Supporting Information for:

Ultrafast Energy-Electron Transfer Cascade in a Multichromophoric Light Harvesting Molecular Square

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Experimental Section

Materials and Methods. Solvents and reagents were purchased and purified and dried according to standard procedures. Column chromatography was performed on standard silica gel columns (particle size 0.063 – 0.2 mm) and with a pump on LiChroprep Si60 columns. The synthesis of the perylene bisimide ligand **L1** has been described recently.[1] [Pt(dppp)][$(OTf)_2$]×$2H_2O$ and 4-

(dimethylamino)pyridinium-4-toluenesulfonate (DPTS) have been synthesized according to the literature. ^{1}H NMR spectra were recorded at 400 or 500 MHz spectrometers using TMS as internal standard and ^{31}P{^{1}H} NMR spectra were measured at 202 MHz. Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (ESI–FTICR–MS) measurements were carried out with a passively shielded Bruker 4.7 Tesla APEX^{TM}II-ESI/MALDI–FT–ICR mass spectrometer with saturated solutions of the complexes in acetone/dichloromethane.

Synthesis. *Pyrene–Perylene Bisimide–Platinum Square (**Sq1**):* **L1** (20.58 mg, 10.0 μmol) and [Pt(dppp)][$(OTf)_2$] ×2H_2O (9.42 mg, 10.0 μmol) were dissolved in dichloromethane (5 mL) and stirred under argon at room temperature for 24 h. After filtration the solvent was concentrated to ca. 1 mL and diethylether (10 mL) was added to precipitate the product. The solid was collected by centrifugation, washed with diethylether (2 × 5 mL) and dried in vacuo. Yield: 20 mg (67%). M.p. > 300 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.15 (br s, 16H; $H_{\alpha\text{-py}}$), 8.08–7.92 (m, 144H; H_{pyr}+H_{per}), 7.70 (br s, 32H; H_{dppp}), 7.58 (br d, ^{3}J(H,H) = 9.2 Hz, 16H; H_{pyr}), 7.46–7.28 (br s, 48H; H_{dppp}), 7.07 (br s, 16H; $H_{\beta\text{-py}}$), 6.87 (d, ^{3}J(H,H) = 9.9 Hz, 32H; H_{ar}), 6.73 (d, ^{3}J(H,H) = 9.9 Hz, 32H; H_{ar}), 3.30 (br s, 16H; H_{dppp}), 3.14 (m, 32H; H_{CH2}), 2.40 (m, 32H; H_{CH2}), 2.20 (br s, 8H; H_{dppp}), 2.01 (m, 32H; H_{CH2}); ^{31}P NMR (202 MHz, $CDCl_3$, 25 °C): δ = –14.4 (s); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 580 (184 000), 544 (130 000), 451 (70 200), 344 (605 000), 328 (446 300), 314 (237 700), 277 (892 300), 266 nm (652 900 mol^{-1} dm^3 cm^{-1}); fluorescence (CH_2Cl_2): λ_{max} = 615 nm; ESI–FTICR–MS (acetone/CH_2Cl_2 1:1): calcd for [*M*–4OTf]$^{4+}$: 2814.84; found 2814.54; calcd for [*M*–5OTf]$^{5+}$: 2222.06; found 2221.87. *M* ($C_{668}H_{456}N_{16}O_{88}S_8F_{24}P_8Pt_4$) = 11855.65.

Steady State Spectroscopy. Electronic absorption spectra were recorded on Perkin Elmer Lambda 40P and Hewlett Packard UV/vis diode array 8453 spectrophotometers. Steady state emission

spectra were obtained from SPEX 1681 Fluorolog spectrofluorimeter equipped with two double monochromator (excitation and emission) and are corrected for the photomultiplier response. Quantum yields of compounds were measured with respect to *N*,*N*'-di(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxyperylene-3,4:9,10-tetracarboxylic acid bisimide (0.96 in chloroform)[2] for the perylene emissions, and anthracene (0.27 in ethanol)[3] for the pyrene emission in optically diluted solutions. All solvents used are spectroscopic grade and purchased from Acros and Merck Uvasol, and distilled when it was necessary. It is important to keep the concentration of the square compounds in solutions in the range of 10^{-6} M or higher for stability reasons. Thus all experiments were performed under conditions were the squares are stable, as can be easily checked by the 5 nm bathochromic shift of the perylene absorptions.

Time-resolved Spectroscopy. Time-resolved fluorescence measurements were performed on a picosecond single photon counting (SPC) setup. The frequency doubled (300-340 nm, 1 ps, 3.8 MHz) output of a cavity dumped DCM dye laser (Coherent model 700) pumped by a mode-locked Ar-ion laser (Coherent 486 AS Mode Locker, Coherent Innova 200 laser) was used as the excitation source. A (Hamamatsu R3809) micro channel plate photomultiplier was used as detector. The instrument response (~17 ps FWHM) was recorded using the Raman scattering of a doubly deionized water sample. Time windows (4000 channels) of 5 ns (1.25 ps/channel) – 50 ns (12.5 ps/channel) could be used, enabling the measurement of lifetimes of 5 ps - 40 ns. The recorded traces were deconvoluted with the system response and fitted to an exponential function using the Fluofit (PicoQuant) windows program.

For the low-temperature lifetime measurements an Oxford-instruments liquid nitrogen cryostat (DN704) was used in combination with picosecond single photon counting (SPC) setup.

In the femtosecond transient absorption measurements, a Spectra-Physics Hurricane Titanium: Sapphire regenerative amplifier system was used as the laser system. The full spectrum setup was based on an optical parametric amplifier (Spectra- Physics OPA 800) as a pump. A residual fundamental light, from the pump OPA, was used for white light generation, which was detected with a CCD spectrograph. The OPA was used to generate excitation pulses at 345 and 575 nm. The laser output was typically 5 μJ pulse^{-1} (130 fs FWHM) with a repetition rate of 1 kHz. A circular cuvette (d = 1.8 cm, 1 mm, Hellma), with the sample solution, was placed in a homemade rotating ball bearing (1000 rpm), to avoid local heating by the laser beam. The solutions of the samples were prepared to have an optical density at the excitation wavelength of ca. 0.5 in a 1-mm cell. The absorbance spectra of the solutions were measured before and after the experiments to check for degradation.

All photophysical data reported here have an error limit of 5 to 10%.

References

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