Controllable Charge-Transfer Mechanism at *Push-Pull* Porphyrin/Nanocarbon Interfaces

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ABSTRACT: Ultrafast charge transfer at the interfaces between 5,15-donor-acceptor *push-pull* porphyrins (Por-tBu and Por-OC8) and nanocarbon materials in the form of fullerene (C₆₀) and graphene carboxylate (GC) are investigated using femtosecond (fs) pump-probe spectroscopy with broadband capabilities. The strong photoluminescence (PL) quenching of the porphyrin indicates electron and/or energy transfer from the photoexcited porphyrin to the nanocarbon materials. More interestingly, the Stern-Volmer plots of PL quenching shows linear and nonlinear patterns upon increasing the concentration of GC or C₆₀ in the porphyrin solution, respectively, clearly indicating static and a combination of static and dynamic quenching at the interfaces with these nanocarbon materials. Using femtosecond transient absorption (TA) spectroscopy, ultrafast electron transfer from a singlet-excited porphyrin to the nanocarbon materials is clearly identified by the fast ground state bleach recovery and the formation of cation radical species. Furthermore, a fs-TA study revealed that both porphyrins show very long-lived ground state bleach (GSB) and excited state absorption (ESA), which can be attributed to the triplet-state formation. This work provides new physical insights into the electron transfer process and its driving force in donor-accepter systems that include nanocarbon materials.

1. INTRODUCTION:

Profound understanding of interfacial charge-transfer processes at donor (D)-acceptor (A) interfaces is very crucial for the advancements of important research areas including photocatalysis, photovoltaic and light emitting diodes.¹⁻⁷ Over the past quarter century, numerous investigations on the unique characteristics of nanocarbons have been undertaken, starting with the advent of 0D fullerenes, followed by 1D carbon nanotubes and 2D graphene.⁸⁻¹⁰ Because the probabilities of arranging electronic and structural features of carbon-based materials are limitless, their role in charge-transfer systems is increasing in importance.¹¹ For instance, as carbon nanostructures are easily obtained from natural products, they will continue to play a major role in future energy supply in terms of sustainability.¹²⁻¹⁴ Costly rare-earth metals and/or toxic materials in contemporary electronic devices can be replaced with carbon nanostructures due to their rich electrochemical characteristics and versatile mechanisms of modification.¹⁵ For these reasons, there has been significant interest in studying molecular-scale carbon-based hybrid materials that could be used in optoelectronic applications.¹⁶⁻²¹

On the other hand, porphyrin molecules possess excellent light-harvesting features owing to the high absorption cross section of their Soret and Q-bands in the UV/Vis spectral region.²² Furthermore, this class of molecules exhibits unique photophysical and electrochemical properties, which are tunable by changing the functional groups on the porphyrin core as well as through interactions with metal ions in the core of the porphyrin macrocycle,^{2, 23} making them valuable molecules for exploring the potential of carbon-based hybrid materials. Previous studies have shown that porphyrins can be used to functionalize carbon materials such as fullerene and graphene²⁴. Moreover, it was proven that photoinduced electron-transfer processes with carbon-

based materials for the development of optoelectronic devices can benefit from the electron-donor characteristic of porphyrins.²⁵⁻²⁷

In addition, *push-pull* porphyrins have recently been in the focus of research due to their versatile use in applications such as dye-sensitized solar cells (DSSCs) and nonlinear optics.²⁸⁻³⁰ This type of molecule consists of an electron donor and an electron acceptor and has gained intense popularity over the last decades owing to its exceptional performance in DSSCs.²⁹ Therefore, charge-transfer interactions with other forerunner nanomaterials, such as graphene carboxylate and fullerene, were investigated in an attempt to combine these two important contemporary materials. The porphyrins selected for this study were [5-(4-carboxyphenylethynyl)-10,20-bis(3,5-di-*tert*-butylphenyl)-15-(*N,N*-dimethylaniliny)porphyrinato]zinc(II) (Por-tBu) and [5-(4-carboxyphenylethynyl)-10,20-bis(2,6-dioctyloxyphenyl)-15-(bis(4-*tert*-butylphenyl)amino)porphyrinato]zinc(II) (Por-OC8). These *push-pull* porphyrins have been previously reported by Meindl *et al.* and represent two novel 5,15-disubstituted *push-pull* porphyrins with different donor units, which have a dipole running along the *meso-meso* axis.³¹ The design of these porphyrins is based on state-of-the-art *push-pull* porphyrins for dye-sensitized solar cells.²⁹ The ground-state and excited-state interactions of these noncovalently linked hybrids between neutral porphyrins and nanocarbon materials (neutral C₆₀ fullerene and negatively charged graphene carboxylate (GC)) were investigated using steady-state spectroscopy and femtosecond transient absorption spectroscopy with broadband capabilities. The affinity of each porphyrin for the nanocarbon surface was determined by steady-state absorption and emission spectroscopies, and efficient quenching of the porphyrin fluorescence was monitored. Stern-Volmer plots demonstrated a combination of diffusion-controlled (dynamic) and static mechanisms for porphyrin/C₆₀ hybrids and static mechanisms for porphyrin/GC system. Finally, time-resolved

femtosecond and nanosecond TA measurements were utilized to validate the electron-transfer process in these porphyrin/nanocarbon hybrid interfaces.

2. EXPERIMENTAL SECTION:

a. Materials:

[5-(4-Carboxyphenylethynyl)-10,20-bis(3,5-di-*tert*-butylphenyl)-15-(*N,N*-dimethylaniliny)porphyrinato]zinc(II) (Por-tBu) and [5-(4-carboxyphenylethynyl)-10,20-bis(2,6-dioctyloxyphenyl)-15-(bis(4-*tert*-butylphenyl)amino)porphyrinato]zinc(II) (Por-OC8) were synthesized as described earlier.³¹ Fullerene (C₆₀) and *N*-methyl-2-pyrrolidone (NMP, anhydrous, 99.5%) were purchased from Sigma-Aldrich. Graphene carboxylate (GC) was obtained from ACS material and tetrahydrofuran (THF, 99%) was supplied by Alfa Aesar. Deionized (DI) water was used during the experiments.

b. Instrumentation:

(i) Steady-state Spectroscopy

Absorption spectra were recorded on a Cary 5000 UV–Visible spectrometer (Agilent Technologies), whereas the steady-state photoluminescence spectra were obtained using a Fluoromax-4 spectrofluorometer (Horiba Scientific). Rectangular quartz cells with a 1 cm optical path were utilized for the measurements.

(ii) Transient Absorption Spectroscopy

Helios spectrometers (Ultrafast Systems, Florida, USA) were used to perform femtosecond transient absorption spectroscopy experiments. The detailed experimental setup of the fs-TA can

be found in the literature.³² Briefly, a white-light continuum probe pulse was generated in a 2-mm-thick sapphire plate utilizing a small fraction of the fundamental output of a Ti:sapphire femtosecond regenerative amplifier, which was operating at 800 nm with 35 fs pulses, and a repetition rate of 1 kHz. Pump pulses at 640 nm were formed in an optical parametric amplifier (Newport Spectra-Physics). In a 2-mm-thick cuvette cell containing the sample solutions, the pump and probe pulses overlapped temporally and spatially. The probe light transmitted from the sample was gathered and focused on a broadband UV–Vis detector to record the change in the absorbance (ΔA). The nanosecond (ns) TA spectroscopic measurements were also performed at 640 nm following laser pulse excitation. The ns-TA spectra were recorded using the pump-probe EOS setup (Ultrafast Systems, Florida, USA), in which a standard probe beam is split into two: one travels through the sample, and the other one is sent directly to the reference spectrometer, which monitors the fluctuations in the probe beam intensity. The detailed experimental setup of the EOS can be found elsewhere.³³

3. RESULTS and DISCUSSION:

The main aim of the present study was to investigate the charge-transfer interaction between two newly synthesized *push-pull* porphyrins (Por-tBu and Por-OC8) with two different types of polymorph nanocarbon materials (fullerene (C₆₀) and graphene carboxylate (GC)). Studies of the porphyrin nanocarbon interactions using C₆₀ and GC were carried out in NMP and a THF:H₂O mixture [1:1 v/v], respectively, owing to better solubility. [Figures 1](#) and [2](#) represent steady-state absorption and emission spectra changes for the investigated porphyrins at 0.002 mM fixed concentration with successive additions of C₆₀ and GC. In the absence of nanocarbon materials, the characteristic Soret and Q-bands of Por-tBu and Por-OC8 are clearly depicted. The Soret and two Q-bands of Por-tBu appear at 449 nm, 583 nm and 634 nm in NMP and at 446 nm, 579 nm

and 630 nm in the THF:H₂O mixture [1:1 v/v] (Figure 1A and 2A left panels). Similarly, for Por-OC8, the Soret and two Q-bands appear at 452 nm, 582 nm and 645 nm in NMP and at 449 nm, 581 nm and 641 nm in the THF:H₂O mixture [1:1 v/v] (Figure 1B and 2B left panels). Increasing the amount of added nanocarbon material gradually in both Por-tBu and Por-OC8 solutions caused the absorption to increase, especially in the UV spectral region where the absorption spectra of C₆₀ and GC are located. Upon successive addition of either C₆₀ or GC to reach the final concentration, a broad signal monotonically decreasing from the UV to the visible region was observed, which was the signal of the tested nanocarbons (see Figure S1). It is worth noting that the neutral porphyrin does not form a ground-state charge-transfer (CT) complex with the nanocarbon material due to weak electrostatic interactions. However, in our earlier work,¹⁸ the positively charged porphyrins could form a CT complex with GC due to strong electrostatic interactions and π - π stacking interactions.³⁴

To further investigate the noncovalent interactions between the porphyrins and the nanocarbon materials, steady-state photoluminescence (PL) measurements were performed. Figure 1A and 1B (right panels) illustrate the emission spectra of Por-tBu and Por-OC8 measured at 625 nm excitation in the presence of C₆₀ at different concentrations. The emission spectra of the same porphyrins were investigated after excitation at 600 nm upon increasing the concentration of GC,

Figure 1: Steady-state absorption (left) and emission spectra ($\lambda_{\text{ex}} = 625 \text{ nm}$) (right) of (A) Por-tBu and (B) Por-OC8 recorded at different C_{60} concentrations (in mg/mL) as indicated. The chemical structures of the porphyrins and the Stern-Volmer plots as a function of the C_{60} concentration of each porphyrin are shown in the insets.

as illustrated in **Figure 2A** and **B** (right panels). The emission of both porphyrins was successively quenched during the addition of C_{60} and GC, providing a clear indication of excited-state interactions between porphyrins and the molecular acceptors. At a C_{60} concentration of 0.346 mg/mL, the quenching efficiencies were estimated to be 84% and 73% and were accompanied by 2 nm and 5 nm spectral redshifts for Por-tBu and Por-OC8, respectively. On the other hand, the estimated efficiencies of quenching were 96% and 91% with 4 nm and 7 nm spectral redshifts for Am1 5,15 and Por-OC8, respectively, at a GC concentration of 0.750 mg/mL. From the results above, it can be seen that slightly larger redshifts are present in the emission spectra of the porphyrin/GC hybrids compared to those of the porphyrin/ C_{60} hybrids. The shifts in the emission spectra can be attributed to the complexation or interaction between the porphyrins and the nanocarbon materials. Therefore, the interactions between the Por-tBu/GC and Por-OC8/GC hybrids seem to be larger than the interactions between the same porphyrins and C_{60} . We also observed that the fluorescence quenching is more efficient for Por-tBu than Por-OC8. This variation in the fluorescence quenching efficiency of the investigated porphyrins can be related to differences in the intermolecular contact between the porphyrin and nanocarbon material. It should be noted that the change in the structure of the porphyrins at the *meso*-position does not change the interaction with the nanocarbon materials significantly.

To gain further insight into the quenching mechanisms, Stern-Volmer plots of the emission quenching of Por-tBu and Por-OC8 upon interacting with C₆₀ were obtained; the results are illustrated in the insets of Figure 1A and B. Each data plot shows a nonlinear change with increasing C₆₀ concentration, which demonstrates a combined effect from both diffusion-controlled (dynamic) and static mechanisms in the excited-state deactivation.³⁵ Stern-Volmer plots were also used to investigate the quenching mechanism of Por-tBu and Por-OC8 by GC (see right panels of the insets in Figure 2A and B). For this type of hybrid material, a linear correlation of the quenching with increasing GC concentration can be observed, which shows that quenching progress occurs according to a static mechanism in the porphyrin/GC mixtures.³⁵⁻³⁶ The efficient PL quenching can be attributed to electron and/or energy transfer from the photoexcited porphyrin to the nanocarbon material. To confirm and evaluate this further, fs and ns-TA spectroscopy were performed.

Figure 2: Absorption (left) and fluorescence after excitation at 600 nm (right) of (A) Por-tBu and (B) Por-OC8 recorded at different GC concentrations (in mg/mL) as indicated. Insets show the respective Stern-Volmer plots.

Insights about excited-state dynamics, such as excited-state charge transfer (CT), charge separation (CS), and charge recombination (CR),³⁷⁻⁴⁰ of the noncovalent interactions of Por-tBu and Por-OC8 with C₆₀ and GC are provided by fs-TA spectroscopic measurements. Figure 3 shows the fs-TA spectra for Por-tBu and Por-OC8 in the absence and presence of C₆₀ and GC. Excitation was performed at 640 nm, which mainly excites the porphyrins. Analysing the TA spectra in different time domains shows strong negative absorption bands at 449 nm and 451 nm for Por-tBu and Por-OC8 in NMP, respectively. These bands can be attributed to the ground-state bleach (GSB) of the Soret band. In addition to the GSB, a broad excited-state absorption (ESA) in the range of 460-550 nm is observed (Figure 3A and D), illustrating the characteristic peaks of the porphyrin molecules.^{18-19, 41-43}

Figure 3: fs-TA spectra recorded after excitation at 640 nm for (A) Por-tBu in NMP, (B) Por-tBu/C₆₀ in NMP, (C) Por-tBu/GC in THF:H₂O [1:1 v/v], (D) Por-OC8 in NMP, (E) Por-OC8/C₆₀ in NMP and (F) Por-OC8/GC in THF:H₂O [1:1 v/v].

fs-TA measurements of these porphyrins were also performed in a THF:H₂O [1:1 v/v] solution with excitation at 640 nm, as shown in **Figure S2**. The kinetics of the GSB and ESA bands occurs in a similar manner observed for the measurement in NMP. The fs-TA measurements of these porphyrins in THF:H₂O [1:1 v/v] within a 5.5 ns time scale (see **Figure S3**) show that the GSB recovers to its initial-state by <30%, which is in agreement with the literature.^{19, 41, 43-44} As shown in **Figure 3B** and **E**, the GSB and ESA of the Por-tBu/C₆₀ and Por-OC8/C₆₀ hybrids recovered and decayed faster than those of the porphyrins alone. This difference can be attributed to electron transfer from the photoexcited porphyrin to C₆₀.^{18-19, 45} Upon photoexcitation, an electron is transferred from the porphyrin

Figure 4: Normalized fs-TA kinetics of (A and C) GSB at 450 nm for Por-tBu and Por-OC8 in NMP, respectively, in the absence (black) and presence (blue) of C₆₀; (B and D) ESA at 490 nm for Por-tBu and Por-OC8 in NMP, respectively, in the absence (black) and presence (blue) of C₆₀; (E and G) GSB at 450 nm for Por-tBu and Por-OC8 in THF:H₂O [1:1 v/v], respectively, in the absence (black) and presence (blue) of GC; and (F and H) ESA at 510 nm for Por-tBu and Por-OC8 in THF:H₂O [1:1 v/v], respectively, in the absence (black) and presence (blue) of GC. Fitted lines are represented in red.

to the C₆₀, forming a charge-separated state, which will later recombine to generate the initial state.⁴⁶ It is obvious here that the CS is quite efficient because the electron received by C₆₀ propagates far from the interface and is therefore too far away for CR with Por-tBu or Por-OC8,

resulting in the lack of recovery.⁴⁷ Similar to the C₆₀ interaction, the bleach recovery of the porphyrin occurs at a faster rate in the presence of GC (Figure 3C and F, for Por-tBu/GC and Por-OC8/GC, respectively) due to complexation on the surface of GC. Further studies were conducted by comparing the kinetic traces of the porphyrins in the presence and absence of these nanocarbon materials. The association of the kinetics traces of Por-tBu and Por-OC8 in the absence and presence of nanocarbon materials (with C₆₀ in NMP and with GC in THF:H₂O mixture) are shown in Figure 4. The kinetics are plotted up to a 200 ps time window to visualize the change at an early time scale. The GSB of Por-tBu and Por-OC8 recorded at 450 nm can be fitted using a biexponential decay function (see Table 1). The recovery up to 5.5 ns (see also Figure S3A) shows a fast component of 20 ± 1.5 ps in NMP and 3 ± 0.2 ps in the THF:H₂O mixture for Por-tBu and 3 ± 0.2 ps in NMP and 4 ± 0.2 ps in the THF:H₂O mixture for Por-OC8 and a long time constant of 1.1 ± 0.1 ns in NMP and 509 ± 50 ps in the THF:H₂O mixture for Por-tBu and 2 ± 0.2 ns in NMP and 2 ± 0.2 ns in the THF:H₂O mixture for Por-OC8. The short time component can be attributed to nonradiative de-excitation through intermolecular H-bonding of the carboxylate group, while the long lifetime component can be assigned to singlet excited state lifetime. On the other hand, the ESA of these porphyrins shows almost no decay at longer time scale (Figure S3B). The long-lived state may reflect the triplet state formation, which is populated through a nonradiative decay channel (ISC; intersystem crossing). Further discussion on the triplet state using ns-TA is demonstrated in the next section. The calculated lifetimes from GSB and ESA kinetics are in good agreement with literature values.^{18-19, 45} It is worth noting that the GSB of both porphyrins in NMP and in the presence of C₆₀ follows biexponential recovery like free porphyrins. The difference is that the time constants are getting shorter than that of the porphyrin alone. More importantly, in the presence of GC, an additional time constant, which varies from 0.2 to 0.25 ps

(Table 1), appears to fit well the kinetics traces. For C₆₀, the short-lived component can be attributed to charge recombination between the donor-acceptor pairs, while the long-lived one may be assigned to the ISC of the porphyrins, which did not undergo electron transfer. However, the presence of a very fast component on the GSB in the presence of GC clearly indicates a faster electron transfer due to complexation. This observation is in good agreement with the steady-state PL study (Figure 1 and 2). Surprisingly, the ESA of Por-tBu and Por-OC8 with C₆₀ decayed, while with GC, an increasing ESA signal was observed. We observed a faster decay (2.3-2.5 ps) of the ESA over the range of 475-550 nm with C₆₀, which can be attributed to the decay of the porphyrin^{•+} radical cation⁴⁸⁻⁴⁹ that forms immediately after photoexcitation which resulted from ultrafast electron injection. On the other hand, the faster bleach recovery of the porphyrin in the presence of GC in contrast to C₆₀ clearly shows complex formation on the GC surface that improved charge separation due to the 2D layer structure of the GC, which promotes electron injection through π - π stacking in a static manner. Faster bleach recovery, formation of the cation radical, and absence of spectral overlap between the donor-acceptor pair are evidence of electron transfer and not energy transfer. From the kinetics study, it is clear that the quenching (electron transfer) in the presence of C₆₀ takes place via a long-range diffusion-controlled mechanism, while in the case of GC, quenching occurs via a short-range static mechanism. Further investigations into the long-range electron-transfer process were performed through ns-TA measurements.

To explore whether the interaction between the porphyrins and the nanocarbon materials is effective via the triplet state, we performed ns-TA spectroscopy. The ns-TA spectra were recorded up to microsecond time scales for Por-tBu and Por-OC8 in the absence and presence of C₆₀, and the results are shown in Figure S4. Figure 5 represents the ns-TA kinetics of free Por-tBu and Por-OC8 as well as mixtures with C₆₀. It is worth mentioning that a slower bleach recovery was noticed

from the fs-TA results for the porphyrin/C₆₀ hybrids compared to the GC complexes, while more than 70% quenching was observed in the steady-state PL study. In addition, the nonlinear pattern of the Stern-Volmer plot of porphyrin/C₆₀ suggested a dynamic quenching for the porphyrin complexes. The ns-TA kinetics of porphyrin/nanocarbon hybrids were obtained up to a 50 ns time window, and the results reflected faster bleach recovery and decay of ESA with C₆₀ (Figure 5) up to tens of ns time scale, confirming the diffusion-controlled electron-transfer process in the system.

Table 1:

Ultrafast time constants of the exponential fitting of the experimental data. The parenthesis indicates the percentage of amplitude.

Sample	Lifetime – fs-TA		Lifetime – ns-TA	
	GSB	ESA	GSB	ESA
Por-tBu in NMP	$\tau_1 = 20 \pm 1.5$ (20%) ps $\tau_2 = 1.1 \pm 0.1$ (80%) ns	$\tau = 1.8 \pm 0.2$ ns	$\tau = 1.2 \pm 0.1$ μ s	$\tau = 1.2 \pm 0.1$ μ s
Por-tBu/C₆₀ in NMP	$\tau_1 = 9.5 \pm 1$ (21%) ps $\tau_2 = 472 \pm 30$ (79%) ps	$\tau_1 = 2.3 \pm 0.1$ (31%) ps $\tau_2 = 55 \pm 4$ (69%) ps	$\tau_1 = 1.8 \pm 0.1$ (24%) ns $\tau_2 = 1 \pm 0.1$ (76%) μ s	$\tau_1 = 2 \pm 0.2$ (24%) ns $\tau_2 = 1 \pm 0.1$ (76%) μ s
Por-OC8 in NMP	$\tau_1 = 3 \pm 0.2$ (15%) ps $\tau_2 = 2 \pm 0.2$ (85%) ns	$\tau = 2.4 \pm 0.2$ ns	$\tau = 1.8 \pm 0.2$ μ s	$\tau = 1.8 \pm 0.1$ μ s
Por-OC8/C₆₀ in NMP	$\tau_1 = 1.1 \pm 1$ (13%) ps $\tau_2 = 1.8 \pm 0.1$ (87%) ns	$\tau_1 = 2.5 \pm 0.2$ (42%) ps $\tau_2 = 90 \pm 8$ (58%) ps	$\tau_1 = 2.5 \pm 0.2$ (14%) ns $\tau_2 = 2 \pm 0.1$ (86%) μ s	$\tau_1 = 1.7 \pm 0.1$ (32%) ns $\tau_2 = 2 \pm 0.2$ (68%) μ s
Por-tBu in THF:H ₂ O	$\tau_1 = 3 \pm 0.2$ (10%) ps $\tau_2 = 509 \pm 50$ (90%) ps	$\tau = 3 \pm 0.2$ ns	$\tau = 0.65 \pm 0.04$ μ s	$\tau = 0.7 \pm 0.04$ μ s
Por-tBu/GC in THF:H ₂ O	$\tau_1 = 0.25 \pm 0.02$ (14%) ps $\tau_2 = 5 \pm 0.5$ (11%) ps	$\tau_{\text{rise}} = 23 \pm 2.3$ (21%) ps $\tau_2 = 3.4 \pm 0.03$ (79%) ns	$\tau = 0.7 \pm 0.03$ μ s	$\tau = 0.7 \pm 0.04$ μ s

	$\tau_3 = 547 \pm 53$ (75%) ps			
Por-OC8 in THF:H ₂ O	$\tau_1 = 4 \pm 0.2$ (14%) ps	$\tau = 1.1 \pm 0.1$ ns	$\tau = 1 \pm 0.04$ μ s	$\tau = 1 \pm 0.06$ μ s
	$\tau_2 = 2 \pm 0.2$ (86%) ns			
Por-OC8/GC in THF:H ₂ O	$\tau_1 = 0.2 \pm 0.02$ (12%) ps	$\tau_{\text{rise}} = 20 \pm 1$ (25%) ps	$\tau = 1 \pm 0.04$ μ s	$\tau = 1 \pm 0.06$ μ s
	$\tau_2 = 13 \pm 1.3$ (18%) ps	$\tau_2 = 819 \pm 17$ (75%) ps		
	$\tau_3 = 500 \pm 49$ (70%) ps			

Finally, the ns-TA kinetics of the same porphyrins in the absence and presence of GC were investigated, as shown in Figure S5. However, no clear change in ns-TA could be observed for Por-tBu/GC and Por-OC8/GC, which confirms the absence of a diffusion-controlled (dynamic) electron-transfer process in these cases. This leads to the conclusion that porphyrins are only adsorbed on the GC surface; therefore, only static electron-transfer process occurs in this system. Finally, the very long-lived species can be attributed to the triplet-excited state of free porphyrin molecules. It should be noted that no change in the lifetime can be detected upon addition of GC. This clearly indicates that electron transfer does not take place

Figure 5: Normalized ns-TA kinetics of (A and C) GSB at 450 nm for Por-tBu and Por-OC8, respectively, in the absence (black) and presence (blue) of C₆₀ in NMP and (B and D) ESA at 490

nm for Por-tBu and Por-OC8, respectively, in the absence (black) and presence (blue) of C₆₀ in NMP after 640 nm laser excitation. Fitted lines are represented in red.

through the triplet state but rather occurs via the singlet-excited state. However, as mentioned previously, a diffusion-controlled process was observed between each porphyrin and C₆₀. This means that each porphyrin and C₆₀ hybrid is located far from each other and needs to diffuse to form a reactive complex with a certain difference for the electron transfer to occur as observed for GSB at 450 nm and ESA at 490 nm (Figure 5). Note that the two time constants (sub ns and μ s) that refer to the singlet state and triplet state lifetimes are given in Table 1.

4. CONCLUSION:

In conclusion, the photoinduced charge-transfer processes at the interface of two newly synthesized *push-pull* porphyrins and nanocarbon materials have been investigated and deciphered. Steady-state PL quenching was observed, which illustrates that electron transfer from the excited porphyrin to the nanocarbon material occurs. In addition, Stern-Volmer plots of porphyrin/GC vary linearly with increasing GC concentration, while a deviation from linearity is found with cumulative addition of C₆₀ to the porphyrin moiety. These results indicate that a static and a combination of static and dynamic quenching are dominant in the presence of GC and C₆₀, respectively and were further confirmed through fs and ns-TA experiments. Faster GSB recovery in fs-TA and no change in ns-TA of the porphyrins in the presence of GC reveals that the ET reactions occur via the noncovalent association of porphyrin/GC from the singlet-excited porphyrin to the GC and that it is of static nature. Importantly, faster GSB recovery of porphyrin/C₆₀ hybrids in both fs and ns-TA was observed, which suggests the combination of static

and diffusion-controlled electron transfer process. These findings provide new physical insights into how to control the electron transfer mechanisms at porphyrin/nanocarbon interfaces, which could be applied to other donor-acceptor systems.

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Notes:

The authors declare no competing financial interest.

Acknowledgements:

The authors are grateful for the financial support from Science Foundation Ireland (SFI, W.J.B. 12/IA/1306 and M.O.S. IvP 13/IA/1894) and King Abdullah University of Science and Technology (KAUST).

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