

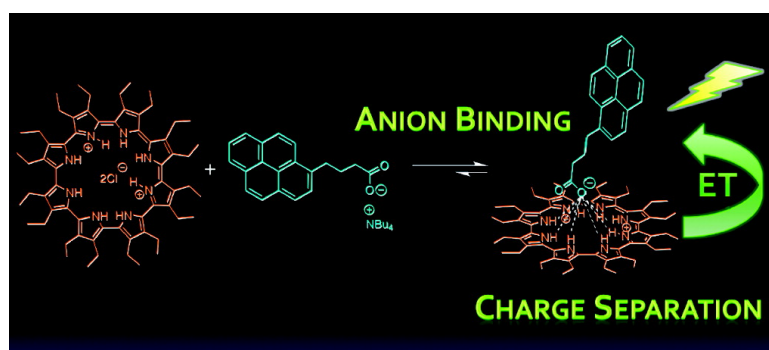
Communication

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“Umpolung” Photoinduced Charge Separation in an Anion-bound Supramolecular Complex

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Recent decades have borne witness to an explosion in research devoted to *mimicking* natural photoinduced electron transfer processes, such as those associated with the early events in photosynthesis.^{1,2} Many of the systems reported in this context have relied on the use of covalently tethered electron donors and acceptors. An alternative strategy, wherein the donors and acceptors are linked through noncovalent forces, has also received attention of late.^{2a,3} This latter approach is attractive in terms of its versatility, flexibility in design, and ease of synthesis. While a number of supramolecular motifs have been explored for this purpose, there are only a few examples where anion binding is used to connect the donor and the acceptor;⁴ to the best of our knowledge, none of these involve the use of an expanded porphyrin as the anion binding element.⁵

Here, we report that the combination of diprotonated [30]octaphyrin(0.0.0.0.0.0.0.0) (cyclo[8]pyrrole; **C8**; Figure 1) and a pyrene carboxylate anion produces a supramolecular ensemble, **C8–Py** (**Py**: denoted the pyrene moiety) that, upon photoexcitation, yields a charge-separated (CS) state. This CS state has two unprecedented novel features: One is the unusual direction of electron transfer to form **C8^{•+}–Py^{•-}**, a CS that is higher in energy than the alternative putative CS species, **C8^{•-}–Py^{•+}**, while the other feature is the long CS lifetime of **C8^{•+}–Py^{•-}** (300 μ s), a species that decays to a long-lived triplet state (lifetime ≥ 200 ms) before returning to the ground-state.

Cyclo[8]pyrrole, was first reported by us in 2002,⁶ and is a system that has shown promise in a variety of applications, including use as a sulfate anion extractant.⁷ The photophysical and electrochemical properties of cyclo[8]pyrrole have been reported previously,^{5,8} whereas its anion binding properties are the subject of an ongoing investigation. In preliminary studies, a high affinity has been observed for carboxylate anions, leading us to consider that this particular expanded porphyrin could be used to construct an anion-binding-based supramolecular electron transfer system. To test this idea, tetra-*n*-butylammonium 1-pyrenebutyrate, **Py**, was chosen as the anionic, electron acceptor “partner”. Figure 1 shows the UV–vis titration between these two species, as well as the resulting binding isotherm. From these spectral changes, an association constant, K_a , of $(2.6 \pm 0.3) \times 10^5 \text{ M}^{-1}$ could be derived⁹ for the formation of **C8–Py**.

The two-electron reduction potential of **C8** in MeCN is -0.05 V vs SCE, while the oxidation potential is 0.46 V vs SCE.^{8a} In the presence of 1 equiv of **Py**, both the oxidation and reduction potentials of **C8** are decreased slightly to 0.44 and -0.03 V vs SCE, respectively. In the presence of **C8**, the reduction potential of **Py** is decreased from -2.18 to -2.14 V vs SCE, while the oxidation potential is increased from 1.24 to 1.28 (cf. Supporting Information, Figure S1). Spectral

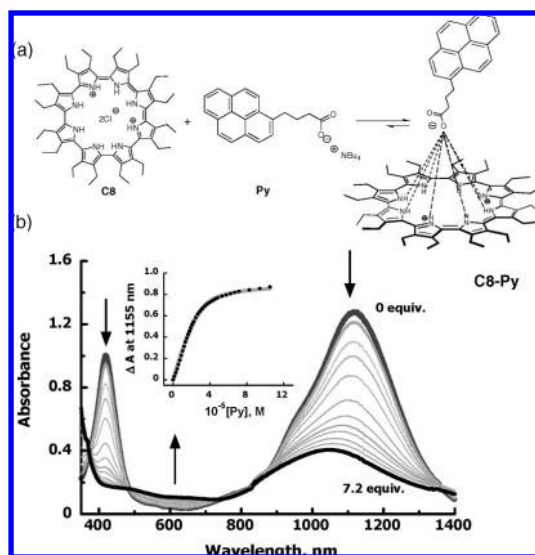


Figure 1. (a) Proposed complex formation; (b) UV–vis titration of tetra-*n*-butylammonium 1-pyrenebutyrate, **Py** into cyclo[8]pyrrole, **C8** at $1.5 \times 10^{-5} \text{ M}$ in MeCN at 298 K. Inset: Curve fit (line) to a 1:1 binding isotherm produced from the change in absorbance at 1155 nm (points).

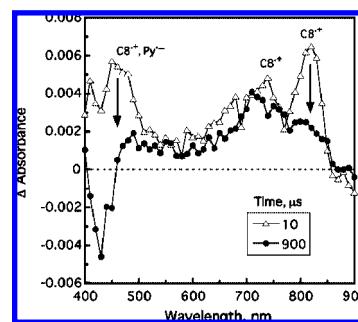


Figure 2. Transient absorption spectra of **C8** and **Py**, in a 1:1 ratio at $5.0 \times 10^{-5} \text{ M}$ in deaerated MeCN at 298 K taken at $10 \mu\text{s}$ (Δ) and $900 \mu\text{s}$ (\bullet) after laser photoexcitation (355 nm, 25 mJ per pulse).

monitoring of the one-electron electrochemical oxidation of cyclo[8]pyrrole or chemical oxidation using $\text{Fe}(\text{bpy})_3^{3+}$ ($\text{bpy} = 2,2'$ -bipyridine) reveals the presence of new features with λ_{max} at 482, 738, and 818 nm (cf. Figures S2, S3).

Transient absorption spectra were recorded after photoexcitation of **C8** and **Py** alone (cf. Figure S4), and in a 1:1 ratio in MeCN (cf. Figure 2). On the basis of the absorption maxima there is clear evidence for formation of **C8^{•+}** (but NOT **C8^{•-}**). Such an observation is consistent with photoinduced electron transfer taking place from **C8**

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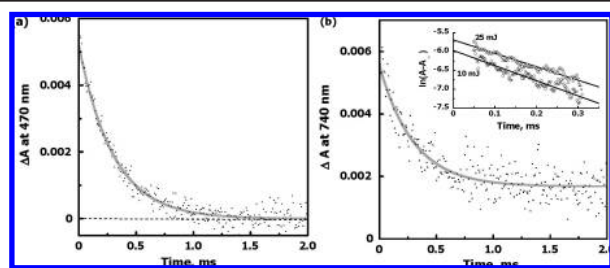


Figure 3. Decay profiles at (a) 470 and (b) 740 nm obtained from the transient absorption spectra of Figure 2. Inset: First-order plots of the spectral changes at 740 nm with different laser intensities.

to the singlet excited-state of **Py** ($^1\text{Py}^*$) to produce the CS state, $\text{C8}^{+\bullet}-\text{Py}^{\bullet-}$; this happens even though the energy of $\text{C8}^{+\bullet}-\text{Py}^{\bullet-}$ (2.58 eV) is higher than that of $\text{C8}^{\bullet-}-\text{Py}^{\bullet+}$ (1.31 eV). The transient absorption due to $\text{Py}^{\bullet-}$ appears at 480 nm and is overlapped with features due to $\text{C8}^{+\bullet}$. The CS state decays to the triplet excited state ($^3\text{C8}^*$) rather than to the ground state, as inferred from the fact that the transient spectrum of the ensemble recorded at 900 μs in Figure 2 agrees with that observed for $^3\text{C8}^*$ produced following photoexcitation of **C8** alone (Figure S4).

Fitting the decay at both 470 and 740 nm to a single exponential results in a charge recombination rate (k_{cr}) of $(3.3 \pm 0.1) \times 10^3 \text{ s}^{-1}$, a value that corresponds to a lifetime for the charge-separated state (τ_{cr}) of 300 μs (Figure 3). Changing the laser power has no effect on the rates, as underscored by the invariance of the first-order plots included in Figure 3. Such findings provide support for the proposal that intramolecular electron transfer takes place within the supramolecular complex. As expected, the use of pyrene-1-butyric acid, instead of the deprotonated form (i.e., **Py**) in conjunction with **C8** under otherwise identical conditions, yielded none of the peaks characteristic of $\text{C8}^{+\bullet}$ following photoirradiation.

The formation of $\text{C8}^{+\bullet}$ following photoexcitation in the presence of **Py** is particularly interesting given the fact that pyrene typically acts as a good electron donor.¹⁰ The charge reversal seen in the present “umpolung” system has also been reported for electron transfer from electron donors to $^1\text{Py}^*$.¹¹ In the specific case of **C8-Py**, the proposed path is similar, namely excitation of a 1:1 solution of **C8** and **Py** at 355 nm affords first the singlet excited-state of pyrene, $^1\text{Py}^*$ (3.46 eV); this is then followed by electron transfer from **C8** to form the CS state, $\text{C8}^{+\bullet}-\text{Py}^{\bullet-}$ (Figure 2). The CS rate constant was determined to be $5.1 \times 10^6 \text{ s}^{-1}$ from the decrease in the fluorescence lifetime of **C8-Py** (140 ns) as compared to that of the reference pyrene (480 ns); see Figure S5. The slow CS was confirmed by femtosecond laser flash photolysis measurements, where little change was observed in the transient absorption due to $^1\text{Py}^*$ in **C8-Py** (see Figure S6). That this pathway is followed, rather than an alternative one leading to the formation of $\text{C8}^{\bullet-}-\text{Py}^{\bullet+}$, is rationalized by the Marcus theory of electron transfer, which predicts that the charge separation to produce the lower energy CS state ($\text{C8}^{\bullet-}-\text{Py}^{\bullet+}$), with a larger driving force of 2.15 eV, is deeply in the Marcus inverted region; this makes the CS rate much slower than the CS rate required to produce the high energy CS state $\text{C8}^{+\bullet}-\text{Py}^{\bullet-}$, which lies in the Marcus normal region and which is characterized by a driving force of 0.88 eV.¹² After initial photoinduced charge separation, recombination occurs via decay to the triplet excited state, $^3\text{C8}^*$,¹³ which then returns to the ground-state extremely slowly, in a time exceeding 200 ms (cf. Figure S8). This mode of recombination is also rationalized by the slower back electron transfer to the ground-state as compared to the triplet excited-state in the Marcus inverted region.^{12–15}

In summary, we have shown that anion binding to an appropriately chosen expanded porphyrin, namely **C8**, can be used to create a

noncovalently linked dyad capable of electron transfer. In the present system, which is predicated on the use of an anionic pyrene derivative, photoexcitation produces a CS state of $\text{C8}^{+\bullet}-\text{Py}^{\bullet-}$ that is higher in energy than the alternative CS state, $\text{C8}^{\bullet-}-\text{Py}^{\bullet+}$. This high energy CS state decays with a lifetime of 300 μs to give a long-lived triplet state. Formation of such a high energy and long-lived CS state justifies further studies with **C8** in conjunction with other potential electron acceptors, as well as efforts to create more elaborate ensembles wherein anion recognition is used in combination with other noncovalent interactions to link together multiple donor and acceptor subunits. Work along these lines is in progress.

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Supporting Information Available: Experimental details, CV data, additional transient spectroscopy and kinetic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Deisenhofer, J.; Norris, J. R., Eds. *The Photosynthetic Reaction Center*; Academic Press: San Diego, 1993.
- (2) Review:(a) Wasielewski, M. A. *Chem. Rev.* **1992**, *92*, 435–461. (b) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198–205. (c) Fukuzumi, S. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2283–2297. (d) Fukuzumi, S.; Kojima, T. *J. Mater. Chem.* **2008**, *18*, 1427–1439. More recent examples: (e) Imahori, H.; Guldi, D. M.; Tamaki, K.; Yoshida, K.; Luo, C.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 6617–6618. (f) Ohkubo, K.; Kotani, H.; Shao, J.; Ou, Z.; Kadish, K. M.; Li, G.; Pandey, R. K.; Fujitsuka, M.; Ito, O.; Imahori, H.; Fukuzumi, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 853–856. (g) Curiel, D.; Ohkubo, K.; Reimers, J. R.; Fukuzumi, S.; Crossley, M. J. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5260–5266.
- (3) Review:(a) Chitta, R.; D’Souza, F. *J. Mater. Chem.* **2008**, *18*, 1440–1471. Examples: (b) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1993**, *115*, 10418–10419. (c) Sanchez, L.; Sierra, M.; Martin, N.; Myles, A.; Dale, T.; Rebek, J., Jr.; Seitz, W.; Guldi, D. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 4637–4641. (d) Seiler, M.; Durr, H.; Willner, I.; Joselevich, E.; Doron, A.; Stoddart, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 3399–3404.
- (4) (a) Kojima, T.; Honda, T.; Ohkubo, K.; Shiro, M.; Kusukawa, T.; Fukuda, T.; Kobayashi, N.; Fukuzumi, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 6712–6716. (b) Rosenthal, J.; Hodgkiss, J. M.; Young, E. R.; Nocera, D. G. *J. Am. Chem. Soc.* **2006**, *128*, 10474–10483.
- (5) Anion binding has been used to create a noncovalent ensemble that undergoes photoinduced energy transfer; see: Springs, S. L.; Gosztola, D.; Wasielewski, M. R.; Král, V.; Andrievsky, A.; Sessler, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2281–2289.
- (6) Seidel, D.; Lynch, V.; Sessler, J. L. *Angew. Chem., Int. Ed.* **2002**, *41*, 1422–1425.
- (7) Eller, L. R.; Stepien, M.; Fowler, C. J.; Lee, J. T.; Sessler, J. L.; Moyer, B. A. *J. Am. Chem. Soc.* **2007**, *129*, 11020–11021.
- (8) (a) Kohler, T.; Seidel, D.; Lynch, V.; Arp, F. O.; Ou, Z.; Kadish, K. M.; Sessler, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 6872–6873. (b) Yoon, Z. S.; Kwon, J. H.; Yoon, M.-C.; Koh, M. K.; Noh, S. B.; Sessler, J. L.; Lee, J. T.; Seidel, D.; Aguilar, A.; Shimizu, S.; Suzuki, M.; Osuka, A.; Kim, D. *J. Am. Chem. Soc.* **2006**, *128*, 14128–14134.
- (9) Johnson, K. A., Ed. *Kinetic Analysis of Macromolecules*; Oxford University Press: Oxford, 2003.
- (10) Wilson, J. N.; Teo, Y. N.; Kool, E. T. *J. Am. Chem. Soc.* **2007**, *129*, 15426–15427.
- (11) Fukuzumi, S.; Satoh, N.; Yuasa, Y.; Ohkubo, K. *J. Am. Chem. Soc.* **2004**, *126*, 7585–7594.
- (12) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.
- (13) The observed absorbance at 740 nm due to $^3\text{C8}^*$ after the charge recombination in Figure 3b was the same as that observed by the photoexcitation of $^3\text{C8}^*$ alone (see Figure S7). This indicates that the radical ion pair decays to the triplet excited state, $^3\text{C8}^*$.
- (14) The triplet energy of $^3\text{C8}^*$ is estimated to be lower than the singlet excited energy of **C8** (0.95 eV).⁸
- (15) A Marcus plot of the logarithm of CS and CR rate constants vs the driving force of electron transfer affords a reorganization energy $\lambda = 0.85 \text{ eV}$ and an electron coupling element $V = 0.13 \text{ cm}^{-1}$ (cf. Figure S9).

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