Organic Semiconductor Nanoparticle Photocatalysts for Hydrogen Evolution from Water

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Abstract

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Photocatalytic water splitting using solar irradiation has the potential to produce sustainable hydrogen fuel on a large scale. Practical solar energy conversion requires the development of new, stable photocatalysts that operate efficiently under a broad range of visible wavelengths. Organic semiconductors are increasingly being employed as photocatalysts due to their earth abundance, aqueous stability, and optical absorptions that can be tuned to the solar spectrum. However, much remains unknown about the mechanism of organic semiconductor photocatalysis, and significant efficiency improvements need to be made before organic photocatalysts can achieve practical solar energy conversion.

In chapter 2 the effect of residual Pd on hydrogen evolution activity in conjugated polymer photocatalysts was systematically investigated using colloidal poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) nanoparticles (NPs). Residual Pd, originating from the synthesis of F8BT via Pd catalysed polycondensation polymerisation, was observed in the form of homogenously distributed Pd NPs within the polymer. Residual Pd was essential for any hydrogen evolution to be observed from this polymer, and very low Pd concentrations (<40 ppm) were sufficient to have a significant effect on the hydrogen evolution reaction (HER) rate. The HER rate increased linearly with increasing Pd concentration from <1 ppm to approximately 100 ppm, at which point the rate began to saturate. Transient absorption spectroscopy experiments
support these conclusions and suggest that residual Pd mediates electron transfer from the F8BT NPs to protons in the aqueous phase.

Photocatalysts formed from a single organic semiconductor typically suffer from inefficient intrinsic charge generation, which leads to low photocatalytic activities. In chapter 3 we demonstrate that incorporating a heterojunction between a donor polymer and non-fullerene acceptor in organic NPs can result in hydrogen evolution photocatalysts with greatly enhanced photocatalytic activity. Control of the nanomorphology of these NPs was achieved by varying the stabilizing surfactant employed during NP fabrication, converting it from a core-shell structure to an intermixed donor/acceptor blend, and increasing H$_2$ evolution by an order of magnitude. The resulting photocatalysts display an unprecedentedly high H$_2$ evolution rate of over 60,000 µmolh$^{-1}$g$^{-1}$ under 350 to 800 nm illumination and external quantum efficiencies over 6% in the region of maximum solar photon flux.
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List of Abbreviations

2,1,3-benzothiadiazole (BT)
Absolute temperature ($T$)
Ascorbic acid (AA)
Carbon nitrides (CNx)
Concentration ($c$)
Conduction band (CB)
Contact potential difference ($V_{CPD}$)
Covalent organic frameworks (COFs)
Cryo-transmission electron microscopy (cryo-TEM)
Dehydroascorbic acid (DHA)
Delay time ($\tau$)
Deuterated EH-IDTBR (dEH-IDTBR)
Diethylamine (DEA)
Donor/acceptor (D/A)
Dynamic light scattering (DLS)
External bias ($V_{DC}$)
External quantum efficiency (EQE)
Extinction coefficient ($\varepsilon$)
Fast fourier transform (FFT)
Frequency resolved TAS (FR-TAS)
Fuel cell electric vehicles (FCEVs)
Gas chromatograph (GC)
Gel permeation chromatography (GPC)
Gibbs free energy $\Delta G$
Grazing incidence X-ray diffraction (GIXRD)
H$_2$ evolution photocatalysts (HEPs)
Hydrogen evolution photocatalysts (HEP)
Hydrogen evolution reaction (HER)
Inductively coupled optical emission spectroscopy (ICP-OES)
Infrared (IR)
International Energy Agency Photovoltaic Power Systems programme (IEA PVPS)
Kelvin Probe Force Microscopy (KPFM)
Levelized cost of electricity (LCOE)
Lower heating value (LHV)
Nanoparticles (NPs)
Nuclear magnetic resonance (NMR)
Number average molecular weight Mn
Number of moles of H$_2$ ($n_{H2}$)
Optical density ($OD$)
Optical path length ($l$)
Overall water splitting (OWS)
Overpotentials ($\eta$)
Oxygen evolution photocatalysts (OEP)
Oxygen evolution reaction (OER)
Partial pressure of H$_2$ ($P_{H2}$)
Parts per million (ppm)
Photoelectrochemical (PEC)
Photo-electron emission spectroscopy in air (PESA)
Photoluminescence (PL)
Photoluminescence quenching yield (PLQY)
Photovoltaics (PV)
Poly \([2,3\text{-bis}(3\text{-octyloxyphenyl})-5,8\text{-quinoxalinediyl}]\text{-2,5\text{-thiophenediyl}}\) (PTQ1)

Poly\([2,6'\text{-}4,8\text{-di}(5\text{-ethylhexylthienyl})\text{benzo[1,2-b;3,3-b]dithiophene}]\text{3-fluoro-2[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]}\) (PTB7-Th)

Poly\(3\text{-hexylthiophene}\) (P3HT)

Poly\(9,9\text{-dioctylfluorene-alt-9-octylcarbazole}\) (F8CBz)

Poly\(9,9\text{-dioctylfluorene-alt-benzothiadiazole}\) (F8BT)

Poly\([2,6\text{-}(4,8\text{-bis}(5\text{-ethylhexyl)thienyl-2-yl})\text{benzo[1,2-b:4,5-b']dithiophene}]-\text{alt-}(5,5\text{-}(1',3'\text{-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione})\) (PBDB-T)

Poly\([\text{bis}(4\text{-phenyl})(2,4,6\text{-trimethylphenyl})\text{amine}]\) (PTAA)

Poly\([N,N'\text{-bis}(2\text{-octyldodecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl}]\text{-alt-}(5,5\text{-}(2,2'\text{-bithiophene}))\) (PNDI(2OD)2T)

Polytetrafluoroethylene (PTFE)

PV + electrolysis (PV-E)

Simulated solar light (AM 1.5g)

Small-angle neutron scattering (SANS)

Sodium 2-(3-thienyl)ethyloxybutylsulfonate (TEBS)

Sodium dodecyl sulfate (SDS)

Solar to hydrogen efficiency (\(\eta\text{STH}\))

Thermal conductivity detector (TCD)

Time resolved TAS (TR-TAS)

Transient absorption spectroscopy (TAS)

Transmission Electron Microscopy (TEM)

Triethanolamine (TEOA)

Tris(dibenzylideneacetone)di palladium(0) (Pd\(_2\)(dba)\(_3\))

Turnover frequency (TOF)

Ultraviolet (UV)

Universal gas constant \(R\)
Valence band (VB)
Volume (V)
Weight average molecular weight Mw
Work function (ϕ)
1. Chapter 1:

   Introduction
1.1 Climate change and the need for renewable energy

Almost 85% of the world’s primary energy is currently generated from the combustion of coal, oil, and natural gas (Figure 1.1a). This releases vast quantities of CO₂ into the atmosphere (Figure 1.1b) and contributes to climate change by increasing the Earth’s average surface temperature via the “greenhouse effect”. The effects of climate change are already being felt, with unprecedentedly high temperatures being measured all over the planet (Figure 1.1c), and an increased frequency and intensity of extreme weather events being observed.
Continuing to burn fossil fuels in line with the world’s relentlessly growing energy demand would have disastrous environmental and economic effects. For this reason,
anthropogenic climate change has been identified as the greatest threat to global health in the 21\textsuperscript{st} century.\textsuperscript{6} Clearly therefore, there is an urgent need to develop sustainable carbon neutral energy sources to avert the consequences of climate change while sustaining global population and economic growth.\textsuperscript{7}

1.2 The potential of solar energy

Solar irradiation is by far the world’s most abundant energy source.\textsuperscript{8,9} The solar energy incident annually on the Earth’s continental surface is almost 1 YJ, over 2000 times the annual global energy consumption of 450 EJ.\textsuperscript{8} This is an order of magnitude greater than wind energy, the second largest source of renewable energy, and far outstrips the total planetary reserves of non-renewable fossil fuels and uranium combined (Figure 1.2). Harnessing this abundance of free and universally accessible sunlight as a carbon neutral energy source is therefore highly desirable.

![Figure 1.2: A comparison of the energy available from various sources. The volume of each cube represents the energy available from each source. Non-renewable sources (coal, gas, nuclear)](image-url)
are expressed with regard to their total reserves. Renewable sources are expressed with regard to their annual potential. Figure adapted from ref. 10
1.3 Harnessing solar energy

Solar energy is currently mostly generated by solar photovoltaics (PV). PV installations have grown exponentially in the past decade (Figure 1.3) driven by a decrease in module cost which has enabled the levelized cost of electricity (LCOE) generated from PV to reach parity with, or even fall below that generated from fossil fuels.\textsuperscript{11}

![Figure 1.3: Evolution of global installed solar photovoltaic capacity in International Energy Agency Photovoltaic Power Systems programme (IEA PVPS) countries and others. Figure reprinted from ref.\textsuperscript{12}](image)

However, the power output of PV installations is governed by the intensity of light incident on the installation, which varies with the annual and diurnal cycles, and according to the weather. This means that, unlike electricity generated from fossil fuels, the power output of PV installations cannot be easily adjusted in real time to match demand. While variable renewable energy sources such as PV only account for a small fraction of the total power generated on a given grid, it is possible to balance their
power output with dispatchable fossil fuel generators such as gas fired power plants. However, if solar energy is to provide power on a scale commensurate with or exceeding that currently generated from fossil fuels, it must be stored and supplied to users on demand.\textsuperscript{13}

1.4 Storing solar energy

1.4.1 Pumped storage hydroelectricity

Pumped storage hydroelectricity accounts for over 86\% of installed global energy storage capacity, and can be used to store electricity generated from PV.\textsuperscript{14} It stores electrical energy in the form of gravitational potential energy by pumping water from a lower to an upper reservoir. During periods of high demand, the stored water is released through a turbine to generate electricity. Pumped storage hydroelectricity is an economical, established way to store large quantities of electricity,\textsuperscript{15} with current global capacity estimated at 9000 GWh.\textsuperscript{16} However, low energy density, stringent geographical requirements, and environmental issues with reservoir construction limit the number of sites suitable for the construction of pumped storage hydroelectric plants.

1.4.2 Battery storage

Batteries are increasingly being deployed to help balance PV power output with demand.\textsuperscript{14} Batteries have higher energy density and more rapid cycling times compared to pumped storage hydroelectricity,\textsuperscript{15} but their high cost has limited their application to short-duration power stabilization which requires batteries with relatively small capacities. The total capacity of utility scale Li-ion battery storage currently installed
worldwide is 2.3 GWh,\textsuperscript{14} and the average system has a duration of only 1.6 h. Using batteries to store the amount of energy required to fully balance PV output with demand over 24h would require batteries with significantly higher capacity which are likely to be prohibitively expensive.\textsuperscript{17}

1.4.3 Hydrogen fuel

Solar energy can be stored as chemical energy in the chemical bonds of a fuel such as hydrogen, which can subsequently be used to generate heat or electricity on demand. Currently, a lack of economical methods for renewable hydrogen generation and storage have limited the amount of energy stored as hydrogen. Only 0.02\% of the world's total energy storage capacity installed since 1958 utilises hydrogen, with a total capacity of only 100 MWh.\textsuperscript{14} However, provided that efficient and economical methods of hydrogen storage and generation from renewable energy sources are developed, hydrogen could be used to store renewable energy indefinitely, and in virtually unlimited amounts. This would have the power to revolutionize the current energy landscape and enable a future “hydrogen economy” in which hydrogen generated from renewable sources replaces fossil fuels to serve as the primary energy carrier.\textsuperscript{18}

1.5 The hydrogen economy

Hydrogen is a versatile energy carrier which can be burned to generate heat, or oxidised with atmospheric oxygen in fuel cells to generate electricity. In both cases the only waste product is water. Hydrogen has the highest gravimetric energy density of any fuel, with a lower heating value (LHV) of 120 MJkg\textsuperscript{-1}; 2.4, 2.8 and 4 times higher than that of
methane, gasoline and coal, respectively. In the short term, renewable hydrogen could be used to lower the carbon intensity of natural gas used for heating applications by mixing it with the natural gas being transported through existing natural gas pipelines. When burned, the hydrogen/methane gas mixture would have a higher heating value and produce less CO$_2$ than pure methane; thereby lowering net carbon emissions.

Through the use of fuel cells, hydrogen can also act as a transport fuel for fuel cell electric vehicles (FCEVs), and provide energy storage on a utility scale as well as for smaller residential buildings and distributed networks. FCEVs have already entered the mass market, albeit on a small scale, and an off-grid residential complex powered solely by PV coupled with long term hydrogen storage is in the process of being constructed. The success of these pilot projects shows that the transition to a hydrogen economy is already possible, but there are still major technological hurdles to be overcome before a hydrogen economy becomes economically viable. Most prominently, a cheap, safe, and scalable method that can efficiently convert renewable energy to hydrogen is lacking. Hydrogen storage also poses a problem because although hydrogen has the highest gravimetric energy density of any fuel, concentrating it in a form which has a high volumetric energy density is challenging. Hydrogen has a critical temperature of 33 K, which means that it can only be liquefied under cryogenic conditions which is energy intensive. For this reason other hydrogen storage technologies such as metal hydrides and molecular organic frameworks are being developed.
1.6 Methods of producing “solar” hydrogen

96% of hydrogen produced globally is currently derived from fossil fuels through carbon intensive processes. Steam methane reforming is the main production method, accounting for 48% of global hydrogen production, and a further 48% is produced from oil reforming and coal gasification. The remaining 4% is produced almost entirely by electrolysis, often as a by-product of chlorine production. Fossil fuel derived hydrogen will play an important role during the transition to a hydrogen economy, but will eventually need to be replaced by hydrogen generated from carbon neutral sources. The relative abundance of solar energy compared to any other renewable energy source means that an efficient method of converting solar energy to hydrogen is highly desirable. There are currently three major methods of producing hydrogen from solar energy, which are discussed in detail below. In each case hydrogen is produced by splitting water into hydrogen and oxygen according to reaction 2.1, which requires a significant input of energy ($\Delta G = +237 \text{ kJ mol}^{-1}$) that is subsequently stored in the form of hydrogen.

\[2 \text{ H}_2\text{O} \rightarrow 2 \text{ H}_2 + \text{ O}_2 \quad (1.1)\]

1.6.1 Thermal decomposition of water

Solar-thermal installations could be used to provide heat to thermally decompose water into hydrogen and oxygen. Single-step thermal decomposition of water (reaction 2.1) has been impeded by the need for a high temperature heat source above 2500 K required to achieve a reasonable degree of dissociation, as well as the difficulty of
separating the explosive high temperature hydrogen + oxygen gas mixture. These restrictions can be lifted by employing thermochemical cycles that split water through a series of consecutive reactions, of which at least one is highly endothermic and proceeds under elevated temperatures. For example, in the zinc/zinc oxide cycle, zinc oxide is first decomposed to zinc and oxygen at 2100-2300 K (reaction 2.2). The zinc can then be reacted with steam to produce hydrogen and regenerate zinc oxide (reaction 9.3). The net result is overall water splitting (OWS) reaction 2.1.

\[
2 \text{ZnO} \rightarrow 2 \text{Zn} + \text{O}_2 \text{(2100-2300 K)} \tag{2.2}
\]

\[
2 \text{Zn} + 2 \text{H}_2\text{O} \rightarrow 2 \text{ZnO} + 2\text{H}_2 \text{(600-700 K)} \tag{2.3}
\]

Although the maximum theoretical solar to hydrogen efficiency (\(\eta_{\text{STH}}\)) of thermochemical cycles is estimated to be 49.5%, difficulties with heat management and intermediate recycling have so far limited \(\eta_{\text{STH}}\) to 2%. Furthermore, limited reactor durability and complex reactor design due to the high temperatures and often corrosive materials employed increase the cost of thermochemical water splitting. Nonetheless, with further cycle and reactor optimization thermochemical cycles may provide a viable option for solar hydrogen generation in the future.\(^{25}\)
1.6.2 PV + electrolysis

![Diagram of solar hydrogen production via PV + electrolysis.]

**Figure 1.4**: Schematic diagram of solar hydrogen production via PV + electrolysis. Solar energy is harvested by an external solar cell.

Water electrolysis is a relatively mature technology which splits water using electrical energy. 4% of hydrogen produced globally is generated via electrolysis, which is the largest share of any hydrogen production method which does not directly rely on fossil fuels.\(^2\) Electrolysers work by applying direct current between two electrodes in contact with water. Under acidic conditions, water is oxidised at the positive electrode (anode) to form oxygen and protons in the oxygen evolution reaction (OER, **reaction 2.4**). Protons are reduced at the negative electrode (cathode) to form hydrogen in the hydrogen evolution reaction (HER, **reaction 2.5**). This results in overall water splitting (OWS, **reaction 2.1**).
When supplied with electricity generated from PV, electrolysis can be used to store solar energy. A schematic of this process is shown in Figure 1.4. The potential of PV + electrolysis (PV-E) combined with hydrogen storage to supply 100% of the energy required for a small housing complex is being demonstrated in a residential complex containing 172 apartments in Sweden.\textsuperscript{20} The relatively high cost of solar panels and fuel cells/electrolysers along with efficiency losses due to their coupling has thus far meant that hydrogen generated in this way has been uneconomical compared to steam methane reforming. However, as the amount of electricity generated from PV increases, and fuel cell/electrolyser cost and durability improves, PV-E is likely to become the preferred option for generating solar hydrogen in the medium term.\textsuperscript{26}

In PV-E, light harvesting and the electrochemistry required to split water are decoupled. This simplifies the optimisation of each component and has enabled the design of laboratory scale systems with \( \eta_{\text{STH}} \) up to 30%, which is the highest \( \eta_{\text{STH}} \) reported for any solar water splitting device.\textsuperscript{27} However, in industrial applications PV + electrolysis comes with additional costs associated with panel cooling and water transport.\textsuperscript{27} For this reason it may become more economically viable to combine light harvesting and water splitting into a single system where the light harvesting semiconductor is directly submerged in water. This can be achieved either photoelectrochemically or photocatalytically.

\[
\text{OER: } 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \tag{2.4}
\]

\[
\text{HER: } 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2 \tag{2.5}
\]
1.6.3 Photoelectrochemical water splitting

Figure 1.5: Schematic diagram of solar hydrogen production via photoelectrochemical water splitting. Light is harvested directly by the photoanode and photocathode, which are connected without any external bias.

Photoelectrochemical (PEC) water splitting utilises semiconductor photoelectrodes that are directly in contact with water, to both harvest light and drive the OER and HER on their surface. OWS can be achieved either by a single photoelectrode connected to a non-photoactive counter electrode such as Pt, or two photoelectrodes connected in series (Figure 1.5). The configuration used depends on the photoelectrode bandgaps, and the position of their conduction and valence bands relative to the water oxidation and reduction potentials. Photoelectrochemical water splitting was first demonstrated by Fujishima and Honda in 1972 using a rutile TiO$_2$ photoanode coupled to a platinum
cathode.\textsuperscript{29} Ultraviolet (UV) photons absorbed by the TiO$_2$ generated holes in its valence band (VB) and electrons in its conduction band (CB). The photogenerated holes oxidised water to drive the OER on the surface of the TiO$_2$ photoanode, and the electrons were extracted with the aid of an applied bias to the Pt cathode where they reduced protons to drive the HER. Using two photoelectrodes connected in series can remove the need for an applied bias, and improve photocatalytic efficiency by improving the efficiency of light harvesting. Current lab scale PEC devices based on high performance III-IV semiconductors and containing precious metal electrocatalysts to improve the kinetics of the HER and OER are able to achieve $\eta_{\text{STH}}$ of up to 19\%, but the high cost and poor stability of these systems is still a major bottleneck to commercialization.\textsuperscript{30} Furthermore, the best PEC devices utilise the same III-IV semiconductors and the same precious metal catalysts as the best solar cells and electrolysers used for PV-E, but the added complications of immersing the light harvesting materials in electrolyte has meant that their $\eta_{\text{STH}}$ has remained significantly lower.\textsuperscript{27,30} Given that installation costs for PV-E and PEC systems are expected to be similar,\textsuperscript{31} this, along with the falling cost of PV and improvements in electrolyser technology make it unlikely that PEC systems will become cost-competitive with PV-E.\textsuperscript{32}
Photocatalytic water splitting

**Figure 1.6**: Schematic diagram of solar hydrogen production via photocatalytic water splitting. Hydrogen and oxygen are produced simultaneously on particles of a photocatalyst.

Photocatalytic water splitting (**Figure 1.6**) relies on a suspension of semiconductor photocatalysts which absorb light and convert it to electrical charges that simultaneously drive the HER and OER on the particle surface. Unlike PEC systems, which have similar installation costs to PV-E, the relative simplicity of the particle bed reactor required for photocatalysis means that photocatalysis could theoretically produce hydrogen at a significantly lower levelized cost.\(^{31,33}\) Recent technoeconomic analyses estimate that photocatalysis could produce hydrogen at a levelized cost that meets the United States Department of Energy target of $\text{USD}$ 2.00 – 4.00 $\text{kg}^{-1}$ while operating at a $\eta$STH as low as 5-10%.\(^{33,34}\) Currently the best performing photocatalysts
that are able to drive OWS achieve $\eta_{\text{STH}}$ on the order of 1-2%.\textsuperscript{34,35} However, as more efficient photocatalysts are developed, photocatalytic water splitting may become a more economical renewable hydrogen generation strategy than PV-E.\textsuperscript{31,33}

1.6.5 Photocatalytic water splitting principles

1.6.5.1 Single semiconductor water splitting

![Figure 1.7](image)

**Figure 1.7:** Photocatalytic water splitting using a single semiconductor photocatalyst. Adapted from ref.\textsuperscript{36}

OWS (reaction 2.1) requires an input of energy ($\Delta G = +237 \text{ kJ mol}^{-1}$). During photocatalytic water splitting this energy is provided by solar energy via the excitation of a semiconductor photocatalyst (Figure 1.7). The semiconductor absorbs photons with energies greater than its bandgap, which excites electrons from the semiconductor valence band (VB) to the conduction band (CB). This generates a bound electron-hole pair (exciton). The exciton must then dissociate into individual charges which diffuse to the photocatalyst surface where the holes can drive the OER (reaction 2.4) and
electrons can drive the HER (reaction 2.5). Optionally, additional co-catalysts can be deposited on the photocatalyst surface to aid exciton dissociation and lower the kinetic barriers to the HER and OER.\textsuperscript{37} Thermodynamic constraints mean that for both the HER and OER to proceed, the semiconductor CB and VB edges must straddle the proton reduction potential (0 - 0.059pH, V versus NHE) and water oxidation potential (1.23 - 0.059pH, V versus NHE) respectively. At pH 7 this translates to a CB edge ≤ -0.41 V versus NHE (≥ -4.03 V versus vacuum) and a VB edge ≥ +0.81 V versus NHE (≤ -5.26 V versus vacuum).\textsuperscript{38,39} Thermodynamically the minimum bandgap required to drive OWS with a single semiconductor is therefore 1.23 eV, but in practice significantly wider bandgap semiconductors are required due to the overpotentials required to kinetically drive the HER, and particularly the OER.\textsuperscript{37} Critically, an effective photocatalyst must also be stable under operation, be formed of earth abundant elements, and have a bandgap that is narrow enough to absorb a significant portion of the solar spectrum. Satisfying all of these requirements with a photocatalyst formed of a single semiconductor is challenging, and despite decades of research no suitable photocatalyst has yet been developed.\textsuperscript{36,40}
1.6.5.2 Heterojunction water splitting

Forming a heterojunction from two or more semiconductors can reduce the number of requirements that have to be met by a single photocatalyst, which may potentially lead to increased $\eta_{\text{STH}}$.

![Diagram of band alignments required for water splitting](image)

**Figure 1.8**: Illustration of band alignments required for a) single semiconductor, b) Z-scheme, c) donor/acceptor heterojunction overall water splitting at pH 7. Representative overpotentials ($\eta$) of 50 mV and 400 mV required to drive the HER and OER respectively with common co-catalysts are indicated by the dashed lines. Ovals represent different semiconductors, with the CB and VB positions of each semiconductor indicated by the upper and lower horizontal lines inside each oval. Y axis not to scale.

As previously discussed, for OWS to proceed with a single photocatalyst (Figure 1.8a), its CB and VB edges must straddle the proton reduction potential (-4.03 V vs. vacuum at pH 7) and water oxidation potential (-5.26 V vs. vacuum at pH 7) respectively, while supplying enough overpotential to kinetically drive the HER and OER. Although
conceptually simple, the difficulty in finding a water-stable semiconductor with a suitable band alignment has meant that most stable photocatalysts capable of driving OWS developed to date have bandgaps > 3 eV which confine their activity almost exclusively to the UV spectrum.\textsuperscript{38,42} UV light accounts for less than 4% of the solar spectrum, which fundamentally limits the $\eta_{STH}$ of these photocatalysts below the minimum target of 5% required for commercial viability.\textsuperscript{33,43}

This has prompted interest in “Z-scheme” photocatalysis (Figure 1.8b) in which the HER and OER occur on separate hydrogen evolution photocatalysts (HEP) and oxygen evolution photocatalysts (OEP). In a Z-scheme only the highest lying (most positive absolute electrochemical potential) CB and lowest lying (most negative absolute electrochemical potential) VB of the semiconductors employed need to straddle the proton reduction and water oxidation potentials respectively. This permits the use of narrower bandgap semiconductors which are able to harness a larger amount of the solar spectrum, particularly if the two semiconductors have complementary absorptions. In a Z-scheme, photoexcitation occurs at both the HEP and the OEP. Holes in the OEP VB oxidise water, and electrons in the HEP CB reduce protons. Both of these reactions are often promoted by the addition of co-catalysts.\textsuperscript{44-47} The remaining electrons in the OEP CB combine with the holes in the HEP VB. Redox mediators, either solid state conductors such as gold or graphene, or solution based redox couples such as Fe$^{3+}$/Fe$^{2+}$ and IO$^{3-}$/I$^-$, can be employed to facilitate this recombination pathway.\textsuperscript{44-47} Charge recombination between the OEP CB and HEP VB in a Z-scheme means that,
assuming 100% quantum efficiency, a Z-scheme needs to absorb twice as many photons to produce the same amount of hydrogen as a single semiconductor that can drive OWS. However, due to the large amount of low energy photons in the solar spectrum that could be harvested by a Z-scheme but are not energetic enough to drive OWS with a single semiconductor, the theoretical maximum $\eta_{STH}$ of Z-schemes is 40% compared to 30% for a single semiconductor photocatalyst.48 Z-schemes could also be designed to allow the HER and OER to take place in separate reactors; thereby removing the need to separate the potentially explosive hydrogen/oxygen mixture generated by single semiconductor water splitting.34

A heterojunction could also be created between two semiconductors that have a type II energy level offset and are both individually capable of driving overall water splitting (Figure 1.8c). The donor/acceptor (D/A) heterojunction thus created may improve exciton dissociation between the two semiconductors, improving $\eta_{STH}$. A D/A heterojunction may be particularly useful for organic photocatalysts which have high exciton binding energies and therefore suffer from poor intrinsic charge generation. A D/A heterojunction approach would have the added advantage that, similarly to a single semiconductor photocatalyst, every photogenerated charge could potentially be used for OWS. However, such a system has not yet been demonstrated with organic semiconductors.

Regardless of which architecture is employed, developing and optimising an efficient OWS photocatalyst is challenging due to the many parameters involved
(semiconductor(s), co-catalyst(s), pH) and the difficulty of diagnosing performance bottlenecks. It is therefore common to develop new photocatalysts by first testing their performance for either the HER or the OER. This is achieved through the use of sacrificial reagents which rapidly scavenge either electrons (when studying the OER) or holes (when studying the HER), thereby providing a chemical bias to the system and removing the need for both the HER and OER to be driven simultaneously.\textsuperscript{47,49,50} This approach is particularly useful when designing individual HEPs or OEPs for Z-scheme water splitting because it allows the photocatalysts to be individually optimised for their specific reactions before being combined in a Z-scheme.\textsuperscript{47} Typical hole scavengers include organic molecules which are thermodynamically and kinetically easier to oxidise than water such as alkyl amines, alcohols, and ascorbic acid.\textsuperscript{50,51} Typical electron scavengers include salts of transition metal ions that are thermodynamically easier to reduce than protons, such as $\text{AgNO}_3$.\textsuperscript{52}
Figure 1.9: Illustration of the chemical bias provided by sacrificial reagents. a) Ag⁺ electron scavenger allowing OEP to drive OER without driving HER. The reduction potential of Ag⁺ (-5.0 eV) is below that of H⁺. b) Ascorbic acid (AA) hole scavenger allowing HEP to drive HER without driving the OER. The oxidation potential of AA to dehydroascorbic acid (DHA -4.4 eV @ pH 7) is above that of H₂O. c) OEP from (a) and HEP from (b) combined with a redox mediator in a Z-scheme to drive overall water splitting at pH 7. Representative η of 50 mV and 400 mV required to drive the HER and OER respectively with common co-catalysts are indicated by the dashed lines. Ovals represent different semiconductors, with the CB and VB positions of each semiconductor indicated by the upper and lower horizontal lines inside each oval. Y axis not to scale.
1.6.6 Materials for photocatalytic water splitting

1.6.6.1 Inorganic photocatalysts

Since the first report of overall water splitting using TiO$_2$ many inorganic semiconductors have been tested as photocatalysts for overall water splitting; in which H$_2$ and O$_2$ evolution both occur on the same semiconductor, and for “Z scheme” water splitting; in which separate photocatalysts are used for H$_2$ and O$_2$ evolution. However, the highest η$_{STH}$ achieved with these materials have remained relatively low (0.4-1.2%). High operational stability and near unity quantum efficiencies at wavelengths < 450 nm have been achieved with semiconductors such as TiO$_2$ and SrTiO$_3$ but their deep VBs give rise to wide bandgaps which confine their photocatalytic activity almost entirely to UV wavelengths, which constitute <4% of the solar spectrum. This fundamentally limits their maximum η$_{STH}$ below the target of 5-10% deemed necessary for commercial viability.

Narrower bandgap inorganic semiconductors such as CdS, CdSe, and Ta$_3$N$_5$ are highly active for hydrogen evolution under visible light, however despite decades of research their susceptibility to self photocorrosion has so far inhibited their use in an efficient particulate overall water splitting photocatalyst. Stable, low cost and efficient OEPs such as WO$_3$ and BiVO$_4$ are active up to 470 and 510 nm respectively, but lack stable HEPs with complementary absorptions and high activities above 500 nm. Given that the rate determining step of OWS is the kinetically slow 4 electron water oxidation step in the OER, the most straightforward way of improving the η$_{STH}$ of OWS is to develop stable, visible light active HEPs which can be used in Z-schemes in combination with the
best OEPs. This has prompted the recent interest in developing visible light active HEPs based on organic semiconductors.

1.6.6.2 Organic photocatalysts

Compared to inorganic semiconductors, organic semiconductors are relatively unexplored as photocatalysts even though they possess some properties that are highly desirable for photocatalytic applications. Most notably, organic semiconductors typically have highly tuneable direct bandgaps which give rise to strong, precisely tuneable absorptions.\(^{70,71}\) Their modular structures also allow them to be modified with properties such as hydrophilicity and porosity, both of which have been shown to be beneficial for hydrogen evolution.\(^{50,72,73}\) Furthermore, organic semiconductors are formed of earth abundant elements and, if soluble, can be processed from organic solvents to create photocatalyst structures not readily accessible to inorganic semiconductors, such as bulk heterojunction NPs.

1.6.6.2.1 Carbon nitrides

Carbon nitrides (CNx),\(^ {74,75}\) are the most widely studied class of organic semiconductors for photocatalytic applications, and have achieved the highest OWS nSTH of any organic photocatalyst to date (2%).\(^ {35}\) CNx are prepared from the polycondensation of various unsaturated amines, and are composed primarily of triazine and heptazine heterocycles linked via sp\(^2\) bonded N atoms.\(^ {76}\) CNx can adopt a range of graphitic to polymeric structures, often within the same sample, depending on the synthetic procedure employed (Figure 1.10).\(^ {74,75,77−79}\) Synthesis from cheap and abundant precursors such as
melamine, melem, and urea, (Figure 1.10) chemical and thermal stability, non-toxicity, and a bandgap that straddles the water redox potentials are properties that make CNx attractive photocatalysts for large scale OWS.\(^{76}\)

**Figure 1.10:** Building blocks and common structural motifs of carbon nitrides. a) melamine b) melem c) melon d) fully condensed triazine based graphitic carbon nitride e) fully condensed heptazine based graphitic carbon nitride.

However, similarly to stable inorganic photocatalysts, CNx typically have wide bandgaps (2.6-2.7 eV) that are difficult to tune and confine their activity mostly to the UV spectrum.\(^{74-76}\) Furthermore, their chemical structures are often inhomogeneous and poorly defined, which can make establishing meaningful structure-activity relationships challenging.\(^{77}\) Recently, CNx with a well-defined alternating triazine-heptazine structure was synthesized by post-calcination of polymeric CNx in a eutectic mixture of NaCl/KCl. The resulting CNx had an intramolecular triazine-heptazine donor-acceptor structure that narrowed its bandgap from 2.75 eV to 2.58 eV, and achieved an external quantum efficiency (EQE) for hydrogen evolution of 60% at 420 nm.\(^{75}\) However, absorption was
mostly limited to wavelengths <460 nm, limiting visible light activity. Incorporating increasing amounts of barbituric acid into CNx successfully narrowed its bandgap to as low as 1.58 eV, enabling visible light absorption up to 700 nm. However, this also decreased the crystallinity of CNx, which increases charge recombination, and led to an overall decrease in photocatalytic activity compared to pure CNx.\textsuperscript{76,80}

Other attempts to improve the visible light activity of CNx have included incorporating thiophene containing units to narrow its bandgap,\textsuperscript{81} and sensitization with visible light absorbing dyes.\textsuperscript{82} However, enhancing the visible light activity of CNx for OWS photocatalyst has so far been unsuccessful, with the highest performing system being based on a composite of unmodified CNx and carbon nanodots.\textsuperscript{35} The difficulty of tuning CNx for high visible light activity spurred the interest in developing photocatalysts based on other organic semiconductors which have well defined chemical structures and can be rationally tuned.

1.6.6.2.2 Covalent organic frameworks

Covalent organic frameworks (COFs) are crystalline porous polymers synthesized via reversible condensation reactions from organic monomers. The size, symmetry, and connectivity of the monomers pre-determine the three-dimensional structure of the framework, and allow positional control over the arrangement of monomers in the COF.\textsuperscript{83} Incorporating conjugated building blocks gives a COF semiconducting properties which in principle allow it to be used as a photocatalyst. Appreciable rates of hydrogen evolution under sacrificial conditions was observed from a range of COFs incorporating
triazine units in the presence of a platinum co-catalyst. Activity was observed up to 550 nm, but low EQEs (maximum 0.45% @ 450 nm) limited the HER rate. More recently, both H\textsubscript{2} and O\textsubscript{2} evolution were driven individually under sacrificial conditions by a triazine containing COF, in the presence of Pt and RuO\textsubscript{x} co-catalysts respectively. The reported EQEs were 6.0% and 3.8% at 420 nm for H\textsubscript{2} and O\textsubscript{2} evolution respectively. However, poor visible light absorption caused the EQEs to drop rapidly at wavelengths >450 nm.

The porosity of COFs allows species dissolved in the electrolyte to penetrate the bulk material, increasing the semiconductor/electrolyte heterojunction area, and potentially improving charge separation. Porosity may also improve contact between the COF and molecular co-catalysts dissolved in the electrolyte, thus enabling improved electron extraction. It was recently shown that a porous triazine COF showed superior hydrogen evolution activity in the presence of a dissolved molecular cobaloxime catalyst than photodeposited Pt. Dye sensitization of a wide bandgap benzo-bis(benzothiophene sulfone) containing COF with a red light absorbing dye increased its HER rate under sacrificial conditions by 61% compared to the pristine COF, and extended visible light activity from 600 to 700 nm. Interestingly, addition of the dye more than doubled the composite’s EQE at 420 nm, even though it did not improve light absorption at this wavelength. This suggests that the type II energy level offset between the dye and the COF may promote exciton separation; increasing the number of photogenerated charges available for hydrogen evolution.
1.6.6.2.3 Conjugated polymer networks

Crosslinked conjugated polymer networks have been tested as photocatalysts for hydrogen evolution under sacrificial conditions. Similarly to COFs, conjugated polymer networks are synthesised from conjugated monomers via polycondensation polymerisation.\(^{50,88}\) However, the coupling reactions are irreversible and result in poorly defined, insoluble polymer structures that are difficult to purify. Furthermore, synthesis via Pd catalysed cross coupling polymerisation often leaves significant amounts of residual Pd within the polymer network that is able to act as a hydrogen evolution co-catalyst.\(^{51,88}\) This complicates the rational comparison of HER rates, and will be discussed in further detail in Chapter 2. Facile synthesis from readily available precursors, straightforward bandgap tunability via statistical copolymerisation, and microporosity afforded by poor chain packing are attractive features of conjugated polymer networks. Recently, OWS with visible light activity up to 650 nm and 0.6% ηSTH was demonstrated on sheet like polymer networks containing alkyne linked 1,3,5-tris-(4-ethynylphenyl)-benzene and 1,3,5-triethynylbenzene units.\(^{89}\)

1.6.6.2.4 Linear conjugated polymers

The first report of hydrogen evolution using an organic photocatalyst for hydrogen evolution was using the linear conjugated polymer polyphenylene in 1985, decades before the first report of hydrogen evolution using CNx in 2009.\(^{74,90}\) Polyphenylene’s wide bandgap restricted its activity to UV light, and inefficient charge separation resulted in a relatively low EQE of <0.04% at 290 nm.\(^{90}\) Nevertheless, polyphenylene
paved the way for conjugated polymers to be used as photocatalysts. Since then much research has focused on optimising the optoelectronic properties of semiconducting linear conjugated polymers for applications including organic solar cells,\textsuperscript{91} organic light emitting diodes,\textsuperscript{92} and organic field effect transistors.\textsuperscript{93} Research from the field of solar cells is particularly applicable to organic photocatalysts because both solar cells and photocatalysts both rely on the same fundamental processes of light harvesting, charge separation and charge transport to convert solar photons into spatially separated electrical charges.\textsuperscript{94}

In general, linear polymers have shown lower photocatalytic performance than polymer networks or COFs containing similar structural units.\textsuperscript{54,87,95,96} For example, a COF containing the benzo- bis(benzothiophene sulfone) moiety displayed a HER rate under sacrificial conditions almost an order of magnitude higher than its linear polymer analogue. The difference in performance was attributed to greater porosity in the COF, which increased the semiconductor/electrolyte interfacial area, as well as greater crystallinity in the COF which may be beneficial for charge transport.\textsuperscript{87} Soluble linear polymers can be processed into NPs in order to increase the available surface area of the photocatalyst, however photocatalytic activities of conjugated polymer NPs have remained low, likely due to the inefficient intrinsic charge generation of organic semiconductors, and a lower surface area to volume ratio compared to COFs.\textsuperscript{96–98} In the absence of a semiconductor donor/acceptor heterojunction, hole scavenging by the sacrificial electron donor is thought to be an essential step towards generating long
lived electrons capable of driving the HER. The high semiconductor/electrolyte interfacial area in COFs, particularly those that are functionalized with hydrophilic groups, may enhance the rate of hole scavenging and thus generate more long lived photons that are capable of driving the HER.

A feature of linear conjugated polymers that has not yet been exploited for photocatalysis is that their solubility allows them to be blended with electron accepting (or donating) small molecules to form a type II energy level offset that drives exciton separation within the photocatalyst bulk. The work in Chapter 3 is based on the premise that introducing a donor/acceptor heterojunction into organic semiconductor NPs will improve exciton separation within the NP and thus increase photocatalytic activity compared to the individual donor and acceptor components.

1.7 Experimental techniques

The experimental techniques used in this thesis range from those commonly used in the field, such as UV-Vis absorption spectroscopy, steady-state photoluminescence (PL) spectroscopy, and dynamic light scattering (DLS), to more specialist techniques required to probe material structure and morphology. Focus will be given to describing the techniques that are less commonly used in the field and their application to the research in this thesis.

1.7.1 Photo-electron emission spectroscopy in air (PESA)

Photo-electron emission spectroscopy in air (PESA) is a useful technique for measuring the work function of semiconductors under ambient conditions. The work function is
the minimum energy required to remove an electron from the semiconductor HOMO to a point outside the semiconductor. During operation, monochromatic UV light at a specific intensity is directed onto a semiconductor thin film on a glass substrate. The photon energy is gradually increased, and when it exceeds the work function (\(\phi\)) of the semiconductor the semiconductor begins to emit photoelectrons. The photoelectrons travel several mm (mean free path of electron in air at atmospheric pressure) towards the positively polarized detector before colliding with an oxygen molecule to generate a superoxide anion (\(O_2^{•−}\)). The superoxide anion continues to travel to the anode under the influence of the applied electric field before being detected by an open detector.\textsuperscript{101} Plotting the standardized photoelectron yield ratio vs excitation energy gives rise to a signal that increases linearly above a certain threshold energy that corresponds to the \(\phi\) of the semiconductor. A typical plot showing the work function of poly(3-hexylthiophene) (P3HT) is shown in Figure 1.11. Once the \(\phi\) has been measured, the semiconductor HOMO level can be estimated using equation 2.12, and the LUMO can be estimated from equation 2.13, where \(E_g\) is the optical band gap measured by UV-Vis spectroscopy.

\[
HOMO \,(eV) = -\phi \tag{2.12}
\]

\[
LUMO \,(eV) = HOMO + E_g \tag{2.13}
\]
Figure 1.11: Plot of photoelectron yield vs. photon energy for P3HT measured by PESA, indicating a $\phi$ of 4.61 eV.

1.7.2 Transient absorption spectroscopy (TAS)

Transient absorption spectroscopy (TAS) can be used to measure the yield and lifetime of excited states (excitons and polarons) within a sample that originate from the absorption of photons. TAS is a nonlinear pump-probe technique in which a laser pump pulse irradiates a sample, promoting a fraction of the electrons therein from the ground state to an electronically excited state. Once excited, electrons can decay back to their ground state via several competing radiative or non-radiative pathways described by the Jablonski diagram. Alternatively, electron or hole transfer to or from a neighbouring material can take place, forming charged electron and hole polarons with their own unique spectral signatures. To “observe” the sample after excitation, a low intensity probe pulse irradiates the sample at a specific delay time ($\tau$) after excitation by the
pump pulse. The optical density (OD) of the sample is recorded by the probe pulse before (OD) and after, (OD*) excitation, and the difference in optical density (ΔOD) between the excited and unexcited sample is calculated according to equation 2.14.

$$\Delta OD = OD^* - OD$$

(2.14)

Hence ΔOD corresponds to the optical density of the excited sample at a specific τ, and is related to the excited state concentration (c), the optical path length (l), and the extinction coefficient (ε) of the excited species present by the Beer-Lambert law (equation 2.15).

$$\Delta OD = \epsilon \cdot c \cdot l$$

(2.15)

To obtain information about the spectral signature of an excited species, frequency resolved TAS (FR-TAS) can be used to measure ΔOD over a range of wavelengths at constant τ. Alternatively, time resolved TAS (TR-TAS) can be used to monitor excited state decay kinetics by measuring ΔOD over a range of τ (fs-ms timescales) at fixed wavelengths. FR-TAS and TR-TAS can also be combined; measuring ΔOD over a range of wavelengths at different delay times to observe decay kinetics across a range of wavelengths. This technique is particularly useful for samples that contain more than one species that absorbs at the wavelength of excitation. A schematic of a TAS setup is shown in Figure 1.12.
Figure 1.12: Schematic illustration of transient absorption spectroscopy setup. The height of each pulse represents its intensity.

1.7.3 Cryo-Transmission Electron Microscopy (Cryo-TEM)

Transmission Electron Microscopy (TEM) uses a beam of electrons to observe the structure of materials on the atomic scale. Samples with narrow cross-sections (thin films, nanoparticles (NPs), or powders) are immobilised on a conductive grid and examined under vacuum. However, “soft” organic molecules such as biopolymers and synthetic organic polymers and small molecules can only be studied in limited detail by TEM due to the high electron doses used, which burn the sample. Furthermore, solvated organic samples such as proteins, emulsions, and synthetic polymer NPs, cannot be imaged by TEM because the vacuum would cause the solvent to evaporate. Cryo-TEM overcomes these limitations by operating under cryogenic conditions to prevent solvent evaporation, and using lower electron doses coupled with advanced image processing to reduce the beam damage sustained by the sample. During sample preparation, a droplet of solution containing the nanostructures of interest is loaded onto a TEM grid, and excess solution is dabbed off (Figure 1.13). A thin aqueous film containing the
nanostructures is retained in the holes of the TEM grid. The grid is then rapidly submerged in liquid nitrogen cooled liquid ethane to vitrify the ice. The rapid cooling vitrifies the water without allowing it to crystallise. This preserves the sample in a hydrated, but cryogenically fixed state that can be observed by TEM under cryogenic conditions. Cryo-TEM is used extensively to study the internal morphology of mixed organic polymer/small molecule NPs in chapter 3.

![Illustrative diagram of sample preparation for cryo-transmission electron microscopy.](image)

**Figure 1.13:** Illustrative diagram of sample preparation for cryo-transmission electron microscopy. *a*) water droplet containing sample loaded onto TEM grid. *b*) Film of water
containing sample on TEM grid. c) cross section of two cells of TEM grid containing sample in vitrified water. Light blue shading represents water. Dark blue dots represent hydrated sample.
1.7.4 Kelvin Probe Force Microscopy (KPFM)

Kelvin Probe Force Microscopy (KPFM) is a scanning probe technique that can be used to map the surface potential or work function of a sample surface. KPFM measures the contact potential difference \( V_{\text{CPD}} \) between a conductive atomic force microscope (AFM) tip and the sample surface. \( V_{\text{CPD}} \) depends on the difference between the sample and tip workfunctions \( \phi_{\text{sample}} \) and \( \phi_{\text{tip}} \) respectively, according to equation 2.16. Where \( e \) is the electronic charge.

\[
V_{\text{CPD}} = \frac{\phi_{\text{sample}} - \phi_{\text{tip}}}{e}
\] (2.16)

If \( \phi_{\text{sample}} \) and \( \phi_{\text{tip}} \) are different (Figure 1.14a), an electric current, \( i \), flows from the lower \( \phi \) to the higher \( \phi \) material when the tip is brought within a short enough distance, \( d \), from the sample surface to allow electron tunnelling between tip and sample. The current flows until the fermi levels are aligned and the system reaches equilibrium. This causes the tip and sample to become charged, and a \( V_{\text{CPD}} \) is formed between the sample and tip (Figure 1.14b). An attractive electrostatic force acts on the contact area between sample and tip due to the \( V_{\text{CPD}} \), which can be nullified if an external bias \( (V_{\text{DC}}) \), equal in magnitude but opposite in direction to \( V_{\text{CPD}} \), is applied between the tip and the sample (Figure 1.14c). Thus \( V_{\text{DC}} \) is equal to the \( \phi \) difference between the tip and the sample, and can be used to calculate \( \phi_{\text{sample}} \) if \( \phi_{\text{tip}} \) is known.\(^{103}\) KPFM will be used in chapter 3 to measure the \( \phi \) of mixed polymer/small molecule NPs with different morphologies.
Figure 1.14: Electronic energy levels of sample and tip a) before contact b) during contact c) after contact and with the application of an external direct current. Vertical axis represents electric potential of negative charge.

1.7.5 Hydrogen evolution measurements

A large part of this thesis was devoted to building and optimising an experimental setup for the measurement of H$_2$ evolution from water. The reactor is based on a design which has been described in detail previously, but a number of modifications were made to improve the accuracy and reproducibility of H$_2$ evolution measurements. Focus here will be given to describing the modifications and how they improve the accuracy of H$_2$ evolution measurements.

The recirculating batch reactor consists of a reaction chamber connected to a gas manifold connected to a vacuum pump and a gas chromatograph (GC). Figure 1.15 and Figure 1.16 show photographs of the experimental setup.
During operation, the sample is illuminated with simulated solar light (AM 1.5g) or broadband visible light (350-800 nm). Any gases evolved in the sample chamber are continuously circulated through the manifold and through the GC sample loop by the recirculating pump. At set time intervals the gasses in the sample loop are injected into the GC column (5Å molecular sieve, Ar carrier gas) and analysed by a thermal conductivity detector (TCD). Using Ar as the carrier gas maximises sensitivity for H$_2$ because of the large conductivity difference between the carrier gas (Ar) and the analyte (H$_2$). The integral of the peak corresponding to H$_2$ on the GC trace is
proportional to the partial pressure of H$_2$ in the system. The exact partial pressure is
determined by comparing the measured peak integral against a calibration curve
measured from a standard gas containing a known concentration of H$_2$ at a series of
different pressures. Multiplying the partial pressure of H$_2$ ($P_{H_2}$) by the total volume of
the system ($V$) gives the number of moles of H$_2$ ($n_{H_2}$) generated according to the perfect
gas law (5) where $R$ and $T$ are the universal gas constant and absolute temperature
respectively.

$$n_{H_2} = \frac{P_{H_2}V}{RT}$$  \hspace{1cm} (5)

The modified reactor has two separate loops in the GC connected to two separate TCDs
to allow the measurement of two samples in parallel; doubling throughput. In the
original reactor design the beam of the light source was cooled with a water filter
housed above the sample chamber. The water was cooled and served to remove
infrared (IR) light from the light source before it reached the sample, in an effort to
prevent sample heating. However, the sample chamber was not cooled and over the
course of the 16-35 h measurement water vapour condensed on the bottom of the
water filter (indicated in Figure 1.16b).
Figure 1.16: Close-up photographs of sample chamber and light source. a) top view. b) side view. Note: The water filter has been left empty to prevent condensation.

This formed water droplets that significantly diffracted the incident light; reducing the accuracy of light intensity measurements. To overcome this problem, the water filter was emptied and the sample chamber was instead cooled from below, by submerging it into a jacketed water bath cooled by a chiller (Figure 1.16). This removed all condensation and allowed the sample to be kept at a constant temperature (288 K) throughout the experiment. The open cooled bath is a simpler, cheaper, and more user friendly solution (easier cleaning, manipulation) compared to a jacketed sample chamber. A sample chamber lid that does not contain a water filter is in the process of being fabricated.
Removing condensation from the bottom of the water filter reduced the uncertainties associated with measuring light intensity. However, it also reduced light scattering which reduced the illuminated sample area to a 625 mm$^2$ square. This meant that new uncertainties were introduced due to non-uniform sample illumination and a poorly defined illuminated area due to possible light scattering outside of the 625 mm$^2$ square. To overcome this issue, a polytetrafluoroethylene (PTFE) insert was designed which filled the sample chamber volume and contained a square opening with a well-defined cross sectional area (400 mm$^2$, Figure 1.17).

![Figure 1.17: Photographs of sample chamber and PTFE insert a) side view of PTFE insert outside of reactor. b) top view of PTFE insert inside reactor.](image)

The opening in the PTFE insert holds all of the sample in the path of the light source and acts as a shadow mask to accurately define the illuminated sample area. It also has the same area and geometry as the active area of a calibrated silicon photodiode that was used to calibrate the incident light intensity to 1 sun. Therefore, with the use of the PTFE insert, the average light intensity across the sample can be accurately adjusted to 1 sun,
and the exact illumination area is unambiguously known. This greatly increases the precision of \( \text{H}_2 \) evolution measurements.
2. Objectives

The central aim of this dissertation is to develop novel organic semiconductor NP photocatalysts capable of producing hydrogen from water under visible light irradiation in the presence of a sacrificial hole scavenger. The dissertation aims to further the understanding of the mechanism by which photocatalysts drive the HER, and to improve the visible light activity of state of the art organic photocatalysts.

In Chapter 2, focus will be given to understanding the mechanism by which conjugated polymer photocatalysts catalyse the HER. Particularly the role that residual Pd, originating from semiconductor synthesis, plays in this mechanism.

In Chapter 3, the effect of introducing a D/A semiconductor heterojunction into conjugated polymer NP photocatalysts is investigated. In organic bulk heterojunction solar cells, D/A heterojunctions increase the efficiency of exciton dissociation by providing a thermodynamic driving force that overcomes the exciton binding energy and favours the spatial separation of positive and negative charges. The same principles should also improve exciton dissociation in D/A heterojunction NP photocatalysts and may lead to enhanced photocatalytic activities. Focus will be given to fabricating D/A heterojunction NPs, characterising the heterojunction morphology, and optimising it to maximise the photocatalytic hydrogen evolution rate.
3. Chapter 2:

The effect of residual palladium catalyst contamination on the photocatalytic hydrogen evolution activity of conjugated polymers
1.8 Contributions to chapter

Transient absorption spectroscopy was carried out by Michael Sachs and Dr Robert Godin. Cryo-TEM images were captured by Dr Dalaver Anjum. Hydrogen evolution measurements were carried out by the dissertation author, initially under the supervision of Dr Muhammad Qureshi. All other work was carried out by the dissertation author.

1.9 Introduction

In recent years there has been a growing interest in developing organic semiconductors capable of driving photocatalytic water splitting due to their low cost, aqueous stability, and tunable band gaps. Graphitic carbon nitrides remain the most well-known and intensely studied class of organic materials for this application. More recently however, new classes of materials are being investigated for hydrogen evolution from water, such as nitrogen doped graphene oxide, covalent organic frameworks, conjugated polymer networks, and linear conjugated polymers. With the notable exception of graphitic carbon nitride, most organic materials have required an additional metal co-catalyst to produce an appreciable \( \text{H}_2 \) evolution rate, often introduced by Pt photodeposition, or the addition of a molecular catalyst. However, recent reports of photocatalysis employing both linear and cross linked conjugated polymers suggest that these systems are able to produce \( \text{H}_2 \) under visible light irradiation without any added co-catalyst, at a much faster rate than commercial graphitic carbon nitride, even when the latter is subjected to Pt photodeposition.
Activity without the need for co-catalysts, which are often precious metals or molecular complexes with limited stability, could be a very attractive feature of such polymer photocatalysts with the potential to vastly reduce the cost and complexity of current photocatalytic systems.

However, a feature of these linear and crosslinked conjugated polymers that has not yet been systematically studied is the presence of significant quantities of residual Pd originating from their synthesis via Pd catalysed polycondensation reactions. It has previously been shown that the molecular Pd catalysts used in these reactions can decompose via deligation and subsequent Ostwald ripening to form metallic Pd particles which are strongly retained within the polymer matrix and are difficult to remove via classical purification techniques. Similarly to Pt, Pd is a highly active proton reduction electrocatalyst. Therefore, it is possible that the residual Pd, dispersed within these polymer structures, facilitates H₂ evolution and removes the need for additional co-catalysts. Much uncertainty remains about the nature of the active site in conjugated polymer systems, and there are conflicting views in the literature on whether or not the residual amounts of Pd play a significant role. No correlation was seen between Pd concentration and hydrogen evolution reaction (HER) rate in a range of conjugated microporous polymers, and in a series of linear polymers containing the 2,1,3-benzothiadiazole (BT) unit, it was concluded that it was H-bonding from water to the N atoms on this unit that facilitated proton reduction, not residual Pd. In the most in depth study to date, a dependency of HER rate on Pd content was
observed when Pd catalyst loadings were altered during the synthesis of a conjugated polymer network. However, altering catalyst loadings changed the degree of polymerisation of the polymer, and may have also altered the network’s microstructure. Consequently, it was impossible to completely decouple the effects these structural changes may have had on HER rate from the effect of residual Pd. Furthermore, due to the crosslinked structure of the polymer it was not possible to reduce the Pd mass fraction below 400 ppm (0.04 wt.%). Therefore, it could not be determined whether these conjugated polymers could drive the HER without Pd, or if Pd only accelerated the HER rate, similarly to Pt in carbon nitrides. The question whether such conjugated polymer systems are intrinsically able to photocatalytically reduce protons to H₂ or require a co-catalyst such as Pd to drive this reaction is therefore of great interest.

In this work, the effect that residual Pd has on the HER rate of conjugated polymers is demonstrated using the linear polymers poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) and poly(9,9-dioctylfluorene-alt-9-octylcarbazole) (F8CBz). At low Pd concentrations, it is unambiguously shown that the HER rate is highly dependent on Pd concentration, and that no hydrogen evolution is observed when all residual Pd is removed. A very low Pd concentration (approximately 200 ppm) appears sufficient to saturate the performance of F8BT. This is approximately 20 times lower than the Pd concentration reported in similar polymers in the literature, which explains why in these polymers there was no observed trend between Pd concentration and HER rate.

Purification methods for conjugated polymer photocatalysts are suggested that will
allow the effects of the semiconductor and the effects of the co-catalyst on HER rate to be decoupled, and thus allow rational comparisons between conjugated polymer photocatalysts to be made.

1.10 Results and discussion

F8BT and F8CBz were synthesized via Suzuki polymerisation according to a published procedure using tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$(dba)$_3$) as the cross coupling catalyst. After purifying F8BT and F8CBz via Soxhlet extraction (see experimental section), over 1000 ppm (0.1 wt.%) of Pd remained within each polymer. To reduce the residual Pd concentration, the polymers were further purified by gel permeation chromatography (GPC) and washed with a solution of diethyldithiocarbamate; a ligand previously shown to chelate and remove residual Pd. A portion of each polymer was retained after each purification stage, and the Pd concentration was analyzed by inductively coupled optical emission spectroscopy (ICP-OES). Purification resulted in a gradual decrease of Pd concentration to below the instrument’s 1 ppm detection limit (Table 3.1) and did not alter the polymer’s molecular structure, as evidenced by the unaltered absorbance spectrum (Figure 3.1) and $^1$H nuclear magnetic resonance (NMR) spectrum (Figure 3.2) before and after purification.
Table 3.1: Residual Pd concentrations in F8BT and F8CBz samples measured by ICP-OES

<table>
<thead>
<tr>
<th>Polymer sample</th>
<th>[Pd] (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F8BT Unpurified</td>
<td>1170</td>
</tr>
<tr>
<td>F8BT GPC</td>
<td>195</td>
</tr>
<tr>
<td>F8BT GPC + Wash</td>
<td>36</td>
</tr>
<tr>
<td>F8BT GPC + Wash 2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>F8CBz Unpurified</td>
<td>1937</td>
</tr>
<tr>
<td>F8CBz GPC</td>
<td>309</td>
</tr>
<tr>
<td>F8CBz GPC + Wash</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>
Figure 3.1: Normalised absorbance spectra of F8BT in THF after each purification stage.
**Figure 3.2**: $^1$H NMR spectrum (400 MHz, CDCl$_3$) of a) F8BT GPC + Wash 2 b) F8BT unpurified.

In addition to the samples in **Table 3.1**, F8BT samples containing 60, 100, and 250 ppm Pd were prepared by reintroducing Pd$_2$(dba)$_3$ to GPC + Wash 2 F8BT. Each F8BT sample was then processed into NPs using a modified nanoprecipitation procedure (see experimental section). TEM images (**Figure 3.3**) of purified and unpurified F8BT samples were taken before and after they were processed into NPs to confirm that residual Pd was present within the polymer in the form of NPs, and that these NPs were retained within the polymer after it was processed into NPs.
Figure 3.3: Dark field TEM images of a) Unpurified b) GPC c) GPC + Wash 2 F8BT films showing the successful removal of Pd NPs. Bright field Cryo-TEM images of F8BT NP suspensions formed from d) unpurified e) GPC f) GPC + Wash 2 F8BT.
TEM images of polymer films formed from purified and unpurified F8BT samples (Figure 3.3a-c) reveal that unpurified F8BT contained a large number of dense NPs (445 particles in 1 µm²) with an average diameter 4.6 nm, which dramatically decreased upon GPC purification (137 particles in 1 µm², average diameter 4.0 nm). No particles were observed in the GPC + Wash 2 F8BT. This is consistent with the ICP-OES measured Pd concentrations, and suggests that the dense NPs consist of Pd and can be removed by the purification steps employed. Cryo-TEM images of polymer NPs formed from purified and unpurified F8BT samples (Figure 3.3d-f) reveal that the F8BT formed rounded particles, with diameters ranging between approximately 30 and 70 nm. It can also be seen that many polymer NPs formed from unpurified F8BT contain one or more dense particles with a diameter of approximately 1-5 nm. These are approximately the same size as those within the unpurified F8BT film before nanoprecipitation, and are therefore attributed to Pd NPs. Far fewer Pd particles were observed in the GPC purified F8BT than the unpurified sample, and no Pd particles were observed in the GPC + Wash 2 sample. Importantly, it can be seen that the Pd NPs are also present at the surface of some of the polymer particles and are therefore optimally situated to act as a catalytic interface between F8BT and protons in the aqueous phase. Figure 3.4 shows that when Pd₂(dba)₃ was reintroduced into the GPC + Wash 2 F8BT, the small dense NPs were also reintroduced. This further suggests that the dense NPs are formed of Pd and originate from the Pd₂(dba)₃ catalyst employed during polymerization.
Figure 3.4: Dark field TEM image of F8BT GPC + Wash 2 film after the re-addition of Pd$_3$(dba)$_3$ (100 ppm Pd). The bright section in the top left corner of the image arises from the carbon grid.
The size distributions of each F8BT NP batch were analyzed by dynamic light scattering (Figure 3.5, Table 3.2).

**Figure 3.5:** F8BT NP size distributions by intensity, measured by DLS. Histograms have been plotted as frequency polygons for greater clarity.
Table 3.2: Summary of DLS NP size distribution data.

<table>
<thead>
<tr>
<th>[Pd] (ppm)</th>
<th>Z-average diameter (nm)</th>
<th>Polydispersity index</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;1</td>
<td>49.6</td>
<td>0.101</td>
</tr>
<tr>
<td>36</td>
<td>55.2</td>
<td>0.160</td>
</tr>
<tr>
<td>60</td>
<td>54.0</td>
<td>0.190</td>
</tr>
<tr>
<td>100</td>
<td>43.1</td>
<td>0.212</td>
</tr>
<tr>
<td>195</td>
<td>57.0</td>
<td>0.142</td>
</tr>
<tr>
<td>250</td>
<td>46.4</td>
<td>0.178</td>
</tr>
<tr>
<td>1170</td>
<td>40.1</td>
<td>0.118</td>
</tr>
</tbody>
</table>

DLS revealed that all of the NP samples had narrow size distributions (PdI <0.3) and similar Z-average diameters of approximately 50±10 nm, which is in good agreement with the NP Cryo-TEM images. Because all of the NP samples have very similar size distributions, any effects that differences in NP size or surface area may have on HER rate are eliminated. Furthermore, since all of the F8BT and F8CBz samples originated from the same initial F8BT or F8CBz batch, and the purification steps did not influence the molecular weight distribution of the polymers, all batches of the same polymer are chemically identical. Any differences in photocatalytic HER rate between these NP samples can therefore be unambiguously assigned to differences in Pd concentration.
Photocatalytic HER rates of the NP samples were measured in the presence of the sacrificial hole scavenger diethylamine (DEA) under broadband visible light irradiation (350-800 nm) from a 300 W Xe lamp.

Figure 3.6: a) \( \text{H}_2 \) evolution from F8BT NPs containing varying amounts of Pt or Pd. Full squares represent samples containing residual Pd. Hollow squares represent samples in which Pd\(_2\)(dba)\(_3\) was added to GPC + Wash 2 F8BT. Stars represent GPC + Wash 2 F8BT NPs with 5 wt.% photodeposited Pt. b) Average \( \text{H}_2 \) evolution rate over 24 h from colloidal F8BT NPs as a function of Pd concentration. **Conditions:** 2 mg F8BT NPs, 30% DEA/H\(_2\)O, 300 W Xe lamp.
**Figure 3.6** shows that the photocatalytic HER rate of F8BT NPs was highly dependent on the concentration of residual Pd within the polymer. Nanoparticles formed from F8BT containing 1170 ppm residual Pd displayed an average HER rate of 176.6 µmol/h.g, producing 8.47 µmol H₂ over 24 h. However, NPs formed from F8BT containing <1 ppm residual Pd were completely inactive, producing <0.02 µmol H₂ (below the GC detection limit) over the same time period. This shows that Pd is an essential component of both the F8BT and the F8CBz NPs without which the HER does not take place. Once Pd was reintroduced into the purified polymer (hollow circles) the HER activity recovered proportionally to Pd concentration; consistent with Pd being the species that facilitates H₂ evolution, and that the loss of photocatalytic activity after purification was not due to the removal of other contaminants or degradation of the polymer. Repeating the experiment with another conjugated polymer synthesized via Pd catalysed Suzuki polymerisation, F8CBz, confirmed that the observed effect of residual Pd on HER rate was not exclusive to F8BT, and that it is therefore likely to occur in a wide range of conjugated polymer photocatalysts.
Figure 3.7: a) H₂ evolution from F8CBz NPs containing varying amounts of residual Pd. b) Average H₂ evolution rate over 24 h from F8CBz NPs as a function of Pd concentration. Conditions: 2 mg F8BT NPs, 30% DEA/H₂O, 300 W Xe lamp.

Figure 3.7 shows that NPs formed from F8CBz containing 1937 ppm residual Pd displayed an average HER rate of 15.92 µmol/h.g, producing 0.76 µmol H₂ in 24 h. However, similarly to F8BT, once the residual Pd concentration reached <1 ppm the F8CBz NPs became inactive. Interestingly, a very low Pd concentration (approximately 200 ppm) appears sufficient to saturate the performance of the F8BT NPs, and even photodeposition of 50,000 ppm (5 wt.% ) Pt, a more efficient HER catalyst, did not produce a significant rate increase compared to 200 ppm Pd. This is in contrast to F8CBz, in which the HER rate increases approximately linearly as the Pd concentration increases from <1 to 1937 ppm. This suggests that the Pd saturation concentration of different polymers may differ widely, in the same way as the optimum loading of photodeposited Pt varies for different organic and inorganic H₂ evolution photocatalysts. Nevertheless, the low Pd saturation concentration of F8BT may explain why in similar systems reported in the literature there was no observed trend
between Pd concentration and HER rate, because in these systems the Pd concentration was on the order of 0.5 wt.%; more than 20 times greater than the 200 ppm saturation limit shown for the F8BT system. It also suggests that even low residual Pd concentrations could greatly lower the efficiency of conjugated polymer photocatalysts for other photocatalytic reduction chemistries, such as CO\textsubscript{2} reduction, in which proton reduction is a competing and unwanted side reaction. In these systems Pd may act as an electron trap, promoting proton reduction instead of the desired reduction chemistry. A schematic illustration of this process is shown in Figure 3.8.

**Figure 3.8:** Illustrative diagram of the potential role of residual Pd as an electron trap during CO\textsubscript{2} reduction. The proton coupled reduction of CO\textsubscript{2} to CO is shown as a representative reaction. \(\eta\) CO\textsubscript{2} and \(\eta\) H\textsuperscript{+} represent CO\textsubscript{2} and proton reduction overpotentials respectively.

For further insights into the influence of residual Pd on the photophysics of the F8BT NPs, we performed TAS measurements.
Figure 3.9: Transient absorption measurements of F8BT NP suspensions. a) Transient spectrum of unpurified F8BT at 1 ms, both in pure H₂O and in an aqueous suspension containing 30% DEA. b) Transient kinetics probed at 750 nm for GPC+wash F8BT suspended in a mixture of 30% DEA in water. The same suspension was first purged with argon (blue trace) and then with oxygen (red trace). All traces were acquired at an excitation wavelength of 460 nm and an excitation intensity of 0.54 mJ cm⁻². The suspension was prepared with an absorbance of 0.42.

As shown in Figure 3.9, experiments on µs – ms time scales reveal the emergence of a long-lived excited state absorption in the presence of DEA which extends throughout the visible and near-infrared spectral range and is characterised by an increasing amplitude towards 500 nm. This long-lived signal only appears upon addition of the electron donor DEA (Figure 3.9a) and is quenched significantly in the presence of oxygen (Figure 3.9b), which, taken together, suggests that this long-lived signal can be assigned to photogenerated electrons on the F8BT polymer (electron polaron). This assignment is in line with the observation of long-lived electrons in carbon nitride systems upon addition of hole scavengers.¹³⁷,¹³⁸ Since previous studies have reported a transient spectrum with a maximum between 600 nm and 800 nm for F8BT polarons,¹³⁹,¹⁴⁰ we
attribute the different spectrum observed here primarily to the aqueous environment in our suspension systems.

To investigate the dependence of the long-lived electron signal upon Pd concentration, we probed the transient kinetics in F8BT NP suspensions with different levels of purification. Kinetics at 750 nm were chosen to avoid the photoluminescence artefacts (photoluminescence maximum $\lambda_{PL} = 550$ nm) that are present at early times for shorter probe wavelengths.
Figure 3.10: Transient kinetics probed at 750 nm for different Pd concentrations in an aqueous suspension containing 30% DEA. All data were obtained at an excitation wavelength of 460 nm and a fluence of 0.54 mJ cm\(^{-2}\). Suspensions were prepared with an absorbance of 0.42 at 460 nm and purged with argon before the experiment.

As shown in Figure 3.10, we observe an increasing signal amplitude with decreasing Pd content. We attribute this increasing signal amplitude to an increased accumulation of long lived photogenerated F8BT electrons in the absence of Pd, consistent with the presence of Pd accelerating photocatalytic hydrogen generation and therefore suppressing the accumulation of long lived electrons. This suppression of long lived electrons in the presence of metal catalyst, correlated with increased hydrogen generation is analogous to results we have reported previously for carbon nitride photocatalysts with Pt and molecular nickel based proton reduction co-catalysts,\(^{138}\) and supports the key role of Pd in catalysing proton reduction in the F8BT NPs studied herein.

1.11 Conclusion

It has been unambiguously shown that residual Pd has a profound effect on the photocatalytic HER rate of conjugated polymers, to an extent that when it is removed, it can change a polymer from highly active to completely inactive. Without Pd present, it is very likely that conjugated polymers without added co-catalysts would have much lower HER efficiencies. Little is known about how molecular Pd catalysts self-assemble into NPs within polymers, and factors such as Pd particle size, and distribution within the polymer matrix (e.g. surface vs bulk), will likely have significant effects on the HER
performance of the polymer. Since these effects cannot effectively be controlled, the presence of residual Pd can make it impossible to make rational comparisons between the photocatalytic performance of different polymers. Therefore, Pd concentrations should at least be quantified, and if possible all of the Pd should be removed using diethyldithiocarbamate or similar washes. Pd can then be replaced with a known quantity of a well-defined co-catalyst such as a molecular hydrogenase or photodeposited Pt to make rational comparisons between polymer semiconductors possible. For some polymers, the only available synthetic route results in precipitation of the polymer during polymerization, and formation of polymer particles which cannot re-dissolve, thus preventing purification to remove residual Pd. In these cases, the performance of the polymer should be saturated by adding an additional co-catalyst, until performance no longer improves to ensure that the polymer’s performance is not limited by a lack of co-catalyst. Furthermore, the presence of Pd could hinder a range of reduction chemistries, including CO₂ reduction, because it may act as an electron trap, promoting proton reduction at the expense of the species of interest.

1.12 Experimental

1.12.1 Materials and methods

All chemicals were purchased from Sigma Aldrich and used without purification unless otherwise stated. Polymer purification by GPC was carried out on a Shimadzu LC-20AD liquid chromatograph equipped with two Agilent PLgel 10 µm mixed-d columns. Polymer samples were digested using an UltraWAVE single reaction chamber microwave digestion
system. Pd concentrations were measured by inductively coupled plasma optical emission spectrometry (Agilent 5110). Sonication was carried out in an ultrasonic bath (Branson 5510). Nanoparticle size was measured by dynamic light scattering (Malvern Zetasizer ZS). TEM and Cryo-TEM images were taken using FEI Titan and Titan Krios transmission electron microscopes respectively.

1.12.2 F8BT synthesis

F8BT was synthesised from its monomers using a modified literature procedure. Monomers were recrystallized from ethanol, and thoroughly dried prior to use. All solvents were thoroughly degassed with nitrogen prior to use. A solution of potassium phosphate (0.529 g, 2.49 mmol) in 2 mL water and 0.5 mL dioxane was added to a mixture of 9,9-Dioctyl-9H-fluorene-2,7-diboronic acid bis(pinacol) ester (1) (400 mg, 0.623 mmol), 4,7-Dibromobenzo[c]-1,2,5-thiadiazole (183 mg, 0.623 mmol), Tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$(dba)$_3$) (5.7 mg, 6.22 µmol, 2 mol% Pd), and tri(o-tolyl)phosphine (P(o-tol)$_3$), (11.4 mg, 37.5 µmol, 6 mol%) in toluene (2 mL). The mixture was stirred vigorously inside a sealed microwave vial for 24 h at 110 °C. The contents were removed, and washed by consecutive Soxhlet extractions with methanol, acetone, and hexane, each for 24 h. The polymer was extracted with chloroform, concentrated under reduced pressure, and precipitated into methanol. The yellow precipitate was filtered to obtain “unpurified” F8BT (Mn = 39.6 kD Mw = 84.4 kD, PDI = 2.13, 507 mg 87% yield).
1.12.3 Polymer purification by gel permeation chromatography

“Crude” polymer (400 mg) was purified by gel permeation chromatography at 80°C, using a 2 mL/min isocratic flow of chlorobenzene. The eluent was collected in fractions, and the central 75% fractions were kept, combined, and the solvent was removed under reduced pressure. The polymer was dissolved in a small amount of chloroform, precipitated into methanol, and filtered to obtain purified “GPC” polymer.

1.12.4 Polymer purification by diethyldithiocarbamate wash

“GPC” purified polymer (150 mg) was dissolved in chloroform (50 mL) and added to a solution of sodium diethyldithiocarbamate trihydrate (0.60 g, 2.35 mmol) in water (60 mL). The biphasic mixture was stirred vigorously at 60°C for 12 h under nitrogen. The chloroform phase was separated, and thoroughly washed with water (5 x 20 mL). The solution was concentrated under reduced pressure, precipitated into methanol, and filtered to obtain the purified “GPC + Wash” purified polymer. This procedure was repeated with “GPC + Wash” purified polymer to give “GPC + Wash 2” purified polymer.

1.12.5 Measurement of residual palladium in polymers

The polymer sample was digested in a microwave digester (UltraWAVE) in a mixture of aqua regia containing a small amount of hydrogen peroxide and sulfuric acid. The digested sample was analysed by ICP-OES to determine the concentration of palladium in the sample.
1.12.6 Addition of Pd to purified F8BT

To add a specific concentration of Pd back into “GPC + wash 2” F8BT (0 ppm residual Pd), a precise aliquot of Pd$_2$(dba)$_3$ solution was added to a solution of “GPC + wash 2” F8BT. For example, to add 100 ppm Pd back into “GPC + wash 2” F8BT, 25.0 µL of Pd$_2$(dba)$_3$ solution (10 ppm in THF) was added to 5.0 mL of “GPC + wash 2” F8BT (500 ppm in THF). The solution was heated in a sealed vial at 60 °C overnight, and the solvent was removed. During this time the Pd$_2$(dba)$_3$ decomposed to Pd$^0$ NPs and became fully mixed into the polymer. The dried polymer was then used to make NPs as described below.

1.12.7 Nanoparticle preparation

Polymer NPs were fabricated by nanoprecipitation using a method similar to one reported previously.$^{141}$ In a typical preparation, a solution of F8BT (500 ppm) and polystyrene-co-maleic anhydride (100 ppm) in tetrahydrofuran (5 mL) was filtered (0.2 µm PTFE syringe filter), then rapidly injected into MilliQ water (40 mL) under sonication in an ultrasonic bath. The mixture was sonicated for a further 2 min, and then heated in an oil bath at 80 °C under constant nitrogen bubbling to remove the THF and concentrate the solution to 10 mL. Finally, the concentrated solution was filtered (0.45 µm glass fibre syringe filter) to remove large agglomerates. If stored in the dark, NP suspensions formed in this way were stable for several months without any signs of aggregation.

1.12.8 Hydrogen evolution measurements

Hydrogen evolution from colloidal F8BT and F8CBz NPs was measured using DEA as a sacrificial electron donor. F8BT or F8CBz NPs (2 mg) in 3:7 DEA:water (15 mL) were loaded
into a recirculating batch reactor (area = 452 mm$^2$) which has been previously reported.$^{104}$

A starting pressure of 100 Torr was used. The suspension was illuminated with a 300 W Xe lamp (385-700 nm) and H$_2$ evolution was quantified by a gas chromatograph equipped with a thermal conductivity detector.
1.12.9 Transient absorption measurements

Transient absorption measurements were conducted using a home-built transient absorption setup with a Nd:YAG laser (OPOTEK Opolette 355 II, 4 – 7 ns pulse width), which uses an optical parametric oscillator to generate 460 nm excitation pulses. These laser pulses are directed to the sample using a liquid light guide. A pyroelectric energy sensor (Ophir Photonics PE9) was used to measure excitation densities, here 0.54 mJ cm$^{-2}$ at 460 nm. The output of a 100 W quartz halogen lamp (Bentham IL1) is used as a probe beam, with monochromators to select the probe wavelength positioned before and after the sample, and detected by a Si photodiode (Hamamatsu S3071). Appropriate long pass filters were placed between sample and detector and scattered laser light was used to start the data acquisition (Thorlabs DET210). Home-built LabVIEW-based software was used to record data: the detector output was amplified (Costronics 1999 amplifier) and sampled on the μs – ms timescale using an oscilloscope (Tektronix DPO 2012B), and the non-amplified signal was recorded on the ms timescale using a DAQ card (National Instruments, NI USB6211). The recorded data was processed in MATLAB and OriginPro 2017.
4. Chapter 3:

Photocatalytic Hydrogen Evolution from Organic Semiconductor Heterojunction Nanoparticles
1.13 Contributions to chapter

Transient absorption spectroscopy and photoluminescence quenching measurements were carried out by Dr Hyojung Cha, Michael Sachs, Lingyu Zou and Sandra Gonzalez Lopez. Small angle neutron scattering was measured by Dr Tyler Martin. Kelvin probe force microscopy and interfacial tension measurements were performed by Dr Calvyn Howells. Cryo-TEM images were captured by Dr Dalaver Anjum and Dr Rachid Sougrat and analysed by the dissertation author. Deuterated EH-IDTBR and TEBS were synthesized by Matthew Bidwell. EH-IDTBR was synthesized by Dr Weimin Zhang. All other work was carried out by the dissertation author.

1.14 Introduction

The development of sustainable energy sources is essential to avert impending climate change while sustaining the global population and economic growth. Solar energy is by far the greatest available source of renewable energy, but its transience limits its utility. If solar energy is to provide power on a scale commensurate with or exceeding that currently generated from fossil fuels, it must be stored and supplied to users on demand. Storing solar energy in the chemical bonds of a fuel is therefore highly desirable. H₂ is the simplest such “solar fuel” and can be generated from water via electrolysis, or using semiconductor photocatalysts, which absorb light and convert it to electrical charges that drive surface redox reactions. A “particulate” system in which photocatalysts are directly dispersed in water is projected to be the cheapest way of producing solar H₂. In the simplest case, OWS can be achieved by a single
photocatalyst that simultaneously oxidises and reduces H₂O into H₂ and O₂. However, the only particulate photocatalysts currently capable of driving OWS are typically based on single component, wide bandgap semiconductors such as TiO₂,²⁹,⁵⁹ SrTiO₃,⁵⁶,⁶⁰ or CNₓ,⁷⁴,⁷⁵ which are almost exclusively active at UV wavelengths that constitute <4 % of the solar spectrum.⁴⁰ This fundamentally limits their maximum ηSTH below the target of 10% deemed necessary for commercial viability.³³,⁴⁰ OWS can also be achieved by two photocatalysts operating in parallel, where the HER and OER take place on separate semiconductors. This “Z-scheme” system is analogous to natural photosynthesis, and can potentially achieve higher ηSTH by employing semiconductors with narrower bandgaps which can absorb a larger proportion of the solar spectrum.⁴⁵–⁴⁷ Stable, low cost and efficient O₂ evolution photocatalysts, such as WO₃,⁶⁴ and BiVO₄,³⁶,⁴⁶,⁶⁵,⁶⁶ are active up to 470 and 510 nm respectively,⁶⁸ but the development of stable, efficient and low cost inorganic H₂ evolution photocatalysts (HEPs) has proved more challenging, particularly for HEPs which exhibit complementary absorptions and high activities above 500 nm.⁴²,⁶¹,⁶²,⁶⁹ This greatly limits the ηSTH of current Z-schemes and has prompted the recent interest in developing visible light active HEPs based on organic semiconductors other than CNₓ,⁷⁵,⁷⁶,¹⁴³ whose bandgaps can be tuned to absorb further into the visible spectrum. Conjugated polymers⁵⁰,⁸⁸,⁹⁵,¹⁴⁴,¹⁴⁵ and COFs⁸⁴,⁸⁷,¹¹³,¹¹⁴ have attracted the most attention due to their modular structures which enable their energy levels and physical properties to be precisely controlled. However, the EQEs of these novel non-CNₓ photocatalysts have been limited by the high exciton binding energies and short exciton diffusion lengths (typically 5-10 nm)¹⁴⁶–¹⁴⁸ of organic semiconductors which cause high
rates of exciton recombination in the semiconductor bulk, and hence inefficient generation of charges that can drive redox reactions at the photocatalyst surface.

**Figure 4.1a.** To overcome this limitation, most research has been focused on improving exciton dissociation at the photocatalyst surface by increasing the semiconductor/electrolyte interfacial area via NP formation, hydrophilicity enhancements and/or by sensitising the photocatalyst surface with a suitable dye to create a D/A semiconductor heterojunction that is able to dissociate excitons at the external photocatalyst/dye interface. Less attention has been given to developing organic non-CN₃ HEPs with internal semiconductor heterojunctions that can drive exciton dissociation and spatially separate charges in the photocatalyst bulk. Conjugated polymer NPs can be readily fabricated with an internal D/A heterojunction by blending donor and acceptor semiconductors together within the same NP.

**Figure 4.1b.** However, this feature has not yet been fully exploited, with most studies to date focusing on optimising the photocatalytic performance of HEP NPs formed of a single conjugated polymer.
Figure 4.1: Illustrations of a) 50nm diameter photocatalyst NP formed of a single organic semiconductor. Assuming an exciton diffusion length of 5 nm, only excitons generated up to 5 nm from the NP surface can dissociate at the semiconductor/electrolyte or semiconductor/Pt interfaces. Excitons generated in the NP core are likely to recombine before reaching an interface. Thus 51% of the NP is “dead volume” that absorbs light but does not contribute to photocatalysis. b) 50 nm diameter photocatalyst NP formed from an intimately mixed donor/acceptor semiconductor blend. The donor/acceptor heterojunction in the NP bulk drives exciton dissociation which spatially separates charges and extends charge lifetime; allowing a larger proportion of charges to reach the NP surface and contribute to photocatalysis.
1.15 Results and discussion

1.15.1 Polymer donor/polymer acceptor heterojunction nanoparticles

Polymer donor/polymer acceptor heterojunction NPs were formed from blends of the donor polymers Poly([2,6′-4,8-di(5-ethylhexylthienyl)benzo[1,2-b;3,3-b]dithiophene]{3-fluoro-2[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediy}] (PTB7-Th), Poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b′]dithiophene))-alt-(5,5-(1’,3’-di-2-thienyl-5’,7’-bis(2-ethylhexyl)benzo[1’,2′-c:4’,5’-c′]dithiophene-4,8-dione]) (PBDB-T), and Poly [[2,3-bis(3-octyloxyphenyl)-5,8-quinoxalinediy1]-2,5-thiophenediy1] (PTQ1) matched with the acceptor polymer Poly{[N,N′-bis(2-octyldecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5′-(2,2′-bithiophene}) (PNDI(2OD)2T). Chemical structures and energy levels of all of the polymers used in this study are shown in Figure 4.2.
Figure 4.2: 

**a)** Chemical structures of PTB7-Th, PBDB-T, PTQ1, and PNDI(2OD)2T

**b)** Highest occupied and lowest unoccupied molecular orbital energy levels of PTB7-Th, PBDB-T, PTQ1, and PNDI(2OD)2T compared to the proton reduction potential (H⁺/H₂), water oxidation potential (O₂/H₂O), and the calculated potential of the two hole oxidation of ascorbic acid to dehydroascorbic acid in solution (A/H₂A) at pH 2 (the experimentally measured pH of 0.2 mol/L ascorbic acid). All energy levels and electrochemical potentials were calculated from the work function measured by PESA and the absorption onset measured by UV-vis, and are expressed on the absolute electrochemical scale (0 V vs. SHE = -4.44 V vs Vac.).
Polymer blends were processed into nanoparticles using the miniemulsion method (detailed in experimental section) employing sodium dodecyl sulfate (SDS) as the stabilising surfactant. The NP size distributions were measured by DLS Table 4.1, Figure 4.3).

**Table 4.1:** DLS parameters of NPs formed with a range of PTB7-Th:PNDI(2OD)2T, PBDB-T:PNDI(2OD)2T and PTQ1:PNDI(2OD)2T ratios using SDS surfactant.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Z-Avg Diameter (nm)</th>
<th>Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNDI(2OD)2T</td>
<td>56.79</td>
<td>0.309</td>
</tr>
<tr>
<td>PTB7-Th</td>
<td>79.01</td>
<td>0.211</td>
</tr>
<tr>
<td>PTB7-Th:PNDI(2OD)2T 0.1:9.9</td>
<td>62.38</td>
<td>0.282</td>
</tr>
<tr>
<td>PTB7-Th:PNDI(2OD)2T 0.75:9.25</td>
<td>43.15</td>
<td>0.297</td>
</tr>
<tr>
<td>PTB7-Th:PNDI(2OD)2T 1.5:8.5</td>
<td>44.68</td>
<td>0.255</td>
</tr>
<tr>
<td>PTB7-Th:PNDI(2OD)2T 3:7</td>
<td>41.06</td>
<td>0.299</td>
</tr>
<tr>
<td>PTB7-Th:PNDI(2OD)2T 5:5</td>
<td>74.94</td>
<td>0.225</td>
</tr>
<tr>
<td>PTB7-Th:PNDI(2OD)2T 8.5:1.5</td>
<td>43.02</td>
<td>0.268</td>
</tr>
<tr>
<td>PBDB-T</td>
<td>33.21</td>
<td>0.581</td>
</tr>
<tr>
<td>PBDB-T:PNDI(2OD)2T 0.1:9.9</td>
<td>48.91</td>
<td>0.313</td>
</tr>
<tr>
<td>PBDB-T:PNDI(2OD)2T 0.425:9.575</td>
<td>48.19</td>
<td>0.411</td>
</tr>
<tr>
<td>PBDB-T:PNDI(2OD)2T 0.75:9.25</td>
<td>38.46</td>
<td>0.423</td>
</tr>
<tr>
<td>PBDB-T:PNDI(2OD)2T 1.5:8.5</td>
<td>40.5</td>
<td>0.323</td>
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<tr>
<td>PBDB-T:PNDI(2OD)2T 3:7</td>
<td>39.63</td>
<td>0.448</td>
</tr>
<tr>
<td>PBDB-T:PNDI(2OD)2T 5:5</td>
<td>35.52</td>
<td>0.477</td>
</tr>
<tr>
<td>PBDB-T:PNDI(2OD)2T 8.5:1.5</td>
<td>30.45</td>
<td>0.52</td>
</tr>
<tr>
<td>PTQ1</td>
<td>49.6</td>
<td>0.204</td>
</tr>
<tr>
<td>PTQ1:PNDI(2OD)2T 0.1:9.9</td>
<td>68.37</td>
<td>0.289</td>
</tr>
<tr>
<td>PTQ1:PNDI(2OD)2T 0.75:9.25</td>
<td>44.96</td>
<td>0.307</td>
</tr>
<tr>
<td>PTQ1:PNDI(2OD)2T 1.5:8.5</td>
<td>57.71</td>
<td>0.342</td>
</tr>
<tr>
<td>PTQ1:PNDI(2OD)2T 3:7</td>
<td>42.41</td>
<td>0.288</td>
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<tr>
<td>PTQ1:PNDI(2OD)2T 5:5</td>
<td>67.38</td>
<td>0.257</td>
</tr>
<tr>
<td>PTQ1:PNDI(2OD)2T 7:3</td>
<td>48.08</td>
<td>0.232</td>
</tr>
<tr>
<td>PTQ1:PNDI(2OD)2T 8.5:1.5</td>
<td>66.63</td>
<td>0.224</td>
</tr>
</tbody>
</table>
Figure 4.3: DLS size distributions by intensity of NPs formed with a range PTB7-Th:PNDI(2OD)2T, PBDB-T:PNDI(2OD)2T and PTQ1:PNDI(2OD)2T ratios using SDS surfactant.
Figure 4.3 shows that all NP batches had similar size distributions consisting of one major peak centred at 60-80 nm, with some samples also displaying a minor peak below 10 nm. The Z average hydrodynamic diameter between NP batches made from the same donor/acceptor combination remained relatively constant at 40-60 nm for PTB7-Th:PNDI(2OD)2T blends, 30-50 nm for PBDB-T:PNDI(2OD)2T blends, and 50-70 nm for PTQ1:PNDI(2OD)2T blends. This is important when comparing the HER rates of NP batches formed from different D:A ratios, because NP size affects the total NP surface area, which would likely affect HER rate. Having samples with similar size distributions minimises this variation and allows the effects of NP composition to be isolated.

The D/A combinations were chosen because all components absorb strongly throughout the visible spectrum (Figure 4.4) and have absorption maxima within the region of maximum solar photon flux (550-850 nm). More importantly, the energy levels of the PTB7-Th, PBDB-T and PTQ1 donor polymers form a type II D/A heterojunction with the PNDI(2OD)2T acceptor. This drives holes to the D polymer HOMO, and electrons to the PNDI(2OD)2T LUMO (Figure 4.2b). The PNDI(2OD)2T LUMO is significantly more reducing (less negative absolute potential) than the proton reduction potential at pH 2 (-4.32 eV) so electrons therein have sufficient potential to drive hydrogen evolution with the aid of a suitable cocatalyst. Because neither donor polymer has a HOMO that is more oxidising (more negative absolute potential) than the water oxidation potential at pH 2 (-5.52 eV) it is not possible to drive oxygen evolution with this system alone. Hydrogen evolution experiments were therefore carried out in the presence of AA
which can be oxidised by holes in the PTB7-Th HOMO and acts as a sacrificial hole scavenger.
Figure 4.4: Absorption spectra of a) PTB7-Th:PNDI(2OD)2T b) PBDB-T:PNDI(2OD)2T c) PTQ1:PNDI(2OD)2T blend NPs with different D:A ratios formed with SDS. For each D:A combination the blend which achieved the maximum HER rate is highlighted with star symbols.

Figure 4.5: Average mass normalized HER rates over 24 h of PTB7-Th:PNDI(2OD)2T, PBDB-T:PNDI(2OD)2T, and PTQ1:PNDI(2OD)2T blend NPs over a range of blend ratios. Conditions: 2 mg D/A blend NPs, 0.2 mol/L ascorbic acid (20 mL), pH 2, 5% (10 µg) Pt, 300 W Xe lamp (350 to 800 nm), 20 cm² reactor. Irradiation spectrum can be found in the experimental section.
Measuring the HER rates of blend NPs composed of a range of PTB7-Th:PNDI(2OD)2T, PBDB-T:PNDI(2OD)2T, and PTQ1:PNDI(2OD)2T mass ratios formed using SDS as a surfactant (Figure 4.5) revealed that in all cases, D/A NPs formed from a D/A blend were significantly more active than single component NPs formed from any of the pristine polymers. The HER rate increase is therefore attributed to enhanced charge generation in the blend NPs driven by their internal D/A heterojunction.

Interestingly, in all three polymer blends, the maximum HER rate was achieved at a PNDI(2OD)2T mass fraction ≥ 85%. This differs greatly from the optimum blend ratio when the same polymers were employed in the active layer of solar cells, where the maximum photovoltaic efficiency was reported at a PNDI(2OD)2T mass fraction of 50% and 30% for PBDB-T:PNDI(2OD)2T and PTQ1:PNDI(2OD)2T blends respectively. In both cases the HER rate was also significantly less tolerant to the blend ratio compared to the corresponding solar cell; dropping rapidly at PNDI(2OD)2T mass fractions ≥ 85%. This suggests that the heterojunction morphology in NPs differs significantly from that in thin films of the same polymers, leading to inefficient charge extraction at blend ratios comprising < 85% PNDI(2OD)2T. The internal morphology of PTQ1:PNDI(2OD)2T NPs was analysed by cryo-transmission electron microscopy (cryo-TEM, Figure 4.6).
Figure 4.6: Cryo-TEM images of NPs a) PNDI(2OD)2T b) PTQ1 c) PTQ1:PNDI(2OD)2T 1:1 d) PTQ1:PNDI(2OD)2T 7.5:92.5 with 5 wt.% photodeposited Pt. The Pt co-catalyst can be seen as dark NPs 2-4 nm in diameter. Profiles along the long axis of the blue rectangles highlighted in each image are shown in Figure 4.7.
This technique was chosen because it can image the NPs in an environment that is close to their native state, and therefore sample preparation is expected to preserve their morphology. NPs formed of pure PTQ1 were roughly spherical and displayed a semicrystalline morphology with a d-spacing of 2.3 nm visible as lines of alternating high and low electron density (dark and light contrast) through the NP projection (Figure 4.7a). Pure PNDI(2OD)2T NPs were ellipsoidal, perhaps due to higher polymer chain rigidity and a higher degree of crystallinity compared to PTQ1. The d-spacing was also clearly visible, with an inter-chain distance of 2.5 nm (Figure 4.7b). The d-spacings of 2.3 nm and 2.5 nm correspond to the lamellar stacking distances measured by grazing incidence X-ray diffraction of PTQ1 (2.4 nm) and PNDI(2OD)2T (2.5 nm) respectively.\textsuperscript{159} NPs formed from a 1:1 blend of PTQ1:PNDI(2OD)2T displayed a shell that resembles PNDI(2OD)2T and an amorphous core, which may correspond to PTQ1 (Figure 4.7b). However, the boundary between the core and shell is not visibly defined due to the similar lamellar stacking distances of PTQ1 and PNDI(2OD)2T, so it is not possible to unambiguously define the position of the PTQ1 domain(s). NPs formed of a 7.5:92.5 PTQ1:PNDI(2OD)2T blend no longer display an amorphous domain in the NP core, and resemble NPs formed of pure PNDI(2OD)2T. However, the fraction of PTQ1 in the blend visibly disrupts the lamellar stacking of PNDI(2OD)2T; as can be seen by the greater number of dislocations visible in the PNDI(2OD)2T lamella in the blend NP compared to the pure PNDI(2OD)2T NP. These observations suggest that at this blend ratio a core-shell morphology is no longer favoured, and PTQ1 is randomly distributed in small domains that disrupt the PNDI(2OD)2T lamellar stacking throughout the NP bulk. This is
consistent with the trend observed in HER rates (Figure 4.5), because as the blend NPs transition from a core-shell morphology at low PNDI(2OD)2T fractions to a more intermixed morphology at high PNDI(2OD)2T fractions, a larger proportion of the holes generated in PTQ1 are able to reach the surface of the NP and contribute to photocatalysis. However, the PNDI(2OD)2T fraction required to favour this transition is likely too high to allow efficient exciton dissociation and charge percolation out of the NP bulk, and therefore the HER rates of the PTB7-Th:PNDI(2OD)2T, PBDB-T:PNDI(2OD)2T, and PTQ1:PNDI(2OD)2T blend NPs are all likely limited by their unfavourable core-shell morphology.
Figure 4.7: Profiles along long axis of areas in blue rectangles highlighted in Figure 4.6. a) PNDI(2OD)2T b) PTQ1 c) PNDI(2OD)2T: PTQ1 1:1 d) PTQ1:PNDI(2OD)2T 7.5:92.5. Numbers in the top right hand corner of each panel correspond to the average d-spacing measured along each profile.

The NP morphology was further characterised by blending PNDI(2OD)2T with polymers which display a clear phase contrast. Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine]
(PTAA) was chosen for its highly amorphous structure, which can be clearly
distinguished from the highly crystalline PNDI(2OD)2T. Poly(3-hexyl)thiophene (P3HT)
was chosen due to its narrow reported lamellar stacking distance (1.66 nm)\textsuperscript{160} which
should be distinguishable from the significantly wider PNDI(2OD)2T lamellar stacking
distance by cryo-TEM. NPs formed from pure PTAA, P3HT, and the corresponding blends
with PNDI(2OD)2T are shown in Figure 4.8. PTAA formed highly amorphous, spherical
NPs, and P3HT formed irregularly shaped, semicrystalline NPs consisting of a large
amorphous domain with several crystallites in which the characteristic P3HT 1.7 nm
lamellar stacking was visible (Figure 4.9a). Blending PTAA with PNDI(2OD)2T resulted in
NPs with a clearly defined core-shell structure consisting of an amorphous core fully
encapsulated by a PNDI(2OD)2T shell; characterised by its strong crystallinity and 2.4 nm
lamellar stacking distance (Figure 4.9b). P3HT:PNDI(2OD)2T NPs displayed a similar
structure, with P3HT adopting an amorphous morphology in the NP core (Figure 4.9b).
It is therefore likely that core-shell morphologies are also present in the PTB7-
Th:PNDI(2OD)2T, PBDB-T:PNDI(2OD)2T, and PTQ1:PNDI(2OD)2T blend NPs used in this
study. However, the systems were not fully characterised because our focus was drawn
to the more highly performing systems described in the remainder of this chapter.
Figure 4.8: Cryo-TEM images of NPs a) PTAA b) P3HT c) PTAA:PNDI(2OD)2T 1:1 d) P3HT:PNDI(2OD)2T 1:1. Profiles along the long axis of the blue rectangles highlighted in b-d are shown in Figure 4.9.
Figure 4.9: Profiles along long axis of areas in blue rectangles highlighted Figure 4.8. a) P3HT b) PTAA:PNDI(2OD)2T 1:1 c) P3HT:PNDI(2OD)2T 1:1.
1.15.2 Polymer donor/small molecule acceptor heterojunction nanoparticles

**Figure 4.10:** a) Chemical structures of PTB7-Th and EH-IDTBR. b) Highest occupied and lowest unoccupied molecular orbital energy levels of PTB7-Th and EH-IDTBR compared to the proton reduction potential (H⁺/H₂), water oxidation potential (O₂/H₂O), and the calculated potential of the two hole oxidation of ascorbic acid to dehydroascorbic acid in solution (A/H₂A) at pH 2 (the experimentally measured pH of 0.2 mol/L ascorbic acid). All energy levels and electrochemical potentials are calculated from the work function measured by PESA and the absorption onset measured by UV-vis, and are expressed on the absolute electrochemical scale (0 V vs. SHE = -4.44 V vs Vac.).

Polymer donor/small molecule acceptor NPs were also fabricated via the miniemulsion process, initially employing SDS as the stabilising surfactant, from the donor polymer PTB7-Th matched with the nonfullerene acceptor EH-IDTBR. The structures and energy levels of the semiconductors used are shown in **Figure 4.10**. The NP size distributions were measured by dynamic light scattering (Figure 4.11, Table 4.2).
Figure 4.11: DLS size distributions by intensity of NPs formed with a range of PTB7-Th/EH-IDTBR ratios. Nanoparticles formed with (a) SDS (b) TEBS.

Figure 4.11 shows that all NP batches formed using SDS had unimodal size distributions and that the Z average hydrodynamic diameter between batches remained relatively constant at 50-70 nm. This is important when comparing HER rates between batches, because NP size affects the total NP surface area, which would likely affect HER rate. Having samples with similar size distributions minimises this variation and allows the effects of NP composition and morphology to be isolated.
Table 4.2: DLS parameters of NPs formed with a range of PTB7-Th/EH-IDTBR ratios using SDS or TEBS surfactants.

<table>
<thead>
<tr>
<th></th>
<th>Zavg.D (nm)</th>
<th>Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB7-Th</td>
<td>67.1</td>
<td>0.285</td>
</tr>
<tr>
<td>85:15</td>
<td>68.2</td>
<td>0.262</td>
</tr>
<tr>
<td>70:30</td>
<td>63.4</td>
<td>0.298</td>
</tr>
<tr>
<td>50:50</td>
<td>50.5</td>
<td>0.282</td>
</tr>
<tr>
<td>30:70</td>
<td>46.9</td>
<td>0.271</td>
</tr>
<tr>
<td>15:85</td>
<td>50.5</td>
<td>0.282</td>
</tr>
<tr>
<td>10:90</td>
<td>45.2</td>
<td>0.293</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Zavg.D (nm)</th>
<th>Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB7-Th</td>
<td>83.3</td>
<td>0.201</td>
</tr>
<tr>
<td>85:15</td>
<td>84.1</td>
<td>0.164</td>
</tr>
<tr>
<td>70:30</td>
<td>82.6</td>
<td>0.229</td>
</tr>
<tr>
<td>60:40</td>
<td>80.6</td>
<td>0.196</td>
</tr>
<tr>
<td>50:50</td>
<td>78.7</td>
<td>0.221</td>
</tr>
<tr>
<td>30:70</td>
<td>81.9</td>
<td>0.228</td>
</tr>
<tr>
<td>15:85</td>
<td>81.4</td>
<td>0.234</td>
</tr>
<tr>
<td>EH-IDTBR</td>
<td>63.8</td>
<td>0.263</td>
</tr>
</tbody>
</table>
The PTB7-Th/EH-IDTBR D/A combination was chosen because both PTB7-Th and EH-IDTBR strongly absorb light throughout the visible spectrum (Figure 4.12) and have absorption maxima within the region of highest solar photon flux (approximately 550-850 nm). More importantly, their energy levels form a type II D/A heterojunction with sufficient HOMO-HOMO (0.64 eV) and LUMO-LUMO (0.66 eV) energy level offsets required for exciton dissociation, which drives holes to the PTB7-Th HOMO, and electrons to the EH-IDTBR LUMO (Figure 4.10b). The EH-IDTBR LUMO is significantly more reducing (less negative absolute potential) than the proton reduction potential at pH 2 (-4.32 eV) so electrons therein have sufficient potential to drive hydrogen evolution with the aid of a suitable cocatalyst. Because the PTB7-Th HOMO is less oxidising (less negative absolute potential) than the water oxidation potential at pH 2 (-5.52 eV) it is not possible to drive oxygen evolution with this system alone. Hydrogen evolution experiments were therefore carried out in the presence of AA which can be oxidised by holes in the PTB7-Th HOMO and acts as a sacrificial hole scavenger.
Figure 4.12: Absorption spectra of PTB7-Th:EH-IDTBR NPs at different PTB7-Th:EH-IDTBR ratios formed with a) TEBS and b) SDS.

Before using the SDS-prepared NPs as photocatalysts, photoluminescence quenching yield (PLQY) measurements (Figure 4.13) were used to confirm that NPs prepared from mixed PTB7-Th:EH-IDTBR solutions formed two-component PTB7-Th:EH-IDTBR NPs, and not a mixture of single component NPs. No PL quenching was observed in mixtures of single component PTB7-Th and EH-IDTBR NPs prepared from neat PTB7-Th or EH-IDTBR solutions because PTB7-Th and EH-IDTBR are confined to separate NPs, and hence cannot form a D/A heterojunction that drives exciton dissociation. In NPs formed from mixed solutions of PTB7-Th and EH-IDTBR, quenching of the combined PTB7-Th and EH-IDTBR emissions was observed for all PTB7-Th:EH-IDTBR blends as can be seen in Figure 4.13. This indicates that charge transfer is occurring between PTB7-Th and EH-IDTBR, which is only possible if PTB7-Th and EH-IDTBR are within the exciton diffusion length (c.a. 5–10 nm)\textsuperscript{147,148} from each other, and hence within the same NP.
Using TEBS as a surfactant narrowed the NP size distributions and slightly increased the $Z_{\text{avg}}$ NP size to 60-80 nm for all PTB7-Th:EH-IDTBR ratios (Figure 4.11). Similarly to NPs formed with SDS, PL quenching measurements showed enhanced exciton dissociation in all PTB7-Th:EH-IDTBR blends compared to mixtures of pure PTB7-Th and EH-IDTBR NPs (Figure 4.13) confirming that the TEBS surfactant also produced mixed PTB7-Th:EH-
IDTBR NPs. However, the NPs formed using TEBS showed greater PL quenching at 15% and 85% EH-IDTBR, which signifies increased mixing between PTB7-Th and EH-IDTBR domains that allows more efficient exciton dissociation at low donor or acceptor fractions. Pure PTB7-Th NPs also showed greatly enhanced PL intensity when formed using TEBS, possibly due to a change in PTB7-Th morphology.

Measuring the HER rates of NPs composed of a range of PTB7-Th:EH-IDTBR mass ratios formed using SDS as a surfactant (Figure 4.14) revealed that in all cases, D/A NPs formed from a PTB7-Th:EH-IDTBR blend were significantly more active than single component NPs formed of either pristine PTB7-Th, pristine EH-IDTBR, or both pristine NPs mixed together. The HER rate increase is therefore attributed to enhanced charge generation in the blend NPs driven by their internal D/A heterojunction.
Figure 4.14: H₂ evolution vs. time from PTB7-Th/EH-IDTBR NPs formed from a range of PTB7-Th:EH-IDTBR ratios using a) SDS c) TEBS surfactant. Average H₂ evolution rates of PTB7-Th/EH-IDTBR NPs formed using b) SDS d) TEBS surfactant over 16 h as a function of blend composition. Conditions: 2 mg PTB7-Th:EH-IDTBR NPs, 0.2 mol/L ascorbic acid (20 mL), pH 2, 5% (10 µg) Pt, 300 W Xe lamp (350 to 800 nm), 20 cm² reactor. Error bars were calculated as a percentage uncertainty based on 6 repeat measurements. Irradiation spectrum can be found in the experimental section.

This is confirmed by PLQY measurements, which show partial quenching of both PTB7-Th and EH-IDTBR excitons at all two component NP blend compositions (Figure 4.13).

Interestingly, the maximum HER rate (3044 ± 332 µmolh⁻¹g⁻¹) occurred at a blend ratio (EH-IDTBR mass fraction of 90%) where there is insufficient PTB7-Th to efficiently
quench all excitons generated in EH-IDTBR, as indicated by the relatively low EH-IDTBR PLQY (52 %, Figure 4.13c). We attributed the suppressed HER rates at <90 % EH-IDTBR to a core-shell NP morphology as indicated from our structural analyses detailed below. This morphology would allow exciton dissociation at the PTB7-Th/EH-IDTBR heterojunction, but would subsequently confine most photogenerated electrons to the EH-IDTBR core, preventing electron extraction to the Pt cocatalyst at the NP surface, leading to low photocatalytic activity. Increasing the EH-IDTBR fraction increases the probability of NPs having a partially exposed EH-IDTBR core that provides a pathway for electron extraction. This gradually increases the HER rate until the EH-IDTBR mass fraction exceeds a threshold value between 85-90 % at which point PTB7-Th can no longer fully encapsulate the EH-IDTBR core; allowing more efficient extraction of both electrons and holes, and leading to the maximum HER rate at 90 % EH-IDTBR.

Core/shell morphologies are common in polymer/small molecule blend NPs prepared from miniemulsions stabilised by SDS.\textsuperscript{162–164} This morphology occurs because the low volatility components phase segregate to minimize interfacial tension between one another, and between the continuous and disperse phases of the emulsion as the organic solvent is removed.\textsuperscript{165–167} The chloroform/water interfacial tension in the presence of SDS was twice as high when the chloroform phase contained EH-IDTBR vs. PTB7-Th (Figure 4.15).
Therefore, when forming NPs from a mixed PTB7-Th:EH-IDTBR solution, it is
thermodynamically favourable for PTB7-Th to segregate to the surface of the emulsified
chloroform droplets in order to minimise their surface tension; eventually forming NPs
with a PTB7-Th rich shell and an EH-IDTBR rich core. We attribute the difference in
interfacial tensions to a greater affinity between the long aliphatic tail of SDS and the

Figure 4.15: a) Surface tensions b) interfacial tensions measured using the ring method. PTB7-Th
and EH-IDTBR were dissolved in the chloroform phase. SDS and TEBS were dissolved in the
water phase.
higher alkyl chain density of PTB7-Th compared to EH-IDTBR. Correspondingly, a surfactant with a short aromatic tail, such as sodium 2-(3-thienyl)ethyloxybutylsulfonate (TEBS)\(^{168}\) was expected to have increased affinity for EH-IDTBR because it can interact more strongly with its exposed aromatic units. In the presence of TEBS, the chloroform/water interfacial tensions were almost identical when the chloroform phase contained EH-IDTBR vs. PTB7-Th (Figure 4.15). Because the affinity of TEBS for PTB7-Th and EH-IDTBR is approximately equal, radial segregation of PTB7-Th or EH-IDTBR within the NP is no longer thermodynamically favoured. Consequently, when TEBS is employed as the stabilising surfactant, PTB7-Th and EH-IDTBR are expected to be more homogenously mixed throughout the NP and to reside at its surface in approximately equal proportions; providing pathways for efficient extraction of both electrons and holes, thereby increasing the HER rate. Employing TEBS during NP formation dramatically enhanced the HER rates of the blend NPs at all PTB7-Th:EH-IDTBR ratios (Figure 4.14b-c), with the maximum HER rate (28,133 ± 3067 \(\mu\)molh\(^{-1}\)g\(^{-1}\)) increasing by almost an order of magnitude compared to NPs formed using SDS. The optimum blend composition also shifted from an EH-IDTBR mass fraction of 90% to 70%; a composition in which there is more efficient exciton dissociation, as evidenced by PL quenching (Figure 4.13), and which has been previously reported to deliver optimal photon conversion efficiency in the active layer of solar cells.\(^{169}\) Both observations are consistent with a transition from an unfavourable core-shell to a more intermixed NP morphology, and demonstrate that optimising the interfacial properties of an emulsified D/A semiconductor blend through judicious surfactant choice can greatly enhance the
HER rate of D/A semiconductor blend NPs. An even greater increase in the relative HER rate upon replacing SDS with TEBS as the stabilising surfactant was observed for P3HT:PCBM NPs (Figure 4.16), which highlights the broad applicability of this technique for optimising the morphology of D/A NP photocatalysts formed from a wide range of solution processable semiconducting polymers and small molecules.

Figure 4.16: \( \text{H}_2 \) evolution vs. time of P3HT:PCBM 1:1 NPs formed using (a) SDS (b) TEBS surfactants.
**Figure 4.17:** Bright field cryo-TEM images of NP photocatalysts showing differences in internal NP morphology. a) PTB7-Th (SDS) b) PTB7-Th (TEBS) c) EH-IDTBR (SDS) d) EH-IDTBR (TEBS) e) PTB7-Th:EH-IDTBR 30:70 (SDS) f) PTB7-Th/EH-IDTBR 30:70 (TEBS) g) PTB7-Th:EH-IDTBR 30:70 (SDS) after deposition of Pt co-catalyst and 20 h H₂ evolution. The periodic spacings in the red (1.6 nm) and green (2.1 nm) rectangles correspond to the lamellar stacking distances of EH-IDTBR and PTB7-Th respectively.¹⁷⁰,¹⁷¹ h) PTB7-Th/EH-IDTBR 30:70 (TEBS) after deposition of Pt co-catalyst and 20 h H₂ evolution. Note: The dark contrast at the bottom of images a,c,e,f,g arises from the carbon TEM grid. High resolution images of a-h and detailed analysis of images c- can be found in Fig. S6-12.

To confirm that the increased HER rates in NPs formed using TEBS vs. SDS were indeed due to a transition from a core-shell to a more intermixed heterojunction NP morphology, the internal morphologies of PTB7-Th:EH-IDTBR NPs fabricated using TEBS and SDS were analysed by cryo- TEM (**Figure 4.17**). This technique was chosen because it can image the NPs in an environment that is close to their native state, and therefore sample preparation is expected to preserve their morphology. No morphological differences were observed between single component PTB7-Th NPs formed using SDS vs. TEBS (**Figure 4.17a-b**). Both have an amorphous internal morphology, as indicated by the round NP shape and relatively featureless NP projection, which suggests that there is little structural order in the polymer microstructure. Single component EH-IDTBR NPs formed using SDS and TEBS (**Figure 4.17c-d**) both had highly crystalline structures with a lattice spacing of 1.6 nm, clearly visible as lines of alternating high and low electron density (**Figure 4.18**).
Figure 4.18: Cryo TEM image analysis of EH-IDTBR (SDS). Image (a) of NP highlighting analysis areas. The area inside the red square was processed using fast fourier transform (FFT). The resulting reciprocal space image is shown in (b). The profile along the long axis of the area in the blue rectangle is shown in (c). Both FFT (0.68 nm⁻¹ spacing) and profile results show a lattice spacing of 1.6 nm along the long axis of the blue rectangle.
Figure 4.19: Cryo TEM image analysis of EH-IDTBR (TEBS). Image (a) of NP highlighting analysis areas. The area inside the red square was processed using FFT. The resulting reciprocal space image is shown in (b). The profile along the long axis of the area in the blue rectangle is shown in (c). Both FFT (0.63 nm$^{-1}$ spacing) and profile results show a lattice spacing of 1.6 nm.

This spacing is consistent with the diffraction peak at $Q = 0.39$ Å$^{-1}$ in the grazing incidence X-ray diffraction (GIXRD) pattern of an annealed EH-IDTBR thin film.$^{170}$

However, EH-IDTBR NPs formed using SDS mostly consisted of a single EH-IDTBR crystal, as indicated by the hexagonal NP projection and the constant lattice orientation throughout the NP, whereas EH-IDTBR NPs formed using TEBS had a more
polycrystalline structure with multiple lattice orientations and visible grain boundaries. The polycrystallinity is attributed to the higher chloroform/water interfacial tension in the presence of TEBS vs. SDS (Figure 4.15). This induces more rapid EH-IDTBR nucleation and hence a more polycrystalline NP structure. Two component PTB7-Th:EH-IDTBR particles formed using SDS typically exhibit a crystalline phase in the particle core surrounded by a thin amorphous shell. The lattice spacing of the crystalline domain is close to that observed in pure EH-IDTBR (1.7 nm), and the lattice planes have the same orientation throughout the crystalline domain, which suggests that the particle core is formed from a single EH-IDTBR crystal (Figure 4.20).
Figure 4.20: Cryo TEM image analysis of 30:70 PTB7-Th:EH-IDTBR (SDS). Image (a) of NP highlighting analysis areas. The area inside the red square was processed FFT. The resulting reciprocal space image is shown in (b). The profile along the long axis of the area in the blue rectangle is shown in (c). Both FFT (0.60 nm\(^{-1}\)) and profile results show a lattice spacing of 1.7 nm.

In a 95 nm diameter particle shown in Figure 4.17e, the crystalline core radius is approximately 42 nm, and the amorphous shell radius is approximately 5 nm. Modelling the particle as a sphere, and assuming equal densities of PTB7-Th and EH-IDTBR (Figure
4.21) shows that the volume of the core and shell domains is consistent with the 30:70 PTB7-Th:EH-IDTBR mass ratio in the blend.

**Figure 4.21:** Cryo TEM image analysis of 30:70 PTB7-Th:EH-IDTBR (SDS) NP. Calculations based on volumes, assuming a spherical particle and equal densities of PTB7-Th and EH-IDTBR.

<p>| | |</p>
<table>
<thead>
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<tbody>
<tr>
<td>NP diameter measured (nm)</td>
<td>95.2</td>
</tr>
<tr>
<td>EH-IDTBR diameter measured (nm)</td>
<td>84.7</td>
</tr>
<tr>
<td>EH-IDTBR diameter predicted (nm)</td>
<td>84.5</td>
</tr>
<tr>
<td>PTB7-Th radius measured (nm)</td>
<td>5.3</td>
</tr>
<tr>
<td>PTB7-Th radius predicted (nm)</td>
<td>5.4</td>
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</tbody>
</table>
Figure 4.22: Cryo TEM image analysis of PTB7-Th:EH-IDTBR 30:70 (SDS) after deposition of Pt co-catalyst and 20 h H₂ evolution. **a** Image of NP highlighting analysis areas. **b** Profile along the long axis of the area in the blue rectangle on the left hand side. Average D-spacing = 1.58 nm **e** Profile along the long axis of the area in the blue rectangle on the right hand side. Average d-spacing = 2.14 nm.

Furthermore, as shown in Figure 4.17, the 30:70 PTB7-Th:EH-IDTBR NPs formed using SDS occasionally display an additional periodic spacing in the shell (2.14 nm) which corresponds to the lamellar stacking distance of PTB7-Th as determined by GIXRD. Both these observations strongly suggest that that the NPs formed using SDS are composed of a crystalline EH-IDTBR core surrounded by an amorphous PTB7-Th shell, which is in agreement with the interfacial tensions measured in the presence of SDS (Figure 4.15) as well as the trend in HER rate vs. blend composition (Figure 4.14). Two component PTB7-Th:EH-IDTBR NPs formed using TEBS comprise a distributed blend of crystalline and amorphous domains. The crystalline domains showed two different lattice spacings: 1.9 nm and 3.2 nm (Figure 4.23), both of which correspond to minor peaks in the GIXRD pattern of an EH-IDTBR film at Q = 0.33 Å⁻¹ and 0.19 Å⁻¹ respectively.
Figure 4.23: Cryo TEM image analysis of 30:70 PTB7-Th:EH-IDTBR (TEBS) NP. Image (a) of NP highlighting analysis areas. (b) FFT of the area in the upper red square. (c) FFT of the area inside
the lower red square. (d) Profile along the long axis of the area in the upper blue rectangle. (e) Profile along the long axis of the area in the lower blue rectangle. FFT (0.53 nm\(^{-1}\) and 0.31 nm\(^{-1}\) spacings) and profiles show a lattice spacing of 1.9 nm and 3.2 nm for the upper and lower regions respectively.

This suggests that the rapid crystallisation invoked by TEBS can give rise to multiple EH-IDTBR polymorphs forming within the NP, as has been previously observed in P3HT:EH-IDTBR blend films.\(^{172}\) Therefore, based on the 30:70 mass ratio of PTB7-Th and EH-IDTBR within the NP, the crystalline regions with 1.9 and 3.2 nm lattice spacings are both assigned to EH-IDTBR. The lack of any apparent radial segregation between the PTB7-Th and EH-IDTBR within the NP, and an approximately equal distribution of PTB7-Th and EH-IDTBR at the NP surface is consistent with the interfacial tensions measured in the presence of TEBS (Figure 4.15) as well the dramatically increased HER rates achieved with NPs formed using TEBS vs. SDS (Figure 4.16).

**Figure 4.24:** Small-angle neutron scattering (a, b) and deconstructed partial scattering functions (c) for PTB7-Th (PTB7-Th):dEH-IDTBR NPs in H\(_2\)O/D\(_2\)O solutions with SDS (a) or TEBS (b) surfactants. In all plots, solid-black lines represent spherical form-factor model fits to the data. In a) and b), the curves are successively shifted by 10\(^{0.5}\) and 10\(^{0.9}\) respectively, while the upper two curves in part c are both shifted by 10\(^{4}\).
Small-angle neutron scattering (SANS) (Figure 4.24) of blend NPs of PTB7-Th and deuterated EH-IDTBR (dEH-IDTBR) in D₂O/H₂O solutions further supports the morphological analysis from the cryo-TEM. In Figure 4.24a, NPs formed using SDS surfactant near the contrast match point of PTB7-Th (volume fraction of 24.7 % D₂O) indicate a spherical dEH-IDTBR core. At contrast conditions near those of dEH-IDTBR (volume fraction of 82.0 % D₂O), a large feature emerges at a middle-q range between (0.02 < q < 0.2) Å⁻¹. Despite the visual appearance of the NPs in Figure 4.17e, no core-shell model could be fit to the full range of data shown. This includes core-shell models with varying number of shell layers and varying mathematical descriptions of the layer interfaces. To further understand the data, we decomposed the contrast series into partial scattering functions (Figure 4.24c) which isolate the contributions from the PTB7-Th (S_{PTB7-Th}(q)) and dEH-IDTBR (S_{dEH-IDTBR}(q)) to the total scattering function, \( \frac{d\Sigma}{\Omega}(q) \). This analysis clearly shows that the mid-q feature arises from the PTB7-Th domain while the dEH-IDTBR scattering is described well by a spherical form-factor model. Taken together, these data describe the particle as having a spherical dEH-IDTBR core and a PTB7-Th domain(s) that displays a broad secondary length-scale. Given the cryo-TEM analysis, this secondary length scale likely still describes a shell-like feature, but there is some additional structural complexity that is not captured in the core-shell models explored here (e.g., local aggregation of PTB7-Th on core-surface, or PTB7-Th/SDS mixed morphologies). The NPs formed using TEBS also showed no significant secondary length scale at any SANS contrast condition (Figure 4.24b). Simultaneous fits
to the spherical form factor model with the radius \( R \) and log-normal dispersity
\[
\left( \frac{dR}{R} \right)
\]
parameters constrained across contrast conditions yield reasonable fits \( R = 10.2 \, \text{nm}, \frac{dR}{R} = 0.57 \). The decomposed partial scattering functions (Figure 4.24c) also show spherical behaviour, with \( S_{dEH-IDTB} (q) \) displaying a better fit than \( S_{PTB7-TH} (q) \). The deviations in \( S_{PTB7-TH} (q) \) along with those of the full scattering curves at intermediate contrast conditions (Figure 4.24b) indicate that there is microstructure that is not perfectly described by a spherical model. These observations are likely related to the multiple amorphous and crystalline domains observed in the cryo-TEM (Figure 4.17f). Overall, the SANS analysis indicates that the blend NPs prepared with TEBS are more intermixed than their SDS counterparts, consistent with the transition from a core-shell NP morphology to a more intermixed D/A heterojunction NP.
Figure 4.25: Topography (a, b) and contact potential difference (V_{CPD}) (c, d) measured by KPFM. Images correspond to NPs prepared using either SDS (a, c) or TEBS (b, d). Gold and indium tin oxide were used as the standard.

KPFM (Figure 4.25) provides further evidence for the difference in morphology between NPs formed using SDS and TEBS. The work function estimated from the mean surface potentials of NP films was found to be larger for NPs formed using TEBS (5.43 eV - calculated from a mean surface potential of 378 mV) compared to NPs formed using SDS (5.01 eV – calculated from a mean surface potential of -41 mV). This suggests a more EH-IDTBR rich surface in the NPs formed using TEBS, because EH-IDTBR has a higher ionisation potential than PTB7-Th (Figure 4.10).

The co-catalyst is an essential component of the overall photocatalytic system because it facilitates electron transfer from the photocatalyst to protons in the aqueous phase by providing sites for proton adsorption. It also enables accumulation of photogenerated electrons; which is required to drive the two electron reduction of 2H^+ to H_2. 51,120,174
Photodeposited Pt was used as the cocatalyst, and the Pt loading was optimised to maximise the HER rate of the best performing PTB7-Th:EH-IDTBR blend (30:70 PTB7-Th:EH-IDTBR TEBS). Increasing the Pt loading from 0% to 10% Pt resulted in an approximately linear increase in the HER rate up to a maximum of $64.4 \pm 7 \text{ mmol h}^{-1} \text{g}^{-1}$ at 10% Pt (Figure 4). Further increasing the Pt loading lowered the HER rate.

**Figure 4.26:** (a) $\text{H}_2$ evolution vs. time (b) Average HER rates over 16 h of optimised NP photocatalysts (PTB7-Th:EH-IDTBR 30:70 TEBS) with varying Pt loadings. Conditions: 2 mg PTB7-Th:EH-IDTBR NPs, 0.2 M ascorbic acid (20 mL), pH 2, 300 W Xe lamp (350-800 nm), 20 cm$^2$ reactor.

The emergence of a maximum in the HER rate of a photocatalyst at a specific co-catalyst loading has been reported in many previous studies.$^{175-178}$ It occurs because at low Pt concentrations, increasing the Pt loading increases the HER rate by increasing the density of $\text{H}_2$ evolution active sites, however excess Pt lowers the HER rate by hindering light absorption of the photocatalyst, and/or causing increased recombination of photogenerated electrons and holes.$^{175}$ The non-zero HER rate of NPs containing 0% Pt ($38.0 \mu\text{mol h}^{-1} \text{g}^{-1}$) is likely due to PTB7-Th containing over 3000 mg/g residual Pd (Table 4.3), which was previously shown to act as an efficient HER co-catalyst.$^{51}$
Table 4.3: Residual Pd concentrations measured by ICP-OES.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Residual Pd content (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB7-Th</td>
<td>3129</td>
</tr>
<tr>
<td>EH-IDTBR</td>
<td>&lt;1</td>
</tr>
<tr>
<td>F8BT</td>
<td>1170</td>
</tr>
</tbody>
</table>

The HER rate of the best performing NPs (30:70 mass ratio PTB7-Th:EH-IDTBR TEBS) with 10% Pt (64,426 ± 7022 µmolh⁻¹g⁻¹) is, to the best of our knowledge, the highest mass normalized HER rate reported to date for any organic HEP under broadband visible light irradiation. Measuring the EQEs of the NPs over a range of wavelengths (Figure 4.27a) revealed that the NPs were highly active throughout the visible spectrum; achieving EQEs of 2.0%, 2.3%, 4.3%, 5.6% and 6.2% at 400, 500, 620, 660, and 700 nm respectively. This is in contrast to state of the art CNx HEPs which can achieve higher EQEs at wavelengths <450nm but are inactive above 500 nm due to their wide bandgaps. High EQEs at wavelengths >500 nm are essential for the photocatalyst to efficiently utilise photons in the region of maximum solar photon flux, and hence achieve high ηSTH. The EQEs of the PTB7-Th:EH-IDTBR NPs at wavelengths ≥500 nm are significantly higher than those reported for any organic HEP to date, and make the PTB7-Th:EH-IDTBR HEPs particularly attractive for use in a Z-scheme in conjunction with an efficient wide bandgap OEP such as WO3 or BiVO4 that is only active at wavelengths <500 nm.
Figure 4.27: a) External quantum efficiencies at 400, 500, 620, 660 and 700 ± 10 nm and absorbance spectrum of PTB7-Th:EH-IDTBR 30:70 mass ratio (TEBS) NP photocatalysts. b) H₂ evolution vs. time. c) Average H₂ evolution rates of a range of photocatalysts measured over 16 h. **Conditions:** PTB7-Th:EH-IDTBR: 2 mg photocatalyst, 10 % Pt, 20 mL 0.2 mol/L AA. P25 TiO₂: 100 mg photocatalyst, 1.5 % Pt, 20 mL 10 % triethanolamine (TEOA). gC₃N₄: 100 mg photocatalyst, 1 % Pt 20 mL 10 % TEOA. F8BT: 2 mg photocatalyst, 5 % Pt, 20 mL
0.2 mol/L AA. Note: HER rates were higher for TiO$_2$ and gC$_3$N$_4$ with TEOA instead of AA as the sacrificial hole scavenger. Irradiance spectra can be found in Figure 4.28.

The HER rate of the optimised PTB7-Th:EH-IDTBR NP photocatalysts was compared to a range of benchmark materials measured in the same reactor, under illumination from the same light source (Figure 4.27b-c). To ensure a fair comparison between photocatalysts, the HER rates were measured under saturated conditions (0 % light transmission through the reactor throughout the photocatalyst’s absorption range).\textsuperscript{104} The Pt loadings of g-C$_3$N$_4$ (1 %)\textsuperscript{182} TiO$_2$ (1.5 %)\textsuperscript{183} and F8BT (5 %)\textsuperscript{51} were chosen based on previously reported optima, and the photocatalytic activities reported for g-C$_3$N$_4$ and TiO$_2$ are the higher of two measurements taken in the presence of different sacrificial reagents (AA or TEOA). HER rates were compared in terms of the absolute amount of H$_2$ produced per hour.\textsuperscript{180} The average HER rate over 16h of the PTB7-Th:EH-IDTBR NP photocatalysts (128.9 µmolh$^{-1}$) was over 4 times higher than that of TiO$_2$ (32.1 µmolh$^{-1}$), almost 10 times higher than that of commercial CNx (13.3 µmolh$^{-1}$), and over 75 times higher than poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) NPs (1.7 µmolh$^{-1}$), a commonly studied conjugated polymer photocatalyst with no internal D/A heterojunction.\textsuperscript{51,97,129} Although the optimum Pt loading (10 %) was significantly higher for the PTB7-Th:EH-IDTBR NPs than for the other photocatalysts, when comparing photocatalytic activities in terms of HER rate per total mass of Pt used (Figure 4.27d) the activity of the PTB7-Th:EH-IDTBR NPs rises even further above the g-C$_3$N$_4$ and TiO$_2$ benchmarks. This is because the strong light absorption and efficient charge generation of the PTB7-Th:EH-IDTBR NPs allows them to produce significantly more
photogenerated charges per unit mass of photocatalyst. This increases the turnover frequency of the Pt co-catalyst (Table 4.4) compared to the benchmark photocatalysts, which is highly advantageous in terms of both cost and scalability.\textsuperscript{184}

**Table 4.4**: Comparison of H\textsubscript{2} evolution activity of optimised PTB7-Th:EH-IDTBR NPs with a range of benchmark materials.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Pt loading (µg)</th>
<th>HER rate (µmolh\textsuperscript{-1})</th>
<th>TOF Pt (h\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB7-Th:EH-IDTBR</td>
<td>20</td>
<td>128.9</td>
<td>125.7</td>
</tr>
<tr>
<td>P25 TiO2</td>
<td>1500</td>
<td>32.1</td>
<td>4.2</td>
</tr>
<tr>
<td>g-C\textsubscript{3}N\textsubscript{4}</td>
<td>1000</td>
<td>13.3</td>
<td>2.6</td>
</tr>
<tr>
<td>F8BT</td>
<td>10</td>
<td>1.7</td>
<td>33.2</td>
</tr>
</tbody>
</table>
1.16 Conclusion

We have demonstrated the fabrication of organic NP HEPs with an internal D/A semiconductor heterojunction, which significantly improves charge generation inside the NP bulk, and thus greatly enhances photocatalytic activity compared to NPs formed from a single organic semiconductor. By varying the stabilizing surfactant employed during NP fabrication, it was possible to optimize the heterojunction morphology from an unfavorable core-shell structure to a more intimately mixed blend. This improved charge extraction from the NPs and increased the HER rate of PTB7-Th:EH-IDTBR NPs by almost an order of magnitude, leading to the unprecedentedly high HER rate of 64,426 ± 7022 µmolh⁻¹g⁻¹ under broadband visible light illumination, photocatalytic activity throughout the visible spectrum, and EQEs exceeding 5% at 660 to 700 nm. The EQEs at wavelengths >500 nm are the highest reported for any organic HEP to date, and may provide a pathway to increased ηSTH of current Z-schemes via improved visible light utilization. Furthermore, the NP fabrication and heterojunction optimization process provides a platform for the vast library of existing soluble organic semiconductors to be combined and processed into NP photocatalysts energetically tailored to drive a wide range of redox chemistries, including OWS if the D HOMO is energetically matched to the O₂ evolution potential.
1.17 Experimental

1.17.1 Nanoparticle fabrication:

Individual stock solutions (500 ppm) of PTB7-Th and EH-IDTBR were prepared in chloroform. The solutions were heated overnight (80 °C) to ensure complete dissolution and filtered (0.2 μm PTFE). Nanoparticle precursor solutions were prepared from the stock solutions by mixing them in the ratio of the desired NP composition. 5 mL of the NP precursor solution was then added to a 0.5 wt.% solution of surfactant (SDS or TEBS) in water (10 mL), and stirred vigorously for 15 min at 40 °C to form a pre-emulsion, which was then sonicated for 5 min with an ultrasonic processor (Sonics VibraCell VCX130PB) to form a stable mini-emulsion. The mini-emulsion was heated at 85 °C under a stream of air to remove the chloroform, leaving a surfactant stabilised NP dispersion in water. Finally, the dispersion was filtered (0.45 μm glass fibre) to remove any large aggregates or debris from the processor tip.

1.17.2 Dynamic light scattering:

The size distribution of each NP batch was measured by dynamic light scattering (DLS, Malvern Zetasizer ZS, Fig. S1, Table S1). Fig. S1 shows that all NP batches had unimodal size distributions and that the $Z_{\text{avg}}$ hydrodynamic diameter between batches remained relatively constant at 50-80 nm regardless of whether SDS or TEBS was used as the stabilising surfactant. TEBS narrowed the NP size distributions and slightly increased the $Z_{\text{avg}}$ NP size for all PTB7-Th:EH-IDTBR ratios, but overall all NP batches were of a similar size. This is important when comparing HER rates between batches, because NP size
affects the total available surface area, which would likely affect the HER rate. Having samples with similar size distributions minimises this variation and allows the effects of NP composition and morphology to be isolated.

1.17.3 Cryo Transmission Electron Microscopy:

Cryo-TEM of the samples was carried out with a Titan Krios 80-300 TEM from Thermo-Fisher Scientific, USA. This microscope is optimized for carrying out cryoTEM analysis of liquid samples. It is also equipped with an energy-filter of model GIF Quantum 968 from Gatan, Inc., USA, underneath the column to filter the energy-loss electrons to improve the contrast in the acquired images. Moreover, behind the GIF column, a highly sensitive direct electron complementary metal oxide semiconductor (CMOS) camera of model K2, also from Gatan, Inc., USA, was installed for the recording of high-resolution images at extremely low electron dose conditions (~1 e/Å²). Specimen preparation of samples for cryoTEM analysis was carried out by using an automated plunge-freezing tool of model Vitrobot Mark-IV. Moreover, the specimens were prepared with a special type of copper TEM-grid of model Quatifoil MultiA. These grids have a carbon layer with various size holes and were chosen with a purpose of varying ice-thickness in the holes. In this way, the chance of organic particles being present in the specimen was dramatically higher than with the single hole-size carbon containing grid. Each specimen was prepared by placing 3.5 micro-litre of solution onto grids followed by 1 second of blotting-time and plunge-freezing into liquid ethane cryogen. The cryoTEM analysis was performed by setting the microscope at the accelerating voltage of 300 kV. Prior to the analysis, the
microscope as well as GIF were aligned to have higher quality images. Furthermore, the images were recorded under so called dose-fractionation conditions. In fact, instead of acquiring a single frame with total electron beam exposure time, the images were acquired in stacks that contained frames whose exposure time was more than ten times smaller than the total exposure time. The acquired stacks were then aligned and summed along z-direction in order to have final images. This exercise of image-recording ensured higher quality images of organic particles with as minimum damage as possible. The total electron dose given to images, acquired at low-magnifications (<50,000X) was kept below 10 e/Å2. Whereas, higher magnification images (>100,000X) received the electron dose of about 20 e/Å2 so as to maintain a good signal-to-noise condition. It is to be noted that the entire image acquisition as well as processing was performed using Gatan Microscopy Suite of version 3.2.

1.17.4 Hydrogen evolution measurements:

Hydrogen evolution from PTB7-Th/EH-IDTBR NPs was measured using AA as a sacrificial electron donor. PTB7-Th/EH-IDTBR NPs with varying PTB7-Th:EH-IDTBR ratios (2 mg) in 0.2 M AA (20 mL) were loaded into a recirculating batch reactor (area = 452 mm²) which has been previously reported.104 The desired Pt loading was achieved by adding a specific amount of aqueous potassium hexachloroplatinate solution (0.401 mg/mL Pt). The reactor was evacuated and purged with Ar 5 times to remove oxygen, and the pressure was set to 100 Torr. The suspension was stirred and illuminated with a 300 W Xe lamp (Asahi Max 303, spectrum shown in Figure 4.28) fitted with a UV-vis mirror module (350-
800 nm) and H₂ evolution was quantified by a gas chromatograph equipped with a thermal conductivity detector. The same method was used to measure H₂ evolution from TiO₂ and g-C₃N₄, except in this case 100 mg of photocatalyst was used, and the reaction was carried out either in 0.2 M AA, or 10 vol.% triethanolamine.

![Figure 4.28](image)

Figure 4.28: Average irradiance over reactor area of Xe lamp used for H₂ evolution and external quantum efficiency measurements.

Turnover frequency (TOF) over 16 h was calculated according to equation 5.1:
$$TOF = \frac{mol H_2 h^{-1}}{mol Pt}$$

1.17.5 EQE measurements:

EQE measurements were carried out in the same way as hydrogen evolution measurements, but with suitable band pass filters fitted to the light source. The sample was first illuminated under unfiltered light (350-800 nm) for 4 h to complete Pt photodeposition. Then the reactor was evacuated and purged with Ar 5 times to remove all of the $H_2$ evolved during this time. The light source was fitted with a band pass filter, and illuminated with filtered light within a narrow wavelength range (irradiance spectra in Fig. S16). The EQE was calculated using Equation 1, where $nH_2$ represents the number of moles of $H_2$ evolved per hour, and $n$ photons represents the total number of photons incident on the reactor per hour. Photon flux was measured using a calibrated spectrometer (Ocean Optics USB2000 calibrated with an Ocean Optics DH3-plus light source) fitted with a fibre optic cable and a 0.4778 cm$^2$ cosine corrector.

**Equation 1:**

$$EQE \, (\%) = \frac{200nH_2}{n \text{ photons}}$$
1.17.6 Kelvin Probe Force Microscopy (KPFM):

Nanoparticles were drop-cast on ITO coated glass substrates and characterised with a SOLVER NEXT SPM (NT-MDT) using an atomic force microscopy (AFM) measuring head. To confirm the core-shell morphology, samples were placed in a plasma-asher (HPT-100, Henniker plasma) for two ten second periods, a few nanometres of material was removed from the surface of the NPs. Topography and surface potential were measured in semi-contact mode using a 20 nm PtIr-coated conductive 0.01-0.025 Ohm-cm Antimony (n) doped Si cantilever (SCM-PIT, Veeco). The cantilever had a resonant frequency and stiffness of 60-100 kHz and 1-5 N/m, respectively. The work-function of the tip was estimated by measuring the contact potential difference ($V_{CPD}$) of a gold standard (5.1 eV) from Digital Instruments Veeco Metrology Group and using the equation 2.10:

$$V_{CPD} = \frac{\Phi_{tip} - \Phi_{sample}}{-e}$$

Where $\phi$ is the work-function and e the charge of an electron. The work-function of the tip was found to be 5.05 eV (mean $V_{CPD}$ for gold = 50 mV). To confirm, a commercial ITO sample was measured and the work-function estimated as 4.84 eV (mean $V_{CPD}$ for ITO = -213 mV).
1.17.7 Surface and interfacial tension measurements:

Surface and interfacial tensions were measured with a Kruss Tensiometer using the ring method. The probe was rinsed in water and heated until it was red hot. The glass vessel used to hold the liquid was cleaned with acetone and rinsed with water. To confirm no contamination, before each measurement, the surface tension of water was measured. The liquid to be measured was placed in the glass vessel, and the temperature allowed to equilibrate for 30 min. The concentration of TEBS or SDS in deionized water was 0.5 wt % and for PTB7-Th or EH-IDTBR 0.5 mg/ml in chloroform. The surface tension measurements were performed by attaching the probe to the balance. The glass vessel containing the liquid to be measured was raised until the probe was just above the liquid. The probe and liquid were slowly brought together until in contact with one another. The interfacial tension was calculated according to equation 2.11.

\[
\sigma = \frac{F_{\text{max}} - F_v}{L \cdot \cos \theta}
\]

(2.11)

Where \( F_v \) is the weight of liquid volume, \( L \) the wetted length, and \( \theta \) the contact angle. \( \theta = 0 \) because the force vector is parallel to the direction of motion. A Harkins and Jordan correction factor is applied to correct for the curvature of the film being greater on the inside than the outside of the ring.
5. Summary and future outlook

The overall aim of this dissertation was to improve the visible light activity of current state of the art organic semiconductor particulate HEPs. Organic NP HEPs were chosen as the class of HEP to optimise due to their well-defined constituent semiconductors which can be systematically tailored to allow rational photocatalyst design.

In Chapter 2, progress was made towards understanding the mechanism of hydrogen evolution from organic semiconductor HEPs. Residual Pd, originating from semiconductor synthesis via Pd catalysed polycondensation polymerization, was shown to act as an efficient H\textsubscript{2} evolution co-catalyst even at ppm level concentrations. Pd had a profound effect on the photocatalytic HER rate of conjugated polymers, to an extent that when it was removed, it could change a polymer from being highly active to completely inactive. The presence of residual Pd should therefore be considered when designing organic HEPs, but also for processes such as CO\textsubscript{2} reduction, where proton reduction is a competing and unwanted side reaction. Guidelines of how to make reliable comparisons between polymer semiconductors synthesized using Pd were proposed, and the author hopes that they will facilitate rational HEP design in the young and chaotic field of organic photocatalysis.

In Chapter 3, novel NP HEPs containing D/A heterojunctions were fabricated from a range of polymer donors and polymer and small molecule acceptors. In all cases, the D/A heterojunction was shown to significantly enhance photocatalytic activity by improving exciton dissociation within the NP. However, NPs prepared using the
common surfactant SDS formed unfavourable core-shell structures which led to low H₂ evolution activity. By varying the stabilizing surfactant employed during NP fabrication, it was possible to optimize the heterojunction morphology from the unfavourable core-shell structure to a more intimately mixed blend. This improved charge extraction from the NPs and greatly increased HER rate. NPs formed from an optimized blend of PTB7-Th:EH-IDTBR achieved an unprecedentedly high HER rate of 64,426 ± 7022 µmolh⁻¹g⁻¹ under broadband visible light illumination, photocatalytic activity throughout the visible spectrum, and EQEs exceeding 5% in the region of maximum solar photon flux. The EQEs at wavelengths >500 nm were the highest reported for any organic HEP at the time of writing, and may provide a pathway to increased ηSTH of current Z-schemes via improved visible light utilization. Furthermore, the NP fabrication and heterojunction optimization process provides a platform for the vast library of existing soluble organic semiconductors to be combined and processed into NP photocatalysts energetically tailored to drive a wide range of redox chemistries, including OWS if the donor HOMO is energetically matched to the O₂ evolution potential.
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