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Tetrabenzo[5.7]Fulvalene: A Forgotten Aggregation Induced-Emission Luminogen

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General Methods

Reactions were performed under an atmosphere of argon in oven-dried glassware, unless otherwise stated. Anhydrous THF or diethyl ether was prepared via pre-drying solvents over CaH_2, then distillation under an inert atmosphere of argon, then stored over 4Å molecular sieves in an oven dried Schlenk tube. Compounds purchased commercially were used without further purification, unless otherwise stated. Solvents for analysis were used after SPS purification, unless otherwise stated.

Analytical thin layer chromatography (TLC) was performed using aluminium plates precoated with silica gel 60 F_{254} (0.2 mm). Flash chromatography employed 230-400 mesh silica gel. Solvent systems used for chromatography are quoted as volume/volume ratios.

NMR spectroscopy was performed at 298 K using an Avance III HD 400 (400.1 MHz, ^{1}H; 100.6 MHz, ^{13}C) or an Avance III 300 (300.13 MHz, ^{1}H; 75.5 MHz, ^{13}C) at the Mark Wainwright Analytical Centre at the University of New South Wales Sydney. ^{1}H NMR data is expressed in parts per million (ppm) downfield shift from tetramethylsilane with residual solvent as an internal reference (δ 7.26 ppm for chloroform, δ 1.94 for acetonitrile) and is reported as position (δ in ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (J in Hz) and integration (number of protons). ^{13}C NMR spectra were recorded at 298 K with complete proton decoupling. Data is expressed in parts per million (ppm) downfield shift relative to the internal reference (δ 77.16 ppm for the central peak of deuterated chloroform and δ 118.26 ppm for the CN-carbon peak in acetonitrile).[3]

UV-visible spectroscopy was performed on a Varian Cary 50 single-beam spectrophotometer at ambient temperature. Fluorescence data were obtained on a Varian Cary Eclipse Fluorescence Spectrophotometer at ambient temperature with slit widths set at 5 nm. Images of compounds were obtained with a Samsung Note8. The absorption spectra of the solid-state samples were obtained by converting from the reflectance spectrum. The reflectance spectra were measured by a UV-visible spectroscopy with integrating sphere (Thermo®Scientific, EVOLUTION 220).

Infrared spectra were obtained on a ThermoNicolet Avatar 370 FT-IR spectrometer and are reported in wavenumbers (cm^{-1}). HRMS were performed at the Bioanalytical Mass Spectrometry Facility within the Mark Wainwright Analytical Centre at the university of

New South Wales on an Orbitrap LTQ XL (Thermo Fisher Scientific, San Jose, CA, USA) ion trap mass spectrometer.

Thin Film Sample Preparation

All the glass slides (MENZEL-GLÄSER Microscope Slides, 76 × 26 mm) used in sampling were cut to 12.5 × 12.5 × 1 mm, cleaned by sonicating sequentially in $CHCl_3$, acetone, $NaOH_{(aq.)}$, distilled water, isopropanol and acetone, then dried using a strong flow of N_2. All the thin-film samples were prepared by spin coating 50 μL casting solutions (5 mM in $CHCl_3$) on top of the above-mentioned glass slides. The spin-coated conditions were 2000 rpm in one minute for deposition process.

PLQY Measurements

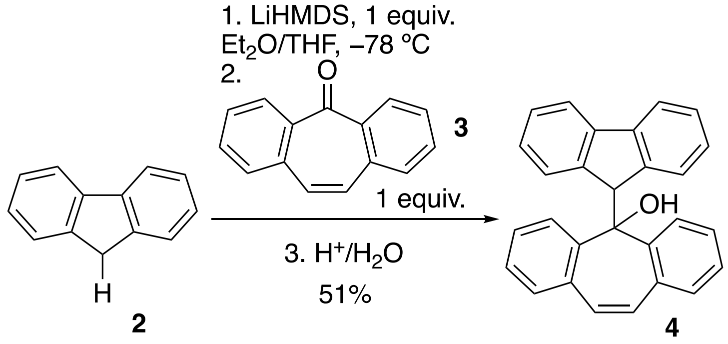
Absolute PLQY measurements of all samples were performed using an integrating sphere accessory (F3018, Horiba Jobin Yvon) on a Fluorolog®-3 fluorometer. The angle of the excitation beam to the normal of the sample surface can be modified using the variable sample holder. All spectra for the absolute quantum yield measurements were corrected for the light source noise, wavelength sensitivity and the transmittance of the filters. The photon counts of all the measurements on the Fluorolog®-3 fluorometer were within the linear response range of the detector (2×10^6 cps).

Time-correlated single photon counting (TCSPC) measurement

The excitation source was a mode-locked and cavity dumped Ti:Sapphire laser (Coherent Mira 900F/APE PulseSwitch) pumped by a Coherent Verdi-10 DPSS Nd:YVO4 laser. The laser output (880 nm wavelength, 5.4 MHz repetition rate) was frequency doubled to provide an excitation wavelength of 405 nm for the solid samples and 400 nm for the solution samples. The individual fluorescence decay curves were collected using the time-correlated single photon counting technique. Synchronization of the laser pulses was achieved using a fast photodiode (Becker & Hickl, PHD-400-N) fed through a nanosecond delay box and constant fraction discriminator (Tennelec TC455) as the stop signal for the time-to amplitude converter (Ortec model 457). The fluorescence decay profiles of the samples were collected at the magic angle relative to the (vertical) excitation polarization. The fluorescence lifetimes were calculated by FAST software (Edinburgh Instruments Ltd) using exponential components analysis.

The following compounds were synthesised according to a modified method previously prepared by Weissman *et al.*[1]

Preparation of 5-(9H-fluoren-9-yl)-5H-dibenzo[a,d]cycloheptene-5-ol



Lithium bis(trimethylsilyl)amide (1.0 M in THF, 10 mL, 1.0 equiv.) was added dropwise to a solution of fluorene (10 mmol, 1.0 equiv.) in dry diethyl ether (16 mL) at -78 °C under an inert atmosphere. The solution was left to stir at room temperature for one hour. 5-dibenzosuberenone (10 mmol, 1.0 equiv.) in dry THF was then added dropwise at -78 °C and was stirred at room temperature for one hour.

Aqueous HCl solution (0.1 M, 10 mL) was then added at -78 °C until the pink colour disappeared. The resulting mixture was filtered, isolating a white powder. The filtrate was then extracted with dichloromethane, dried over Na_2SO_4 and the solvent removed, which revealed a colourless solid. This was combined with the white powder and recrystallised from hot toluene to yield the tertiary alcohol as a colourless crystalline solid.

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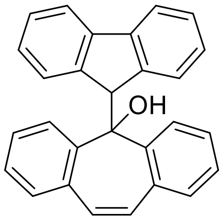
[1] I. Agranat, M. Rabinovitz, M. Weissman, *Tetrahedron Lett.* **1972**, *13*, 273-276.



Yield 51%;

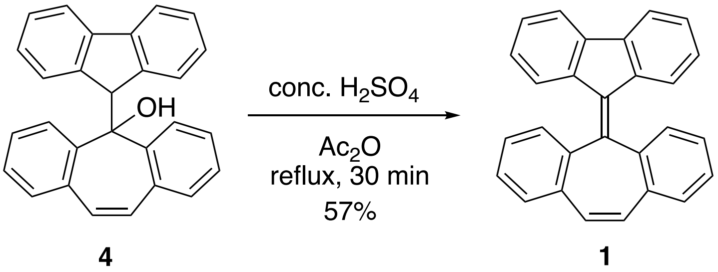
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.79 – 7.73 (m, 2H), 7.67 (d, *J* = 7.6, 2H), 7.58 – 7.52 (m, 2H), 7.47 – 7.41 (m, 4H), 7.31 (s, 2H), 7.26 (t, *J* = 7.6, 2H), 6.87 (td, *J* = 7.6, 1.2 Hz, 2H), 5.58 (dd, *J* = 7.6, 0.9 Hz, 2H), 5.24 (s, 1H), 1.78 (br. s, 1H) ppm;

^{13}C NMR (101 MHz, CDCl$_3$) δ 143.1, 142.5, 141.4, 133.1, 132.4, 129.2, 129.1, 127.7, 127.21, 126.5, 126.3, 125.8, 119.6, 77.9, 49.4 ppm;

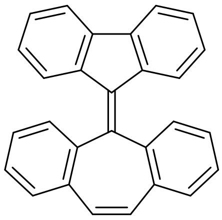
HRMS (ESI+) (m/z): Anal. Calcd. for $C_{28}H_{20}O^+Na$ 395.1412, found 395.1405;

IR: 3571, 3022, 2936 cm^{-1}.

Preparation of Tetrabenzo[5.7]fulvalene



Concentrated sulfuric acid (98%, 2 drops) was added to the alcohol (1.0 mmol) in freshly distilled acetic anhydride (2 mL). The solution was then heated to 145 °C until a white precipitate was formed in the purple solution. The volatile organic compounds were then removed by vacuum filtration, and the precipitate was washed with diethyl ether. The precipitate was then purified by recrystallisation with hot toluene, yielding a colourless crystalline solid. Characterisation data corresponded to that of literature.[1]



Yield 57%;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 – 7.63 (m, 2H), 7.62 – 7.58 (m, 2H), 7.56 – 7.51 (m, 2H), 7.51 – 7.40 (m, 4H), 7.23 (td, *J* = 7.5, 1.0 Hz, 2H), 7.04 (s, 2H), 6.94 – 6.87 (m, 2H), 6.46 (d, *J* = 7.9 Hz, 2H) ppm;

^{13}C NMR (101 MHz, CDCl$_3$) δ 141.3, 140.7, 138.1, 138.0, 133.7, 132.6, 130.9, 128.7, 128.6, 127.9, 127.5, 127.1, 126.6, 125.3, 119.3 ppm;

HRMS (ESI) (m/z): Anal. Calcd. for $C_{28}H_{18}{}^{+}H$ 355.1487, found 355.1481;

IR 3480, 3361, 3051, 1625, 1594, 1476, 1443 cm^{-1};

UV-Vis λ_{abs} = 317 nm;

Fluorescence λ_{ex} = 317 nm, λ_{em} = 480 nm;

PLQY $\Phi_{soln} < 0.1\%$, $\Phi_{AIE} = 43.2\%$, $\Phi_{tf} = 20.2\%$, $\Phi_{cryst} = 34.7\%$.

AIE study of Tetrabenzo[5,7]fulvalene

From a stock solution of tetrabenzo[5,7]fulvalene (0.1 mM in THF), varying amounts of THF and deionised water were used to make a series of solutions with a total concentration of fulvalene of 0.05 mM. These solutions were freshly prepared then immediately analysed.

Single Crystal X-ray Diffraction

All crystallography data was obtained on a Bruker D8Quest diffractometer equipped with an Incoatec molybdenum microfocus source (MoKα; λ = 0.71073 Å). The data was merged and extracted using SHELXL package. The structures were solved with Olex2 program using SHELXT solution package. All non-hydrogen atoms were refined anisotropically. Atomic coordinates, bond lengths and angles and displacement parameters for tetrabenzo[5.7]fulvalene has been deposited at the Cambridge Crystallographic Data Centre (CCDC No. 1910665). This data can be obtained free-of-charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033. This data includes the CIF file for the relevant compound, which includes details of refinement procedures used for that particular structure.

NMR Spectra

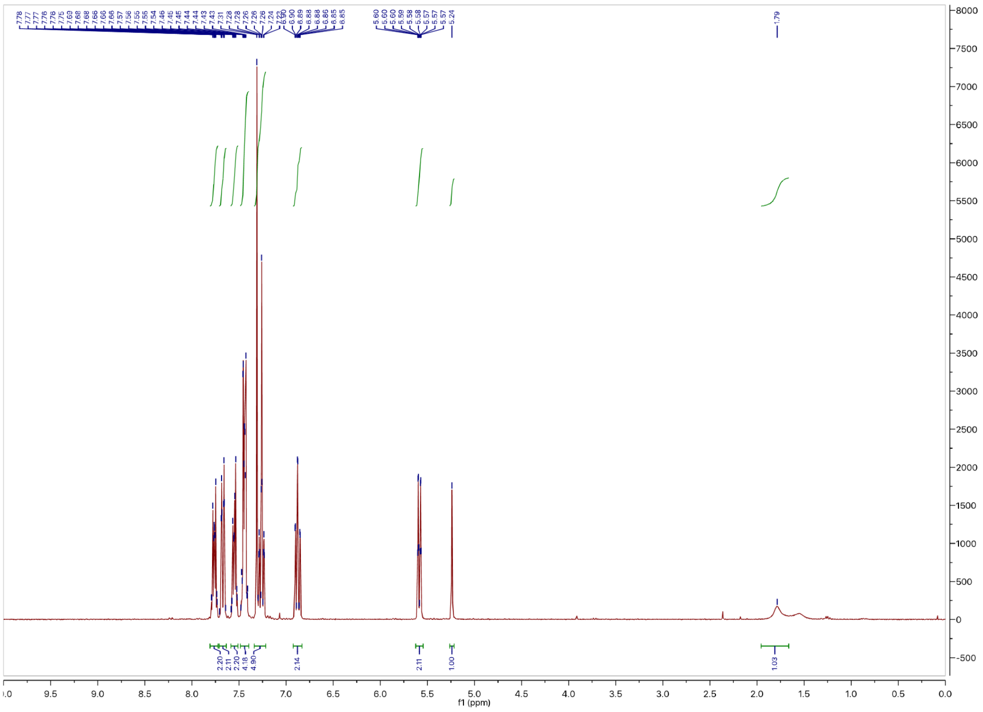


Figure S1. ^{1}H NMR ($CDCl_3$, 298K, 400 MHz) of 5-(9H-fluoren-9-yl)-5H-dibenzo[a,d]cycloheptene-5-ol

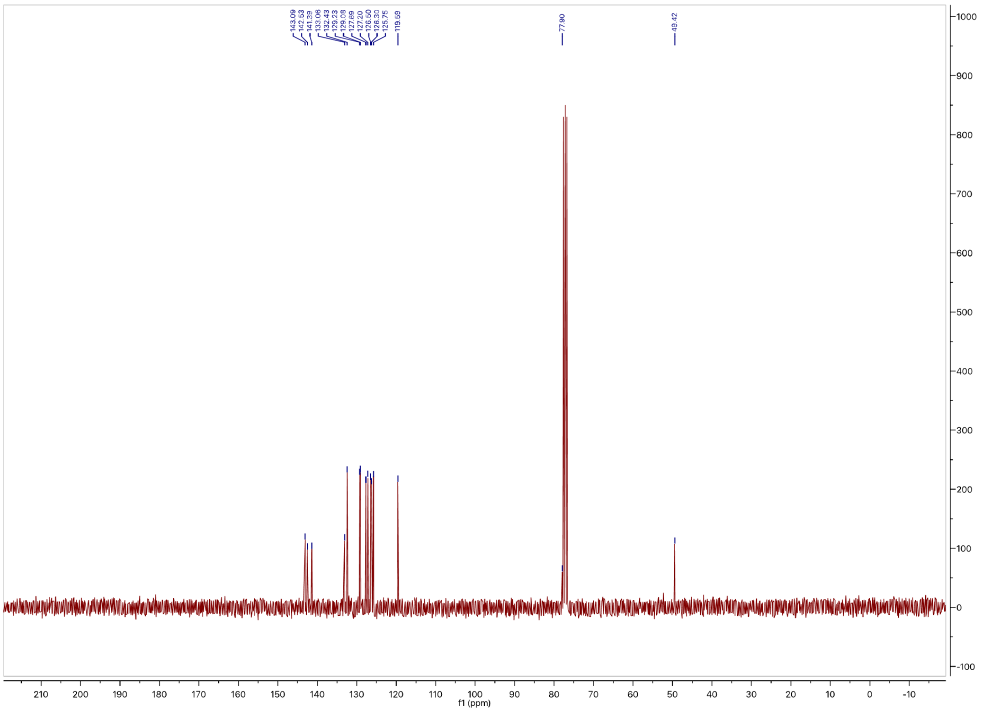


Figure S2. ^{13}C NMR ($CDCl_3$, 298K, 100 MHz) of 5-(9H-fluoren-9-yl)-5H-dibenzo[a,d]cycloheptene-5-ol

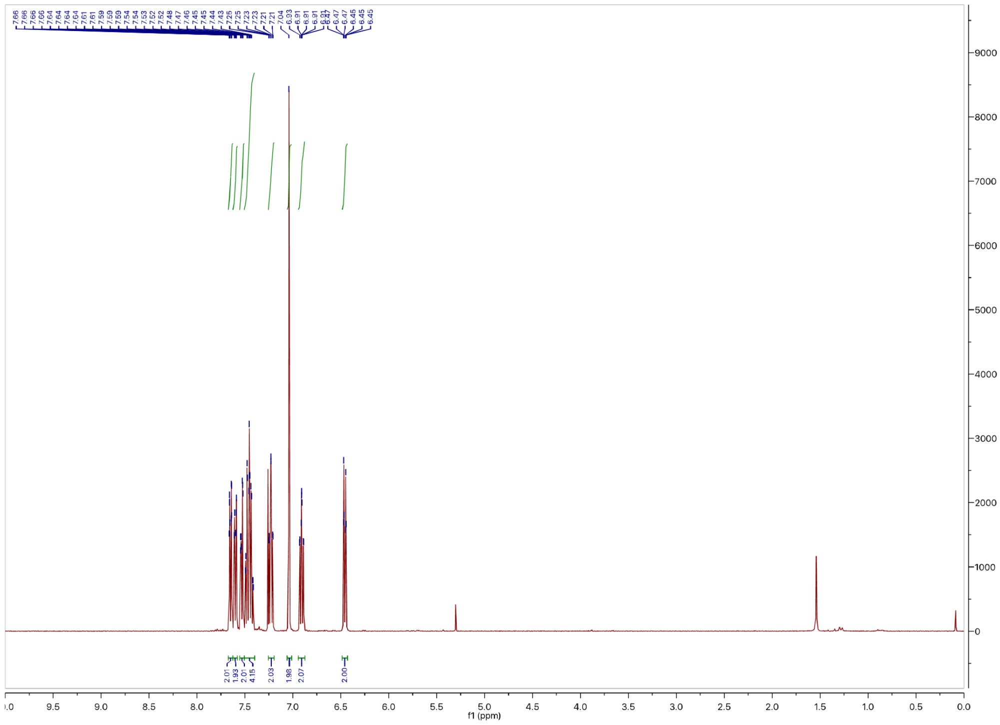


Figure S3. ^{1}H NMR ($CDCl_3$, 298K, 400 MHz) of tetrabenzo[5.7]fulvalene

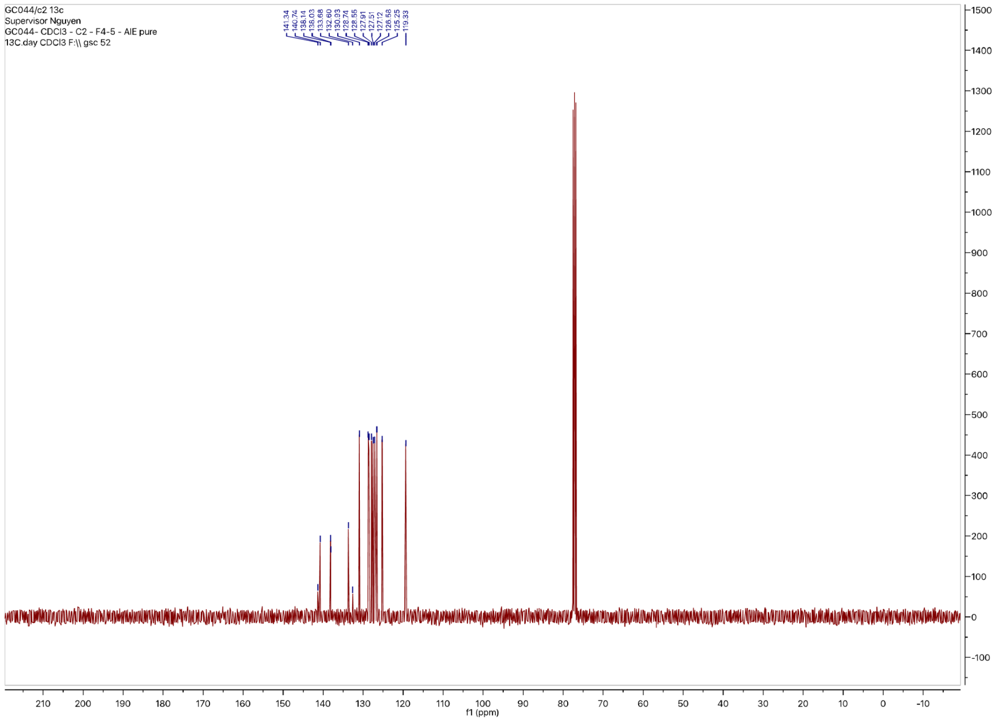


Figure S4. ^{13}C NMR ($CDCl_3$, 298K, 100 MHz) of tetrabenzo[5.7]fulvalene

UV-vis Absorption Spectra of Tetrabenzo[5.7]fulvalene in Thin-film and Crystal

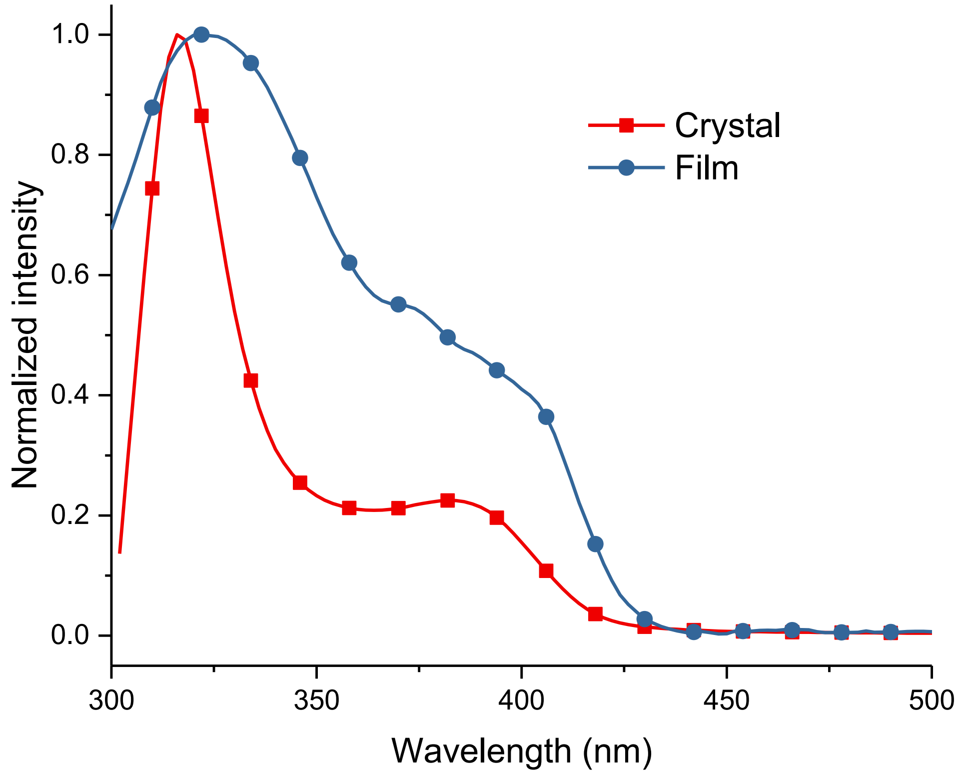


Figure S5. UV-vis absorption spectra of tetrabenzo[5.7]fulvalene **1** in thin-film and crystal

Normalised UV-visible absorption spectra of tetrabenzo[5.7]fulvalene **1** in crystalline powder and in amorphous thin film are depicted in Figure S5. The absorption spectra of the solid-state samples were converted from the reflectance spectra measured by a UV-visible spectroscopy with integrating sphere (Thermo®Scientific, EVOLUTION 220).

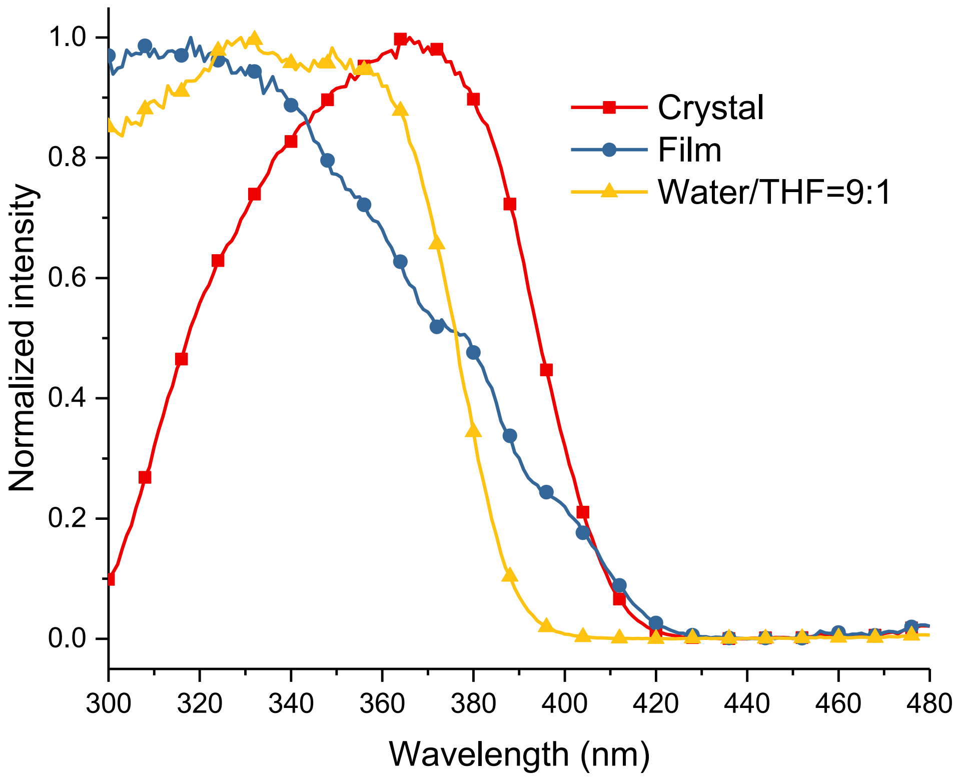


Figure S6. Excitation spectra of tetrabenzo[5.7]fulvalene **1** in crystalline powder, amorphous thin film and water/THF (9:1) blend solution.

The excitation spectrum in pure THF was omitted as the emission intensity was too low to detect. The emission detection wavelength was 500 nm. Both the absorption spectra of the amorphous film and the crystalline powder showed a new absorption band at around 385 nm, indicating the formation of a new species, which may be attributed to the aggregates of tetrabenzo[5.7]fulvalene. The absorption spectrum of the crystalline powder was sharper than the amorphous film, due to a more confined molecular configuration of tetrabenzo[5.7]fulvalene in the crystalline packing. The excitation spectra of tetrabenzo[5.7]fulvalene in crystalline powder matched with the second absorption band, suggesting the aggregates were the main source of the emission.

Excited State Lifetimes of Tetrabenzo[5.7]fulvalene

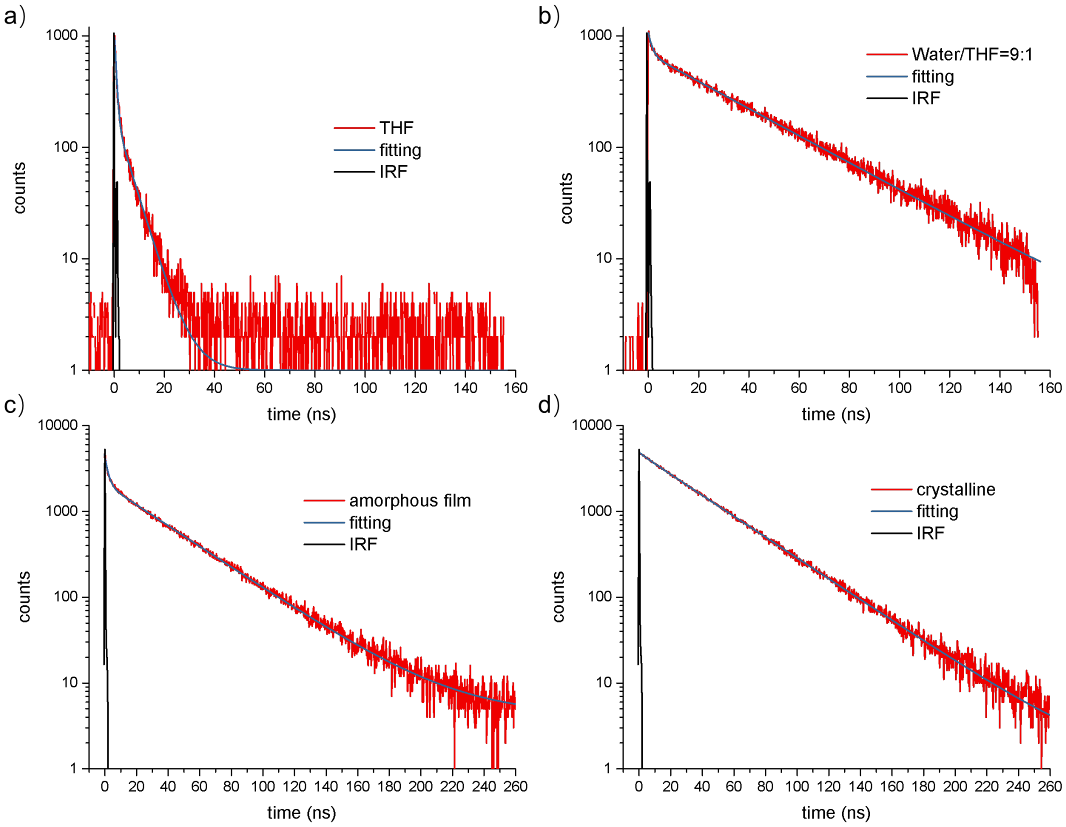
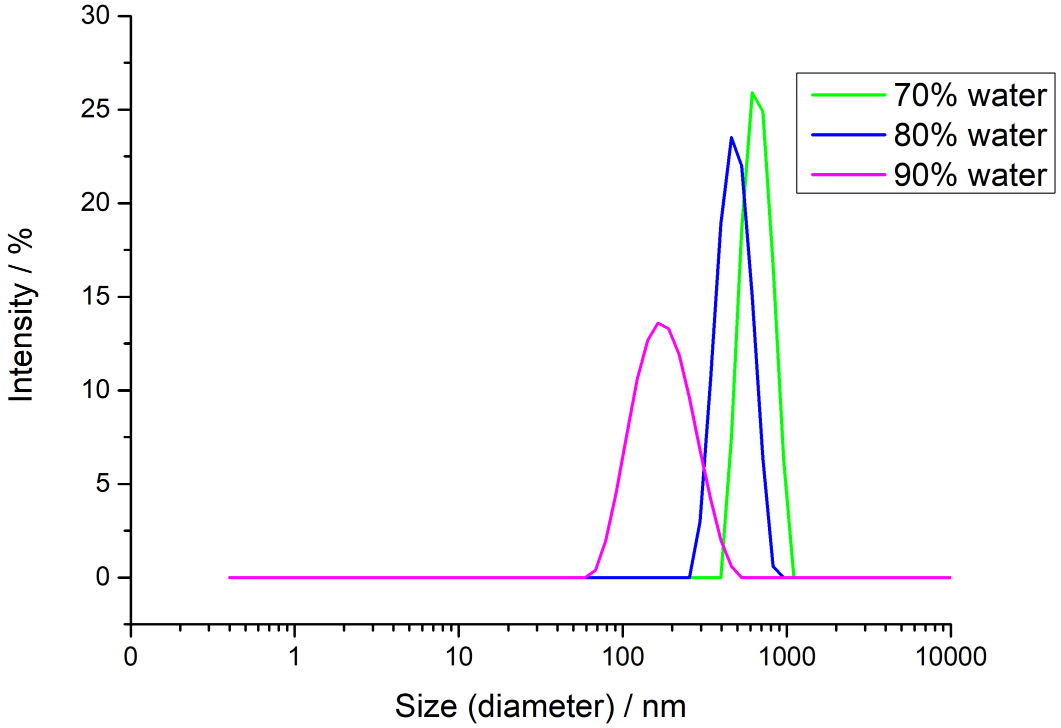


Figure S7. Fluorescence decay profiles obtained from the TCSPC measurement of tetrabenzo[5.7]fulvalene in a) 0.05 mM THF solution, b) 0.05 mM water/THF=9:1 mixture solution, c) amorphous film and d) crystalline powder.

The fluorescent lifetime of tetrabenzo[5.7]fulvalene in aggregated states were all around 32-35 ns and much longer than in the 0.05 mM THF solution (2.3 ns). This is typical for AIE-type compounds, due to the absence of the non-radiative pathway in the aggregates, leading to an increase in the fluorescent lifetime and PLQY.

Dynamic Light Scattering Analysis of Tetrabenzo[5.7]fulvalene Aggregates



Percentage of water f_w	Average size (nm)	Polydispersity
70%	832	0.317
80%	615	0.375
90%	164	0.141

Figure S8. Dynamic Light Scattering Analysis of Tetrabenzo[5.7]fulvalene Aggregates

The hydrodynamic diameters Dh of tetrabenzo[5.7]fulvalene aggregates in THF solutions with varying water content (v/v 70-90%) was determined using a Zetasizer Nano ZSP particle size analyser (laser, angle = 173°) using a 1 mL four sided quartz cuvette at 25 °C. All samples were measured at 0.1 mM concentration.