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Dynamic Clicked Surfaces Based on Functionalised Pillar[5]arene

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Electronic Supplementary Information

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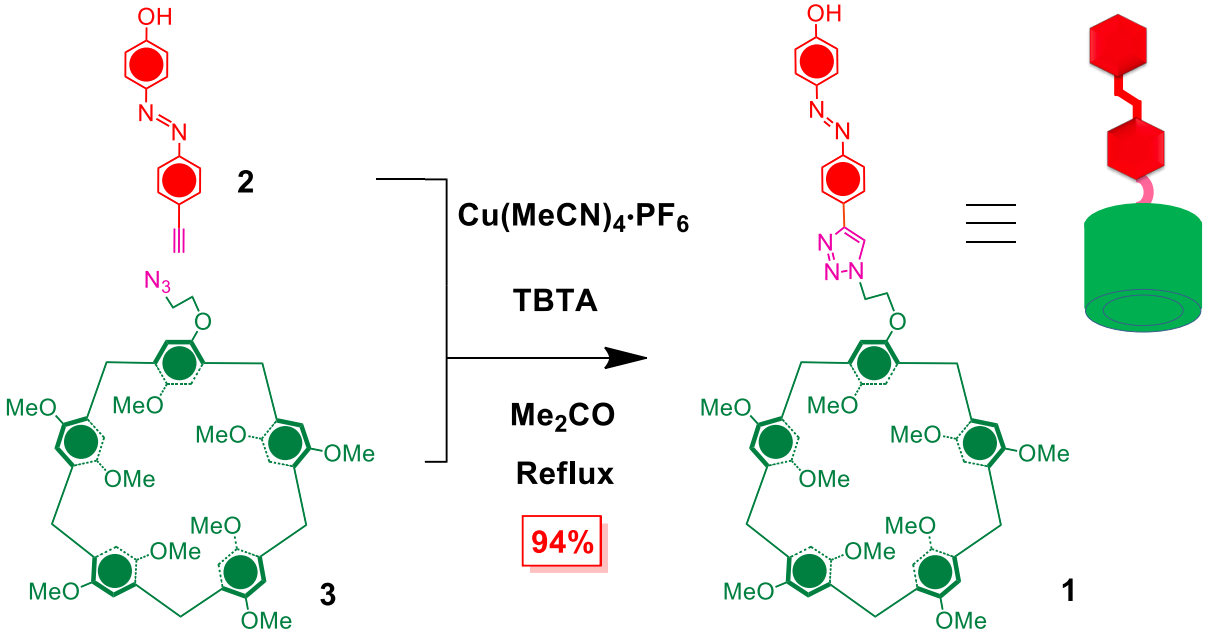
General Methods

Reagents were purchased from Aldrich and used without further purification. 4-hydroxy-4′-ethynyl azobenzene[S1] (**2**) and azido-pillar[5]arene[S2] (**3**) were synthesised according to the literature procedures. The THF was dried using a commercial solvent purification system (SG Water, Inc.). The H_2O used was triply distilled. The UV lamp is a Blak-Ray series, model B100A/R and 365 nm longwave UV, purchased from UVP, LLC. UV spectra were recorded with TU-1800pc UV-Vis Spectrophotometer at 298 K. The stock solutions (10^{-2} mol•L^{-1}) of **1** were prepared with triply distilled H_2O. All sample solutions for the investigation of the CAC were freshly prepared by diluting the stock solutions according to literature procedures.[S3]

1D and 2D nuclear magnetic resonance (NMR) spectra were recorded at 298 K on Bruker Avance III 500 spectrometer with working frequencies of 500 MHz for ^1H and 125 MHz for ^{13}C nuclei. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvent ($CDCl_3$: δ 7.26 ppm; Tetrahydrofuran-d_8: δ 1.73 and 3.58 ppm; D_2O: δ 4.79 ppm), and coupling constants were recorded in Hertz (Hz). All ^{13}C NMR spectra were recorded with the simultaneous decoupling of ^1H nuclei. The following abbreviations were used to explain the multiplicities: s, singlet; d, doublet; t, triplet; b, broad peaks; m, multiplet or overlapping peaks. Electrospray Ionization (ESI) mass spectra were obtained on an Agilent LC-TOF high-resolution mass spectrometer.

Negative-stained TEM and Cryo-TEM were measured on a Hitachi H-8100 electron microscope (100—200 kV) equipped with slow scan CCD and using cold cathode field emission as the gun. The samples for negative-stained TEM were prepared by dropping a droplet of the orange yellow sample solution onto a TEM grid (copper grid, 300 meshes, coated with carbon film), immediately staining with 2% uranyl acetate in H_2O (about 2 μL) and allowing to air-dry. SEM images were obtained on a FEI Quanta 600 SFEG scanning electron microscope (0.2—30 kV) equipped with both solid-state BSED and low vacuum LFSED as detectors. Atomic force microscopy was performed by using a multimode Nanoscope IIIA system operated in tapping mode using silicon cantilevers. DLS measurements were carried out with a Zetasizer Nano ZS instrument purchased from Malvern Instruments Ltd. at 298 K using a 633 nm ‘red’ laser. The mean hydrodynamic radius was calculated with Zetasizer software.

Compounds Synthesised



Synthesis of 1

1: 4-hydroxy-4′-ethynyl azobenzene (**2**, 25 mg, 0.11 mmol) and **3** (90 mg, 0.11 mmol), tetrakis(acetonitrile) copper(I) hexafluorophosphate (4.1 mg, 0.011 mmol) and tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl] amine (TBTA) were dissolved in Me_2CO (20 mL). The mixture was then stirred under reflux for 2 days. The solution was then poured into H_2O (200 mL). The aqueous phase was extracted (3 × 200 mL) with CH_2Cl_2. The combined organic layers were dried (Mg_2SO_4) and the solvent was removed in vacuum. The mixture was subjected to column chromatography (SiO_2, gradient elution from 2% up to 20% MeOH in CH_2Cl_2) to afford **1** (108.3 mg) in 94% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.16 (s, 1H), 7.97 (t, J = 10 Hz, 4H), 7.91 (d, J = 10 Hz, 2H), 7.01 (d, J = 5 Hz, 2H), 6.86-6.74 (m, 8H), 6.44 (t, J = 5 Hz, 2H), 4.35 (d, J = 5 Hz, 2H), 3.83-3.78 (m, 12H), 3.72-3.59 (m, 26H), 3.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.2, 152.3, 151.6, 151.2, 151.0, 150.7, 132.1, 128.9, 128.6, 128.4, 128.1, 127.8, 127.6, 126.2, 125.1, 123.2, 121.6, 115.9, 115.2, 114.6, 114.4, 114.2, 114.1, 113.8, 67.2, 55.9, 50.1, 29.9. HR-MS (ESI): $C_{60}H_{61}N_5O_{11}$ calcd for m/z = 1028.4440, found m/z = 1028.4443 $[M + H]^+$.

Figure S1—S9

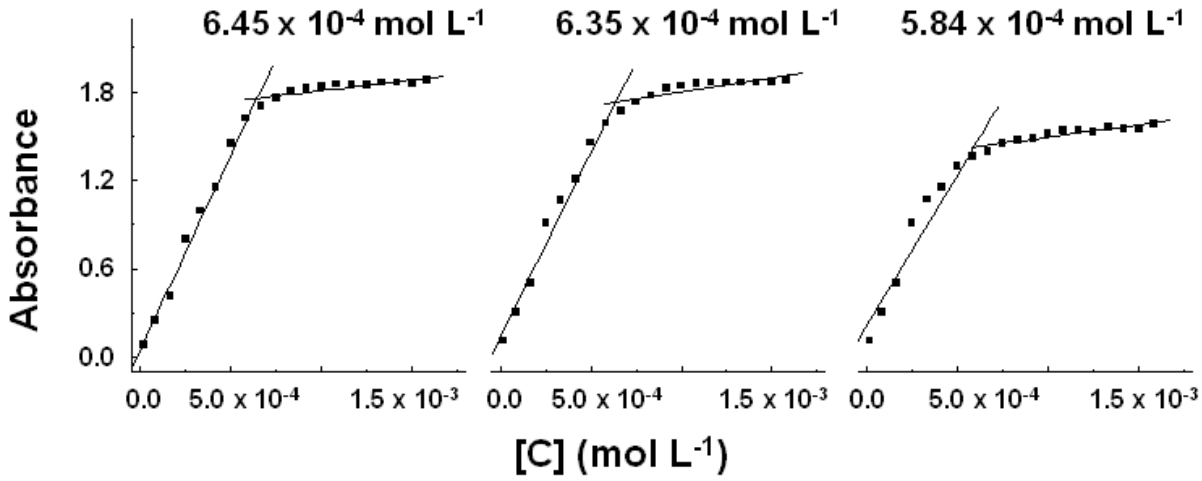


Fig. S1 The critical assembly concentration (CAC) of **1** in the 1/2 (v/v) mixture of H_2O and THF was determined in three separate trials, giving an average value of 0.62 $\pm$ 0.03 mM by detection of the maximum absorption band in the UV-vis spectra.

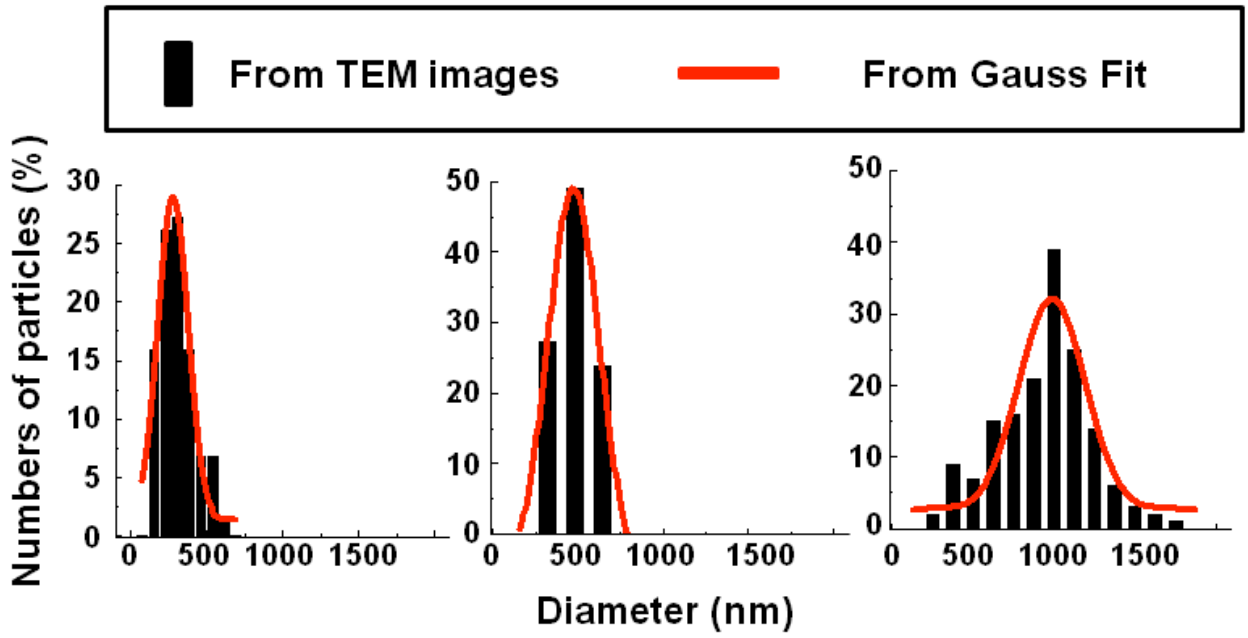


Fig. S2 Size distributions of **1** cast on a TEM grid from a 1:2 H_2O / THF mixture (2 mM) in visible light atmosphere (left), irradiated by UV (365 nm) for 1 h (middle) and then exposed in visible light for another 1 h (right).

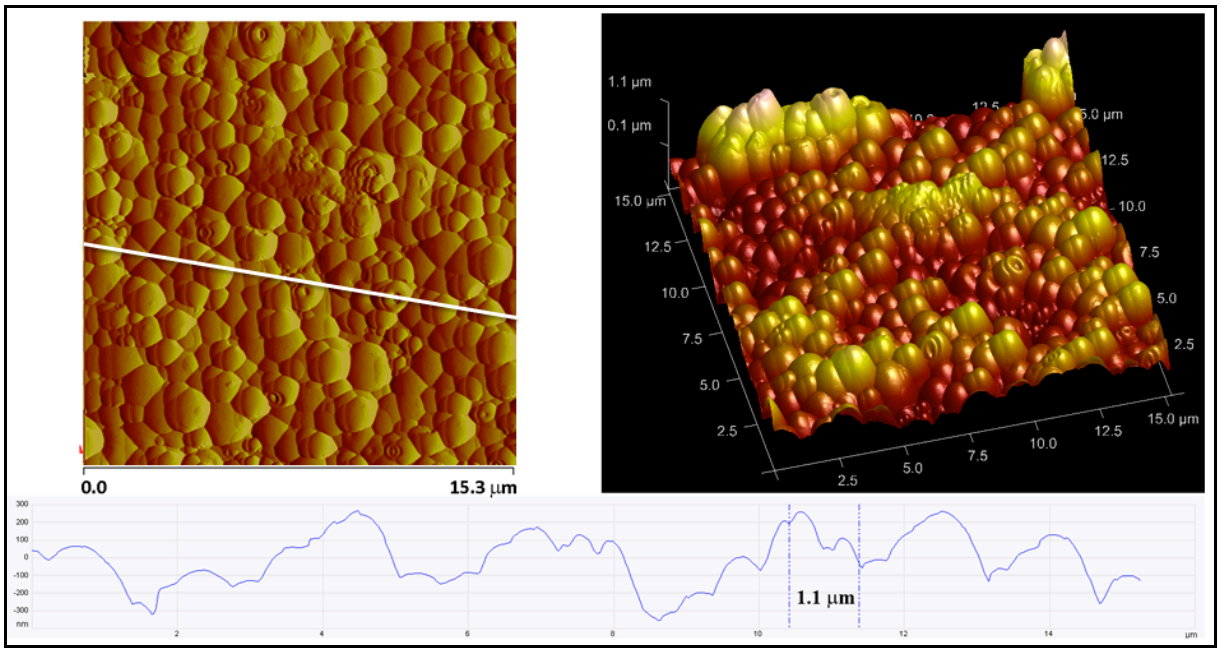


Fig. S3 The orange-yellow sample solution was dropped onto a silicon plate and allowed to air-dry. Air tapping mode AFM images of assemblies of **1** (upper left, planar image with scale bar = 15.3 μm; upper right, steric image; bottom, a line profile extracted along the marked white trace in the upper left image).

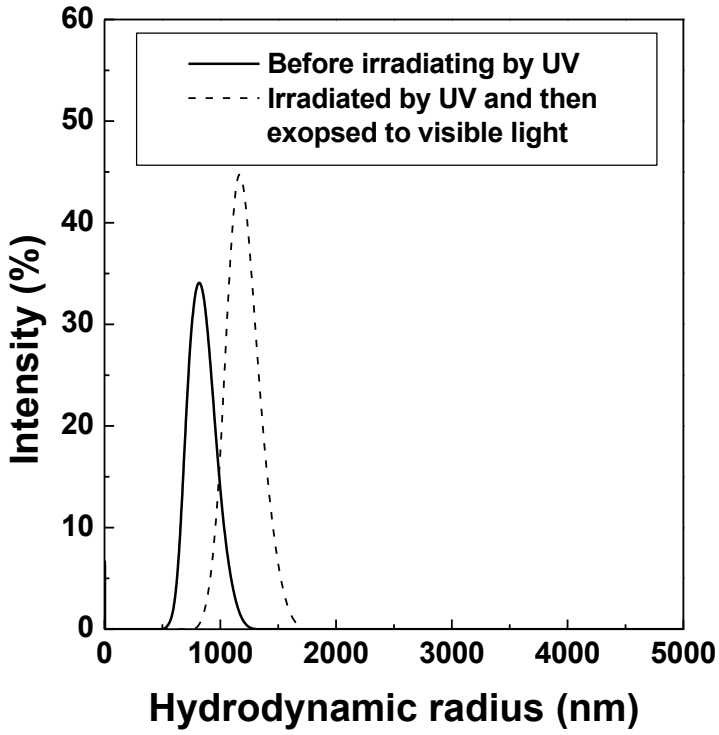


Fig. S4 DLS size distributions of **1** (molar ratio = 1:1) in the 1:2 H_2O / THF mixture (2 mM) before irradiating by UV (solid line), after irradiating by UV and exposing in visible light (dash line).

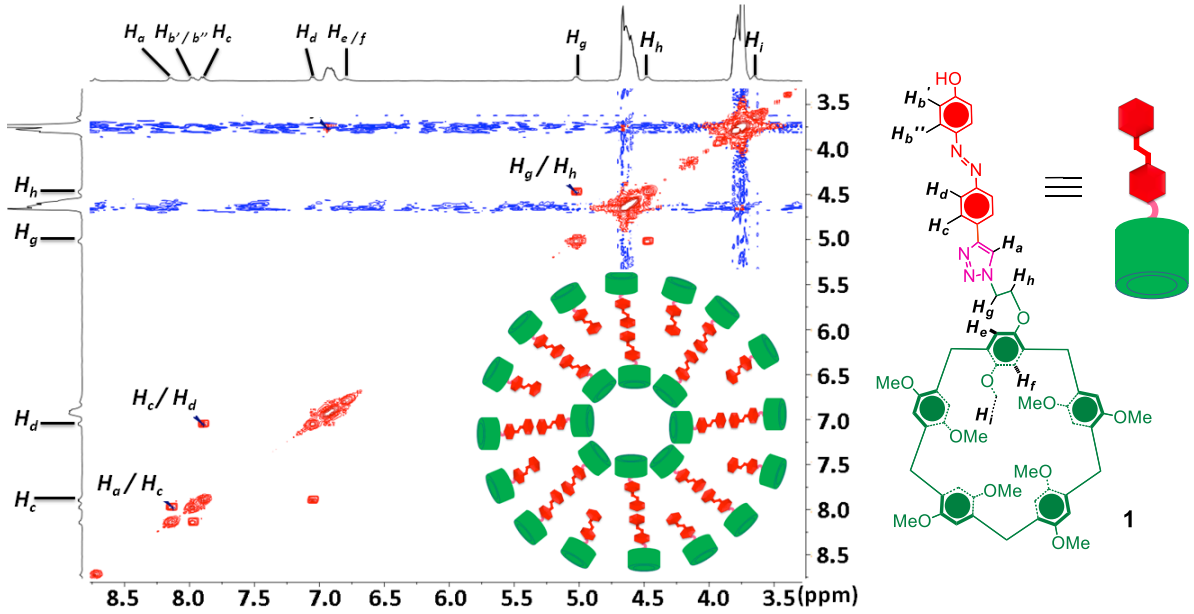


Fig. S5 2D NMR NOESY spectrum of **1** at ambient temperature. Inset: proposed structure of lamellar assemblies formed by **1**.

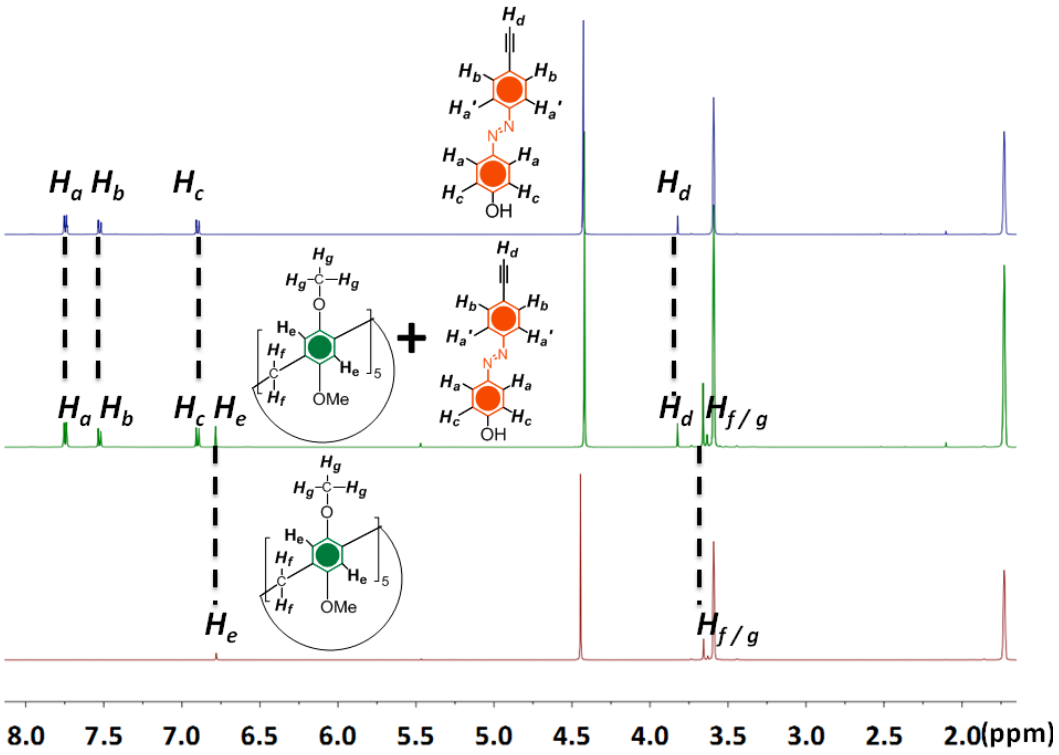


Fig. S6 ^{1}H-NMR spectra (500 MHz, r. t.) of 1:1 **2** and DMpillar[5]arene mixture (2 mM) in 1:2 (v/v) D_2O / THF-d_8 mixed solvent in comparison with the individual **2** and the individual DMpillar[5]arene.

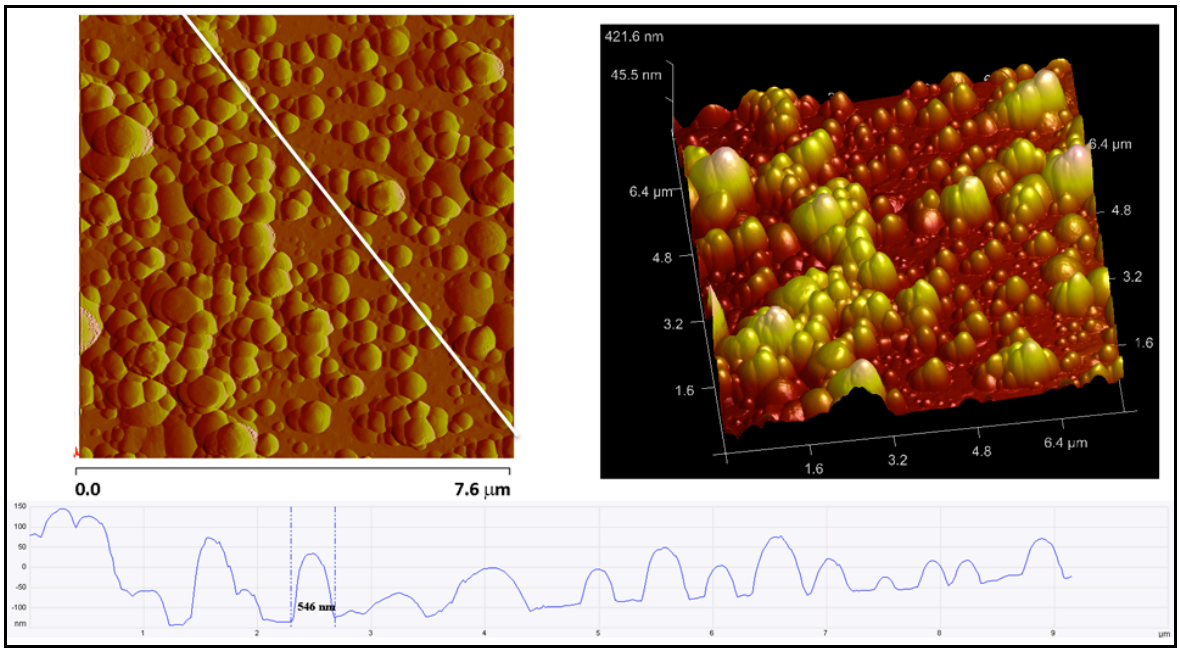


Fig. S7 The sample solution, **1** in the 1/2 (v/v) mixture of water and THF (2 mM), was irradiated by the UV lamp for 1 hour at rt. One droplet of the solution was cast on a silicon plate and carefully air-dried in the absence of light. Immediately, AFM detection with air tapping mode was performed. Air tapping mode AFM images of assemblies of **1** (upper left, planar image with scale bar = 7.6 mm; upper right, steric image; bottom, a line profile extracted along the marked white trace in the upper left image).

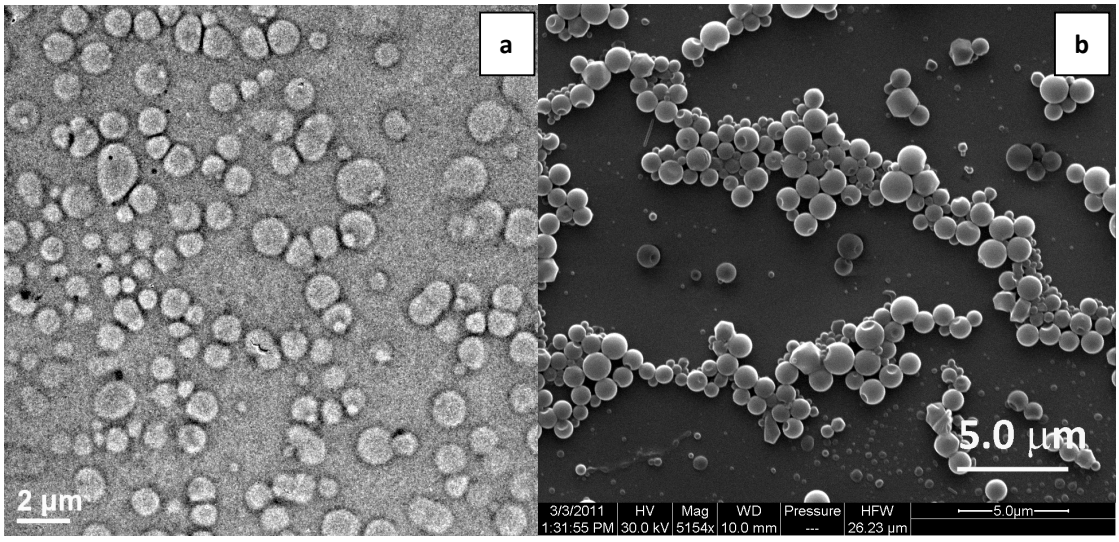


Fig. S8 Micro-morphology of **1** in the 1:2 H_2O / THF mixture (2 mM) after exposing in visible light once again for 1 h: negative stained TEM image (a) and gold sputtering SEM images (b, scale bar = 5 µm).

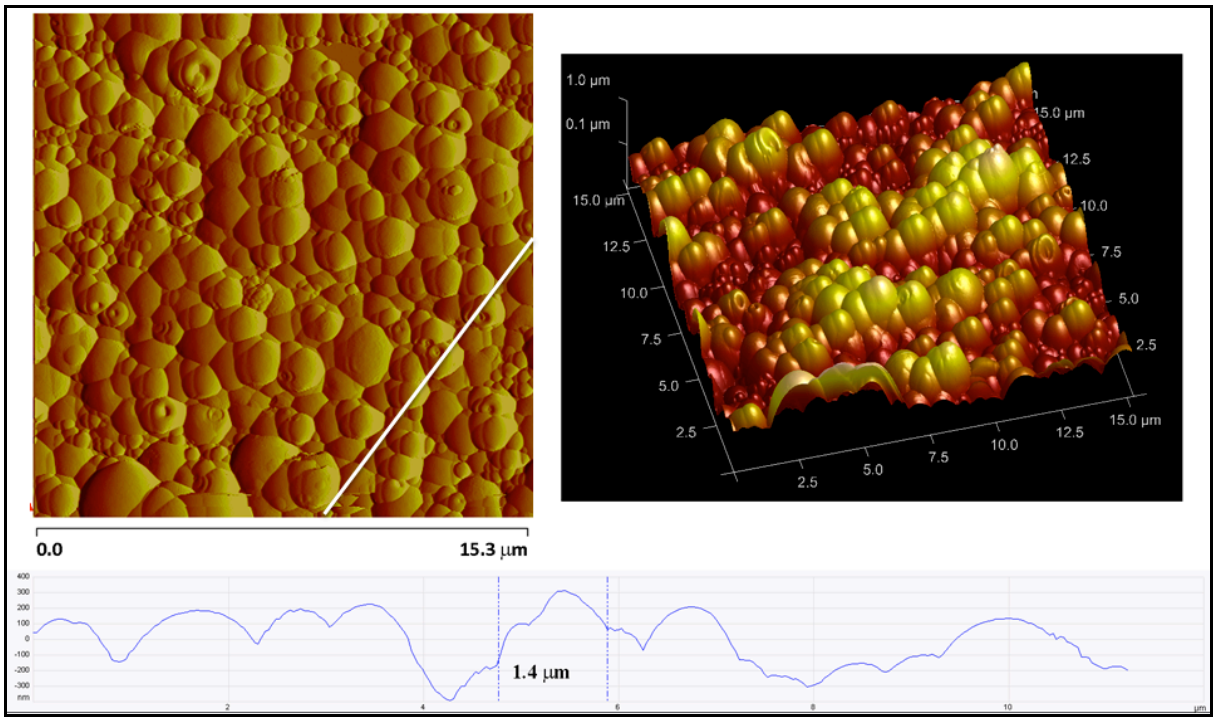


Fig. S9 Air tapping mode AFM images of assemblies of **1** which were exposed to visible light (upper left, planar image with scale bar = 15.3 µm; upper right, steric image; bottom, a line profile extracted along the marked white trace in the upper left image).

Table S1

Table S1. Morphologies and sizes of aggregates obtained by TEM, SEM, ESEM and AFM.

Conditions	*Morphology*	*Size (D / nm)*
Visible light	Hollow spheres (TEM)	150~600 (TEM)
	Hollow spheres (SEM)	180~700 (SEM)
	Hollow spheres (ESEM)	300~1000 (ESEM)
	Hollow spheres (AFM)	300~1000 (AFM)
UV (365 nm)	Solid spheres (TEM)	300~650 (TEM)
	Solid spheres (SEM)	200~600 (SEM)
	Solid spheres (AFM)	300~700 (AFM)
Visible light	Hollow spheres (TEM)	250~1700 (TEM)
	Hollow spheres (SEM)	300~1500 (SEM)
	Hollow spheres (AFM)	300~1800 (AFM)

References

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[S2] N. L. Strutt, R. S. Forgan, J. S. Spruell, Y. Y. Botros, J. F. Stoddart, *J. Am. Chem. Soc.*, 2011, **133**, 5668.

[S3] (a) P. Mukerjee, M. J. Gumkowski, C. C. Chan, R. Sharma, *J. Phys. Chem.*, 1990, **94**, 8832; (b) B. W. Liu, Y. Chen, B. E. Song, Y. Liu, *Chem. Commun.*, 2011, **47**, 4418.