SUPPORTING INFORMATION

Engineering Spherical Nanostructures via Hydrogen-bonding
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I. Synthesis

Compounds were fully characterized (m.p., IR, $^1$H and $^{13}$C NMR, ES-MS). NMR spectra were obtained on a Jeol JNM-EX400 (400 MHz $^1$H-NMR) and on a Varian Gemini 200 spectrometer (50 MHz $^{13}$C-NMR). Chemical shifts are reported in ppm using the solvent residual signal as an internal reference (CDCl$_3$: $\delta_\text{H} = 7.26$ ppm, $\delta_\text{C} = 77.16$ ppm). The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), br (broad signal). IR spectra (KBr) were recorded on a Perkin Elmer 2000 spectometer. Mass spectrometry measurements: Electron Impact (EI) performed on a Ion trap GCQ Finnigan Thermoquest at 70 eV were recorded at Università degli Studi di Trieste by Dr. Fabio Hollan. Melting Point (m.p.) was measured on a Büchi SMP-20. THF and NEt$_3$ were distilled from Na/benzophenone and CaH$_2$ respectively. Compound 2$^1$ and precursor 2,6-Diacetylamino-4-ethynlypyridine have been synthesized following the protocols reported by us.$^2$

1,4-Bis(dodecyloxy)-2,5-Bis[(2,6-Di(acetylamino)pyridine-4-yl)-ethynyl]benzene (1)

To a degassed solution of dry Et$_3$N (4 mL) and THF (4 mL), 1,4-Bis(dodecyloxy)-2,5-diiodobenzene 5 (0.2 g, 0.29 mmol), [Pd(PPh$_3$)$_4$] (0.014 g, 0.012 mmol), and CuI (4 mg, 0.023 mmol) were added and the mixture degassed a second time. 2,6-Di(acetylamino)-4-ethynlypyridine (0.16 g, 0.73 mmol) was then added, the reaction mixture degassed one last time, and refluxed overnight at 85 °C under Ar. The reaction colour turned bright yellow. Following this the crude mixture was filtered over celite, concentrated under vacuum and purified by CC (cyclohexane: EtOAc, 5:5, then EtOAc) yielding 1 (0.171 g, 68 %) as a bright yellow solid. m.p. > 240 °C; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 8.1 (s, 4H; Py-H); 7.6 (s, 4H; CH$_3$CONH-Py); 7.0 (s, 2H, Ar-H), 4.1 (t, 4H, OCH$_2$(CH$_2$)$_{10}$CH$_3$), 2.2 (s, 12H; CH$_3$CONH-Py), 1.9 (m, 4H, OCH$_2$CH$_2$(CH$_2$)$_9$CH$_3$), 1.3 (br, 36H, O(CH$_2$)$_2$(CH$_2$)$_9$CH$_3$), 0.9 (t, 6H, O(CH$_2$)$_{11}$CH$_3$); $^{13}$C-NMR (50 MHz, CDCl$_3$): $\delta$ 168.28, 153.66, 149.45, 136.13, 117.33, 113.62, 111.49, 92.95, 90.57, 69.83, 32.11, 29.83, 29.56, 29.51, 29.29, 26.14, 24.97, 22.88, 14.32; IR (cm$^{-1}$): v 3285.3, 2959.1, 2926.5, 2220.3, 2162.1, 1708.1, 1685.4, 1612.1, 1554.9, 1419.2, 1249.8, 869.7, 843.0, 759.1, 642.1; MS (70 eV, EI): Found 877 (M$^+$), C$_{52}$H$_{72}$N$_6$O$_8$ requires = 877.16.
1,4-Bis(dodecyloxy)-2,5-Bis[(2,6-Di(acetylmethylamino)pyridine-4-yl-)ethynyl] benzene (3)

I (20 mg, 0.023 mmol) was dissolved in dry THF (0.5 mL) and NaH (5 mg, 0.23 mmol) was added. Following this, MeI (28 µl, 0.46 mmol) was added and the mixture was allowed to stir at room temperature under Ar overnight. Purification of the crude reaction by CC (cyclohexane: EtOAc, 8:2, then 5:5) afforded 3 (0.010 g, 48 %) as a yellow oil. $^1$H-NMR (200 MHz, CDCl$_3$): $\delta$ 7.35 (s, 4H; Py-H); 7.0 (s, 2H; Ar-H), 4.1 (t, 4H; Ar-OCH$_2$(CH$_2$)$_{10}$CH$_3$), 3.4 (s, 12H; CH$_3$CONCH$_3$-Py), 2.2 (s, 12H; CH$_3$CONCH$_3$-Py), 1.9 (m, 4H; Ar-OCH$_2$CH$_2$(CH$_2$)$_6$CH$_3$), 1.3 (br, 36H; Ar-O(CH$_2$)$_2$(CH$_2$)$_9$CH$_3$), 0.9 (t, 6H; Ar-O(CH$_2$)$_{11}$CH$_3$); $^{13}$C-NMR (50 MHz, CDCl$_3$): $\delta$ 170.82, 154.79, 153.98, 135.23, 118.79, 117.06, 113.66, 91.94, 91.36, 69.71, 35.52, 32.07, 29.83, 29.51, 29.33, 26.16, 23.86, 22.85, 14.29; IR (cm$^{-1}$): $\nu$ 3434.9, 2925.6, 2854.4, 2215.6, 1676.3, 1593.2, 1400.0, 1376.1, 1217.8, 1014.8; MS (70 eV, EI): Found 933 (M$^+$), C$_{56}$H$_{80}$N$_6$O$_6$ requires = 933.27.

II. Spectrometric Characterization

The solutions for spectroscopic studies were prepared by injecting microlitre amounts (10/20 µL) of 1 mM solutions in THF of each compound into 3 mL of cyclohexane. Electronic absorption and emission measurements were carried out, respectively, on a Lambda 950 UV/VIS/NIR spectrophotometer (Perkin Elmer) and on an Edinburgh FLS920 spectrofluometer (continuous 450 W Xe lamp), equipped with a Peltier-cooled Hamamatsu R928 photomultiplier tube (185-850 nm). The temperature of the solutions was varied with HAAKE F3-C digital heated/refrigerated water bath (Haake Mess-Technik GmbH u.Co., Germany) which can be manually connected to cuvette holder and controlled externally. Emission quantum yields were determined according to the approach described by Demas and Crosby$^3$ using Ruthenium ($\Phi_{em} = 0.028$ in air-equilibrated acid water solution, 1 N H$_2$SO$_4$) as standard. All the solvent (THF and cyclohexane) are spectrophotometric grade Sigma-Aldrich, (99+%) and were used as received.
**Fig S1.** Absorption and emission spectra of 1 (in black) and 2 (in gray) in cyclohexane. $\lambda_{\text{exc}} = 355$ nm.

**Fig S2.** Changes with temperature in absorption (left) and emission spectra (right, $\lambda_{\text{exc}} = 333$ nm) of molecule 3 alone in cyclohexane.
**Fig. S3.** Absorption spectra of 3, 2, 1:2 molecular adduct between 3 and 2 and the algebraic sum of 3 and 2.

### III. Additional microscopic characterization

The samples for microscopic studies were prepared by heating CHX solutions to 80 °C to break any kind of aggregate formed; the samples were then slowly cooled down to room temperature to induce the formation of the thermodynamically favoured nanostructures. For TEM analysis, a drop (10 µl) of each solution was placed on a carbon coated nickel grid (3.00 mm, 200 mesh). After drying at room temperature, the samples were observed with a TEM Philips EM 208 microscope (accelerating voltage of 100 kV). The samples for AFM imaging were prepared by drop-casting each solution (10 µl) onto a freshly cleaved mica piece (0.5 cm × 0.5 cm), allowed to dry for a few minutes and then investigated by using Digital Instruments (Veeco) Nanoscope IIIa (Tapping Mode) with Veeco RTESP7 Tips.
**Fig S4.** TEM images of self assembled structures of 1 in cyclohexane recorded from different areas of the same sample.

**Fig S5.** Tapping mode AFM images of self assembled structures of 1 in cyclohexane recorded from different areas of the same sample.
**Fig S6.** TEM images of self assembled structures of the molecular adduct between 1 and 2 in the ratio 1:2 in cyclohexane recorded from different areas of the same sample.

**Fig S7.** Tapping mode AFM images of self assembled structures of the molecular adduct between 1 and 2 in the ratio 1:2 in cyclohexane recorded from different areas of the same sample.
Fig S8. TEM images of self assembled structures of the molecular adduct between 1 and 2 in the ratio 1:1 in cyclohexane recorded from different areas of the same sample.

Fig S9. Tapping mode AFM images of self assembled structures of the molecular adduct between 1 and 2 in the ratio 1:1 in cyclohexane recorded from different areas of the same sample.
Fig S10. Tapping mode AFM images of a solution of 2 in cyclohexane drop-casted on to freshly cleaved mica surface.

References

