Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Tunable aggregation-induced emission of star-shape luminogen based on cyclohexanehexone substituted with AIE active tetraphenylethene functionality

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General Methods & Materials: Hexaketocyclohexane octahydrate, chloroform, methanol, dichloromethane, tetrahydrofuran and hexane were purchased from Aldrich and used without purification, unless otherwise specified. The UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 40p spectrometer. ^{1}H NMR, ^{13}C-NMR spectra were recorded on a Bruker spectrometer using chloroform-d as solvent and tetramethylsilane as an internal standard. The solvents for spectroscopic studies were of spectroscopic grade and used as received. Mass spectra (MS) were obtained by using Bruker AutoFlex Matrix Assisted Laser Desorption/Ionisation (MALDI) Time of Flight (TOF)- Mass Spectrometer (MALDI-TOF-MS). The X-ray diffraction (XRD) pattern spectra were performed on a Bruker D8 FOCUS diffractometer using a Cu target radiation source (λ= 0.15418 nm).

UV-vis absorption spectroscopy: A 0.2 mL aliquot of the stock solution of **HTCA** (conc. = 10^{-3} M) was transferred to various ratios of THF/water in different volumetric flasks, and made up to 2 mL volume. The solutions were allowed to equilibrate for 2 h prior to the spectroscopic measurements.

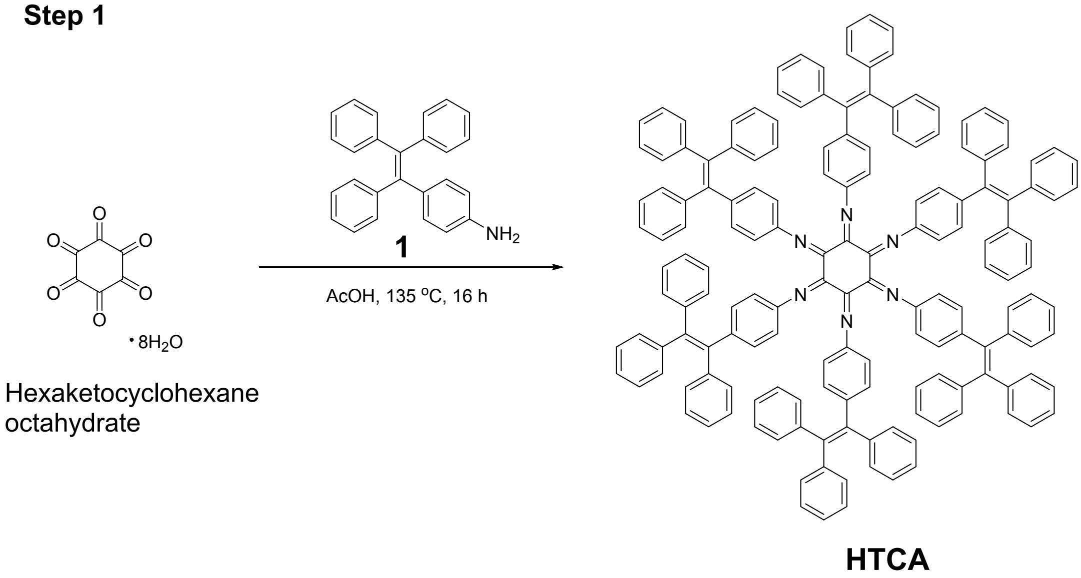
Fluorescence Spectroscopy: Fluorescence emission spectra were recorded on a Horiba Jobin Yvon FluoroMax®-4–Spectrofluorometer. All experiments were performed in a quartz cell with a 1 cm path length with 339 nm excitation wavelength. All the solutions were prepared in a similar manner to that in the UV–vis study.

Scanning Electron Microscopy (SEM): A 0.2 mL aliquot of the stock solution of **HTCA** was transferred separately to four different volumetric flasks of (i) THF/water

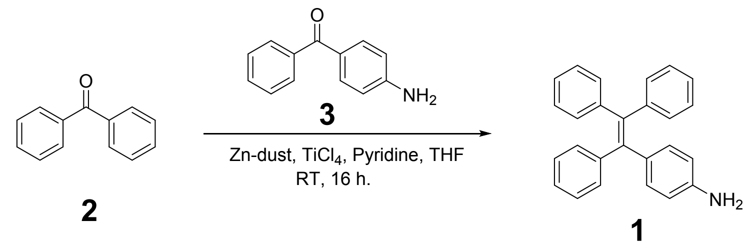
(50% water), *v/v*), (ii) THF/water (70% water) and (iii) THF/water (90% water) and made up to 2 mL volume with respective solvents. The solutions were allowed to equilibrate for 2 h prior to the Scanning Electron Microscopy (SEM) measurements. SEM measurements were performed on a FEI Nova NanoSEM (Hillsboro, USA) or Philips with operating at high vacuum and SEM and images were collected. Freshly prepared 0.5 µL of **HTCA** sample were sputter coated with gold for 10 s at 0.016 mA Ar plasma (SPI, West Chester, USA) after drop-casting the solutions on glass coverslip and solvent evaporation.

Synthesis of **HTCA** target molecule:

Step 1



Step 2



Step-1: Synthesis of *N^1^,N^2^,N^3^,N^4^,N^5^,N^6^*-hexakis(4-(1,2,2-triphenylvinyl) phenyl)cyclohexane-1,2,3,4,5,6-hexaimine (**HTCA**): Compound hexaketocyclohexane octahydrate (0.1 g, 0.595 mmol) and TPVA **1** (1.4 g, 4.17 mmol) was heated to reflux in deoxygenated AcOH (10 mL) at 135 °C for 16 h. Reaction completion was checked by TLC analysis. After completion reaction was quenched with water. Solid precipitates out was filtered through Buchner funnel and dried under vacuum. Crude solid was purified by column chromatography followed by preparative TLC to afford pure compound as an off white solid (0.446 g, yield 35%). ^{1}HNMR (300 MHz, $CDCl_3$) δ (TMS, ppm) 7.16 (d, *J* = 8.4 Hz, 12H), 7.11 – 6.91 (m, 90H), 6.88 (d, *J* = 8.6 Hz, 12H); ^{13}CNMR (75 MHz, $CDCl_3$) δ ^{13}C NMR (75 MHz, CD_2Cl_2) δ 168.4, 144.2, 144.1, 139.8, 136.9, 132.1, 131.6, 131.5, 128.1, 128.0, 127.9, 126.8, 126.7, 119.0; Elemental Analysis for $C_{162}H_{114}N_6$: Calcd: C, 90.72; H, 5.36; N, 3.92; Found: C, 90.74; H, 5.39; N, 3.91; HRMS (MALDI-TOF, m/z): [M^+] calcd for $C_{162}H_{114}N_6$: 2142.91, found 2142.91;

Step-2: Synthesis of 4-(1, 2, 2-triphenylvinyl) aniline (**TPAV**) **1:** A 2-necked round bottom flask was charged with Zn powder (8.04 g, 123.37 mmol) and THF (460 mL) under an argon atmosphere. The mixture was cooled to -5 °C to 0 °C, and $TiCl_4$ (6.72 mL, 61.68 mmol) was added slowly by syringe with the temperature maintained under 10 °C. The suspended mixture was warmed to r.t. and stirred for 0.5 h, then heated to reflux for 2.5 h. The mixture was again cooled to -5 °C to 0 °C, charged with pyridine (4 mL), and stirred for 10 min. The solution of **2** (4.0 g, 21.95 mmol) and **3** (3.5 g, 17.78 mmol) in THF (60 mL) was added slowly. When the addition was complete, the mixture was heated to reflux for 16 h. Reaction completion was checked by TLC analysis. After completion, reaction was quenched by addition of 10% aq K_2CO_3 and extracted with DCM. Organic layer was dried over sodium sulphate and evaporated on rota vapour to obtain crude compound which was purified by flash chromatography to afford pure compound **1** as a yellow solid. (5 g yield 65 %.) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19–6.98 (m, 15H), 6.86–6.77 (m, 2H), 6.48–6.40 (m, 2H), 3.59 (s, 2H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 144.7, 144.3, 144.2, 144.1, 140.9, 139.3, 134.0, 132.5, 131.5, 131.4, 131.3, 127.7, 127.6, 127.5, 126.2, 126.0, 114.3; HRMS (MALDI-TOF, m/z): [M^+] calcd for $C_{26}H_{21}N$: 347.17, found: 348.20 $(M+H)^+$.

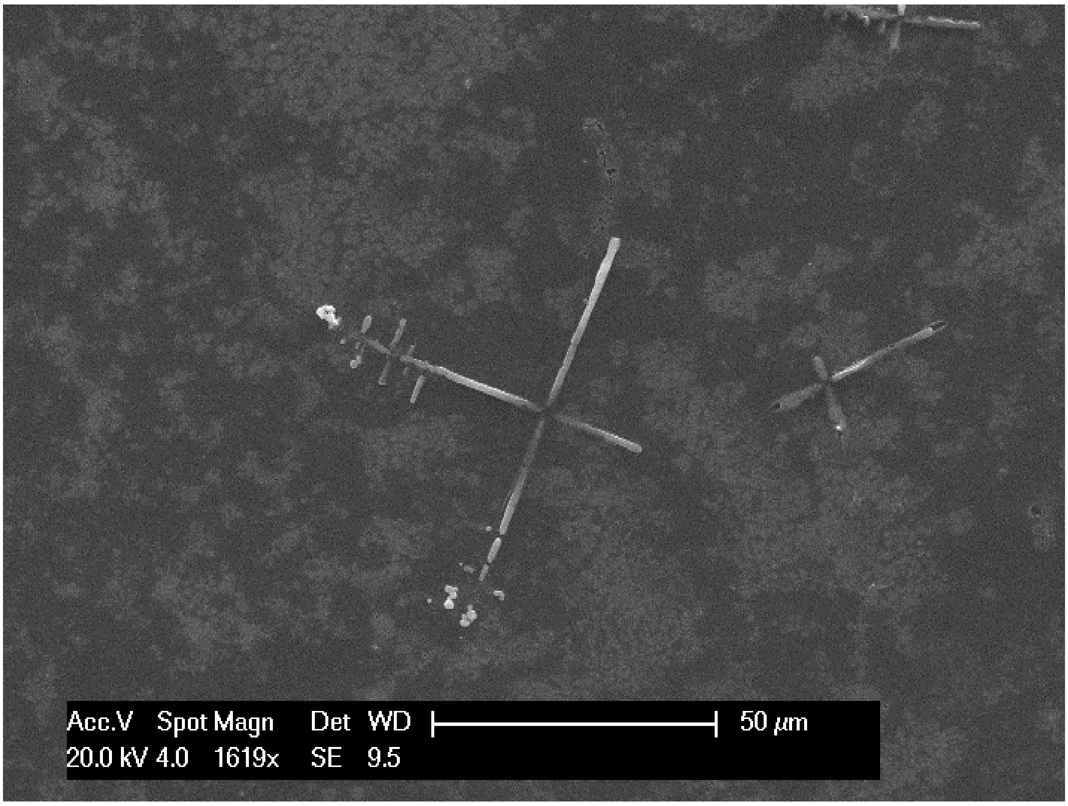


Fig. S1 SEM image of HTCA (10^{-5} M) from water/THF mixes with water fractions of $f_w = 50\%$.

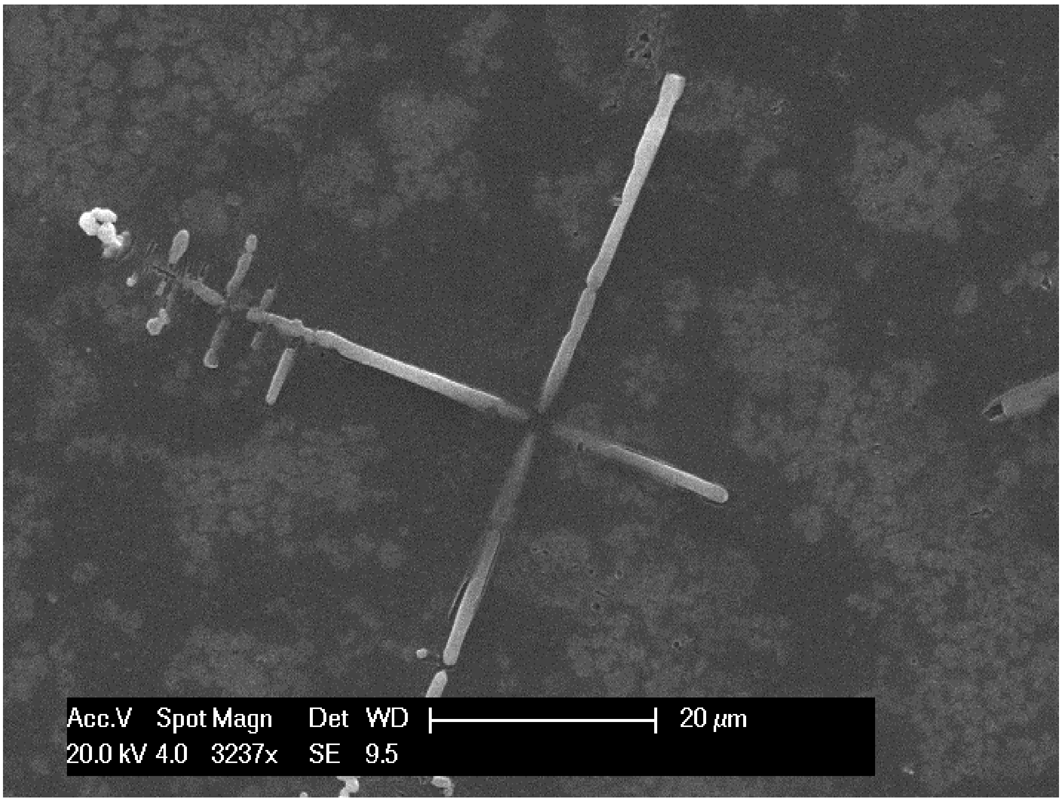


Fig. S2 SEM image of HTCA (10^{-5} M) from water/THF mixes with water fractions of $f_w = 50\%$.

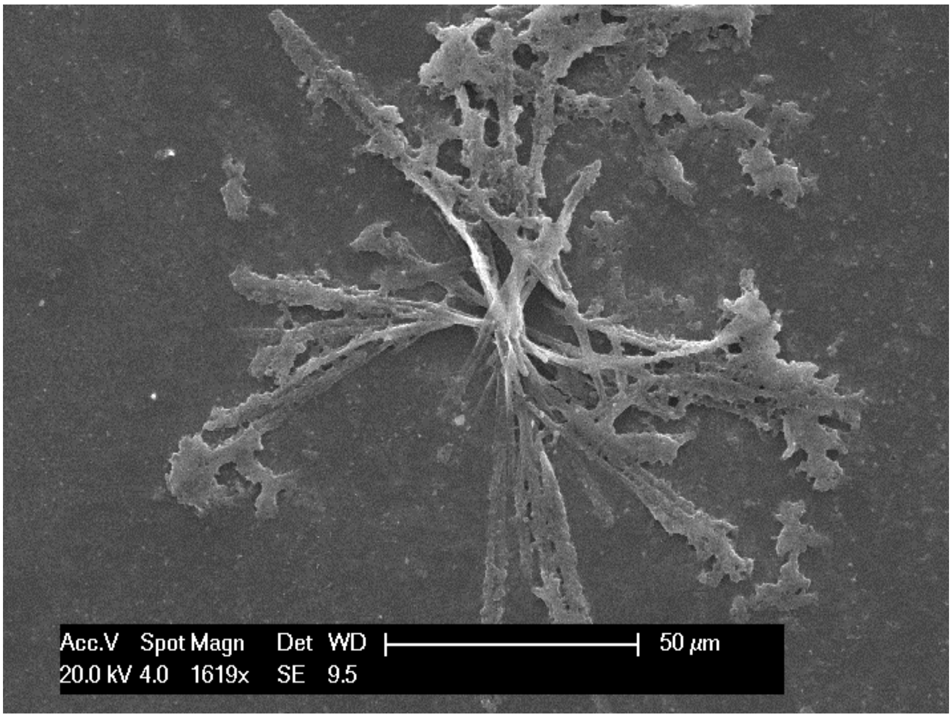


Fig. S3 SEM image of HTCA (10^{-5} M) from water/THF mixes with water fractions of f_w = 70%.

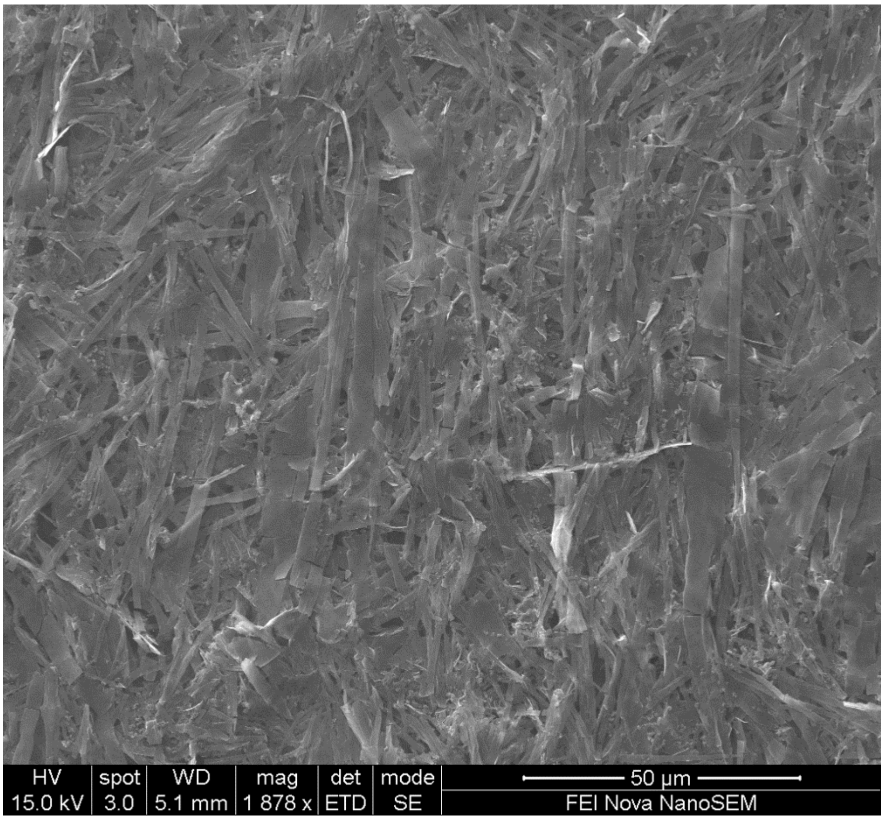


Fig. S3 HTCA (10^{-3} M) from water/THF mixes with water fractions of f_w = 80%.

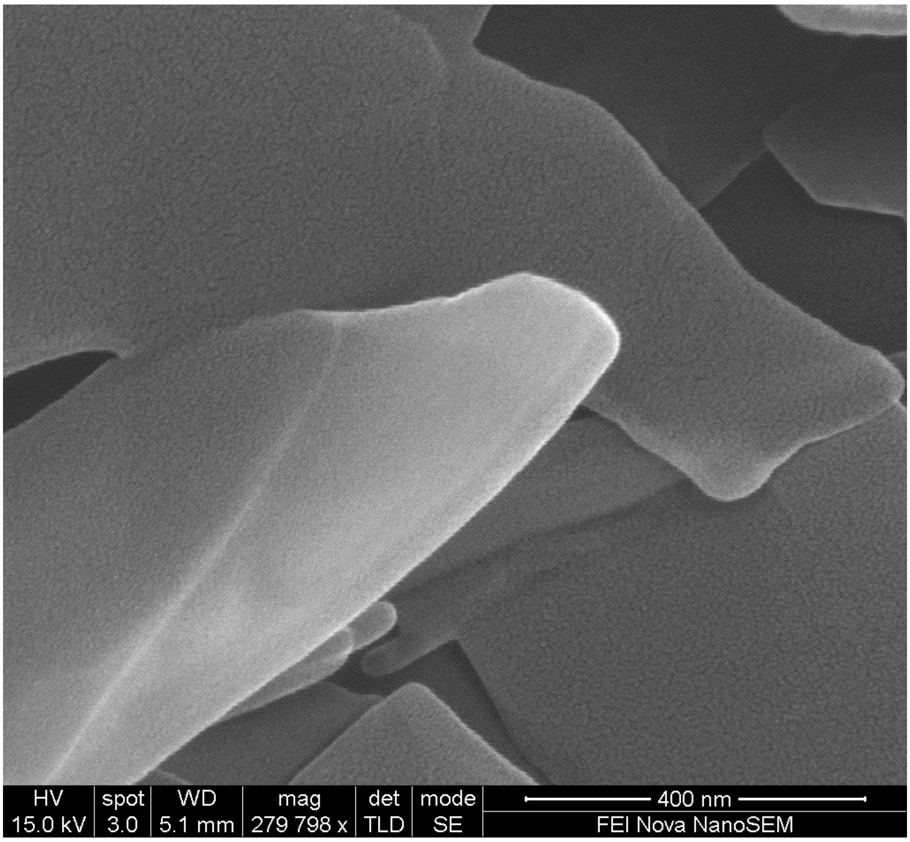
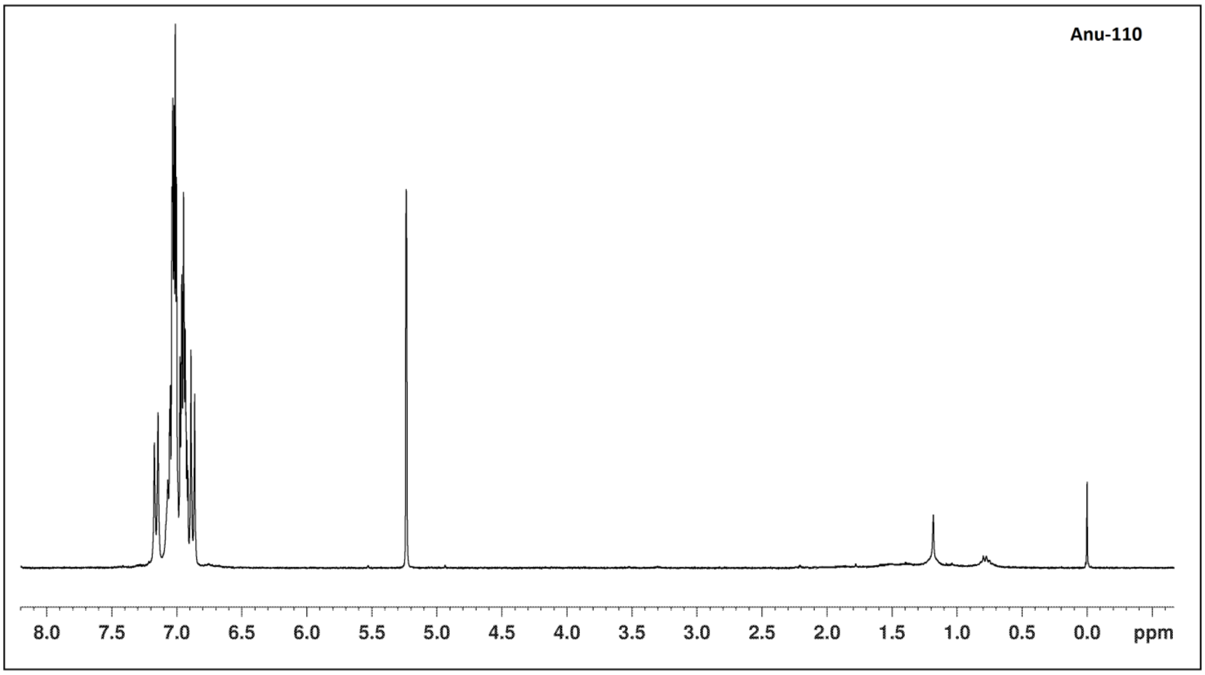
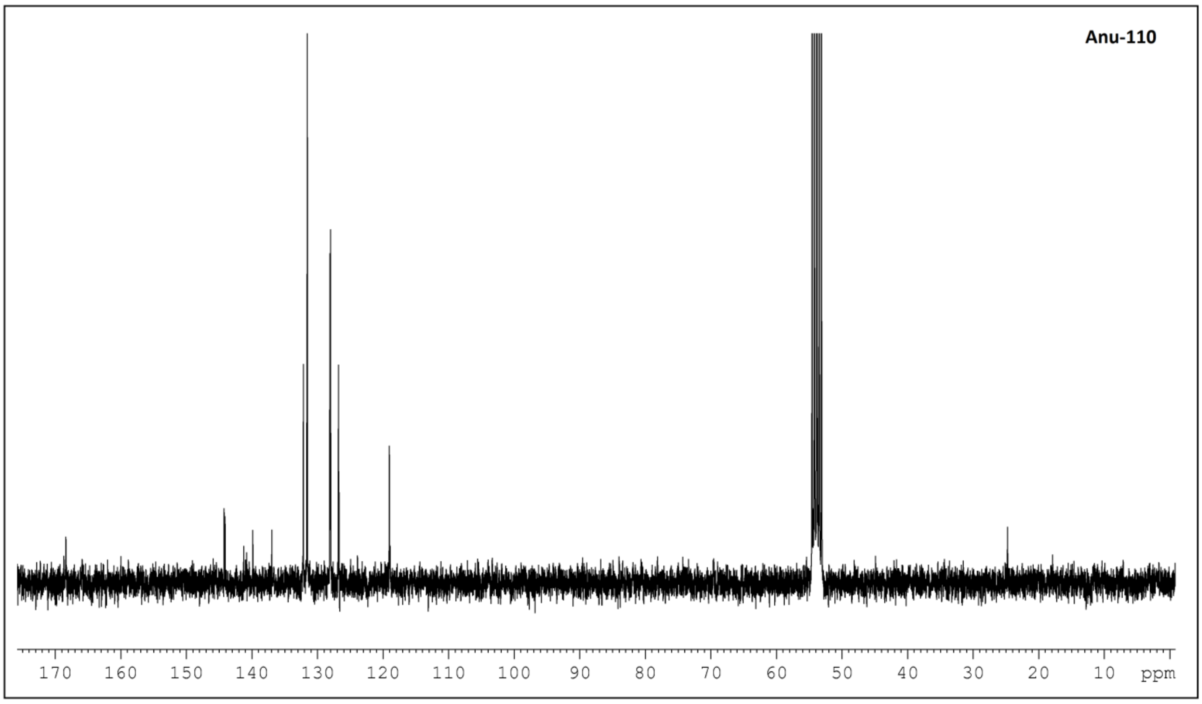


Fig. S3 Enlarged SEM image of HTCA (10^{-3} M) from water/THF mixes with water fractions of $f_w = 80\%$.

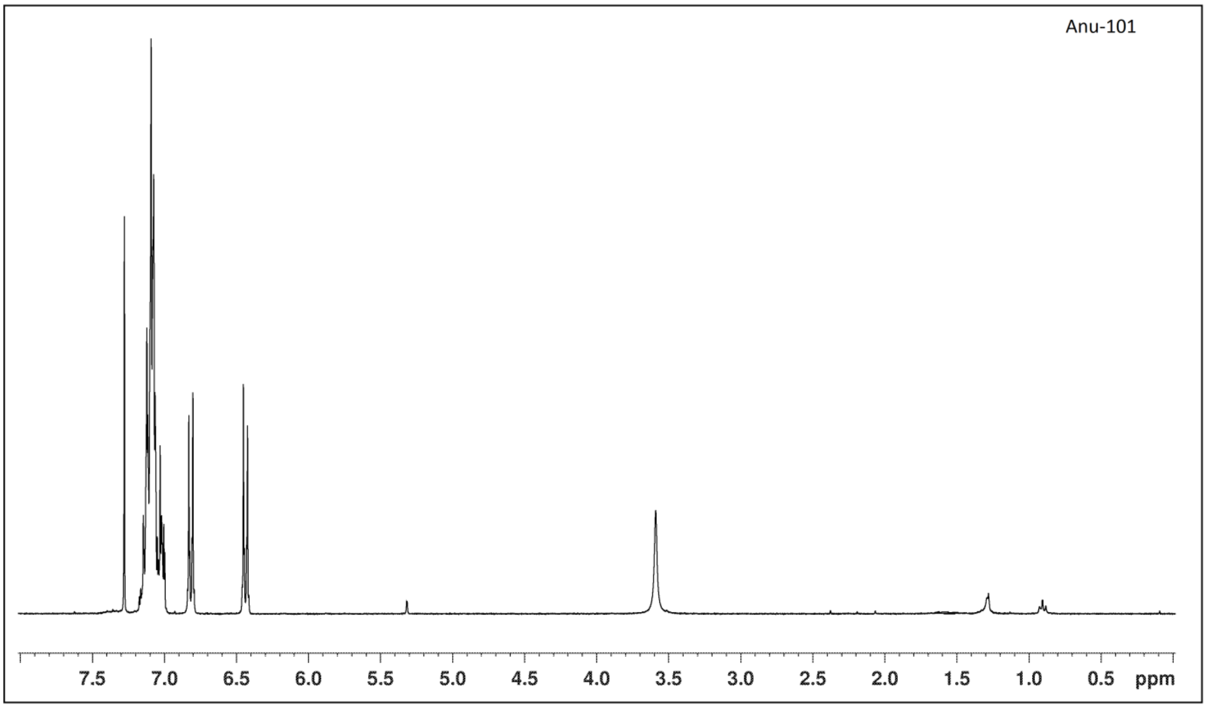
^{1}H NMR of **HTCA**



^{13}CNMR of **HTCA**



^{1}HNMR of TPVA



^{13}CNMR of TPVA