Supporting Information

Two-Dimensional Self-Organization of Rectangular OPE Amphiphiles into Microcrystalline Lamellae

Gustavo Fernández,^a Fátima García,^a Fátima Aparicio,^a Emilio Matesanz,^b and Luis Sánchez^{a*}

^a Departamento de Química Orgánica, Facultad de C.C. Químicas, Universidad Complutense, E-28040 Madrid (Spain). Fax: (+) 34913944103; e-mail:

lusamar@quim.ucm.es

^bC.A.I. Difraccion de Rayos X, Facultad de Ciencias Químicas, Universidad Complutense, E-28040 Madrid (Spain)

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1. Supplementary figures



Scheme S1. Synthesis of amphiphiles 1 and 2.



Figure S1. FTIR spectra (film) of amphiphiles 1 and 2.



Figure S2. Normalized UV-Vis absorption spectra of **1** and **2** (298 K, 1 x 10^{-4} to 2.25 x 10^{-8} M) in 2-PrOH (a and c), and methylcyclohexane (b and d). Arrows indicate the direction of change with increasing concentration. The inset shows the fit of $\Delta\epsilon$ at a wavelength of 328 nm to the isodesmic model.



Figure S3. a) Normalized distribution of R_H of **1** (~10⁻⁵ M in H₂O); b) linear correlation of the inverse of time *vs.* the square of the scattering vector (R = 0.9667).



Figure S4. SEM images showing the 2D sheets in water (~10⁻⁵ M) (a) and MCH (~10⁻⁴ M) (b). c) Molar fraction of aggregated molecules (α_n) plotted as a function of concentration of **1** in 2-PrOH and MCH. The inset in (c) shows the average number of amphiphiles per stack (*N*) as a function of concentration of **1**. The curves have been calculated by fitting the normalized extinction coefficients to the isodesmic model at wavelengths of 328 nm for both 2-PrOH and MCH.



Figure S5. SEM images (298 K) of a drop-cast of an aqueous solution of **1** (~ 10^{-5} M) on glass plate. (a) Large area, (b) and (c) selected sheets.



Figure S6. SEM images (298 K) of a drop-cast of a solution of **1** (\sim 10⁻⁴ M) in methylcyclohexane on glass plate. (a) Large area, (b) and (c) selected sheets.



Figure S7. Confocal fluorescence microscopy images of **1** in methylcyclohexane (~ 10^{-4} M). The micrographs on the right depict selected expanded views.



Figure S8. TEM images of cryo-ultramicrotomed films of untreated **1** embedded into an epoxy resin.



Figure S9. TEM images from an aqueous solution of **1** ($\sim 10^{-5}$ M) onto carbon-coated copper grids at 80 kV. The TEM image on the right corresponds to the rectangle in the image on the left.



Figure S10. Electron diffraction pattern of the crystalline lamellae formed from $\sim 10^{-5}$ M aqueous solution of **1**. The numbers in brackets corresponds to the *hkl* Miller's indexes also observed by XRD.







Figure S12. HR-TEM images of the crystalline lamellae formed from $\sim 10^{-5}$ M aqueous solution of **1**. Images (b) and (d) depict the expanded regions marked with a black rectangle in (a) and (c), respectively. The inset in (b) represents the density profile of the lamellae along the black line.



Figure S13. X-ray diffraction patterns (298 K) of **2** plotted against the angle 2 θ . The inset shows the expanded region of large angles and a schematic illustration of the *p*2 oblique unit cell.

h	k	1	$2\theta_{exp}$	d _{exp} (Å)	d _{calcd} (Å)	d _{exp} – d _{calcd} (Å)
1	0	0	1.83	48.275	48.183	0.091
0	1	0	3.65	24.206	24.292	-0.085
1	2	0	7.56	11.693	11.705	-0.012
5	0	0	9.12	9.696	9.637	0.060
-4	2	0	10.10	8.758	8.667	0.091
6	0	0	10.99	8.050	8.031	0.020
5	2	0	11.90	7.437	7.455	-0.018
-3	3	0	12.15	7.284	7.308	-0.023
6	2	0	13.37	6.622	6.620	0.003
8	1	0	15.21	5.825	5.811	0.015
8	2	0	16.56	5.353	5.341	0.012
-9	1	0	16.88	5.252	5.257	-0.005
1	5	0	18.35	4.835	4.821	0.013
10	1	0	18.87	4.703	4.703	0.000
10	2	0	19.96	4.448	4.439	0.009
8	4	0	20.96	4.238	4.222	0.017
-11	2	0	21.34	4.164	4.155	0.008
-9	4	0	21.84	4.069	4.069	0.000
-4	6	0	22.94	3.877	3.868	0.008

Table S1. X-ray	diffraction	data for	oblique	planar l	lattice of	f com	pound 1	1 (2	298 K).

^a d_{exp} and d_{calcd} are the distances of the observed reflections, and calculated for the *p*2 oblique unit cell with lattice parameters a = 4.8 nm, b = 2.4 nm and γ = 91.5°.

h	k	1	$2\theta_{exp}$	d _{exp} (Å)	d _{calcd} (Å)	d _{exp} – d _{calcd} (Å)
1	0	0	2.26	39.090	38.869	0.222
0	1	0	4.10	21.551	21.882	-0.332
2	0	0	4.47	19.768	19.434	0.333
3	0	0	6.91	12.792	12.956	-0.164
0	2	0	8.09	10.929	10.941	-0.013
-1	2	0	8.39	10.538	10.644	-0.105
-4	3	0	14.83	5.973	5.949	0.024
-7	2	0	17.70	5.011	5.034	-0.023
4	4	0	18.94	4.685	4.687	-0.002
-8	2	0	19.67	4.513	4.508	0.005
-9	1	0	20.81	4.268	4.270	-0.001
6	4	0	21.68	4.099	4.099	0.000

Table S2. X-ray diffraction data for oblique planar lattice of compound 2 (298 K).

^a d_{exp} and d_{calcd} are the distances of the observed reflections, and calculated for the p2

oblique unit cell with lattice parameters a = 3.8 nm, b = 2.2 nm and γ = 92.3°.

2. Experimental Section

General. All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh or Scharlau 60, 230-240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminum coated Merck Kieselgel 60 F254 plates. 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. Matrix Assisted Laser Desorption Ionization (coupled to a Time-Of-Flight analyzer) experiments (MALDI-TOF) were recorded on a Bruker REFLEX spectrometer. SEM images were obtained from on a JEOL JSM 6335F microscope working at 10kV. The microtomed samples of untreated 1 (ca. 40 nm thick) were quenched in liquid nitrogen (Leica Ultracut S) and transferred to to carbon-coated Cu-grid substrates for TEM imaging on a FEI Tecnai 20T microscope operating at 200 kV. TEM images from samples in solution were performed on a JEOL 2000-FX electron microscope, operating at an acceleration voltage of 200 kV. For the observation of aggregates, a drop of sample solution (10⁻⁴ M) was placed on a copper grid coated with carbon and air-dried. Powder XRD scans were performed with a Panalytical X'Pert PRO diffractometer in reflection mode with Cu radiation.





1,2-dibromo-4,5-diiodobenzene, compounds **3a**, **3b**, **4**, and **6a** were prepared according to previously reported synthetic procedures (see: O. S. Miljanic, K. P. Vollhardt, G. D. Whitener, *Synlett*, **2003**, 29-34; J. A. Marsden, J. J. Miller, L. D. Shirtcliff, M. M. Haley *J. Am. Chem. Soc.* **2005**, *127*, 2464–2476; T. Haino, M. Tanaka, Y. Fukazawa, *Chem. Commun.* **2008**, 468-470; G. Fernández, F. García, L. Sánchez, *Chem. Commun.* **2008**, 6567-6569) and showed identical spectroscopic properties to those reported therein. Although the synthesis of compound **6b** has been reported in an international patent (Int. Appl. **2000**, WO 2000024745 A1 20000504) we prepared this compound by utilizing a similar procedure to those reported for compound **6a** (see G. Fernández, F. García, L. Sánchez, *Chem. Commun.* **2008**, 6567-6569).

1-(decyloxy)-4-(2-(2-(2-(4-(decyloxy)phenyl)ethynyl)-4,5-bis(2-(triisopropylsilyl)ethynyl)phenyl)ethynyl)benzene (5a)



Compound **3b** (2.50 g, 5.13 mmol), compound **4** (4.06 g, 11.30 mmol), tetrakis-(triphenylphosphine)-palladium(0) (0.59 g, 0.51 mmol) and copper (I) iodide (0.05 g, 0.26 mmol) were dissolved in triethylamine (100 mL). The reaction mixture was subjected to several vacuum/argon cycles. It was heated at 50 °C and stirred overnight. After evaporation of the solvent under reduced pressure, the residue was washed with NH₄Cl, extracted with methylene chloride and dried over MgSO₄. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, hexane) affording **5a** as a brown solid (3.90 g, 80%); ¹H NMR (CDCl₃, 300 MHz) δ 7.63 (2H, H_a, s), 7.51 (4H, H_b, d, J=8.8 Hz), 6.88 (4H, H_c, d, J=8.8 Hz), 3.99 (4H, H_d, t, J=6.5),1.81 (4H, H_e, q, J=6.7 Hz), 1.49-1.30 (28H, H_{f+g+h+j+k+l}, m), 1.16 (42H, H_n, s), 0.93-0.85 (6H, H_{m+o},m); ¹³C NMR (CDCl₃, 75 MHz) δ 160.0, 136.6, 133.6, 125.8, 125.0, 115.0, 105.0, 97.3, 96.0, 86.8, 68.5, 32.3, 30.0, 29.8, 29.7, 29.6, 26.4, 23.1, 19.2, 14.5, 11.7; FTIR (neat) 671, 830, 884, 1004, 1170, 1248, 1289, 1388, 1467, 1512, 1605, 2151, 2209, 2862, 2930 cm⁻¹.

1-(decyloxy)-4-(2-(2-(2-(4-(decyloxy)phenyl)ethynyl)-4,5-diethynylphenyl)ethynyl)benzene (5b)



A solution of Bu₄NF (40 mL, 1M in THF) was added to a solution of compound **5a** (3.90 g, 4.10 mmol) in THF anhydrous (150 mL). The reaction mixture was stirred under argon atmosphere for 15 minutes. After evaporation of the solvent under reduced pressure, the residue was washed with NaCl and water, extracted with diethyl ether and dried over MgSO₄. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, hexane:methylene chloride 1:2) affording **5b** as a yellow solid (2.1 g, 80%); ¹H NMR (CDCl₃, 300 MHz) δ 7.66 (2H, H_a, s), 7.48 (4H, H_b, d, J=8.8 Hz), 6.86 (4H, H_c, d, J=8.8 Hz), 3.97 (4H, H_d, t, J=6.5), 3.40 (2H, H_n, s), 1.79 (4H, H_e, q, J=6.5 Hz), 1.53-1.19 (28H, H_{f+g+h+j+k+l}, m), 0.88 (6H, H_m, t, J=6.9); ¹³C NMR (CDCl₃, 75 MHz) δ 159.7, 135.4, 133.3, 126.2, 124.0, 114.7, 96.2, 86.1, 82.6, 81.1, 68.2, 31.9, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7, 14.2, 5.0; FTIR (neat) 657, 724, 768, 830, 894, 1020, 1046, 1141, 1175, 1248, 1286, 1470, 1514, 1604, 2210, 2854, 2924, 3289 cm⁻¹.

1-(2-(4,5-bis(2-(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)ethy-nyl)-2-(2-(4-(decyloxy)phenyl)ethynyl)phenyl)ethynyl)-4-(decyloxy)benzene (1)



Compound **5b** (0.73 g, 1.14 mmol) and compound **6a** (1.50 g, 2.34 mmol) were dissolved in triethylamine (20 mL). The mixture was subjected to several vacuum/argon cycles and tetrakis-(triphenylphosphine)-palladium(0) (0.27 g, 0.23 mmol) and copper (I) iodide (0.02 g, 0.12 mmol) were added. The reaction mixture was heated at 50 °C and stirred overnight. After evaporation of the solvent under reduced pressure, the residue was washed with NH₄Cl, extracted with methylene chloride and dried over MgSO₄. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, hexane:methylene chloride 1:1) affording 1 as a brown solid (0.80 g, 31%).¹H NMR (CDCl₃, 300 MHz) δ 7.69 (2H, H_a, s), 7.50 (8H, H_{b+n}, d, J=8.7 Hz), 6.90 (4H, H_{c.o}, d, J=8.5 Hz), 6.87 (4H, H_{c.o}, d, J=8.5 Hz), 4.17 (4H, H_p, t, J=4.6), 3.98 (4H, H_d, t, J=6.5), 3.88 (4H, H_a, t, J=4.6 Hz), 3.53-3.79 (16H, H_{r+s+t+u}, m), 3.39 (6H, H_w, s), 1.80 (4H, H_e, q, J=6.5 Hz), 1.53-1.19 (28H, H_{f+q+h+i+k+l}, m), 0.90 (6H, H_m, t, J=6.96); ¹³C NMR (CDCl₃, 75 MHz) δ 160.0, 159.6, 134.8, 133.6, 125.5, 125.4, 115.8, 115.3, 115.1, 115.0, 95.8, 95.6, 87.1, 87.0, 72.3, 71.3, 71.0, 70.9, 70.0, 68.5, 67.9, 59.4, 32.3, 30.0, 29.8, 29.7, 29.6, 26.4, 23.1, 14.5; FTIR (neat) 647, 722, 831, 891, 925, 1059, 1132, 1174, 1250, 1295, 1468, 1514, 1568, 1605, 2206, 2853, 2920 cm^{-1} . HRMS: calcd. for $C_{72}H_{90}O_{10}$ [M], 1114.6529; found, 1114.6531.

1-(2-(4,5-bis(2-(4-(2-methoxyethoxy)phenyl)ethynyl)-2-(2-(4-(decyloxy)phenyl)ethynyl)phenyl)ethynyl)-4-(decyloxy)benzene (2)



Compound **5b** (0.73 g, 1.14 mmol) and compound **6b** (0.70 g, 2.5 mmol) were dissolved in triethylamine (20 mL). The mixture was subjected to several vacuum/argon cycles and tetrakis-(triphenylphosphine)-palladium(0) (0.13 g, 0.11 mmol) and copper (I) iodide (0.01 g, 0.06 mmol) were added. The reaction mixture was heated at 50 °C and stirred overnight. After evaporation of the solvent under reduced pressure, the residue was washed with NH₄Cl, extracted with methylene chloride and dried over MgSO₄. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, hexane:methylene chloride 1:1) affording **2** as a yellow solid (1.07 g, 92%). ¹H NMR (CDCl₃, 300 MHz) δ 7.58 (2H, H_a, s), 7.52 (8H, H_{b+c}, d, J=8.9 Hz), 6.92 (4H, H_{d+e}, d, J=8.9 Hz), 6.88 (4H, H_{e+d}, d, J=8.9) 4.15 (4H, H_f, t, J=4.5 Hz), 3.98 (4H, Hg, t, J=6.5 Hz), 3.77 (4H, H_h, t, J=4.54Hz), 3.47 (6H, H_i, s), 1.80 (4H,

H_j, q, J=6.9 Hz), 1.47-1.29 (28H, H_{k+l+m+n+o+p+q}, m), 0.90 (6H, Hr, t, J=6.5 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ 159.6, 159.2, 134.37, 133.2, 125.2, 125.1, 115.5, 115.0, 114.8, 114.7, 95.5, 95.3, 86.8, 86.6, 71.0, 68.2, 67.4, 59.3, 31.9, 29.6, 29.6, 29.4, 29.3, 29.2, 26.1, 22.7, 14.1 ; FTIR (neat) 649, 722, 811, 830, 892, 925, 1037, 1060, 1108, 1131, 1174, 1199, 1250, 1295, 1372, 1468, 1514, 1567, 1605, 2206, 2853, 2922 cm⁻¹. HRMS: calcd. for C₆₄H₇₄O₆ [M], 938.5480; found, 938.5510.

 ^{13}C NMR (CDCl_3, 75 MHz, 298 K) of compound 1

 ^{13}C NMR (CDCl_3, 75 MHz, 298 K) of compound $\boldsymbol{2}$

