Supplementary information

Unveiling emissive H-aggregates of benzocoronenediimide, their photophysics and ultrafast exciton dynamics

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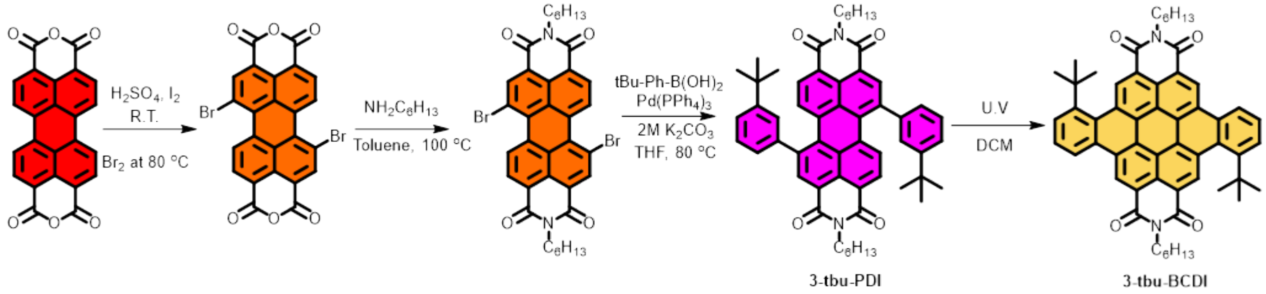
***Materials and methods*:** All solvents and general chemicals were obtained from commercial sources and used as obtained. Silica gel (200-400 mesh) was used for column chromatographic separation. Bruker 400/600 MHz spectrometer was used for ^{1}H-NMR and ^{13}C-NMR spectra. Tetramethylsilane (TMS) was used as an internal reference and residual proton in $CDCl_3$ (δ= 7.26 ppm) was used as a reference peak. MALDI-TOF (Bruker) was used for mass spectra. UV-visible spectra were obtained on Shimadzu 1800 and steady-state fluorescence spectra were recorded on a Horiba Fluoromax-4. A nano-LED-based time-correlated single-photon counting (TCSPC) spectrometer (Deltaflex, HORIBA) was used for fluorescence decay studies. Monitoring the scattered excitation light from the suspended SiO_2 particles in water gave us the instrument response function (IRF). All decay fittings were carried out using Global Fitting. Ultrafast excited state dynamics were resolved using visible-pump visible-probe transient absorption spectroscopic setup (from CDP corporation, Russia) coupled to a femtosecond amplified laser system from Amplitude Technologies, France. Briefly, samples were excited with 100 fs laser pulses at 470 nm (500 nJ/pulse energy), and transient spectra in entire visible wavelengths were recorded using a femtosecond white light continuum as probe pulse at different time delays of pump and probe pulse. Sample solution in a 1 mm thick rotating cell (absorbance ~0.2 at excitation wavelength) was placed at pump-probe overlap region. Polarizations of pump and probe beam were kept at magic angle to avoid temporal dynamics associated with depolarization dynamics. The transient spectra were corrected for the temporal chirp of probe wavelengths. The transient kinetics at different wavelengths were fitted with sum of exponentials convoluted with Gaussian instrument response function of 150 fs. All spectroscopic measurements were carried out at ambient condition and at room temperature (298K).

Synthesis and characterizations



Scheme 1: Synthesis of ***t*-But-BCDI**

Synthesis of ***t*-But-BCDI***:* In a Schlenk tube were added Br_2-PDI (0.120 g, 0.17 mmol), 3-tert-butylphenylboronic acid (0.064 g, 0.36 mmol), K_2CO_3 (0.52 g, 0.36 mmol) and $Pd(PPh_3)_4$ (30 mg, 0.028 mmol). The Schlenk tube was capped with rubber septum and then evacuated. THF (3 mL) and water (0.5 mL) were added via syringe. The Schlenk tube was evacuated and purged with argon three times. The reaction mixture was heated to 80 °C for 18 hours, and the progress of the reaction was monitored by TLC. Afterward, the reaction mixture was extracted with DCM, and the organic layer was dried with sodium sulfate and concentrated. The crude compound (**3-t-BuPDI**) was dissolved in DCM (100 mL) and exposed to UV-visible light at room temperature to synthesize the title compound (24 h). The compound was then purified through column chromatography using DCM, resulting in the isolation of the pure ***t*-But-BCDI** as an orange solid with a yield of 99%. ***t*-But-BCDI** is poorly soluble in common organic solvents. Melting point above 200 °C; ^{1}H-NMR (600 MHz, $CDCl_3$, *δ ppm*): 9.63 (s, 1H), 9.57 (s, 1H), 8.88 (s, 1H), 8.73 (d, 1H, *J* = 9 Hz), 8.57 (s, 1H), 8.07 (d-d, 1H, *J* = 9.6 Hz), 8.03 (d, 1H, *J* = 8.4 Hz), 7.82 (d, 1H, *J* = 8.4 Hz), 7.55 - 7.50 (m, 2H), 7.33 (s, 1H), 7.2 (d, 1H, *J* = 6.6 Hz), 4.39 – 4.37 (t, 2H, *J* = 7.8 Hz), 4.31 – 4.28 (t, 2H, *J* = 7.8, 8.4 Hz), 1.93 – 1.88 (m, 2H), 1.85 – 1.80 (m, 2H), 1.75(s, 9H), 1.68 – 1.51 (m, 3H), 1.45 – 1.39 (m, 8H), 1.30 (s, 8H), 0.95 – 0.92 (q, 6H); FTIR (cm^{-1}): 2969, 2922, 2847, 1707, 1652, 1605, 1442, 1333, 1252, 776; MALDI-TOF mass calcd. For $C_{56}H_{54}N_2O_4$ (819.04) found 819 (M^+).

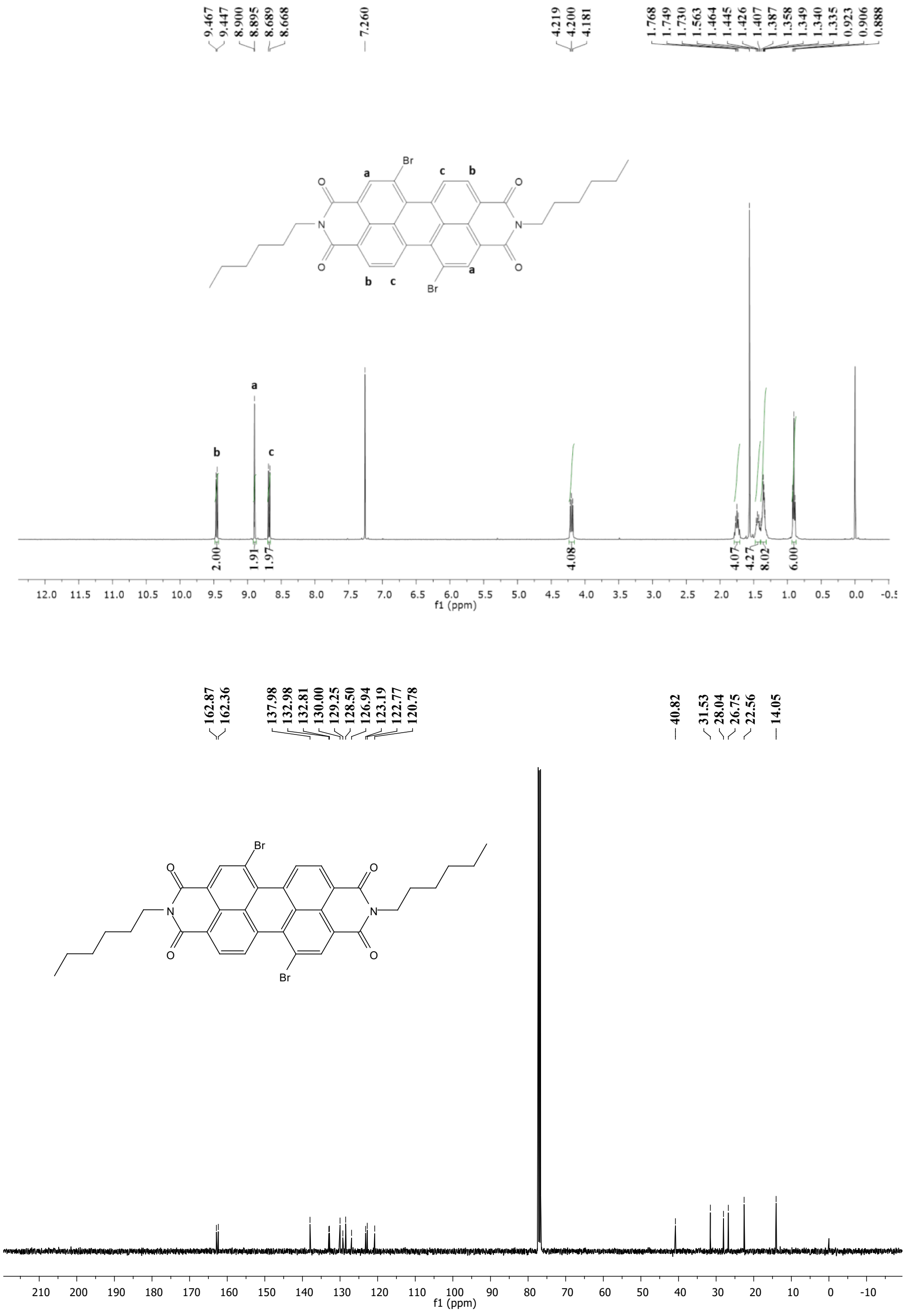


Figure SI 1: ^{1}H-NMR (above) and ^{13}C-NMR (below) spectra of **Br_2-PDI** in $CDCl_3$.

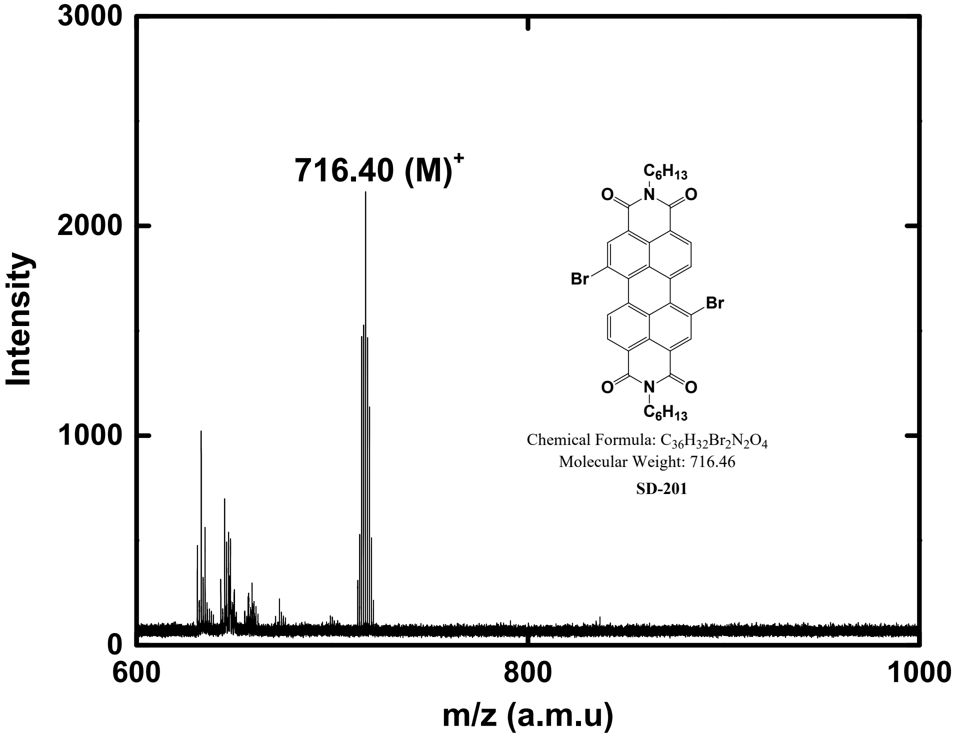


Figure SI 2: MALDI – TOF spectra of **Br_2-PDI.**

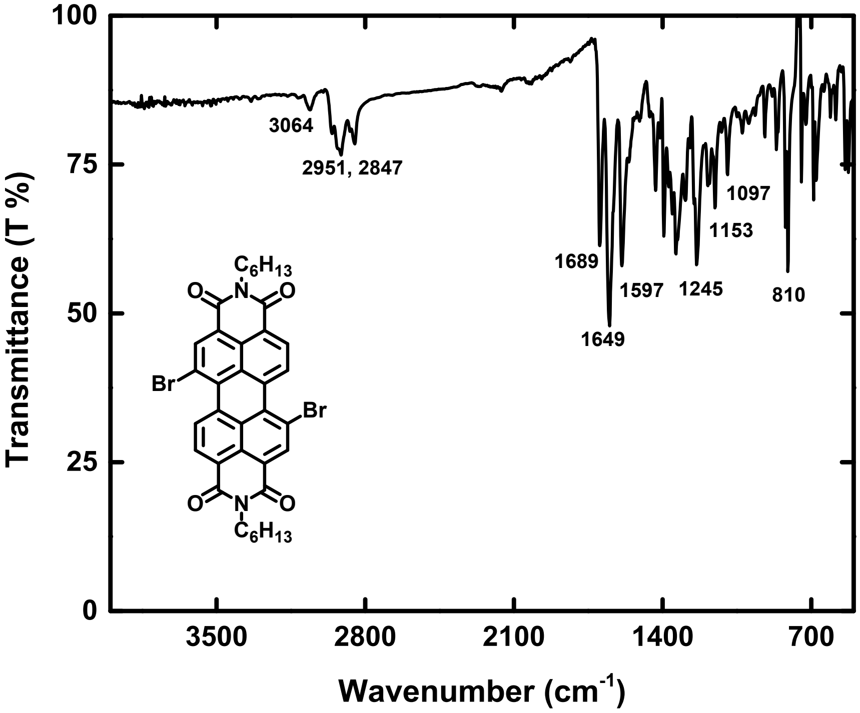


Figure SI 3: FTIR spectra of **Br_2-PDI**

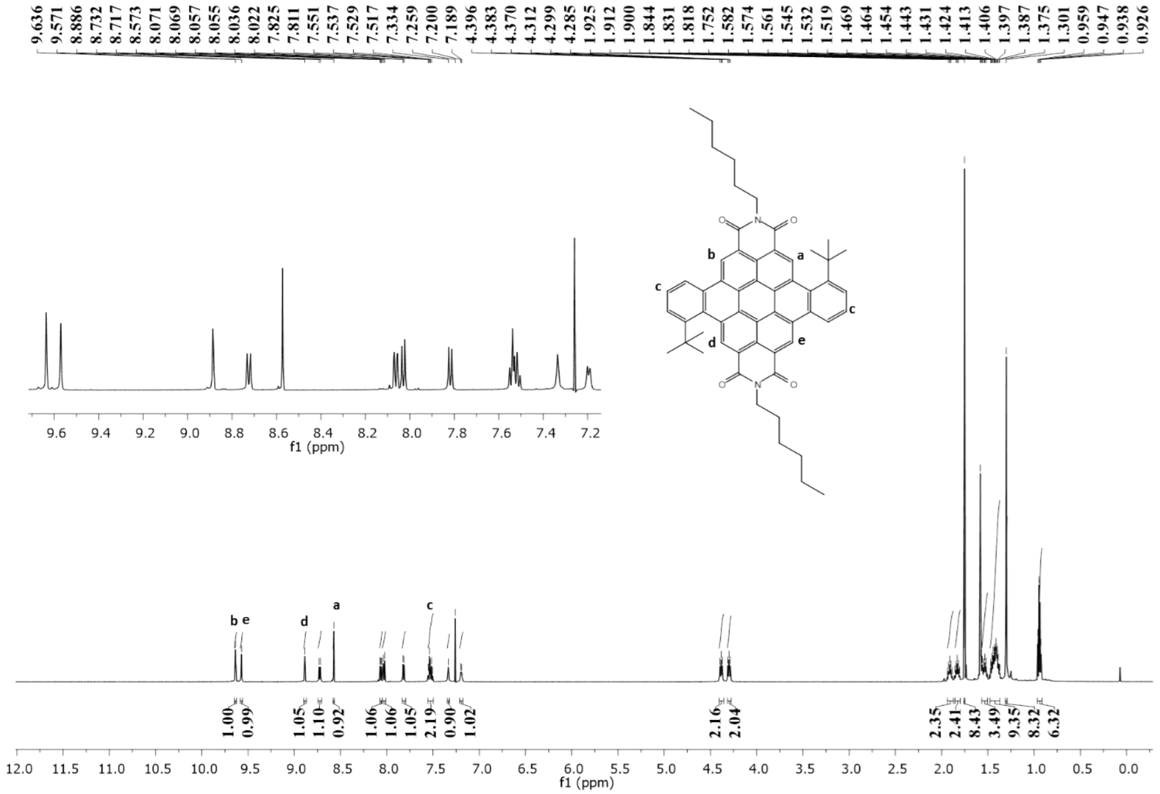


Figure SI 4: ^{1}H-NMR of ***t*-But-BCDI** in CDCl$_3$

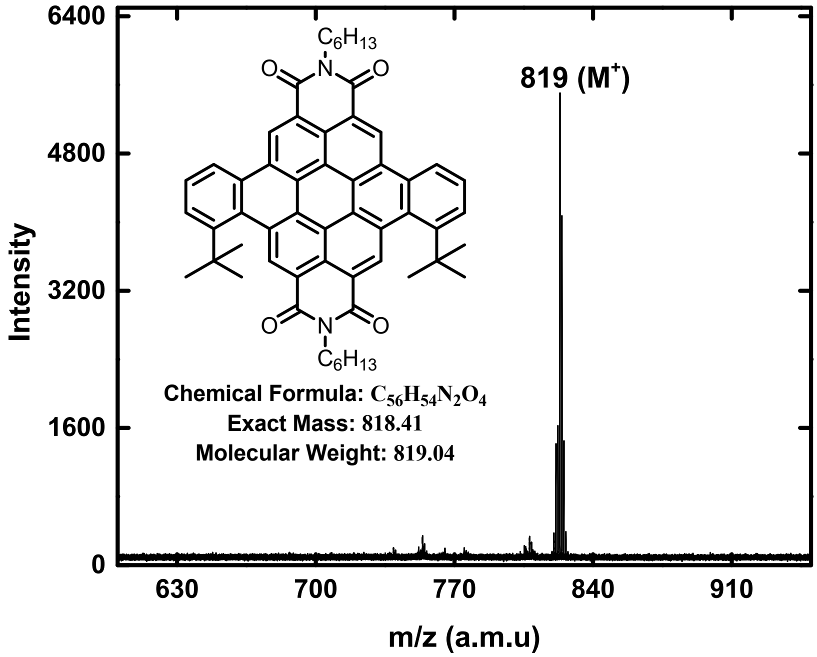


Figure SI 5: MALDI – TOF spectra of ***t*-But-BCDI**

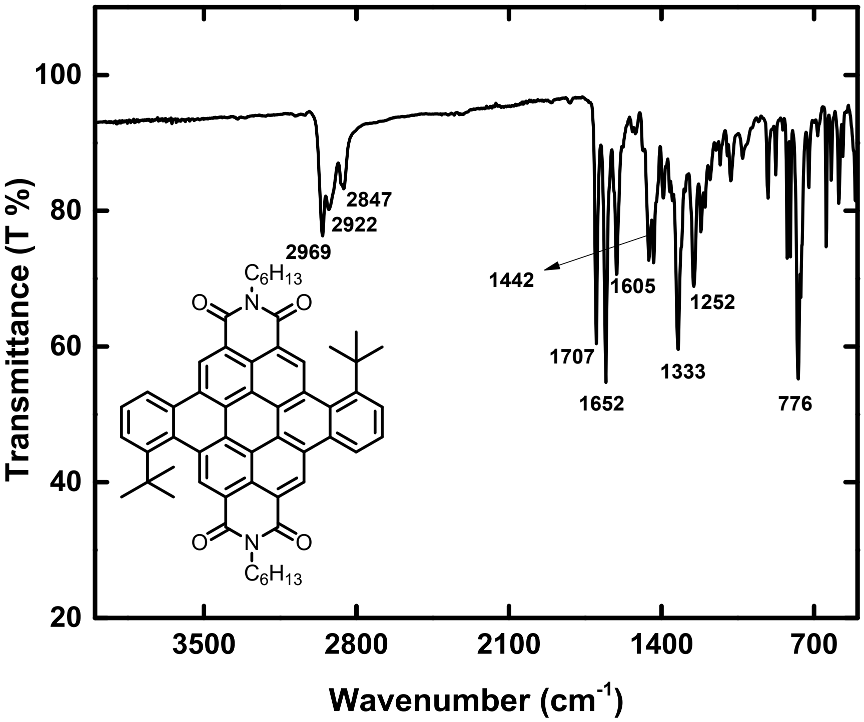


Figure SI 6: FTIR spectra of ***t*-But-BCDI**

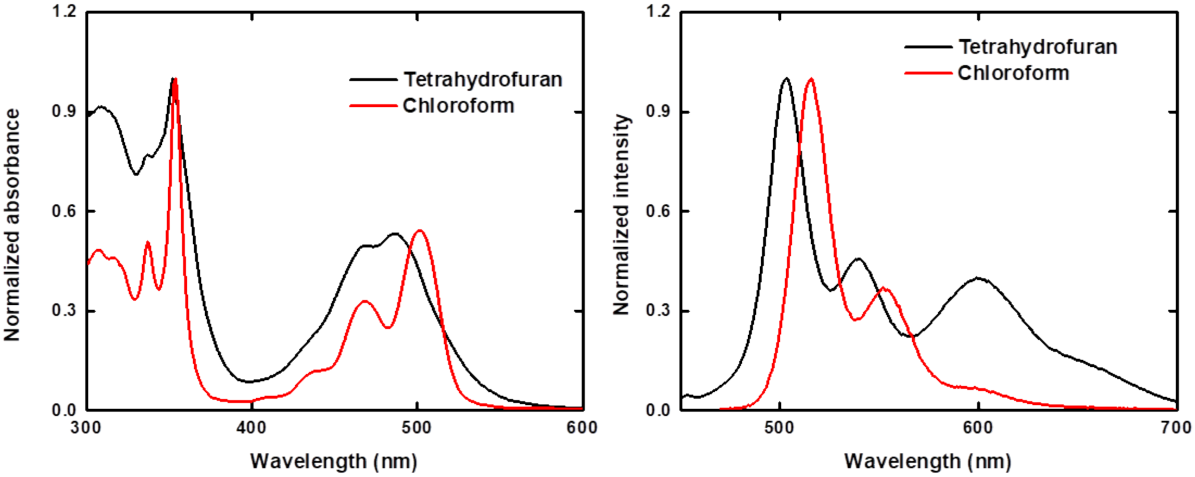


Figure S7: Absorption and emission spectra of ***t*-But-BCDI** in $CHCl_3$ and THF.

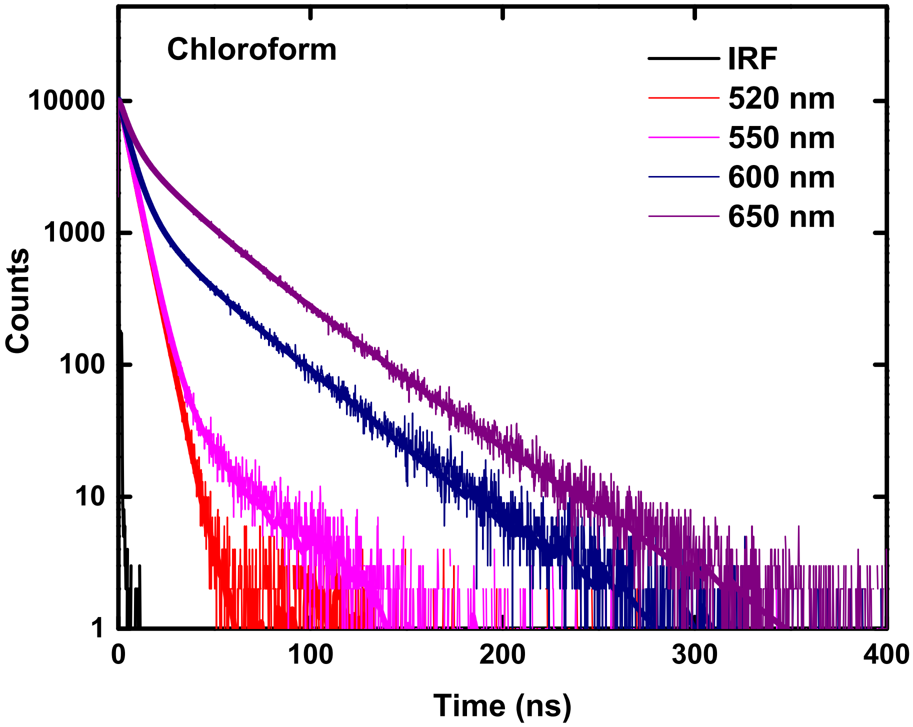


Figure S8: Fluorescence lifetime decay of ***t*-But-BCDI** in Chloroform

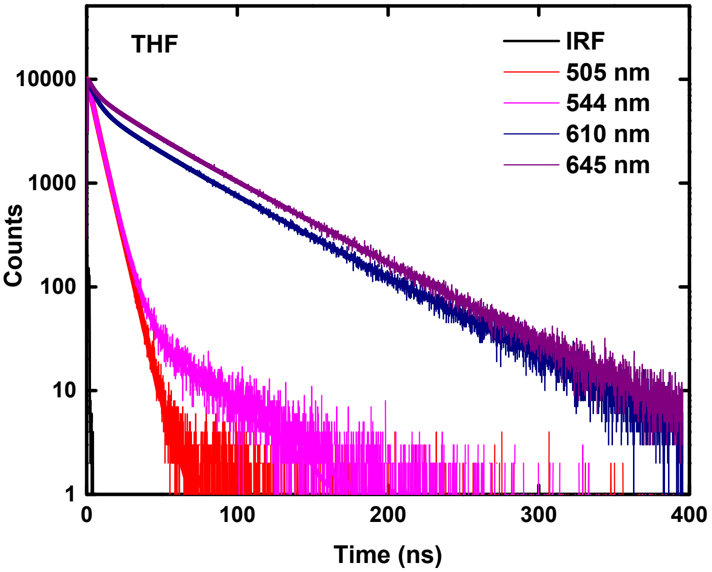


Figure S9: Fluorescence lifetime decay of ***t*-But-BCDI** in THF

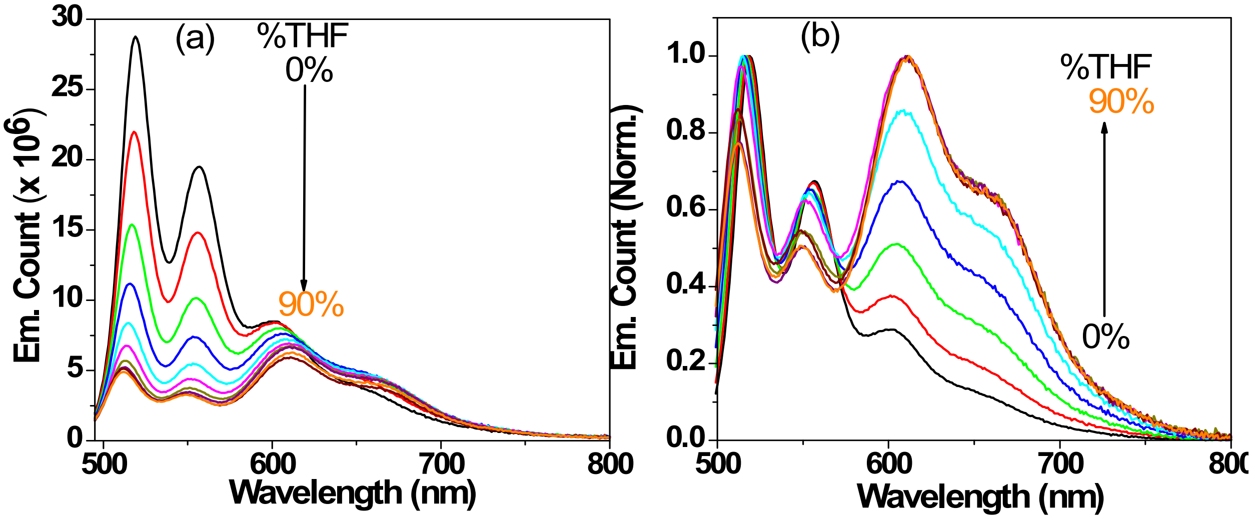


Figure S10: (a) Emission spectral change of ***t*-Bu-BCDI** as a function of solvent composition in chloroform/THF mixture. (b) Peak normalized emission spectra. Sample concentration was kept ~5 μM for all measurement and excitation wavelength was 480 nm.

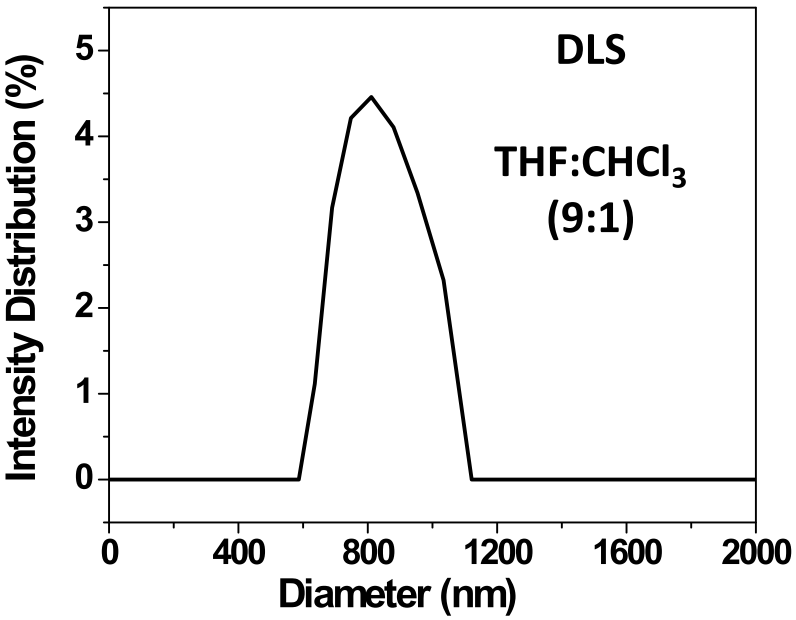


Figure S11: Size distribution of aggregates measured by Dynamic light scattering of ***t*-But-BCDI** in THF: $CHCl_3$ (9:1)