Supporting Information

Luminescent and conductive supramolecular polymers from an *N*-annulated perylenedicarboxamide

Fátima García,^a Julia Buendía,^a Samrat Ghosh,^b Ayyappanpillai Ajayaghosh,^{b,*} and Luis Sánchez^{a,*}

 ^aDepartamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, E-28040 Madrid (Spain). E-mail: <u>lusamar@quim.ucm.es</u>
 ^bPhotosciences and Photonics Group, Chemical Sciences and Technology Division National Institute for Interdisciplinary Science and Technology (NIIST), CSIR, Trivandrum-695019 (India). E-mail: ajayaghosh@niist.res.in

Contents:

1 Supplementary Figures and Tables	S-2
Synthetic scheme	S-2
¹ H NMR spectra	S-2
AFM images	S-3
UV-Vis spectra	S-3
CIE diagram and I-V curves	S-4
2. Experimental section	S-5
3. Synthetic details and characterization	S-7
4. Collection of spectra	S-9

1. Supplementary Figures and Tables



Scheme S1. Synthesis of the *N*-annulated perylenedicarboxamide 1.



Figure S1. Partial ¹NMR spectra of **1** at different concentration (CDCl₃, 300 MHz, 298 K).

Figure S2. AFM images of the aggregates formed by NPDC **1** onto HOPG at different magnifications (298 K, toluene, 1×10^{-5} M). The right part of the panel depicts the height profiles along the green lines in the left part.

Figure S3. (a) UV-Vis spectra of **1** in MCH/chloroform mixtures $(1.25 \times 10^{-4} \text{ M}, 298 \text{ K})$. The black and red lines depict the UV-Vis spectra of **1** in pure MCH and pure chloroform, respectively. (b) Denaturation curve obtained for **1** in MCH/chloroform mixtures.

Electronic Supplementary Material (ESI) for Chemical Communications This journal is C The Royal Society of Chemistry 2013

Figure S4. UV-Vis spectra of 1 in chloroform and toluene (1 x 10⁻⁴ M, 298 K).

Figure S5. (a) CIE chromaticity diagram of the toluene gel of NPDC **1**. The blue dot indicates the luminescent CIE coordinates. (b, c) Conductive Atomic Force Microscopy images (CAFM) of the toluene gel of NPDC **1** onto HOPG as surface.

3. Experimental section

General. All solvents were dried according to standard procedures. Reagents were used as purchased. NMR spectra were recorded on a Bruker Avance 300 (¹H: 300 MHz; ¹³C: 75 MHz) spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. FT-IR spectra were recorded on a Bruker Tensor 27 (ATR device) spectrometer. UV-Vis spectra were recorded on a Varian Cary 50 spectrophotometer. High resolution mass spectra (HRMS) were recorded on a FTMS Bruker APEX Q IV spectrometer. UV-Vis spectra were registered on a Jasco-V630 spectrophotometer equipped with a Peltier thermoelectric temperature controller. The spectra were recorded in the continuous mode between 200 and 800 nm, with a wavelength increment of 1 nm, a response time of 4 s, and a bandwidth of 1 nm. A 1 mm path length quartz cuvette (Hellma) was used. Thermal experiments were performed at constant heating rates of 1 K/min in methylcyclohexane. Atomic Force Microscopy was performed on a SPM Nanoscope IIIa multimode microscope working on tapping mode with a RTESPA tip (Veeco) at a working frequency of ~235 kHz. The fluorescence quantum yield of 1 (ϕ_s) was calculated in CHCl₃ or and MCH by using a standard reference (fluorescein in water, ϕ_r =0.93). The experiments were performed by using optically matching solutions and the quantum yield was calculated by using the equation: $\phi_s = \phi_r (A_r F_s / A_s F_r) (\eta_s^2 / \eta_r^2)$; being A_s and A_r the absorbance (OD = 0.1) of the sample and reference solutions, respectively, at the same excitation wavelength (@470). F_s (8.7883 x 10⁸) and F_r (1.30095 x 10⁹) are the corresponding relative integrated fluorescence intensities, and η is the refractive index of the solvents $[\eta_r=1.3330 \text{ (water)}, \eta_s=1.490 \text{ (chloroform)}, \eta_s=1.422 \text{ (MCH)}]$. Fluorescence lifetimes were measured by using IBH (FluoroCube) time-correlated picosecond single photon counting (TCSPC) system. The corresponding solutions were excited with a pulsed diode laser 440 nm, <100 ps pulse duration with a repetition rate of 1 MHz. The detection system consists of a microchannel plate photomultiplier (5000U-09B, Hamamatsu) with a 38.6 ps response time coupled to a monochromator (5000M) and TCSPC electronics (DataStation Hub including Hub-NL, NanoLED controller and preinstalled Fluorescence Measurement and Analysis Studio (FMAS) software). The fluorescence lifetime values were determined by deconvoluting the instrument response function with mono- and bi-exponential decay using DAS6 decay analysis software. The quality of the fit has been judged by the fitting parameters such as χ^2 (<1.2) as well as

S-5

the visual inspection of the residuals. Conductive Atomic Force Microscopy images were recorded under ambient conditions using a NTEGRA (NT-MDT). Micro-fabricated diamond coating was doped with nitrogen cantilever tips (DCP11) and employed an operator-activated external circuit to switch to contact mode for point contact electrical characterization of the selected positions. The morphology shown is slightly different from that on mica probably due to the interaction of the gelator molecules with HOPG. The value of the conductivity (s) can be calculated by using the equation: $\sigma = d/A_t R$ (S/cm); being d is the thickness of the film (20-30nm), A_t is the area of the C-AFM probe $(A_t = pr^2 \text{ where } r = 70 \text{ nm})$; *R* is the resistance of the sample calculated from graph R=V/I by calculating the slope at any point. Substituting the values in the above equation a value of σ = 2.16 x 10⁻⁶ S/cm was obtained. For the four-probe conductivity measurement, a xerogel of 1 was prepared on a glass slide. The xerogel was placed on the base plate of the four probe instrument and the probes were located on the flat surface of the film. Current was passed through the two outer electrodes, and the floating potential was measured across the inner pair. In this measurement, a known current was applied and the potential across the probes was determined. This experiment was repeated three times and the average resistance values were taken. The value of the resistivity (ρ) was calculated from the equation $\rho = (V / I) \times \pi t/ln2$ (cm/S), being t = thickness of the film (estimated in 20 μ m.) The conductivity (σ) was calculated from the equation $\sigma = 1 / \rho_{actual}$ (S/cm). By using these two equations, values of $\rho = 0.52 \times 10^6$ (cm/S) and, consequently, of $\sigma = 1.92 \times 10^{-6}$ (S/cm), were calculated. The cooperative self-assembly of 1 in solution has been investigated by applying the method reported for BTA-based systems.^{S-1} In this model, the dynamic equilibrium between free monomers and the supramolecular polymer and the growth of the

corresponding polymer are considered. The nucleation and elongation reactions, are described by the constants K_1 and K_2 , and the parameter σ that expresses the degree of cooperativity. The relevant equations that allow extracting the thermodynamic parameters are:

$$K_{1} = e^{-(\Delta H^{0} - T\Delta S^{0})/(RT)}$$
 Eq. 1

$$K_{2} = K_{1}e^{\Delta H^{0}_{mm}/(RT)}$$
 Eq. 2

$$\sigma = \frac{\dot{K}_{1}}{K_{1}} = \frac{\dot{K}_{2}}{K_{2}} = e^{\Delta H^{0}_{mnc}/(RT)}$$
 Eq. 3

S-1 a) A. J. Markvoort, H. M. M. ten Eikelder, P. A. J. Hilbers, T. F. A. de Greef and E. W. Meijer, *Nat. Commun.* 2011, **2**, 509; b) H. M. M. ten Eikelder, A. J. Markvoort, T. F. A. de Greef and P. A. J. Hilbers, *J. Phys. Chem. B* 2012, **116**, 5291.

4. Synthetic details and characterization

Compounds 2^{2} , 3^{1} , 4^{3} , and 5^{2} were prepared according to previously reported synthetic procedures and showed identical spectroscopic properties to those reported therein.

(4-(decylcarbamoyl)phenyl)boronic acid (6)

4-(Dihydroxyboryl)benzoic 10.00 mmol), 1-Ethyl-3-(3acid (1.66 g, dimethylaminopropyl)carbodiimide hydrochloride (2.11 g, 11.00 mmol) and 4-Dimethylaminopyridine (1.34 g, 11.00 mmol) were dissolved in dry methylene chloride (40 mL) and dry DMSO (10 mL) under Argon atmosphere. The mixture was cooled to 0 °C and stirred for 15 minutes. Then, decylamine (2.0 mL, 10.00 mmol) was added portionwise. The reaction mixture was stirred at room temperature for 48 hours. The organic layer was washed with water, HCl 1 M and the precipitate was filtered compound **6** as a white solid (1.40 g, 46%) ¹H NMR (CD₃OD, 300 MHz) δ 8.45 (1H, br), 7.80 (2H, m), 7.71 (2H, m), 3.41 (2H, m), 1.65 (2H, m), 1.49-1.22 (14H, br), 0.92 (3H, t, J = 6.6 Hz); ¹³C NMR (CD₃OD, 75 MHz) δ 170.4, 137.3, 135.0, 127.3, 41.2, 41.1, 33.1, 30.7, 30.7, 30.6, 30.5, 30.5, 28.2, 23.8, 14.5; FTIR (neat) 487, 650, 711, 784, 856, 920, 1015, 1120, 1272, 1372, 1541, 1623, 2470, 2568, 2821, 2853, 2923, 2956, 3038, 3319, 3462, 3527, 3668 cm⁻¹.

² Jiang, W.; Qian, H.; Li, Y.; Wang, Z. J. Org. Chem. 2008, 73, 7369-7372.

³ Li, Y.; Wang, Z. Org. Lett. **2009**, *11*, 1385-1387.

4,4'-(1-decyl-1*H*-phenanthro[1,10,9,8-*cdefg*]carbazole-3,10-diyl)bis(*N*-decylbenzamide) (1)

Exact Mass: 923.63 Molecular Weight: 924.35

Compound 5 (0.12 g, 0.32 mmol), compound 4 (0.39 g, 1.27 mmol), Tetrakis(triphenylphosphine)palladium(0) (37 mg, 0.032 mmol), K₂CO₃ (0.22 g, 1.60 mmol) were dissolved in THF (80 mL) and water (3 mL) under Argon atmosphere. The reaction mixture was heated at reflux 48 hours. After evaporation of the solvent under reduced pressure, the residue was washed with water, extracted with chloroform, and dried over MqSO₄. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, chloroform) affording compound **1** as a brown solid (110 mg, 37%); ¹H NMR (CDCl₃, 300 MHz) δ 8.67 (2H, H_d, d, J = 7.8 Hz), 8.10 (2H, H_b, d, J = 8.2Hz), 7.99 (4H, H_f, d, J = 8.1 Hz), 7.79 (4H, H_e, d, J = 8.1 Hz), 7.77 (2H, H_c, t, J = 8.0 Hz), 7.73 (2H, H_a, s), 6.35 (2H, H_a, t, J = 5.6 Hz), 4.61 (2H, H_c, t, J = 6.9 Hz), 3.56 (4H, H_h, m), 2.06 (2H, H_s, m), 1.72-1.18 (46H, H_{i-p+t-z}, br), 0.90 (6H, H_q, m), 0.83 (3H, Hg, t, J = 7.0 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ 167.8, 145.5, 136.9, 133.9, 132.3, 131.0, 130.9, 127.8, 127.5, 125.2, 124.3, 121.5, 117.5, 114.5, 42.4, 40.6, 32.3, 30.5, 30.2, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 27.5, 23.8, 23.5, 23.1, 23.0, 14.5, 11.5; FTIR (neat) 639, 671, 721, 763, 802, 850, 1020, 1100, 1165, 1264, 1305, 1462, 1502, 1545, 1635, 1733, 2854, 2924, 3297 cm⁻¹. HRMS: calcd. for $C_{64}H_{81}N_3NaO_2$ [M+Na]⁺, 946.62210; found, 946.61956.

