



Supporting Information

© Wiley-VCH 2007

69451 Weinheim, Germany

Supramolecular Construction of Fluorescent J-Aggregates

Based on Hydrogen-Bonded Perylene Dyes

Theo E. Kaiser, Hao Wang, Vladimir Stepanenko, and Frank Würthner*

Universität Würzburg, Institut für Organische Chemie and Röntgen Research Center
for Complex Material Systems, Am Hubland, 97074 Würzburg, Germany.

*E-mail: wuerthner@chemie.uni-wuerzburg.de

Table of Content

1. FT-IR Spectroscopy	S2
2. ¹ H NMR Spectroscopy	S4
3. Scanning Probe Microscopy	S6
4. UV/vis Spectroscopy	S8
5. Fluorescence Spectroscopy	S8
6. Additional References	S13

1. FT-IR Spectroscopy

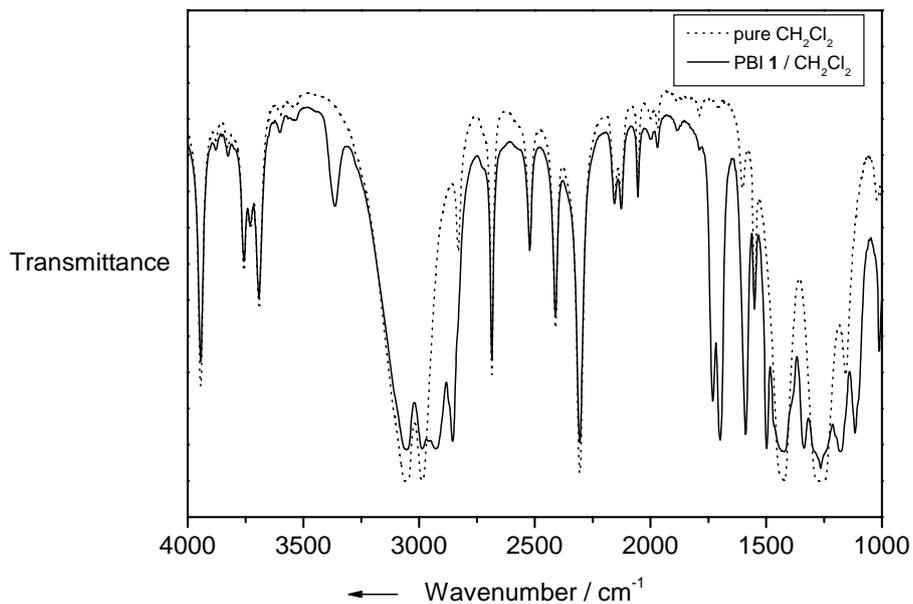


Figure S1. FT-IR spectra of CH₂Cl₂ (dotted line) and solution of perylene bisimide **1** (10⁻³ M) in CH₂Cl₂ (solid line) at room temperature.

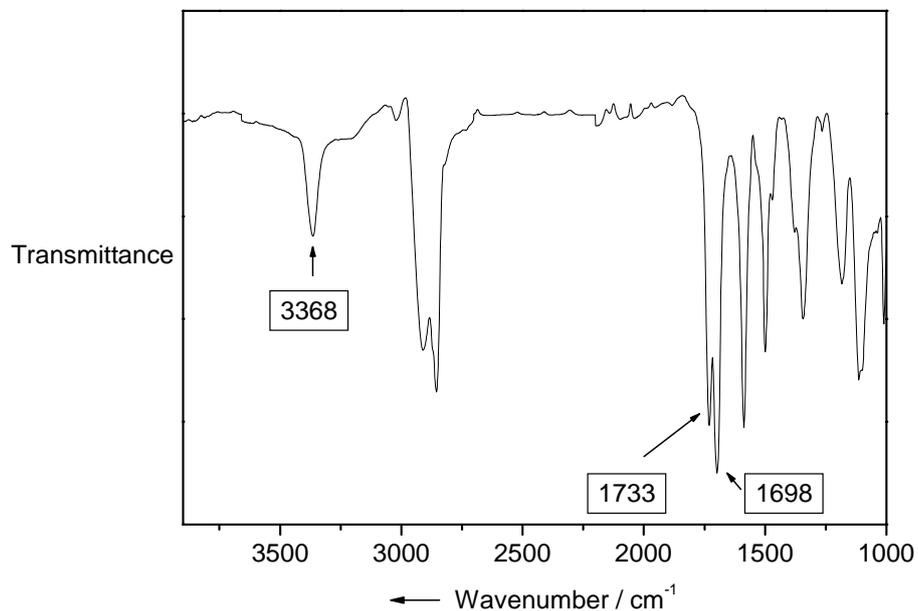


Figure S2. FT-IR spectrum of perylene bisimide **1** in CH₂Cl₂ after subtracting the solvent spectrum (data taken from Figure S1).

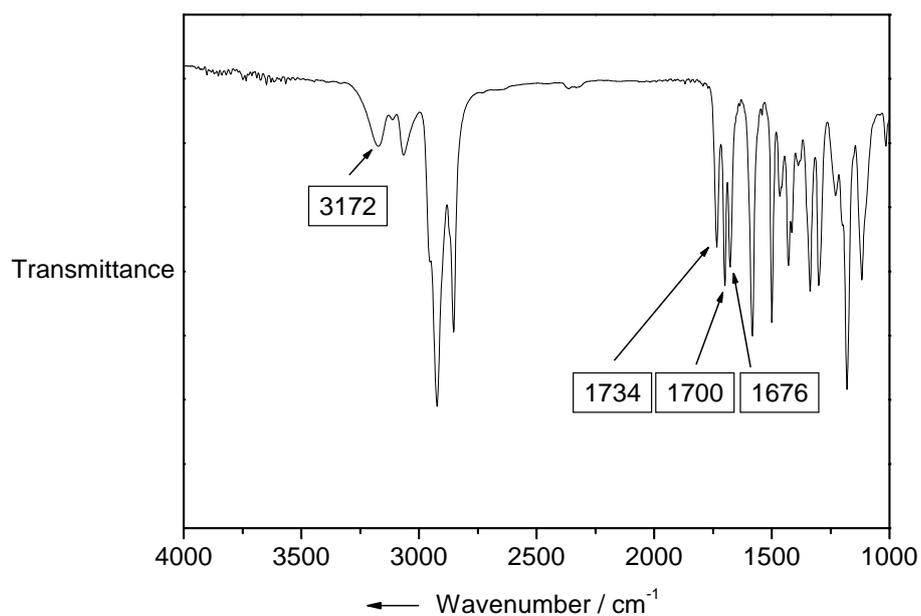


Figure S3. FT-IR spectrum of perylene bisimide **1** (10^{-2} M) in MCH at room temperature. Arrows indicate N-H and C=O vibration modes.

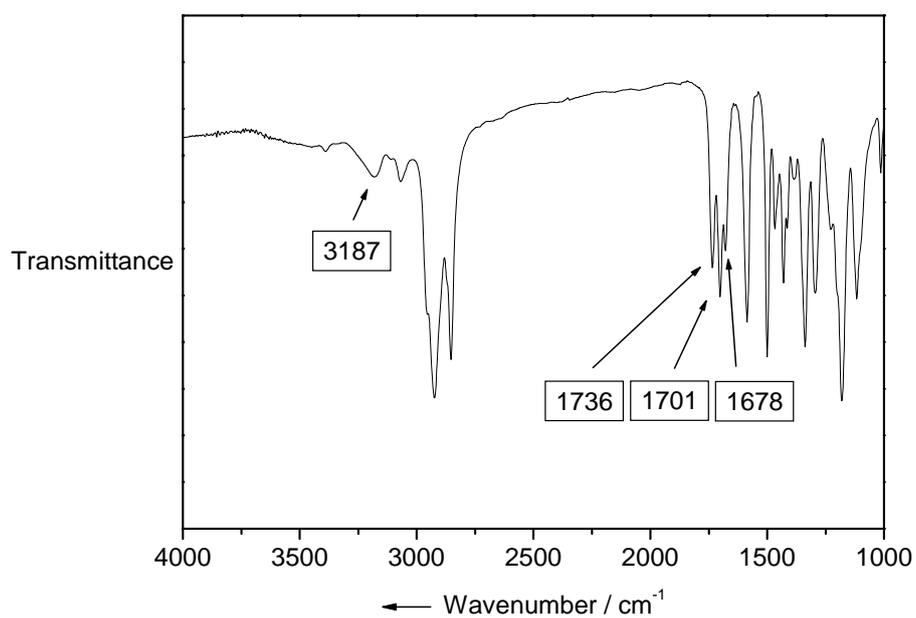
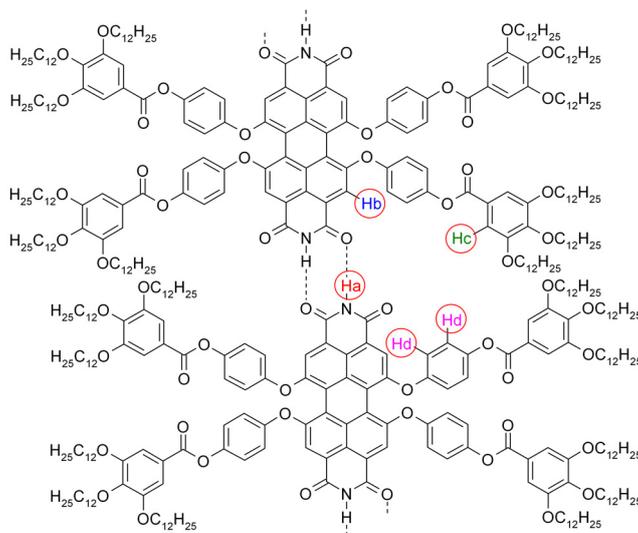


Figure S4. FT-IR spectrum of perylene bisimide **1** in solid state at room temperature. Arrows indicate N-H and C=O vibration modes.

2. ^1H NMR Spectroscopy



Structure of perylene bisimide **1** with the relevant protons highlighted.

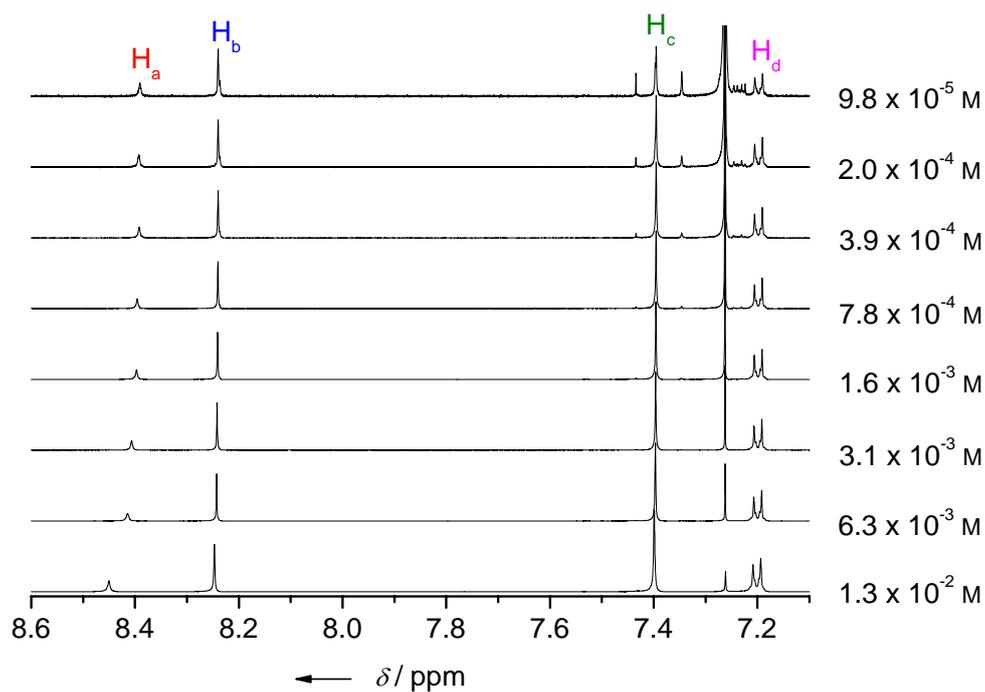


Figure S5. Variable concentration (9.8×10^{-5} M to 1.3×10^{-2} M) ^1H NMR spectra of perylene bisimide **1** in CDCl_3 . The signal of N-H protons is shifted from 8.39 ppm to 8.45 ppm upon increasing the concentration.

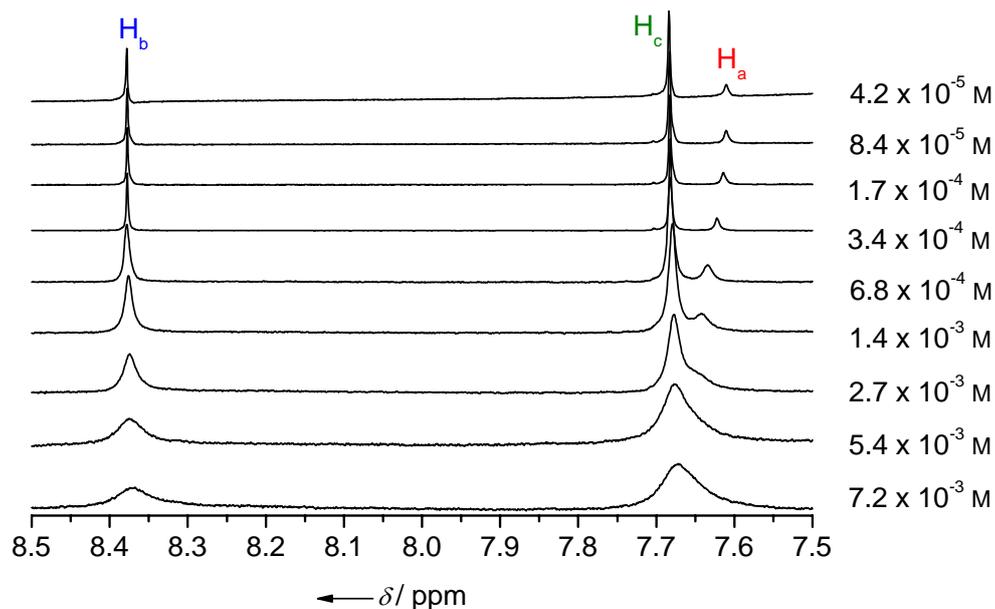


Figure S6. Variable concentration (4.2×10^{-5} M to 7.2×10^{-3} M) ^1H NMR spectra of perylene bisimide **1** in toluene- d_8 .

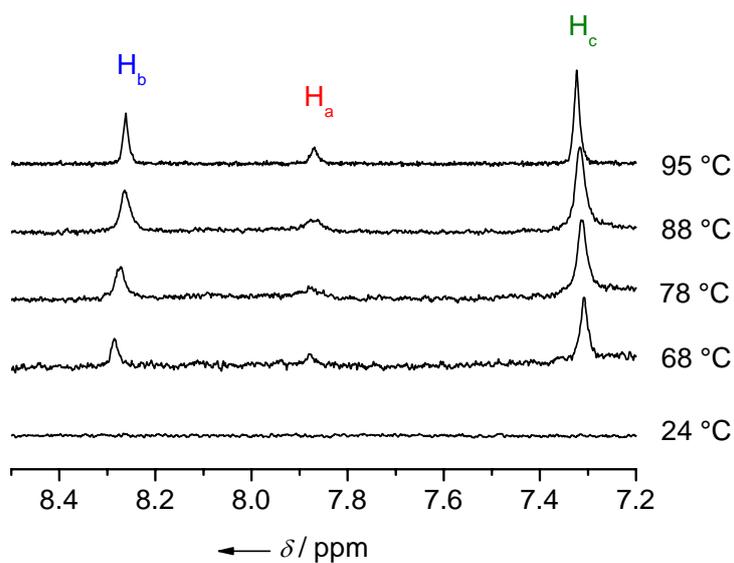


Figure S7. Temperature-dependent (95 °C to 24 °C) ^1H NMR spectra of perylene bisimide **1** (1.3×10^{-4} M) in MCH- d_{14} . Upon formation of aggregates, only proton signals of alkyl chains at high field could be observed (not shown here).

3. Scanning Probe Microscopy

Atomic Force Microscopy (AFM)

AFM measurements were carried out under ambient conditions by using a Veeco MultiMode™ Nanoscope IV system operating in tapping mode in air. Silicon cantilevers (Olympus corporation, Japan) with a resonance frequency of ~ 300 kHz were used. The 512×512 pixel images were collected at a rate of 2 scan lines per second. Solutions of perylene dye **1** in MCH were spin-coated onto silicon wafer (NanoWorld AG, Switzerland) (9×10^{-6} M, 2000 rpm).

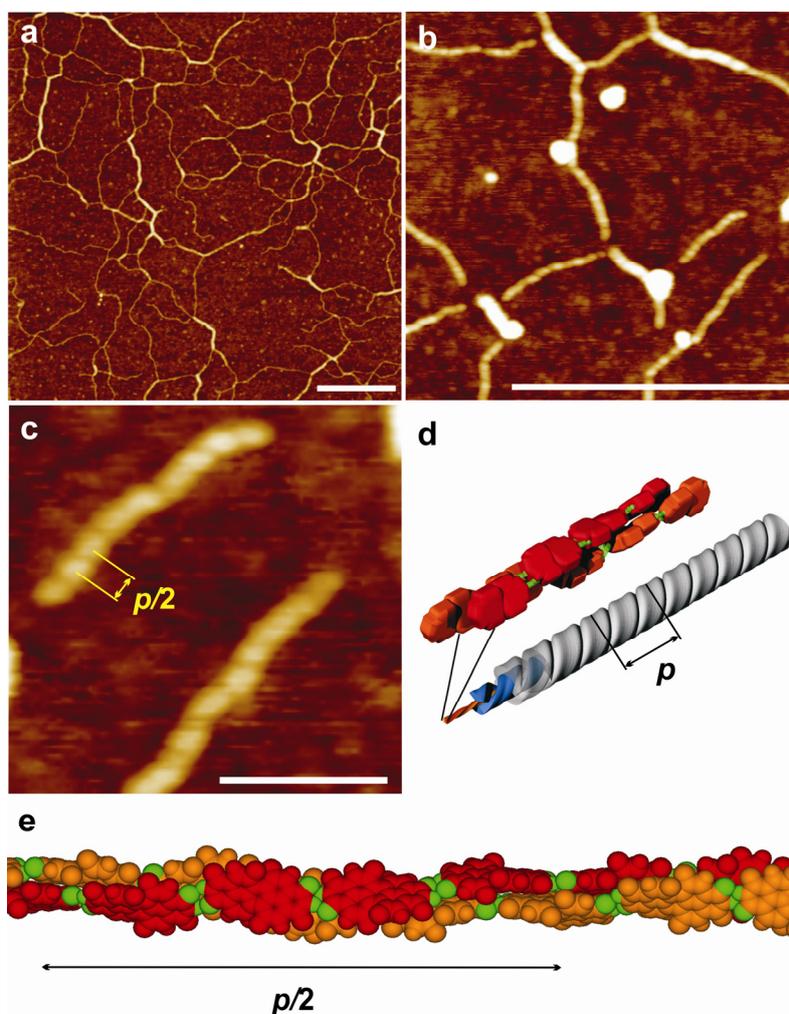


Figure S8. (a,b) Tapping-mode AFM images of self-assemblies of **1** on silicon wafer spin-coated (2000 rpm) from a 9×10^{-6} M solution in MCH. The scale bars (white)

represent 300 nm, z scale is 6 nm. Image (c) shows a magnified section of image (b), with a scale bar representing 45 nm. In (d), the aggregate model (taken from Figure 1b) is shown with distance p representing the helical pitch. The periodic top-to-top length (corresponds to the half pitch $p/2$) of the helical structures in (b,c) was measured as 6.5 ± 1.7 nm. This is in good agreement with the calculated value of 6 nm from AMBER force field calculations (HyperChemTM Release 7.03 for Windows) for the molecular model of dye **1** aggregate structure (e). For this graphic, Accelrys DS ViewerPro 5.0 was used.^[S1] Perylene cores including oxygens at bay positions and free carbonyl oxygens are shown in red and orange, and hydrogen-bonded carbonyl oxygens and imide hydrogens in green. Aryloxy substituents are omitted for clarity. Cross-section analysis (Figure 3b) provided an average height value of 2.0 ± 0.2 nm and an average width value of 8.4 ± 2.6 nm, which is in agreement with the calculated values (3.0 nm and 5.7 nm), if one considers the following points:

- I. Due to the AFM tip broadening effect, the actual width of aggregates is usually smaller than the apparent one.^[S2-S6]
- II. AFM imaging of perylene bisimide **1** on silicon wafer (Figure 3 and Figure S8a-c) was carried out in the repulsive regime. In this regime, the tip probes the repulsion that is dictated by Pauli's exclusion principle which closely resembles the geometric shape of the sample.^[S2] The lower than expected experimental values for the heights and higher values for the widths are possibly due to the deposition of the flexible C₁₂H₂₅ chains on the surface and the compression of the aggregate by AFM tip during scanning.^[S6]

4. UV/vis Spectroscopy

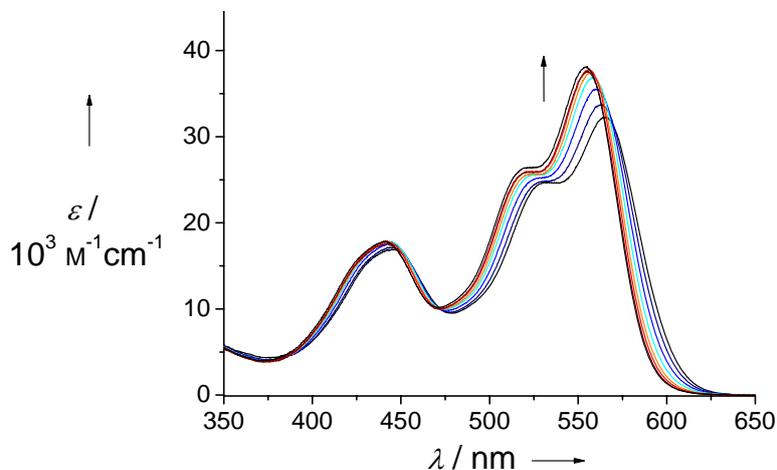


Figure S9. Temperature-dependent UV/vis spectra of reference dye **2** (2.9×10^{-4} M) in MCH at 20 °C to 90 °C. Arrow indicates changes upon increasing temperature.

5. Fluorescence Spectroscopy

Fluorescence emission and excitation spectra were recorded on a PTI QM4-2003 fluorescence spectrometer equipped with a Peltier system as temperature controller and were corrected against photomultiplier and lamp intensity. A long wavelength range emission corrected Hamamatsu photomultiplier R928 was used. Fluorescence quantum yield of perylene bisimide **1** monomer was determined in CH_2Cl_2 vs *N,N'*-bis(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxyperylene-3,4:9,10-tetra-carboxylic acid bisimide ($\Phi_{\text{fl}} = 0.96$ in CHCl_3)^[S7] and that of perylene bisimide **1** aggregate in methylcyclohexane (MCH) was measured vs Nile blue perchlorate ($\Phi_{\text{fl}} = 0.27$ in $\text{C}_2\text{H}_5\text{OH}$)^[S8] under magic angle set-up (54.7°). The given quantum yields were averaged from values measured at three different excitation wavelengths with OD of 0.02 – 0.05 in the absorption maximum (standard deviation $\sigma = 1\text{-}3\%$).

Fluorescence polarization experiments

The fluorescence anisotropy r is a measure for the depolarization of the fluorescence emission and is defined as follows:^[S9]

$$r = \frac{I_{VV} - G \cdot I_{VH}}{I_{VV} + 2 \cdot G \cdot I_{VH}} \quad \text{with} \quad G = \frac{I_{HV}}{I_{HH}}$$

In this equation, I is the fluorescence intensity at a specific wavelength and the indices are related to the vertical or horizontal orientation of the excitation (first index) and the emission polarizer (second index) with respect to the excitation-emission plane. G is an instrument factor which compensates for polarization effects of the emission optics. Fluorescence anisotropy was determined on PTI/QM4 fluorescence spectrometer equipped with two Glan-Thomson polarizers. Correction for the G factor was obtained automatically. Fluorescence intensities were averaged for 60 s at 2 points/s, bandwidth was set to 4 or 6 nm, and all measurements were performed at 25 °C by using a Peltier system as temperature controller that is incorporated in the sample holder.

Time-resolved fluorescence lifetime

Fluorescence lifetimes were measured with a PTI LaserStrobe fluorescence spectrometer system containing a PTI GL-3300 nitrogen laser (337.1 nm, pulse width 600 ps, pulse energy 1.45 mJ) coupled with a dye laser PTI GL302 (pulse width 500 ps, pulse energy 220 μ J at 550 nm) as an excitation source and stroboscopic detection. Laser output was tuned within the emission curves of the laser dyes supplied by the manufacturer (PLD 421, 500, 579, 665, 735). Details of the Laser Strobe systems are described on the manufacturer's web site and in the literature.^[S10] The instrument

response function was collected by scattering the exciting light of a dilute, aqueous suspension of colloidal Silica (LUDOX). Decay curves were evaluated using the software supplied with the instrument applying least square regression analysis. The quality of the fit was evaluated by analysis of χ^2 , DW factor and Z value and by inspection of residuals and autocorrelation function. The experiments were performed at room temperature and all samples were degassed by nitrogen gas flow for 5 min prior to measurement.

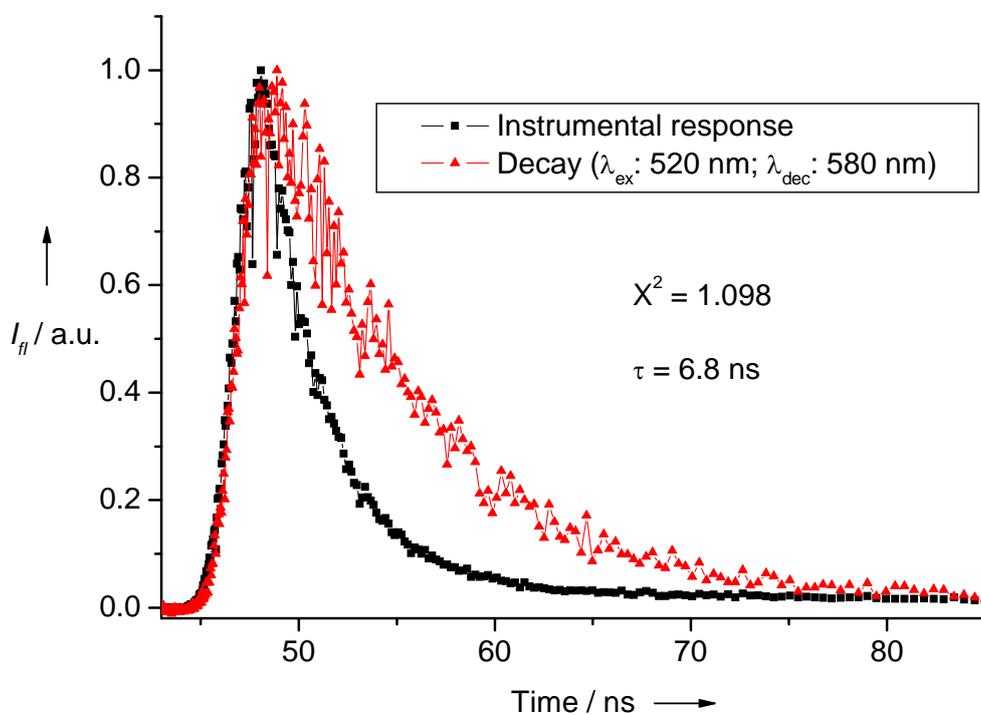


Figure S10. Fluorescence intensity decay curves for perylene bisimide **1** monomer in MCH at 25 °C. Detection wavelength $\lambda_{\text{det}} = 580 \text{ nm}$ and fitted with a single-exponential decay function.

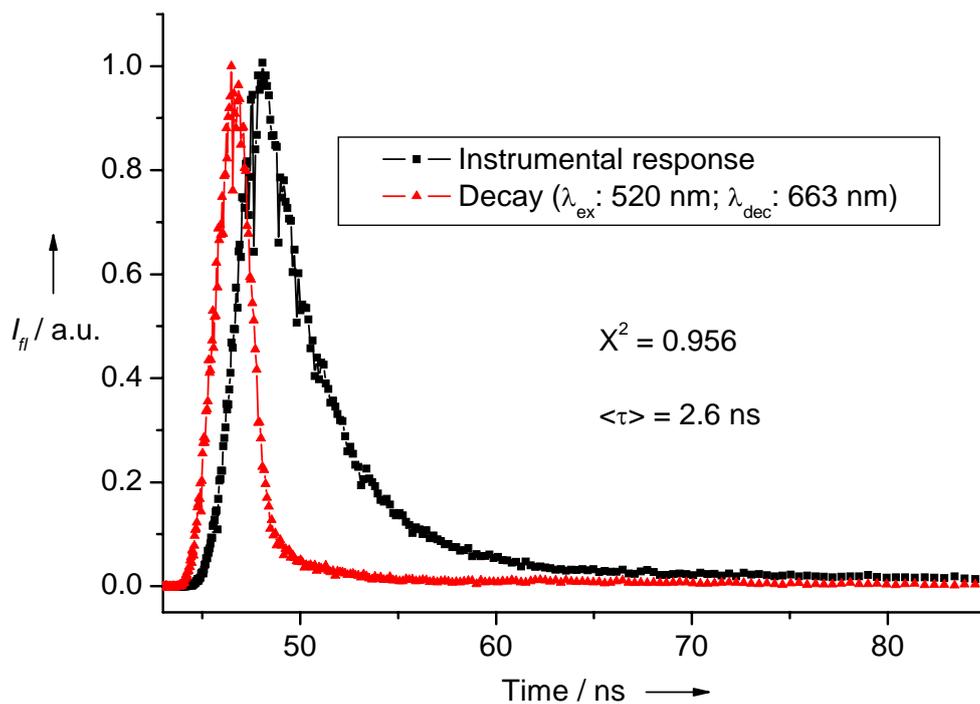


Figure S11. Fluorescence intensity decay curves of perylene bisimide **1** aggregate in MCH at 25 °C. Detection wavelength $\lambda_{\text{det}} = 663$ nm and fitted with two-exponential decay function and then the τ_{agg} could be calculated as a weighted mean fluorescence lifetime. From curve fitting, two fluorescence lifetimes 2.24 ns (93.5 %) and 6.92 ns (6.5 %) could be obtained for perylene bisimide **1** aggregate. The mean fluorescence lifetime of aggregate is calculated as follows:^[S11]

$$\tau_{\text{agg}} = \langle \tau \rangle = (A \times \tau_1) + (B \times \tau_2) = (0.9354 \times 2.237) + (0.06456 \times 6.917) = 2.6 \text{ ns}$$

Absolute fluorescence quantum yield determination

Absolute fluorescence quantum yields were determined on a Hamamatsu Absolute PL Quantum Yield Measurement System CC9920-02. The system is made up of an excitation source that uses a 150 W CW Xenon light source, a monochromator (250-700 nm, FWHM 10 nm), an integrating sphere, and a multi-channel spectrometer capable of simultaneously measuring multiple wavelengths between 300

and 950 nm and counting the number of absorbed and emitted photons. With this system the absolute fluorescence quantum yield of a concentrated ($c = 2.7 \times 10^{-5}$ M) sample of perylene dye **1** aggregates in MCH was determined to 0.85 ± 0.02 upon excitation at $\lambda = 600$ nm under ambient conditions (room temperature, no degassing). For comparison, a dilute solution ($c = 1.1 \times 10^{-6}$ M in CHCl_3) of the fluorescence standard

N,N'-bis(2,6-diisopropylphenyl)-1,6,7,12-(tetraphenoxy)perylene-3,4:9,10-tetra-carboxylic acid bisimide was determined under identical conditions and a fluorescence quantum yield of 1.01 ± 0.02 was obtained upon excitation at $\lambda = 550$ nm (literature value:^[S7] 0.96 - 1.01).

6. Additional References

- [S1] DiscoVery Studio ViewerPro; Accelrys Inc.: San Diego, CA, **2002**;
(www.accelrys.com).
- [S2] L. Chen, C. L. Cheung, P. D. Ashby, C. M. Lieber, *Nano Lett.* **2004**, *4*,
1725-1731.
- [S3] I. Kvien, B. S. Tanem, K. Oksman, *Biomacromolecules* **2005**, *6*, 3160-3165.
- [S4] D. J. Keller, F. S. Franke, *Surf. Sci.* **1993**, *294*, 409-419.
- [S5] D. Keller, *Surf. Sci.* **1991**, *253*, 353-364.
- [S6] T. Shibata-Seki, J. Masai, K. Yoshida, K. Sato, H. Yanagawa, *Jpn. J. Appl. Phys.* **1993**, *32*, 2965-2968.
- [S7] a) G. Seybold, G. Wagenblast, *Dyes Pigments* **1989**, *11*, 303-317; b) R. Gvishi, R. Reisfeld, Z. Burshtein, *Chem. Phys. Lett.* **1993**, *213*, 338-344.
- [S8] R. Sens, K. H. Drexhage, *J. Luminescence* **1981**, *24*, 709-712.
- [S9] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Kluwer Academic/Plenum Publishers, New York, **1999**.
- [S10] a) Photon Technology International, Inc. (www.pti-nj.com); b) R. G. Bennett, *Rev. Sci. Instrum.* **1960**, *31*, 1275-1279.
- [S11] E. Da Como, M. A. Loi, M. Murgia, R. Zamboni, M. Muccini, *J. Am. Chem. Soc.* **2006**, *128*, 4277-4281.