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To what extent can charge localization influence electron injection efficiency at graphene-porphyrin interfaces?

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Controlling the electron transfer process at donor-acceptor interfaces is a research direction that has not yet seen much progress. Here, with careful control of the charge localization on the porphyrin macrocycle using β -Cyclodextrin as an external cage, we are able to improve the electron injection efficiency from cationic porphyrin to graphene carboxylate by 120%. The detailed reaction mechanism is also discussed.

1 Introduction

Charge transfer (CT) at donor (D)-acceptor (A) interfaces is central to the function of photovoltaic and light emitting devices.¹⁻⁴ Understanding and controlling this process on the molecular level is crucial, not only for optimizing the performance of many energy-challenged relevant devices,⁵⁻⁷ but also for enhancing many photocatalytic processes.^{8, 9} Several efforts have recently been made to control the rate of charge and energy transfer at donor-acceptor interfaces.¹⁰⁻¹⁴ More specifically, *Ricks et al.* prepared a series of molecules to test the effect of cross-conjugated bridges on the charge transfer rate in D-A systems.¹⁵ They found that by changing the electronic coupling of a cross-conjugated 1,1-diphenylethene bridge, interfacial charge-transfer rate could be significantly reduced. Similar studies have been applied to quantum dot (QD) and a triruthenium molecular-cluster interfaces.¹⁶ In this case, a correlation between the rate of photoinduced electron transfer from CdSe QDs to oxo-centered triruthenium clusters (Ru_3O) and the structure of the coordinating head group of the ligand, by which the Ru_3O clusters adsorb on QDs, is carefully deciphered.¹⁶ However, controlling the efficiency of the interfacial charge-transfer process is a research direction that has not yet seen much progress. In this communication, we use β -Cyclodextrin (β -CD) as an external cage to block intramolecular charge transfer (ICT) between the macrocycle and its positively charged meso units of 5,10,15,20-tetra(1-methyl-4-pyridino)porphyrin (TMPyP). Subsequently, electron density is localized on the cavity of TMPyP and its oxidation potential is reduced, significantly increasing the availability of donating electrons to the electron acceptor component. Next, we explore the interaction of the resulting configuration (TMPyP- β -CD) with graphene carboxylate (GC) as an

electron-acceptor unit in aqueous solution after 650 nm of photoexcitation. We found that electron injection efficiency from TMPyP to GC in the presence of β -CD is 120% higher than without β -CD.

2 Results & Discussion

Fig. 1A illustrates how TMPyP absorption changes with successive addition of β -CD in aqueous media at pH 10 and a fixed porphyrin concentration; this is visualized by a decrease in the intensity of the Soret band.

Fig. 1 Absorption (left) and fluorescence ($\lambda_{\text{ex}} = 580 \text{ nm}$) (right) of TMPyP in the presence of CD (A), GC (B), and CD-GC (C).

It is worth pointing out that we observed a clear saturation in the emission intensity after the addition of 9 mM β -CD to the TMPyP solution as shown in Fig. 1A. As there was no further interaction observed between CD and TMPyP after addition of 9mM CD, we selected this concentration of CD for the further investigation with GC. The Q-region showed no observable spectral change, indicating that porphyrin symmetry was unchanged by interaction with β -CD. As a result of complexation with β -CD, the observed spectral change in Soret band intensity can be attributed to the change in the local environment around the pyridinium unit.^{17–19} Moreover, we expect that the electron density localized on the porphyrin macrocycle is highest in the β -CD complex, and hence electron-donating properties should be enhanced. To investigate this prediction, two different experiments were performed where a fixed concentration of GC was added successively to a solution of TMPyP and to a solution containing the TMPyP- β -CD complex. Addition of GC resulted in a decrease in Soret band intensity for both solutions (Fig. 1B and 1C). Using the same fixed concentration of GC, a comparison of the absorption spectra reveals the development of a new band at 440 nm for the TMPyP- β -CD complex, but only a 2-nm red shift was observed for TMPyP alone; this clearly indicates the difference between the ground state interaction of TMPyP and GC in the presence or absence of β -CD. We performed a controlled experiment by successive addition of GC to β -CD in aqueous media and observed no change in the absorption spectra of GC or β -CD as shown in Fig. S1. This observation excludes any assumption that a change in the interaction efficiency between TMPyP and GC in the presence of CD is due to side interactions between CD and GC.

On the other hand, a significant change in the shape and intensity of the emission spectrum is observed after addition of CD compared to that of TMPyP alone (right panel of Fig. 1A). As reported for TMPyP, porphyrin macrocycle electron density shifts towards the electron-accepting peripheral meso units through ICT that result in the recorded broad emission.²⁰ When β -CD is added, a complex is formed where the hydrophobic cavity of β -CD hosts the pyridinium units of TMPyP.^{17–19} These added units put a constraint on the free rotation of pyridinium that limits mixing between low-lying CT and S_1 , causing the observed structured shape of the emission spectrum.¹⁷ This restriction on the free rotation and the suppression of ICT has been recently reported to explain the apparent enhanced emission intensity.^{21, 22} The fluorescence (Flu) quenching observed in the TMPyP and TMPyP- β -CD experiments in the presence of added GC, indicates a strong excited-state interaction that results in the formation of a weak or nonluminescent complex. Based on Flu quenching of the free porphyrin monitored in the presence of a consistent concentration of GC, we estimate the efficiencies of quenching to be 40% and 90% for TMPyP and the TMPyP- β -CD complex, respectively. In a previous work, we proved that the interaction between GC and TMPyP is triggered by an electrostatic attraction that continues through π - π stacking of porphyrin on the surface of GC.²³ Hence, the estimated difference in efficiency can be related to the increased localization of electron density on the cavity of TMPyP and the ease of porphyrin oxidation in the TMPyP- β -CD complex compared to free TMPyP; this is evident from the change in oxidation potentials shown by the cyclic voltammetry measurements discussed below. Furthermore, we found that fluorescence quenching of TMPyP by GC exhibited a mixed-static dynamic mechanism²³ unlike our time-resolved data, which indicate that the TMPyP- β -CD and GC interaction mechanism is static in nature. We verified the static mechanism of the interaction by extracting the fluorescence lifetime of the TMPyP-CD complex in the presence and absence of GC using time-correlated single photon counting (TCSPC) (see Fig. S4). The resulting kinetic decay curves show the

same time constant, which supports the static nature of the interaction. Raman spectra also confirmed the interactions for both free TMPyP and the TMPyP-CD-GC complex (Fig. S2); a detailed discussion of the Raman study can be found in the SI.

Femtosecond transient absorption (fs-TA) spectroscopy provides direct, detailed information about the excited-state charge transfer, charge separation, and charge recombination (CR).^{24–27} Therefore, we performed an fs-TA spectroscopy with broadband capabilities and a 120-fs resolution time. Fig. 2 shows the recorded spectra after a 650-nm pulsed excitation; the detailed experimental setup is described elsewhere.^{28, 29} Comparisons between TA spectra for free TMPyP and the TMPyP- β -CD complex are shown in Fig. 2 (left panel); using the same experimental conditions. The excited state absorption (ESA) at 465 nm and 470 nm for TMPyP and TMPyP-CD; respectively corresponds to S_2 population³⁰ and the broad weak absorption extending over 500–600 nm with depletion peaks corresponds to the ground state absorption of the Q-region. In both solutions no spectral change is observed up to 1.0 ns. This is expected from the long lifetime of the singlet excited states of TMPyP and indicates no change in the excited state in the presence of β -CD; however, in the presence of the same concentration of GC, immediate changes indicate fast excited-state deactivation (Fig. 2 right panel).

Fig. 2 Femtosecond transient absorption spectra recorded after 650-nm pulsed-laser 120 fs excitation for TMPyP, TMPyP-CD, TMPyP-GC, and TMPyP-CD-GC.

Photoexcitation of these complexes at 650 nm, which mainly excites porphyrin, resulted in bleaching at 425 nm for TMPyP-GC and 443 nm for TMPyP- β -CD-GC, corresponding to the ground-state bleach (GSB) of these complexes as shown in Fig. 2. In both cases, a broad positive spectral feature extends from 460–600 nm, a typical signature for the excited-state absorption of TMPyP.^{21, 22} It is worth mentioning here that ESA is red-shifted compared to the spectrum without GC, ensuring strong electrostatic interaction between GC and TMPyP as well as TMPyP- β -CD. Moreover, Fig. 2 (right

panels) and Fig. 3 illustrate that the ultrafast ground-state bleach recovery of TMPyP- β -CD-GC is much larger than for TMPyP-GC, which can be attributed to the more efficient interaction by TMPyP- β -CD-GC. We performed TA studies on GC alone after excitation at 650 nm and found no ground state bleaching (GSB) for it at the concentration used in this experiment. However, by increasing GC concentration, we observed GSB at less than 400 nm as shown in Fig. S5, far from the GSB of TMPyP-CD. Clear experimental evidence for the electron transfer process at the TMPyP-GC interface, especially in the presence of β -CD, is obtained from the measured TA spectra after a 475-nm pulse excitation (Fig. S3). While the TA of TMPyP and TMPyP-CD in the absence GC show the characteristic excited-state signal of porphyrin,³¹ new spectral features are observed in their complexes with GC in the range of 500–600 nm that can safely be assigned to the porphyrin cation radical.²³ We extended the TA experiment in NIR region and observed broad spectral feature as shown in Fig. S6 which has similar kinetic behavior as radical cation observed at 550 nm. These spectral features may be due to graphene anion radical or combination of both anion and cation radicals.

Fig. 3. Kinetic traces of free TMPyP (black) after the addition of CD (blue), GC (green), and TMPyP-CD-GC (violet); the monitoring wavelength is indicated on each graph.

We collected kinetic traces of TMPyP at GSB recovery and excited-state TA decay to break down the dynamics of the electron transfer process (Fig. 3). The time profile for TMPyP, collected at 490 nm, showed similar kinetics before and after the addition of β -CD, further confirming the absence of an excited-state interaction between TMPyP and β -CD. However, when cationic porphyrins interacted with GC kinetic traces collected from the excited-state absorption and GSB recovery showed fast dynamics compared with the excited state of free porphyrins. On the other hand, kinetic traces of the TMPyP- β -CD complex with GC had a much higher GSB recovery compared with the TMPyP-GC complex. Meanwhile, TMPyP- β -CD-GC demonstrated a new feature that has been

assigned to the cation radical of TMPyP at 550 nm (formed within the temporal resolution of our machine at about 120 fs). This very fast dynamic indicates close contact between GC and porphyrins,³² which agrees with the static nature of the quenching mechanism, as indicated by ground-state absorption and TCSPC.

The decay of the ground-state bleach recovery of TMPyP-GC exhibits two time constants: one is very fast about 90 ps due to CR, while the other is relatively long extending to nanoseconds due to the unreacted porphyrin, which points to an inefficient interaction. In the presence of the same concentration of GC, in TMPyP-CD-GC hybrid, the fast component observed about 40 ps. In this case, one can anticipate the complete absence of a porphyrin excited-state signal as an indication of a highly efficient interaction with GC. This agrees with the steady-state measurements that show high quenching efficiency of TMPyP- β -CD with added GC. It also follows with the static nature of the quenching mechanism unlike the mixed dynamic static mechanism proven for the TMPyP-GC complex.²³

In order to explain the higher efficiency of electron transfer at TMPyP- β -CD and GC interfaces, we conducted cyclic voltammetry (CV) for TMPyP alone and for the TMPyP-CD complex (S7). By comparing the curves, we observed that the peak-to-peak separation of the TMPyP-CD configuration is 30 mV lower than for TMPyP alone. Since the electron transfer process is directly correlated with the peak-to-peak separation,³³ these results suggest the possibility of a higher electron injection in the configuration of TMPyP- β -CD to GC than TMPyP alone. Similarly, by comparing the CV plots for both TMPyP-GC and TMPyP-CD-GC, we observed that the peak-to-peak separation of the TMPyP-CD-GC hybrid is also lower than for TMPyP-GC alone as shown in Fig. S7. These results suggest the possibility of a higher electron injection in TMPyP-CD-GC compared to TMPyP-GC configurations.

Fig. 4. A schematic diagram of electron transport at the porphyrins-GC interface with and without CD.

It is believed that in the TMPyP- β -CD configuration, β -CD encapsulates the meso unit of TMPyP (see Fig. 4), causing a

disturbance in the intramolecular charge transfer between the macrocycle and its positively charged meso units. Subsequently, electron density is localized on the cavity of TMPyP and its oxidation potential is reduced, thereby significantly increasing the availability of donating electrons to the GC.

3 Conclusion

In conclusion, with careful control of the charge localization of the TMPyP cavity using β -CD as an external cage, we successfully improved the interfacial-electron injection efficiency from cationic TMPyP to GC by 120% compared to TMPyP alone. In this case, β -CD not only restricts free pyridinium rotation, but also blocks ICT between the macrocycle and the meso substituents of TMPyP; subsequently, electron density is localized on the cavity of TMPyP and its oxidation potential is reduced, increasing the ability to donate electrons to GC. Interestingly, unlike the interaction between TMPyP and GC, which is static and dynamic in nature, the interaction of TMPyP- β -CD with GC takes place via an efficient static mechanism. Finally, the novel new insights in this study holds promise for a variety of potential application that principally rely on interfacial charge transfer, such as photocatalysis.

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