

# An unusual one-donor-two-acceptors interaction in a pair of covalently bridged naphthalenediimide dimers

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## I. Materials and methods

Reagents were received from Sigma Aldrich Chemical Co. and used without further purification. Solvents were purchased from commercial sources and purified following reported protocol.<sup>1</sup> Spectroscopic grade solvents were used for physical studies.

NMR spectra were measured on AVANCE III 500 BRUKER spectrometer and the data were calibrated against TMS.

UV/visible absorption spectroscopy was performed on a Perkin-Elmer Lambda 35 spectrometer.

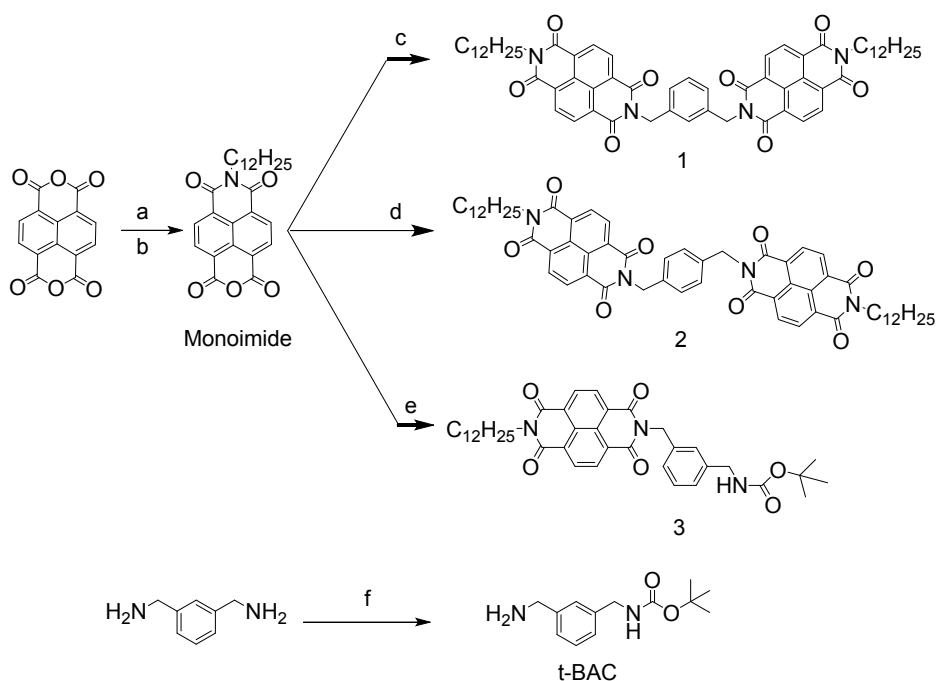
Photoluminescence studies were performed on a Perkin-Elmer LS55 spectrophotometer.

Mass spectrometric data were acquired using an electron spray ionization (ESI) technique on a MASSLYNX 4.0 (WATER Micromass Q-ToF-micro™ (+ve) mode mass spectrometer (Micro mass).

FT-IR spectra were recorded in KBr pellets on a Perkin Elmer Spectrum 100 FT-IR spectrometer.

Time resolved fluorescence decay experiments were carried out using a time-correlated single-photon counting (TCSPC) spectrometer (5000, IBH). 408 nm Laser was used as the excitation source and an MCP photomultiplier was used as the detector. The instrument response function (IRF) was detected by placing a scatterer, and the FWHM of the IRF was 70 ps.

## II. Syntheses scheme



a)  $C_{12}H_{25}NH_2$ , 1:1 PrOH/ $H_2O$ , 343K, Ar b) Glacial AcOH reflux c) m-xylenediamine, DMF, 393K  
d) p-xylenediamine, DMF, 393K e) t-BAC, DMF 393K f) di-tert-butyl dicarbonate,  $CHCl_3$ , 273K, 16 hr

### III. Syntheses details and characterization

#### Monoimide

The synthesis is based on the reported procedure<sup>2</sup>, which was significantly modified. n-Dodecylamine (12 mmol, 2.224g) was added to a suspension of 1,4,5,8-naphthalenetetracarboxylic dianhydride (3.73 mmol, 1g) in a mixture of water (10 ml) and n-propanol (10 ml) at RT, under Ar flow. The suspension was heated to 343K for 24 hr to obtain a brown precipitate. The reaction mixture was cooled down to RT and acidified to pH 1 with 5 ml c. HCl, and further stirred for 1 h at RT. The solid was filtered off and stirred in acetic acid (50 ml) at reflux condition for 1 hr. to a form deep brown solution. The mixture was then refrigerated overnight to ensure complete precipitation. The crude product was extracted in CH<sub>2</sub>Cl<sub>2</sub> (200 ml) and washed with water (200 ml). The organic layer was collected, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and reduced in volume under reduced pressure. Addition of ethanol (50 ml) and evaporation of CH<sub>2</sub>Cl<sub>2</sub> gave a suspension of the desired product in ethanol, which was filtered off, washed with ethanol, hexane and ether. The raw product obtained at this stage was used for subsequent reactions without further purification.

#### Compound 1

Monoimide (2 mmol, 0.871g) was taken in a 100 ml round-bottom flask with DMF (20 ml) and stirred under Ar atmosphere at 328 K for 30 mins until the suspension turned into a clear solution. To this a solution *m*-xylenediamine (1 mmol, 0.136g) in 2 ml DMF was slowly added with stirring. The entire system was refluxed under Argon at 393K for 4 hours. The progress of the reaction was monitored using TLC. After another 2hr the reaction mixture was refrigerated to obtain a brown precipitate that was washed with cold methanol and hexane. Resulting mixture was purified using column chromatography (Silica gel 100-200 mesh)(Yield: 0.048g, 2.4 %).<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, TMS):  $\delta$  (ppm) = 8.74 (8H, m), 8.01 (1H, s), 7.83-7.77 (2H, dd  $J$  = 20Hz), 7.49 (1H, t,  $J$  = 10 Hz), 5.44 (4H, s), 4.19 (4H, m), 1.75-1.69 (4H, m), 1.41-1.22 (36 H, m), 0.86 (6 H, t,  $J$  = 6.0 Hz); <sup>13</sup>CNMR (CDCl<sub>3</sub>)  $\delta$  (ppm) = 162.68, 162.83, 162.80, 137.62, 136.68, 135.16, 131.28, 130.88, 130.36, 129.29, 126.87, 126.20, 43.48, 40.99, 31.86, 29.58, 29.29, 29.53, 29.47, 29.29, 29.26, 28.01, 27.03, 22.63, 14.08. ESI-MS (MeOH, 0.1% DMSO):  $m/z$  (Calc): C<sub>60</sub>H<sub>66</sub>N<sub>4</sub>O<sub>8</sub> [M] 970.4881; found: 970.4836[M]<sup>+</sup>, 969.4800[M-H]<sup>+</sup>. Anal. Calc. for C<sub>60</sub>H<sub>66</sub>N<sub>4</sub>O<sub>8</sub>: C, 74.20 ; H,6.85; N, 5.77% found C, 74.22 ; H,6.83 ; N, 5.79%. Melting point >250 °C

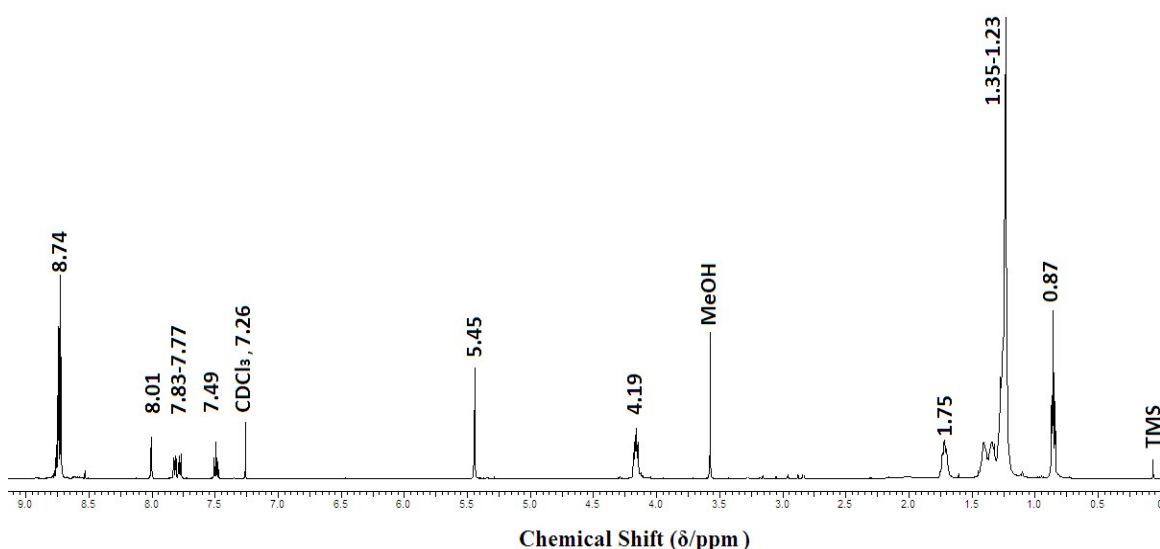


Figure S1:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298K) spectrum of 1

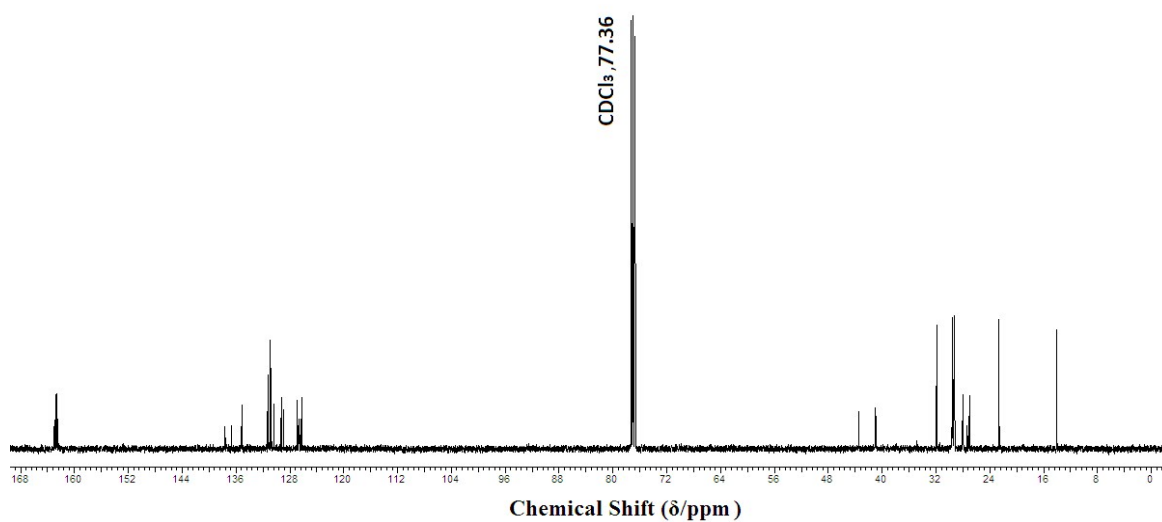


Figure S2:  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 298K) of 1

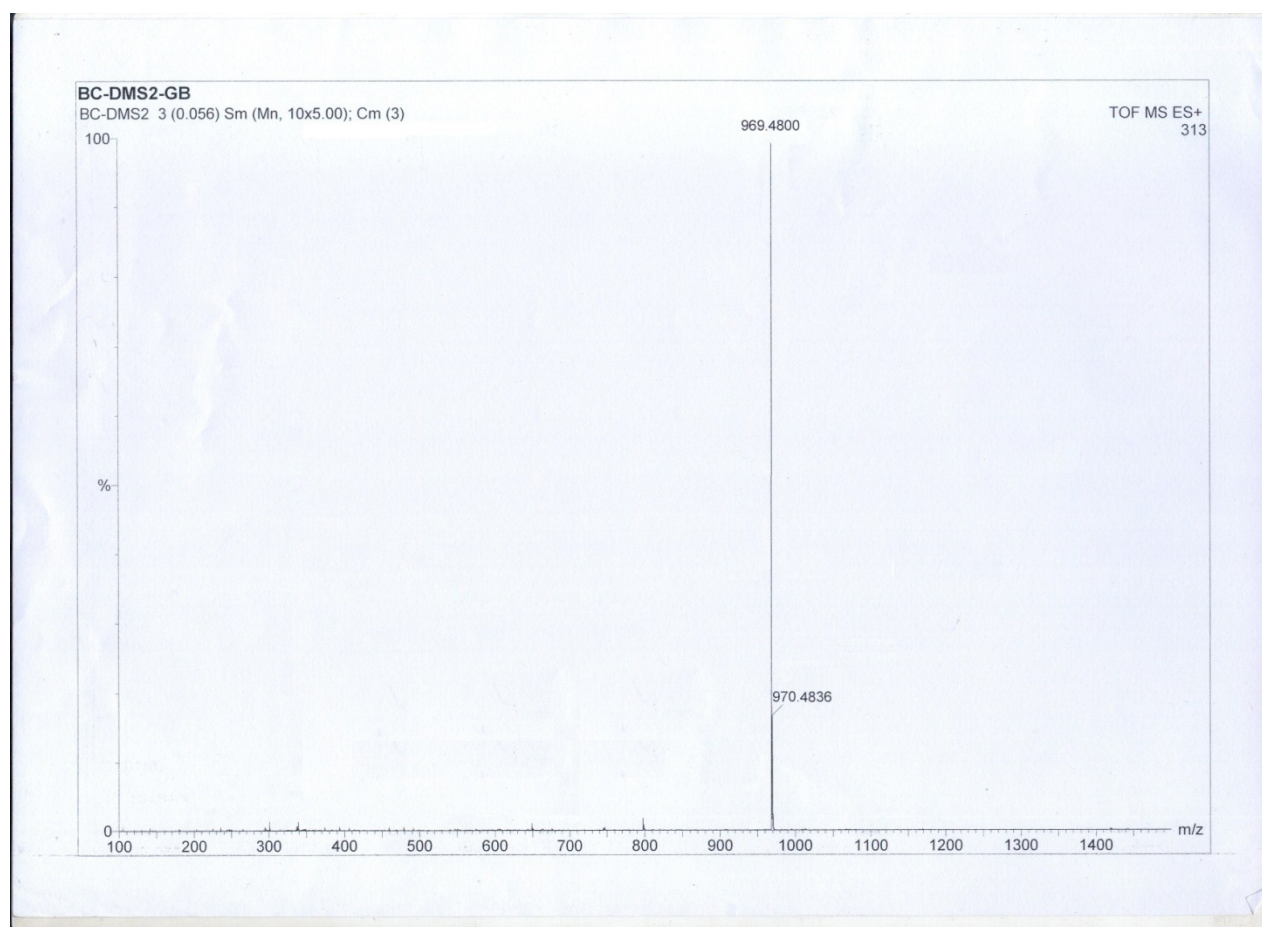


Figure S3: ESI-MS of Compound 1.

## Compound 2

Monoimide (2 mmol, 0.871 g) was taken in a 100 ml round-bottom flask with DMF (20 ml) and stirred under Ar atmosphere at 328 K for 30 mins until the suspension turned into a clear solution. To this a solution *p*-xylenediamine (1 mmol, 0.136 g) in 2 ml DMF was slowly added with stirring. The entire system was refluxed under Argon at 393K for 4 hours. The progress of the reaction was monitored using TLC. After another 2hr the reaction mixture was refrigerated to obtain a brown precipitate that was washed with cold methanol and hexane. Resulting mixture was purified using column chromatography (Silica gel 100-200 mesh) (Yield: 0.062g, 3.1 %).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz, TMS):  $\delta$  (ppm) = 8.77 (8H, m), 7.83 (2H, d  $J$  = 10Hz), 7.69 (2H, d  $J$  = 10Hz), 5.45-5.33 (4H, s), 4.18 (4H, m), 1.75 (4H, m), 1.35-1.22 (36 H, m), 0.87 (6 H, t,  $J$  = 6.0 Hz);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm) = 162.65, 143.16, 131.35, 130.94 130.02, , 129.47, 128.42, 128.04, 126.77, 43.78, 41.02, 31.88, 29.59, 29.31, 27.05, 22.65, 14.08. ESI-MS (MeOH, 0.1% DMSO):  $m/z$  (Calc):  $\text{C}_{60}\text{H}_{66}\text{N}_4\text{O}_8$  [M] 970.4881; found: 970.4844[M] $^+$ , 969.4844[M-H] $^+$ . Anal. Calc. for  $\text{C}_{60}\text{H}_{66}\text{N}_4\text{O}_8$ : C, 74.20; H, 6.85; N, 5.77% found C, 74.18; H, 6.87; N, 5.75%. Melting point >250 °C.

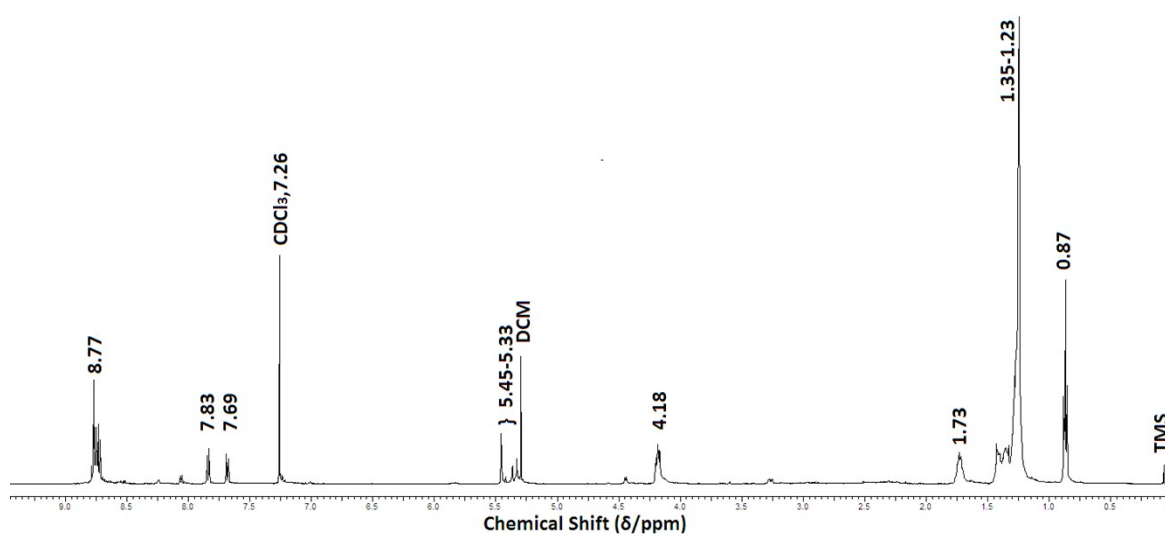


Figure S4:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ , 298K) spectrum of 2

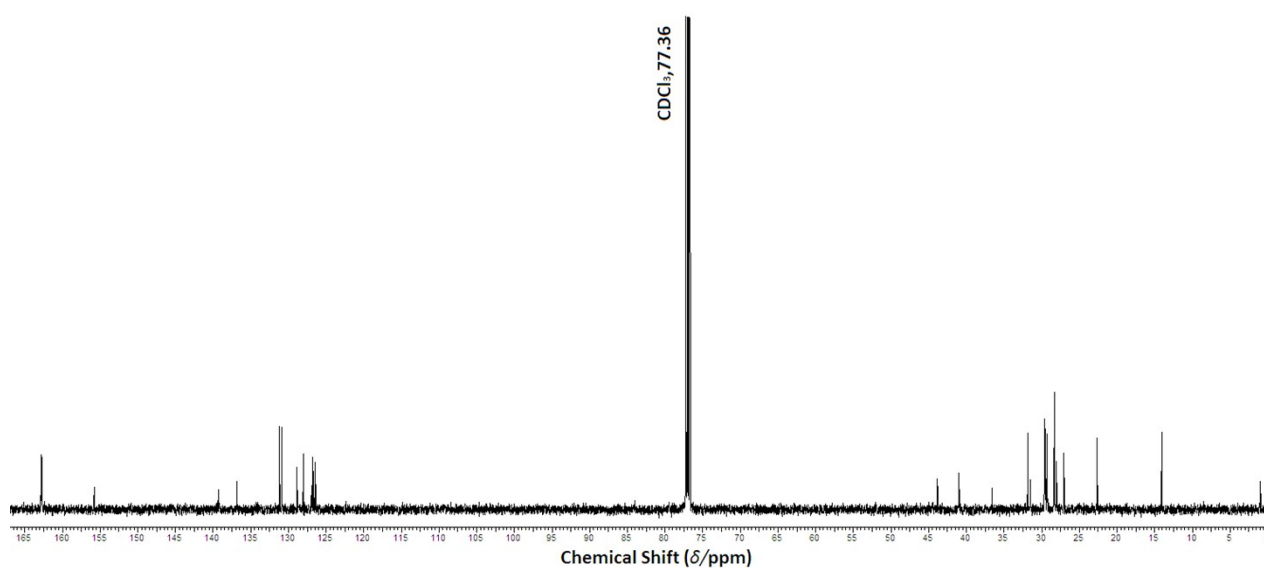
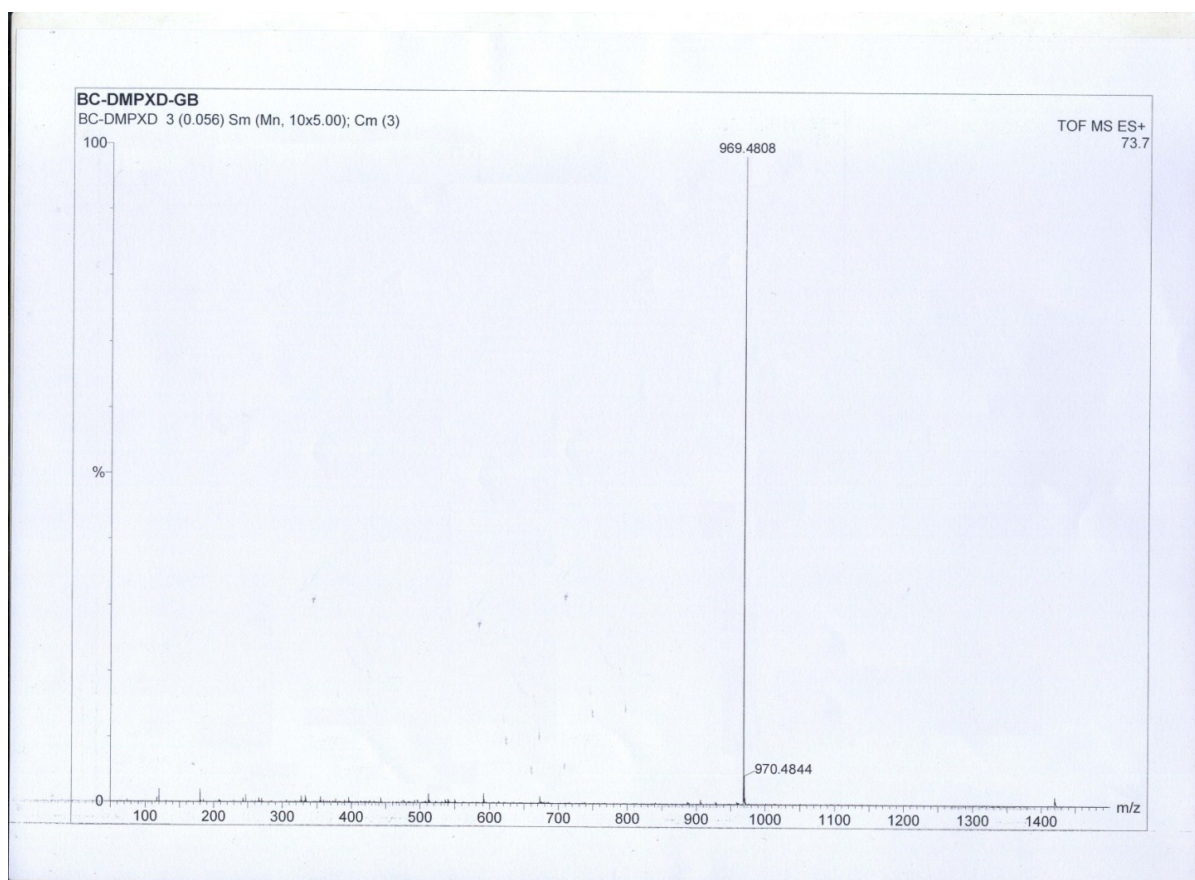


Figure S5:  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ , 298K) of 2



**Figure S6:** ESI-MS of Compound 2.

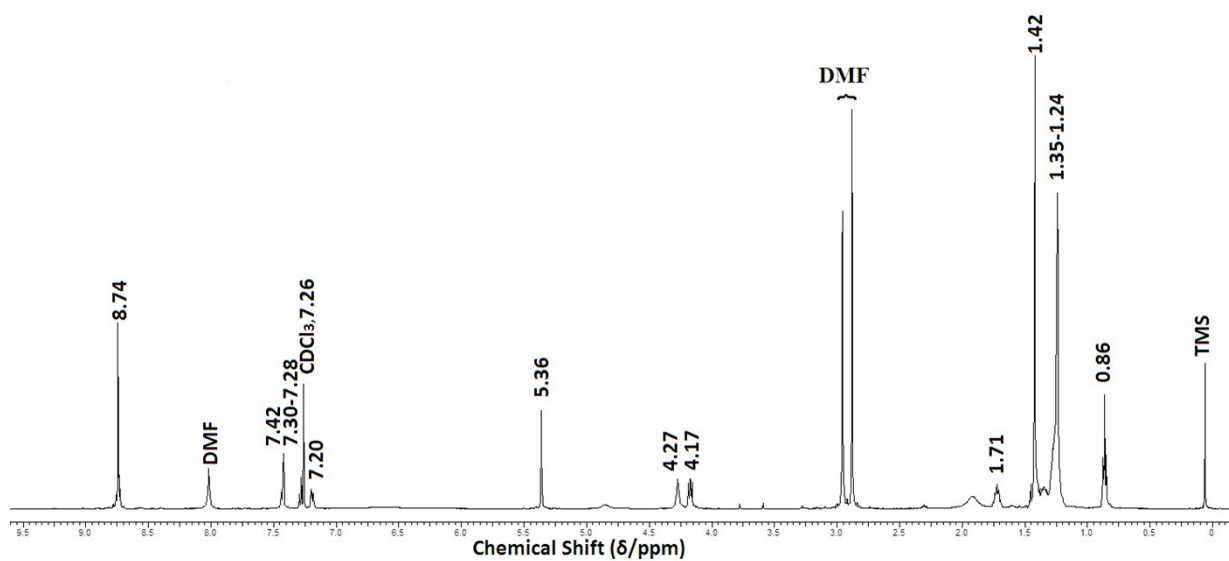
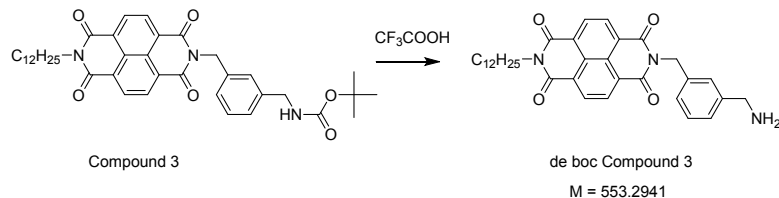
### **tBAC**

To a solution of *m*-xylenediamine (90 mmol, 12.25g) in  $\text{CHCl}_3$  (400 ml), a solution of di-*tert*-butyldicarbonate (22 mmol, 4.83g) in  $\text{CHCl}_3$  (80 ml) was added dropwise at 273 K over a period of 3 hrs. After stirring for 16 h at RT, the reaction mixture was washed with brine (4x100 ml) and water (1x100 ml), dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuum to afford a yellow viscous oily liquid, which was purified by column chromatography to obtain 4.2 gm (90%) of *tert*-Butyl 3-aminomethyl benzylcarbamate (tBAC) as a colourless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.21-7.10 (4H, s), 4.19 (2H, s), 3.72 (2H, s), 1.37 (9H, s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 156.3, 144.1, 139.6, 129.1, 126.5, 79.8, 46.7, 45.0, 28.8. ESI-MS (MeOH, 0.1% DMSO):  $m/z$  (Calc):  $\text{C}_{13}\text{H}_{20}\text{N}_2\text{O}_2$  [M] 237.160; found: 237.0650.

### **Compound 3**

Monoimide (10 mmol, 4.35 g) and tBAC (20 mmol, 4.72g) were taken together in a flask and stirred with dry DMF (15 ml), heated at 393K for 18 hrs. under Ar flow. The reaction mixture upon cooling gives a precipitate, which was washed with 20 ml of cold 10 % methanol in hexane solution to eliminate excess amine. Resulting precipitate was purified by column chromatography.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, TMS):  $\delta$  (ppm) = 8.74 (4H, m), 7.42(1H, s), 7.30-7.28(2H, m), 7.20(1H, s), 5.36(2H, s), 4.27(2H, br s), 4.17(2H, t,  $J=6$ ), 1.71 (2H, m), 1.42(9H, s), 1.35-1.24 (18H, m), 0.86 (3H, t,  $J = 5.0$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 162.83, 139.33, 136.85, 131.17, 130.88, 128.86, 128.03, 126.76, 126.44, 43.83, 40.99, 36.60, 31.87, 29.58, 28.03, 27.04, 2, 22.64, 14.07. ESI-MS (MeOH, 0.1% DMSO):  $m/z$  (Calc):  $\text{C}_{39}\text{H}_{47}\text{N}_3\text{O}_6$  [M] 653.3465; found: 657.3944[M+4H] $^+$ , 658.4149[M+5H] $^+$ , Anal. Calc. for  $\text{C}_{39}\text{H}_{47}\text{N}_3\text{O}_6$ : C, 71.64; H, 7.25; N, 6.43% found C, 71.62; H, 7.23; N, 6.45%. Melting point >250  $^\circ\text{C}$ .

Further we repeated the ESIMS measurement of 3, this time upon addition of excess  $\text{CF}_3\text{COOH}$ . As expected,  $\text{CF}_3\text{COOH}$  spontaneously deprotects the amine group in 3, as shown in the scheme below. The new mass spectrum shows the presence of the de boc-Compound 3 (Figure S10). ESI-MS (MeOH, 0.1% DMSO):  $m/z$  (Calc):  $\text{C}_{34}\text{H}_{39}\text{N}_3\text{O}_4$  [M] 553.2941, found 554.2424  $[\text{M}+\text{H}]^+$ , 555.2430  $[\text{M}+2\text{H}]^+$ , 537.2191  $[\text{M}-\text{NH}_2]^+$ .



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Figure S7:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298K) spectrum of 3

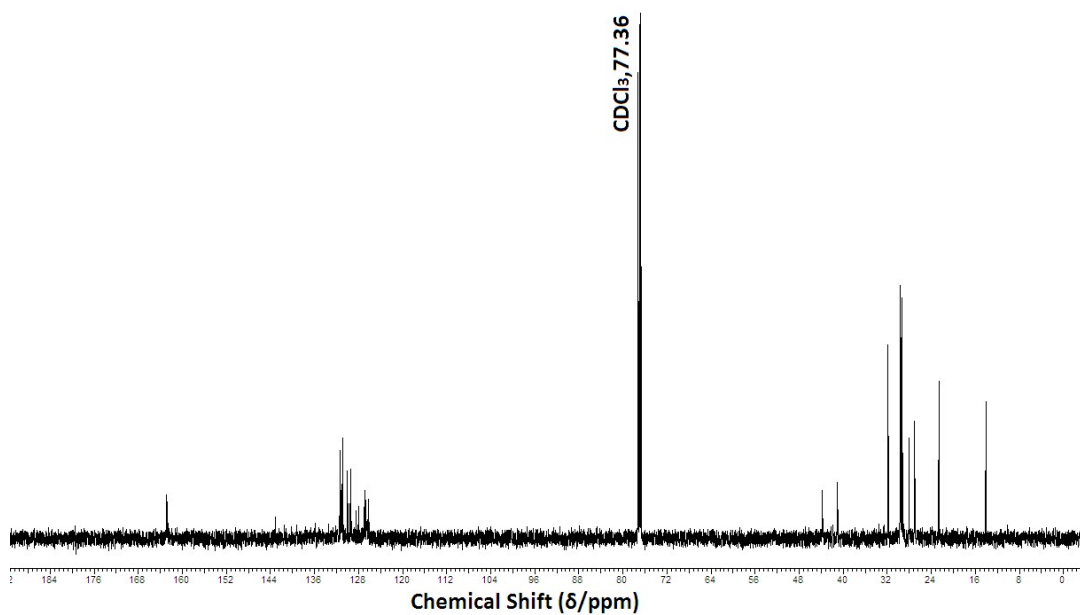




Figure S8:  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 298K) of 3

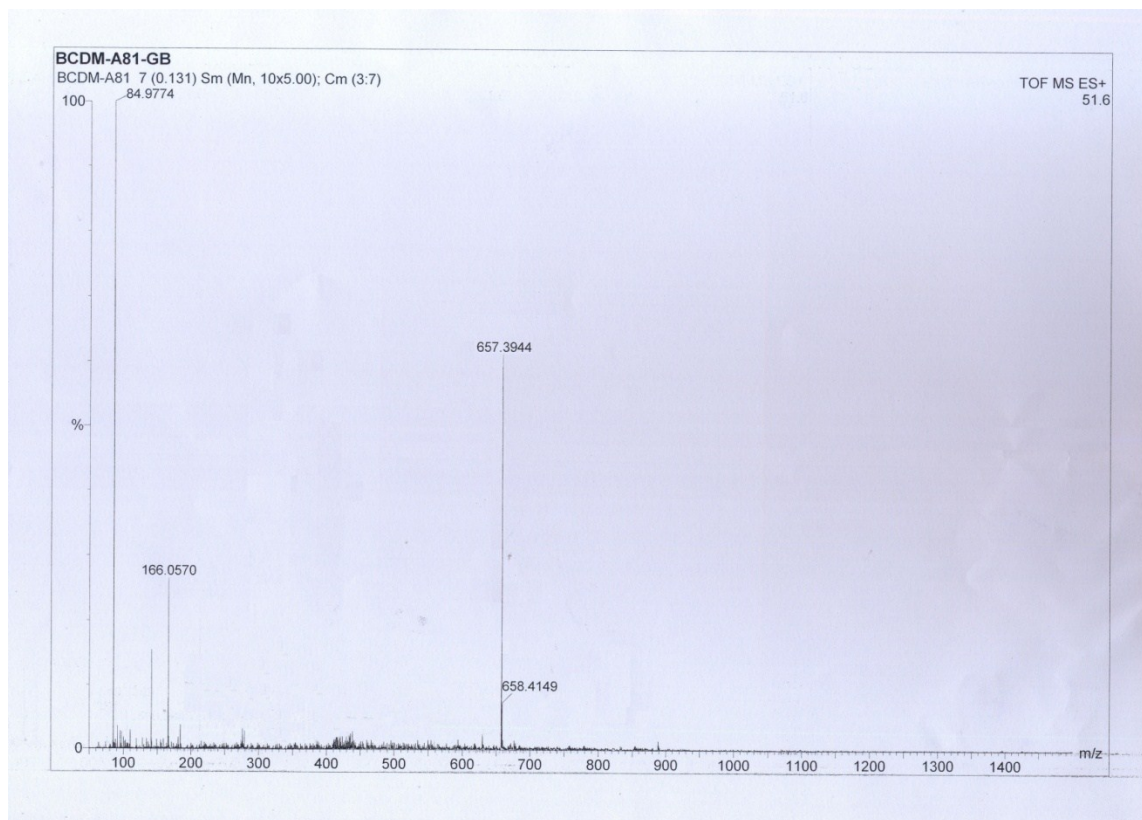


Figure S9: ESI-MS of Compound 3.

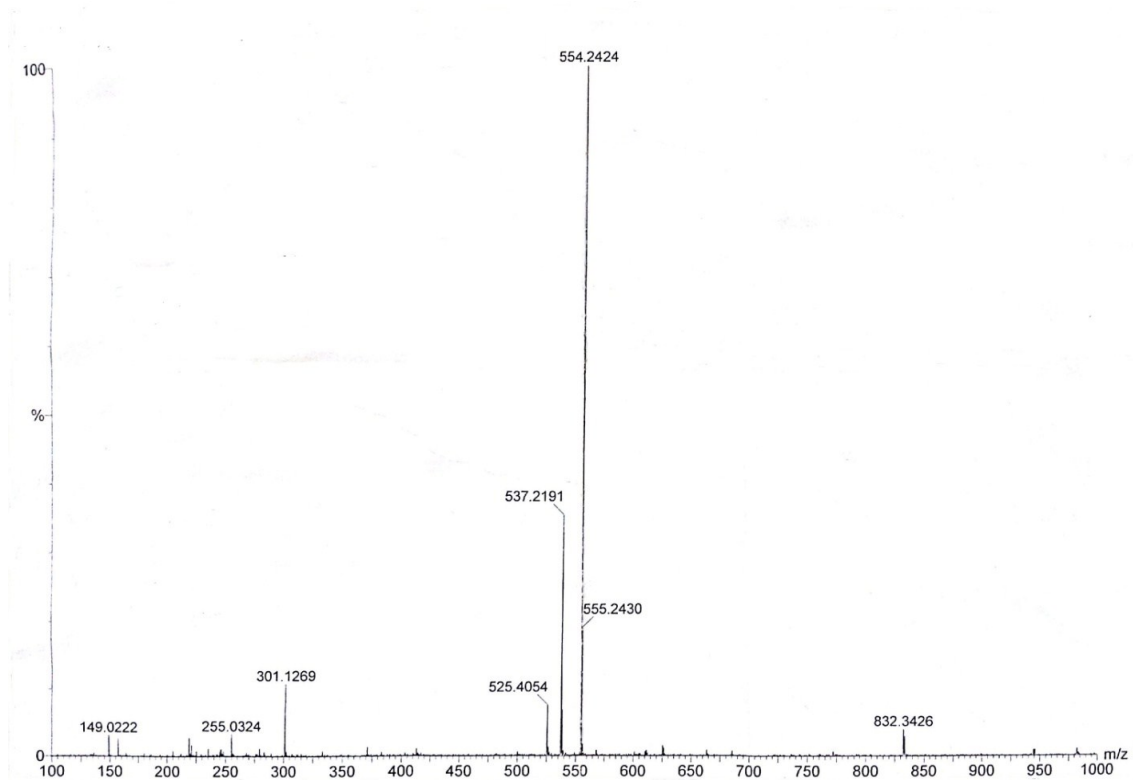




Figure S10: ESI-MS of de-boc compound 3.

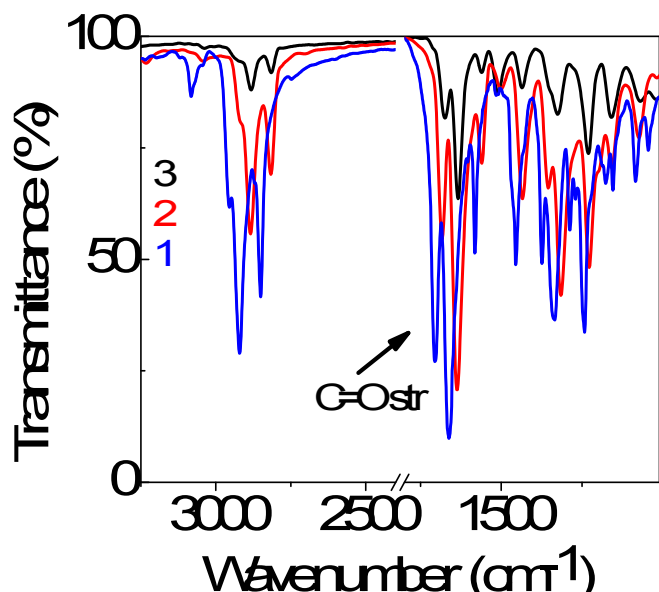


Figure S11: FTIR spectra of 1, 2 and 3.

Asymmetric stretching of the imide C=O group appears at  $\sim 1650\text{ cm}^{-1}$ , which also couples to the electronic transitions (absorption and PL) of 1, 2 and 3.

#### V. Spectroscopic behaviour compound 1 and 2 in different solvents.

- Absorbance (Fig. S8a) and PL (Fig. S8b) spectra of compound 1 were also measured in THF, a polar non halogenated solvent. Absorption feature of compound 1 also shows vibronics at 380,360,340 nm which are clear indicative of underlying NDI chromophores and also a weak red shifted feature at 470-510 nm. These features are similar to the absorption spectra of compound 1 taken in CH<sub>2</sub>Cl<sub>2</sub>. Further similarities of PL and PLE spectrum of compound 1 in THF and CH<sub>2</sub>Cl<sub>2</sub> are clear indicative of the fact that the interactions are not due to halogen solvent and pi-core which is generally known as halogen-pi interactions.

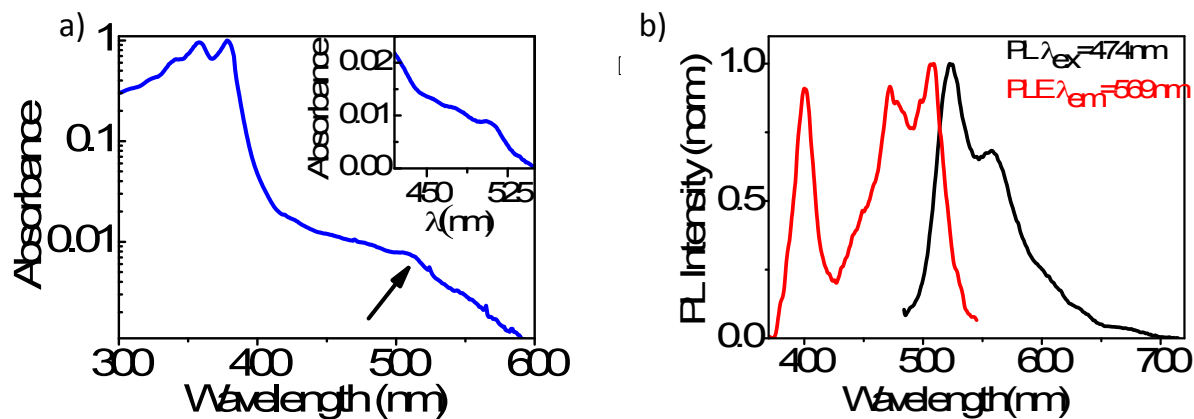


Figure S12: (a) Absorbance (b) PL and PLE spectra of compound 1 in THF.

- PL spectra (Fig. S13a and b) of compound 1 and 2 exhibit relatively weak solvatochromism. This is similar to mono-amino-core-substituted NDIs, [3] where the interaction between the amino substitution and the NDI core is of a partial charge-transfer character.

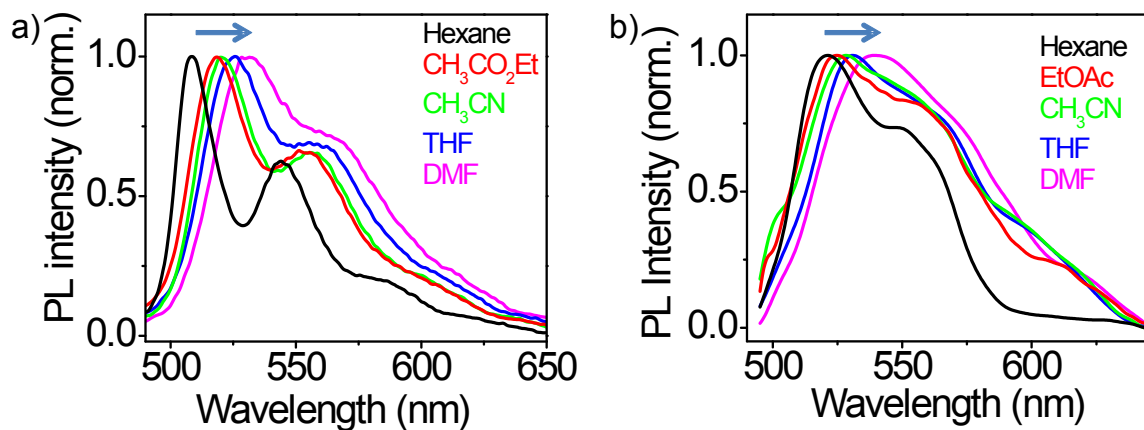


Figure S13: PL solvatochromism for compounds (a) 1 and (b) 2.

- D-A species in concentrated  $\text{CH}_2\text{Cl}_2$  solution

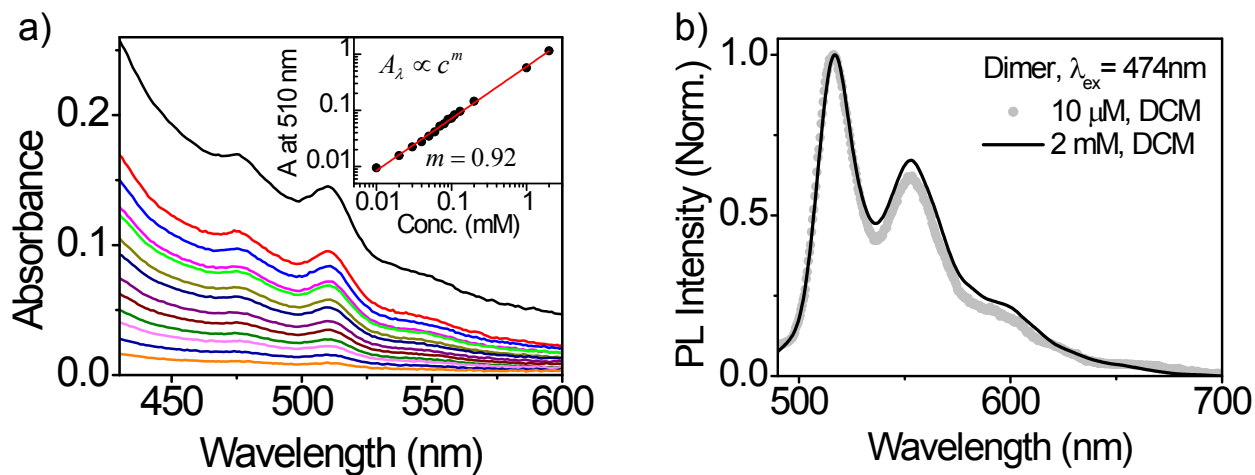
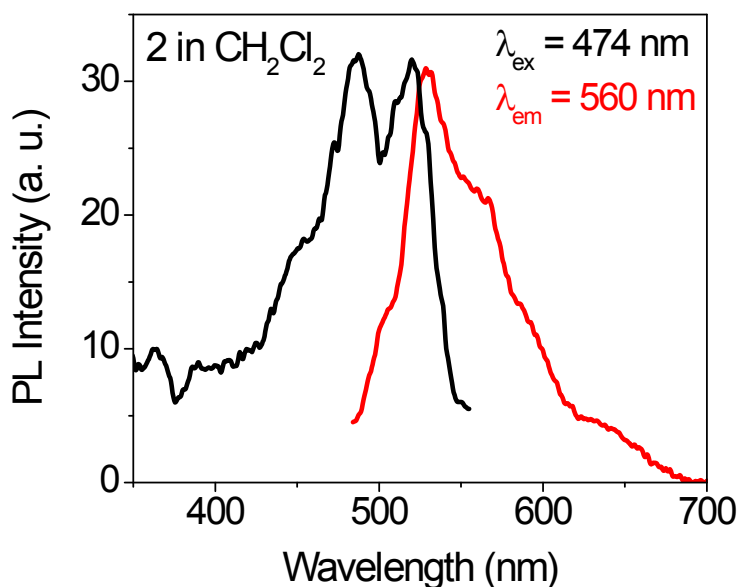


Figure S14 (a) Absorption spectrum of the D-A species of 1 is independent of concentration in 10-200  $\mu\text{M}$  range. Inset: A good agreement with Beer Lambert's law in 10  $\mu\text{M}$  to 2 mM concentration range (b) PL spectra at extreme concentrations are identical to each other.

- Emissive state of *p*-xylylene dimer, 2.

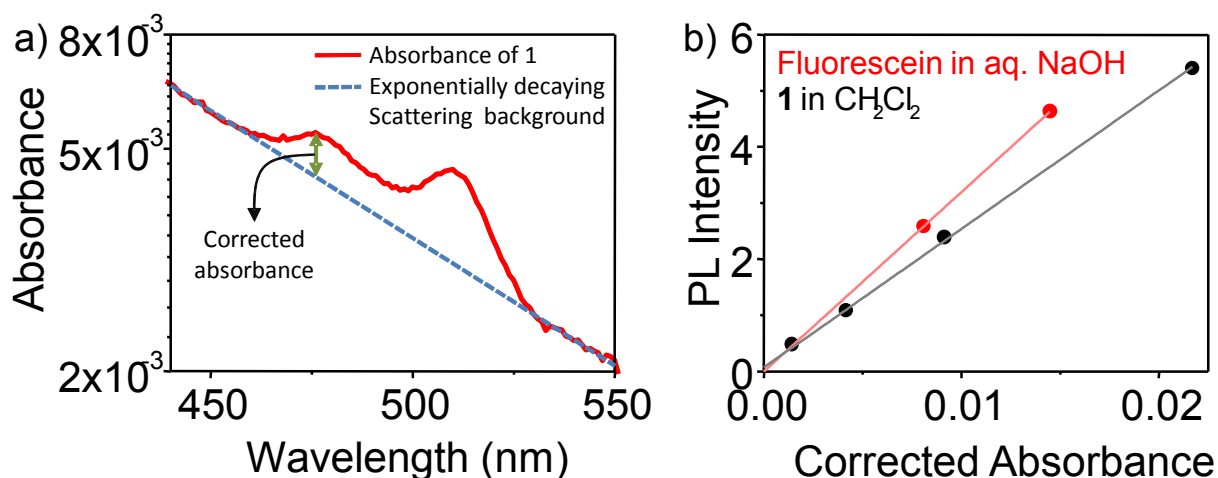


**Figure S15.** PL and PLE spectra of 2 in dilute  $\text{CH}_2\text{Cl}_2$  reveal a very similar emissive state as 1. Both PL and PLE spectra of 2 are  $\sim 12$  nm red-shifted compared to 1, consistent with the observed shift in the corresponding absorption spectra.

#### V. PL quantum efficiency

PL quantum efficiency (PLQE) of the D-A species was measured against fluorescein in aq. NaOH (PLQE = 0.91). The weak absorption feature of the D-A species rides over an exponentially decaying scattering background, which is of comparable magnitude. This necessitates an appropriate background correction for determination of the actual absorbance of the D-A species. The exponentially decaying scattering background in 450-550 nm region was subtracted from the measured absorption spectrum to obtain the corrected absorbance (see Fig. S11a). PLQE of the weak red shifted species was determined from the ratio of slopes in Fig. S11b.

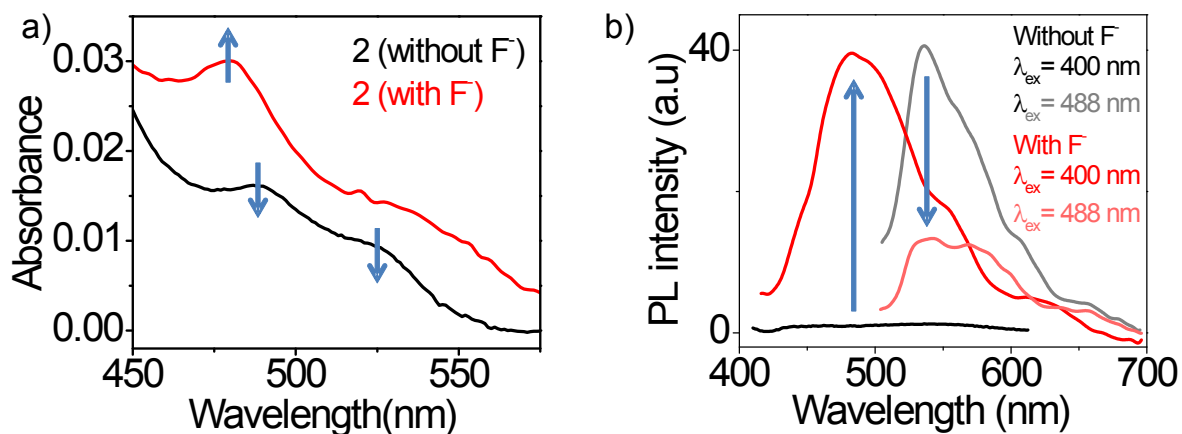
We calculated PLQE using both corrected and as-obtained absorbance values, as 0.78 and 0.11 respectively. Despite the low absorbance of the D-A species, such a high PLQE suggests the absence of any dominant non-radiative relaxation process.



**Figure S16(a):** Determination of the corrected absorbance for 1 after subtracting an exponentially decaying scattering background. Note the logarithmic scale for Absorbance. **(b)** A plot of integrated PL intensity against absorbance.

## VI. Fluoride ion binding with dimer 2

Fluoride ion binding with 2 was carried out in dilute ( $\sim 10 \mu\text{M}$ )  $\text{CH}_2\text{Cl}_2$  solution. As expected, the effect is similar to that observed in the case of dimer 1.  $\text{F}^-$  being a competing donor, disrupts the intrinsic one-donor-two-acceptor interaction in both dimers (1 and 2). Consequently, the weak absorbance of the D-A interaction is replaced by that of  $\text{NDI-F}^-$  complex (Fig. , revised ESI). PL corresponding to D-A species (488 nm excitation) diminishes, and that of isolated NDI (390 nm excitation) grows upon addition of  $\text{F}^-$ .



**Figure S17.** Fluoride ion binding with dimer 2. (a) Absorption spectrum (b) PL spectrum for two different excitation wavelengths, 400 and 488 nm.

## VII. References:

- [1] M. J. Frisch *et al.*, Gaussian Inc., Wallingford CT, 2010.
- [2] N. M. Shavaleev, H. Adams, J. Best, J. A. Weinstein, *J. Organomet. Chem.*, 2007, **692**, 921.
- [3] T. D. M. Bell, S. Yap, C. H. Jani, S. V. Bhosale, J. Hofkens, F. C. DeSchryver, S. J. Langford and K. P. Ghiggino, *Chem. As. J.*, 2009, **4**, 1542.