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Supporting Information

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Self-Assembly of Tripodal Squaraines: Cation Assisted Amplification of Molecular Chirality and Spherical to Helical Morphology Change

Ayyappanpillai Ajayaghosh, Parayalil Chithra and Reji Varghese*

[*] Dr. A. Ajayaghosh, P. Chithra and R. Varghese.

Photosciences and Photonics Group,

Chemical Sciences and Technology Division,

Regional Research Laboratory, CSIR,

Trivandrum 695019 (India)

Fax: (+91) 471-490186

E-mail: aajayaghosh@rediffmail.com

1. Experimental Section

General

Solvents and the reagents were purified and dried by usual methods. All starting materials were obtained from commercial suppliers and used as received. All melting points were determined with Mel-Temp-II melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR were measured on a 300 MHz Bruker Avance DPX Spectrometer. High Resolution Mass Spectra were recorded with a JEOL JMS600. FT-IR spectra were recorded using a Shimadzu IR Prestige-21 Fourier Transform Infrared spectrophotometer. Elemental analyses were done using a Perkin-Elmer series-II 2400 CHN analyzer. The emission spectra were measured on a SPEX-Fluorolog F112X spectrofluorimeter. Fluorescence quantum yields were determined using optically matching solutions of 4,4-[bis-(*N,N*-dimethylamino)phenyl] squaraine dye (Φ_f = 0.70 in chloroform) as standard at an excitation wavelength of 570 nm. MALDI-TOF mass spectrometry was conducted on a perspective Biosystems Voyager DE-Pro-MALDI-TOF mass spectrometer using α-Cyano-4-hydroxy cinnamic acid as the matrix.

2. Description on Experimental Techniques

i) Atomic Force Microscopy (AFM)

Atomic Force Microscopy images were recorded under ambient conditions using a Digital Instrument Multimode Nanoscope IV operating in the tapping mode regime. Micro-fabricated silicon cantilever tips (MPP-11100-10) with a resonance frequency of 299 kHz and a spring constant of 20-80 Nm^{-1} were used. The scan rate varied from 0.5 to 1.5 Hz. AFM section analyses was done offline. Samples for the imaging were prepared by drop casting the solution of **1b** and **1c** in acetonitrile as well as the respective Ca^{2+} complexes on freshly cleaved mica at the required concentrations and the solvent was removed by vacuum.

ii) Transmission Electron Microscopy (TEM)

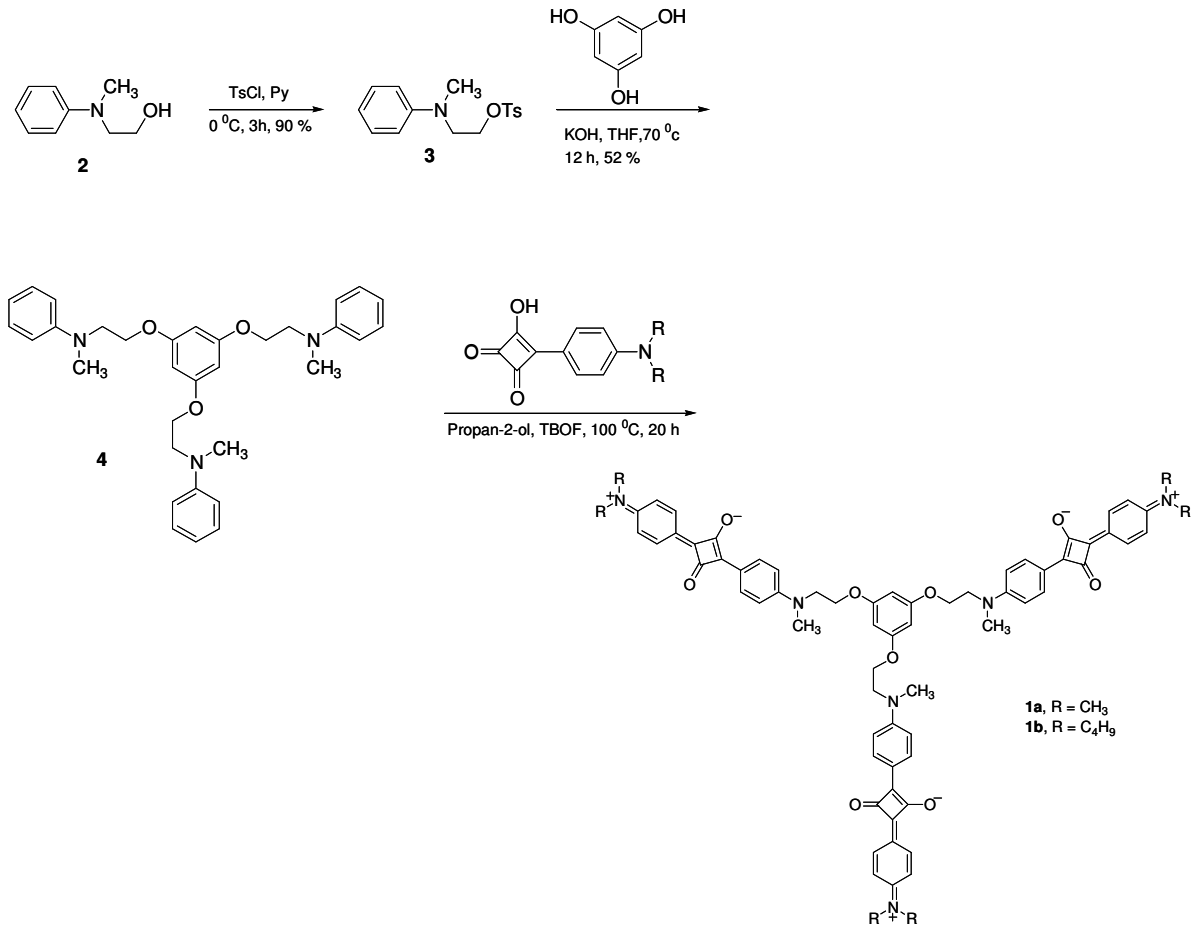
TEM measurements were carried out using JEOL JEM1011 with an accelerating voltage of 80 kV. The samples were prepared by drop casting acetonitrile solution of **1c** (2 x 10^{-6} M) onto a carbon coated copper grid. TEM images were obtained without staining.

iii) X-Ray Diffraction (XRD)

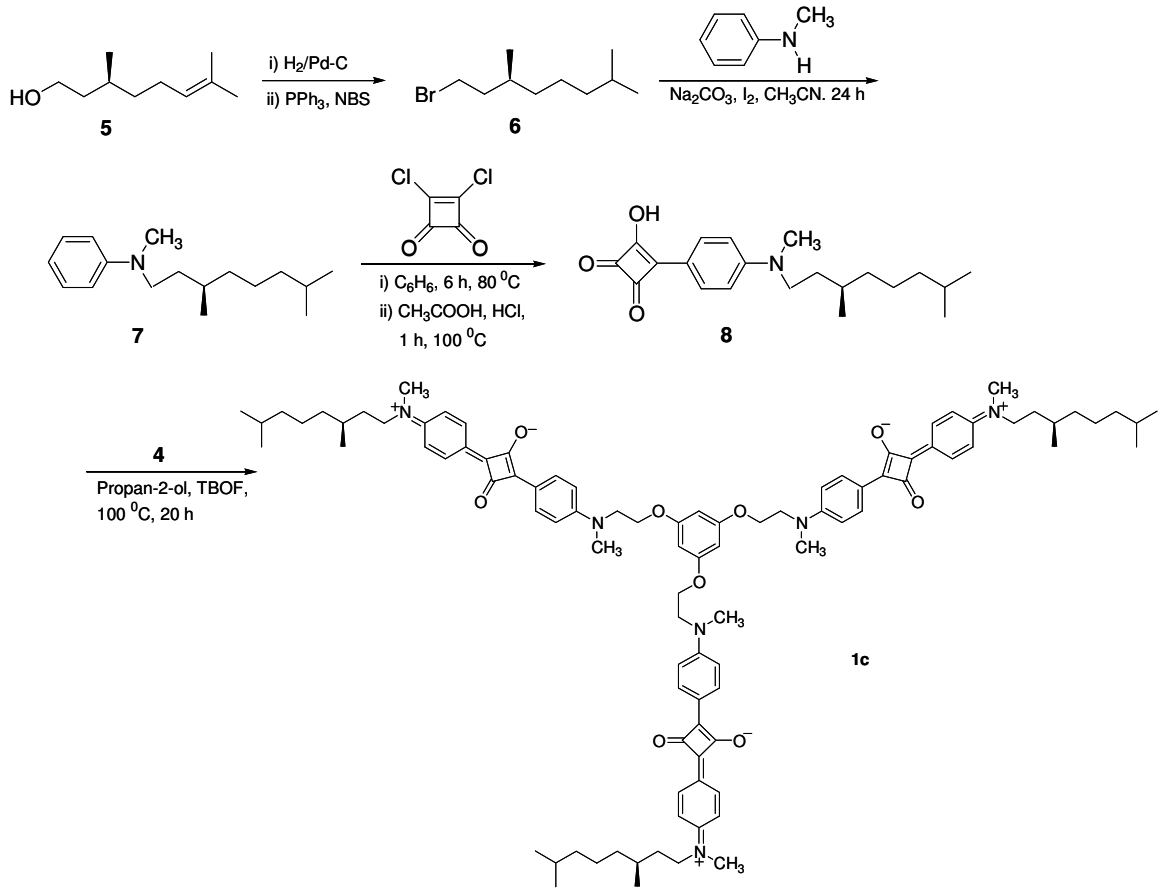
Powder X-ray diffractogram of **1c** was recorded on a Phillips diffractometer using Ni filtered Cu Kα radiation.

3. Synthesis and characterization

Scheme 1: Syntheses of 1a and 1b



Scheme 2: Synthesis of 1c



Synthesis of 1,3,5-tris[(2-(*N*-methyl-*N*-phenyl)amino) ethoxy]benzene (4)

A suspension of phloroglucinol (250 mg, 1.98 mmol), **3** (1.81 g, 5.95 mmol) and potassium hydroxide (2 g) in THF (100 mL) was stirred under reflux for 12 h under an argon atmosphere. After removal of the solvent under reduced pressure, water (50 mL) was added to hydrolyze the excess tosylate to the corresponding alcohol. After extracting with dichloromethane, the organic layer was dried over sodium sulfate. Evaporation of the solvent provided the crude products that were purified by column chromatography using ethyl acetate / hexane (1/19) over silica gel (100-200 mesh) to give the pure product as pale-yellow oil.

Yield: 540 mg (52%); FT-IR (neat): $\overline{\nu}_{max}$ 2866, 1731, 1602, 1514, 1426, 1259, 1045, 927, 878, 672, cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.94 (s, 9H, $-NCH_3$), 3.47-3.51 (t, J = 5.5, 6H, $-NCH_2$), 3.58-3.64 (t, J = 5.5, 6H, $-OCH_2$), 6.68-

6.71 (m, 9H, aromatic), 7.18–7.27 (t, *J* = 8.5, 9H, aromatic) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 39.07, 52.92, 68.7, 93.08, 96.25, 109.7, 112.68, 116.50, 128.84 ppm. HRMS–FAB: $[M]^+$ calcd for $C_{17}H_{29}N_3O_3$, 525.30; found: 525.15

Synthesis of (*S*)-(–)-1-bromo-3,7-dimethyloctane (6): The chiral handle was obtained from (*S*)-(–)citronellol, which was first catalytically hydrogenated and then brominated as per reported procedures.[1]

Synthesis of compound 7: A mixture of *N*-methyl aniline (1.2 g, 12 mmol), **6** (2.8 g, 12 mmol), sodium carbonate (2 g) and iodine (50 mg) in 50 mL acetonitrile was refluxed for 24 h. After cooling, the residue was filtered and the solvent removed. The mixture was extracted with dichloromethane and the organic layer was dried over sodium sulfate. The solvent was removed under reduced pressure and purified by column chromatography over silica gel (100–200 mesh) using hexane to give the product as a pale yellow liquid.

Yield: 89 %; FT-IR (KBr) $\bar{\nu}_{max}$ = 2956, 2662, 1590, 1401.3, 1350, 1260.5, 1182, 833, 787.9, 516.9 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.9–1.27 (d, 9H, $-CH_3$), 1.29– 1.6 (m, 10H, $-CH_2$ and –CH), 2.9 (s, 3H, $-NCH_3$), 3.23–3.38 (m, 2H, $-NCH_2$), 6.63– 6.69 (m, 3H, aromatic), 7.18– 7.24 (m, 2H, aromatic) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.1, 20.2, 29.5, 69, 77.4, 106.9, 132.8, 153.8, 164.6 ppm. HRMS–FAB: $[M]^+$ calcd for $C_{17}H_{29}N$, 247.45; found: 247.61.

Synthesis of compound 8: Squaryl chloride (600 mg, 4 mmol) and the chiral aniline derivative **7** (1.5 g, 4 mmol) were dissolved in 50 mL dry benzene and refluxed for 6 h. After cooling, the reaction mixture was poured into ice water and the two layers formed were separated. The organic layer was washed with water and treated with a mixture of acetic acid (20 mL), hydrochloric acid (1 mL) and 20 mL water. This mixture was refluxed for 2 h, and cooled to room temperature. The product was isolated by filtration, washed with ether and dried.

Yield: 65 %; FT-IR (KBr) $\bar{\nu}_{max}$ = 2953, 2648, 2503, 1762.9, 1573.9, 1427, 1136, 1028, 866 cm^{-1}.; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.82-0.9 (d, 9H, $-CH_3$) 1.1-1.14 (t, 4H, $-CH_2$) 1.17-1.53 (m, 6H, $-CH_2$), 3.01 (s, 3H, $-NCH_3$), 3.43- 3.45 (t, 2H,$-NCH_2$), 6.88- 6.91 (d, 2H, aromatic), 7.85- 7.88 (d, 2H, aromatic) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.23, 19.42, 22.4, 24, 27.32, 31.92, 32.63, 36.47, 39.77, 50.45, 109, 112.8, 115.5, 117.9, 119.26, 127.87, 149.8, 173.1, 194.56. HRMS-FAB: $[M]^+$ calcd for $C21H29NO_3$, 343.21; found: 344.61.

Syntheses of 1a, 1b and 1c:

1,3,5-tris[(2-(*N*-methyl-*N*-phenyl)amino)ethoxy]benzene (**4**) was refluxed with the corresponding *N,N*-(dialkylaminophenyl)-4-hydroxycyclobut-3-en-1,2-dione in propan-2-ol (50 mL)in the presence of tributyl orthoformate (TBOF) for 20 h resulting in the formation of the squaraine dyes **1a**, **1b** and **1c**, which were purified over silica gel (100-200 mesh) using chloroform/ methanol (9/1) as the eluent.

1a: Yield: 17 %; m.p. > 320 °C (decomp); FT-IR (KBr) $\bar{\nu}_{max}$ 2956, 2662, 1712, 1589, 1401.3, 1350, 1260.5, 1182, 833, 787.9, 516.9 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 3.1 (s, 27H, $-NCH_3$), 3.45-3.46 (t, 12H, $-OCH_3$ and $-NCH_3$), 6.71-6.78 (m, 15H, aromatic), 8.35-8.39 (m, 12H, aromatic) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 39.6, 51.2, 52.2, 69, 76.5, 93.1, 103.3, 106.9, 112.3, 119.4, 132.8, 133.7, 153.8, 164.6, 178, 183 ppm. Anal. Calculated for ($C_{69}H_{66}N_6O_9$): C, 73.78; H, 5.92; N, 7.48. Found: C, 73.67; H, 5.98; N, 7.41.

1b: Yield: 11 %; m.p. > 320 °C (decomp); FT-IR (KBr) $\bar{\nu}_{max}$ 3513, 2955, 1710, 1587, 1402.3, 1349, 1182, 834, 786.9 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.96-1.01(t, 18H, $-CH_3$), 1.31-1.43 (m, 24H, $-CH_2$), 3.1 (s, 9H, $-NCH_3$), 3.41-3.67 (m, 24H, $-NCH_2$ and $-OCH_2$), 6.1(s, 3H, aromatic), 6.71- 6.78 (m, 15H, aromatic), 8.36-8.39 (m, 12H, aromatic) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 20.2, 29.5, 39.6, 51.2, 76.9, 106.9, 112.3, 112.4, 120.1, 132.7, 133.6,

153.8, 183.3, 187.3 ppm. Anal. Calculated for ($C_{87}H_{102}N_6O_9$): C, 75,95; H, 7.47; N, 6.11. Found: C, 75,86; H, 7.50; N, 6.09.

1c:Yield: 21 %; mp >320 °C (decomp); FT-IR (KBr) $\bar{\nu}_{max}$ = 2953, 2924, 2673, 1720, 1587.4, 1435, 1384, 1355.3, 1284.5, 1182, 1126.4, 933, 835, 785, 503.4 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 0.86-0.88(d, 18H, $-CH_3$), 0.96-0.98(d, 9H,$-CH_3$), 1.25-1.71 (m, 30H, $-CH_2$), 3.1 (s, 18H, $-NCH_3$), 3.51-3.67(m, 18H, $-NCH_2$ and $-OCH_2$), 6.72-6.78 (m, 15H, aromatic), 8.35- 8.4 (d, 12H, aromatic) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.2, 19.6, 22.6, 24.6, 27.9, 29.6, 30.9, 33.9, 37.1, 39.6, 52.3, 69, 92.8, 94.6, 96.4, 104.4, 107.4, 110.8, 113, 119, 120.1, 124, 128.7, 132.9, 133.5, 183.3, 194.3, 197.2, 199.3 ppm. MALDI-TOF MS (MW = 1500.99): m/z = 1501.07 $[M]^+$

Reference:

[1] A. R. A. Palmans, J. A. J. M. Vekemans, E. E. Havinga, E. W. Meijer, *Angew. Chem.* **1997**, *109*, 2763-2765; *Angew. Chem. Int. Ed.* **1997**, *36*, 2648-2651.

Additional Figures

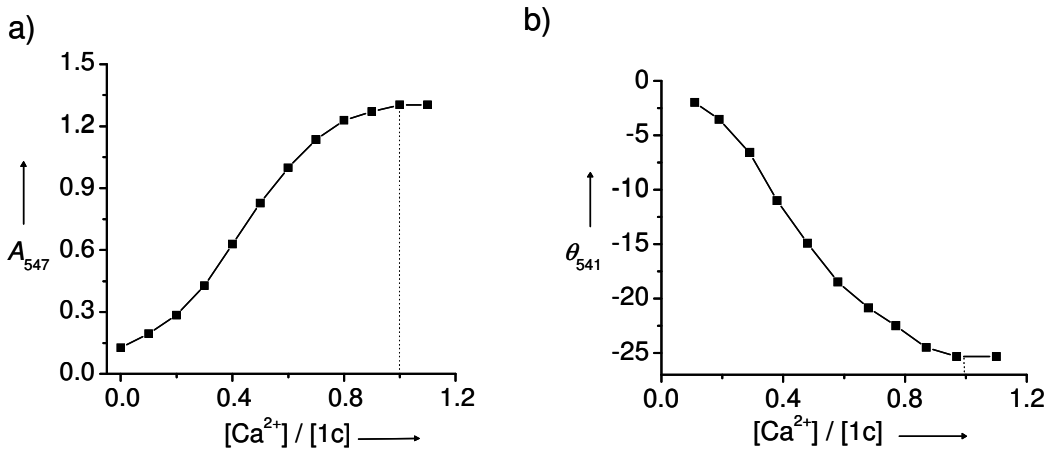


Figure S1. Plots of a) absorbance at 547 nm and b) CD intensities at 541 nm against the ratio of $[Ca^{2+}]$ to **1c**.

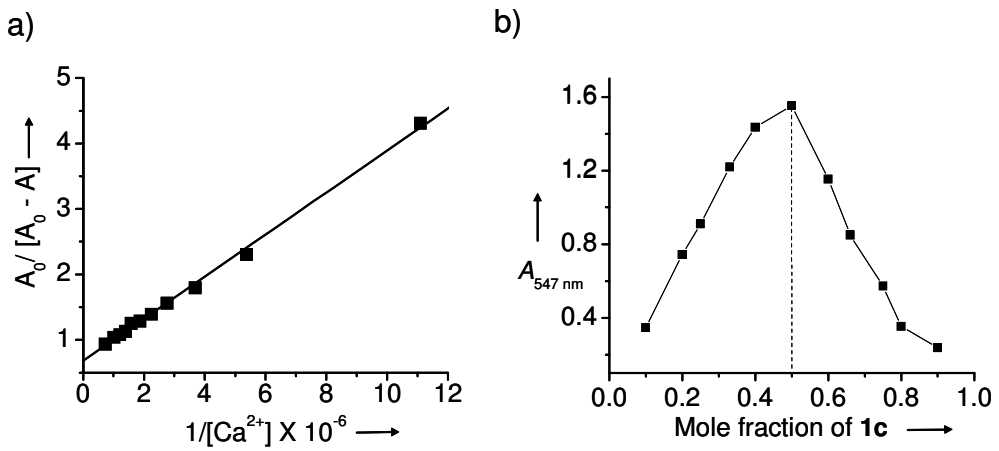


Figure S2. a) Benesi–Hildebrand plot obtained for 1:1 binding of **1c** with Ca^{2+} in acetonitrile. b) Job plot showing 1:1 binding of **1c** with Ca^{2+}.

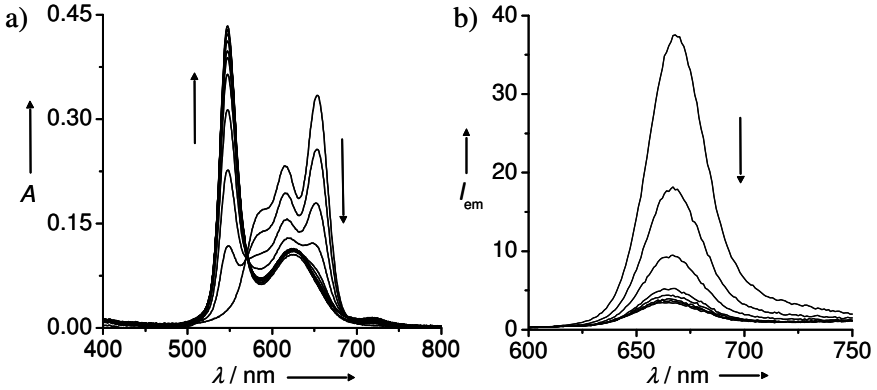


Figure S3. Changes in the a) absorption and b) emission spectra of **1b** (0.9 x 10^{-6} M) in acetonitrile upon addition of $Ca(ClO_4)_2$ (0–1 x 10^{-6} M).

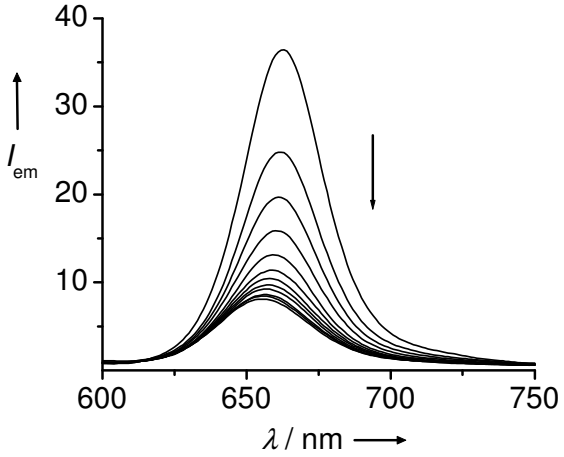


Figure S4. Changes in the emission spectrum of **1c** (3.6 x 10^{-6} M) upon addition of $Ca(ClO_4)_2$ (0–4 x 10^{-6} M)in acetonitrile.

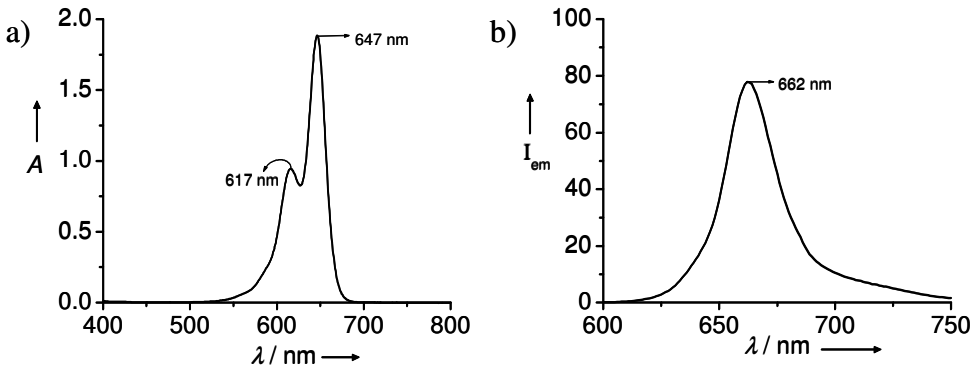


Figure S5. Absorption and emission spectra of **1c** (1.2 x 10^{-6} M) in chloroform.

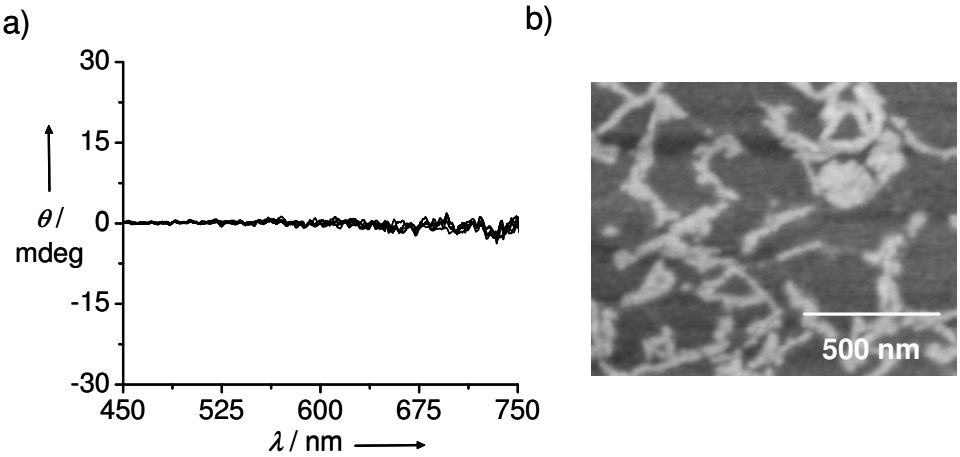


Figure S6. a) CD spectra of **1c** (3.6 x 10^{-6} M) in acetonitrile-water mixtures of different composition (0-12 % water) at 298 K (path length 10 mm). b) Tapping mode AFM image of **1c** from acetonitrile-water.

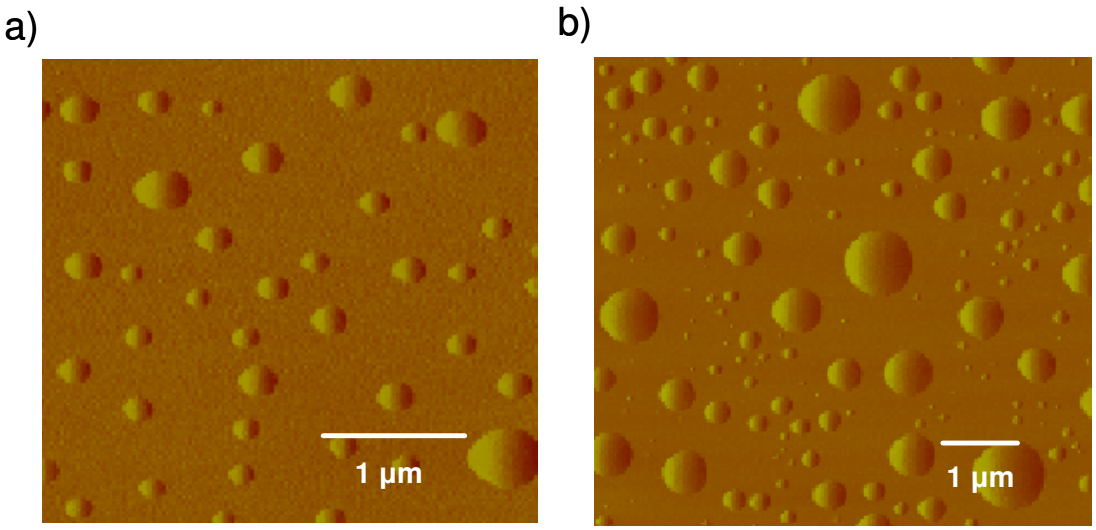


Figure S7. Tapping mode AFM phase images corresponding to Figure 2a and 2b of the main text.

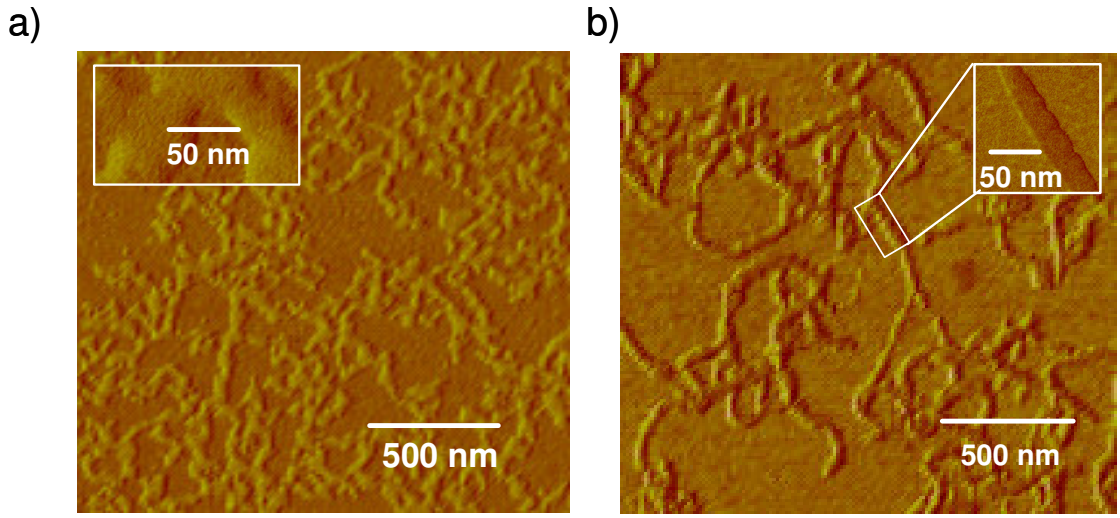


Figure S8. Tapping mode AFM phase images corresponding to Figure 3a and 3b of the main text.

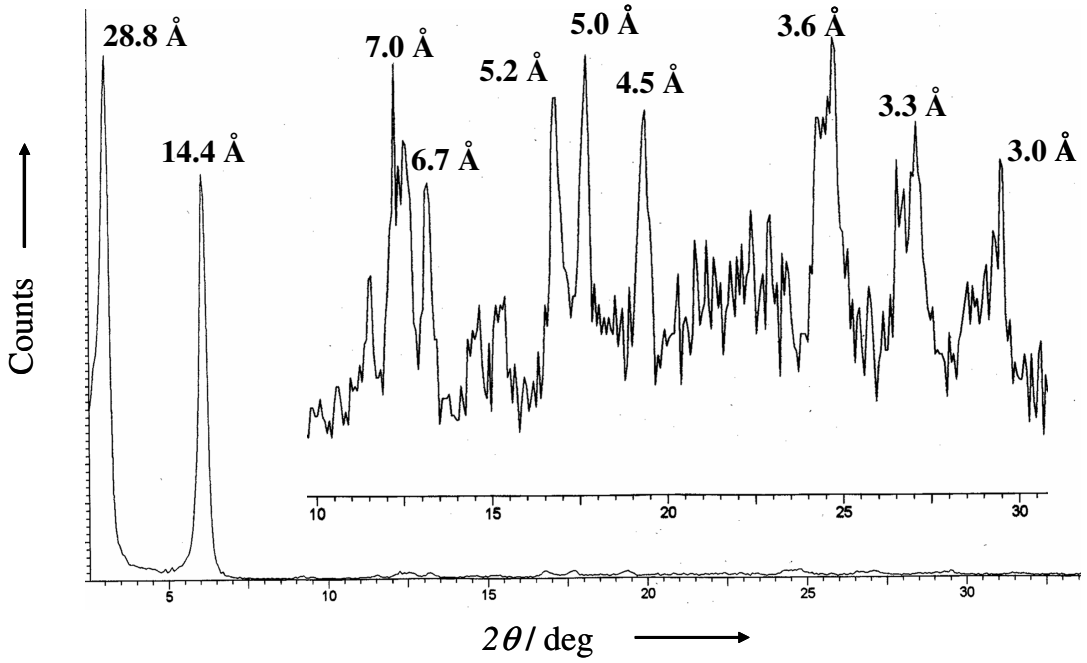


Figure S9. Powder XRD pattern of **1c**.