Supplementary Material (ESI) for Chemical Communications

Naphthalene-bis-hydrazimide: Radical anions and ICT as New Bimodal Probes for Differential Sensing of a Library of Amines

Supporting Information

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Experimental Details:

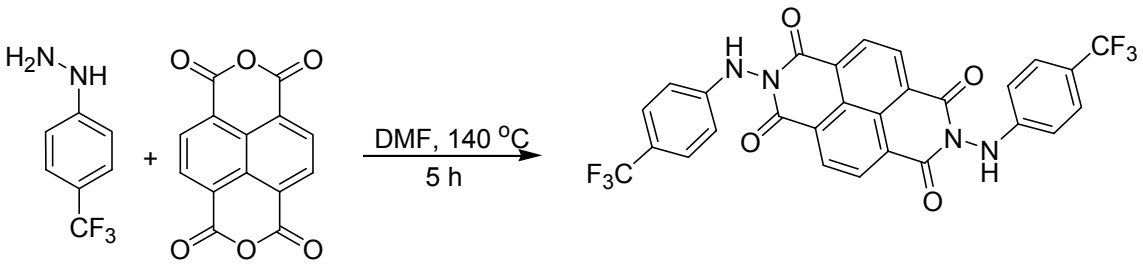
General: All chemicals were sourced from Sigma-Aldrich, Spectrochem India or Thomas-Baker-India and were used as received. Thin layer chromatography (TLC) was carried out on aluminium plates coated with silica gel mixed with fluorescent indicator having particle size of 25 μm and was sourced from Sigma-Aldrich. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer in DMSO-d_6 with TMS as a standard. MALDI-TOF mass spectral data were obtained using a Bruker made Autoflex TOF/TOF instrument with laser repetition rate of 50 psec. α-Cyano-4-hydroxycinnamic acid was used as the matrix for MALDI-TOF mass spectrometry. UV-Vis spectroscopy was performed on a Shimadzu UV-2401 PC model, with all the reported spectra taken instantaneously. Infrared spectra were recorded in KBr pellet using Varian 3100 FT-IR instrument.

Cyclic Voltammetry: Cyclic voltammetry (CV) was carried out using a computer-controlled potentiostat (Autolab) and a standard three electrode arrangement. CV measurements used both platinum working and auxiliary electrodes and a saturated calomel reference electrode. All electrochemical measurements were carried out in N_2-purged dry THF with 0.1M Bu_4NBF_4 as the supporting electrolyte. The scan rate for the measurements was typically 50-200mV/s.

Theoretical Calculations: The semiempirical Parametric Model 3 (PM3) and Zerner's Intermediate Neglect of Differential Overlap (ZINDO/S) in Configuration Interaction mode.

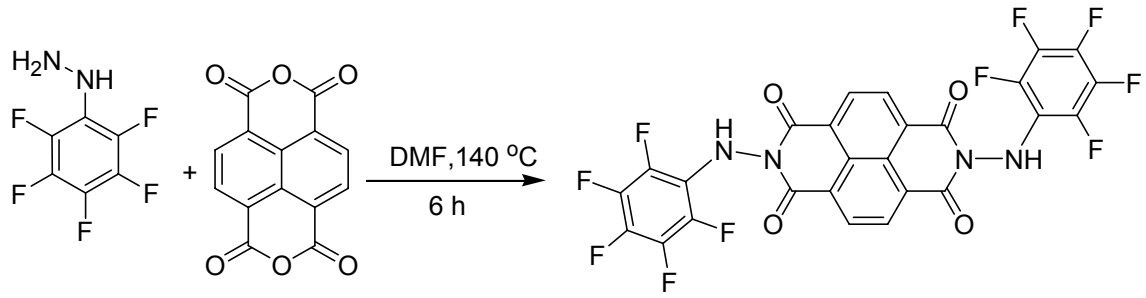
VPD procedure: Thin film of **1a** was deposited on a glass substrate by vacuum evaporation technique at 10^{-6} mbar pressure and room temperature. The thickness of the film was controlled by a resistively heated Mo boat. The rate of evaporation was 1 A° s^{-1}.

Synthesis of 1a:



4-Trifluromethylphenylhydrazine (0.60 g, 3.35 mmol) was transferred to a 50 mL R.B. flask containing 1,4,5,8-naphthalenetetracarboxylic dianhydride (0.30 g, 1.12 mmol) in 20 mL DMF in Ar atmosphere. The reaction mixture was heated on a magnetic stirrer at 140 ^{o}C for 5 h and cooled to RT. This solution was transferred to 100 mL water and extracted with EtOAc. The organic layer was washed with brine solution (5x 50 mL), dried over anhydrous $MgSO_4$ and the solution was evaporated using rotary evaporator. This crude product obtained was purified by column chromatography [silica gel 100-200, using $CHCl_3$/MeOH (9:1), R_f = 0.19] and further recrystallized with $CHCl_3$. A dark brown precipitate was formed. Yield: 70%. Mp: 322 ^{o}C. ^{1}HNMR (300 MHz, DMSO-*d_6*, 300 K, TMS): δ = 9.33 (s, 2H, NH), 8.78 (s, 4H, *Nap*), 7.51 (d, 4H, J = 8.4 Hz, *Ph*), 7.03 (d, 4H, J = 8.4 Hz, *Ph*). ^{13}CNMR (300 MHz, DMSO-*d_6*, 300 K, TMS): δ = 162.01, 150.38, 131.05, 127.05, 126.25, 123.02, 119.76, 119.34, 112.23. MS (MALDI–TOF matrix: α-Cyano-4-hydroxycinnamic acid): calculated for $C_{28}H_{14}F_6N_4O_4$ (m/z) 584.34, found 584.99. FTIR (KBr pellet) υ = 3346.49 (NH_{str}), 1724.09, 1689.63 ($C{=}O_{str}$), 1622.34, 1321.23 cm^{-1}. UV-vis (THF): $\lambda_{max}(\varepsilon)$ = 375 nm (22,359 M^{-1}cm^{-1}), 355 nm (20162 M^{-1}cm^{-1}). Anal. calcd. for $C_{28}H_{14}F_6N_4O_4$: C 57.54, H, 2.42, N, 9.59

Synthesis of 1b:



2,3,4,5,6-Pentafluorophenyl hydrazine (0.55 g, 3.36 mmol) was transferred to a 50 mL R.B. flask containing 1,4,5,8-naphthalenetetracarboxylic dianhydride (0.30 g, 1.12 mmol) in 20 mL DMF in Ar atmosphere. The reaction mixture was heated on a magnetic stirrer at 140 ^{o}C for 6 h and cooled to RT. This solution was transferred to 100 mL water and extracted with EtOAc. The organic layer was washed with brine solution (5x 50 mL), dried over anhydrous $MgSO_4$ and the solution was evaporated using rotary evaporator. After drying under vacuum, the crude product was washed with $CHCl_3$ and then with MeOH. The obtained solid was dried and further purified by column chromatography [silica gel 100-200, $CHCl_3$/MeOH (9:1), R_f = 0.22]. A pale yellow product was obtained. Yield: 49%. Mp: 308 ^{o}C. ^{1}HNMR (300 MHz, DMSO-d_6, 300 K, TMS): δ = 9.20 (s, 2H, NH), 8.81 (s, 4H, *Naph*). MS (MALDI–TOF matrix: α-Cyano-4-hydroxycinnamic acid): calculated for $C_{28}H_{14}F_6N_4O_4$ (m/z) 628.33, found 628.01. FTIR (KBr pellet) υ = 3305.91 (NH_{str}), 1732.65, 1691.57 (>C=O_{str}), 1522.50, 1486.95, 1329.71 cm^{-1}. UV-vis (THF): $\lambda_{max}(\varepsilon)$ = 375 nm (17307.14 $M^{-1}cm^{-1}$), 354 nm (16034.29 $M^{-1}cm^{-1}$). Anal. calcd. for $C_{26}H_6F_{10}N_4O_4$: C 49.70, H, 0.96, N, 8.92

Synthesis of 1c:

Compound **1c** (N,N'-Bis(phenylmethyl)naphthalene-1,4,5,8-tetracarboxylic diimide) was synthesized according to the procedure reported by:

Ya-Lien Lee et. al. *J. Phy. Chem. C* **2008**, *112*, 1694-1699.

Preparation of solutions: The solutions for the UV-vis spectroscopic studies were prepared as follows: **i)** For studies with amines having molarity greater than 7, a 3.59 mM solution of **1a** was prepared in THF or THF/H_2O (9:1) or THF/H_2O (1:1). 200 µL of **1a** was taken in a cuvette (path length = 1mm) and the amine concentration was kept at 1.80 M for all the cases. The final concentration of **1a** was 2.66 mM and final volume of the solution 270 µL. As an example, the initial

concentration of n-butyl amine = 10.08 M. 48 μL of butyl amine, 22 μL of solvent [THF, THF/H_2O (9:1) or THF/H_2O (1:1)] were added to 200 μL of **1a** and the UV-vis spectrum was taken.

b) Compound 1a, 0.4 mg was weighed in a small vial. Amine and solvent [THF, THF/H_2O (9:1) or THF/H_2O (1:1)] were added to this vial and making the final concentrations 1.80 M, 2.66 mM for amine and **1a** respectively in 270μL solution. This solution was transferred to cuvette (path length=0.1 cm) and the UV-vis spectrum were taken. Similar procedure was repeated for the other amines in this class.

Table ST1: Comparison of *pK_a*, *Molar volume, Molecular length*, and S*pectroscopic response* of **1a** in dry THF and THF:H_2O (9:1).

Amines	**pK_a[a]**	**Vol[b]**	**Length[c]**	**$(A-A_0)/A_0$**	**$(A-A_0)/A_0$**
				THF	**THF:H_2O (9:1)**
n-Propylamine (**2**)	10.57	63.937	4.882	20.14	99.52
n-Butylamine (**3**)	10.64	74.906	6.34	46.18	100.67
n-Hexylamine (**4**)	na	115.165	9.332	58.05	102.98
n-Octylamine (**5**)	10.61	116.496	11.899	69.00	83.33
n-Dodecylamine (**6**)	na	197.785	16.548	78.00	65.94
Tertiarybutylamine (**7**)	10.68	80.139	4.193	4.73	6.11
Cyclohexylamine (**8**)	10.63	83.706	6.029	7.10	49.11
Benzylamine (**9**)	9.34	102.688	7.114	6.14	25.62
β-Me-phenethylamine (**10**)	9.83	130.484	7.225	10.68	33.19
Ethylenediamine (**11**)	9.93	54.453	4.753	10.045	*
Putrescine (**12**)	10.65	86.883	7.271	204.50[d]	130.58
Diethylamine (**13**)	11.0	74.23	5.496	4.50	4.42
di-n-propylamine (**14**)	11.03	89.393	9.293	6.64	2.07
di-n-Butyl amine (**15**)	na	146.372	10.645	7.14	1.10
di-n-Hexylamine (**16**)	na	200.516	17.012	7.32	*
di-n-Octylamine (**17**)	na	271.723	19.882	10.32	*
Piperidine (**18**)	11.07	83.714	4.862	7.91	7.54
Morpholine (**19**)	8.3	59.516	4.834	1.77	0.22
Diisopropylamine (**20**)	11.1	105.522	6.553	1.50	2.48
Triethylamine (**21**)	10.8	97.625	6.325	1.09	0.89
Pyridine (**22**)	5.23	71.502	4.306	0.02	0.37

Reference:

a) H. K. Hall Jr., *J. A.m. Chem. Soc.* 1957, **79**, 5441.

b) & c) Volume and molecular length of the amines are in

d) $(A-A_0)/A_0$ at 470 nm.

e) Nonspecific binding of anions with the sensor **1a/1b** prevented use of buffer in the mixed aqueous system. However, we confirmed that steric factors play a dominant role over the pk_a of the amines.

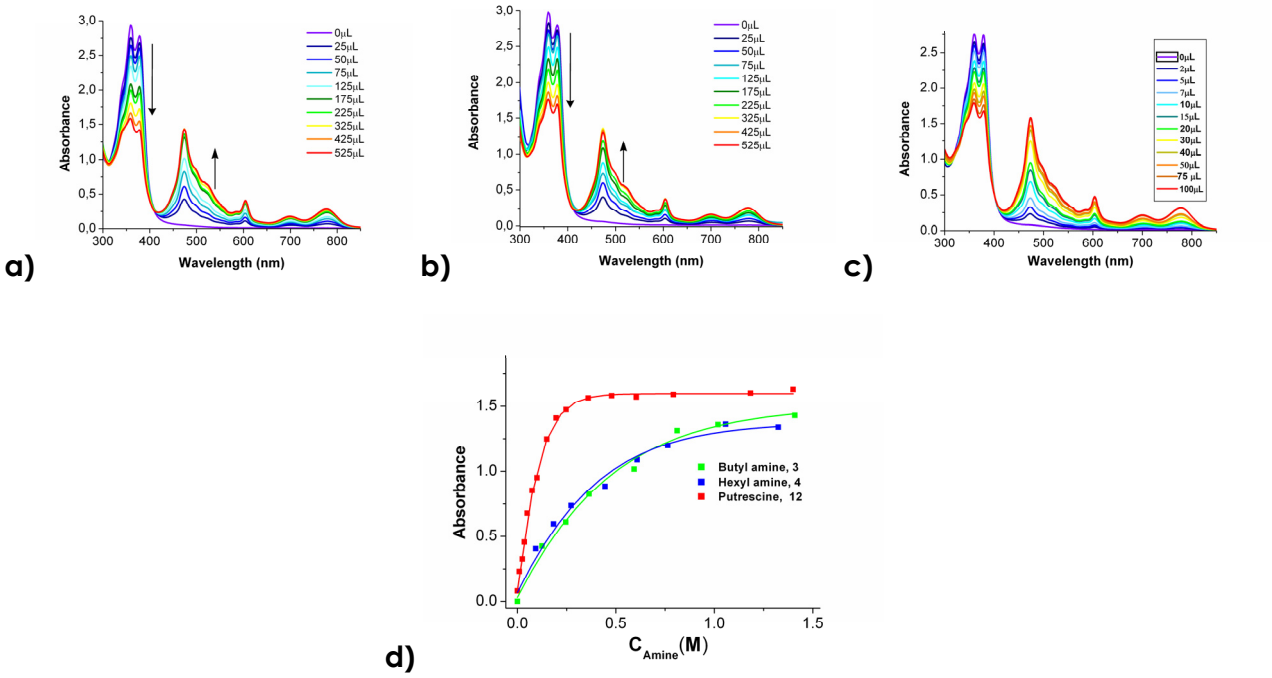


Figure SI 1: UV-vis spectra showing the spectral response of **1a** with gradual addition of a) n-butyl amine **3**, **b)** n-hexylamine **4, c)** Putrescine **12** in DMSO, d) Determination of the binding constants. [Minimum of 25 eqv. of **12** and 250 eqv. of other straight chain 1^0 amines are required to visualize the chromogenic changes during amine sensing].

Binding Constants (K_a)* of **1a** with amines **3**, **4** and **12** in DMSO		
1a. 3	**1a.4**	**1a.12**
3.4 ± 0.3	3.7 ± 0.3	14.5 ± 0.3

*Determined by Non-linear least square fitting of (1:1) binding saturation curves.

The signature peaks for the radical anions of the NDI moiety in the presence of amines matches completely with the earlier reports:

Reference:

(*a*) D. Gosztola, M. P. Niemczyk, W. Svec, A. S. Lukas and M. R. Wasielewski, *J. Phys. Chem., A* 2000, **104**, 6545; (b) G. Andric, J. F. Boas, A. M. Bond, G. D. Fallon, K. P. Ghiggino, C. F. Hogan, J. A. Hutchison, M. A. –P. Lee, S. J. Langford, J. R. Pilbrow, G. J. Troup and C. P. Woodward, *Aust. J. Chem.*, 2004, **57**, 1011.

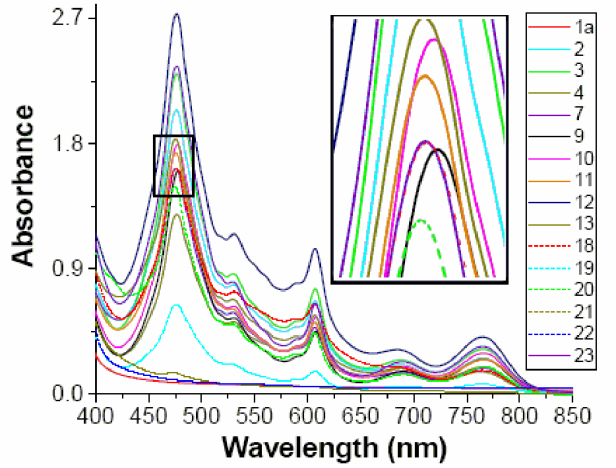


Figure SI 2: UV-vis spectra of **1a** with various amines (**2**-**23**) in THF:H_2O (1:1).

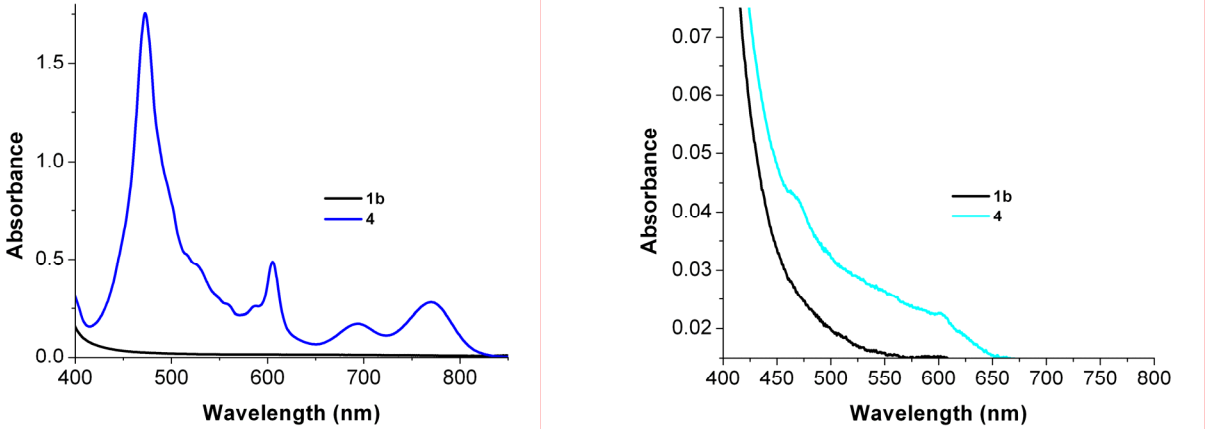


Figure SI 3: UV-vis spectra of **1b** with n- Hexylamine, **4** in a) THF:H_2O (1:1) and b) THF.

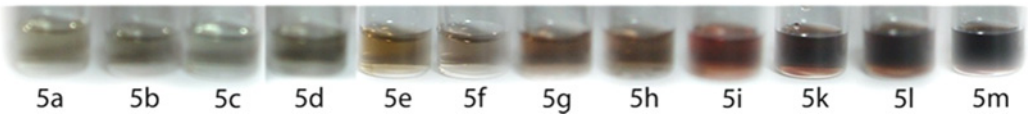


Figure SI 4: Photographs of **1a** with amine **5** generated by tuning the solvent polarity; a) $CHCl_3$, b) DCM, c) $CHCl_3$:THF(9:1) d) DCM:THF(9:1) e) THF:DMSO(9:1) f) THF:MeOH(9:1) g) MeOH:DMSO(9:1) h) MeOH:THF(9:1) i) DMSO j) DMSO:THF(9:1) k) DMSO:MeOH (9:1) l) DMSO:H_2O (9:1)

Table ST2: Determination of RGB values of **5a**-**5l**: Gradual changes from the original light yellow colour of the sensor **1a** to light blue, red and dark red shades.

Entry	R	G	B
5a	98	96	74
5b	66	68	54
5c	98	101	90
5d	54	54	43
5e	75	59	34
5f	86	74	54
5g	65	48	38
5h	56	44	31
5i	49	29	23
5k	23	23	24
5l	22	22	24
5m	19	21	25

Reference: a) The RGB values were determined by using the software **Colour Contrast Analyser** (1:1), downloaded from www. visionaustralia.org.au

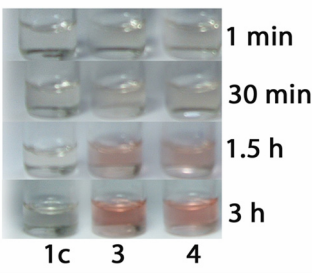


Figure SI 5: Photographs of **1c** with various amines (**3**, **4**, **12**, **18** and **21**) in THF:H_2O (9:1) showing the slow radical anion generation process.

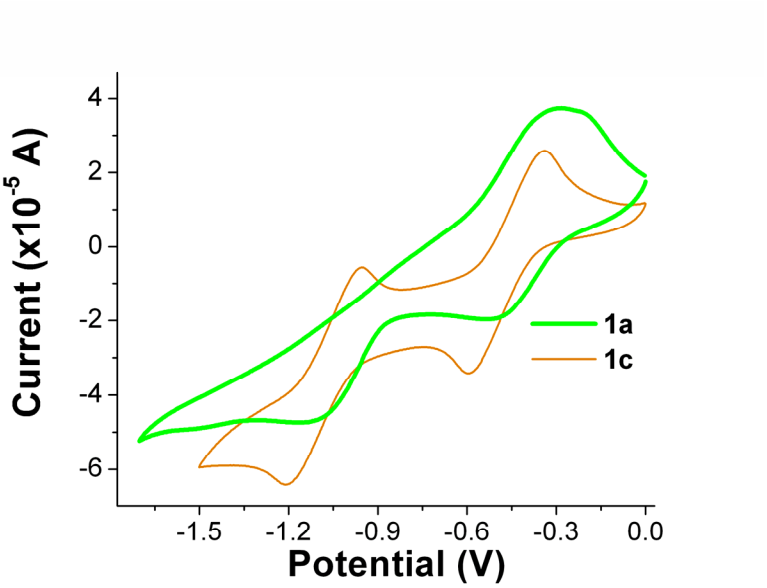


Figure SI 6: Cyclic Voltammetric studies of a) **1a** and b) **1c** 0.5 mM in dry THF with $Bu_4N^+BF_4^-$ (0.1 M) as the supporting electrolyte under Ar atmosphere.

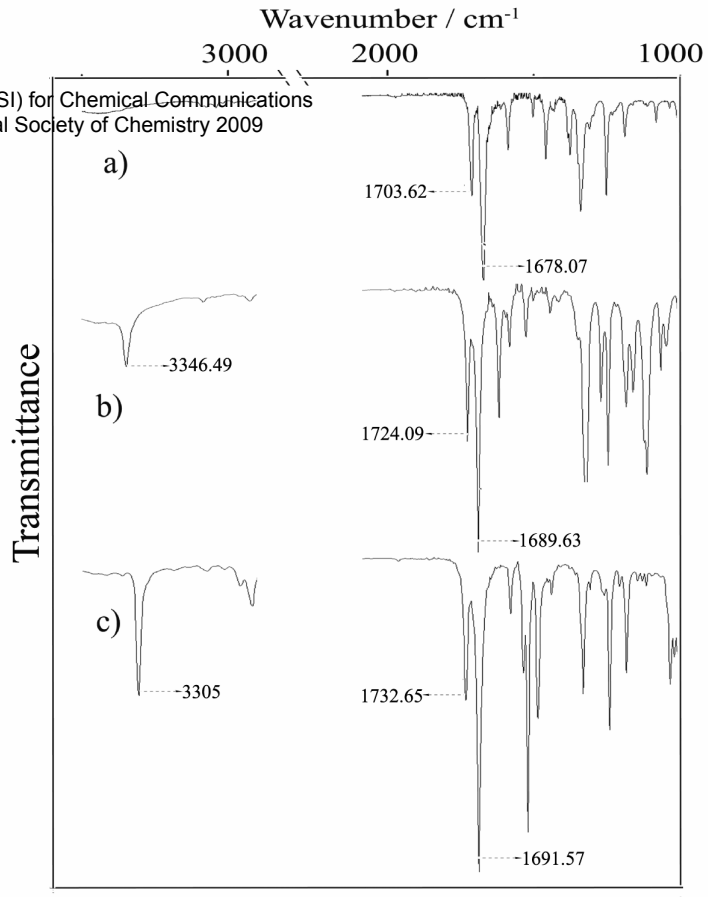


Figure SI 7: IR spectra of a) **1c**, b) **1a** and c) **1b** clearly showing the effect of electron withdrawing inductive effect on the carbonyl groups of the NDI moiety [Carbonyl groups are the centers of electron acceptance during radical anion formation].

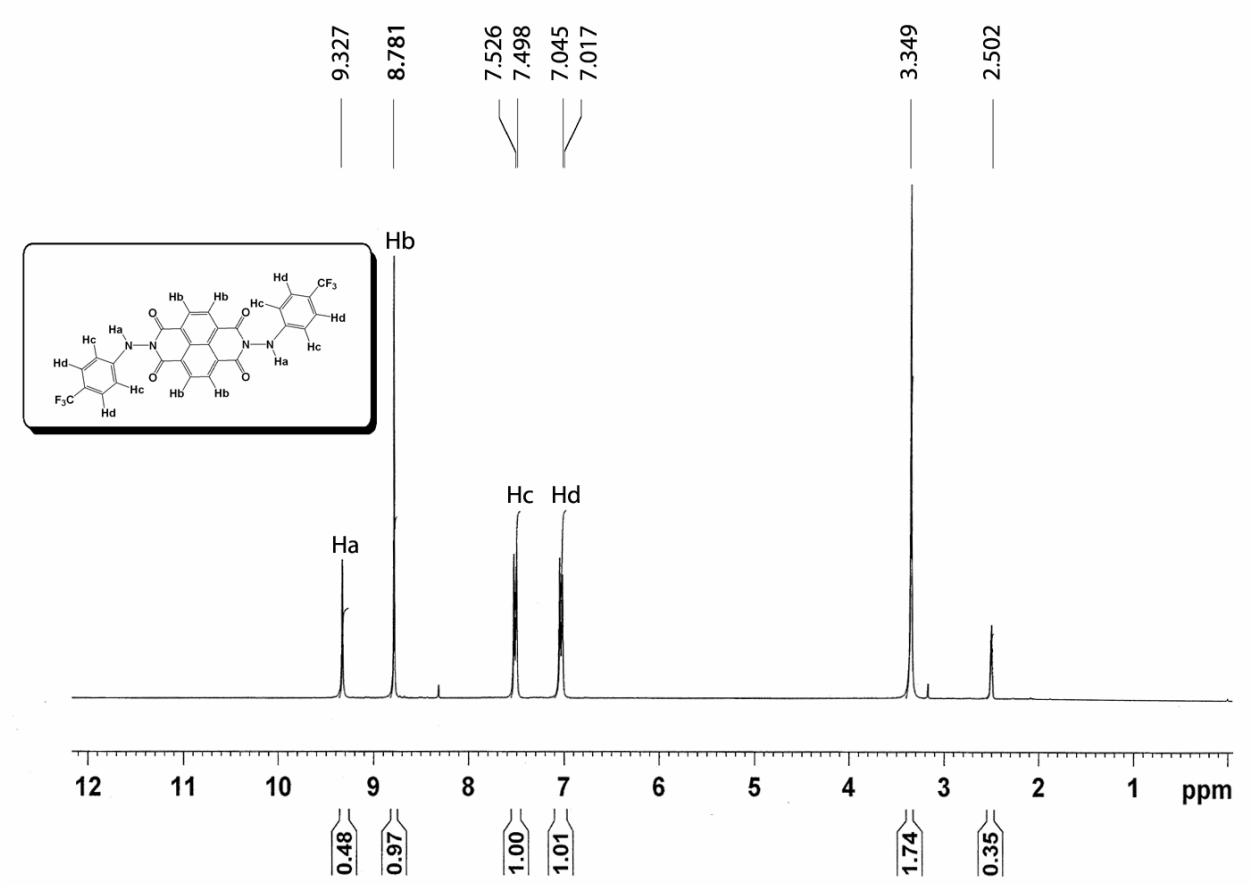


Figure SI 8: 300 MHz ^{1}H NMR spectra of compound **1a** in DMSO.

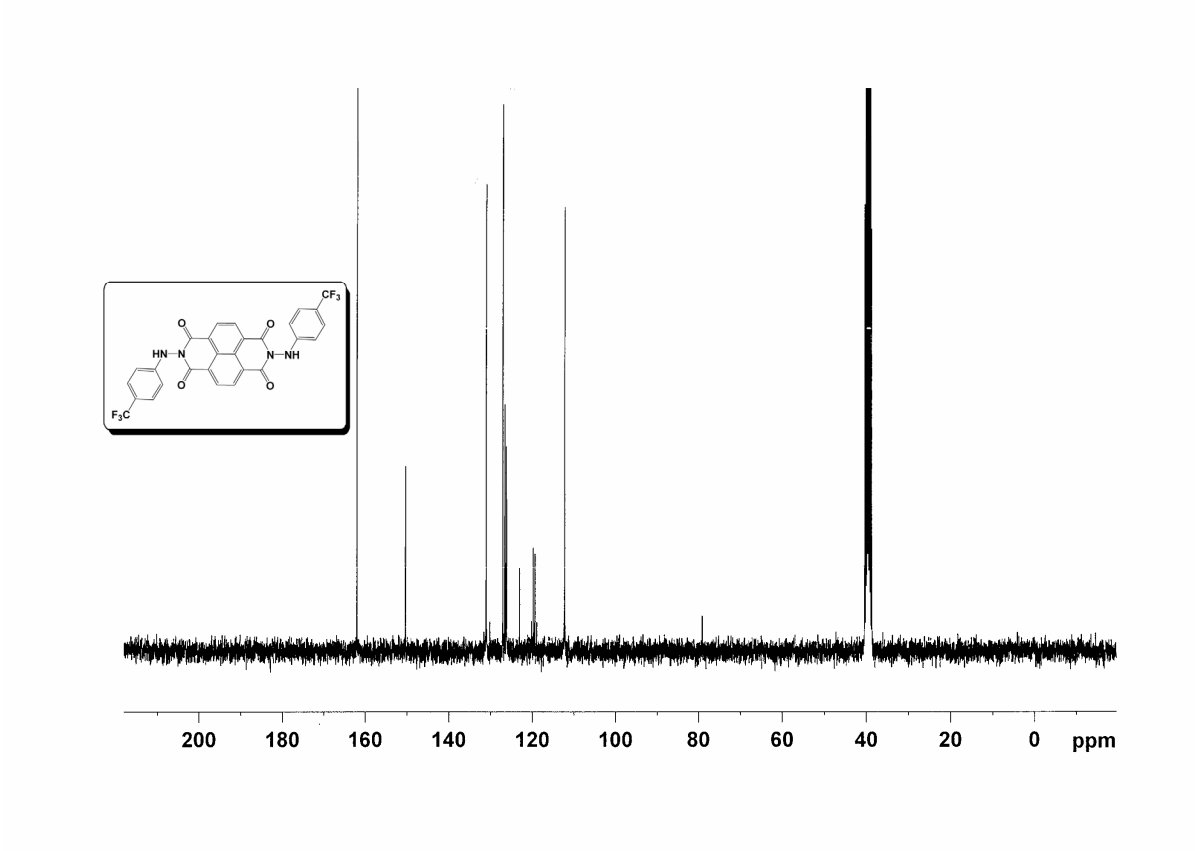


Figure SI 9: 75 MHz ^{13}C NMR spectra of compound **1a** in DMSO.

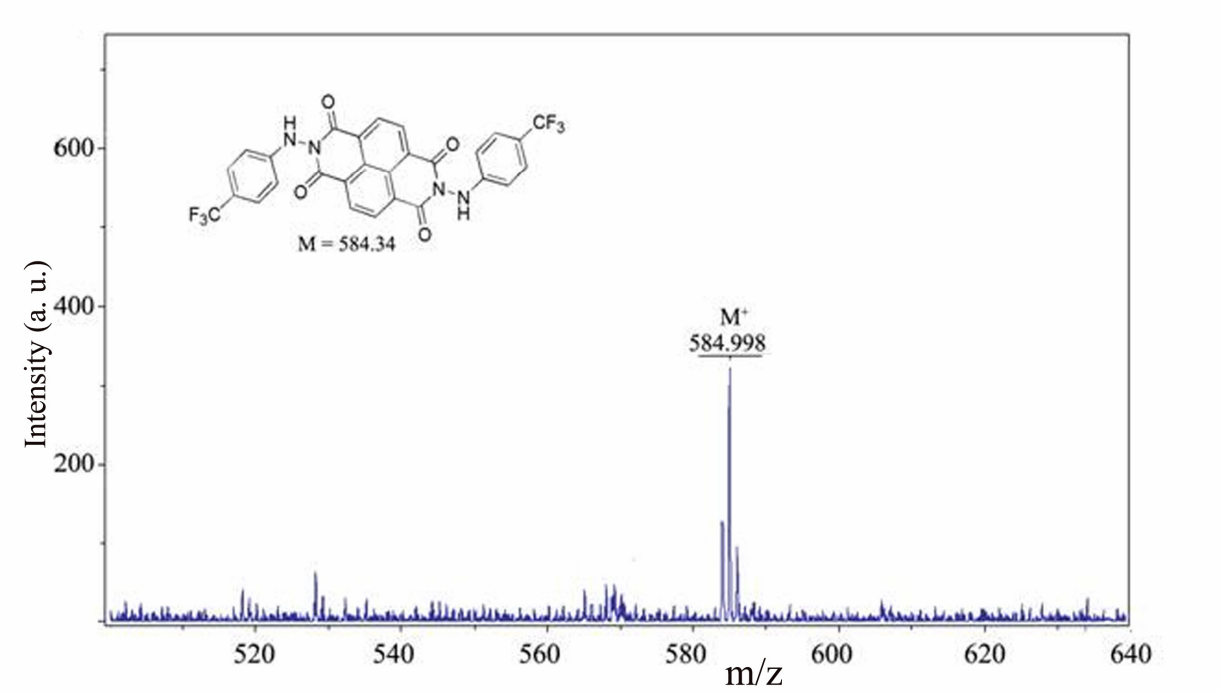


Figure SI 10: MALDI-TOF Mass spectra of compound **1a**.