Supporting Information For:

Photo-induced Charge Transfer and Nonlinear Absorption in Dyads Composed of a Two-photon Absorbing Donor and a Perylene Diimide Acceptor

Chun Huang,[‡] Matthew M. Sartin,[‡] Nisan Siegel, Matteo Cozzuol, Yadong Zhang, Joel M. Hales, Stephen Barlow, Joseph W. Perry*, Seth R. Marder*

School of Chemistry and Biochemistry and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, GA 30332-0400, USA

Corresponding author e-mail addresses: joe.perry@chemistry.gatech.edu, seth.marder@chemistry.gatech.edu

‡ These authors contributed equally to this work.

CONTENTS

I. Experimental Details

Ia. General.

Most organic and inorganic chemicals were obtained from Aldrich and Alfa Aesar. Palladium-based catalysts were purchased from Strem Chemicals and used without further purification. The ^{1}H and ^{13}C NMR spectra were collected on a Bruker 400 MHz or Bruker 500 MHz spectrometer using tetramethylsilane (TMS, $\delta = 0$ ppm) as an internal standard. Mass spectra were measured on a VG Instruments 70-SE using the electron-impact (EI) mode or on an Applied Biosystems 4700 Proteomics Analyzer using MALDI mode. Elemental analyses were carried out by Atlantic Microlabs using a LECO 932 CHNS elemental analyzer. Solution UV-Vis. absorption spectra were recorded on a Varian Cary 5E spectrophotometer. Solution emission and excitation spectra were measured using Fluorolog-2 from Spex (Edison, NJ). Electrochemical measurements were carried out under nitrogen in deoxygenated 0.1 M solutions of tetra-*n*-butylammonium hexafluorophosphate in dry CH_2Cl_2 using a computer-controlled BAS 100B electrochemical analyzer, a glassy-carbon working electrode, a platinum-wire auxiliary electrode, and a Ag wire anodised with AgCl as a pseudo-reference electrode. Potentials were referenced to the ferrocenium/ferrocene couple by using ferrocene as an internal standard. TGA measurements were performed on an NETZSCH STA 449C analyzer under a nitrogen flow of 40 mL/min with a heating rate of 5 ^{o}C/min. DSC measurements were performed on a TA Instruments DSC Q200 analyzer under a nitrogen flow of 50 mL/min with a heating and cooling rate of 5 ^{o}C/min.

Ib. Nonlinear Optical Measurements.

Two-photon absorption spectroscopy. Two-photon absorption (2PA) spectra were acquired using the reference-based two-photon excited fluorescence (2PEF) method.[1-2] The source of excitation light was a nanosecond pulsed optical parametric oscillator (Quanta-Ray MOPO 730) pumped by a Q-switched Nd:YAG laser (Quanta-Ray PRO250). The 2PEF method determines the 2PA spectra of unknowns by measuring the fluorescence emitted by the unknowns under two-photon excitation conditions and comparing it to the fluorescence emitted by a known reference compound under the same conditions. The 2PEF measurements of the model compounds were made in toluene (Sigma-Aldrich spectroscopic grade) solution at chromophore concentrations of 80–110 μM. The data reported here comprise several collections of over 200 pulses at each wavelength. 1,4-Bis(2-methylstyryl)benzene (Sigma-Aldrich, 99%) in cyclohexane (Sigma-Aldrich, spectroscopic grade) and fluorescein[3] (Acros, laser grade) in aqueous NaOH solution (pH 11) were used as references for the 630–680 nm and 690–1040 nm ranges, respectively. The 2PA cross-section values of 1,4-bis(2-methylstyryl)benzene reported by Kennedy[4] were reduced in scale by a factor of 10, as described by Fisher.[5] The uncertainties in the measured cross sections are approximately ±15% for the model compounds and approximately ± 40% for the dyads, owing in this case to the large uncertainty in the very low fluorescence quantum yields.

Femtosecond transient absorption measurements. The excitation source for femtosecond transient absorption measurements was generated by an optical parametric amplifier (TOPAS, Newport) pumped by a Ti:Sapphire regenerative amplifier (Spitfire, Newport), operating at 1 kHz repetition rate. The 800 nm Spitfire output could be converted by the TOPAS over the range of 465–2900 nm. For wavelengths below 465 nm, the TOPAS output was frequency doubled using a BBO crystal. Approximately 5% of the 800 nm Spitfire output was used to generate the white-light continuum probe beam (420–950 nm) in a sapphire plate. The laser pulse width in this spectral region was 120 fs. Transient data were collected using a commercially available Helios spectrometer (Ultrafast Systems, Sarasota, FL). The width of the instrument response function was 200 fs, and the maximum time delay was 3.2 ns. At each temporal delay, the signal was averaged for 1 s. The pump beam was chopped at 500 Hz to alternate between signal and reference data. A correction factor for the chirp of the white light was generated using the ultrafast response of toluene. All samples were prepared in 2 mm cuvettes and deaerated with N_2. The pump wavelengths were 390 nm for Dyad **1** (34 μM, OD = 0.35), Dyad **2** (34 μM, OD = 0.36), and **Donor model** (30 μM, OD = 0.32) and 530 nm for **PDI model** compound (29 μM, OD = 0.39). The pump energy for all samples was ca. 3.3 μJ/pulse.

Nanosecond Transmittance Measurements. The excitation source for nonlinear optical transmittance measurements was the same as that for nanosecond transient absorption. A mechanical shutter reduced the pulse repetition rate to 1 Hz to minimise damage to the sample. The dyads were prepared as deaerated 2 mM solutions in 1 cm cuvettes, with transmittance > 0.9 at the excitation wavelength of 750 nm. The laser was focused into the center of the cuvette using f/5 geometry, and the transmitted light was detected by a New Focus photoreceiver (San Jose, California), sampled using a Stanford Research Systems boxcar averager (Sunnyvale, CA), and recorded using an analog to digital converter and computer. A beam splitter placed before the sample redirected part of each pulse to a reference photoreceiver to normalise for fluctuations in the input energy of each pulse. The focus of the laser was positioned in the center of the 1.0 cm cell by translating the cell through the focus along the axis of the beam, while exciting the sample with 1 μJ pulses (z-scan). Reverse saturable absorption reduced the transmitted signal while the sample was passing through the focus, so the position where the focus was in the middle of the cuvette could be determined from the middle of the region of reduced transmittance.

Microcapillaries for long interaction length nonlinear transmittance measurements, with inner diameter 20 μm and $n_{\text{cladding}} = 1.44$, were obtained from Polymicro Technologies and cut to a length of 18 mm. These were placed upright in 7 mM solutions of the dyads in toluene and left overnight to uptake the solution via capillary force. These were placed in a sealed cell filled with dyad solution to ensure no leakage occurred. The excitation pulse was coupled into the microcapillary using a 10× microscope objective, and the transmitted light was collected using a 20× objective. Transmittance through the capillary was verified by imaging the output beam with a CCD camera. The camera was then replaced with a photoreceiver for the measurement of energy-dependent transmittance.

Ic. Synthesis.

2,7-Dibromo-9-(6-bromohexyl)-9*H*-carbazole. 2,7-Dibromo-9*H*-carbazole[6] (1.62 g, 5.00 mmol) and KOH (0.28 g, 5.0 mmol) were stirred in anhydrous DMF (20 mL) at 0 °C. Then 1,6-dibromohexane (2.5 g, 10 mmol) was added in one portion, and the resultant mixture was stirred overnight at room temperature. The mixture was poured into water (300 mL), and ethyl acetate (200 mL) was used to extract the product. The organic phase was washed with water (6 × 100 mL) and dried over Na_2SO_4. After the solvent was removed, the residue was recrystallised from hexane (100 mL) to afford a white solid (1.94 g, 79%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, J = 8.5 Hz, 2H), 7.50 (s, 2H), 7.33 (dd, J = 8.5, 1.0 Hz, 2H), 4.20 (t, J = 7.0 Hz, 2H), 3.38 (t, J = 6.5 Hz, 2H), 1.88 (m, 4H), 1.51 (m, 2H), 1.47 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ

141.3, 122.6, 121.5, 121.3, 119.7, 111.9, 43.2, 33.6, 32.5, 28.6, 27.9, 26.4. HRMS (EI) calcd. for $C_{18}H_{18}Br_3N$ (M^+): 484.8989, found: 484.8979. Anal. Calcd. for $C_{18}H_{18}Br_3N$: C, 44.30; H, 3.72; N, 2.87. Found: C, 44.26; H, 3.67; N, 2.93.

2-[6-(2,7-Dibromo-9*H*-carbazol-9-yl)hexyl]isoindoline-1,3-dione. 2,7-Dibromo-9-(6-bromohexyl)-9*H*-carbazole (1.60 g, 3.30 mmol) was dissolved in anhydrous DMF (10 mL) and cooled to 0 °C. Potassium 1,3-dioxoisoindolin-2-ide (1.3 g, 7.0 mmol) was then added in one portion. The resultant mixture was stirred overnight at room temperature and then poured into water (200 mL). The white solid was collected by filtration and purified by column chromatography on silica gel, eluted with CH_2Cl_2 / hexane (1:2) to give a white solid (1.64 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, J = 8.0 Hz, 2H), 7.83 (m, 2H), 7.69 (m, 2H), 7.48 (d, J = 1.5 Hz, 2H), 7.31 (dd, J = 8.0, 1.5 Hz, 2H), 4.19 (t, J = 7.5 Hz, 2H), 3.68 (t, J = 7.0 Hz, 2H), 1.84 (m, 2H), 1.66 (m, 2H), 1.42 (m, 4H). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 168.4, 141.3, 133.9, 132.1, 123.2, 122.5, 121.5, 121.3, 119.7, 111.9, 43.2, 37.7, 28.7, 28.4, 26.7, 26.6. HRMS (EI) calcd. for $C_{26}H_{22}Br_2N_2O_2$ (M^+): 552.0048, found: 552.0023. Anal. Calcd. for $C_{26}H_{22}Br_2N_2O_2$: C, 56.34; H, 4.00; N, 5.05. Found: C, 56.37; H, 4.09; N, 5.05.

6-(2,7-Dibromo-9*H*-carbazol-9-yl)hexan-1-amine. 2-[6-(2,7-Dibromo-9*H*-carbazol-9-yl)hexyl]isoindoline-1,3-dione (1.67 g, 3.00 mmol) and hydrazine monohydrate (2.2 mL) were heated in refluxing ethanol (60 mL) for 4 h. After the reaction mixture was cooled to –10 °C, the white solid was filtered and washed with cold methanol to give a white solid (1.24 g, 99%) which was used in the synthesis of compound **B** without further purification, due to the poor solubility.

Compound A. *N*-(1-Undecyl-dodecyl)-perylene-3,4-dicarboxyanhydride-9,10-dicarboximide[7] (0.356 g, 0.50 mmol), 4-(2,7-dibromo-9*H*-carbazol-9-yl)aniline[6] (0.413 mg, 1.00 mmol), anhydrous zinc (II) acetate (80 mg, 0.44 mmol), and imidazole (3.0 g) were heated under N_2 at 180 °C overnight. The reaction mixture was then allowed to cool to ca. 130 °C and poured into 4N aqueous HCl (160 mL). The red precipitate was collected by filtration and washed sequentially with 2N aqueous HCl (3 × 10 mL), water (3 × 10 mL), and methanol (2 × 10 mL). The solid was then dissolved in $CHCl_3$ (5 mL) and a minimum amount of silica gel was added to absorb the liquid. After the solvent was removed under reduced pressure, the dried silica gel was added to the top of a hexane-packed silica gel column, and the column was eluted with $CHCl_3$ to give a red solid (0.53 g, 89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.78 (d, J = 8.0 Hz, 2H), 8.72–8.66 (m, 6H), 7.95 (d, J = 8.5 Hz, 2H), 7.75 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 1.0 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 7.42 (dd, J = 8.5, 1.0 Hz, 2H), 5.18 (m, 1H), 2.26 (m, 2H), 1.86 (m, 2H), 1.29–1.21 (m, 36H), 0.83 (t, J = 6.5 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 165.0, 164.1, 163.9, 141.8, 137.2, 135.8, 134.9, 134.6, 134.5, 132.4, 132.3, 131.6, 131.2, 130.2, 129.9, 128.9, 128.0, 127.0, 126.7, 124.6, 124.4, 123.9, 123.8, 123.6, 123.5, 123.3, 122.3, 122.0, 121.8, 120.6, 116.4, 113.6, 113.5, 55.3, 32.8, 32.3, 30.2, 30.1 (3 peaks) 30.0, 29.8, 27.5, 23.2, 14.7 (the observation of three carbonyl carbon resonances is consistent with previous work on perylene bis(dicarboxyimide)s using similar swallow-tailed *N*-substituents and it has been attributed to restricted rotation of the N—C_{alkyl} bonds.[8] Two aromatic carbon peaks and one alkyl carbon were not observed, presumably due to overlapping coincidental resonances). HRMS (MALDI) calcd. for $C_{65}H_{65}Br_2N_3O_4$ (M^+): 1109.33, found: 1109.35. Anal. Calcd. for $C_{65}H_{65}Br_2N_3O_4$: C, 70.20; H, 5.89; N, 3.78. Found: C, 69.99; H, 5.92; N, 3.8**1**

Compound B. *N*-(1-Undecyl-dodecyl)-perylene-3,4-dicarboxyanhydride-9,10-dicarboximide[7] (0.713 g, 1.00 mmol), 6-(2,7-dibromo-9*H*-carbazol-9-yl)hexan-1-amine (0.500 g, 1.2 mmol), anhydrous zinc (II) acetate (200 mg, 1.10 mmol), and imidazole (10.0 g) were heated under N_2

at 180 °C overnight. The reaction mixture was allowed to cool to ca. 130 °C and poured into 4 N aqueous HCl (160 mL). The red precipitate was collected by filtration and washed with water (3 × 30 mL) and then with methanol (3 × 30 mL). The solid was then dissolved in $CHCl_3$ (10 mL) and a minimum amount of silica gel was added to absorb the liquid. After the solvent was removed under reduced pressure, the dried silica gel was added to the top of a hexane-packed silica gel column and eluted with $CHCl_3$ / hexane (3:2 and then 2:1, and finally $CHCl_3$ / ethyl acetate (20:1). After the solvent was removed, **Compound B** was obtained as a red solid (0.81 g, 72%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.65–8.56 (m, 8H), 7.83 (d, J = 8.0 Hz, 2H), 7.49 (s, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.16 (m, 1H), 4.19 (m, 4H), 4.16 (t, J = 7.5 Hz, 2H), 2.25 (m, 2H), 1.85 (m, 4H), 1.74 (m, 2H), 1.47 (m, 4H), 1.30–1.17 (m, 34H) 0.83 (t, J = 6.0 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 164.6, 163.4 (2 close peaks), 141.3, 134.7, 134.3, 131.8, 131.4, 131.1, 129.5, 129.3, 126.4, 126.3, 124.0, 123.1, 122.9, 122.5, 121.4, 121.2, 119.7, 111.9, 55.0, 43.3, 40.3, 32.4, 31.9, 29.6 (3 peaks), 29.5, 28.6. 27.8, 27.0, 26.9, 26.7, 25.0, 22.6, 14.1. (The observation of three carbonyl carbon resonances is consistent with previous work on perylene bis(dicarboxyimide)s using similar swallow-tailed *N*-substituents and it has been attributed to restricted rotation of the N—C_{alkyl} bonds.[8] One alkyl carbon resonance was not observed, presumably due to overlapping coicnidental resonances). HRMS (MALDI) calcd. for $C_{65}H_{73}Br_2N_3O_4$ (M^+): 1117.402, found: 1117.379. Anal. Calcd. for $C_{65}H_{73}Br_2N_3O_4$: C, 69.70; H, 6.57; N, 3.75. Found: C, 69.86; H, 6.49; N, 3.67.

Dyad 1. Compound **A** (0.33 g, 0.30 mmol), *N,N*-di(4-*n*-butylphenyl)-4-vinylaniline[9] (0.77 g, 2.0 mmol), tri-*o*-tolylphosphine (60 mg, 0.20 mmol), and palladium(II) acetate (22 mg, 0.010 mmol) were placed in a two-neck round-bottomed flask equipped with a condenser. After evacuating and refilling the flask with nitrogen three times, DMF (9.0 mL) and triethylamine

(3.0 mL) were added by syringe. The resultant mixture was then heated under N_2 at 100 °C for 24 h. After the mixture was allowed to cool to room temperature, it was poured into methanol (100 mL) and the resultant solid was collected by filtration. The solid was then dissolved in toluene and purified using column chromatography on silica gel, with toluene / hexane (3:1) as the eluent. After the solvent was removed under reduced pressure, the resultant solid was heated in refluxing ethanol for 2 h; **Dyad 1** was collected by filtration as a red solid while the solution was hot (298 mg**,** 58%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70–8.62 (m, 8H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.64 (s, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 4H), 7.17 (s, 4H), 7.11 (d, *J* = 8.5 Hz, 8H), 7.02 (d, *J* = 8.5 Hz, 8H), 6.98 (d, *J* = 8.5 Hz, 2H), 5.18 (m, 1H), 2.92 (t, *J* = 7.5 Hz, 8H), 2.26 (m, 2H), 1.86 (m, 2H), 4.39 (t, *J* = 6.0 Hz, 2H), 3.63 (m, 2H) 3.03 (t, *J* = 6.0 Hz*,* 2H), 2.26 (m, 2H), 2.04 (m, 2H), 1.87 (m, 2H), 1.63 (quintet, *J* = 7.5 Hz, 8H), 1.41–1.2 (m, 34H), 0.96 (t, *J* = 7.5 Hz, 12H), 0.84 (t, *J* = 7.5 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 163.9, 163.0, 162.8, 147.0, 144.5, 141.0, 137.3, 137.0, 135.4, 134.7, 133.5, 133.2, 131.3, 130.1, 129.8, 129.2, 128.9, 128.5, 137.3, 127.2, 126.5, 126.1, 125.8, 123.9, 122.8, 122.5,122.4, 122.1, 121.9, 119.6, 118.2, 107.1, 54.2, 34.4, 33.0, 31.7, 31.2, 28.9 (4 closely spaced peaks), 28.6, 26.3, 22.0, 21.8, 13.4, 13.3. (The observation of three carbonyl carbon resonances is consistent with previous work on perylene bis(dicarboxyimide)s using similar swallow-tailed *N*-substituents and it has been attributed to restricted rotation of the N—C_{alkyl} bonds.[3] Two aromatic carbon and one alkyl carbon resonance were not observed, presumably due to overlapping coincidental resonances). HRMS (MALDI) calcd. for $C_{121}H_{129}N_5O_4$ (M–H$^+$): 1716.000, found: 1715.998. Anal. Calcd. for $C_{121}H_{129}N_5O_4$: C, 84.62; H, 7.57; N, 4.08; Found: C, 84.53; H, 7.65; N, 4.12.

Dyad 2. Compound **B** (0.33 g, 0.30 mmol), *N,N*-di(4-*n*-butylphenyl)-4-vinylaniline[9] (0.77 g, 2.0 mmol), tri-*o*-tolylphosphine (60 mg, 0.20 mmol), and palladium (II) acetate (22 mg, 0.010 mmol) were placed in a two-neck, round-bottomed flask equipped with a condenser. After evacuating and refilling the flask with nitrogen three times, DMF (9 mL) and triethylamine (3 mL) were added by syringe. The mixture was then heated under N_2 at 100 °C for 24 h. After the mixture was allowed to cool to room temperature, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel, eluted with $CHCl_3$ / hexane (1:1 and then 4:3). After the solvent was removed under reduced pressure, the resulting solid was refluxed in ethanol for 2 h; Dyad **2**, as a red solid, was collected by filtration while the solution was hot (210 mg, 41%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.6–8.4 (m, 8H), 7.94 (d, J = 8.0 Hz, 2H),7.49 (s, 2H), 7.42 (d, J = 9.0 Hz, 4H),7.37 (d, J = 8.0 Hz, 2H), 7.19 (s, 4H), 7.08 (d, J = 7.0 Hz, 8H), 7.0–6.7 (m, 12H), 5.2–5.1 (m, 1H), 4.35 (t, J = 7.0 Hz, 2H), 4.16 (t, J = 7.0 Hz, 2H) 2.58 (t, J = 7.5 Hz, 8H), 2.3–2.2 (m, 2H) , 1.95–1.94 (m, 2H), 1.87–1.83 (m, 2H), 1.77–1.73 (m, 2H), 1.60 (quintet, J = 8.0 Hz, 8H), 1.4–1.2 (m, 48H), 0.95 (t, J = 7.5 Hz, 12H), 0.84 (t, J = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 164.6, 163.5, 163.4, 147.6, 145.2, 141.4, 137.7, 137.6, 135.4, 134.6, 134.4, 131.8, 131.4, 131.1, 130.9, 129.5, 128.3, 129.1, 128.9, 127.7, 127.6, 127.2, 126.4, 126.3, 124.6, 123.9, 123.1, 122.9, 122.5, 122.2, 120.2, 117.5, 106.5, 54.8, 43.0, 40.3, 35.0, 33.7, 32.3, 31.9, 29.6, 29.5, 29.3, 28.8, 27.7, 27.0, 26.9, 26.7, 22.7, 22.4, 14.1, 14.0. (The observation of three carbonyl carbon resonances, along with three additional aromatic resonances, can be attributed to restricted rotation of the N—C_{alkyl} bonds.[3] Two alkyl carbon resonances were not observed, presumably due to overlap). HRMS (MALDI) calcd. for $C_{121}H_{137}N_5O_4$ (M^+): 1724.067, found: 1724.075. Anal. Calcd. for $C_{121}H_{137}N_5O_4$: C, 84.22; H, 7.95; N, 4.09. Found: C, 84.02; H, 8.08; N, 4.05.

Donor Model. 2,7-Dibromo-9-*n*-hexyl-9*H*-carbazole[10] (0.41 g, 1.0 mmol), *N,N*-di(4-*n*-butylphenyl)-4-vinylaniline[9] (1.0, 2.6 mmol), tri-*o*-tolylphosphine (60 mg, 0.20 mmol), and palladium (II) acetate (22 mg, 0.010 mmol) were charged to a two-neck round-bottomed flask equipped with a condenser. After evacuating and refilling the flask with nitrogen three times, DMF (12 mL) and triethylamine (4 mL) were added by syringe. The mixture was then heated under N_2 at 100 °C for 12 h. After the mixture was allowed to cool to room temperature, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel, using $CHCl_3$ / hexane (1:20 and then 1:5) as eluents to give **Donor model** as a yellow solid (0.44 g, 44%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.00 (d, J = 8.0 Hz, 2H), 7.38 (s, 2H), 7.43–7.40 (m, 6H), 7.19 (s, 4H), 7.11 (d, J = 8.0 Hz, 8H), 7.02–6.99 (m, 12H), 4.35 (t, J = 7.0 Hz, 2H), 2.59 (t, J = 7.5 Hz, 8H), 1.93 (quintet, J = 7 .5 Hz, 2H), 1.61 (quintet, J = 6.5 Hz, 8H), 1.4–1.2 (m, 14H), 0.95 (t, J = 7.0 Hz, 12H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 148.2, 145.6, 142.0, 138.4, 135.9, 131.2, 129.6, 127.9, 127.8, 127.5, 125.1, 122.6, 122.5, 120.6, 118.0, 106.8, 43.4, 35.4, 34.1, 32.0, 29.3, 27.3, 22.9, 22.8, 14.2, 14.1. (Two aromatic carbon resonances were not observed, presumably due to overlapping coincidental resonances). HRMS (MALDI) calcd. for $C_{74}H_{83}N_3$ (M^+): 1013.659, found: 1013.665. Anal. Calcd. for $C_{74}H_{83}N_3$: C, 87.61; H, 8.25; N, 4.14. Found: C, 87.35; H, 8.18; N, 4.11.

PDI Model. (*N,N'*-Bis(1-undecyl-dodecyl)-perylene-3,4,9,10-tetracarboxylic diimide): A mixture of perylene-3,4,9,10-tetracarboxydianhydride (6.0 g, 15 mmol), 1-undecyl-dodecylamine (12 g, 35 mmol), anhydrous zinc (II) acetate (1.6 g, 8.7 mmol) and imidazole (70 g) were heated at 180 °C for 5 hours before it was allowed to cool to room temperature and treated with 2 N aqueous HCl solution (400 mL). The mixture was then extracted with chloroform (2 × 200 mL). The organic phase was washed with water (3 × 100 mL) and dried over $MgSO_4$. The solvent was then removed under reduced pressure and the residue was purified by flash chromatography on silica gel, using $CHCl_3$ / hexane (1:1 and then 2:1) as eluent to give **PDI model** as a red solid (12 g, 77%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.64 (m, 8H), 5.18 (m, 2H), 2.22 (m, 4H), 1.86 (m, 4H), 1.4–1.1 (m, 72H). 0.80 (t, J = 6.6 Hz, 12H). The ^{1}H NMR spectrum of this product is consistent with that reported in the literature.[11]

Generation of radical ions. The radical anion of the **PDI model** compound was generated in anhydrous THF solution by reduction with cobaltocene in a nitrogen atmosphere glove box. The radical cation of the **Donor model** compound was generated in anhydrous dichloromethane by oxidation with tris(*p*-bromophenyl)aminium hexachloroantimonate. The absorption spectra of the radical ions were recorded a Varian Cary 5E UV-Vis-NIR spectrophotometer using 1.0 cm pathlength cells.

II. Additional Spectra of Oxidised and Reduced Species.

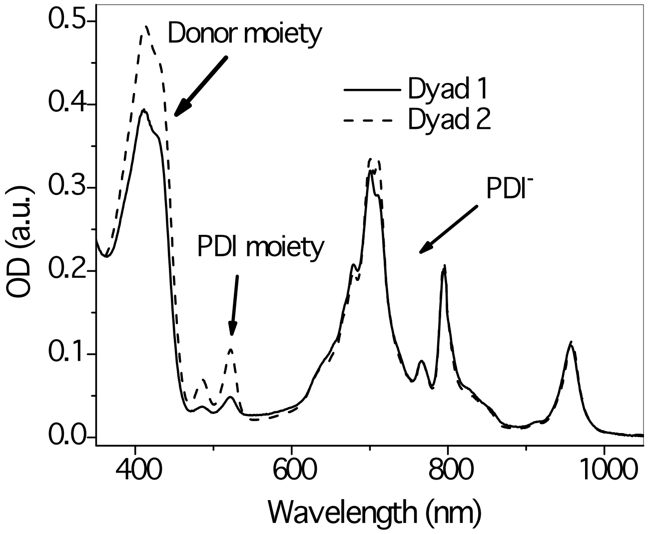

Fig. S1. The absorption spectra of the radical anions of **Dyad 1** (solid) and **Dyad 2** (broken) generated via chemical reduction using cobaltocene in THF.

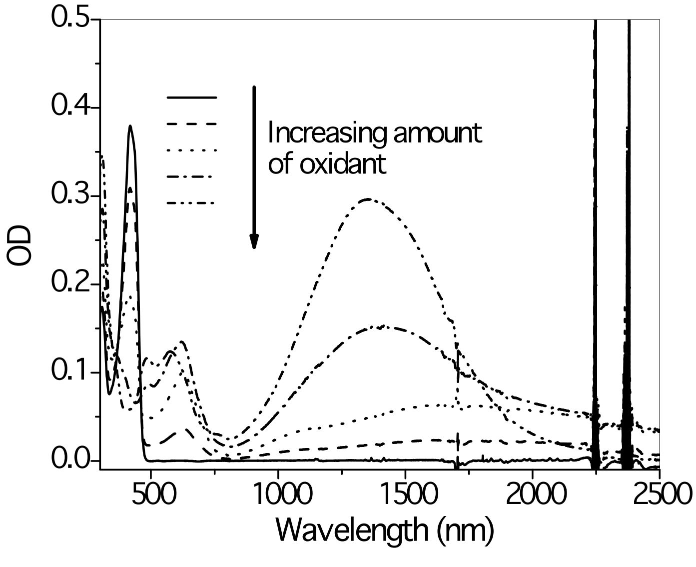

Fig. S2. Absorption spectra of neutral **Donor model** and following oxidation with increasing amounts of tris(*p*-bromophenyl)aminium hexachloroantimonate in dichloromethane.

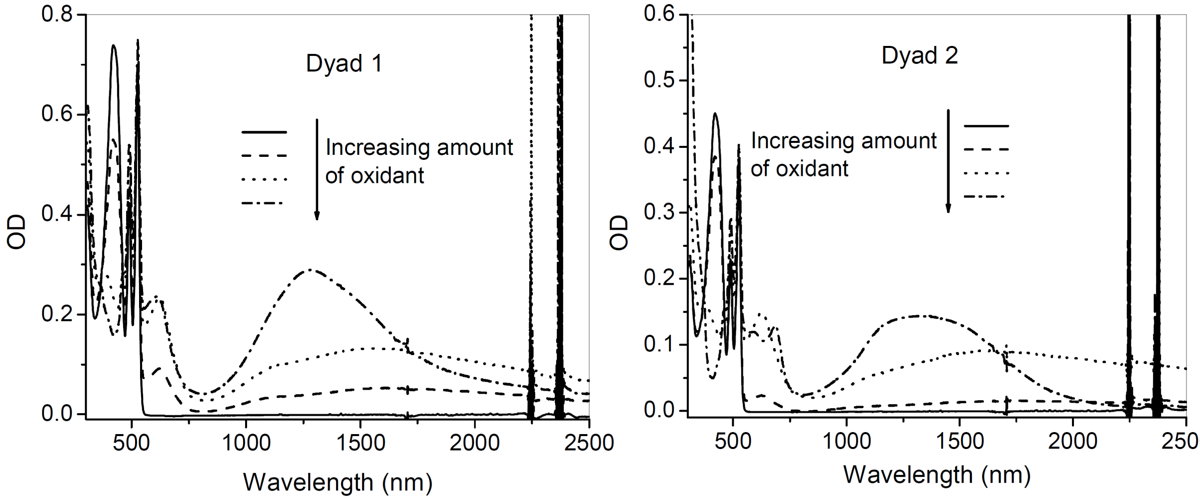

Fig. S3. Absorption spectra of neutral **Dyad 1** (left) and **Dyad 2** (right) and following oxidation with increasing amounts of tris(*p*-bromophenyl)aminium hexachloroantimonate in dichloromethane.

III. Additional Transient Absorption Data and Simulations.

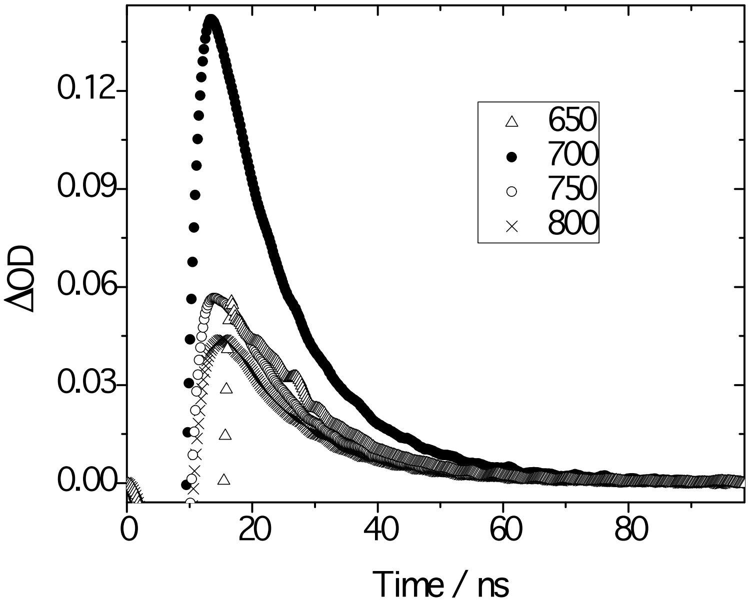

Fig. S4. The Nanosecond pulse transient absorption decay following excitation at 355 nm (OD = 0.11) of 2 μM **Dyad 1** in toluene using 900 μJ/pulse.

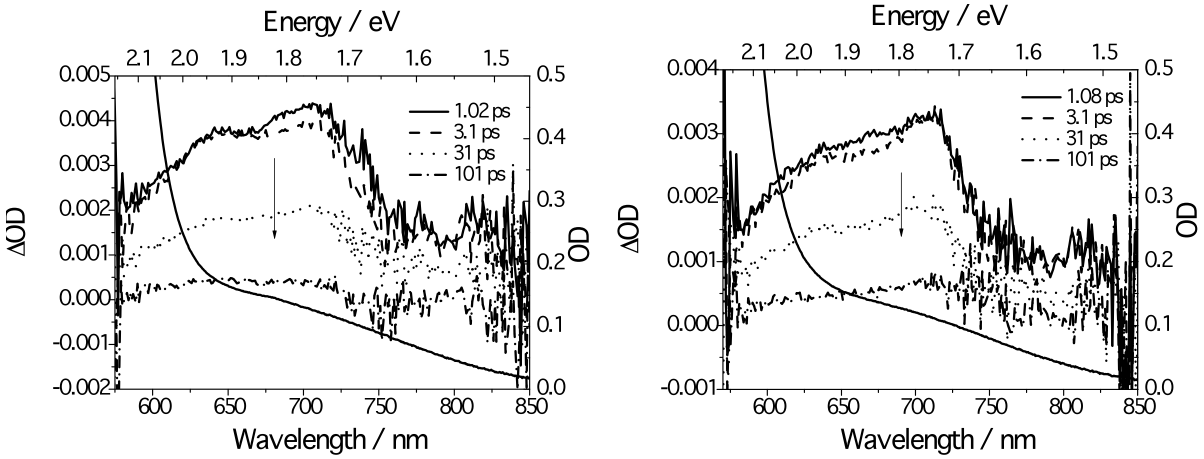

Fig. S5. Transient absorption spectra of 9.6 mM **Dyad 1** in toluene (left) and 9.7 mM **Dyad 2** in toluene (right) obtained by direct excitation of the band assigned to intermolecular charge transfer at 750 nm.

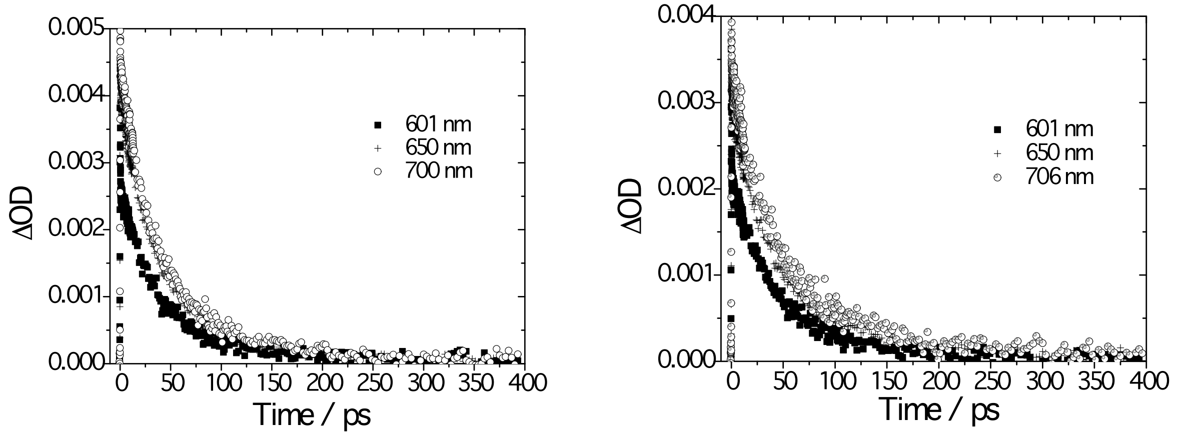

Fig. S6. Decay of transient absorption following 750 nm excitation of intermolecular charge transfer band. 9.6 mM **Dyad 1** in toluene (left) exhibits decays with time constants of 30 ps and 120 ps. 9.7 mM **Dyad 2** in toluene (right) decays with time constants of 40 ps and 160 ps.

IV. Simulations of Nonlinear Transmission Data

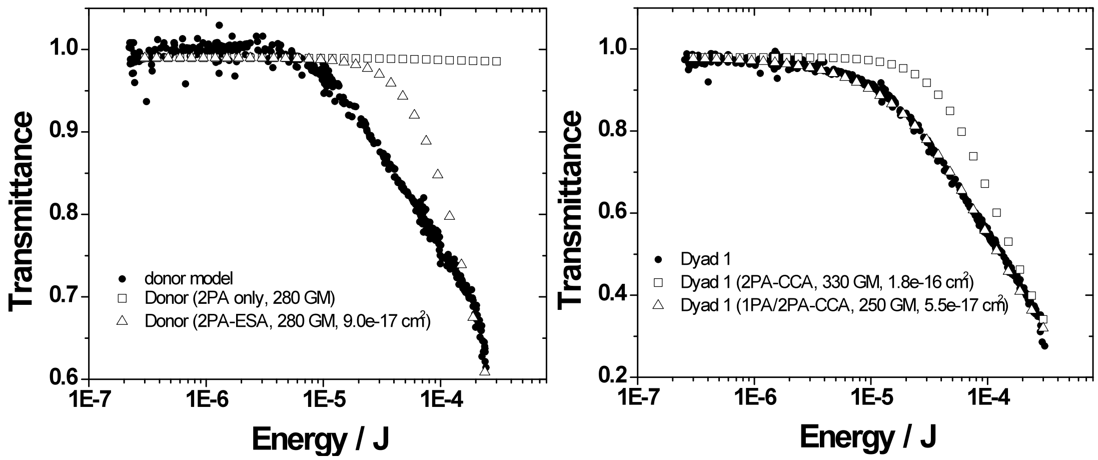

Fig. S7. Comparison of experimental (filled symbols) and simulated (open symbols) energy-dependent transmittance data for 800nm, 6 ns pulses focused in an f/5 geometry into the middle of a 1 cm pathlength cell containing 2 mM solutions of **Donor model** (left) and **Dyad 1** (right). **Donor model** simulations show the NLA due to 2PA alone (open squares) and the effect of the 2PA-induced long-lived ESA (open triangles). **Dyad 1** simulations include the effects of 2PA and radical-ion absorption (open squares), and the effect of additional photogenerated radical ions (open triangles) formed due to the weak ground-state charge-transfer-complex absorption at this wavelength.

V. References for Supporting Information

1 M. Rumi, S. Barlow, J. Wang, J. W. Perry and S. R. Marder, *Adv. Polym. Sci.*, 2008, **213**, 1.

2 M. Rumi, J. E. Ehrlich, A. A. Heikal, J. W. Perry, S. Barlow, Z. Hu, D. McCord-Maughon, T. C. Parker, H. Rockel, S. Thayumanavan, S. R. Marder, D. Beljonne and J.-L. Brédas, *J. Am. Chem. Soc.*, 2000, **122**, 9500.

3 C. Xu and W. W. Webb, *J. Opt. Soc. Am. B* 1996, **13**, 481.

4 S. M. Kennedy and F. E. Lytle, *Anal. Chem.* , 1986, **58**, 2643.

5 W. G. Fisher, E. A. Wachter, F. E. Lytle, M. Armas, and C. Seaton, *Appl. Spectrosc.* 1998, **52**, 536.

6 H. Jian and J. M. Tour, *J. Org. Chem.*, 2003, **68**, 5091.

7 M. J. Tauber, R. F. Kelley, J. M. Giaimo, B. Rybtchinski, and M. R. Wasielewski, *J. Am. Chem. Soc.* , 2006, **128**, 1782.

8 L. D. Wescott and D. L. Mattern, *J. Org. Chem* **2003**, *68*, 10058.

9 M. Behl, E. Hattemer, M. Brehmer, and R. Zentel, *Macromol. Chem. Phys.* 2002, **203**, 503.

10 W. Tang, T. Lin, L. Ke and Z.-K. Chen, *J. Polym. Sci. Part A: Polym. Chem.*, 2008, **46**, 7725.

11 R. F. Kelley, W. S. Shin, B. Rybtchinski, L. E. Sinks and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2007, **129**, 3173.