Phosphorescent perylene imides

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Experimental methods

Compounds **PIx**,[1] and **PIa**[2] were available from a former study.[3] C_{60} was from SES RESEARCH, Houston, Texas. Spectroscopic grade toluene, methanol, dichloromethane, were from C. Erba; 3-methylpentane and ethyl iodide were from Aldrich. All solvents were used without further treatment. A SpexFluorolog II spectrofluorimeter, equipped with a Hamamatsu R928 phototube, was used to detect prompt and time delayed luminescence up to 850 nm. A phosphorimeter accessory 1934D (Spex) was used to detect delayed luminescence. Emission spectra in the NIR range were measured by a FLS920 spectrofluorimeter (Edinburgh) equipped with an Hamamatsu R5509-72 supercooled photomultiplier tube at 193 K and a TM300 emission monochromator with a grating blazed at 1000 nm. Uncorrected spectra, unless otherwise specified, are presented. Absorbance of the order of 0.3 at the excitation wavelength was used. The samples for measurements at 77K were contained in Pyrex tubes dipped in liquid nitrogen in a quartz Dewar. The emission was collected at right angle. Phosphorescence lifetimes were measured by using an IBH 5000F time-correlated single-photon counting apparatus, by using a pulsed SpectraLED excitation source at $\lambda = 464$ nm for **PIx** and $\lambda = 370$ nm for **PIa**. Laser flash photolysis in the nanosecond range was performed by a Surelite (Continuum) pumped Optical Parametric Oscillator (6 ns pulse duration, excitation at 467 or 476 nm, 0.6 mJ/pulse) in a right angle configuration between analysis and excitation. The samples were bubbled with Ar for ca. 15 minutes and sealed in homemade 10 mm optical path cells.

Estimated errors are 10% on lifetimes and ± 2 nm in the maxima wavelength.

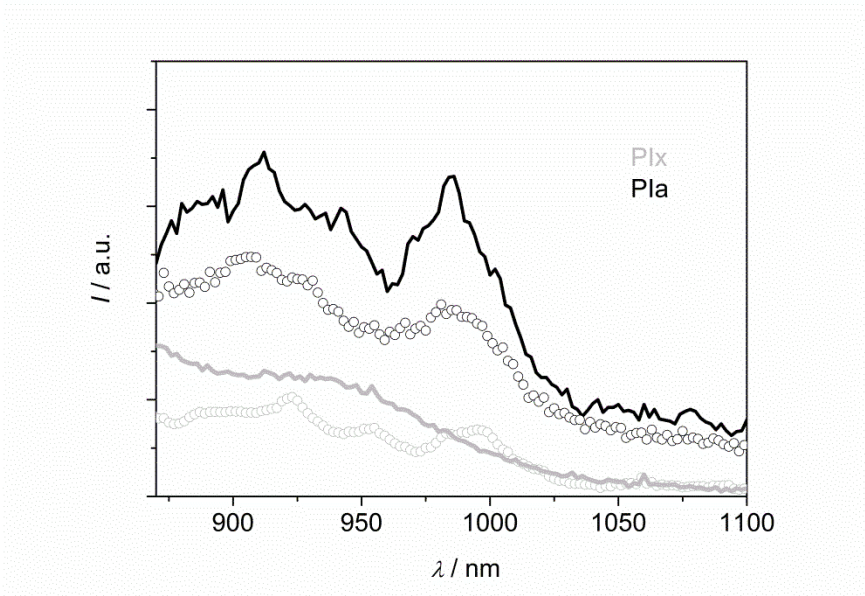

Figure S1. Luminescence spectra in the NIR region of 77 K glassy matrixes of **PIa** (o) and **PIx** (○) in TL, **PIx** in 3-methylpentane (grey line), **PIa** in dichloromethane/methanol (1:1) (black line).

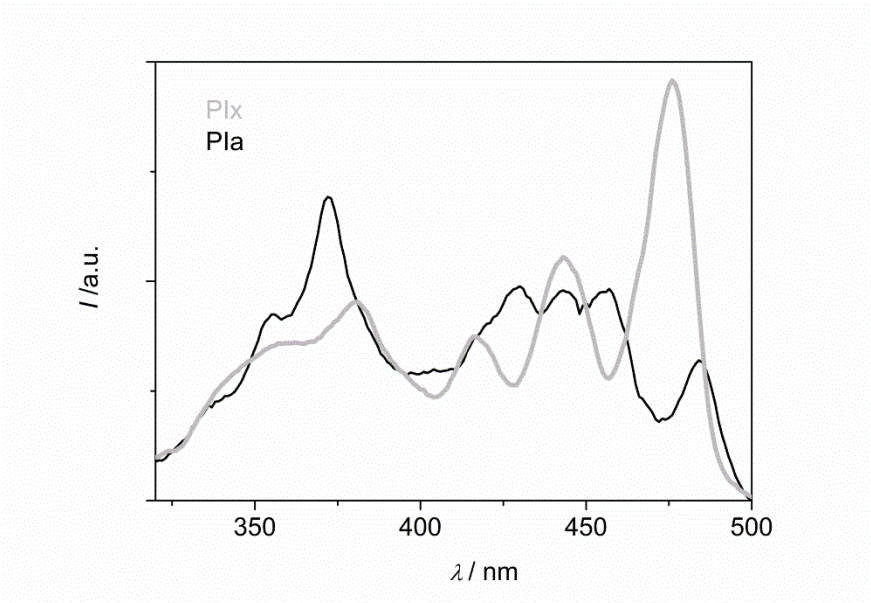

Figure S2. Excitation spectra registered at 686 nm for **PIa** and at 737 nm for **PIx** in a solid matrix at 77 K of dichloromethane, methanol and ethyl iodide (1:1:2).

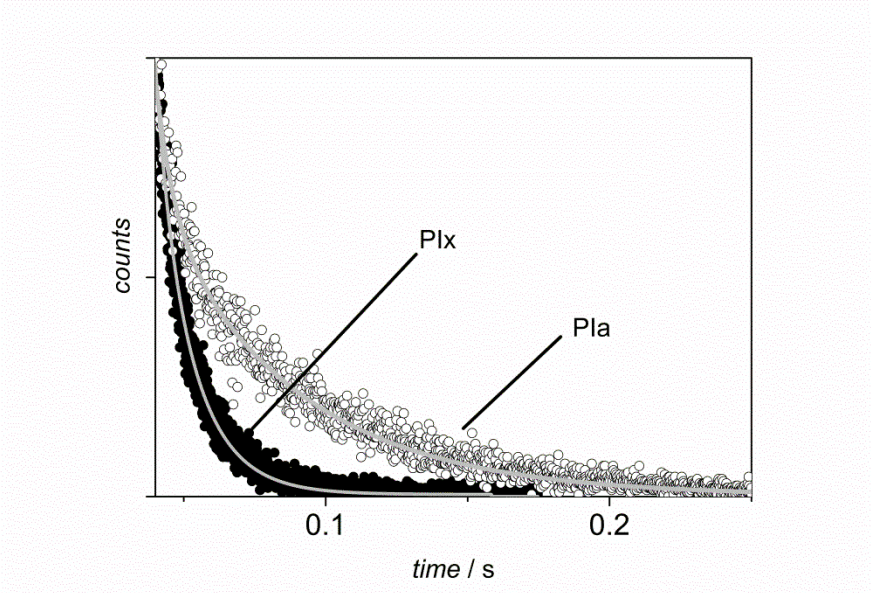

Figure S3. Time resolved phosphorescence at λ_{em}= 737 nm for **PIx** and 690 nm for **PIa** in a dichlorolmethane/methanol (1:1) glass at 77 K. The fitted exponential lifetimes (grey lines) are 13.5 ms for **PIx** and 49.0 ms for **PIa**.

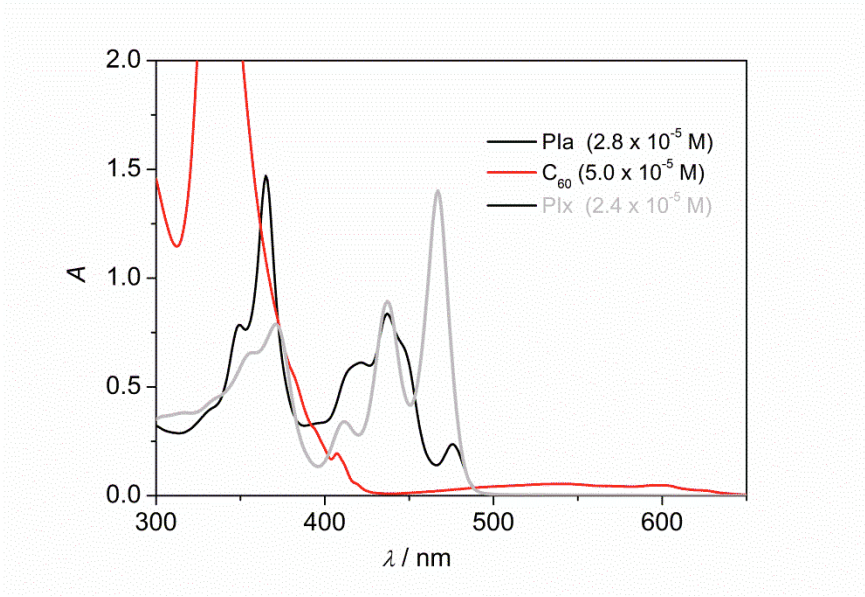

Figure S4. Absorption spectra of the various components in the TL solutions used for the flash-photolysis sensitization experiments.

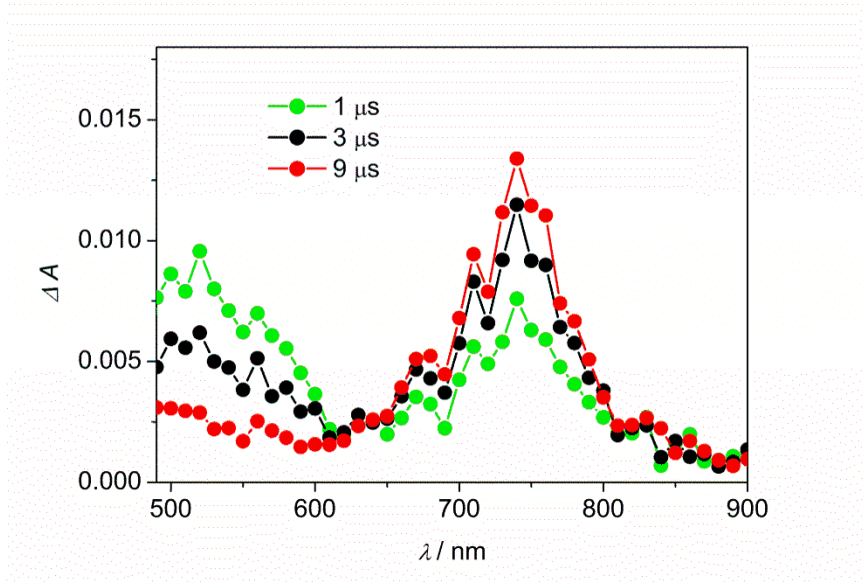

Figure S5. Transient absorption spectra in TL air-free solutions of **PIa** (2.8×10^{-5} M) containing C_{60} (5×10^{-5} M) in TL at 298 K at variable delay times. λ_{exc}= 476 nm, A = 0.26, energy = 0.6 mJ/pulse.

References

1 H. Langhals and S. Kirner, *Eur. J. Org. Chem.*, 2000, 365-380.

2 H. Langhals and B. Böck, " Preparation of orthogonal benzoperylenehexacarboximides for dyes" Ger. Offen. DE 102010023469.9 (June 11, 2010), Chem. Abstr. 2011, 156, 36516.

3 L. Flamigni, A. Zanelli, H. Langhals and B. Böck, *J. Phys. Chem. A*, DOI: 10.1021/jp210132w.