One-dimensional luminescent nanoaggregates of perylene bisimides

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Synthesis and Characterization of the Compounds 2, 3, and 4.

3,4,5-Tris(1'-dodecynyl)-nitrobenzene (2): 1,2,3-Triiodonitrobenzene^[S1] (3.0 g, 6.0 mmol), dodec-1-yne (3.30 g, 19.8 mmol), bis(triphenylphosphine)-palladium(II)-dichloride (252 mg, 0.30 mmol), copper(I) iodide (115 mg, 0.60 mmol) were mixed in 80 mL triethylamine under argon atmosphere and stirred at 80 °C for 4 h. After cooling to room temperature, the solid precipitate was removed by filtration and the solution was concentrated by rotary evaporation. The residue was purified by silica gel column chromatography with *n*-hexane /acetone (10:1) as an eluent to obtain a brown oil (3.40 g, 93%). ¹H NMR (400 MHz, CDCl₃, 300 K, TMS): $\delta = 8.08$ (s, 2H, Ar-H), 2.54 (t, 2H, *J* = 7.0 Hz, C=CCH₂), 2.46 (t, 4H, *J* = 7.0 Hz, C=CCH₂), 1.65 (m, 6H, CH₂), 1.49 (m, 6H, CH₂), 1.4-1.1 (m, 36H, CH₂), 0.88 (t, 9H, *J* = 6.7 Hz, CH₃). MS (EI, 70 eV): m/z (%): 615.6 (100) [M]⁺; elemental analysis (%) calculated for C₄₂H₆₅NO₂ (616.0): C 81.90, H 10.64, N 2.27; found: C 81.50, H 11.05, N 2.36.

3,4,5-Tridodecylaniline (**3**): 3,4,5-Tri(1'-dodecynyl)-nitrobenzene **2** (1.60 g, 2.60 mmol) was placed in a flask containing 0.40 g of 10% palladium on carbon and 80 mL of dry ethanol and 20 mL of dry ethyl acetate. The flask was affixed with balloons filled with hydrogen gas and the mixture was stirred at room temperature for 24 h. Then the Pd/C in the reaction mixture was removed by filtration and the solvent was removed by rotary evaporation. The resulting brown oil was purified by silica gel column chromatography with

n-hexane/CH₂Cl₂ (1:1) as an eluent to give slightly yellow oil which became a white solid when stored in refrigerator. (0.96 g, 53%). ¹H NMR (400 MHz, CDCl₃, 300 K, TMS): $\delta = 6.41$ (s, 2H, Ar-H), 2.48 (m, 6H, Ar-CH₂), 1.7-1.1 (m, 60H, CH₂), 0.88 (m, 9H, CH₃), a very broad signal was observed for NH₂ protons at 4.0-3.0 ppm. MS (EI, 70 eV): m/z (%): 598.1 (100) [M]⁺; elemental analysis (%) calculated for C₄₂H₇₉N (598.1): C 84.34, H 13.31, N 2.34; found: C 84.37, H 13.32, N 2.32.

N,*N*[•]-**Di**(3,4,5-tridodecylphenyl)-perylene-3,4:9,10-tetracarboxylic acid bisimide (4): A mixture of perylene-3,4:9,10-tetracarboxylic acid bisanhydride (0.13 g, 0.33 mmol), aniline **3** (0.40 g, 0.67 mmol) and zinc acetate (73 mg, 0.33 mmol) in 15 mL quinoline was stirred at 180 °C for 4 h. After cooling to room temperature, the reaction mixture was poured into 30 mL MeOH. The precipitate was collected by filtration, washed with methanol (3 × 20 mL), and then dried in vacuum. The crude product was further purified by silica gel column chromatography (CH₂Cl₂ as eluent) and then slowly precipitated from 10 mL CH₂Cl₂/methanol (1: 1) to give a red powder (280 mg, 56%). ¹H NMR (400 MHz, CDCl₃, 300 K, TMS): $\delta = 8.74$ (d, 4H, J = 8.0 Hz, H_{pery}), 8.66 (d, 4H, J = 8.2 Hz, H_{pery}), 6.97 (s, 4H, Ar-H), 2.66 (m, 12H, Ar-CH₂), 1.8-1.2 (m, 120H, CH₂), 0.88 (m, 18H, CH₃). MS (FAB, matrix: *p*-octyloxynitrobenzene): 1551.2 m/z, [M]⁺ (calculated for C₁₀₈H₁₆₂N₂O₄ 1551.3). Elemental analysis (%) calculated for C₁₀₈H₁₆₂N₂O₄ (1552.5): C 83.56, H 10.52, N 1.80; found: C 83.13, H 10.75, N 1.89. UV/Vis (CH₂Cl₂): $\lambda_{max}(\varepsilon) = 527$ (96300), 491 (58100), 460 (21000), 434 (6100), 369 (5000 M⁻¹ cm⁻¹). Fluorescence (CH₂Cl₂): $\lambda_{max} = 532$ nm; quantum yield: $\Phi_{\rm f} = 0.63$.

General Methods. NMR spectra were recorded at 300 K on Bruker Avance 400 (400 MHz) or DMX 600 (600 MHz, for temperature dependent measurements) spectrometers and the spectra were calibrated against TMS. For the temperature dependent measurements the spectra were calibrated against the chemical shift of residual methylcyclohexane (MCH) in $[D]_{14}$ -MCH at 1.60 ppm. UV/Vis spectra were measured on Perkin Elmer Lambda 40P spectrophotometer equipped with a Peltier System as the temperature controller. Differential scanning calorimetery (DSC) measurements were performed by using a TA Q1000 calorimeter. The vapour pressure osmometry measurements were performed on a Knauer vapour pressure osmometer with a universal temperature (40, 50 and 60 °C) im terms of *R* (ohm) vs molal osmotic concentration (moles per kg MCH) was constructed up to 0.01 molal.

UV/Vis Aggregation Study.

A set of absorption spectra for PTCDI **4** was recorded at different concentrations $(2.0 \times 10^{-7} \text{ mol } \text{L}^{-1} \text{ to } 5.0 \times 10^{-3} \text{ mol } \text{L}^{-1})$ and temperatures (10 to 70 °C) in MCH. The apparent absorption coefficients obtained from the spectra were fitted by nonlinear regression analysis to the isodesmic model according to the Equation 1.

$$\varepsilon(c) = \frac{2Kc + 1 - \sqrt{4Kc + 1}}{2K^2 c^2} (\varepsilon_{\rm f} - \varepsilon_{\rm a}) + \varepsilon_{\rm a}$$
⁽¹⁾

Here, $\varepsilon(c)$ is the apparent absorption coefficient and *c* is the total concentration of PTCDI **4**. The constants *K*, ε_{f} and ε_{a} are the aggregation constant, the absorption coefficients for the free

and the aggregated species, respectively, which can be obtained from the curve fitting. The average aggregation number N at certain concentration $c_{\rm T}$ was calculated with Equation 2.

$$N = \frac{1}{2} \left(1 + \sqrt{4Kc_T + 1} \right)$$
 (2)

Fluorescence Measurements. The steady state fluorescence spectra, lifetime and the fluorescence anisotropy were measured on a PTI QM4/2003 spectrofluorometer equipped with two Glan-Thomson polarizers under magic angle and front face setup due to the high optical densities of the samples. All fluorescence spectra were corrected. The fluorescence quantum yields were determined by the optical dilution method by using fluorescein (Φ_f = 0.92 in 1*N* aqueous NaOH) as standards.^[S2] The given quantum yields are averaged value of data obtained at three different excitation wavelengths.

Atomic Force Microscopy (AFM) Study.

AFM measurements were performed under ambient conditions using a Veeco MultiMode Nanoscope IV system operating in tapping mode in air. Silicon cantilevers (OMCL-AC160TS) with a resonance frequency of ~300 kHz were used. Solution of perylene bisimide **4** in MCH was spin-coated onto a HOPG (highly ordered pyrolytic graphite) surface under 7000 rpm.



Fig. S1 Fraction of aggregated molecules $\alpha_{agg.}$ for perylene bisimide 4 as a function of concentration in MCH. The curve was calculated by fitting the apparent absorption coefficients at $\lambda = 517$ nm to the isodesmic model.

Table S1 Aggregation constant K of compound 4 in MCH at different temperatures.

<i>T</i> (°C)	10	20	30	40	50	60	70
K (L mol ⁻¹)	2.6×10^{5}	1.2×10^{5}	4.4×10^4	2.3×10^4	1.2×10^{4}	6.2×10^{3}	3.6×10^{3}



Fig. S2 Van't Hoff plot for the temperature dependence of the aggregation constant K of 4 in MCH.

Table S2 Average aggregation number N of compound 4 at a concentration of 5.0×10^{-3} M in MCH obtained from UV/Vis and VPO measurements.

Т	Ν		
	UV/Vis	VPO	
40 °C	11.2	9.2	
50 °C	8.1	7.1	
60 °C	6.1	6.2	



Fig. S3 Differential scanning calorimetry (DSC) traces of PCTDI **4**: first heating and cooling (solid line) and second heating (dashed line).

References

- [S1] C. Niemann, C. E. Redemann, J. Am. Chem. Soc. 1941, 63, 1549-1552.
- [S2] J. N. Demas, G. A. Crosby, J. Phys. Chem. 1971, 75, 991-1024.