Supporting Information

Photoinduced Interactions in a Pyrene-Calix[4]arene-Perylene Bisimide Dye System: Probing Ground State Conformations with Excited State Dynamics of Charge Separation and Recombination

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1. Synthesis

Materials and methods

Compounds 1[1] **and 2**[2,3] were synthesized according to literature procedures. All compounds were characterized by ^{1}H-NMR spectroscopy and high-resolution mass spectrometry (HR-MS). Solvents were purified and dried according to standard procedures.[4] Column chromatography was performed with silica gel 60 (0.035 - 0.070 mm); HPLC on SiO_2 columns, normal phase (NP). NMR spectra were recorded on a Bruker DMX 600 (600.1 MHz) spectrometer. Chemical shifts δ were calibrated against the residual tetrachloroethane-*d*$_2$ peak (^{1}H-NMR: $\delta = 6.00$ ppm, ^{13}C-NMR: $\delta = 74.20$ ppm). Mass spectra were performed with a Bruker microTOF$_{LC}$ instrument.

Compound 3 (PBI-c):

Under an argon atmosphere 22.0 mg (0.031 mmol, 1 equiv.) of compound **1**, 25.0 mg (0.046 mmol, 1.5 equiv.) of perylene monoimide **2** and one drop of triethylamine in toluene (0.2 mL) were heated to 105 °C for 38 h. The solvent was removed by rota-evaporation, and the resulting solid was purified by column chromatography with CH_2Cl_2/ethylacetate 99:1 and precipitated from CH_2Cl_2/methanol. Compound **3** was obtained as a light red powder (22.0 mg, 0.018 mmol, 58%). $C_{80}H_{87}N_3O_{10}$ (1250.56). Mp 119 – 122 °C. TLC (CH_2Cl_2): $R_f = 0.24$. **^{1}H-NMR** (600 MHz, tetrachloroethane-*d*$_2$, 79 °C): δ (ppm) = 8.74 – 8.71 (m, 4H; Per-*H*); 8.68 – 8.66 (m, 4H; Per-*H*); 6.86 (bs, 2H; Ar-*H*); 6.81 (bs, 2H; Ar-*H*); 6.73 (bs, 1H; Boc-N*H*); 6.60 – 6.55 (m, 6H; Ar-*H*); 5.23 – 5.18 (m, 1H; Undecyl-C*H*); 4.59 and 3.26 (AX, 4H, ^2J = 13.4 and 13.5 Hz; Ar-C*H*$_2$-Ar); 4.52 and 3.21 (AX, 4H, ^2J = 13.3 and 13.4 Hz; Ar-C*H*$_2$-Ar); 4.06 (t, 2H, ^3J = 7.5 Hz; O-C*H*$_2$); 3.97 (t, 2H, ^3J = 7.4 Hz; O-C*H*$_2$); 3.91 (t, 4H, ^3J = 7.1 Hz; O-C*H*$_2$); 2.31 – 2.25 (m, 2H; Undecyl-C*H*$_2$); 2.06 – 1.92 (m, 8H + 2H; Propyl-C*H*$_2$ and Undecyl-C*H*$_2$); 1.57 (s, 9H; Boc-*tert*-Butyl-*H*); 1.43 – 1.34 (m, 12H; Undecyl-C*H*$_2$); 1.11 (t, 6H, ^3J = 7.4 Hz; Propyl-C*H*$_3$); 1.08 – 1.04 (m, 6H; Propyl-C*H*$_3$); 0.91 – 0.89 (m, 6H; Undecyl-C*H*$_3$). **HR-MS** (ESI in acetonitrile/$CHCl_3$): calcd for $C_{80}H_{88}N_3O_{10}$ $[M+H]^+$ m/z = 1250.6470; found 1250.6464.

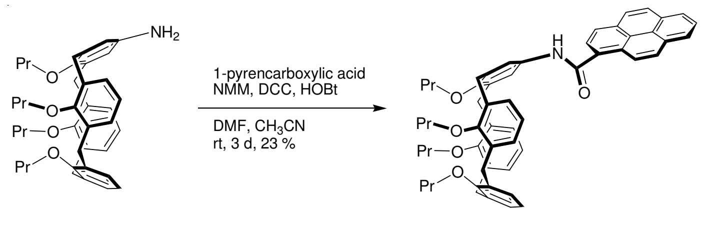
Compound 5 (Py-c-PBI):

To a solution of 22.0 mg (0.018 mmol) of compound **3** in 2 mL dry CH_2Cl_2 were added 3 mL of CF_3COOH under an argon atmosphere. The mixture was stirred for 3 h at room temperature, poured into ice water and adjusted to pH > 9 with NH_3 solution (25%). CH_2Cl_2 (50 mL) was added to the mixture and the resulting organic phase was washed with water and brine, and dried over Na_2SO_4. The solvent was removed by rota-evaporation and the resulting crude product **4** was dried and used for the next step without further purification.

Under an argon atmosphere 3.2 mg (0.013 mmol, 1 equiv.) of 1-pyrenecarboxylic acid, 2.6 mg (0.026 mmol, 2 equiv.) of *N*-methylmorpholine (NMM), 2.6 mg (0.013 mmol, 1 equiv.) of *N*,*N'*-dicyclohexylcarbodiimide (DCC) and 1.7 mg (0.013 mmol, 1 equiv.) of 1-hydroxybenzotriazole

(HOBt) in a 2:1 mixture of dry DMF and dry acetonitrile (0.3 mL) were stirred at room temperature for 0.5 h. A solution of 15.0 mg (0.013 mmol, 1 equiv.) of the crude product **4** in dry DMF (1.2 mL) was added, and the reaction mixture was stirred at room temperature for 5 d. The reaction mixture was filtered and CH_2Cl_2 (70 mL) was added to the filtrate and washed with brine and water, and dried over Na_2SO_4. The crude product was purified by column chromatography with CH_2Cl_2/ethylacetate 97:3, precipitated three times from CH_2Cl_2/*n*-hexane, and was further purified by HPLC with CH_2Cl_2. Compound **5** was obtained as a violet powder (8.0 mg, 5.8 µmol, 33% over two steps). $C_{92}H_{87}N_3O_9$ (1378.69). Mp 270 – 272 °C. TLC (CH_2Cl_2/ethylacetate 95:5): $R_f = 0.84$. **^{1}H-NMR** (600 MHz, tetrachloroethane-*d*$_2$, 79 °C):[5] δ (ppm) = 8.75 – 8.74 (m, 2H; H64 and H69, Per-*H*); 8.56 (s, 1H; H84, N*H*); 8.32 (bs, 2H; H63 and H70, Per-*H*); 8.02 – 7.99 (m, 2H; H5 and H6, Pyrenyl-*H*); 7.76 – 7.75 (m, 1H; H14, Pyrenyl-*H*); 7.71 – 7.69 (m, 1H; H12, Pyrenyl-*H*); 7.61 – 7.60 (m, 1H; H11, Pyrenyl-*H*); 7.57 – 7.54 (m, 1H; H15, Pyrenyl-*H*); 7.45 – 7.43 (m, 1H; H10, Pyrenyl-*H*); 7.33 – 7.32 (m, 1H; H16, Pyrenyl-*H*); 7.25 – 7.24 (m, 2H; H25 and H38, Ar-*H*); 7.20 – 7.19 (m, 2H; H29 and H40, Ar-*H*); 6.99 – 6.98 (m, 1H; H9, Pyrenyl-*H*); 6.95 – 6.93 (m, 2H; H30 and H39, Ar-*H*); 6.55 (s, 2H; H19 and H23, Ar-*H*); 6.50 (s, 2H; H33 and H35, Ar-*H*); 5.29 – 5.24 (m, 1H; H81, Undecyl-C*H*); 4.66 and 3.39 (AX, 4H, ^2J = 13.4 and 13.6 Hz; H43 and H44, Ar-CH_2-Ar); 4.65 and 3.36 (AX, 4H, ^2J = 13.0 and 13.2 Hz; H45 and H46, Ar-CH_2-Ar); 4.27 – 4.19 (m, 4H; H93 and H99, O-CH_2); 3.93 (t, 2H, ^3J = 6.6 Hz; H96, O-CH_2); 3.87 (t, 2H, ^3J = 6.9 Hz; H102, O-CH_2); 2.34 – 2.30 (m, 2H; H82 and H83, Undecyl-CH_2); 2.18 – 2.11 (m, 4H; H94 and H100, Propyl-CH_2); 2.06 – 1.99 (m, 4H + 2H; H97 and H103, Propyl-CH_2, and H82 and H83, Undecyl-CH_2); 1.49 – 1.35 (m, 12H; H85 – H87 and H89 – H91, Undecyl-CH_2); 1.25 (t, 3H, ^3J = 7.4 Hz; H98, Propyl-CH_3); 1.19 (t, 3H, ^3J = 7.4 Hz; H104, Propyl-CH_3); 1.05 (t, 6H, ^3J = 7.4 Hz; H95 and H101, Propyl-CH_3); 0.93 (t, 6H, ^3J = 7.0 Hz; H88 and H92, Undecyl-CH_3). **^{13}C-NMR** (150 MHz, tetrachloroethane-*d*$_2$, 79 °C): δ (ppm) = 168.60 (C17); 164.29 (br, C74 and C76); 163.44 (Per-*C*); 157.99 (C27 and C42); 155.66 (C31); 153.64 (C21); 137.12 (C26 and C37); 136.31 (C28 and C41); 134.61 (Per-*C*); 134.21 (C20 and C22); 134.14 (C32 and C36); 133.79 (br, Per-*C*); 133.38 (C1); 131.86 (C4); 131.68 (C24); 131.57 (br, C64 and C69); 130.49 (C8); 130.15 (C13); 129.86 (C25 and C38); 129.58 (Per-*C*); 128.88 (C29 and C40); 128.51 (C34); 128.04 (Per-*C*); 127.91 (C12); 127.78 (C9); 127.76 (C2); 127.71 (C33 and C35); 126.96 (C10); 126.41 (Per-*C*); 126.38 (C15); 125.35 (C14); 125.09 (C6 or C16); 125.07 (C6 or C16); 125.01 (Per-*C*); 124.60 (C5); 124.44 (C19 and C23); 124.09 (C3); 123.96 (Per-*C*); 123.91 (C11); 123.66 (C7); 123.11 (C63 and C70); 122.46 (C30 and C39); 122.01 (br, Per-*C*); 120.62 (Per-*C*); 116.90 (Per-*C*); 116.70 (Per-*C*); 116.49 (Per-*C*); 78.00 (C102); 77.64 (C96); 76.79 (C93 and C99); 74.46 (Per-*C*); 55.21 (C81); 32.73 (C82 and C83); 31.98 (C86 or C87 and C90 or C91); 31.50 (C43 and C44); 31.43 (C45 and C46); 26.94 (C85 and C89); 23.86 (C97); 23.79 (C103); 23.28 (C94 and C100); 22.75 (C86 or C87 and C90 or C91); 14.21 (C88 and C92); 11.14 (C98); 11.00 (C104); 10.23 (C95 and C101). **HR-MS** (ESI in acetonitrile/$CHCl_3$): calcd for $C_{92}H_{88}N_3O_9$ $[M+H]^+$ m/z = 1378.6554; found 1378.6510.

Synthesis of the reference compound **7**:



6 **7**

Compound **6** was synthesized according to literature procedures.[1,6]

Compound 7 (Py-c):

Under an argon atmosphere 20 mg (0.082 mmol, 1 equiv.) of 1-pyrenecarboxylic acid, 17 mg (0.17 mmol, 2 equiv.) of *N*-methylmorpholine (NMM), 17 mg (0.082 mmol, 1 equiv.) of *N*,*N'*-dicyclohexylcarbodiimide (DCC) and 11 mg (0.082 mmol, 1 equiv.) of 1-hydroxybenzotriazole (HOBt) in a 2:1 mixture of dry DMF and dry acetonitrile (0.5 mL) were stirred at room temperature for 0.5 h. A solution of 50 mg (0.082 mmol, 1 equiv.) of the compound **6** in dry DMF (1.0 mL) was added, and the reaction mixture was stirred at room temperature for 3 d. The reaction mixture was filtered and CH_2Cl_2 (30 mL) was added to the filtrate and washed with brine and water, and dried over Na_2SO_4. The crude product was purified by column chromatography with CH_2Cl_2/methanol 99:1, precipitated two times from CH_2Cl_2/*n*-hexane, and was further purified by HPLC with CH_2Cl_2. Compound **7** was obtained as a white powder (16 mg, 0.019 mmol, 23%). $C_{57}H_{57}NO_5$ (836.07). Mp 127 – 128 °C. TLC (CH_2Cl_2): $R_f = 0.55$. **^{1}H-NMR** (600 MHz, tetrachloroethane-*d*$_2$, 79 °C): δ (ppm) = 8.55 – 8.54 (m, 1H; Pyrenyl-*H*); 8.29 – 8.28 (m, 2H; Pyrenyl-*H*); 8.24 – 8.19 (m, 3H; Pyrenyl-*H*); 8.16 – 8.09 (m, 3H; Pyrenyl-*H*); 7.28 (bs, 1H; N*H*); 7.00 – 6.54 (br, 11H; Ar-*H*); 4.55 and 3.25 (bs, 4H; Ar-C*H*$_2$-Ar); 4.52 and 3.21 (AX, 4H, ^2J = 13.4 and 13.5 Hz; Ar-C*H*$_2$-Ar); 3.97 (bs, 4H; O-C*H*$_2$); 3.92 (t, 2H, ^3J = 7.1 Hz; O-C*H*$_2$); 3.88 (t, 2H, ^3J = 7.2 Hz; O-C*H*$_2$); 1.99 – 1.93 (m, 8H; Propyl-C*H*$_2$); 1.12 – 1.07 (m, 6H; Propyl-C*H*$_3$); 1.04 (t, 6H, ^3J = 7.5 Hz; Propyl-C*H*$_3$). **HR-MS** (ESI in acetonitrile/$CHCl_3$): calcd for $C_{57}H_{57}NNaO_5$ $[M+Na]^+$ m/z = 858.4134; found 858.4128.

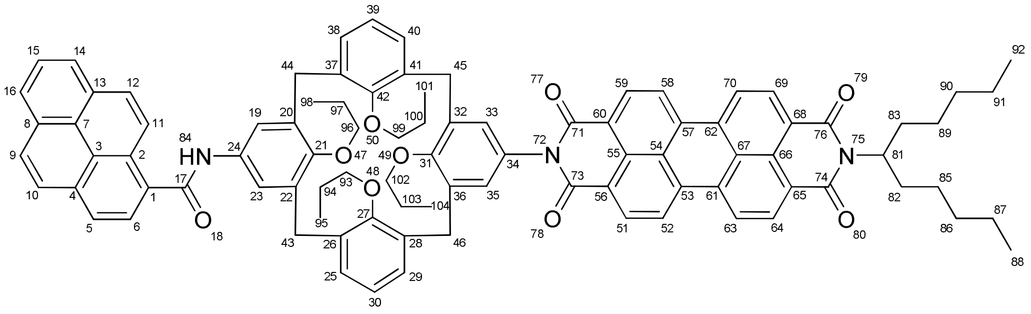


Figure S1.1. *Compound **5** (**Py-c-PBI**) with atom numbering.*[7]

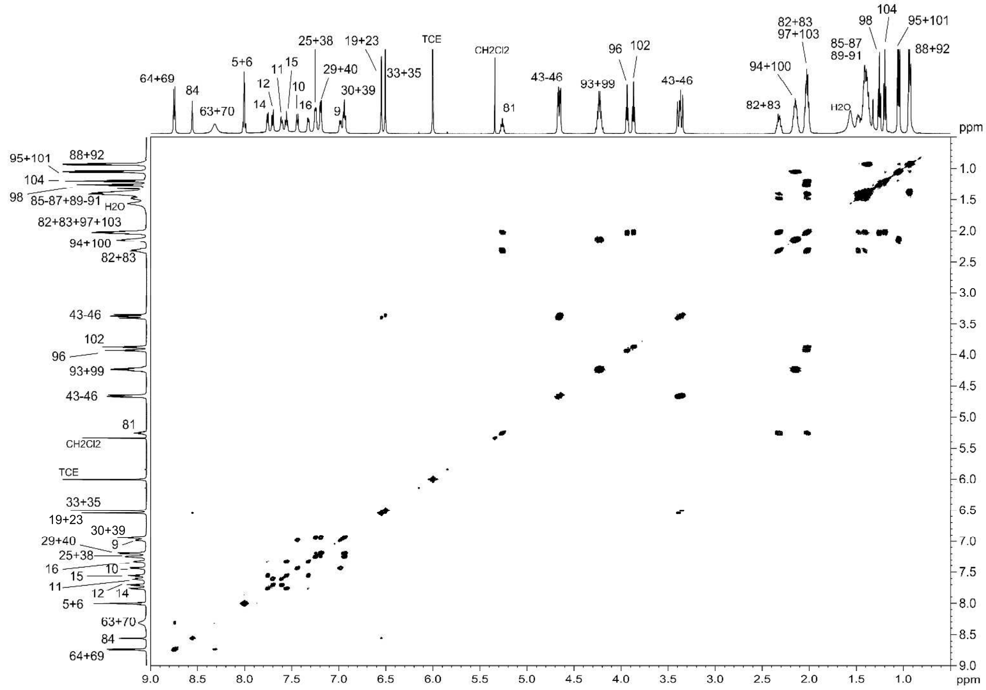


Figure S1.2. *(^1H, ^1H)-COSY NMR spectrum of compound **5**.*

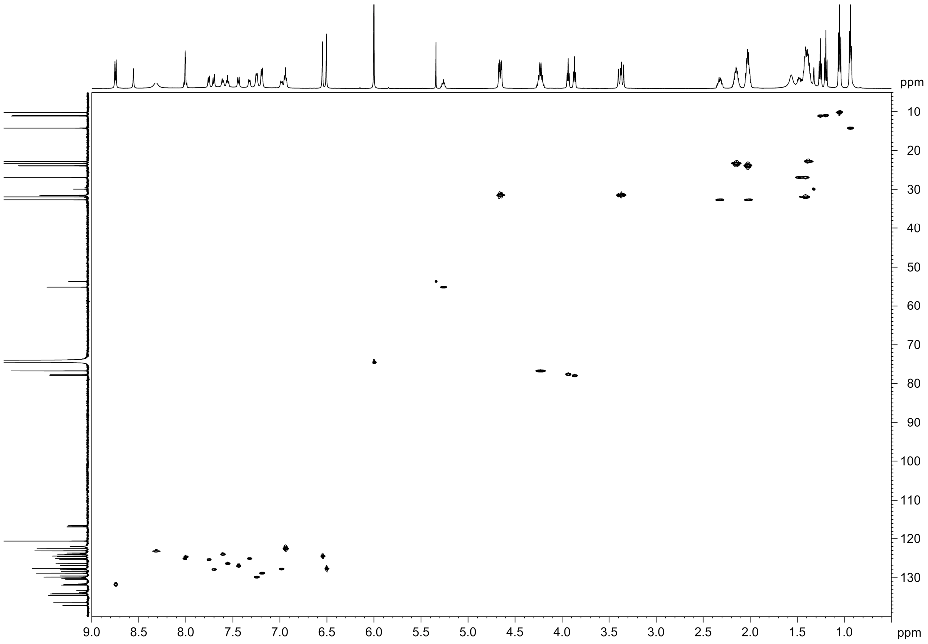


Figure S1.3 *(^{1}H, ^{13}C)-HSQC NMR spectrum of compound* ***5****.*

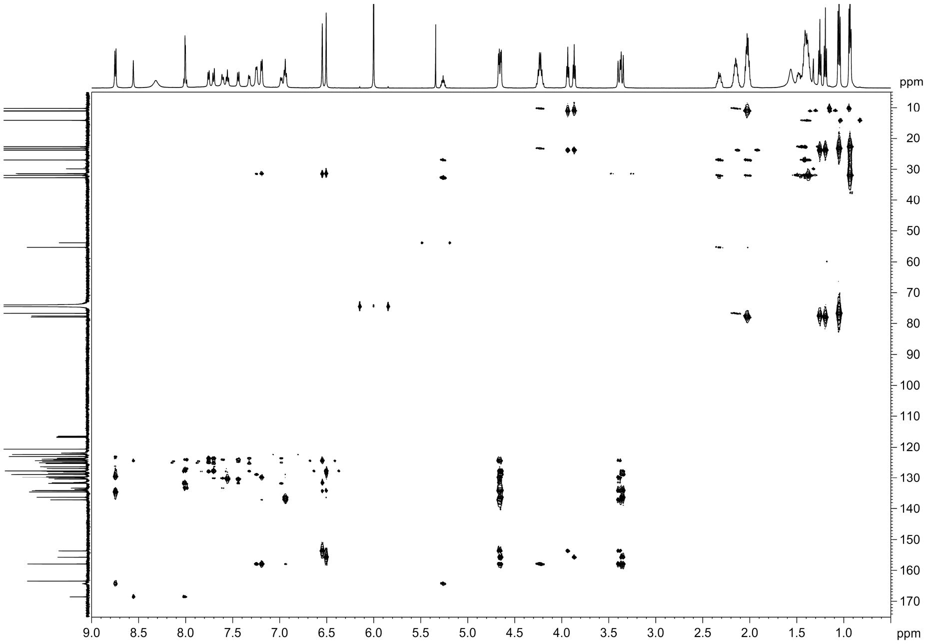


Figure S1.4. *(^{1}H, ^{13}C)-HMBC NMR spectrum of compound* ***5****.*

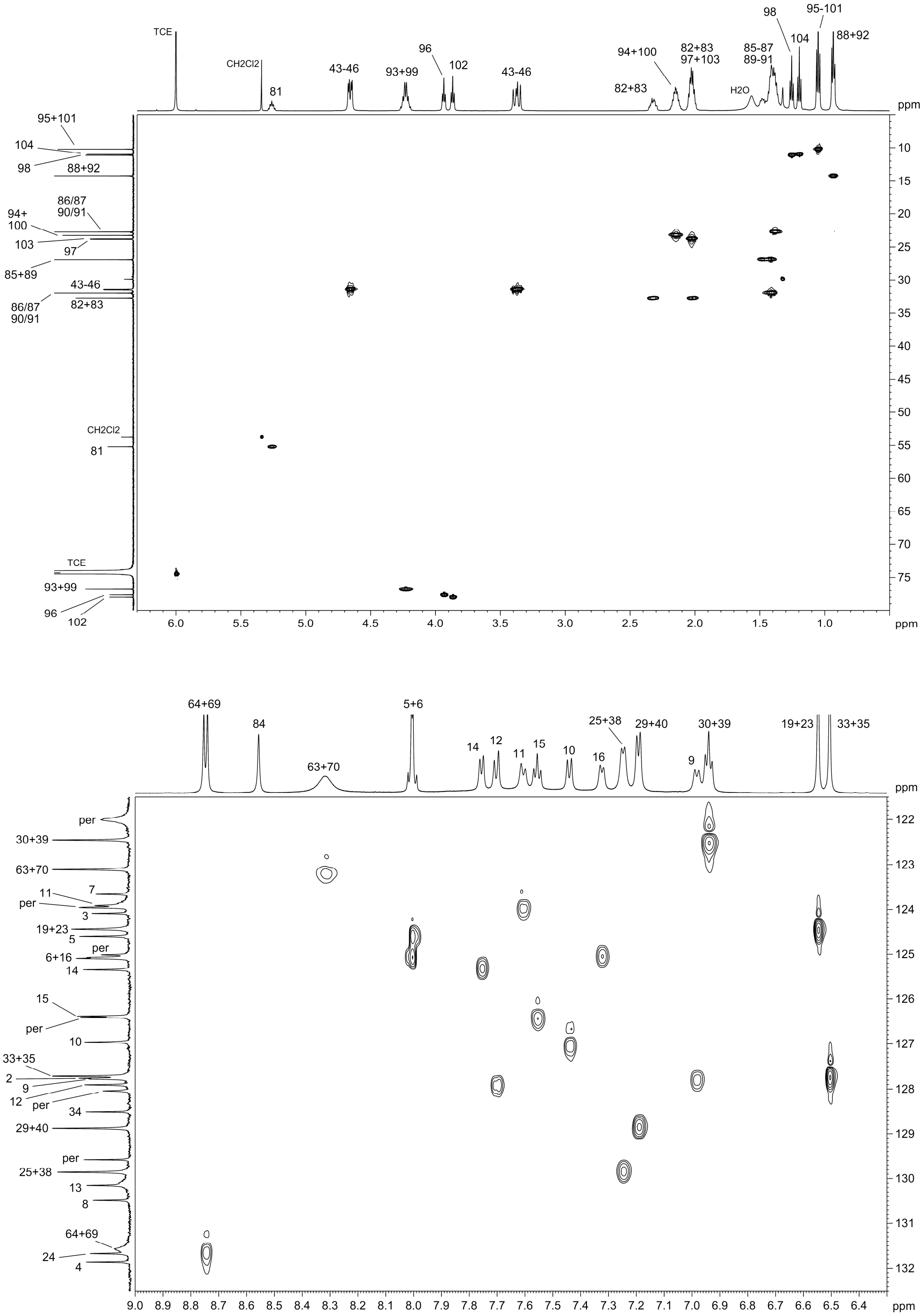


Figure S1.5. *Enhanced areas of the (^1H, ^{13}C)-HSQC spectrum of compound* ***5***.[8]

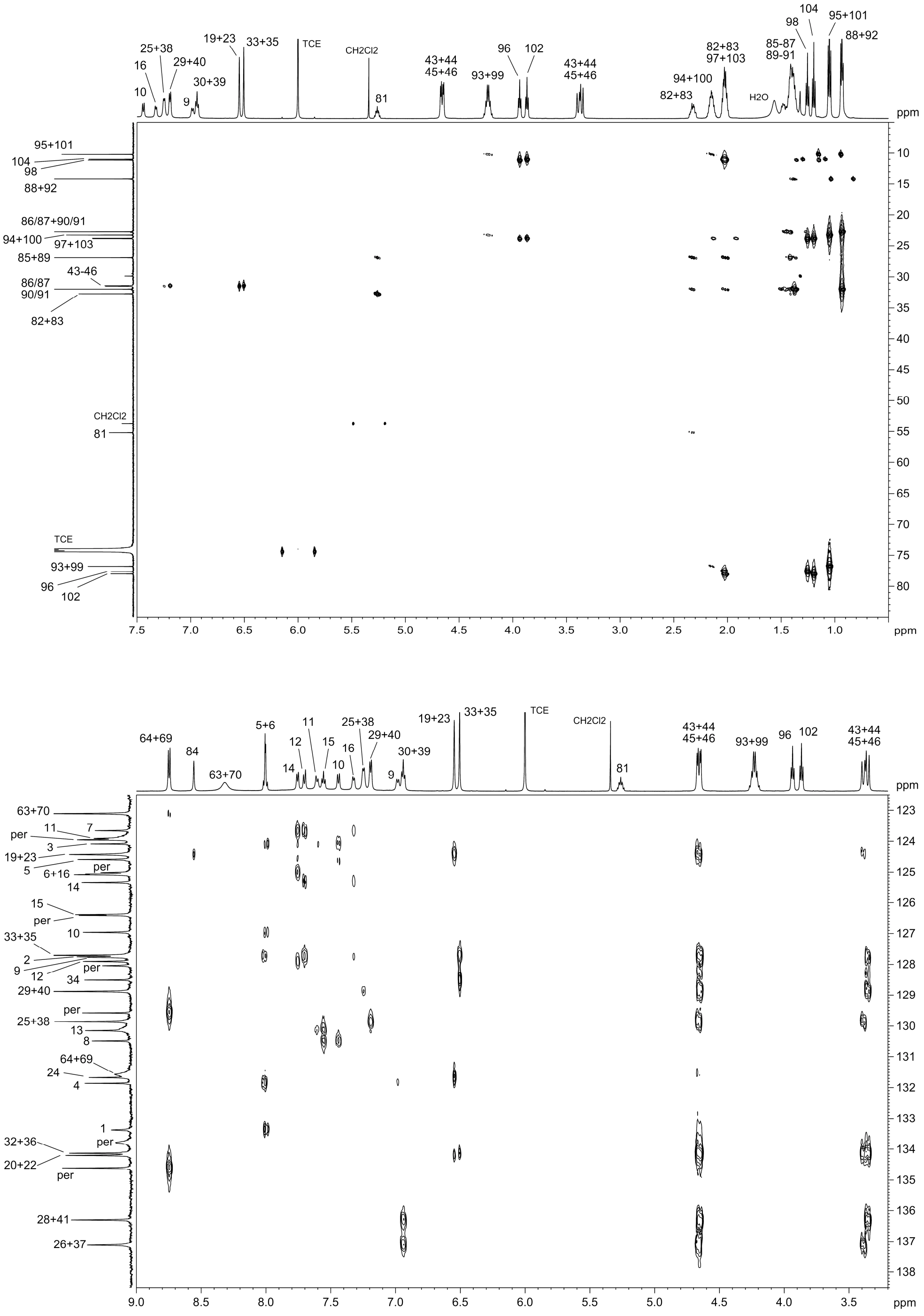


Figure S1.6. *Enhanced areas of the (^1H, ^{13}C)-HMBC spectrum of compound* ***5***.[8]

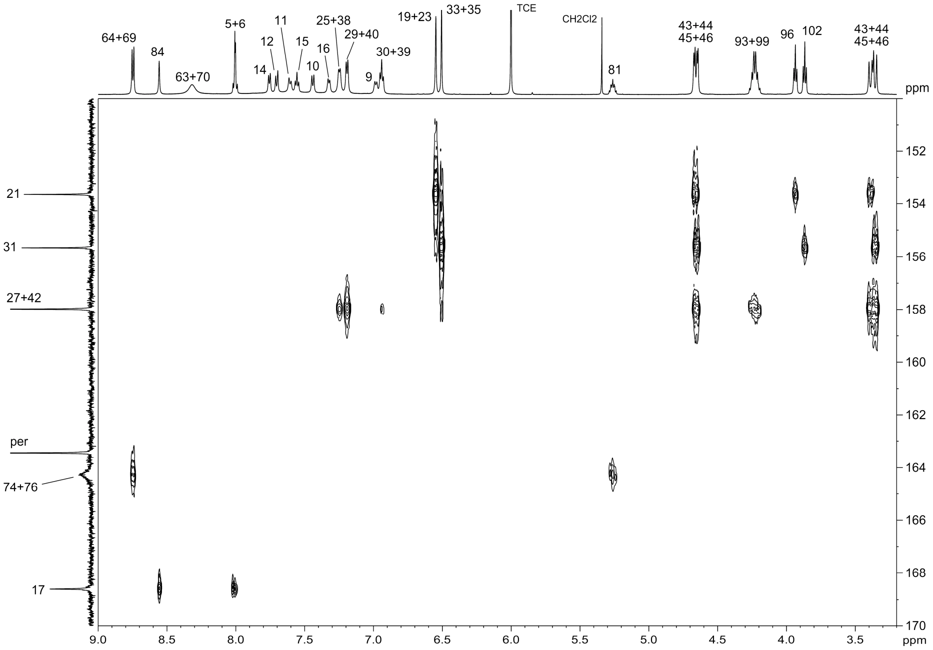


Figure S1.7. *Enhanced area of the (^{1}H, ^{13}C)-HMBC spectrum of compound* ***5****.*[8]

2. Photophysical properties of Py-c-PBI and Py-c

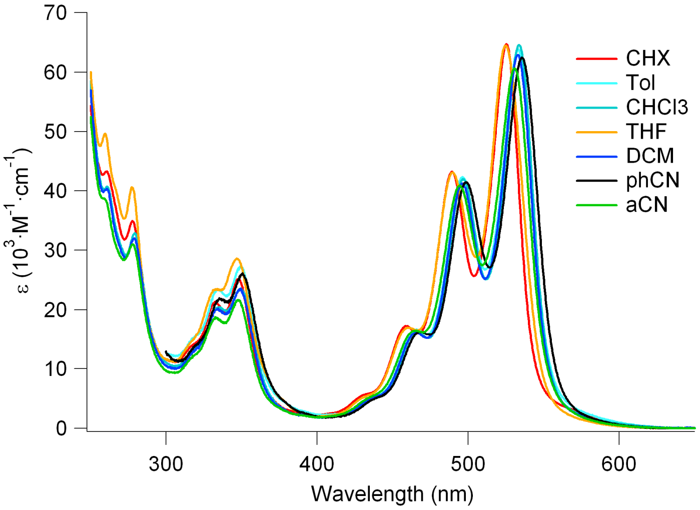


Figure S2.1. *Absorption spectra of* ***Py-c-PBI*** *in different solvents.*

For solutions of the compound in toluene and in benzonitrile, the absorption spectra of the pyrene unit were observed in the region above 300 nm due to the high absorption of these solvents. Although the absorption profiles of **Py-c-PBI** in the solvents are similar, there are still some differences. The Figure S2.1 shows that if taking the solution of **Py-c-PBI** in DCM as a reference, the perylene peaks in THF, CHX and ACN have hypsochromic effects, *i.e.* are displaced by about 6 nm (in THF and CHX) and 2 nm (in ACN) to short wavelength whereas in phCN, there is a slight bathochromic shift (about 2 nm to longer wavelength). In the other solvents, *i.e* TOL and $CHCl_3$ there is no significant difference from DCM.

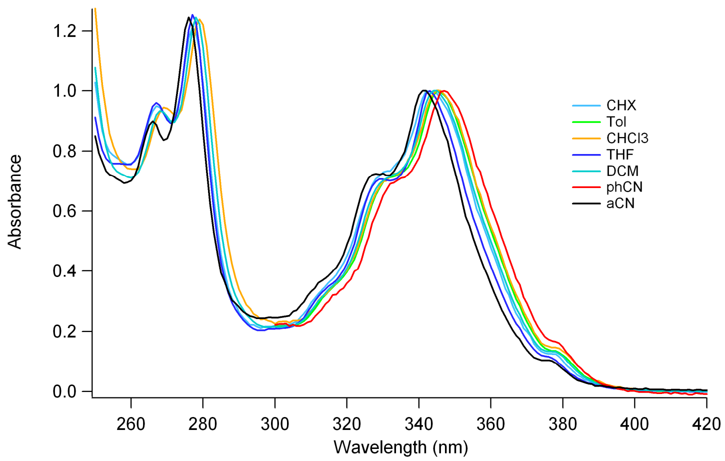


Figure S2.2. *Absorption spectra of **Py-c** in different solvents.*

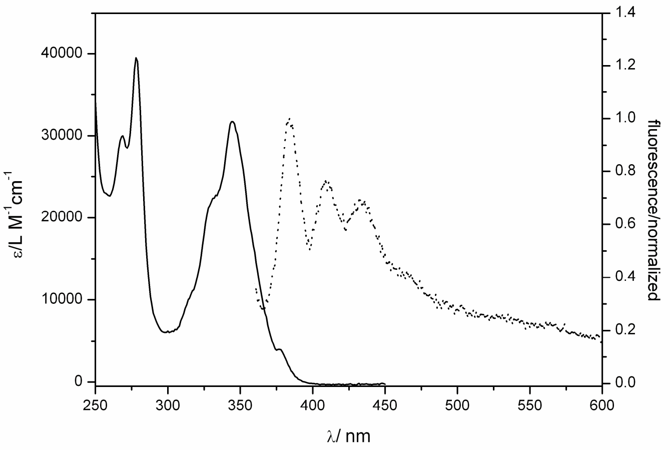


Figure S2.3. *Fluorescence (dash line) (excited at 340nm) together with absorption spectra of **Py-c** (solid black line).*

Table S2.1. *Absorption coefficients and quantum yields of* ***Py-c*** *in seven solvents.*

Solv	**CHX**	**TOL**	**CHCl3**	**THF**	**DCM**	**phCN**	**ACN**
λ/nm (ε/ $M^{-1}cm^{-1}$)	277 (38400)		279 (38400)	277 (39900)	278 (39500)		276 (39200)
	342 (32100)	345 (31700)	345 (31100)	343 (31900)	345 (31700)	347 (32100)	341 (31500)
ϕ_f(a)	1.5×10^{-3}	1.2×10^{-3}	0.6×10^{-3}	1.2×10^{-3}	0.7×10^{-3}	-	0.8×10^{-3}

(a) excitation wavelength 320nm, excitation and emission slits are 12 nm and 2 nm, respectively. *Absorbance at excitation wavelength was 0.07 – 0.1 at room temperature.*

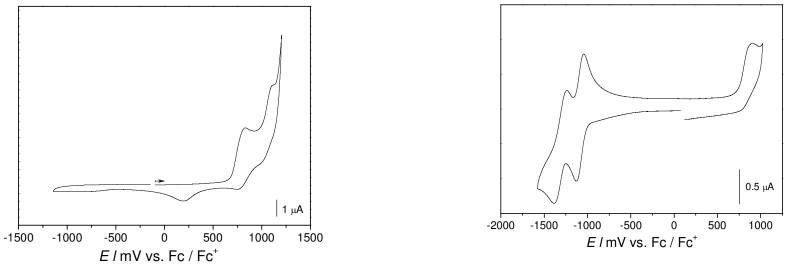


Figure S2.4. *Cyclic voltammograms in CH_2Cl_2 (vs. Fc/Fc$^+$). Left:* ***Py-c*** *(c = 1.8 x 10^{-4} M). Right:* ***Py-c-PBI*** *(c = 1.4 x 10^{-4} M). Scan Rate 100 mV s^{-1}; working electrode: Pt disc, ∅ 1 mm; auxiliary electrode: Pt wire; reference electrode: Ag/AgCl; electrolyte: TBAHFP (0.1 M).*

Table S2.2. *Redox properties of the compounds* ***Py-c-PBI*** *and* ***Py-c*** *in CH_2Cl_2 (vs. Fc/Fc$^+$).*[a]

cmpd	E_{red} (PBI$^-$/PBI^{2-})	E_{red} (PBI/PBI$^-$)	E_{ox} (PBI/PBI$^+$)	E_{ox}[b] (Py/Py$^+$)	***onset of the irrev. oxidation of the calix[4]arene***
Py-c-PBI	−1.31	−1.09		+0.90	+1.13
Py-c				+0.79	+1.13

[a] Scan Rate 100 mV s^{-1}; working electrode: Pt disc, ∅ 1 mm; auxiliary electrode: Pt wire; reference electrode: Ag/AgCl; electrolyte: TBAHFP (0.1 M). [b] Irreversible oxidation.

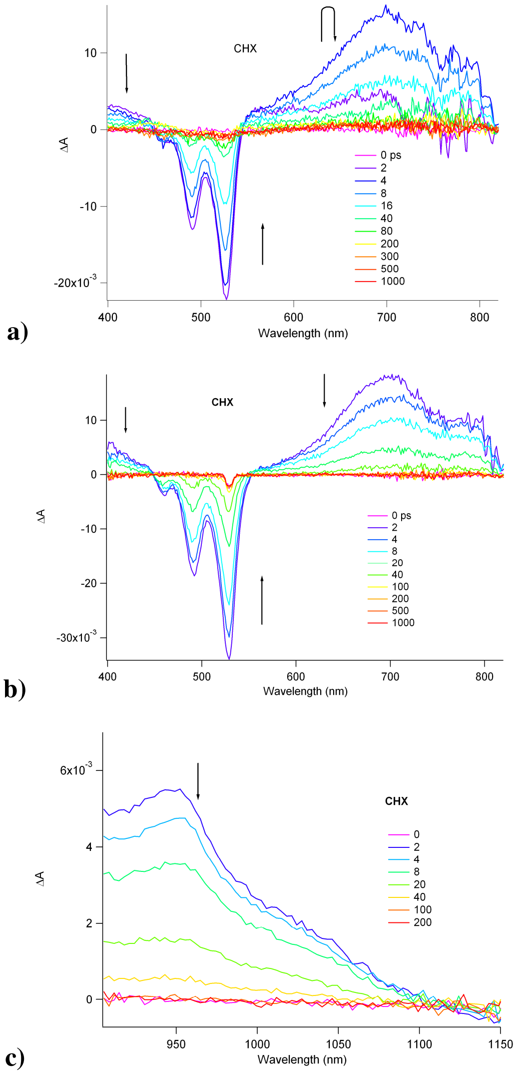


Figure S2.5. *Femtosecond transient spectroscopy of* ***Py-c-PBI*** *in CHX (a) λ_{exc} = 350 nm (b) λ_{exc} = 530nm, visible detection and (c) λ_{exc} = 530 nm, NIR detection.*

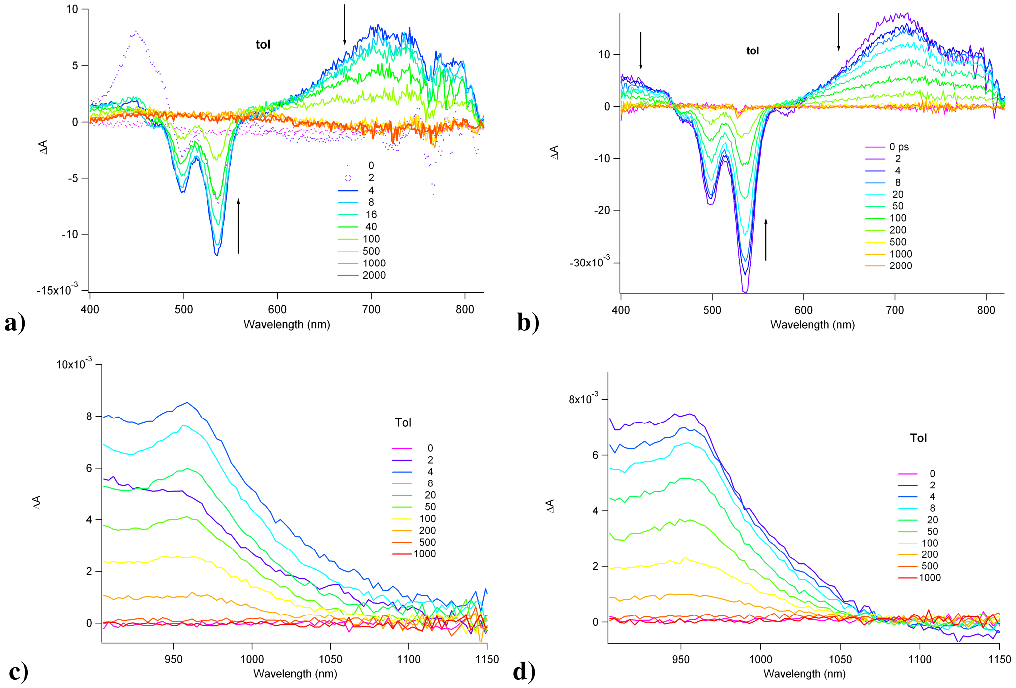


Figure S2.6*. Femtosecond transient spectroscopy of* ***Py-c-PBI*** *in TOL (a) λ_{exc} = 350 nm, vis detection*

(b) λ_{exc} = 530 nm, visible detection (c) λ_{exc} = 350 nm, NIR detection (d) λ_{exc} = 530 nm, NIR detection.

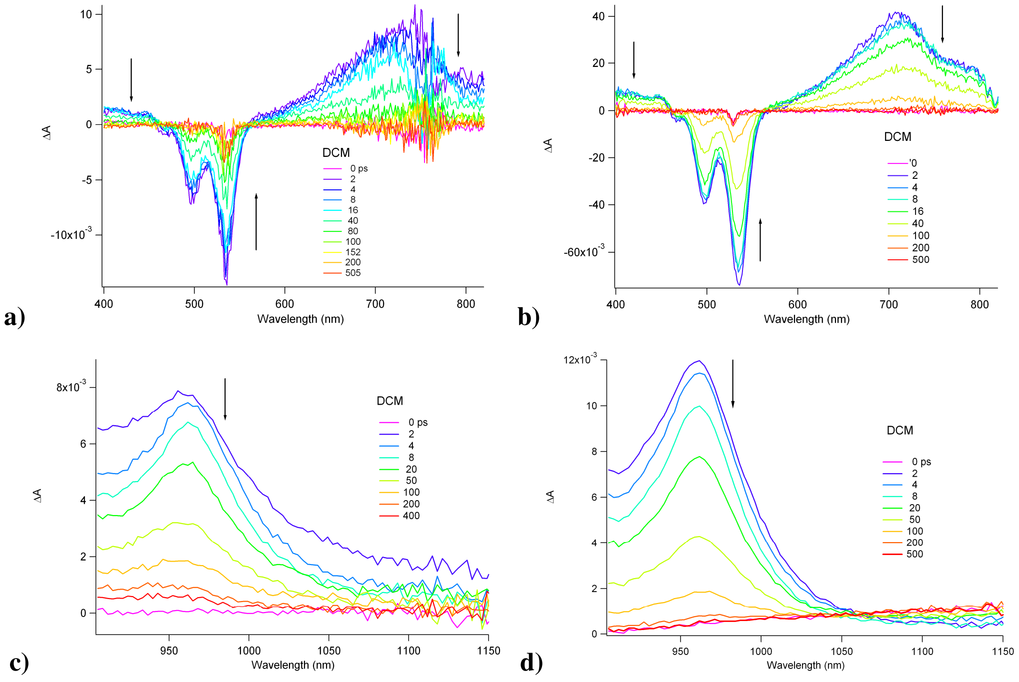


Figure S2.7. *Femtosecond transient spectroscopy of* ***Py-c-PBI*** *in DCM (a)* λ_{exc} *= 350 nm, vis detection and (b)* λ_{exc} *= 530 nm, visible detection (c)* λ_{exc} *= 350 nm, NIR detection (d)* λ_{exc} *= 530 nm, NIR detection.*

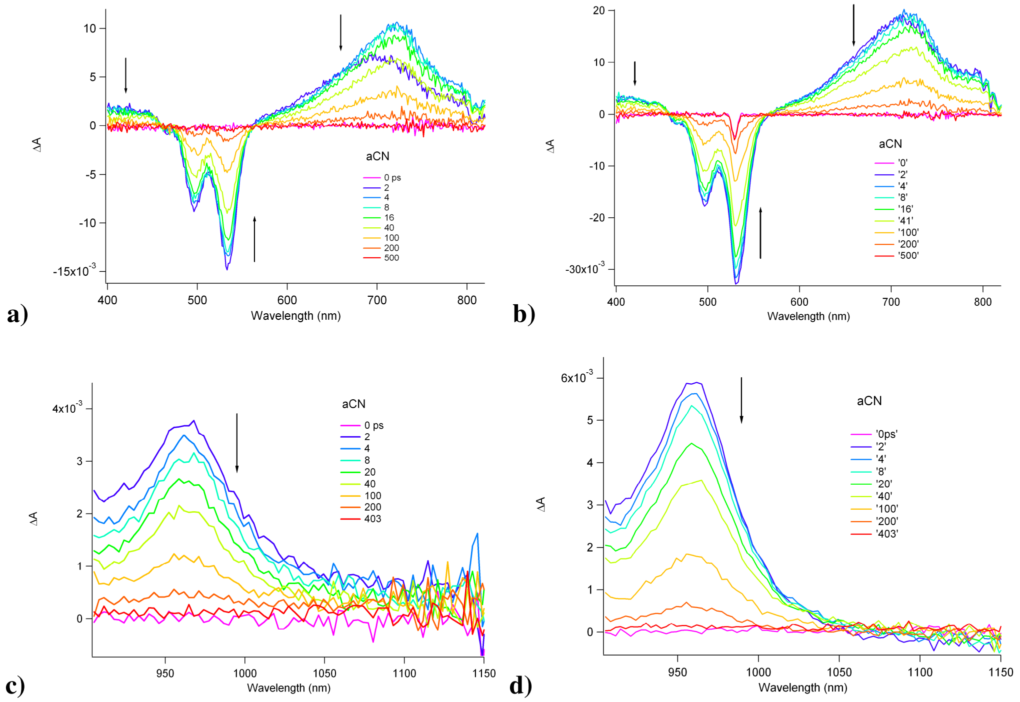


Figure S2.8*. Femtosecond transient spectroscopy of* ***Py-c-PBI*** *in ACN (a)* λ_{exc} *= 350 nm, vis detection and (b)* λ_{exc} *= 530 nm, visible detection (c)* λ_{exc} *= 350 nm, NIR detection (d)* λ_{exc} *= 530 nm, NIR detection.*

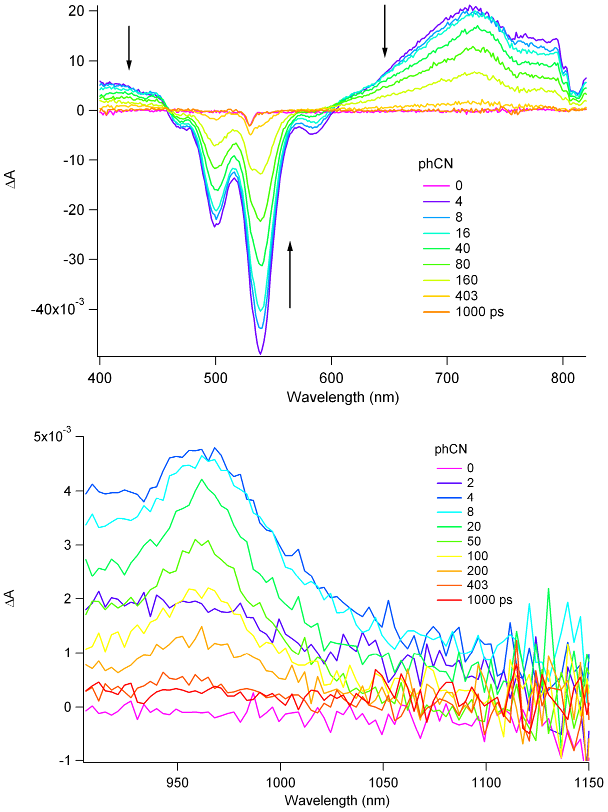


Figure S2.9. *Femtosecond transient spectroscopy of* ***Py-c-PBI*** *in phCN at λ_{exc} = 530 nm, (a) vis detection and (b) NIR detection.*

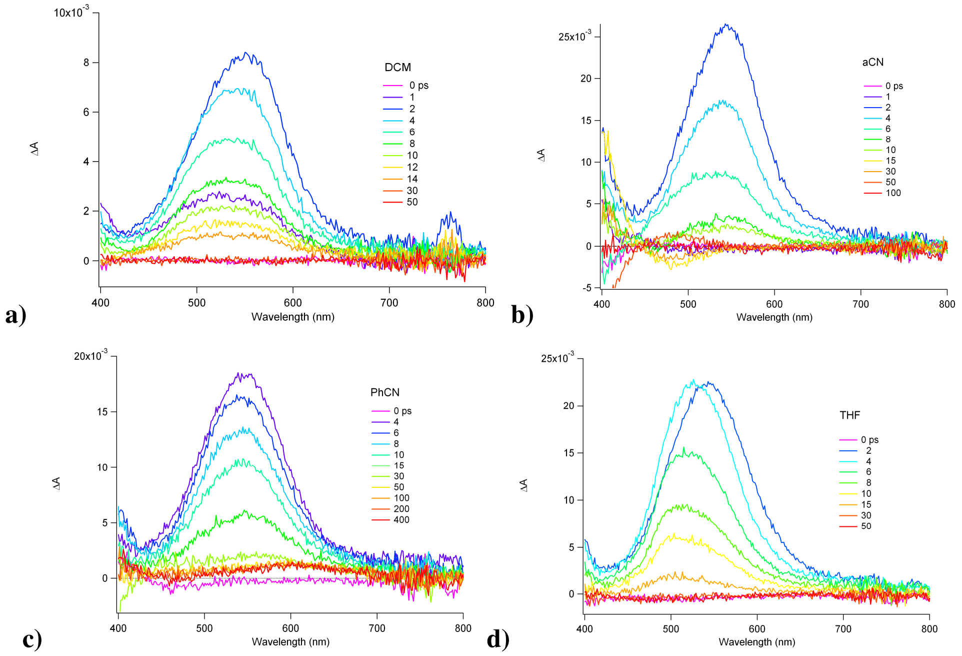


Figure S2.10. *Femtosecond transient spectroscopy of* ***Py-c*** *in (a) DCM; (b) ACN ; (c) in PhCN; and (d) in THF;* λ_{exc} *= 350 nm.*

The femtosecond transient absorption spectra of **Py-c** in some solvents show the totally different features from the **Py-c-PBI** system (in which pyrene unit acts as an electron donor). The absorption band at ca. 550 nm belongs to the pyrene radical anion[9]. In the system **Py-c**, the electron transfer occurs from calix[4]arene to pyrene, i.e. pyrene acts as an acceptor.

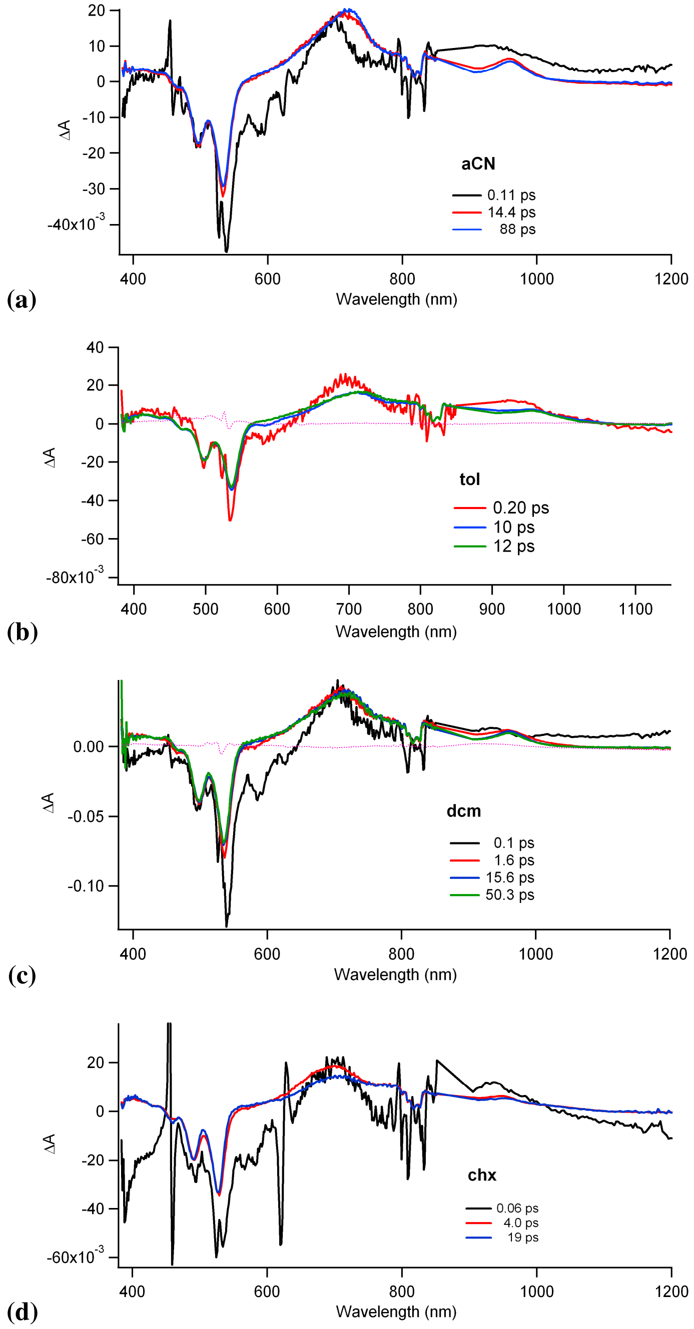


Figure S2.11. *Target analysis SADS of* ***Py-c-PBI*** *in (a) ACN; (b) TOL ; (c) DCM; and (d) CHX; upon 530 nm excitation.*

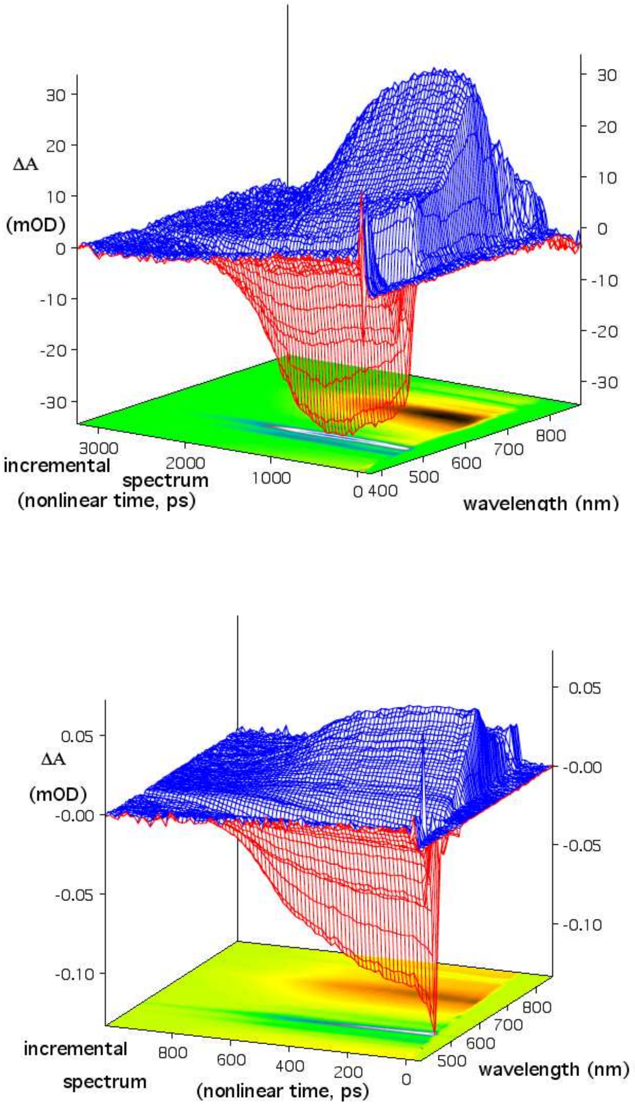
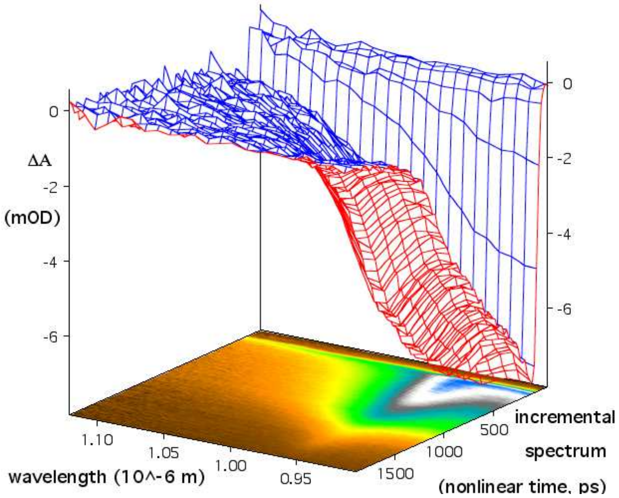


Figure S2.12A. *3D-representation of the data matrix (visible detection) of* ***Py-c-PBI*** *in THF, upon 350 nm excitation (top) and upon 530 nm excitation (bottom).*



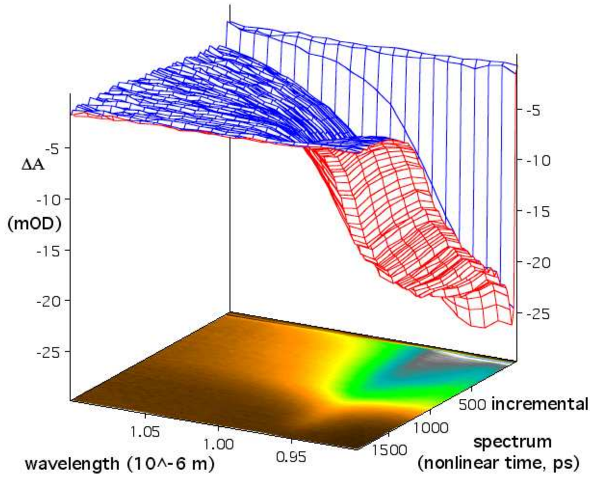


Figure S2.12B. *3D-representation of the data matrix (NIR detection multiplied by -1) of* ***Py-c-PBI*** *in THF, upon 350 nm excitation (top) and upon 530 nm excitation (bottom).*

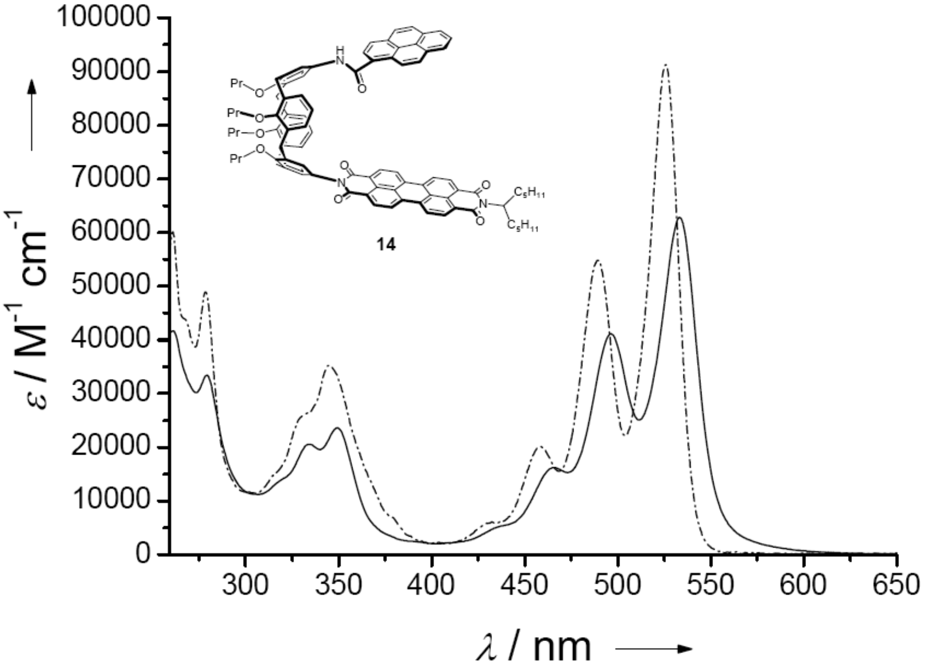


Figure S2.13. *Absorption spectra of* ***Py-c-PBI*** *in DCM (solid line) together with the sum spectrum (dash-dot line) of the two separate reference chromophores* ***PBI-c*** *and* ***Py-c****.*

Energetics for Py-c

An estimate of the Gibbs energy of photoinduced electron transfer ($\Delta_{ET}G^0$) for **Py-c** is given here. For the **Py-c** system the donor is presumed to be the 4-methoxy-N,N-dimethyl aniline (anisole is not a good model for the donor in **Py-c**).

For the **Py-c** system, the standard electrode potentials ($E^0(D^{+\cdot}/D)$ and $E^0(A/A^{-\cdot})$ are estimated to be +0.33 V [10] vs SCE (D/D$^+$) and –2.09V [11] vs SCE (Py/Py$^-$), respectively, in the reference solvent acetonitrile with a relative permittivity ε_{ref} of 37.5. The zero – zero transition energy E_{00} of the Py chromophore is ~ 3.26 eV.

The center-to-center distance R_{cc} between the donor and acceptor was determined from geometries of **Py-c** optimized by using a semi-empirical AM1 method giving the value of 7.67 Å. The effective radii of the donor (r^+) and acceptor (r^-) are estimated using a spherical approach[12]. These values are 3.98 Å for pyrene (density 1.271 g/cm^3 [13]), and 3.74 Å for the donor (for the density was estimated to be 0.995 g/cm^3.

Table 2. *The driving force for charge separation ($\Delta G_{cs} = \Delta_{ET}G^0$), the Gibbs energy of activation ($\Delta G^{\#}$) of the* ***Py-c*** *system upon Py (A) excitation in different solvents.*

Solv	ε^a	n^b	$E_{00}{}^c$ [Py] (eV)	ΔG_{cs} (eV)	λ (eV)	$\Delta G^{\#}$ (eV)
CHX	2.02	1.43	3.26	0.04	0.295	0.093
TOL	2.38	1.49	3.26	-0.11	0.351	0.040
$CHCl_3$	4.86	1.44	3.26	-0.53	0.833	0.027
THF	7.58	1.41	3.26	-0.69	1.036	0.030
DCM	8.93	1.42	3.26	-0.72	1.052	0.025
phCN	25.20	1.53	3.26	-0.87	1.067	0.009
ACN	35.94	1.34	3.26	-0.89	1.338	0.037

[a] at 25°C [21], [b] at 20°C [21]; [c] estimated from intersection between absorption and emission spectra of Py, $\lambda_i = 0.3$ eV.

Table 3. *The lifetimes of the processes occurring in* ***Py-c*** *extracted from global and target analysis (excitation at 350 nm).*

Solv	τ_{s2} (ps)	τ_{cs} (ps)	τ_{cr1} (ps)	τ_{cr2} (ps)
THF	0.3	1.8	2.5	6.9
DCM	0.2	2	2	7.7
ACN	0.4	0.5	2.8	154

THF: tetrahydrofuran; DCM: dichloromethane; ACN: acetonitrile.

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