

Supplementary Information

Hierarchical supramolecular structuring and dynamical properties of water soluble polyethylene glycol – perylene self-assemblies

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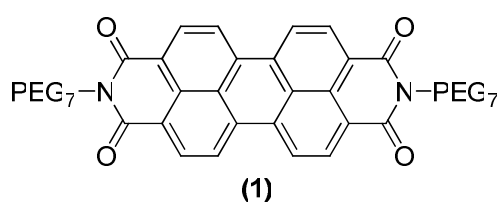
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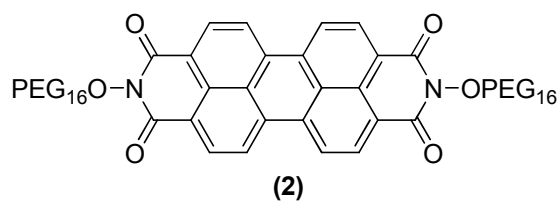
Synthetic procedure

All *reagents and solvents* were purchased at the highest commercial quality and used without further purification unless otherwise noted. Dry solvents were obtained using a double column SolvTech purification system. Yields refer to purified spectroscopically (¹H NMR) homogeneous materials. *Thin Layer Chromatographies* were performed with TLC silica plastic sheets (Polygram SIL G/UV₂₅₄, Macherey-Nagel). In most cases, irradiation using a *Bioblock VL-4C* UV-Lamp (6 W, 254 nm and/or 365 nm) as well as Ce-molybdate stainings were used for visualization. *Ultra Performance Liquid Chromatographies coupled to Mass Spectroscopy* (UPLC-MS) were carried out on a *Waters Acquity UPLC-SQD* apparatus equipped with a PDA detector (190-500 nm, 80Hz), using a reverse phase column (Waters, BEH C18 1.7 μm, 2.1mm x 50 mm), and the MassLynx 4.1 – XP software. *Preparative Ultra Performance Liquid Chromatographies* were performed using a *Waters AutoPurify* apparatus equipped with a UV detector (set at 300 nm), a 3100 mass spectrometer, a reverse phase

column (Waters, Sun Fire Column 5.0 μm , 4.9mm x 150 mm) running with a water/methanol gradient as eluent, and the MassLynx 4.1 – XP software. *MALDI* mass spectra were recorded on a Bruker Daltonics AutoflexII TOF spectrometer. ^1H NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz and ^{13}C spectra at 100 MHz in CDCl_3 (or MeOD) at 25°C. The spectra were internally referenced to the residual proton solvent signal. For ^1H NMR assignments, the chemical shifts are given in ppm. Coupling constants J are listed in Hz. The following notation is used for the ^1H NMR spectral splitting patterns: singlet (s), doublet (d), triplet (t), multiplet (m), large (l).

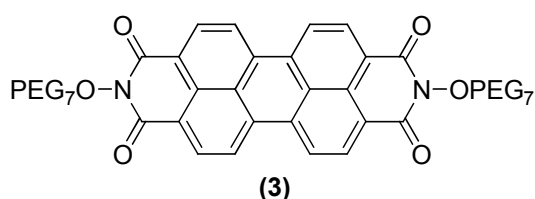


2,5,8,11,14,17,20-heptaodocosan-22-amine (1.97 mmol, 688 mg) and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA, 1.97 mmol, 773 mg) were dissolved in pyridine (15 mL), and the reaction mixture was heated to reflux for 24h. The mixture was then cooled down to room temperature and diluted with dichloromethane, then filtered through Celite to remove the excess of PTCDA. The filtrate was concentrated under reduced pressure and crude product was purified by preparative HPLC to yield compound **1** (176 mg, 17%) as a red solid. ^1H NMR (400 MHz, CDCl_3 , 25°C): δ = 8.62 (d, 3J =8.0 Hz, 4H), 8.54 (d, 3J =7.6 Hz, 4H), 4.45 (t, 3J =6.0 Hz, 4H), 3.85 (t, 3J =6.0 Hz, 4H), 3.72-3.50 (m, 48H), 3.34 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3 , 25°C): δ = 163.6, 134.8, 131.6, 129.6, 126.6, 123.4, 123.3, 72.2, 70.8, 70.4, 68.1, 59.3, 39.6; ESI-MS: m/z calcd for $\text{C}_{54}\text{H}_{70}\text{N}_2\text{O}_{18}$: 1057.45 $[\text{M}+\text{Na}^+]$, found: 1057.25; MALDI-TOF: m/z calcd for $\text{C}_{54}\text{H}_{70}\text{N}_2\text{O}_{18}$: 1057.45 $[\text{M}+\text{Na}^+]$, found: 1057.55.



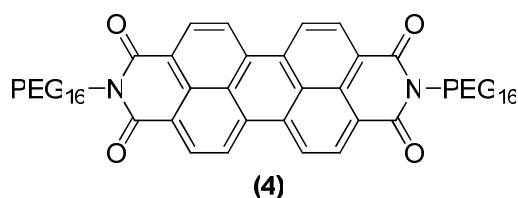
3,6,9,12,15,18,21,24,27,30,33,36,39,42,45,48-hexadecaioxanonatetracontan-1-

hydroxylamine (0.65 mmol, 495 mg) and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA, 0.65 mmol, 255 mg) were dissolved in pyridine (5 mL), and the reaction mixture was heated to reflux for 24h. The mixture was then cooled down to room temperature and diluted with dichloromethane, then filtered through Celite to remove the excess of PTCDA. The filtrate was concentrated under reduced pressure and crude product was purified by preparative HPLC to yield compound **2** (118 mg, 19%) as a red solid. ^1H NMR (400 MHz, CDCl_3 , 25°C): δ = 8.73 (d, $^3J=8.0$ Hz, 4H), 8.68 (d, $^3J=8.2$ Hz, 4H), 4.47 (t, $^3J=4.6$ Hz, 4H), 3.97 (t, $^3J=4.6$ Hz, 4H), 3.73 (t, $^3J=4.8$ Hz, 4H), 3.67-3.57 (m, 112H), 3.52 (t, $^3J=4.6$ Hz, 4H), 3.36 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3 , 25°C): δ = 160.0, 134.6, 131.7, 128.4, 126.3, 123.6, 123.5, 76.3, 72.0, 70.8, 70.6, 69.3, 59.1; ESI-MS: m/z calcd for $\text{C}_{90}\text{H}_{142}\text{N}_2\text{O}_{38}$: 1881.92 $[\text{M}+\text{Na}^+]$, found: 1881.71; MALDI-TOF: calcd for $\text{C}_{90}\text{H}_{142}\text{N}_2\text{O}_{38}$: 1881.91 $[\text{M}+\text{Na}]^+$, found 1881.85.



2,5,8,11,14,17,20-Heptaodocosan-22-hydroxylamine (0.74 mmol, 271 mg) and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA, 0.74 mmol, 290 mg) were dissolved in pyridine (6 mL), and the reaction mixture was heated to reflux for 24h. The mixture was then cooled down to room temperature and diluted with dichloromethane, then filtered through Celite to remove the excess of PTCDA. The filtrate was concentrated under reduced pressure and crude product was purified by preparative HPLC to yield compound **3** (212 mg, 52%) as a red solid. ^1H NMR (400 MHz, CDCl_3 , 25°C): δ = 8.70 (d, $^3J=8.0$ Hz, 4H), 8.65 (d, $^3J=6.8$ Hz, 4H), 4.47 (t, $^3J=4.6$ Hz, 4H), 3.96 (t, $^3J=4.6$ Hz,

4H), 3.73 (t, $^3J=4.8$ Hz, 4H), 3.68-3.57 (m, 40H), 3.52 (t, $^3J=4.6$ Hz, 4H), 3.35 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3 , 25°C): δ = 159.7, 134.0, 131.4, 128.0, 125.6, 123.2, 76.3, 71.9, 70.6, 70.5, 70.4, 69.1, 59.0; ESI-MS: m/z calcd for $\text{C}_{54}\text{H}_{70}\text{N}_2\text{O}_{20}$: 1089.44 $[\text{M}+\text{Na}^+]$, found: 1089.31; MALDI-TOF: calcd for $\text{C}_{54}\text{H}_{70}\text{N}_2\text{O}_{20}$: 1089.44 $[\text{M}+\text{Na}]^+$, found 1089.40.



3,6,9,12,15,18,21,24,27,30,33,36,39,42,45,48-hexadecaoxanonatetracontan-1-amine (0.93 mmol, 700 mg) and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA, 0.93 mmol, 365 mg) were dissolved in pyridine (7 mL), and the reaction mixture was heated to reflux for 24h. The mixture was then cooled down to room temperature and diluted with dichloromethane, then filtered through Celite to remove the excess of PTCDA. The filtrate was concentrated under reduced pressure and crude product was purified by preparative HPLC to yield compound **4** (135 mg, 16%) as a red solid. ^1H NMR (400 MHz, CDCl_3 , 25°C): δ = 8.68 (d, $^3J=8.0$ Hz, 4H), 8.63 (d, $^3J=8.0$ Hz, 4H), 4.45 (t, $^3J=6.1$ Hz, 4H), 3.84 (t, $^3J=6.0$ Hz, 4H), 3.72-3.51 (m, 120 H), 3.36 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3 , 25°C): δ = 163.5, 134.7, 131.5, 129.5, 126.5, 123.4, 123.3, 72.1, 70.8, 70.3, 68.1, 59.2, 39.5; ESI-MS: m/z calcd for $\text{C}_{90}\text{H}_{142}\text{N}_2\text{O}_{36}$: 1849.92 $[\text{M}+\text{Na}^+]$; found: 1849.78; MALDI-TOF: m/z calcd for $\text{C}_{90}\text{H}_{142}\text{N}_2\text{O}_{36}$: 1849.92 $[\text{M}+\text{Na}^+]$; found: 1849.49.

Small-Angle Neutron Scattering (SANS) measurements

SANS measurements have been performed on the PAXE spectrometer at the Laboratoire Léon Brillouin (LLB, CEA Saclay, France). Three configurations were used: the first with a sample-to-detector distance of 5 m, a wavelength of 13 Å and a collimation distance of 5.00 m; the second at 5 m and 5 Å and the last one at 1.2 m and 5 Å with a collimation distance of 2.50 m, providing a large accessible q-range

varying from $4 \cdot 10^{-3}$ to 0.4 \AA^{-1} . The neutron wavelength distribution $\Delta\lambda/\lambda$ was 0.11. Data treatment has been done with a homemade program (Pasinet) following standard procedures (see [1] for details).

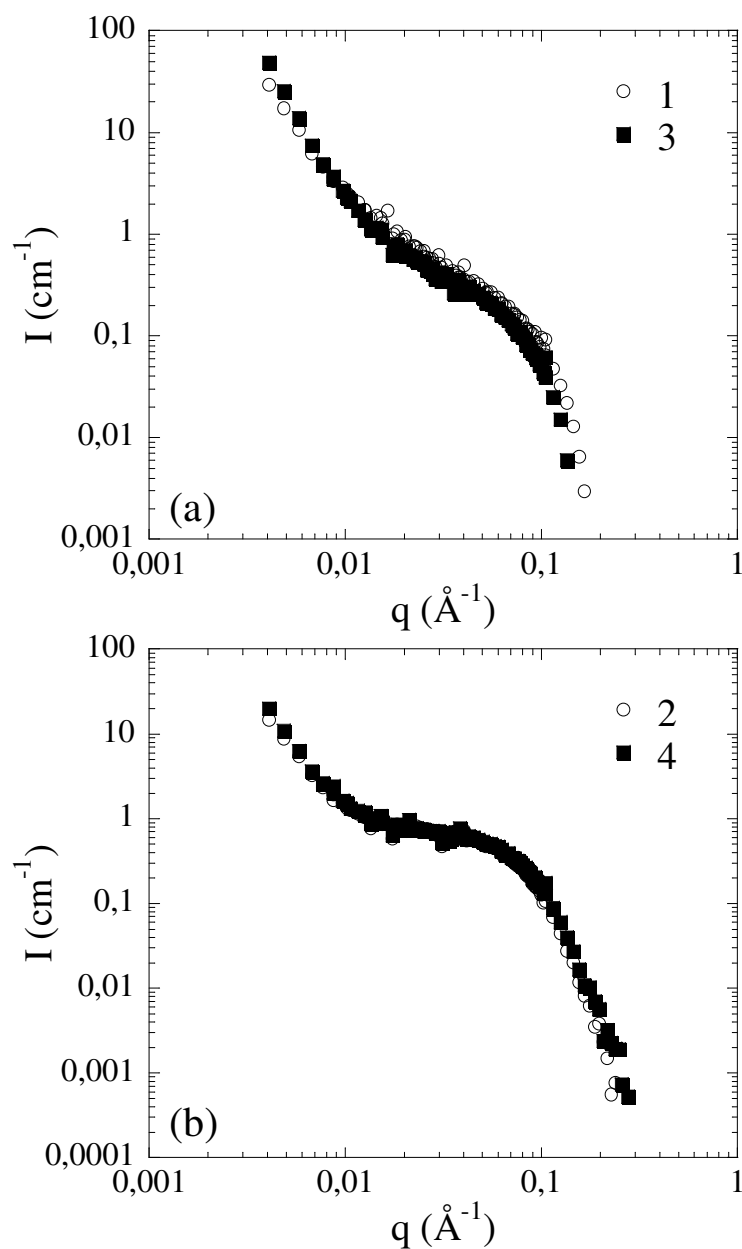


Fig. S1: SANS Scattering intensity as a function of q for compounds **1** and **3** (a) and **2** and **4** (b) at $C=10\text{mM}$ and $T=21^\circ\text{C}$.

The structural behavior is not affected by working either with the PEG-amine or with the PEG-hydroxylamine linked to the perylene core as shown by the superimposition of the data for compounds **1** and **3** and compounds **2** and **4** respectively in Fig. S1 (a) and (b).

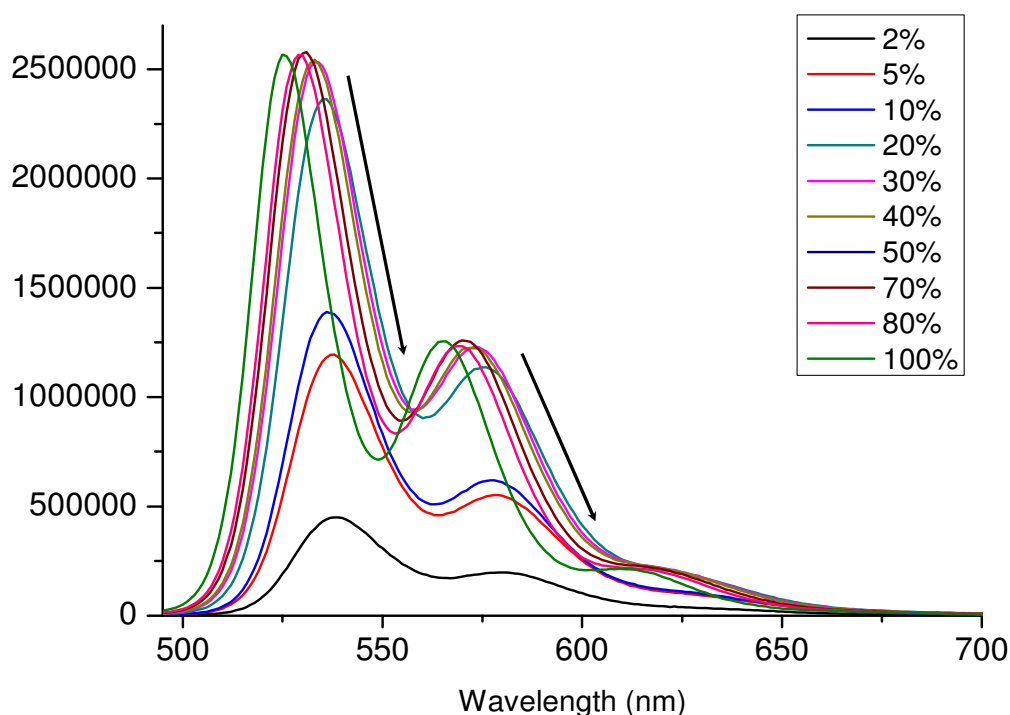


Fig. S2: Fluorescence spectra of compound **3** at 10^{-6} M in water with increasing amounts of THF (2 to 100%). The arrows indicate the decrease of the absorption bands of the perylene unit with increasing amounts of water due to π - π stacking effect. Excitation wavelength=490 nm.

References

- [1] N. Jouault, R. Nguyen, M. Rawiso, N. Giuseppone and E. Buhler, *Soft Matter*, 2011, **7**, 4787-4800.