A Rigid Chlorin−Naphthalene Diimide Conjugate. A Possible New Noncovalent Electron Transfer Model System

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Described in this paper is the synthesis and study of a rigid "coplanar" noncovalent electron-transfer model system. This putative noncovalent complex juxtaposes a novel donor (chlorin) and acceptor (naphthalene diimide) via a three-point hydrogen bonding interaction (CDCl$_3$, $K_a = 364 \pm 47$ M^{-1}). It was studied by steady state fluorescence, time-resolved luminescence, and transient absorption methods. The results of the studies are consistent with (1) forward intraensemble electron transfer (ET) taking place rapidly following photoexcitation of the chlorin donor at 575 nm ($k_{ET} = 7.6 \times 10^8$ s^{-1}; $\Delta G_{cs} \sim -457$ mV; $\Phi = 0.91$) and (2) back electron transfer occurring even more rapidly.

Introduction

Long-range biological electron transfer reactions in proteins are of fundamental importance and play critical roles in such ubiquitous processes as photosynthesis and oxidative phosphorylation.[1] Despite this importance, a detailed understanding of these reactions remains elusive. For instance, considerable effort continues to be devoted to understanding how specific pathways linking a donor and an acceptor, serve to mediate the overall electron transfer (ET) process.[2] One way in which this critical issue is being addressed is through the synthesis and study of simple, noncovalently constructed model systems.[3−6] Here, the overriding objective has been to

Scheme 1
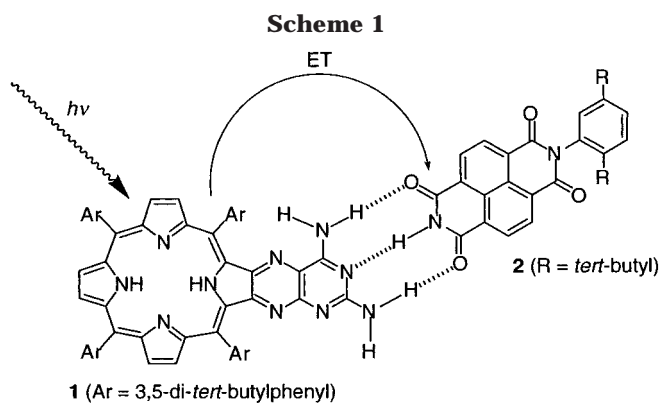
I

determine whether pathways containing hydrogen bonds or other noncovalent contacts are competitive (in terms of allowable ET rates) with those containing only σ-bonds.[7] Unfortunately, even in the context of model systems, this is a point that remains contentious.

In this work the synthesis of a new, rigid noncovalent model system (ensemble **I**, Scheme 1) is described. It employs chlorin **1** as the singlet excited-state electron donor and the diimide **2** as the acceptor. The donor and acceptor are juxtaposed by a three-point hydrogen bond-

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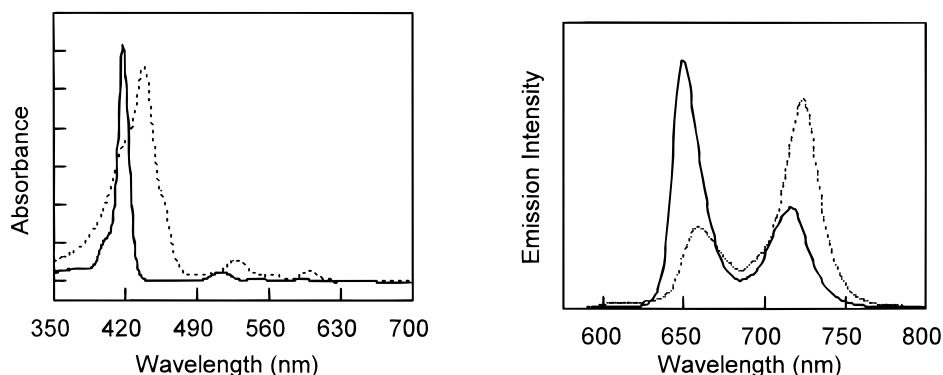
Figure 1. Overlay of 5,10,15,20-tetraphenyl-21*H*,23*H*-porphyrin [—, 1.14×10^{-6} M] and (**1**) [- - -, 2.59×10^{-6} M] in toluene (left trace) and overlay of the fluorescence profile of 5,10,15,20-tetraphenyl-21*H*,23*H*-porphyrin (H$_2$TPP) [—, 2.41×10^{-4} M] and (**1**) [- - -, 2.27×10^{-4} M] in toluene (right trace).

Scheme 2
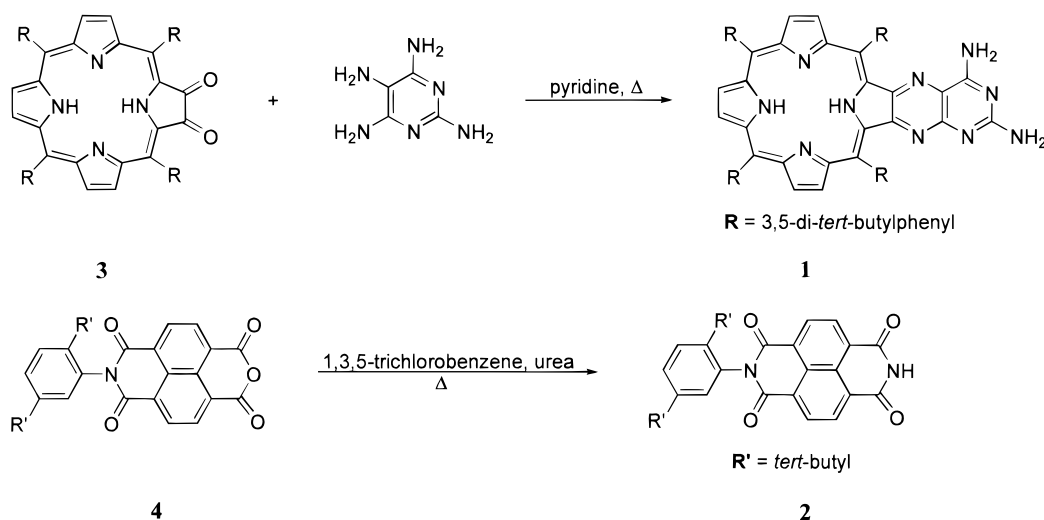
ing interaction which is designed to stabilize a "coplanar" supramolecular complex (ensemble **I**) with a ca. 7 Å edge-to-edge distance between the redox active chlorin and diimide components. Irradiation of this complex at 573 nm gives rise to spectroscopic changes that are readily interpretable in terms of rapid ($k_{\text{et}} = 7.6 \times 10^8$ s^{-1}) forward electron transfer followed by even faster charge recombination (back ET).

Results and Discussion

The preparation of the key monomers **1** and **2** is summarized in Scheme 2. Briefly, chlorin **1** was prepared in 85% yield by condensing commercially available 2,4,5,6-tetraaminopyrimidine with **3** (17,18-dioxotetraphenylchlorin[8]) in pyridine at reflux. Acceptor **2**, on the other hand, was obtained in two steps. First, intermediate **4** was generated in 28% yield by condensing 2,5-di-*tert*-butylaniline with 1,4:5,8-naphthalenetetracarboxylic acid dianhydride.[2] This latter material was then converted to the diimide **2** by treating with urea in boiling 1,3,5-trichlorobenzene.[6]

To the best of our knowledge, the present paper is the first in which porphyrins/chlorins such as **1** have been studied in the context of noncovalent ET studies.[9] Accordingly, the absorption and emission spectral charac-

teristics of **1** were recorded and compared to those of tetraphenylporphyrin (H$_2$TPP). As can be seen from an inspection of Figure 1, there is a large bathochromic shift in the absorption spectra of **1** versus H$_2$TPP with the greatest difference being manifest in terms of a ca. 20 nm red-shift in the Soret absorption (λ_{max} values of 439 and 419 nm were recorded for **1** and H$_2$TPP, respectively). The emission profiles of these two species also differ somewhat as illustrated in Figure 1.

Evidence for the formation of complex **I** in CDCl$_3$ came from ^{1}H NMR spectroscopic studies. Specifically, as illustrated in Figure 2, analysis of the downfield shift for the diimide imine proton as a function of increasing chlorin (**1**) concentration provided support for a 1:1 binding model and yielded an association constant K_a of 364 ± 47 M^{-1}.[10] While such findings are consistent with expectations, diimide compounds are notorious for π-stacking in solution.[11] Therefore, to alleviate concerns that such stacking could be taking place in the present instance, the aromatic naphthalene protons of **2** were also monitored during the course of the ^{1}H NMR titrations. In point of fact, no discernible changes in these latter

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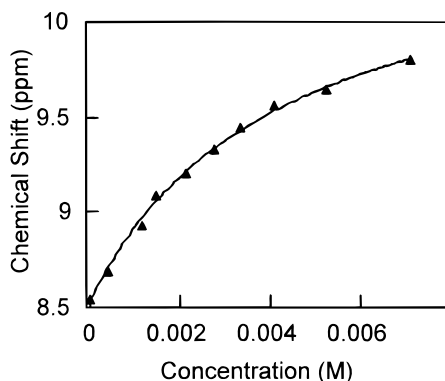
Figure 2. ^{1}H NMR binding isotherm for **1** with **2** in CDCl$_3$ at 25 °C. Nonlinear least-squares analysis, carried out in accord with methods described preciously,[10] gave an association constant $K_a = 364 \pm 47$ M^{-1}.

signals were seen (as a function of concentration). This is interpreted in terms of the extent of π stacking between **1** and **2** being small or nonexistent under the conditions of the experiment.

Steady-state fluorescence quenching experiments indicated that the fluorescence of **1** is quenched to a greater extent by **2** when compared to the case where **1** was replaced by H$_2$TPP. This difference leads us to propose that the hydrogen bond derived recognition site of **1** allows for the ready formation of the putative complex **I** and, as a result, more efficient ET-based quenching of the chlorin singlet excited state. Addition of hydrogen bond competitors (i.e. methanol, uracil) served to restore the fluorescence of **1**.

Single-photon counting experiments performed in toluene further served to support a model where the formation of complex **I** allows for rapid intraensemble ET. The chlorin **1** is similar to H$_2$TPP in that, in the absence of a quencher, its emission profile is monoexponential with a lifetime of 13.2 ns. Addition of the chlorin excited-state quencher, diimide **2**, resulted in the observation of a biexponential emission decay profile for **1** (excitation wavelength, 573 nm and emission monitored at 640 nm). Under these conditions, it was found that the amplitude (i.e. preexponential portion), but not the magnitude, of the fast component lifetime (τ_1; 1.2 ns) increased as the concentration of the quencher (**2**) was increased. Similarly, the amplitude of the slower component (τ_2; ca. 13 ns) was found to decrease as a function of increasing quencher concentration. Analysis of the relevant single photon counting data in a manner analogous to that previously described[5] yielded an association constant of 663 M^{-1} (toluene) for the formation of complex **I**. This value is of a comparable magnitude to that determined in CDCl$_3$ ($K_a = 364 \pm 47$ M^{-1}), a more polar solvent, using the ^{1}H NMR based methods discussed above.
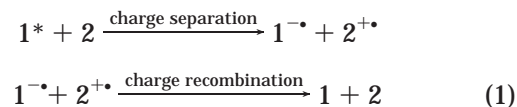
In analogy to what was seen under steady-state conditions, disruption of the noncovalent complex **I** by addition of a hydrogen bond competitor (e.g., methanol or uracil) restored the monoexponential fluorescence decay profile of **1**. Additionally, titration of the porphyrin with a diimide acceptor lacking the uracil-type hydrogen bonding recognition site (i.e. *N,N'*-diphenyl-1,5:4,8-tetracarboxynaphthalenedicarboximide) did not alter the basic monoexponential nature of the fluorescence decay profile typically observed for **1**. Instead, under these conditions the monoexponential decay was found to decrease in a

linear fashion consistent with diffusional "Stern–Volmer" quenching. On the basis of these results and previous precedent,[5] the shorter lifetime (τ_1; 1.2 ns) is assigned to **1** bound in complex **I**, and the longer lifetime (τ_2; 13 ns) is attributed to the free chlorin **1**.

To the extent the above assignments are correct, the most likely explanation for the observed effects is that rapid intracomplex photoinduced electron transfer occurs from the singlet excited state of **1** to the diimide acceptor **2** within assembly **I**. The rate constant for this electron-transfer reaction ($\Delta G_{cs} \cong -457$ mV)[12] was determined to be ca. 7.6×10^8 s^{-1} with a quantum yield of 0.91 ($\Phi = \tau_1 k_{ET}$).[5,13]

Similar experiments were also performed in dichloromethane and yielded analogous results. In particular, the lifetime (but not the amplitude) of the short component was found to remain constant during a titration in which the concentration of **2** was steadily increased from 0 to 1.23×10^{-2} M. Thus, from the lifetime recorded (0.31 ns), a rate constant for intraensemble ET (k_{ET}) of ca. 3.1×10^9 s^{-1} with a quantum yield, ($\Phi = \tau_1 k_{ET}$), of 0.97 could be calculated.[13]

While the single-photon counting experiments provide evidence consistent with electron transfer taking place rapidly within the ensemble **I**, it is important to appreciate that this evidence is only circumstantial. Unfortunately, all efforts to observe a diimide-derived radical anion[14] using time-resolved spectroscopy met with failure. As detailed below, this failure does not reflect the fact that species **2** cannot be reduced to the radical anion. Rather, it is rationalized in terms of the back ET reaction (**2**$^{-\bullet}$ + **1**$^{+\bullet}$ → **2** + **1**) being so fast in toluene or dichloromethane that no appreciable concentration of the charge separated species (**2**$^{-\bullet}$ + **1**$^{+\bullet}$) ever builds up to an observable level (eq 1).

$$1^* + 2 \xrightarrow{\text{charge separation}} 1^{-\bullet} + 2^{+\bullet}$$

$$1^{-\bullet} + 2^{+\bullet} \xrightarrow{\text{charge recombination}} 1 + 2 \qquad (1)$$

Evidence that a radical anion of **2** may be formed under appropriate conditions came from spectroelectrochemical analyses. Using such methods it was found that the diimide **2** exhibits virtually no light absorption between 400 and 700 nm. However, reduction of **2** with a single electron provides a species, **2**$^{-\bullet}$, with a λ_{max} of 476 nm ($\epsilon \sim 10^4$ M cm^{-1}, cf. Figure 3) that, in principle, could provide a very diagnostic "handle" for observing a photoinduced chlorin–diimide ET event, provided the rate of charge recombination (back ET) is such that an appreciable concentration is allowed to build up.

(12) The excited-state energy for **1** was estimated to be approximately 1.95 eV from the intersection of the absorption and emission spectra, cf. Figure 1. To determine the ground-state oxidation potential for **1** (+926 mV) and the ground-state reduction potential for **2** (−567 mV), cyclic voltammetry experiments were performed in dichloromethane/TBAPF$_6$ (Ag/AgCl, Pt electrode). For the forward ET reaction in **I**, a driving force of −457 mV was calculated using the following equation:

$$\Delta G_{CS} = -E_{1/2}(A^-/A) - ((E_{0,0}) - E_{1/2}(D/D^+))$$

(13) Calculated using the expression: $k = 1/\tau_2 - 1/\tau_1$.
(14) Osuka, A.; Nakajima, S.; Okada, T.; Taniguchi, S.; Nozaki, K.; Ohno, T.; Yamazaki, I.; Nishimura, Y.; Mataga, N. *Angew. Chem., Int. Ed. Engl* **1996**, *35*, 92–95, and references therein.
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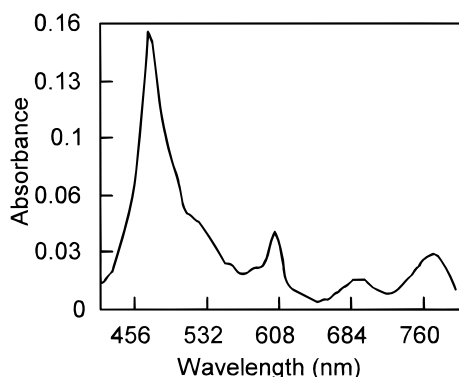
Figure 3. Spectroelectrochemical absorption spectrum for **2** $(1.59 \times 10^{-4}$ M) in anhydrous argon-degassed dichloromethane (25 °C) with 0.15 M TBAPF$_6$ as the electrolyte.
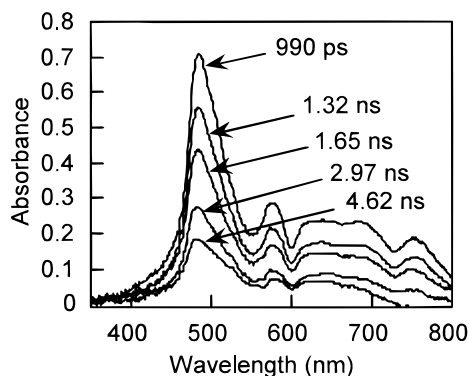
Figure 4. Picosecond transient absorption data for **I** in anhydrous argon-degassed toluene. Concentrations of chlorin (**1**) and quencher (**2**) were 4.84×10^{-5} M and 2.7×10^{-3} M, respectively. Excitation was effected at 532 nm.

In the hope that back ET reaction would be slow enough to allow the radical anion of **2** to be observed, picosecond transient absorption experiments involving **I** were performed. Figure 4 shows transient absorption spectra recorded for **I** following excitation with a 532 nm laser pulse. As can be appreciated from an inspection of this figure, there is no evidence for an appreciable concentration of the reduced diimide species (**2**$^{-\bullet}$). In fact, the spectra recorded for **I** are identical in all respects to those obtained using pure **1**, with the notable exception that the decay of the singlet excited state for **1** in ensemble **I** is faster. Presumably, this latter result simply reflects the fact that (forward) intraensemble ET is both favorable and fast.

Analysis of the decay traces of Figure 4 at a variety of wavelengths where both the excited chlorin and putative anion absorb revealed a monoexponential decay with an excited-state lifetime of 1.4 ns that is in excellent agreement with the fast τ_1 observed (for chlorin **1** in ensemble **I**) by single-photon counting methods (vide supra). A slow component, corresponding to τ_2 in the single-photon counting experiments, is also observed. If an observable population of reduced diimide **2** were present then one would have expected a more complex transient absorption decay profile for the early time events. Such complexity should be manifest at 476 nm where the strongest anion-ascribable absorption feature is found. However, even at this wavelength no kinetic (i.e. nonexponential) or spectral complexity is observed. It thus becomes necessary to assume that either forward electron transfer is not occurring or that subsequent

charge recombination (back ET) occurs even more quickly than the original charge separation process. On the basis of the steady-state fluorescence and single-photon counting studies described above, we favor the latter interpretation.

Conclusion

This present paper outlines a new approach to the construction of rigid noncovalent electron-transfer ensembles. While the present prototypic ensemble works well in terms of allowing photoinduced ET, it falls short in terms of establishing a long-lived charge separated state. Current efforts are therefore focused on the construction of alternative systems, containing different donor−acceptor pairs, that might allow the presumed radical cation−radical anion pair to be better observed.

Experimental Section

General Methods.[15] Proton NMR binding studies were performed using titrations carried out in accord with previously reported methods.[10] In these titrations the relevant binding isotherms were obtained by monitoring the downfield shift of the imide proton in **2**, (initial concentration, 1.62 mM) as the concentration of **1** was varied from 0 to 7.2 mM. Analysis by nonlinear least-squares fitting procedures[10] confirmed the proposed 1:1 binding stoichiometry and yielded an association constant of 364 ± 47 M^{-1}.

Fluorescence lifetimes were measured by time-correlated single-photon counting using a mode-locked, synchronously pumped, cavity-dumped Rhodamine 6G dye laser. The excitation wavelength used for the present chlorin-based systems was at 573 nm while the emission was monitored at a variety of wavelengths between 600 and 700 nm.

Transient absorption studies were performed with a mode-locked, frequency-doubled Nd:YAG laser (pulse width 30 ps). Excitation was at 532 nm.

Materials. Toluene was distilled from sodium. Pyridine and dichloromethane were distilled from calcium hydride. Anhydrous N,N-dimethylformamide, dichloromethane, tetraaminopyrimidine, 1,4:5,8-naphthalenetetracarboxylic acid dianhydride, and tetraphenylporphyrin were purchased from Aldrich Chemical Co. (Sure-Seal).

8,11,14,17-Tetrakis(3,5-di-*tert*-butylphenyl)-2,4-diaminopteridino[2,3-*b*]porphyrin (1). A 50 mL round-bottom flask was charged with **3**[8] (400 mg, 0.365 mmol), 2,4,5,6-tetraaminopyrimidine sulfate (174 mg, 0.73 mmol), and 25 mL of anhydrous pyridine. This mixture was heated at reflux under an argon atmosphere for 24 h. The pyridine was then removed in vacuo. The resulting residue was taken up in chloroform and washed 2×100 mL of water. The organic layer was dried over Na$_2$SO$_4$. After filtration and removal of solvent, this brown material was taken up in a minimum of chloroform and loaded onto a silica gel:hexanes column. A brown product was eluted off the column using 50% ethyl acetate/hexanes (v/v) (TLC-silica gel, R_f = 0.43, 5% MeOH, CHCl$_3$ (v:v)) to yield 371 mg (85%) of **1**. The purified material obtained in this way was recrystallized by allowing the benzene to evaporate off from a solution containing the chlorin product in a mixture of benzene/acetonitrile. This yielded **1** in the form of small brown needles. ^{1}H NMR (250 MHz, CDCl$_3$): δ −2.54 (2H, br s), 1.50−1.55 (72H, m), 5.20−5.35 (2H, br s), 6.35−6.45 (2H, br s), 7.79 (2H, t (J = 1.75 Hz)), 7.88 (1H, t (J = 1.79 Hz)), 7.97 (1H, t (J = 1.75 Hz)), 8.04 (2H, d (J = 1.79 Hz)), 8.07 (2H, d (J = 1.77 Hz)), (2H, d (J = 1.77 Hz)), 8.08 (2H, d (J = 1.78 Hz)), 8.75−8.78 (3H, m), 8.93 (1H, d (J = 4.95 Hz)), 9.00 (2H, s) ppm. ^{13}C NMR (250 MHz, CDCl$_3$): δ 31.74, 31.88, 35.17, 35.23, 116.91, 119.62, 120.23, 120.40, 120.45, 121.12, 121.16, 122.31, 123.13, 128.05, 128.14, 128.24, 128.48, 128.57, 129.45, 129.60, 129.81, 134.06, 134.58, 134.61, 137.95, 138.54, 139.26, 140.33, 140.85, 140.87, 141.19, 142.07, 144.45, 144.98, 147.14, 148.76, 148.89, 149.36, 154.74,

155.45, 157.91, 162.82, 163.81 ppm. Mass Spectrum (FAB): m/z (relative intensity) 1198 (M^+, 100). Exact mass (FAB) for $C_{80}H_{96}N_{10}$: calcd 1197.7839, found 1197.7854. Anal. Calcd for $C_{80}H_{96}N_{10}$: C, 80.23; H, 8.08; N, 11.69. Found: C, 80.20; H, 7.98; N, 11.64. λ_{max} (ϵ) 438.5 (221000 M^{-1} cm^{-1}), 527.5 (19847 M^{-1} cm^{-1}), 564 (5930 M^{-1} cm^{-1}), 599 (9387 M^{-1} cm^{-1}), 651 (589 M^{-1} cm^{-1}) nm. Cyclic voltammetric measurement: (0.15 M TBAPF$_6$ in CH$_2$Cl$_2$; Pt working electrode; Ag/AgCl reference; Pt wire counter electrode; sweep rate of 150 mV/s); $E_{1/2}$ = +926 mV, $E_{1/2}$ = +1061 mV.

N-(2,5-Di-*tert*-butylphenyl)-1,5-dicarboxy-4,8-naphthalenedicarboximide Anhydride (4). A 500 mL round-bottom flask was charged with 1,4:5,8-naphthalenetetracarboxylic acid dianhydride (19.44 g, 73 mmol) and 100 mL of anhydrous N,N-dimethylformamide (DMF) and stirred under an argon atmosphere. After warming to 80 °C, 2,5-di-*tert*-butylaniline (5 g, 24.3 mmol) in 50 mL of anhydrous DMF was added dropwise over 30 min. The mixture was stirred at 80 °C for an additional 12 h. The DMF was removed under high vacuum. The resulting residue was suspended in 50 mL of CH$_2$Cl$_2$ and loaded onto a silica gel:hexanes column. Byproducts were removed by eluting with 10% ethyl acetate/hexanes (v/v). The product was then eluted off using 50% ethyl acetate/hexanes (v/v). This gave 3.06 g (28% yield) of **4**. ^{1}H NMR (250 MHz, CDCl$_3$): δ 1.25 (9H, s), 1.33 (9H, s), 7.03 (1H, d (J = 2.16 Hz)), 7.53 (1H, dd (J = 8.47, 2.20 Hz)), 7.64 (1H, dd (J = 8.54 Hz)), 8.86 (4H, s) ppm. ^{13}C NMR (63 MHz, CDCl$_3$): δ 31.29, 31.83, 123.48, 126.97, 127.67, 127.91, 128.52, 129.48, 131.87, 133.56, 144.48, 151.04, 159.40, 163.76 ppm. Mass spectrum CIMS (CH$_4$): m/z (relative intensity, %) 456 [M + 1, 100]; HRCIMS: for $C_{28}H_{26}NO_5$ cald: 456.1811, found: 456.1806. Cyclic voltammetric measurement: (0.15 M TBAPF$_6$ in CH$_2$Cl$_2$; Pt working electrode; Ag/AgCl reference; Pt wire counter electrode; sweep rate of 150 mV/s); $E_{1/2}$ = −455 mV, $E_{1/2}$ = −927 mV.

N-(2,5-Di-*tert*-butylphenyl)-1,5-dicarboxy-N-hydrogen-4,8-dicarboxynaphthalenediimide (2). A 25 mL round-bottom flask was charged with **4** (300 mg, 0.659 mmol), urea (1 g, 16.7 mmol), and 10 mL of 1,3,5-trichlorobenzene (freshly distilled from CaH$_2$). This reaction mixture was heated at reflux under an argon atmosphere for 1 h and then cooled to room temperature. The trichlorobenzene was removed in vacuo. The residue was taken up in 100 mL of chloroform and washed with 100 mL of 10% NaHCO$_3$ followed by 2 × 100 mL of water. The organic layer was dried over Na$_2$SO$_4$, filtered, and evaporated to dryness. The resulting crude material was loaded onto a 50% ethyl acetate/hexanes (v/v) silica gel column and eluted using the same solvent mixture. After collection of the appropriate fractions and removal of solvent, a light-yellow powder was obtained and recrystallized from cold toluene to give **2** in the form of yellow-feathery needles (248 mg, 83%). ^{1}H NMR (250 MHz, CDCl$_3$): δ 1.27 (9H, s), 1.32 (9H, s), 6.99−7.00 (1H, dd (J = 2.17 Hz)), 7.48−7.52 (1H, dd (J = 2.20, 8.51 Hz)), 7.60 (1H, d (J = 8.54 Hz)), 8.38 (4H, q (J = 7.61 Hz)), 8.95 (1H, s) ppm. ^{13}C NMR (63 MHz, CDCl$_3$): δ 31.19, 31.74, 34.28, 35.57, 126.69, 127.53, 128.99, 130.89, 131.40, 131.97, 143.73, 150.40, 162.44, 163.64 ppm. Mass spectrum FAB-MS (NBA, 70 eV): m/z (*relative intensity*, %) 455 [M + 1, 100]; HRCIMS: for $C_{28}H_{27}N_2O_4$: calcd 455.1971, found: 455.1968. Anal. Calcd for $C_{28}H_{26}N_2O_4$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.86; H, 6.03; N, 6.02. Cyclic voltammetric measurement: (0.15 M TBAPF$_6$ in CH$_2$Cl$_2$; Pt working electrode; Ag/AgCl reference; Pt wire counter electrode; sweep rate of 200 mV/s); $E_{1/2}$ = −567 mV, $E_{1/2}$ = −985 mV.

Supporting Information Available: Proton NMR chemical shift data for the aromatic protons of **2**; steady-state fluorescence data for quenching of **1** by **2**; ^{1}H NMR spectra for **1** and **2**; single photon counting and transient absorption data for **I** (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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