

SUPPORTING INFORMATION

Engineering Spherical Nanostructures via Hydrogen-bonding

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I. Synthesis

Compounds were fully characterized (m.p., IR, ^1H and ^{13}C NMR, ES-MS). NMR spectra were obtained on a Jeol JNM-EX400 (400 MHz ^1H -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 spectrometer. 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-ethynylpyridine 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_3N (4 mL) and THF (4 mL), 1,4-Bis(dodecyloxy)-2,5-diodobenzene **5** (0.2 g, 0.29 mmol), $[\text{Pd}(\text{PPh}_3)_4]$ (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-ethynylpyridine (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; ^1H -NMR (400 MHz, CDCl_3): δ 8.1 (*s*, 4H; Py-*H*); 7.6 (*s*, 4H; $\text{CH}_3\text{CONH-Py}$); 7.0 (*s*, 2H, Ar-*H*), 4.1 (*t*, 4H, $\text{OCH}_2(\text{CH}_2)_{10}\text{CH}_3$), 2.2 (*s*, 12H; $\text{CH}_3\text{CONH-Py}$), 1.9 (*m*, 4H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.3 (*br*, 36H, $\text{O}(\text{CH}_2)_2(\text{CH}_2)_9\text{CH}_3$), 0.9 (*t*, 6H, $\text{O}(\text{CH}_2)_{11}\text{CH}_3$); ^{13}C -NMR (50 MHz, CDCl_3): δ 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}): ν 3285.3, 2959.1, 2925.6, 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^+), $\text{C}_{52}\text{H}_{72}\text{N}_6\text{O}_6$ requires = 877.16.

1,4-Bis(dodecyloxy)-2,5-Bis[(2,6-Di(acetylmethylamino)pyridine-4-yl)ethynyl] benzene (3)

1 (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 μ l, 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. $^1\text{H-NMR}$ (200 MHz, CDCl_3): δ 7.35 (*s*, 4H; Py-*H*); 7.0 (*s*, 2H; Ar-*H*), 4.1 (*t*, 4H; Ar- $\text{OCH}_2(\text{CH}_2)_{10}\text{CH}_3$), 3.4 (*s*, 12H; $\text{CH}_3\text{CONCH}_3\text{-Py}$), 2.2 (*s*, 12H; $\text{CH}_3\text{CONCH}_3\text{-Py}$), 1.9 (*m*, 4H; Ar- $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.3 (*br*, 36H; Ar- $\text{O}(\text{CH}_2)_2(\text{CH}_2)_9\text{CH}_3$), 0.9 (*t*, 6H; Ar- $\text{O}(\text{CH}_2)_{11}\text{CH}_3$); $^{13}\text{C-NMR}$ (50 MHz, CDCl_3): δ 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}): ν 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^+), $\text{C}_{56}\text{H}_{80}\text{N}_6\text{O}_6$ 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 a Edinburgh FLS920 spectrofluorometer (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 Crosby³ using Ruthenium ($\Phi_{\text{em}} = 0.028$ in air-equilibrated acid water solution, 1 N H_2SO_4) as standard. All the solvent (THF and cyclohexane) are spectrophotometric grade Sigma-Aldrich, (99+%) and were used as received.

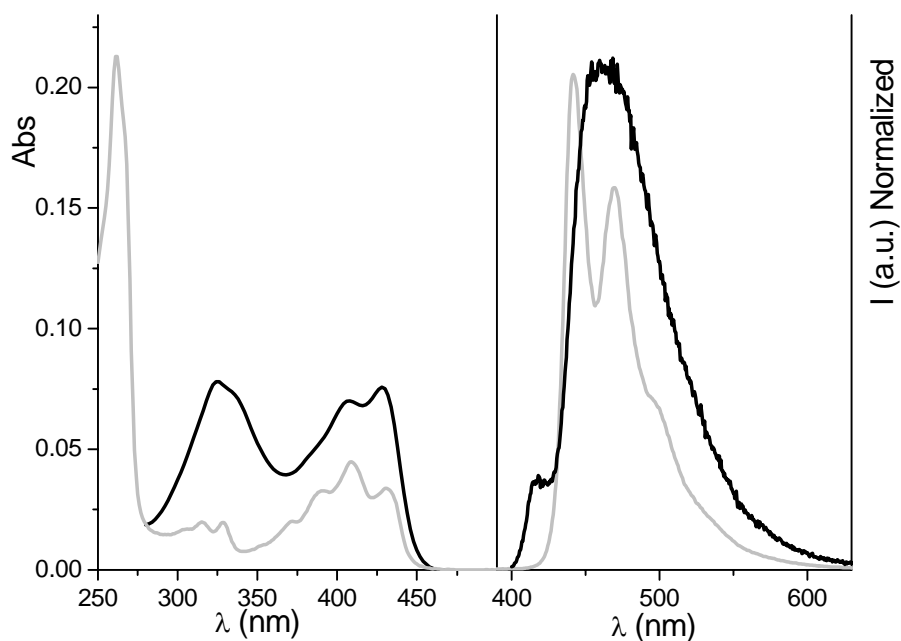


Fig S1. Absorption and emission spectra of **1**(in black) and **2** (in gray) in cyclohexane. $\lambda_{exc} = 355$ nm.

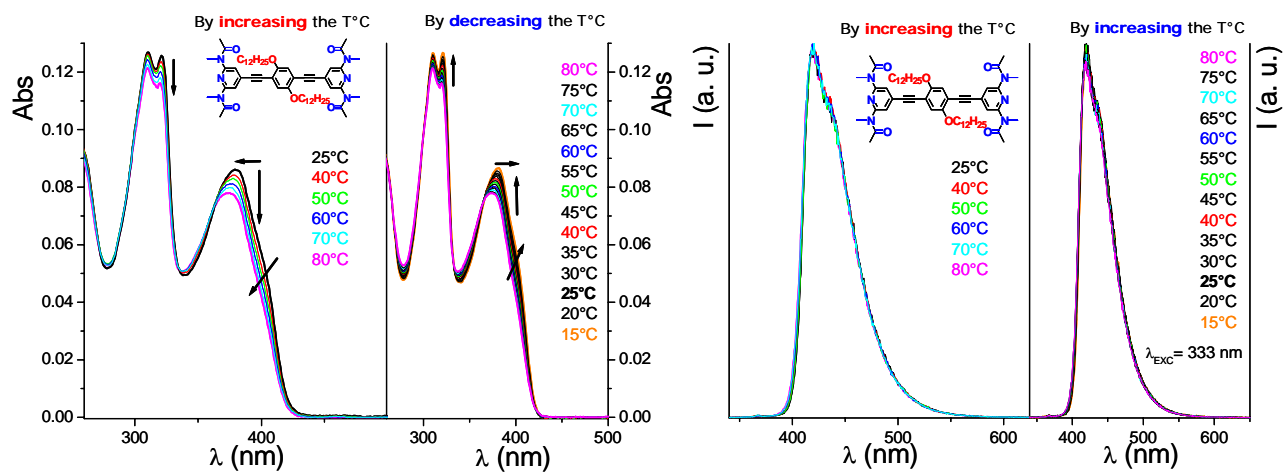


Fig S2. Changes with temperature in absorption (left) and emission spectra (right, $\lambda_{exc} = 333$ nm) of molecule **3** alone in cyclohexane.

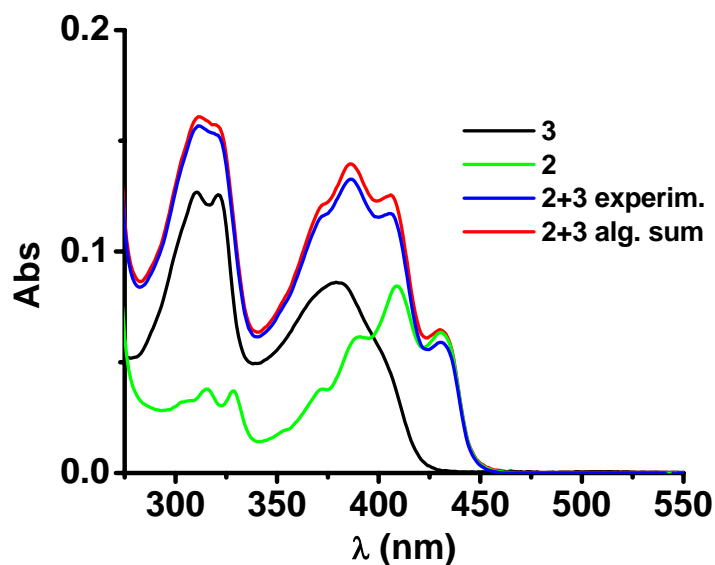


Fig. S3. Absorption spectra of **3**, **2**, 1:2 molecular adduct between **3** and **2** and the algebraic sum of **3** and **2**.

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.

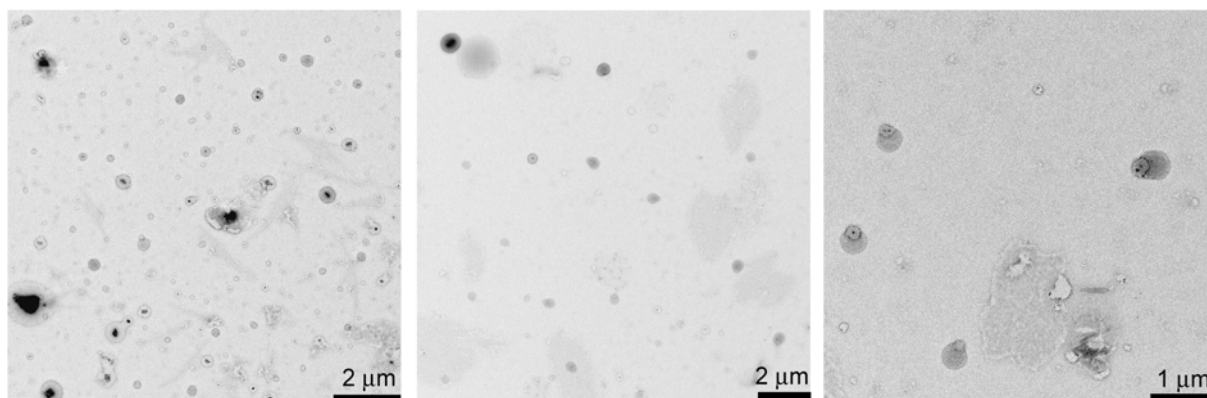


Fig S4. TEM images of self assembled structures of **1** in cyclohexane recorded from different areas of the same sample.

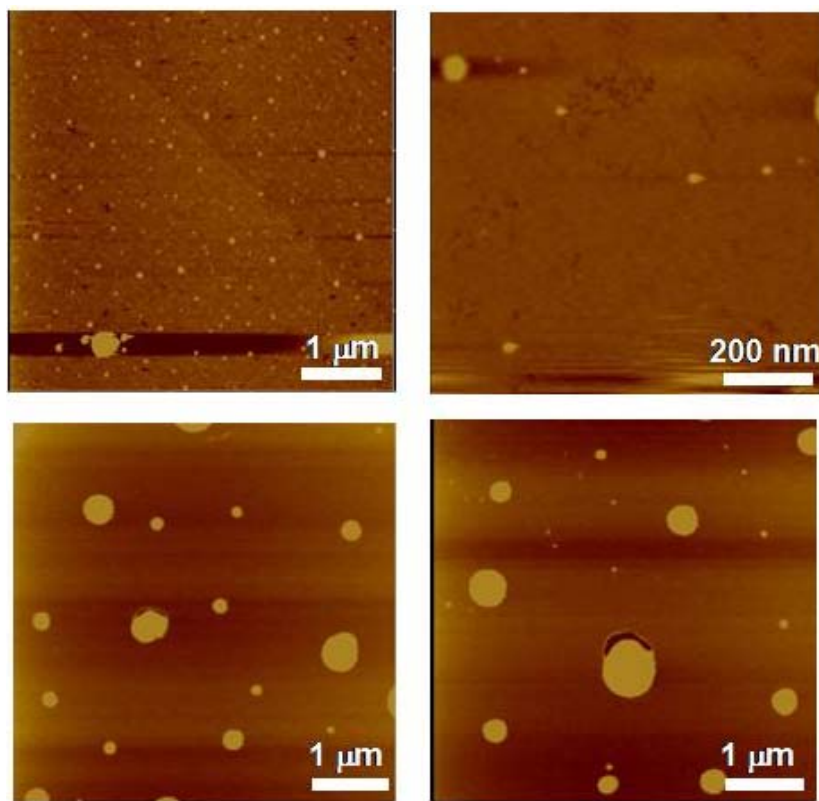


Fig S5. Tapping mode AFM images of self assembled structures of **1** in cyclohexane recorded from different areas of the same sample.

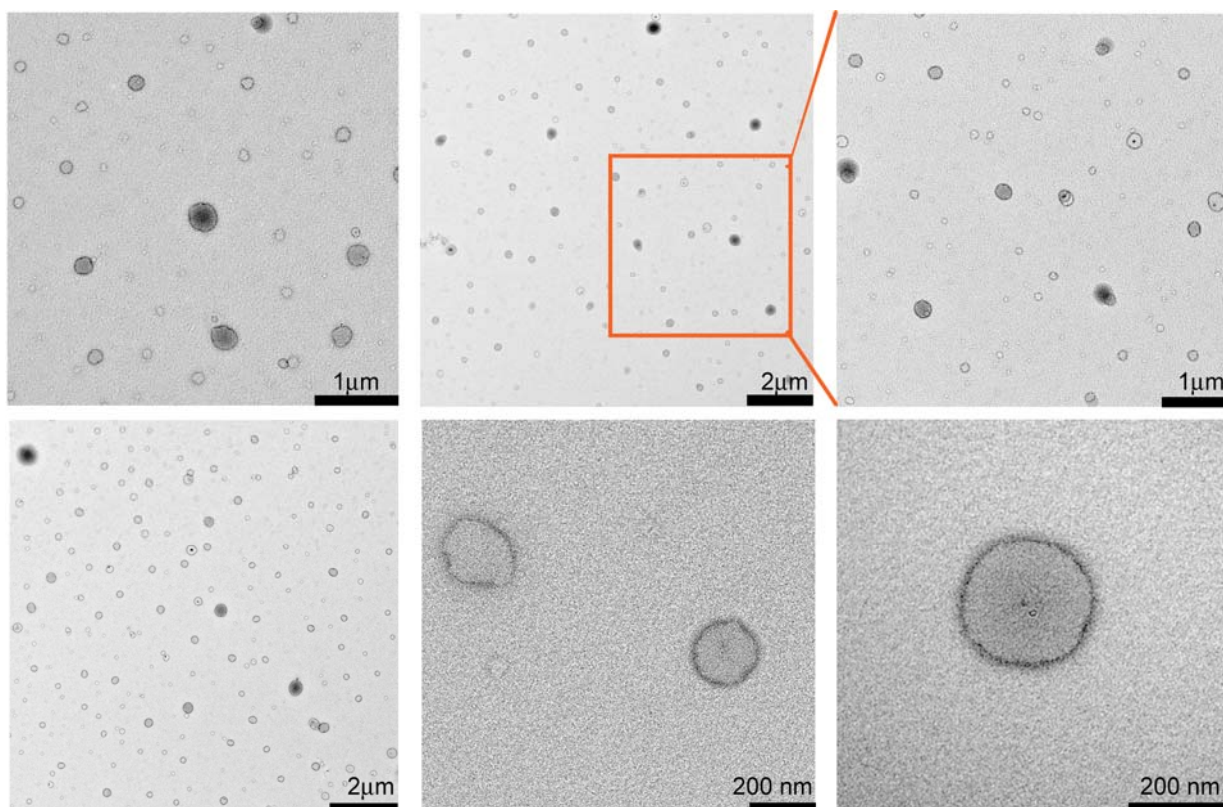


Fig S6. TEM images of self assembled structures of the molecular adduct between **1** and **2** in the ratio 1:2 in cyclohexane recorded from different areas of the same sample.

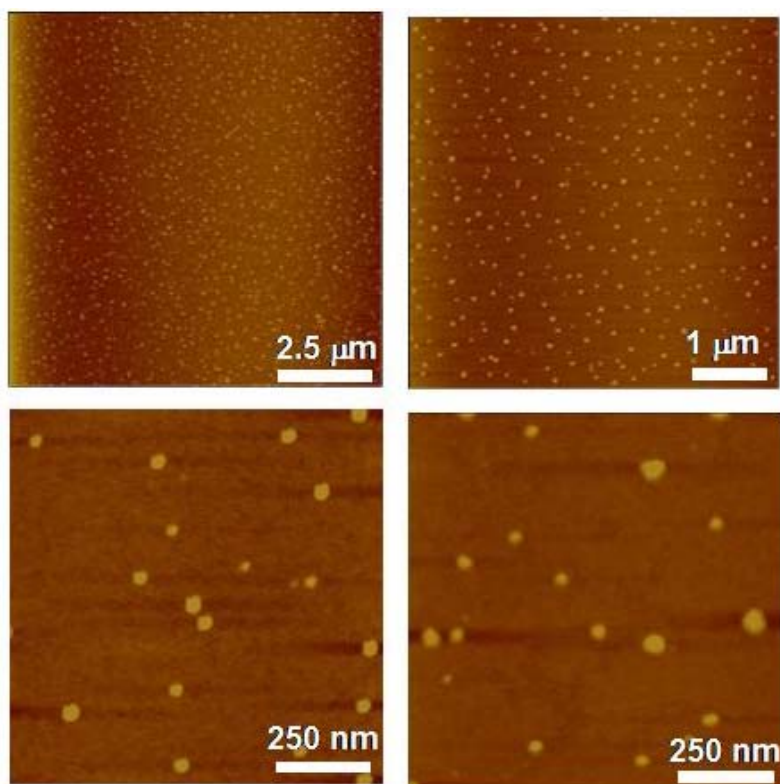


Fig S7. Tapping mode AFM images of self assembled structures of the molecular adduct between **1** and **2** in the ratio 1:2 in cyclohexane recorded from different areas of the same sample.

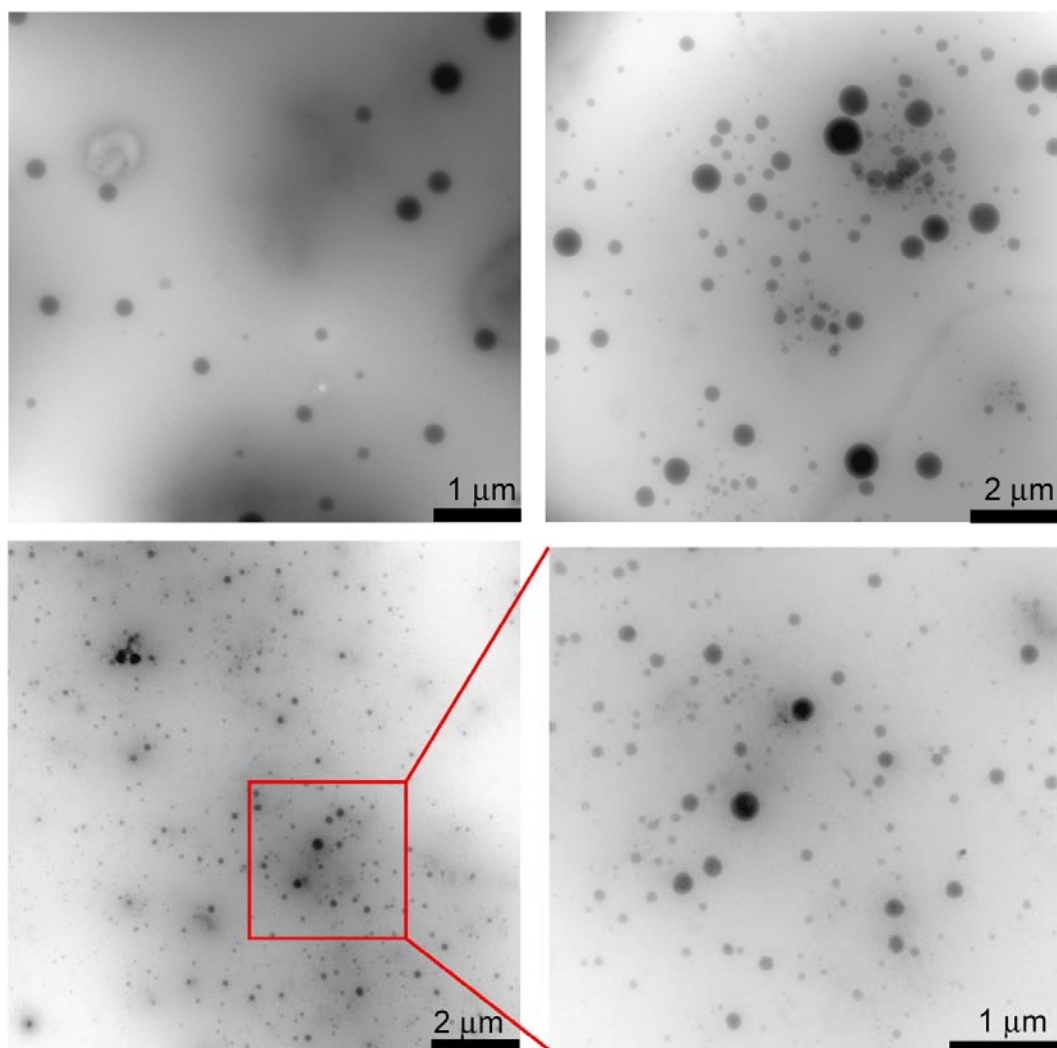


Fig S8. TEM images of self assembled structures of the molecular adduct between **1** and **2** in the ratio 1:1 in cyclohexane recorded from different areas of the same sample

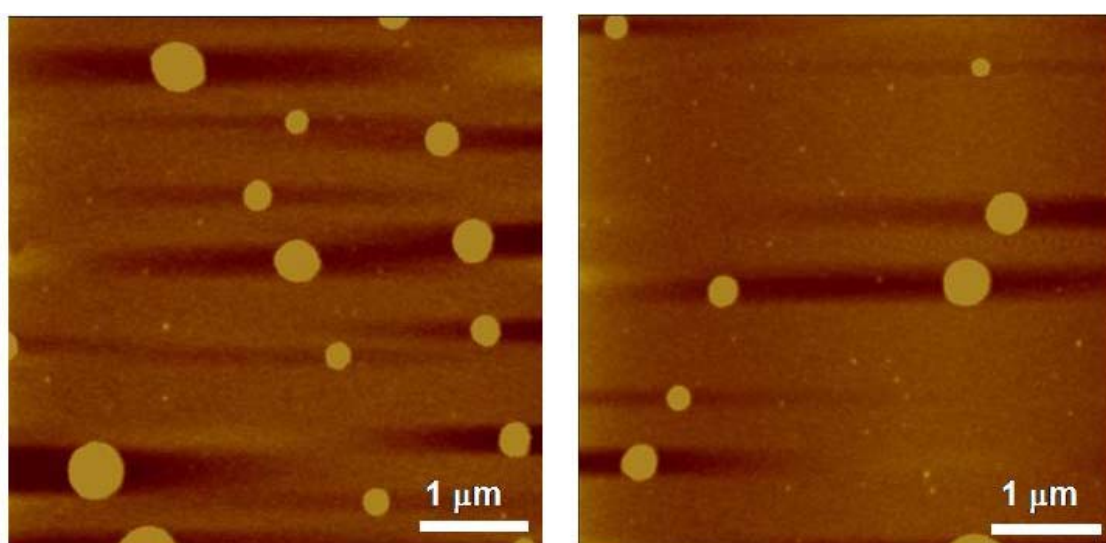


Fig S9. Tapping mode AFM images of self assembled structures of the molecular adduct between **1** and **2** in the ratio 1:1 in cyclohexane recorded from different areas of the same sample.

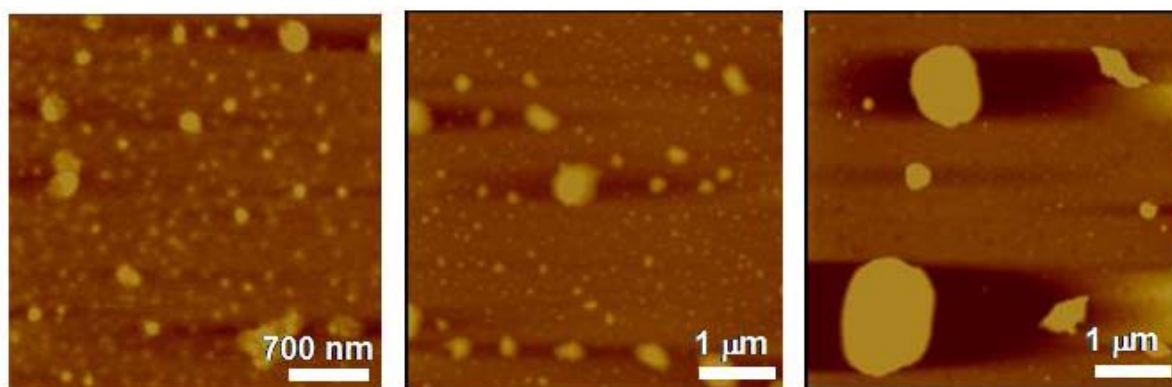


Fig S10. Tapping mode AFM images of a solution of **2** in cyclohexane drop-casted on to freshly cleaved mica surface.

References

1. A. Llanes-Pallas, M. Matena, T. Jung, M. Prato, M. Stöhr and D. Bonifazi, *Angew. Chem. Int. Ed.*, 2008, **47**, 7726-7730.
2. A. Llanes-Pallas, C. A. Palma, L. Piot, A. Belbakra, A. Listorti, M. Prato, P. Samori, N. Armaroli and D. Bonifazi, *J. Am. Chem. Soc.*, accepted.
3. J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991-1024.