Supporting Information for

Excited State Interactions in Calix[4]arene–Perylene Bisimide Dye Conjugates: Global and Target Analysis of Supramolecular Building Blocks

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Materials and Methods:

Compounds **oc2**[S1], **oref**[S2] and **oPMI**[S3] were synthesized according to literature procedures, compound **oPBA** was commercially available. All compounds were characterized by ^{1}H NMR and high resolution mass spectrometry. Solvents were purified and dried according to standard procedures. Column chromatography was performed with silica gel 60 (0.035 - 0.070 mm); PTLC on 20 x 20 cm plates, height 1 mm, silica gel 60 (0.035 - 0.070 mm). High performance liquid chromatography (HPLC) was performed on SiO_2 columns, normal phase (NP), with p.a. grade purified solvents. NMR spectra were recorded on a 400 MHz spectrometer. Mass Spectra were performed on a Finnigan MAT MS 8200 or on a Bruker microTOF$_{LC}$. For UV/vis absorption and fluorescence experiments spectroscopy grade solvents were used.

UV/vis absorption spectra were taken on a conventional UV/vis absorption spectrophotometer. **Steady state fluorescence emission** spectra were recorded on a PTI QM4-2003 fluorescence spectrometer and are corrected against photomultiplier and lamp intensity. A long wavelength range emission corrected photomultiplier R928 was used. Fluorescence quantum yields were determined in CH_2Cl_2 vs. *N,N'*-(2,6-diisopropylphenyl)- 1,6,7,12-tetraphenoxyperylene-3,4:9,10-tetracarboxylic acid bisimide (Φ_{fl} = 0.96 in $CHCl_3$) or fluorescein (Φ_{fl} = 0.92 in 0.1N NaOH) as reference.[S4] The given quantum yields are averaged from values measured at three different excitation wavelengths with OD 0.02–0.05 in the absorption maximum (standard deviation σ = 1–3 %).

Fluorescence lifetimes were measured with a streak camera system (details described in the literature).[S5] As excitation source a Spectra-Physics Hurricane Titanium:Sapphire regenerative amplifier system was used. The excitation wavelength of 530 nm was made with an optical parametric amplifier (Spectra-Physics OPA 800). The excitation light was imaged onto the cell with a mirror and the emission light was collected with a fiber coupled to the spectrograph of the streak setup. To get the best temporal resolution at short times, the streak camera was run in “dump mode”. In which, the sync signal from the hurricane setup is combined with the trigger signal from a triggering diode to gain optimal resolution yielding a system response of approximately 150 ps. Typical laser output was 5 μJ per pulse (130 fs FWHM) with a repetition rate of 1 kHz. The samples were placed into 10 mm quartz cells and were degassed for 15 minutes with argon gas prior to the measurements. Steady state absorbance measurements were performed before and after the laser experiments to rule out possible degradation of the sample.

Femtosecond transient absorption experiments were performed with a Spectra-Physics Hurricane Titanium:Sapphire regenerative amplifier system. The full spectrum setup was based on an optical parametric amplifier (Spectra-Physics OPA 800) as the pump. The residual fundamental light, from the pump OPA, was used for white light generation, which was detected with a CCD spectrograph (Ocean Optics). The polarization of the pump light was controlled by a Berek Polarization Compensator (New Focus). The Berek-Polarizer was always included in the setup to provide the Magic-Angle conditions. The probe light was passed over a delay line (Physik Instrumente, M-531DD) that provides an experimental time window of 1.0 ns with a maximal resolution of 0.6 fs/step. The OPA was used to generate excitation pulses at 530 nm. The laser output was typically 5 μJ pulse^{-1} (130 fs FWHM) with a repetition rate of 1 kHz. The samples were placed into cells of 2 mm path length (Hellma) and were stirred with a stir bar. Samples were prepared to have an optical density of *ca.* 0.3 – 0.6 at the excitation wavelength and were degassed for 15 minutes with argon gas prior to the measurements. The UV/vis absorption spectra of the samples were measured before and after the laser experiments and were found to be virtually identical, thus ruling out a possible degradation or chemical change of the samples. All photophysical data reported here have a 5 to 10 % error limit, unless indicated otherwise. The experiments were performed at room temperature. The power dependence was determined and it was found that the spectral and kinetic behaviour was independent of the laser power used. Four different laser powers were applied by modulating the maximum laser power of the pump beam with a neutral density filter wheel.

For the **global and target analysis** all time-gated spectra were collated in a matrix, which was globally fitted using a sequential kinetic scheme with increasing lifetimes. From this the lifetimes and the evolution-associated difference spectra (EADS) were estimated. The instrument response function (IRF) is described by a Gaussian shape, and the white light dispersion over the spectral range is modelled by a third order polynomial. With increasing lifetimes, and thus decreasing rates, the first EADS decays with the first lifetime and corresponds to the difference spectrum at time zero with an ideal infinitely small IRF. The second EADS is formed with the first lifetime and decays with the second lifetime, etc. The final EADS represents the difference spectrum of the longest living species. The error in the lifetimes obtained from the fitting procedure does not exceed 10%. EADS may not represent pure species, except for the final EADS, and they are interpreted as a weighted sum (with only positive contributions) of species-associated difference spectra (SADS). The quality of the fit was judged by inspection of the singular vectors of the matrix of residuals, which had to be structureless. Next, in target analysis a kinetic scheme was used in combination with spectral assumptions to estimate microscopic rate constants and SADS. A full description of the method has been given elsewhere.[S6]

Data collections for the **Crystal Structure** determination were carried out at the X-ray diffraction beamline of the Elettra Synchrotron, Trieste (Italy), using the rotating crystal method with the monochromatic wavelength of 1.000 Å. Data were collected on a CCD MAR detector. Measurements were performed at 100 K using a nitrogen stream cryo-cooler. Cell refinement, indexing and scaling of the data sets were carried out using Denzo[S7] and Scalepack[S7]. The structures was solved by direct methods using SHELXS[S8] and refined by the full-matrix least-squares method based on F^2 with all observed reflections.[S8] The hydrogen atoms were placed at geometrically calculated positions. All the calculations were performed using the WinGX System, Version 1.70.01.[S9] Crystal data for compound **oc2**: $C_{104}H_{102}N_2O_{12}$, M = 1571.88, monoclinic; space group $P2_1$, $a = 10.707(4)$, $b = 11.962(4)$, $c = 32.120(5)$ Å, $\beta = 91.17(2)$ $V = 4113(2)$ Å^3, Z = 2, $\rho_{calcd} = 1.269$ g/cm^3, $F(000) = 1672$. Final $R = 0.1226$, $wR2 = 0.3304$, $S = 1.173$ for 943 parameters and 21133 reflections, 6648 unique [R(int) = 0.0420], of which 5193 with $I > 2\sigma(I)$. Full crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC reference number 645676).

Spectro-electrochemical experiments were performed in a specially designed sample compartment consisting of a cylindrical quartz cell, a platinum disc electrode (∅ 6 mm), a gold-covered metal (V2A) plate as the auxiliary electrode and a Ag/AgCl pseudo-reference electrode. All spectra were recorded in reflection mode and the optical path-length was varied by adjusting the vertical position of the working electrode with a micrometer screw. The potential applied was varied in steps of 10-100mV and a UV/vis/NIR absorption spectrum was recorded ca. 1 minute after increasing the potential. All compounds were checked for reversibility of the spectra.

Cyclic voltammetry (CV) was performed with a standard commercial electrochemical analyser in a three electrode single-component cell under argon. Dichloromethane (HPLC grade) was used as solvent that was dried over calcium hydride and degassed prior to measurement. The supporting electrolyte tetrabutylammoniumhexafluorophosphate (TBAHFP) was recrystallized from ethanol/water and dried in high vacuum. The measurements were carried out at a concentration of 10^{-4} M with ferrocene as internal standard for the calibration of potential. Working electrode: Pt disc; reference electrode: Ag/AgCl; auxiliary electrode: Pt wire.

Synthesis and chemical characterisation:

*Compound **oc***:

A suspension of 100 mg (1.65×10^{-4} mol, 1 equiv.) of 5-monoamino-25,26,27,28-tetrakis(propyloxy)-calix[4]arene, 135 mg (2.48×10^{-4} mol, 1.5 equiv.) of *N*-(1-pentyl-hexyl)-1,6,7,12-perylene-3,4:9,10-tetracarboxylic acid imide anhydride and 61 mg (3.30×10^{-4} mol, 2 equiv.) of $Zn(OAc)_2$ (H_2O-free) was heated in 0.7 mL distilled quinoline at 165°C for 11 h under an argon atmosphere. The cooled reaction mixture was poured into 2N HCl and stirred for 30 minutes at 40 °C. To this solution 50 mL of CH_2Cl_2 were added and the resulting organic phase was washed with water and brine and dried over $MgSO_4$. The crude product was purified by column chromatography with CH_2Cl_2/ethylacetate 99:1 and precipitated from CH_2Cl_2/methanol. Compound **oc** was obtained as a light red powder (160 mg, 1.41×10^{-4} mol, yield 85 %). $C_{75}H_{78}N_2O_8$ (1135.43). Mp = 208 – 220°C. TLC CH_2Cl_2/Ethyl acetate 99:1; $R_f = 0.56$. **^{1}H-NMR** (400MHz, $CDCl_3$, 25°C): δ (ppm) = 8.77 – 8.63 (m, 8H; Per-*H*); 7.11 and 7.08 (d and s, 4H, $^3J = 7.5$ Hz; Ar-*H*); 6.92 (t, 1H, $^3J = 7.5$ Hz; Ar-*H*); 6.35 and 6.30 (t and dd, 4H, $^3J = 7.5$ Hz and $^3J = 7.5$ Hz / $^4J = 1.8$ Hz; Ar-*H*); 6.16 (dd, 2H, $^3J = 7.3$ Hz / $^4J = 1.6$ Hz; Ar-*H*); 5.24 – 5.16 (m, 1H; N-C*H*) 4.53 and 3.20 (AX, 4H, $^2J = 13.4$ and 13.5 Hz; Ar-CH_2-Ar); 4.48 and 3.17 (AX, 4H, $^2J = 13.4$ and 13.5 Hz; Ar-CH_2-Ar); 4.11 and 4.03 (each t, 4H, $^3J = 8.2$ and 8.1 Hz; O-CH_2); 3.72 – 3.66 (m, 4H; O-CH_2); 2.30 – 2.22 (m, 2H; Alkyl-*H*); 2.06 – 1.84 (m, 10H; Propyl-*H* and Alkyl-*H*); 1.37 – 1.24 (m, 12H; Alkyl-*H*); 1.10 (t, 6H, $^3J = 7.4$ Hz; Propyl-*H*); 0.94 and 0.91 (each t, 6H, each $^3J = 7.5$ Hz; Propyl-*H*); 0.84 (t, 6H, $^3J = 7.3$ Hz; Propyl-*H*). **HR-MS** (ESI in $CHCl_3$/acetonitrile): calcd for $C_{75}H_{78}N_2O_8Na$ (m/z) 1157.5656 $[M+Na]^+$; found 1157.5650. **Analysis**: calcd (%) for $C_{75}H_{78}N_2O_8$ (1135.43): C 79.34; H 6.92; N 2.47; found: C 79.25; H 7.04; N 2.52. **UV/vis** (CH_2Cl_2): λ (nm) [ε ($M^{-1}cm^{-1}$)] = 526 [91600], 489 [55200], 458 [20000]. **Fluorescence** (CH_2Cl_2): λ_{max} (nm) = 535; $\Phi_{Fl} = 0.03$.

Electrochemistry and Spectro-electrochemistry:

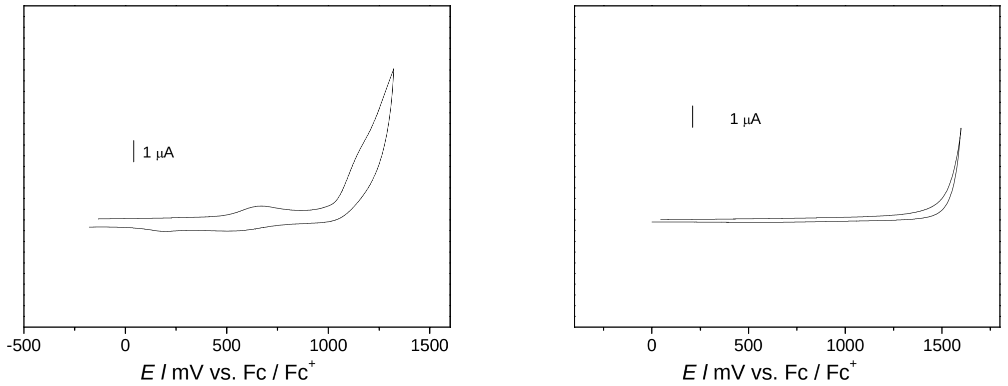

Figure S1. Cyclic voltammograms in CH_2Cl_2. (Left): Tetrapropyloxy-calix[4]arene, concentration = 1.60 x 10^{-3} M. Scan rate 250 mV s^{-1}. (Right): pure solvent. Scan rate 100 mV s^{-1}. Working electrode: Pt disc, ∅ 1 mm; auxiliary electrode: Pt wire; reference electrode: Ag/AgCl; supporting electrolyte TBAHFP (0.1 M).

Molecular Modeling

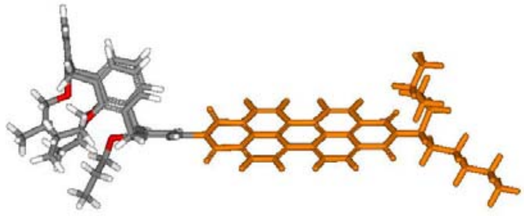

Figure S2. Energy minimized structure obtained from force field calculations (Macromodel 8.0, potential MMFF) of compound **oc.** The PBI unit is colored for clarity.

Femtosecond transient absorption data

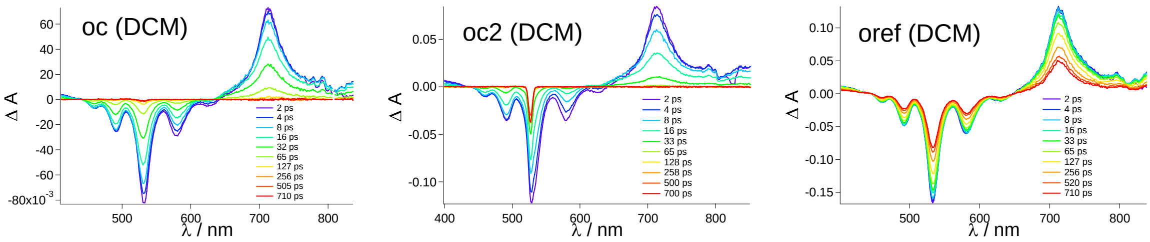

Figure S3. Femtosecond transient absorption spectra and corresponding time delays in CH_2Cl_2 (DCM) after photo-excitation at 530 nm **Left**: compound **oc**. **Middle**: compound **oc2**. **Right**: compound **oref**. For compound **oc2 t**he scattered laser pulse is observed.

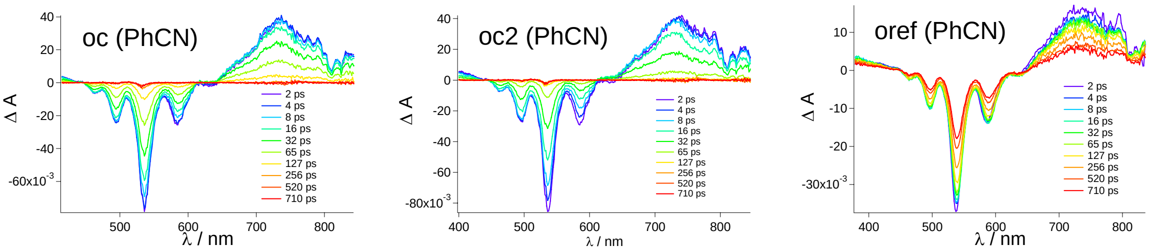

Figure S4. Femtosecond transient absorption spectra and corresponding time delays in benzonitrile (PhCN) after photo-excitation at 530 nm **Left**: compound **oc**. Middle: compound **oc2**. **Right**: compound **oref**.

SADS

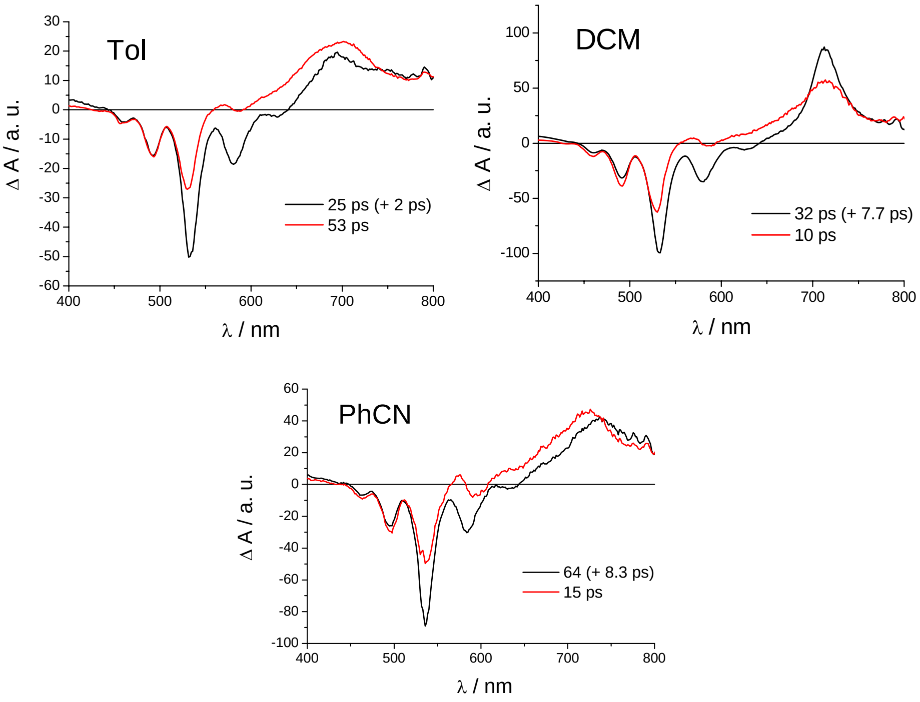

Figure S5. Species-associated difference spectra (SADS) obtained from the *simultaneous* target analysis of femtosecond transient absorption data of compounds **oc** and **oc2** with the related lifetimes given exemplarily for compound **oc** in toluene (Tol, top left), in CH_2Cl_2 (DCM, top right), and in benzonitrile (PhCN, bottom). SADS in toluene are repeated from Figure 6B for comparison. Shown are processes after photoexcitation at 530 nm. Features due to Raman scattering were omitted for clarity. The black SADS represents the biexponentially decaying excited state **o*c**, and the red SADS belongs to the **oc** CT state.

References

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