Electronic Supporting Information

Direct micro-scale monitoring of molecular aggregation, its growth and diffusion via aggregation-induced emission†

Mane Jyothi, Mari Annadhasan, Vuppu Vinay Pradeep and Rajadurai Chandrasekar*

Functional Molecular Nano/Micro Solids Laboratory, School of Chemistry, University of Hyderabad, Prof. C. R. Rao Road, Gachibowli, Hyderabad- 500 046, India.
E-mail: r.chandrasekar@uohyd.ac.in

Experimental Details

1. Materials: 2-(4-bromophenyl)acetonitrile, (4-formylphenyl)boronic acid, potassium carbonate, 1-bromo-3,5-bis(trifluoromethyl)benzene and tetrakis(triphenylphosphine) palladium were obtained from Sigma Aldrich and used as received. Column chromatography was performed using Merck silica gel (particle size 100-200 mesh). For UV-Vis and Fluorescence measurements HPLC grade solvents were used.

2. Solid-state absorbance and emission studies

The solid-state absorbance spectra were collected using a Shimadzu UV-3600 spectrometer in a diffuse reflectance UV−visible (DR−UV−vis) mode. The reflectance spectra were converted to an absorbance spectrum using the Kubelka−Munk function. The solid-state emission spectra were collected using FLUOROMAX spectrofluorimeter (HORIBA, Jobin Yvon). Spin-coating was performed on a quartz substrate using a spin coater (Laurell Technologies Corporation; model WS-400B-6NPP/LITE/8K). The solid-state quantum yield was calculated with an inbuilt integrated sphere.

3. Crystal structure analysis:

Single-crystal X-ray diffraction data were collected on a Rigaku Oxford XtaLAB ProPilatus3 R 200K-A detector system equipped with a CuKα (λ = 1.54184 Å) MicroMax-003 microfocus sealed

tube operated at 50 kV and 0.6 mA. Data were collected at 293 K, and the reduction performed using *CrysAlisPro* the structure was solved and refined using the OLEX software.

4. Structural morphology studies

The size and morphology of micro-crystals were examined by using a Zeiss field-emission scanning electron microscope (FESEM) operating at 3 kV. The samples were prepared freshly by self-assembly method and after solvent evaporation, the gold coating was carried out for imaging.

5. Confocal micro spectroscopy studies

The time-series experiments were carried out using a backscattering set-up of the Wi-Tec alpha 200 SNOM laser confocal optical microscope facility equipped with a Peltier-cooled CCD detector. 405 nm laser was used as an excitation source with maximum input power of 0.100 mW. The excitation and collection of signals from the output of the microstructure were performed by an upright microscope (20×; NA: 0.6). The output signal collection was performed using 20× objective for every 0.3 ms and the signal was sent to a CCD detector through a multimode optical fibre of diameter 100 μm (core). The time taken to complete one time series was from 0-300 s and the experiment was done multiple times and the spectra were summed up to get a new spectrum showing the accurate time for the aggregated microstructures. All measurements were performed in air and images were processed by using WI-TEC 2.0 software.

6. Fluorescence lifetime imaging microscopy (FLIM):

PL decays and PL lifetime images were recorded on a time-resolved (Micro-Time 200, Pico Quant) confocal fluorescence lifetime imaging microscopy (FLIM) setup, which was equipped with an inverted microscope (Olympus IX 71). Measurements were performed at room temperature, on a micro particles deposited cover-slip. The samples were excited by a 405 nm ps diode pulse laser (power ~ 5 μw) with a stable repetition rate of 20 MHz (FWHM: 176 ps) through a water immersion objective (Olympus UPlans Apo; 60×; NA 1.2). Signal from the samples was collected by the same objective and passed through the dichroic mirror, filtered by using a 430 nm long-pass filter to cut off any exciting light. The signal was then focused onto a 50 μm diameter pinhole to remove the out-of-focus signal, recollimated, and directed onto a (50/50) beam splitter prior to entering two single-photon avalanche photodiodes (SPADs). The data acquisition was carried out with a SymPhoTime software controlled PicoHarp 300 time-correlated single-photon counting

(TCSPC) module in a time-tagged time-resolved mode. The overall resolution of the setup was 4 ps.

5. Synthesis:

Synthesis of 3',5'-bis(trifluoromethyl)-[1,1'-biphenyl]-4-carbaldehyde (4): A mixture of 1-bromo-3,5-bis(trifluoromethyl)benzene **2** (1.5 g, 6.67 mmol), (4-formylphenyl)boronic acid **3** (1.18 g, 7.33 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.05 g, 0.004 mmol) was dissolved in 45 mL of tetrahydrofuran. After addition of 15 mL of aqueous 2N potassium carbonate solution, the reaction mixture was stirred at 85 ^{o}C and refluxed for 1 day. The cooled crude mixture was poured into 200 mL of water and extracted with ethyl acetate (150 mL), then dried over anhydrous sodium sulfate. Finally, silica gel column chromatography (n-hexane: EtOAc 3:1) gave the product as a white powder (1.55 g, 5.93 mmol) in 89% yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm]: 10.08 (s, 1H, formyl), 8.05-8.00 (m, 4H, Ar-H), 7.79 (s, 1H, Ar-H), 7.77 (d, 2H, Ar-H).

Synthesis of (Z)-3-(3',5'-bis(trifluoromethyl)-[1,1'-biphenyl]-4-yl)-2-(4-bromophenyl) acrylonitrile (1): To a solution of 3',5'-bis(trifluoromethyl)-[1,1'-biphenyl]-4-carbaldehyde **4** (1.3195 g, 5.0 mmol) and 2-(4-bromophenyl)acetonitrile **5** (1.0782, 5.5 mmol) in dry ethanol was added freshly prepared 20 ml of sodium ethoxide (1.1g, 16 mmol) solution. The reaction mixture was stirred for 40 minutes at 40 ^{o}C. After cooling to room temperature, precipitate was filtered, and washed with cold ethanol and water to give **1** as a green solid (1.38 g, 2.79 mmol) in 94% yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ [ppm]: 8.04-8.08(t, 4H, J=10 Hz, Ar-H), 7.92(s, 1H, Vinyl-H), 7.74-7.76 (d, 2H, J=10 Hz, Ar-H), 7.59-7.63 (q, 5H, J=5 Hz, Ar-H).

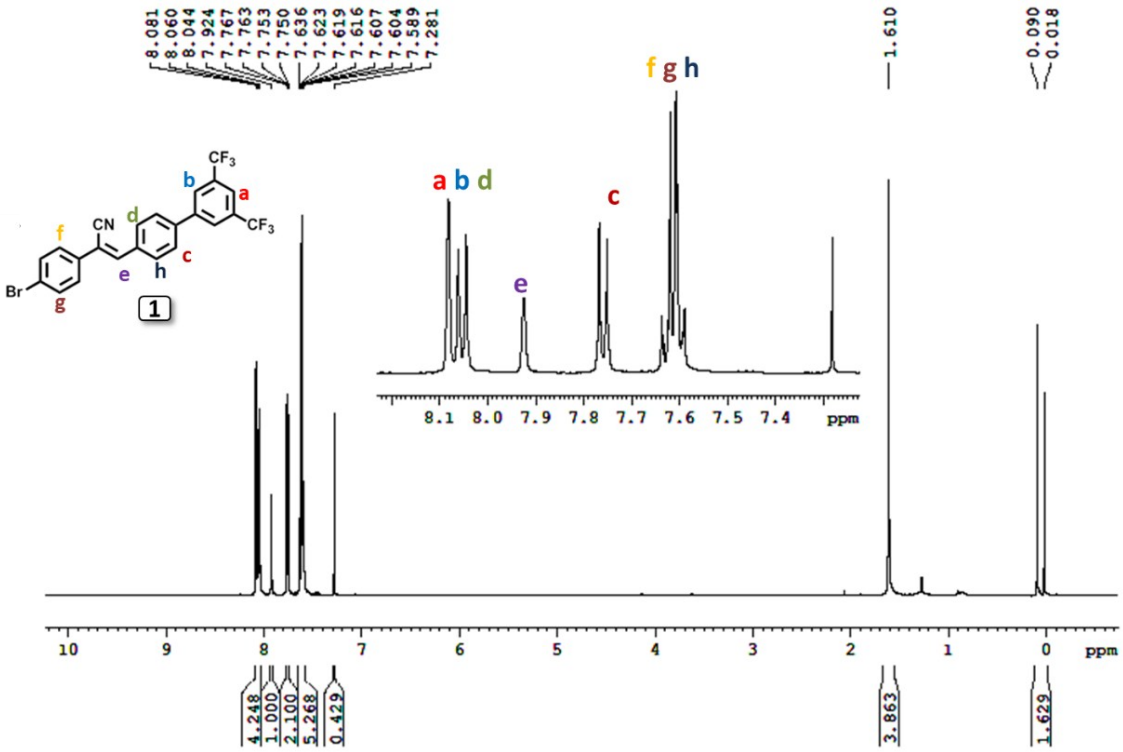

Figure S1: ^{1}H-NMR ($CDCl_3$) spectra of **1**.

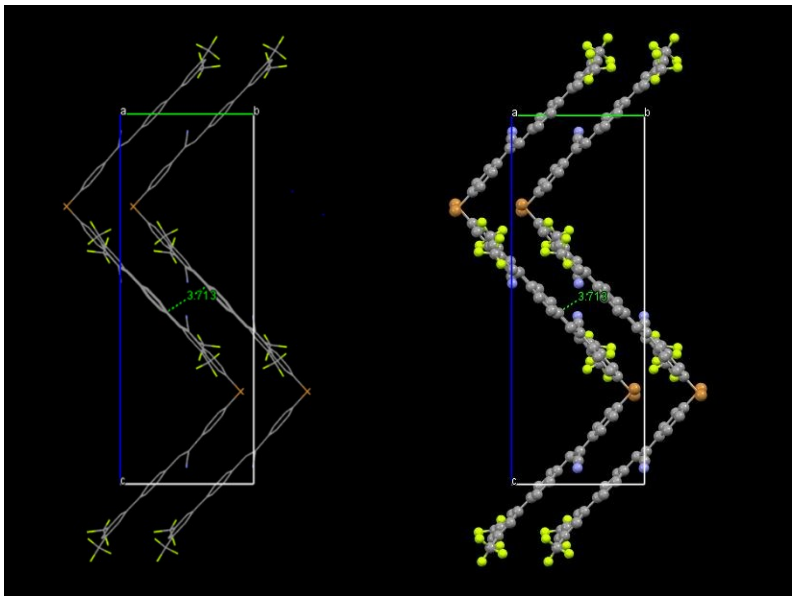

Figure S2: Solid-state packing of 1 revealing pi-pi interactions (3.713 Å).

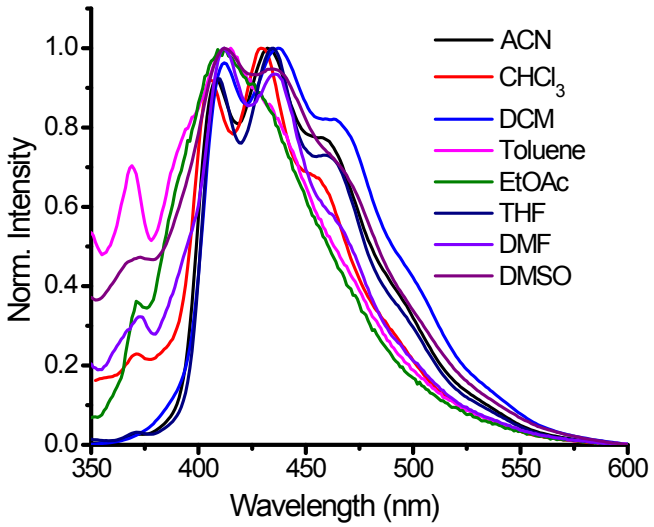

Figure S3: Fluorescence spectra of **1** in different solvents.

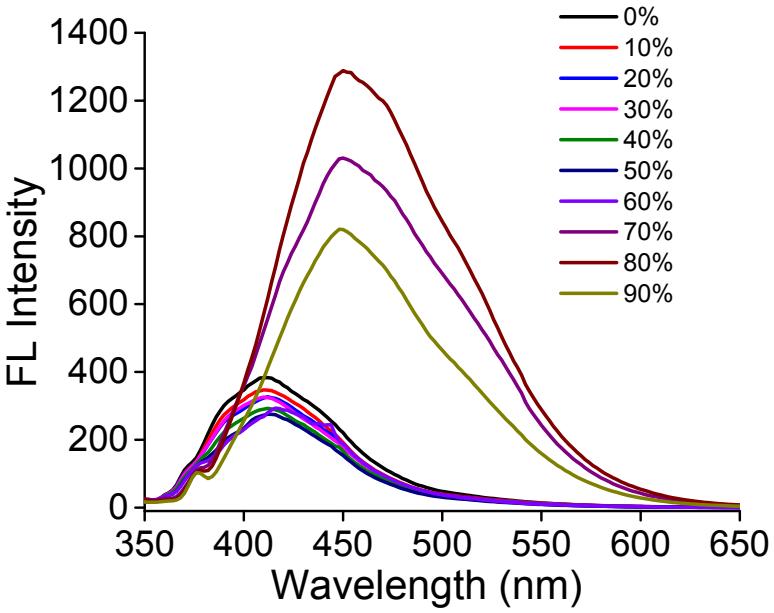

Figure S4: FL spectra of **1** in acetonitrile with different ratios of water. 90% addition of water leads to visible aggregates.

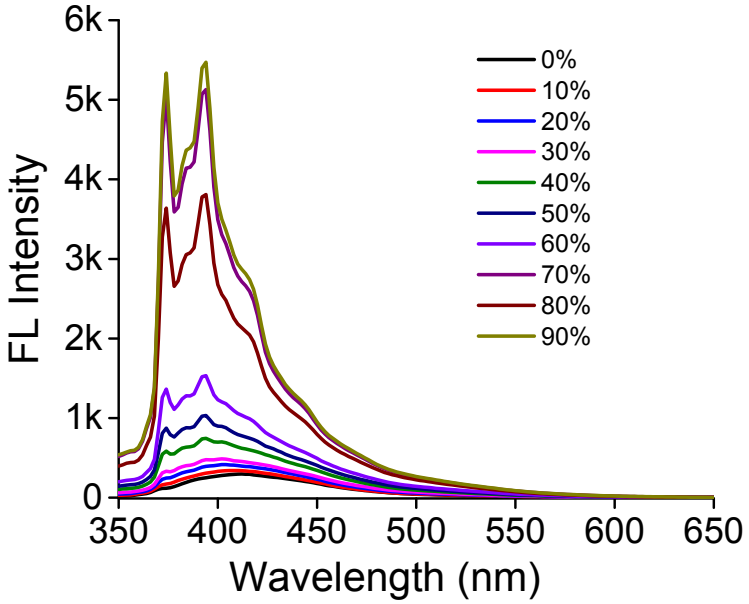

Figure S5: FL spectra of **1** with different ratios of ACN/Ethylene glycol (EG, viscosity = 16.1 mPa·s at 25°C).

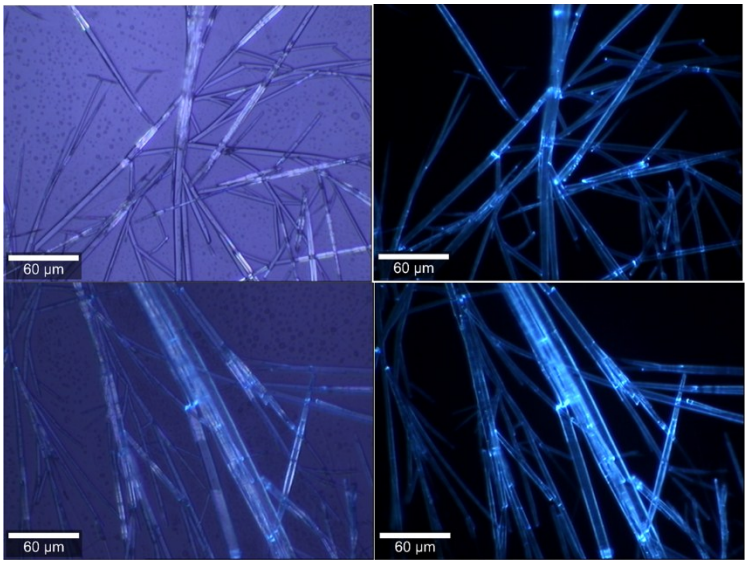

Figure S6: Optical micrographs of crystals of **1** (left) and the corresponding FL image (right).

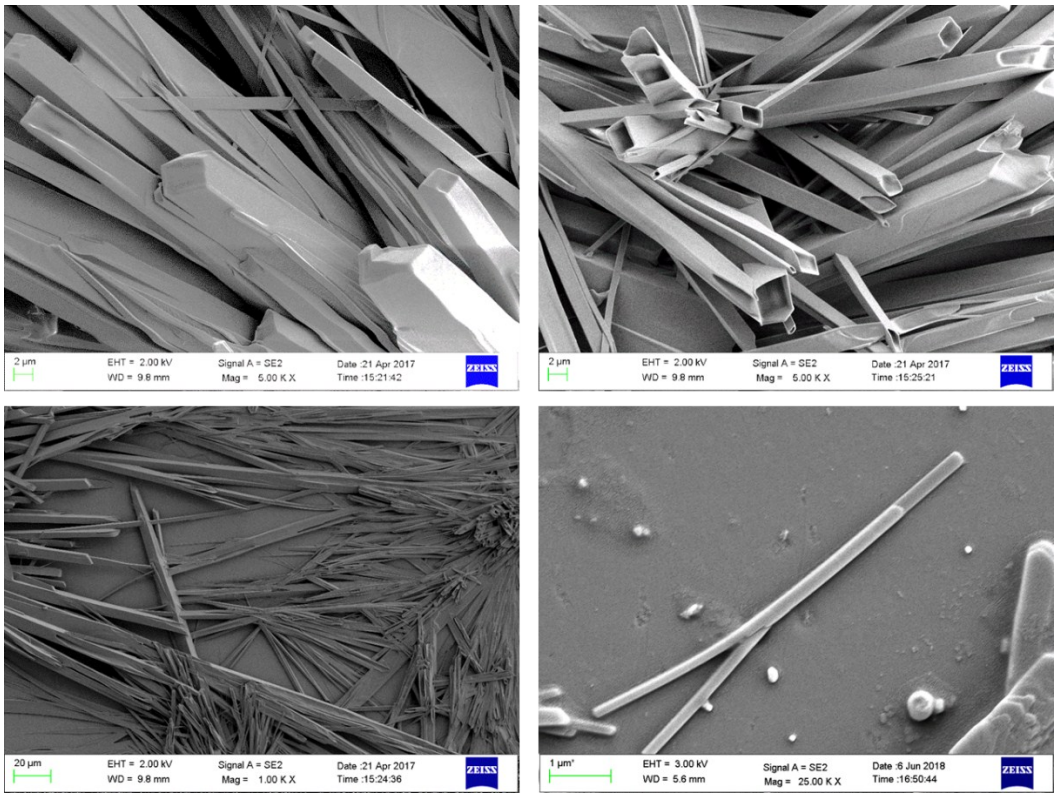

Figure S7: FESEM images of self-assembled micro-crystals of **1**.

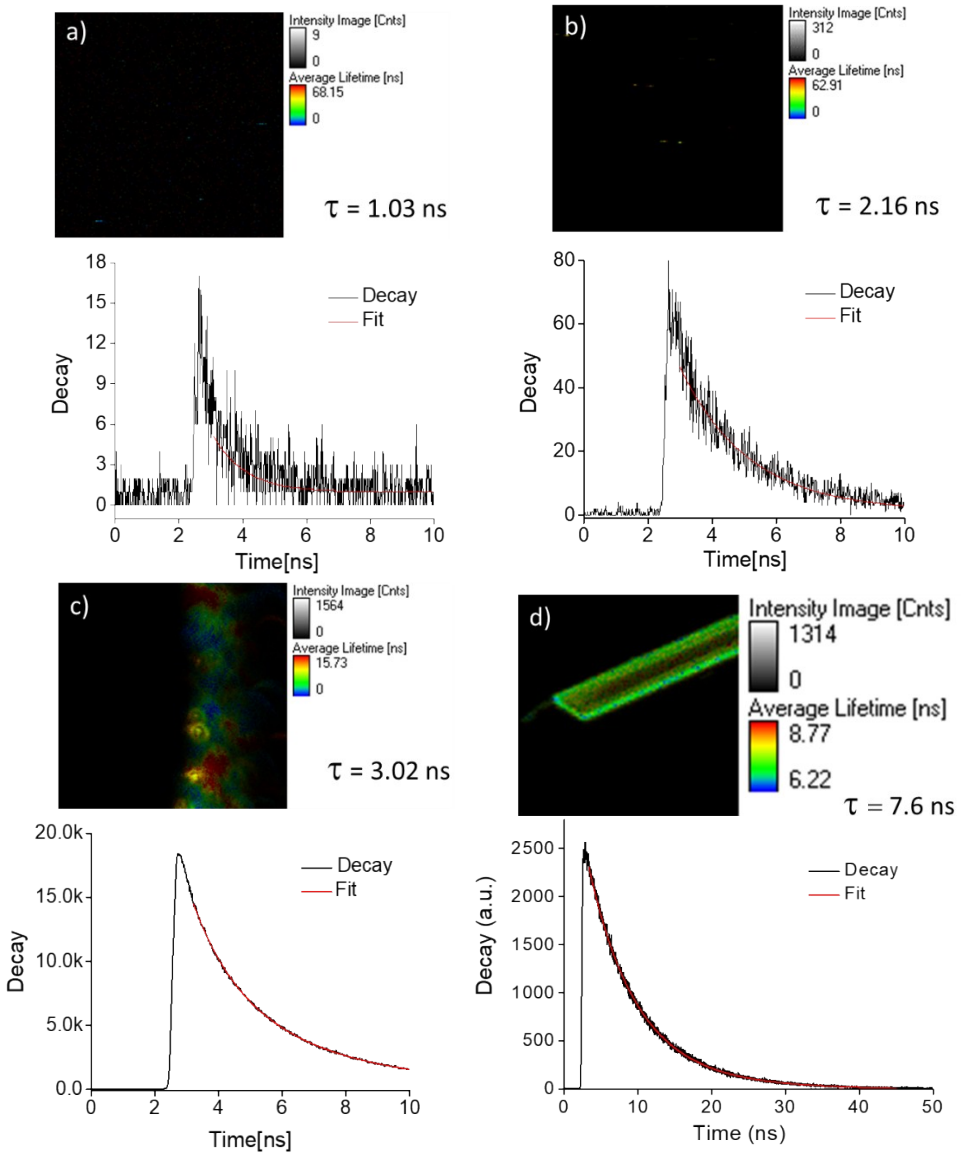

Figure S8: Time-dependent FL life-time data of molecule **1** in ACN/H_2O (1:1) at a) 2:00 min, b) 4:20 min, c) 19.00 min and d) after complete evaporation of the solvent.

The time-dependent AIE decay traces obtained from microscopic measurements reflect an average over a large distribution of local fluorescence kinetics. The fitted decay curves showed heterogeneity in the FL lifetime values not only for the growing aggregates but also for a grown single aggregate (crystal).

Table S1 Crystallographic Parameters

Compound	1
Crystal system	Monoclinic
Temperature (K)	298
Space group	C2/c
Colour	Pale green
Unit cell	a = 15.327 (4) Å b = 9.852(2) Å c = 28.274(7) Å α=90°; β=104.113°; γ =90°
Volume (Å^3)	4141.39
Density (g/cm^3)	1.674
Z, Z'	8, 0
R-Factor	7.36