ELECTRONIC SUPPLEMENTARY INFORMATION

Template-Free Hierarchical Self-Assembly of a Pyrene Derivative into Supramolecular Nanorods

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EXPERIMENTAL

General.

Pyrene butyric acid (PBA), dicyclohexyl carbodiimide (DCC), 3-aminopropyl-triethoxysialne (APTES, \geq 98%) were purchased from Sigma-Aldrich (Switzerland). All used analytical grade solvents were used without any further purification unless otherwise mentioned. Dichloromethane (DCM) was dried over CaH2 and distilled for 4 hours. Reactions were followed by thin-layer chromatography (TLC) carried out on Polygram® G/UV254 pre-coated polyester plates. Flash silica gel chromatography was performed over Macherey Nagel silica C60 (40-63 μ m). Nanopure water was produced with a Millipore Synergy purification system (resistivity \geq 18 M Ω cm). Elma® S30H Elmasonic bath sonicator was used. Fourier transform infrared spectra were measured in attenuated total reflection (ATR) mode using a single reflection diamond ATR device (Golden Gate) and a Varian 670-IR spectrometer. NMR spectra were recorded on a Bruker 400 MHz spectrometer and are reported as chemical shift in parts per million (ppm). All coupling constants (J) are reported in hertz (Hz). The abbreviations s (singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quartet) and m (multiplet) are used to describe multiplicities. Mass spectra (m/z) were recorded on a thermoquest LCQ Deca instrument using positive electrospray ionization (ESI). Melting point was measured using a Büchi 530 apparatus and measurements were carried out in triplicate to ensure the reproducibility of the result.

Procedure for the synthesis of the pyrene derivative 1.

PBA (17.34 mmol, 5 g) was dissolved in freshly dried DCM (700 mL) in a round bottom flask under a nitrogen atmosphere at 0°C. DCC (17.34 mmol, 3.6 mg) was then added and the mixture was stirred for 15 min before APTES (17.34 mmol, 4.1 mL) was added. The suspension was then stirred for 30 min at 0°C before the reaction mixtures was allowed to warm up at 25°C and stirred for additional 24h. The reaction mixture was then cooled at 0°C for 2 hours and the resulting precipitate (DCU) was eliminated by filtration. The mixture was placed at 0°C overnight and was then filtrated. The purification was achieved by flash chromatography using ethyl acetate/cyclohexane mixture (3/7) as eluent, yielding a yellowish powder (2.12 g, 25% yield). [M+Na]+= 514.1. Elemental analysis calcd (%) for C29H37NO4Si: C 70.84, H 7.59, N 2.85; found: C 70.71, H 7.55, N 2.94. Mp: 91°C, TLC ethyl acetate/cyclohexane (6:4) Rf = 0.38.

Self-assembly of 1.

1 mL solution of pyrene derivative **1** in ethanol (5 mg/ml) was prepared and was then added to 9 mL water in a 20 mL glass vial. The suspension was subjected to an ultrasonic treatment for 1h. The suspension was then recovered and centrifuged for 3 min at 20,000 g, the supernatant was removed and the resulting white solid was dried under vacuum at 20°C.

Silica layer growth.

Nanorods were suspended in 12 mL (0.25 mg/mL) of a 2-(N-morpholino)ethanesulfonic acid (MES) buffer (15 mM) and triton X-100 (10 μ L, 0.1%) was added. The suspension was subjected to sonication for 10 min. The suspension was left to stir at 400 rpm for 30 min at 20°C (pH 6). Tetraethoxysilane (12 μ L) was added and the suspension was stirred for 2h. (3-aminopropyl)triethoxysilane (4 μ L) was added and the mixture was stirred at 400 rpm at 10°C for 50h. The nanorods were centrifuged at 20,000 g for 3 min and the supernatant was removed. The solid was suspended in 1 mL nanopure water and centrifuged again, this last step was repeated one more time before the solid was dried under vacuum at 20°C.

Microscopic characterization.

Nanorod structures were imaged using a Zeiss SUPRA^{*} 40VP scanning electron microscope, 5 μ L of each sample were spread on freshly cleaved mica sheets, dried under ambient conditions and sputter-coated with a gold-platinum alloy for 30 s at 15 mA (SC7620 Sputter coater). Micrographs were acquired using the InLens mode with an accelerating voltage of 10 kV. Transmission electron microscope measurements were performed on a Zeiss EM900 microscope equipped with an Olympus Megaview III CCD camera. 10 μ L of suspension of supramolecular structures was dropped on the copper grid and left to dry in air before characterization. Optical micrographs for the crystal colour change were acquired with an Olympus SZX12 stereo microscope equipped with an Olympus UC30 camera.

UV-visible absorbance and fluorescence characterization.

Absorbance and fluorescence intensity were measured using a Biotek Synergy[™] H1 Hybrid Multi-Mode Microplate Reader. All measurements were performed at 25°C. Absorbance characterization was performed using Greiner Bio-one 96 well UV-Star microplates and spectra were recorded between 250 and 500 nm. For the spectrum in ethanol, pyrene derivative 1 was solubilized in ethanol (concentration 0.1 mM) and an aliquot of 200 µL was then analysed. For the spectrum in water (ethanol 10 vol. %) pyrene derivative 1 was first solubilized in ethanol, the latter solution was then added to water to reach a concentration of 0.1 mM and a final ratio vol. water/ethanol 90:10. The suspension was stirred at 600 rpm for 1 h before measurement. For the spectrum in water (ethanol 10 vol. %) under ultrasonication, pyrene derivative 1 was first solubilized in ethanol, and the latter solution was then added to water while under ultrasonication (concentration: 0.1 mM, ratio vol. water/ethanol 90:10). The suspension was subjected to ultrasonic treatment for 1h before measurement. Fluorescence characterization was performed using Greiner Bio-one 96 well black microplates, samples were excited at 366 nm and spectra were recorded between 350 and 550 nm. Fluorescence spectra were first obtained by solubilizing pyrene derivative 1 in ethanol and concentrations of 0.2, 0.4, 1, 2, 5 and 10 mM were prepared. For the spectra obtained after ultrasonication pyrene derivative 1 was solubilized in ethanol and was added to water under ultrasonication (ratio vol. water/ethanol 90:10). Different solutions of pyrene derivative 1 in ethanol were prepared to obtain the following concentrations: 0.2, 0.4, 1, 2, 5 and 10 mM. The suspension was subjected to ultrasonic treatment for 1h before measurement.

Dynamic light scattering measurements.

Measurements were carried out by means of Zetasizer nano-ZS (Malvern instruments) on suspensions of the produced nanorods in water (ethanol 10 vol. %). Measurements were carried out in triplicate to ensure reproducibility.

X-ray crystallography.

Data were collected at 100(2) K by shutterless scans using a Bruker D8 diffractometer equipped with a PHOTON 100 detector and operating with a silicon 111 monochromator and synchrotron radiation of wavelength 0.77490 Å. Diffraction data on the air-stable dried nanorods and crystal powder were collected using a Bruker D8 Advance powder diffractometer, operating with Ge-monochromated Cu Kalpha1 radiation (wavelength = 1.5406 Å) and a LynxEye linear detector. Data were collected over the angular range 5-85 degrees in two theta.





Figure S1. ¹H NMR spectrum of 1.

¹H NMR (400 MHz, DMSO-d₆): δ = 8.38 (d, J=9.4 Hz, 1H, Ar), 8.25-8.30 (m, 2H, Ar), 8.22 (dd, J=8.5, 3.4 Hz, 2H, Ar), 8.13 (d, J=2.0 Hz, 2H, Ar), 8.03-8.09 (m, 1H, Ar), 7.94 (d, J=7.9 Hz, 1H, Ar), 7.85 (s, 1H, NH), 3.72 (q, J=6.9 Hz, 6H, 3xCH₂), 3.25-3.37 (m, 2H, CH₂), 3.00-3.10 (m, 2H, CH₂), 2.17-2.28 (m, 2H, CH₂), 1.96-2.08 (m, 2H, CH₂), 1.41-1.52 (m, 2H, CH₂), 1.06-1.15 (t, 9H, 3xCH₃), 0.50-0.59 (m, 2H, CH₂) ppm.



Figure S2. ¹³C NMR spectrum of 1.

¹³C NMR (400 MHz, DMSO-d₆): δ = 171.64 (CO), 136.54 (Ar C), 130.85 (Ar C), 130.39 (Ar C), 129.26 (Ar C), 128.11 (Ar C), 127.43 (Ar C), 127.40 (Ar C), 127.14 (Ar C), 126.45 (Ar C), 126.07 (Ar C), 124.87 (2 x Ar C), 124.71 (Ar C), 124.21 (Ar C), 124.12 (Ar C), 123.43 (CH₂), 57.63 (3 x CH₂), 41.24 (CH₂), 35.03 (CH₂), 32.23 (CH₂), 27.62 (CH₂), 22.79 (CH₂), 18.13 (3 x CH₃), 7.37 (Si-CH₂) ppm.



Figure S3. ESI mass chromatogram of the pyrene silane derivative 1.

Conditions					
Ethanol	Peak (nm)	264	274	326	340
	Peak-to-valley ratio	1.4	2.42	1.68	2.22
Aqueous medium (ethanol 10%)	Peak (nm)	268	280	332	350
	Peak-to-valley	1.27	1.45	1.16	1.38

Table S1. Peak-to-valley ratio values for **1** in ethanol and in aqueous medium (ethanol 10%). The peak-to-valley ratio values were obtained by considering the ratio of the absorption corresponding to each peak to that of the adjacent trough.



Figure S4. Dynamic light scattering measurement of the colloidal suspension of 1.



Figure S5. FE-SEM micrographs of **1** without (a, b) and with ultrasonic treatment (c, d, e and f). Scale bar represents 4 μ m (a, b), 2 μ m (c), 400 nm (d) and 200 nm (e, f).



Figure S6. FTIR spectrum of powder of **1** (black line) and supramolecular rods of **1** (grey line). Vibration bands corresponding to the main peaks. Si-O 1070 cm⁻¹, C=C aromatic 1550 cm⁻¹, C=O amide 1640 cm⁻¹, C-H alkane 2920 cm⁻¹, N-H amide 3050 cm⁻¹, C-H aromatic 3270 cm⁻¹. Slight spectral changes evidenced the constraint in bond vibration when the molecules are arranged in a packed structure. The changes remain minor probably because of the existence of non-covalent interaction also in the bulk powder.



Figure S7. ¹H NMR of 1-based assemblies solubilized in DMSO-d₆.



Figure S8. X-ray powder diffraction spectra of nanorods (black) and crystals (simulated, grey) of 1.



Figure S9. UV-vis simulated spectrum of 1.



Figure S10. FE-SEM micrograph of the nanorods after silica layer growth (scale bar: 400 nm). The clear differences observed between the pristine nanorods that present a flat surface and the nanorods after surface modification allowed to confirm the effective silica layer growth around the nanorods.

 Table S2. Crystal data and structure refinement for 1 (CCDC 1483530) and unit cell parameters for 1*.

Identification code	PySi 1	PySi 1*
Empirical formula	C ₂₉ H ₃₇ NO ₄ Si	C ₂₉ H ₃₇ NO ₄ Si
Formula weight	491.68	491.68
Temperature/K	100(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group	Pc	Pc
a/Å	19.1439(7)	19.1717(18)
b/Å	9.6535(3)	9.6578(6)
c/Å	30.1293(10)	30.180(3)
α/°	90	90
β/°	107.678(2)	107.482(10)
γ/°	90	90
Volume/Å ³	5305.1(3)	-
z	8	-
ρ _{calc} g/cm ³	1.231	-
µ/mm⁻¹	0.153	-
F(000)	2112.0	-
Crystal size/mm ³	0.3 × 0.05 × 0.02	-
Radiation	Synchrotron ($\lambda = 0.7749$)	-
20 range for data collection/°	4.48 to 51.166	-
Index ranges	-21 ≤ h ≤ 21, -10 ≤ k ≤ 10, -33 ≤ l ≤ 33	-
Reflections collected	36515	-
Independent reflections	15242 [R _{int} = 0.0503, R _{sigma} = 0.0604]	-
Data/restraints/parameters	15242/62/1102	-
Goodness-of-fit on F ²	1.034	-
Final R indexes [I>=2σ (I)]	$R_1 = 0.0975$, $wR_2 = 0.2590$	-
Final R indexes [all data]	R ₁ = 0.1186, wR ₂ = 0.2765	-
Largest diff. peak/hole / e Å ⁻³	0.83/-0.85	-
Flack parameter	0.60(6)	-

Quality data for 1* was of low quality, even using synchrotron radiation, and the best R1 achieved was ~21%.