

Supporting information

Effect of Differential Self-Assembly on Mechanochromic Luminescence of Fluorene-Benzothiadiazole based Fluorophores

Karattu Chali Naeem^{†,‡}, Kadaikkara Neenu[†], Vijayakumar C. Nair^{,†,‡}*

[†] Photosciences and Photonics Section, CSIR-National Institute for Interdisciplinary Science and Technology (NIIST), Trivandrum 695 019, India.

[‡] Academy of Scientific and Innovative Research (AcSIR), CSIR-NIIST Campus, Thiruvananthapuram 695019, Kerala, India.

E-mail: cvijayakumar@niist.res.in

Table of contents

Scheme S1: Synthesis of **FB-C6** and **FB-C12**.

Figure S1: Absorption spectra, emission spectra and time-resolved fluorescence decay profile of **FB-C6** and **FB-C12** recorded in various solvents.

Figure S2: Changes in emission and absorption spectra of **FB-C6** and **FB-C12** in DMF-water mixture.

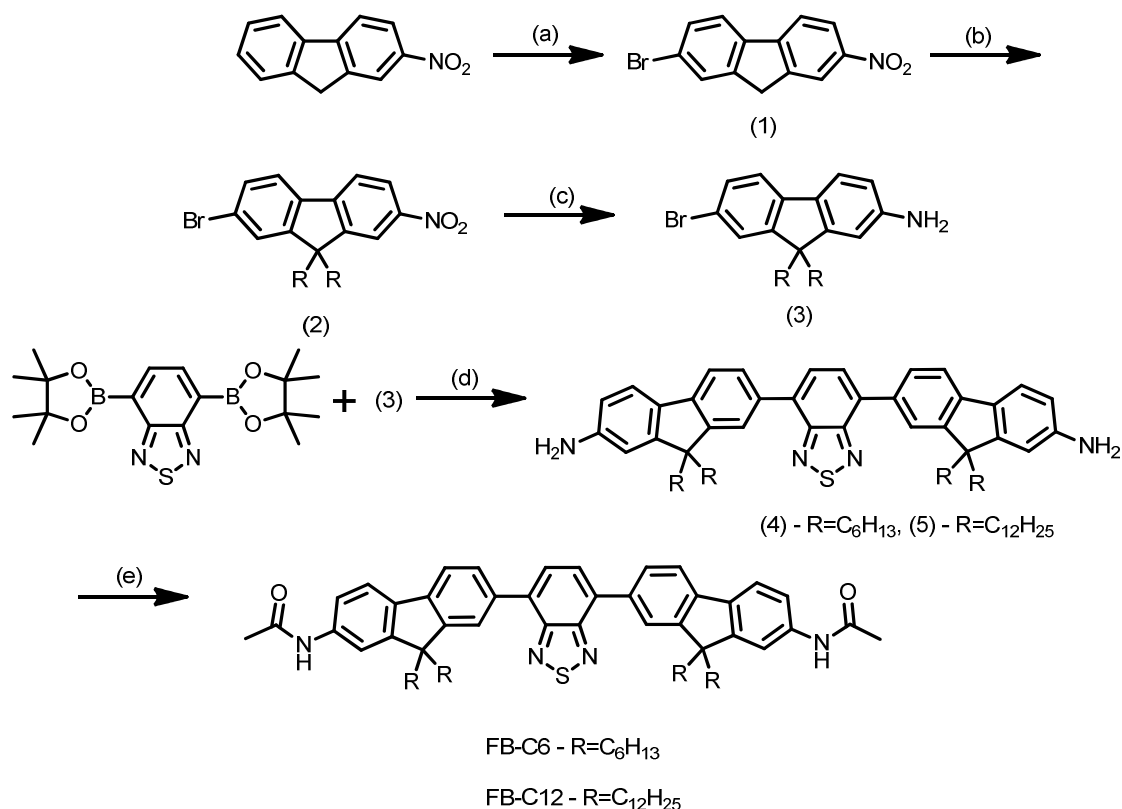
Figure S3: Time-resolved fluorescence decay profile of **FB-C6** and **FB-C12** in the presence of 0% and 20% water fraction.

Figure S4: Solid state absorption spectra of pristine and ground samples of **FB-C6** and **FB-C12**.

Figure S5: Powder x-ray diffraction pattern of **FB-C6** and **FB-C12** at different conditions.

Table S1: Fluorescence lifetime of **FB-C6** and **FB-C12** before and after grinding.

Synthesis and characterization: **FB-C6** and **FB-C12** were synthesized in good yields by Suzuki coupling of 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole with 7-bromo-9,9-dialkyl-9*H*-fluoren-2-amine followed by amide formation reaction with acetic acid. Both compounds were characterized by ¹H NMR, ¹³C NMR, FT-IR and mass spectrometry (see ESI for details of synthesis and characterization). They were soluble in common organic solvents such as toluene, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF) etc. 2-Bromo-7-nitro-fluorene,¹ 2-Bromo-7-nitro-9,9-didodecylfluorene and 2-bromo-7-amino-9,9-dihexylfluorene are previously reported by Takeuchi *et al.*² We followed the same procedure and characterized the molecules by ¹H NMR, ¹³C NMR and Mass spectral analysis.



Scheme S1: Synthesis of **FB-C6** and **FB-C12**; *Reagents and conditions:* (a) Br₂, CH₂Cl₂; (b) RBr, KOH, KI, DMSO, rt, 12h; (c) SnCl₂, EtOH:EtOAc (1:1), Reflux, 3d; (d) Pd(PPh₃)₄, K₂CO₃, THF, H₂O, reflux, 2d; (e) Acetic acid, *N,N*-diisopropylethylamine, HATU, CH₂Cl₂, 0 °C to rt, 8h.

Synthesis of 2-bromo-7-nitro-9,9-dihexylfluorene (2):

Compound 2 was prepared by following the procedure reported by Takeuchi *et al.*² 2-Bromo-7-nitrofluorene (12.0 g, 41.30 mmol, 1.0 equiv.) was added to a mixture of powdered KOH (9.3 g, 165.20 mmol, 4.0 equiv.) and KI (1.0 g, 6.20 mmol, 0.15 equiv.) in DMSO (105 mL). 1-Bromohexane (21.7g, 86.73 mmol, 2.1 equiv.) was then added and stirred for 8 h. After extraction with water/CH₂Cl₂, the organic layer was washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the crude oily product was

purified by column chromatography (silica gel, 25% CHCl₃-hexane). The pure product was obtained as pale yellow viscous liquid. Yield: 63%; ¹H NMR (500 MHz, CDCl₃): δ [ppm] = 8.26 (d, J = 8 Hz, 1H), 8.20 (s, 1H), 7.74 (d, J = 8.5 Hz, 1H), 7.65 (d, J = 8.5 Hz, 1H), 7.54 (d, J = 7Hz, 2H), 1.96-2.02 (m, 4H), 1.28-1.59 (m, 12H), 0.77- 0.88 (m, 6H), 0.53-0.61 (m, 4H). ¹³C NMR (125MHz, CDCl₃): δ [ppm] = 14.13, 22.61, 23.86, 29.65, 31.62, 39.98, 56.02, 118.30, 119.96, 122.48, 123.43, 123.70, 126.59, 130.73, 137.73, 146.45, 147.41, 151.63, 154.40; HRMS: m/z = 457.1698 (calc. =457.16).

Synthesis of 2-bromo-7-amino-9,9-dihexylfluorene (3):

Compound 3 was also prepared by following the procedure reported by Takeuchi *et al.*² 2-Bromo-7-nitro-9,9-dihexylfluorene (6.2 g, 10.00 mmol, 1.0 equiv.) was dissolved in a degassed mixture (1:1) of EtOH/EtOAc (36 mL) by stirring under Ar atmosphere. SnCl₂ (15.0 g, 80.00 mmol, 8.0 equiv.) was added to this and the reaction mixture was refluxed for 3 days. After adding 1M NaOH, the resultant white precipitate was filtered off and washed with EtOAc. The filtrate was then extracted with 1M NaOH, washed with water and followed by brine. The combined organic fractions were dried over anhydrous Na₂SO₄, solvent removed under reduced pressure and the crude product was purified by column chromatography (silica gel, 75% CHCl₃-hexane). The pure product was obtained as light brown colored oil. Yield: 95%; ¹H NMR (500 MHz, CDCl₃): δ [ppm] = 7.46 (d, J = 8 Hz, 1H), 7.35 (m, 3H), 6.74 (m, 2H), 3.76 (s, 2H), 1.85 - 1.90 (m, 4H), 1.0-1.25 (m, 12H), 0.76-0.78 (m, 6H), 0.58-0.61 (m, 4H). ¹³C NMR (125 MHz, CDCl₃): δ [ppm] = 14.16, 22.77, 23.71, 29.36, 30.08, 40.55, 55.13, 109.68, 114.15, 119.07, 119.67, 120.59, 125.87, 129.63, 131.46, 140.63, 146.18, 152.11, 152.35; HRMS: m/z = 427.1932 (calc. = 427.19).

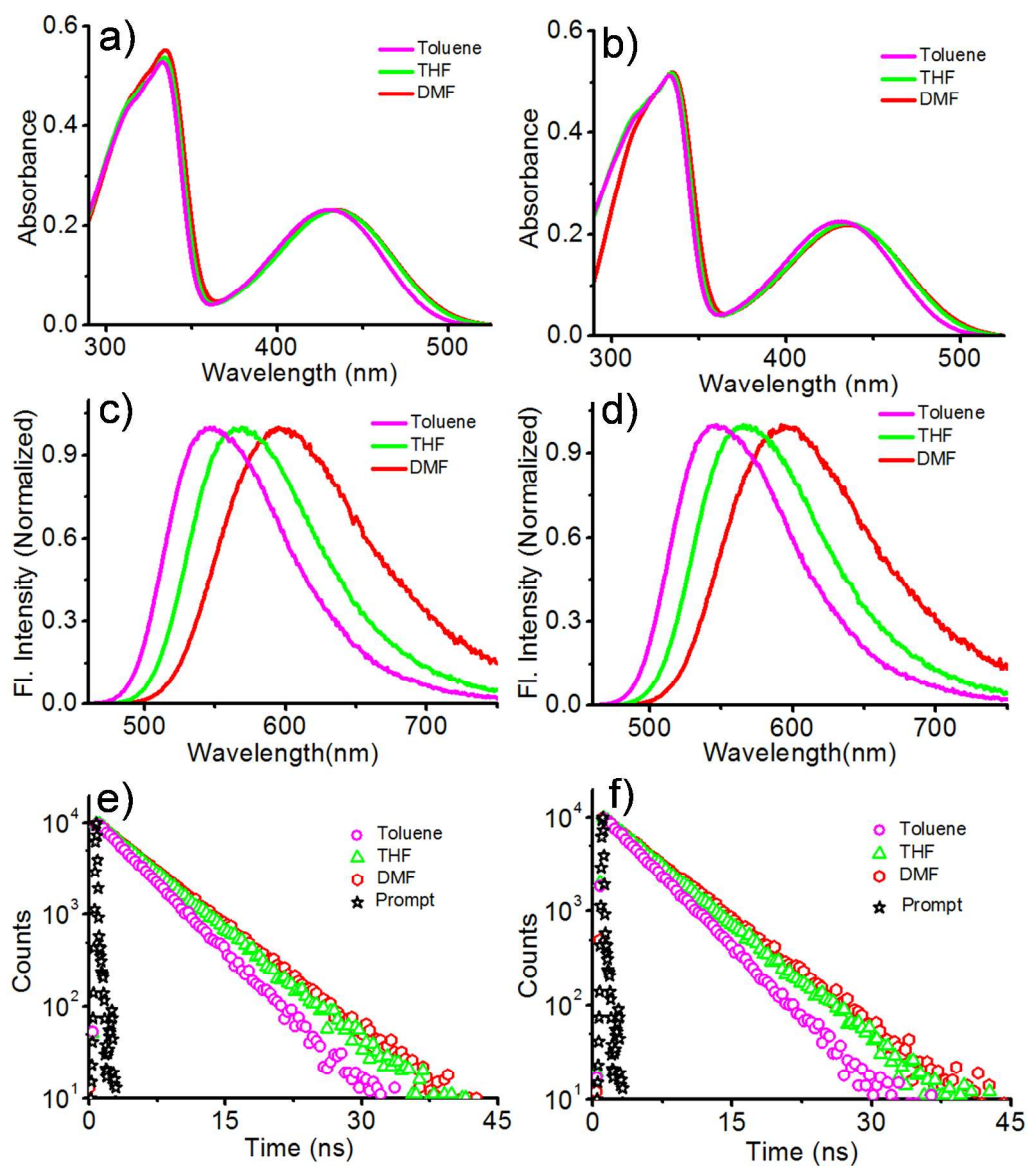


Figure S1: Absorption spectra of a) **FB-C6** and b) **FB-C12**; emission spectra of c) **FB-C6** and d) **FB-C12**; time-resolved fluorescence decay profile of e) **FB-C6** and f) **FB-C12** recorded in various solvents.

Aggregation in DMF-Water mixture

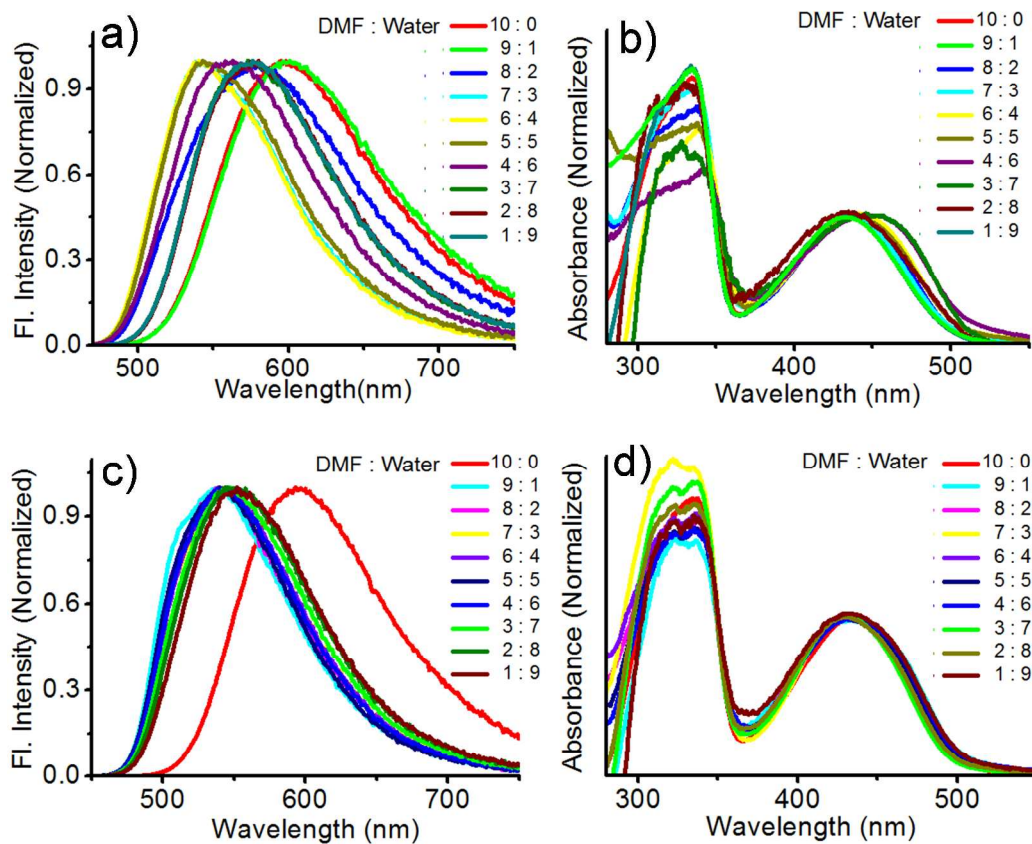


Figure S2: Changes in emission spectra of a) **FB-C6** and c) **FB-C12**; corresponding absorption spectra of b) **FB-C6** and d) **FB-C12** in DMF-Water mixture at different ratios. (Conc. = 2×10^{-5} M; $\lambda_{\text{ex}} = 430$ nm; $l = 10$ mm).

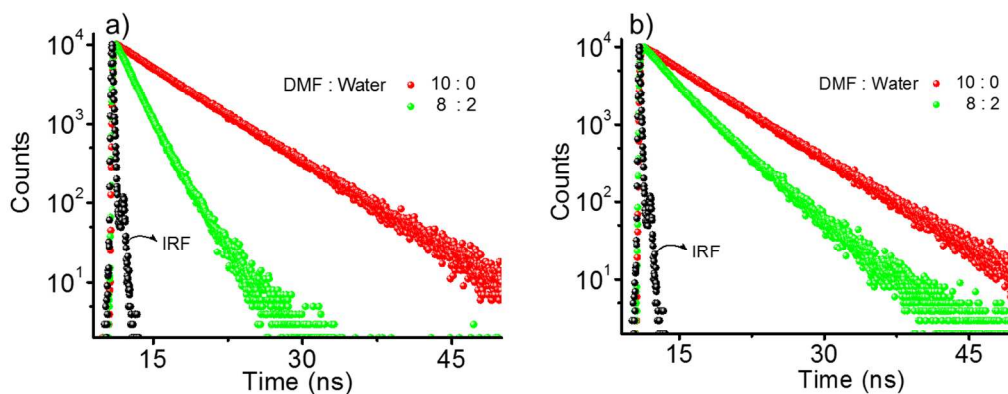


Figure S3: Time-resolved fluorescence decay profile of a) **FB-C6** and b) **FB-C12** in the presence of 0% and 20% water fraction (conc. = 2×10^{-5} M).

The time resolved fluorescence lifetime of **FB-C6** and **FB-C12** molecules in DMF (conc. = 2×10^{-5} M) in the presence of 0% and 20% water fraction (both molecules exhibit significant quenching in the presence of 20% water fraction) were monitored and compared. At 0% water fraction, **FB-C6** and **FB-C12** exhibited monoexponential decay with lifetime of 5.52 and 5.57 ns respectively, whereas, the decay becomes biexponential and the average lifetime was reduced to 1.65 ns and 3.16 ns, respectively. This indicates the proximity of the chromophores due to aggregation facilitates non-radiative decay of the excited state.

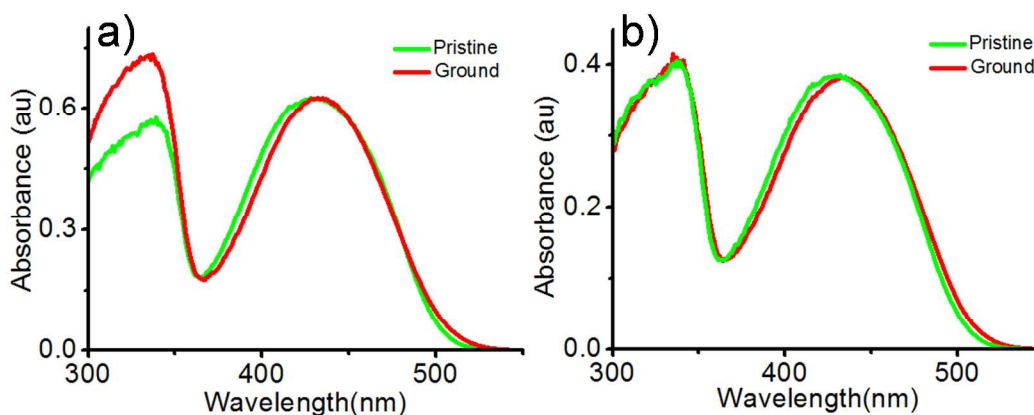


Figure S4: Solid state absorption spectra of pristine and ground samples of a) **FB-C6** and b) **FB-C12**

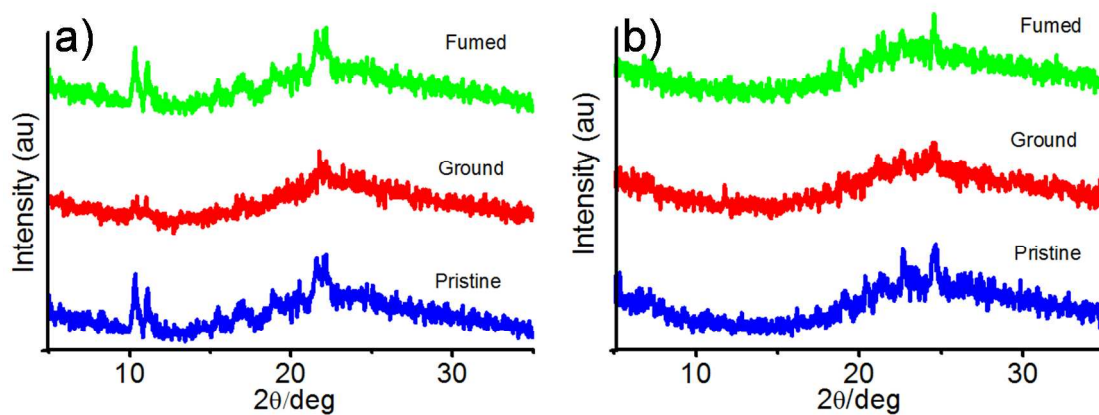


Figure S5: Powder X-ray diffraction pattern of a) **FB-C6** and b) **FB-C12** under different conditions

Table S1: Fluorescence lifetime of **FB-C6** and **FB-C12** before and after grinding

Compounds	Before grinding		After grinding	
	τ (ns)	τ_{av} (ns)	τ (ns)	τ_{av} (ns)
FB-C6	1.86 (60%),	3.35	2.20 (27%),	4.50
	4.33 (40%)		4.89 (71%), 5.41 (2%)	
FB-C12	1.47(64%),	2.87	2.95 (45%),	4.10
	3.83 (36%)		1.23 (10%), 4.90 (45%)	

References:

- (1) Saroja, G.; Pingzhu, Z.; Ernsting, N. P.; Liebscher, J. Synthesis of Alkylated Aminofluorenes by Palladium-Catalyzed Substitution at Halofluorenes. *J Org Chem* **2004**, *69* (3), 987–990.
- (2) Balan, B.; Vijayakumar, C.; Ogi, S.; Takeuchi, M. Oligofluorene-Based Nanoparticles in Aqueous Medium: Hydrogen Bond Assisted Modulation of Functional Properties and Color Tunable FRET Emission. *J Mater Chem* **2012**, *22* (22), 11224–11234.