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Porous-Hybrid Polymers as Platforms for Heterogeneous Photochemical Catalysis

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Abstract. A number of permanently porous polymers containing Ru(bpy)₃ photosensitizer or a cobaloxime complex, as a proton-reduction catalyst, were constructed via one-pot Sonogashira-Hagihara (SH) cross-coupling reactions. This process required minimal workup to access porous platforms with control over the apparent surface area, pore volume, and chemical functionality from suitable molecular building blocks (MBBs) containing the Ru or Co complexes, as rigid and multi-topic nodes. The cobaloxime molecular building block, generated through *in situ* metalation, afforded a microporous solid that demonstrated noticeable catalytic activity towards hydrogen-evolution reaction (HER) with remarkable recyclability. We further demonstrated, in two cases, the ability to affect the excited state lifetime of the covalently-immobilized Ru(bpy)₃ complex attained through deliberate utilization of the organic linkers of variable dimensions. Overall, this approach facilitates construction of tunable porous solids, with hybrid composition and pronounced chemical and physical stability, based on the well-known Ru(bpy)₃ or the cobaloxime complexes.

Key words: porous-organic polymers, Ru complexes, photochemical heterogeneous catalysis, solid-state NMR, hydrogen evolving cobaloxime catalysts.

Introduction

Current and future global energy demands necessitate innovations to tap most available energy resources effectively and responsibly.¹⁻² In creating such innovations, scientists are actively exploring new technologies to design and develop new materials for harvesting solar energy. Despite the extensive efforts devoted to accomplish this goal, utilizing solar energy efficiently and cost-competitively has yet to be realized.³⁻⁵ In addition to photoelectrical applications of Ru dyes⁶⁻⁸, Ru and Co complexes have desirable photocatalytic properties for photochemical energy conversion applications, primarily for photocatalytic water splitting.⁹⁻¹⁰ Of particular interest are heterogeneous photocatalysts that can easily be separated and recycled from a reaction mixture.¹¹⁻¹³

In efforts to address certain demanding applications, like gas storage and separation, CO₂ capture, catalysis, and energy conversion, a large number of porous solids, namely metal-organic frameworks (MOFs),¹⁴ conjugated microporous polymers (CMPs),¹⁵ porous cross-linked polymers (PCPs),¹⁶⁻¹⁷ and porous-organic polymers (POPs),¹⁸ are being actively investigated. Porous solids, in general, are amenable to the bottom-up assembly from judiciously designed molecular building blocks (MBBs). POPs are an emerging class of polymeric materials accessible through covalent linkage of pre-selected MBBs.

POPs commonly exhibit rigid structures, high thermal and chemical stabilities, low densities, and in certain cases permanent porosity with specific surface areas surpassing those of well-known zeolites and porous silicates.¹⁹⁻²¹ Recent reports outlined several synthetic pathways to construct POPs including the Sonogashira-Hagihara (SH) cross-coupling reaction.²² This approach, as being further exploited here, opens the door for utilization of a wider range of functional MBBs, namely brominated aromatic moieties, as compared with previous systems reported by Lin and co-workers that demonstrated photocatalytic activity of PCPs constructed through cobalt-catalyzed alkyne trimerization reaction.¹⁶⁻¹⁷ Our approach allowed the simultaneous incorporation of different building blocks into the solids backbone by including different brominated aromatic building blocks in the one-pot synthesis reported herein. Moreover, the multi-topic nature of the brominated Ru or Co complexes (up to 6 and 4 extension points, respectively) utilized in this study resulted in enhanced microporosity of the solids, in contrast to previous systems utilizing lower connectivity of the building blocks and consequently resulting in nonporous solids.¹⁷

In order to generate artificial photosynthesis systems, several attempts were made to mimic the energy transfer processes of photo-generated excitons in naturally occurring photosystems.²³⁻²⁶

Scheme 1. Synthesis scheme for PRP-1 (left) and a geometrically optimized polymer fragment model showing extension points highlighted in yellow (right). Nitrate ions are omitted for clarity; C (gray), H (white), N (blue), Ru (deep red).

A platform material that is amenable to rational design is thus of significance, facilitating optimization of intermolecular interactions towards applications in photochemical catalysis. Furthermore, a porous solid platform offers the potential for stability against several catalyst degradation processes, including leaching out of the support and/or self-induced degradation.^{18, 27} The broad range of chemistry that can be implemented to fine tune certain platform materials includes (i) the degree of conjugation, length, connectivity, and functionality of the linkers, (ii) the various types of chromophores (iii) the large number of derivatives available for each chromophore, and (iv) the possibility of introducing heterogeneity into the structures by utilizing mixed chromophores. A number of MOFs based on certain chromophores have been recently reported and their photocatalytic behavior explored.^{25, 28-30} Such solids with crystalline structures rely on coordination bonds between functional organic molecules, as linkers, and metal ions/clusters, as nodes, to sustain their structure. This very nature of MOFs can cause electronic isolation of the chromophores as well as, in some cases, chemical instability in certain environments, like moisture, acidic, or alkaline solutions, due to the reversible nature of the coordination bond. Our focus here is directed towards porous platform solids constructed through covalent linkage of designed multitopic chromophore, namely the Ru-polypyridyl photosensitizer,³¹ linked through proper organic linkers to generate a family of five porous, ruthenium-based, polymers (PRP 1-5). A structure-dependence of excited state lifetime is demonstrated for two of the reported PRPs. Additionally, we investigated the potential to construct a porous, cobaloxime-based, polymer (PCoP) incorporating the known proton reduction catalyst, the cobaloxime.³² Finally, the catalytic performance of the PCoP was investigated and demonstrated remarkable catalytic behavior in terms of the turn-over-number in hydrogen evolving reaction, and recyclability under certain conditions.

Results and Discussion

In this report, we developed a one-pot synthesis strategy based on previously established SH cross-coupling pathways to construct porous organic polymers,^{53,54} where under carefully selected reaction conditions,³³⁻³⁴ porous polymers from bridging alkyne linkers and brominated Ru-polypyridyl or cobaloxime derivatives were successfully constructed, **Scheme 1**. In our approach, we expanded the realm of previously utilized cross-coupling reactions of rigid and directional molecular building blocks (MBBs)^{22, 33-34} into more intricate ruthenium-based, and cobaloxime-based brominated metal complexes. This new approach afforded extended porous solids containing the Ru-polypyridyl or cobaloxime functionalities as integral parts of the polymers' backbone. Construction of porous solids from the aforementioned building blocks was accomplished under relatively mild reaction conditions that preserved the functionality and directionality of the building blocks. Indeed, five different compounds, PRPs 1-5, were isolated and characterized by several characterization techniques. Additionally, the cobaloxime-based polymer, PCoP, was synthesized then characterized similarly.

Due to the irreversible C–C bond formation step, POPs constructed through cross-coupling reactions are widely amorphous solids insoluble in most common solvents.³⁵ This aspect, while desirable for ease of separation and recyclability, however, precluded utilization of several solution or diffraction based structure characterization techniques. However, a wide range of structural characterization techniques including spectroscopic techniques like Fourier-transform infrared (FTIR), solid-state NMR, UV-Vis spectroscopy and energy-dispersive X-ray (EDX) spectroscopy were used to characterize the reported compounds. Other used characterization techniques including scanning electron microscopy (SEM), gas sorption, elemental analysis, and thermogravimetric analysis techniques, facilitated drawing a more detailed picture for the chemical composition of the obtained compounds.

Figure 1. N_2 gas sorption isotherms for the porous polymers **PRP1-5** and for **PCoP**.

In particular, the reaction between tris-(4,4'-dibromo-2,2'-dipyridyl) ruthenium (II) nitrate and 1,3,5-triethynyl benzene resulted in a deep-brown solid, **PRP-1**. The isolated solid was found to be insoluble in water and common organic solvents including DMF, DMSO, acetone, DCM, acetonitrile, MeOH, and EtOH. Similar reaction conditions with different alkyne linkers and/or additional spacers were utilized to construct compounds **PRP2-5** (please refer to Supporting Information, SI). The materials obtained were isolated by simple filtration and were subjected to solvent/guest exchange to remove resid-

ual solvent and/or precursors. To extend our previous methodology into the realm of porous cobaloxime-containing polymers, *in situ* metalation of the 1,2-bis(4-bromophenyl)ethane-1,2-dione dioxime by cobalt ions was first attempted (SI). When followed by addition of the terminal alkyne and proper catalyst, the targeted cobaloxime-based porous polymer was isolated as deep-brown solid, **PCoP**. N_2 sorption isotherms for **PRP 1-5** and **PCoP** were collected and are shown in **Fig 1**. The Brunauer–Emmett–Teller (BET) model applied to the N_2 isotherm of the prototypal **PRP-1** demonstrated a type I-like

isotherm³⁶ with calculated BET surface area of 541 m²/g. Similar analysis of compounds **PRP 2-5** indicated surface area values in the range of 348 to 826 m²/g. In **PRP-2**, the ditopic 1,4-diethynylbenzene was used as the bridging alkyne linker. The observed reversible type II-like isotherm³⁶ for **PRP-2** could potentially indicate the presence of a mixed microporous/mesoporous pore system or alternatively can be attributed to gas condensation within the voids between sub micrometer agglomerates.³⁷ This behavior could be ascribed to structural defects resulting from less than complete cross-coupling of the six-connected nodes through the linear ditopic alkyne linker. In compound **PRP-3**, the 3,4-dibromothiophene molecule was added to the reaction mixture to introduce the thiophene ring as a ditopic linker. Thiophene was selected due to its wide utilization as a molecular component in organic solar cells and molecular wires. Additionally, it appears that the directionality of the 3,4-dibromothiophene ring led to some backbone twist during formation of **PRP-3**, thus increasing its surface area as compared to **PRP-1**. In an additional example, the triphenylamine extended linker was used to construct **PRP-4** which demonstrated increased surface area and pore volume as compared to **PRP-1** (644 m²/g, 0.43 cm³/g for **PRP-4** as compared to 541 m²/g, 0.34 cm³/g for **PRP-1**). In compound **PRP-4**, the triphenylamine MBB, utilized as an extended three-connected linker, was judiciously selected due to its wide utilization as an electron donor species (hole transport medium) in organic photovoltaic cells. The observed N₂ sorption isotherm for **PRP-3,4** can be classified as type IV-like character demonstrating H2-type hysteresis.³⁷ This behavior is common among porous organic polymers and can be associated with swelling of the polymers rather than taken to indicate presence of mesoporosity inside the material.³⁷ In **PRP-5**, the heteroleptic Ru(NCS)₂(bpy)₂ coordination cluster was utilized for its known photoactivity,³⁸ and resulted in a microporous polymer with fully reversible, type-I N₂ sorption isotherm (BET surface area of 349 m²/g). The pore size distribution in **PRP-5** is remarkable as it indicates uniform and narrow distribution at ranges of 5, 10 and 15 Å (SI). The reduced apparent surface area of **PRP-5** relative to the rest of the reported compounds here can be attributed to the reduced number of extension points (four brominated aromatic carbons as compared to six in the earlier examples) from which polymer growth and inter-chain linkage commenced. The N₂ sorption isotherm for **PCoP**, Fig. 1, demonstrated a type I-like character. For **PCoP** the calculated apparent BET surface area and total pore volume were found to be 874 m²g⁻¹, and 0.5 cm³g⁻¹, respectively.

The solid-state ¹³C-CPMAS-NMR spectra collected for **PRPs 1-5**, shown in Fig 2, clearly indicated the targeted assembly of molecular building blocks into extended networks. The observed ¹³C chemical shifts include those for internal alkyne (80-90 ppm), aromatic carbons (120-140 ppm) and aromatic carbons (α) to the nitrogen atoms in the bpy rings (C6 and C2 expected at ~150 and ~157 ppm, respectively).³⁹ Comparison between the relative ¹³C peak intensities at the

Figure 2. Stacked ¹³C-CP-MAS NMR spectra of **PRPs 1-5**.

five **PRPs** indicates an increase in the ratio of aromatic, ¹³C signals (~120 ppm) relative to the other ¹³C signals moving from **PRP-1** to **PRP-4**. This is in agreement with the expected increase in the number of aromatic secondary carbons per polymeric repeat unit from **PRP-1** to **PRP-4**, further supporting the repeat unit structures proposed for the respective **PRPs**. The distinctly observed signal (~143 ppm) in the ¹³C-CPMAS NMR spectrum of **PRP-5** falls within the range expected for isothiocyanate ions. This observation further supports the proposed structure of **PRP-5**, to contain Ru-coordinated isothiocyanate. The presence, if any, of unreacted brominated aromatic carbon atoms (expected chemical shift at ~135 ppm) cannot be ascertained from the collected spectra due to masking by signals from other parts of the polymers. The ¹³C-CPMAS spectrum for **PCoP** is shown in the SI and demonstrated peaks at chemical shifts of 89.47 ppm (attributed to the internal alkyne *sp* carbon atoms) and at 129.7 ppm (assigned to the aromatic carbons in the backbone). The broadness of the observed peaks indicated relatively heterogeneous texture of the material and can be ascribed to polymer length/connectivity polydispersity. No additional peaks were detected in the spectrum and the absence of other characteristic peaks could potentially be ascribed to broadening to the signal due to interactions with the Co center.

The successful assembly of the MBBs into **PRPs 1-5** and in **PCoP** was also evidenced by attenuated total reflectance FTIR spectroscopy (SI). Linkage through alkyne groups was shown from the absence or the strong attenuation of the terminal alkyne ν_{C-H} stretching band (observed at 3272 cm⁻¹ for 1,3,5-triethynylbenzene and at 3260 cm⁻¹ for 1,4-diethynylbenzene) and the detection of the ν_{C≡C} stretching band shifted towards higher wave numbers in the products as compared to reactants (From 2105~2112 cm⁻¹ in starting alkynes to 2170~2200 cm⁻¹ in the products). Additional infrared spectroscopic markers in the FTIR spectra of the isolated

Figure 3. Transient absorption spectra for **PRP-1,4** and **PCoP** and the triplet state decay curves for **PRPs-1, 3, 4** and **PCoP**.

compounds included a nitrate stretching band at $\sim 820\text{ cm}^{-1}$ and bpy-centered bands, $\nu_{(\text{C-C}/\text{C-N})}$, at $1570\text{--}1600\text{ cm}^{-1}$ and $\nu_{(\text{C-C}/\text{Ru-N})}$ at 1480 cm^{-1} .⁴⁰ Additionally, in **PRP-5**, a strong absorption band observed at 2094 cm^{-1} was assigned to the $\nu_{\text{C=N}}$ stretching of the isothiocyanate ion. For the **PCoP**, additional characteristic IR spectroscopic markers were observed, including broad $\nu_{\text{O-H}}$ stretching band centered at 3300 cm^{-1} and a $\nu_{\text{C=N}}$ stretch-

ing band at 1670 cm^{-1} , further supporting the incorporation of the oxime functionality into the isolated solid.

As time-resolved laser spectroscopy is an extremely powerful technique to probe the excited state deactivation pathways directly, we performed ultrafast pump-probe experiments with femtosecond and broadband capabilities to record the time-resolved, excitation-induced difference spectra. Detailed information about the experimental setup can be found elsewhere.⁴¹⁻⁴² The transient absorption and the excited state decay data for **PRP-1,3,4**, recorded following 340 nm optical excitation pulses, are shown in **Fig. 3**. As can be clearly seen, the triplet state lifetime of **PRPs-3, 4** are almost seven times larger than that of **PRP-1** ($1.21\text{ }\mu\text{s}$, $1.18\text{ }\mu\text{s}$, and 168 ns , respectively), indicating the dependence of the triplet-state lifetime on the backbone structure and hence microenvironment of the chromophore in the PRPs.

Indeed, the more widely spaced chromophores in **PRPs-3, 4** displayed prolonged excited-state lifetimes. One possible explanation for this observation is that enhanced excited state stabilization through solvation by enclathrated solvent molecules is more pronounced in **PRPs-3, 4** with larger pore volumes and surface area values. Alternatively, enhanced geometrical separation of the chromophores, in **PRPs-3, 4** as compared to **PRP-1**, could be responsible for the observed increase in the excited state lifetime. This is to be expected assuming certain relaxation pathways, like the Dexter triplet-to-triplet energy transfer process, to be weaker in **PRP-3, 4** with more spaced chromophores. It is worth pointing out that the triplet state lifetime values of our compounds, especially **PRPs-3, 4** are much longer than triplet state lifetimes of other derivatives of the Ru photosensitizer that are commonly used in dye-sensitized solar cells.^{38, 43} It is relevant here to mention recent reports on almost nonporous Ru-based conjugated polymers (CPs)^{17, 44} which demonstrated good photochemical catalytic activity. Efficient excited-state migration via Dexter triplet-to-triplet energy transfer among the chromophore framework was postulated in these polymers.²⁹⁻³¹ Similarly, the excited-state lifetime of the **PCoP** was measured (101 ns) and was found to relax relatively quickly to its ground state.

To characterize the surface morphology of some of the constructed solids, field-emission (FE-SEM) images were obtained for **PRP-1** and **PCoP**, **Fig. 4**. The FE-SEM image of the **PRP-1** revealed relatively smooth surface morphology indicative of small particle/grain size. The FE-SEM image of the **PCoP** revealed rough surface texture indicative of larger particle/grain size. Additionally, EDX color-coded elemental analysis maps were recorded for the aforementioned two solids, **Fig. 4**. The EDX maps clearly indicated mostly carbon composition of the compounds analyzed, with noticeable presence of Ru in **PRP-1** and Co in **PCoP**. Additionally, the EDX analysis for both solids indicated the presence of Br, ascribed to polymer chain termination with brominated aromatic molecules, SI.

Figure 4. SEM images of PRP-1 (a) and the PCoP (b) and the corresponding color-coded EDX elemental analysis maps (labeled images).

The proton reduction photocatalytic activity of **PCoP** was studied under standard conditions using $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as a photosensitizer under visible-light irradiation ($\lambda > 415 \text{ nm}$) (table 1). In the first system, an organic solvent, acetonitrile (ACN), was combined with triethanolamine (TEOA) acting both as a sacrificial electron donor and a proton donor, respectively (5:1, v/v). Under these conditions **PCoP** proved active, as $0.90 \mu\text{mol H}_2/\text{mg}$ was produced after 5 hours irradiation (entry 1 in Table 1). Based on EDX analyses, our material was shown to contain $\sim 1.9 \pm 0.4 \text{ wt\%}$ cobalt, thus the activity translated in 2.8 TON in 5 hours reaction time. If TEOA was replaced by triethylamine (TEA) (entry 2 in Table 1) or ascorbic acid (entry 3 in Table 1) in the presence of water as the proton donor, almost no catalytic activity could be observed in the same period of irradiation time. In the second system water under moderately acidic conditions (pH 3.0-5.0) was used as the solvent. Interestingly, when the catalyst **PCoP** was assayed in water containing 0.1 M ascorbic acid (entry 4-8 in table 1), especially when the pH of the solution was at 4 and 4.5, an impressive H_2 production ($10.17 \mu\text{mol}/\text{mg}$, 32 TON, and $7.49 \mu\text{mol}/\text{mg}$, 24 TON, respectively) was observed during 5 hours photolysis. This pH-dependence is well known⁴⁵: indeed at too acidic pH, the reducing power of ascorbic acid is weakened. At too basic pH, catalysis is limited by the availability of protons in the system. In both solvent conditions, no H_2 was detected in the absence of the catalyst **PCoP**, or the photosensitizer $\text{Ru}(\text{bpy})_3\text{Cl}_2$, or when the reactions were undertaken in the dark. Under the optimal conditions, using 10 mM of the photosensitizer, a time curve was obtained for long term experiments, **Fig. 5**, showing a sustained production of H_2 . An initial rate of $0.14 \mu\text{mol H}_2/\text{mg}/\text{h}$ and 21 TONs after 62 hours were obtained using the ACN/TEOA system, while the water/ascorbate system was about 20 times more efficient, with an initial rate of $2.46 \mu\text{mol}/\text{mg}/\text{h}$ and 62 TONs after 10 hours. However, the former proved much more photostable, as the

Table 1. Photocatalytic H_2 production under different solvent systems^a

Entry	Solvent system	H_2 production ($\mu\text{mol}/\text{mg cat.}$)
1	ACN/TEOA ^b	0.90
2	ACN/ H_2O /TEA ^c	0
3	ACN/ H_2O /ascorbic acid, pH 4.0 ^d	0.02
4	H_2O /ascorbic acid, pH 3.0 ^e	0
5	H_2O /ascorbic acid, pH 3.5 ^e	1.43
6	H_2O /ascorbic acid, pH 4.0 ^e	10.17
7	H_2O /ascorbic acid, pH 4.5 ^e	7.49
8	H_2O /ascorbic acid, pH 5.0 ^e	0

^aPhotocatalytic H_2 production in the presence of **PCoP** as a catalyst, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ as a photosensitizer, and a 415 nm cutoff filter.

^bVolumetric ratio of ACN/TEOA is 5 : 1

^cVolumetric ratio of ACN/ H_2O /TEA is 4.5 : 4.5 : 1

^dVolumetric ratio of ACN/ H_2O is 1 : 1, 0.1 M ascorbic acid, pH adjusted by NaOH

^e0.1 M ascorbic acid, pH adjusted by NaOH

PCoP under this condition could be recycled for at least 5 times (16 hours photolysis each run) with maintaining full activity, **Fig. 6a**. The retention of the activity of the solid catalyst after 5 days of cumulative photolysis time proves the impressively good photostability of **PCoP** in this system. In contrast in the water/ascorbate system, the catalyst lost more than half of its activity during the second run and was totally inactivated during the third one, **Fig. 6b**. It is possible that the acidic condition of the system, while favoring proton reduction, affected the integrity of the catalyst, under irradiation. The stability of the **PCoP**-based system is remarkable. Recently heterogeneous coordination polymers and functionalized metal-organic frameworks (MOFs) have been reported to

Figure 5. Catalytic activity for the PCoP towards H₂ production in the two systems reported. Conditions: Ru(bpy)₃Cl₂ (10mM), filter > 415nm. Black squares: H₂ evolution in a 5:1 (v:v) ACN/TEOA solvent system under N₂ saturated conditions. Red circles: H₂ evolution in an H₂O/ascorbic acid (0.1 M) pH 4 solvent system under N₂ saturated conditions.

Figure 6. H₂ production measured during recyclability experiments. (a) ACN/TEOA solvent system (runs of 16 hours photolysis each), (b) H₂O/ascorbic acid (0.1 M) pH 4 solvent system (runs of 16 hours photolysis each).

function as catalysts for light-driven hydrogen generation, however in general with much less stability. For example, a Cu(II) coordination polymer was inactivated after 5 hours reaction.⁴⁶ Incorporation within MOFs of dinuclear iron complexes mimicking the active site of hydrogenases gave catalysts for photocatalytic hydrogen generation. However, the reaction stopped after a very short reaction time (< 2hours) due to catalyst deactivation.⁴⁷⁻⁴⁸ Finally, it is interesting to note that while molecular cobaloximes are good catalysts as well, they also suffer, within comparable photochemical conditions, from low stability, with full inactivation after a few hours.⁴⁹⁻⁵⁰ We also found that the cobaloxime precursor of PCoP was active using the ACN/TEOA system and Ru(bpy)₃Cl₂ as the photosensitizer under the conditions used with PCoP (SI). As the amount of Co was comparable to that provided by the PCoP catalyst, the data show that the free cobaloxime was slightly less efficient. Furthermore, it was found to be much less stable as H₂ production stopped after about 10 hours reaction. It was recently demonstrated that stabilization of these homogeneous molecular catalysts can be obtained using axial

N-ligands such as imidazole derivatives.⁵¹ Such a strategy might also be used to further improving the PCoP catalyst. A recent report by Cooper and co-workers demonstrated photochemically-active family of linear, planarized conjugated polymers of fluorene, carbazole, dibenzo[b,d]thiophene and dibenzo- [b,d]thiophene sulfone functionalities. The reported polymers were investigated for photochemical hydrogen evolution, where among the reported polymers the most active dibenzo[b,d]thiophene sulfone copolymer showed the most activity.⁵² Our PCoP performed with comparable TOF to most of the reported polymers by Cooper and Co-workers in terms of μmol H₂/hr produced for each mg of catalyst used, with the exception being the most two active polymers P6 and P7. As our PCoP catalyst is microporous with relatively large surface area, in contrast to the non-porous polymers studied in this recent report, there is a wide potential to tune and further enhance its catalytic activity through controlled diffusion of redox shuttles, electrolytes, and/or photosensitizers.

CONCLUSION

In conclusion, we describe, for the first time and to the best of our knowledge, an approach to constructing permanently porous polymers of the ruthenium-tris(2,2'-bipyridyl), Ru(bpy)₃ and cobaloxime with large surface areas, variable backbone functionality and long-lived excited state lifetimes that can potentially be exploited for applications in heterogeneous photocatalysis. In addition, our approach utilizes one-pot Sonogashira-Hagihara cross-coupling synthesis, with minimal workup through simple filtration and solvent/guest exchange, making it very appealing for large-scale production. Our results clearly indicate a lifetime dependence of the chromophores on the chemical nature of the backbone, and furthermore photocatalytic activity towards proton reduction and recyclability of the porous catalyst is explored.

EXPERIMENTAL SECTION

All air-sensitive manipulations were performed under a dry N₂ atmosphere using standard Schlenk line techniques. Chemicals were purchased from Alfa-Aesar (triphenylphosphine, 1,3,5-triethynylbenzene, 1,4-diethynylbenzene); Sigma-Aldrich bis(triphenylphosphine)palladium(II) dichloride, silica gel, ethanol, THF, absolute ethanol; Fisher-UK (methanol, potassium nitrate, RuCl₃, DMF, acetonitrile); Combi-Blocks (4,4'-dibromo-2,2'-dipyridine), Acros Organics (CuI); VWR(triethylamine Chromanorm®, HPLC grade). All reagents were used as received without further purification. Nitrogen and CO₂ gasses for sorption were purchased from Air-Liquide (N₂ AlphaGaz2 (99.999%) and CO₂ (99.995%)). Gas sorption analysis was performed on Micromeritics ASAP2020 and the variable temperature CO₂ isotherms were recorded in insulated dewar connected to LAUDA RA-8 circulating chiller. UV-Vis spectra were acquired on ThermoScientific Evolution600 UV-Vis spectrophotometer equipped with inte-

grating sphere for solids. Infra-red absorption spectra were recorded on ThermoScientific **Nicolet is-10**. Thermogravimetric analyses were conducted on Thermal Analysis-**Q50**. Synthetic reactions were performed under nitrogen atmosphere in oven-dried glassware.

Tris(4,4'-dibromo-2,2'-bipyridine) ruthenium (II) nitrate:

In a glass pressure vessel fitted with Teflon screw cap (50 mL) charged with a magnetic stirrer was added absolute ethanol (40 mL) and the solvent degassed through 3 cycles of freeze-pump-thaw and kept under nitrogen. To this degassed solvent was added 4,4'-dibromo-2,2'-bipyridine (0.314 g, 1 mmol) and tetrakis-(dimethylsulfoxide) ruthenium(II) chloride (0.154 g, 0.32 mmol) and the vessel closed under nitrogen. The reaction mixture was maintained at 70° C for 24 hours (color changes to deep red-brown). The solution was then cooled to room temperature, filtered through a fritted funnel and the ethanol removed under reduced pressure. The crude solid was loaded on silica as acetonitrile solution then the silica dried under reduced pressure. The crude product loaded on silica was subjected to column chromatography on silica with a mobile phase consisting of saturated aqueous K(NO₃): water: acetonitrile (1:1:20) and the second band was collected. Evaporation of the solvent gave a deep red solid (0.194 g, yield 60%, based on a molecular formula weight of 1167 g mol⁻¹). ESI/FT-MS: [C₃₀H₁₈Br₂N₆Ru]²⁺ found 521.783252, calculated 521.783215.

Synthesis of PRP-1

In a glass pressure vessel fitted with Teflon screw cap (100 mL) charged with a magnetic stirrer a mixture of DMF (15 mL) and Et₃N (5 mL) was prepared. The vessel was capped with silicon septum, and the solvent mixture was evacuated and backfilled with nitrogen three times through a needle, then was kept under nitrogen for 10 min. To this mixture and under nitrogen atmosphere was added tris-(4,4'-dibromo-2,2'-bipyridine) ruthenium (II) nitrate (0.09 g, 0.077 mmol), 1,3,5-triethynylbenzene (0.023 g, 0.155 mmol, 2 equiv.), bis(triphenylphosphine)palladium(II) dichloride (0.014 mmol, 10 mg), triphenylphosphine (0.02 mmol, 0.005 g) and CuI (0.025 mmol, 0.005 g), the flask was then evacuated/backfilled with nitrogen and sealed and the mixture was stirred at 80 °C for 24 h (deep red-brown precipitate and clear colorless solution). The reaction vessel was then cooled to room temperature, opened to air and filtered through a fritted funnel and washed with DMF-Acetone-MeOH-DCM then kept under MeOH for one week prior to gas sorption measurements. The total dry weight of the solid was found to be 64mg, 88% yield/calculated based on combined weights of the starting materials excluding terminal bromine and hydrogen atoms.

Photolysis

The photochemical reactions are performed using a 300W, high-pressure Xe arc lamp. The beam is passed through an infrared filter, a collimating lens, a filter holder equipped with a 415 nm cutoff filter. Samples are prepared in a 1 cm path length quartz cubic cuvette, which is placed in a temperature

controlled cuvette holder maintained at 20 °C with a circulated water bath. Samples are prepared by adding 0.8 mL solution containing photosensitizer [Ru(bpy)₃]Cl₂ and solid polymer, and by saturating with N₂ for 10 minutes. After photolysis, H₂ measurement is performed by gas chromatography (Shimadzu GC-2014) with a thermal conductivity detector.

ASSOCIATED CONTENT

Supporting Information.

Additional experimental details, UV-vis spectra, FT-IR spectra, mass and solid-state NMR spectra, pore size distribution, XPS and EDX analysis, and TGA traces are available. This material is available free of charge via the Internet at <http://pubs.acs.org>

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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References

1. Witze, A., Energy: That's Oil, Folks. *Nature* **2007**, *445* (7123), 14-17.
2. Lewis, N. S.; Crabtree, G.; Nozik, A. J.; Wasielewski, M. R.; Alivisatos, P.; Kung, H.; Tsao, J.; Chandler, E.; Walukiewicz, W.; Spitler, M.; Ellingson, R.; Overend, R.; Mazer, J.; Gress, M.; Horwitz, J.; Ashton, C.; Herndon, B.; Shapard, L.; Nault, R. M. Basic Research Needs for Solar Energy Utilization. Report of the Basic Energy Sciences Workshop on Solar Energy Utilization, April 18-21, 2005; **2005**. United States. doi:10.2172/899136
3. Lewis, N. S., Powering the Planet. *MRS Bulletin* **2007**, *32* (10), 808-820.
4. Crabtree, G. W.; Lewis, N. S., Solar Energy Conversion. *Phys. Today* **2007**, *60* (3), 37-42.
5. Lewis, N. S.; Nocera, D. G., Powering the Planet: Chemical Challenges in Solar Energy Utilization. *Proc. Natl. Acad. Sci.* **2006**, *103* (43), 15729-15735.
6. O'regan, B.; Grätzel, M., A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO₂ Films. *Nature* **1991**, *353* (6346), 737-740.
7. Grätzel, M., Photoelectrochemical Cells. *Nature* **2001**, *414* (6861), 338-344.
8. Barbe, C. J.; Arendse, F.; Comte, P.; Jirousek, M.; Lenzenmann, F.; Shklover, V.; Grätzel, M., Nanocrystalline Titanium Oxide Electrodes for Photovoltaic Applications. *J. Am. Ceram. Soc.* **1997**, *80* (12), 3157-3171.
9. Hara, M.; Waraksa, C. C.; Lean, J. T.; Lewis, B. A.; Mallouk, T. E., Photocatalytic Water Oxidation in a Buffered Tris(2, 2'-ipyridyl) Ruthenium Complex-Colloidal IrO₂ System. *J. Phys. Chem. A* **2000**, *104* (22), 5275-5280.

10. Takata, T.; Tanaka, A.; Hara, M.; Kondo, J. N.; Domen, K., Recent Progress of Photocatalysts for Overall Water Splitting. *Catal. Today* **1998**, *44* (1), 17-26.
11. Sun, Q.; Dai, Z.; Meng, X.; Xiao, F.-S., Porous Polymer Catalysts with Hierarchical Structures. *Chem. Soc. Rev.* **2015**, *44* (17), 6018-6034.
12. Zhang, Y.; Ying, J. Y., Main-Chain Organic Frameworks with Advanced Catalytic Functionalities. *ACS Catal.* **2015**, *5* (4), 2681-2691.
13. Wang, X.-S.; Chrzanowski, M.; Yuan, D.; Sweeting, B. S.; Ma, S., Covalent Heme Framework as a Highly Active Heterogeneous Biomimetic Oxidation Catalyst. *Chem. Mater.* **2014**, *26* (4), 1639-1644.
14. Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'keeffe, M.; Yaghi, O. M., Modular Chemistry: Secondary Building Units as a Basis for the Design of Highly Porous and Robust Metal-Organic Carboxylate Frameworks. *Acc. Chem. Res.* **2001**, *34* (4), 319-330.
15. Dawson, R.; Laybourn, A.; Clowes, R.; Khimyak, Y. Z.; Adams, D. J.; Cooper, A. I., Functionalized Conjugated Microporous Polymers. *Macromolecules* **2009**, *42* (22), 8809-8816.
16. Xie, Z.; Wang, C.; deKrafft, K. E.; Lin, W., Highly Stable and Porous Cross-Linked Polymers for Efficient Photocatalysis. *J. Am. Chem. Soc.* **2011**, *133* (7), 2056-2059.
17. Wang, C.; Xie, Z.; deKrafft, K. E.; Lin, W., Light-Harvesting Cross-Linked Polymers for Efficient Heterogeneous Photocatalysis. *ACS Appl. Mater. Interfaces* **2012**, *4* (4), 2288-2294.
18. Kaur, P.; Hupp, J. T.; Nguyen, S. T., Porous Organic Polymers in Catalysis: Opportunities and Challenges. *ACS Catal.* **2011**, *1* (7), 819-835.
19. Cote, A. P.; El-Kaderi, H. M.; Furukawa, H.; Hunt, J. R.; Yaghi, O. M., Reticular Synthesis of Microporous and Mesoporous 2d Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2007**, *129* (43), 12914-12915.
20. Kuhn, P.; Antonietti, M.; Thomas, A., Porous, Covalent Triazine-Based Frameworks Prepared by Ionothermal Synthesis. *Angew. Chem. Int. Ed.* **2008**, *47* (18), 3450-3453.
21. Spitler, E. L.; Dichtel, W. R., Lewis Acid-Catalysed Formation of Two-Dimensional Phthalocyanine Covalent Organic Frameworks. *Nature Chem.* **2010**, *2* (8), 672-677.
22. Wu, D.; Xu, F.; Sun, B.; Fu, R.; He, H.; Matyjaszewski, K., Design and Preparation of Porous Polymers. *Chem. Rev.* **2012**, *112* (7), 3959-4015.
23. Aratani, N.; Kim, D.; Osuka, A., Discrete Cyclic Porphyrin Arrays as Artificial Light-Harvesting Antenna. *Acc. Chem. Res.* **2009**, *42* (12), 1922-1934.
24. Gust, D.; Moore, T. A.; Moore, A. L., Solar Fuels Via Artificial Photosynthesis. *Acc. Chem. Res.* **2009**, *42* (12), 1890-1898.
25. So, M. C.; Wiederrecht, G. P.; Mondloch, J. E.; Hupp, J. T.; Farha, O. K., Metal-Organic Framework Materials for Light-Harvesting and Energy Transfer. *Chem. Commun.* **2015**, *51* (17), 3501-3510.
26. Balzani, V.; Bergamini, G.; Ceroni, P.; Vögtle, F., Electronic Spectroscopy of Metal Complexes with Dendritic Ligands. *Coord. Chem. Rev.* **2007**, *251* (3-4), 525-535.
27. Alkordi, M. H.; Liu, Y.; Larsen, R. W.; Eubank, J. F.; Eddaoudi, M., Zeolite-Like Metal-Organic Frameworks as Platforms for Applications: On Metalloporphyrin-Based Catalysts. *J. Am. Chem. Soc.* **2008**, *130* (38), 12639-12641.
28. Wang, J.-L.; Wang, C.; Lin, W., Metal-Organic Frameworks for Light Harvesting and Photocatalysis. *ACS Catal.* **2012**, *2* (12), 2630-2640.
29. Kent, C. A.; Liu, D.; Ma, L.; Papanikolas, J. M.; Meyer, T. J.; Lin, W., Light Harvesting in Microscale Metal-Organic Frameworks by Energy Migration and Interfacial Electron Transfer Quenching. *J. Am. Chem. Soc.* **2011**, *133* (33), 12940-12943.
30. Kent, C. A.; Mehl, B. P.; Ma, L.; Papanikolas, J. M.; Meyer, T. J.; Lin, W., Energy Transfer Dynamics in Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2010**, *132* (37), 12767-12769.
31. Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J., Photochemistry of Tris(2, 2'-bipyridine) Ruthenium (2+) Ion. *J. Am. Chem. Soc.* **1982**, *104* (18), 4803-4810.
32. Artero, V.; Chavarot-Kerlidou, M.; Fontecave, M., Splitting Water with Cobalt. *Angew. Chem. Int. Ed.* **2011**, *50* (32), 7238-7266.
33. Jiang, J. X.; Su, F.; Trewin, A.; Wood, C. D.; Campbell, N. L.; Niu, H.; Dickinson, C.; Ganin, A. Y.; Rosseinsky, M. J.; Khimyak, Y. Z., Conjugated Microporous Poly (Aryleneethynylene) Networks. *Angew. Chem. Int. Ed.* **2007**, *46* (45), 8574-8578.
34. Jiang, J.-X.; Su, F.; Trewin, A.; Wood, C. D.; Niu, H.; Jones, J. T.; Khimyak, Y. Z.; Cooper, A. I., Synthetic Control of the Pore Dimension and Surface Area in Conjugated Microporous Polymer and Copolymer Networks. *J. Am. Chem. Soc.* **2008**, *130* (24), 7710-7720.
35. Dawson, R.; Cooper, A. I.; Adams, D. J., Nanoporous Organic Polymer Networks. *Progress in Polymer Science* **2012**, *37* (4), 530-563.
36. Iupac Commission on Colloid and Surface Chemistry Including Catalysis. *Pure Appl. Chem.* **1985**, *57* (4), 603-619.
37. Wood, C. D.; Tan, B.; Trewin, A.; Su, F.; Rosseinsky, M. J.; Bradshaw, D.; Sun, Y.; Zhou, L.; Cooper, A. I., Microporous Organic Polymers for Methane Storage. *Advanced Materials* **2008**, *20* (10), 1916-1921.
38. Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M., Conversion of Light to Electricity by cis-X₂ bis(2, 2'-bipyridyl-4, 4'-dicarboxylate)ruthenium (II) Charge-Transfer Sensitizers (X= Cl-, Br-, I-, CN-, and SCN-) on Nanocrystalline Titanium Dioxide Electrodes. *J. Am. Chem. Soc.* **1993**, *115* (14), 6382-6390.
39. Pazderski, L.; Pawlak, T.; Sitkowski, J.; Kozerski, L.; Szlyk, E., ¹H NMR Assignment Corrections and ¹H, ¹³C, ¹⁵N NMR Coordination Shifts Structural Correlations in Fe (II), Ru (II) and Os (II) Cationic Complexes with 2, 2'-bipyridine and 1,10-phenanthroline. *Magn. Reson. Chem.* **2010**, *48* (6), 450-457.
40. Omberg, K. M.; Schoonover, J. R.; Treadway, J. A.; Leasure, R. M.; Dyer, R. B.; Meyer, T. J., Mid-Infrared Spectrum of [Ru (Bpy) 3] 2+*. *J. Am. Chem. Soc.* **1997**, *119* (30), 7013-7018.
41. Mohammed, O. F.; Xiao, D.; Batista, V. S.; Nibbering, E. T. J. Excited-State Intramolecular Hydrogen Transfer (ESIHT) of 1,8-dihydroxy-9,10-anthraquinone (DHAQ) Characterized by Ultrafast Electronic and Vibrational Spectroscopy and Computational Modeling. *J. Phys. Chem. A* **2014**, *118*, 3090-3099.
42. Sun, J.; Yu, W.; Usman, A.; Isimjan, T. T.; DGobbo, S.; Alarousu, E.; Takanabe, K.; Mohammed, O. F., Generation of Multiple Excitons in Ag₂S Quantum Dots: Single High-Energy Versus Multiple-Photon Excitation. *J. Phys. Chem. Lett.* **2014**, *5* (4), 659-665.
43. Kallioinen, J.; Benkö, G.; Sundström, V.; Korppi-Tommola, J. E.; Yartsev, A. P., Electron Transfer from the Singlet and Triplet Excited States of Ru (dcbpy)₂ (NCS)₂ into Nanocrystalline TiO₂ Thin Films. *J. Phys. Chem. B* **2002**, *106* (17), 4396-4404.

44. Wang, J.-L.; Wang, C.; deKrafft, K. E.; Lin, W., Cross-Linked Polymers with Exceptionally High Ru(bipy)₃²⁺ Loadings for Efficient Heterogeneous Photocatalysis. *ACS Catal.* **2012**, 2 (3), 417-424.
45. Reynal, A.; Pastor, E.; Gross, M. A.; Selim, S.; Reisner, E.; Durrant, J. R., Unravelling the PH-dependence of a Molecular Photocatalytic System for Hydrogen Production. *Chem. Sci.* **2015**, 6 (8), 4855-4859.
46. Dong, X.-Y.; Zhang, M.; Pei, R.-B.; Wang, Q.; Wei, D.-H.; Zang, S.-Q.; Fan, Y.-T.; Mak, T. C. W., A Crystalline Copper(II) Coordination Polymer for the Efficient Visible-Light-Driven Generation of Hydrogen. *Angew. Chem. Int. Ed.* **2016**, 55 (6), 2073-2077.
47. Pullen, S.; Fei, H.; Orthaber, A.; Cohen, S. M.; Ott, S., Enhanced Photochemical Hydrogen Production by a Molecular Diiron Catalyst Incorporated into a Metal–Organic Framework. *J. Am. Chem. Soc.* **2013**, 135 (45), 16997-17003.
48. Sasan, K.; Lin, Q.; Mao, C.; Feng, P., Incorporation of Iron Hydrogenase Active Sites into a Highly Stable Metal–Organic Framework for Photocatalytic Hydrogen Generation. *Chem. Commun.* **2014**, 50 (72), 10390-10393.
49. Bhattacharjee, A.; Chavarot-Kerlidou, M.; Andreiadis, E. S.; Fontecave, M.; Field, M. J.; Artero, V., Combined Experimental–Theoretical Characterization of the Hydrido-Cobaloxime [HCo(dmgh)₂(PnBu₃)]. *Inorg. Chem.* **2012**, 51 (13), 7087-7093.
50. Bartelmess, J.; Francis, A. J.; El Roz, K. A.; Castellano, F. N.; Weare, W. W.; Sommer, R. D., Light-Driven Hydrogen Evolution by BODIPY-Sensitized Cobaloxime Catalysts. *Inorg. Chem.* **2014**, 53 (9), 4527-4534.
51. Panagiotopoulos, A.; Ladomenou, K.; Sun, D.; Artero, V.; Coutsolelos, A. G., Photochemical Hydrogen Production and Cobaloximes: The Influence of the Cobalt Axial N-Ligand on the System Stability. *Dalton Trans.* **2016**, 45 (15), 6732-6738.
52. Sprick, R. S.; Bonillo, B.; Clowes, R.; Guiglion, P.; Brownbill, N. J.; Slater, B. J.; Blanc, F.; Zwijnenburg, M. A.; Adams, D. J.; Cooper, A. I., Visible Light Driven Hydrogen Evolution Using Planarized Conjugated Polymer Photocatalysts. *Angew. Chem. Int. Ed.* **2016**, 55 (5), 1792-1796.

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