A Tetrastable Naphthalenediimide: Anion Induced Charge Transfer, Single and Double Electron Transfer for Combinational Logic Gates

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Supporting Information

Contents

Experimental Section

General: Chemicals were sourced either from Fluka, Sigma-Aldrich, Spectrochem India or Thomas-Baker-India and were used as received. The tetrabutylammonium fluoride was sourced from Sigma-Aldrich. 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. NMR (^{1}H, ^{13}C, DEPT-135 and APT) spectra were recorded on a Bruker 500 MHz spectrometer in $CDCl_3$ with TMS as a standard. MALDI-TOF mass spectral data were obtained using a Bruker Autoflex TOF/TOF instrument with laser repetition rate of 50 psec. α-Cyano-4-hydroxycinnamic acid and 1,8,9-Anthracenetriol were used as the matrix for MALDI-TOF mass spectrometry. Infra-Red spectra were recorded in KBr pellets using a Varian 7000 FT-IR instrument.

UV-vis-NIR and Fluorescence Spectroscopy: UV-vis-NIR spectra were taken using a JASCO V-670 model spectrometer. The spectroscopic experiments were carried out in UV Grade DMF or THF, which were sourced from Spectrochem, India. The steady state fluorescence spectra were measured using a Varian Cary Eclipse Fluorescence Spectrometer. All UV-vis-NIR spectroscopic experiments were performed in a quartz cuvette with 1.0 mm optical path length and fluorescence studies were carried out in a 1.0 cm quartz cuvette.

Electrochemistry: The electrochemical properties were studied using a computer-controlled potentiostat (CHI 650C) and a standard three electrode arrangement that consisted of both platinum working and auxiliary electrodes and a saturated calomel reference electrode (SCE). All electrochemical measurements were carried out in Ar-purged dry DMF with 0.1 M Bu_4NPF_6 as the supporting electrolyte. The scan rate for cyclic voltametry (CV) experiments was typically 200-300 mV/s. Differential Pulse Voltametry (DPV) was carried out keeping peak amplitude 50 mV, peak width 0.01 sec, pulse period 0.05 sec and increment E at 20 mV.

X-ray Crystallography: Crystals of **1a** were grown from a THF solution by slow evaporation method at ~ 10 ^{o}C. The crystals were highly sensitive, losing the solvent and crystallanity on taking out from the mother liquor. A number of crystals were tried in crystallographic oil and at low temperature. The reported data set was collected by mounting the crystal with paratone oil in a quartz capillary at 100 K. X-ray data were collected on a Bruker's Apex-II CCD diffractometer using Mo Kα (λ = 0.71069 Å). The data were corrected for Lorentz and polarization effects and empirical absorption corrections were applied using SADABS from Bruker. A total of 14031 reflections were measured out of which 3964 were independent and 2163 were observed [I>2 σ(I)] for theta 25.46° The structures were solved by direct methods using SIR-92 [1] and refined by full-matrix least squares refinement methods based on F^2, using SHELX-97 [2]. Refinement showed high disorder in the terminal $-CF_3$ group which could be resolved by splitting each F on two positions with their site occupancies and U_{iso} refined as free variables. Two THF molecules were also located as solvent molecules in the asymmetric unit with some degree of disorder which could not be resolved. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed geometrically with their U_{iso} values 1.2 times of the phenylene and methylene carbons. All calculations were performed using Wingx [3] package. Important crystal and refinement parameters are given in Table 1. A final refinement of 296 parameters gave R1 = 0.1315, wR2 = 0.3415 for the observed data and R1 = 0.2018, wR2 = 0.3870 for all data which are on the higher side due to unstable nature of the crystal. However, the final difference Fourier showed no significant residual electron density and esds and thermal parameters are good. The crystal structure showed SAV of 35 $Å^3$, which are due to the packing forces.

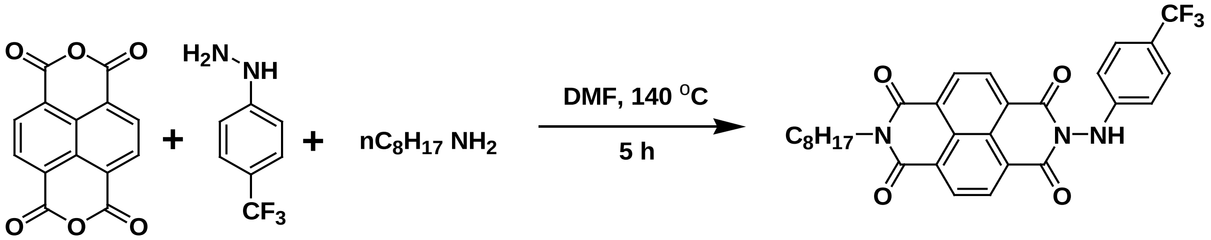
References:

1. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Cryst*. **1994**, *27*, 435.

2. G. M. Sheldrick, SHELXL-97: Program for crystal structure refinement, University of Göttingen, Germany, 1997.

3. L. J. Farrugia, *J. Appl. Cryst.* **1999**, *32*, 837.

Synthesis of 1c



4-Trifluromethylphenylhydrazine (0.36 g, 2.03 mmol) and octyl amine (0.31 mL, 1.90 mmol) were transferred to a 100 mL R.B. flask containing 1,4,5,8-naphthalenetetracarboxylic dianhydride (0.50 g, 1.86 mmol) in 25 mL DMF under N_2 atmosphere. The reaction mixture was heated on a magnetic stirrer at 140 ^{O}C for 5 h and cooled to RT. The solution was evaporated under vacuum. The solid obtained was washed with excess of MeOH. Further purification of the above product was carried out by preparative TLC (silica gel G, $CHCl_3$-MeOH (63:1). Yield: 320 mg (32 %). M.pt: 230 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, TMS): $\delta = 8.83$ (q, 4H, *Nap*), 7.51 (d, 2H, $J = 8.5$ Hz, *Ph*), 7.02 (s, 1H, *NH*), 6.94 (d, 2H, $J = 8.5$ Hz, *Ph*), 4.21 (m, 2H, NCH_2), 1.8 – 1.1 (m, 12H, CH_2), 0.88 (t, 3H, CH_3). ^{13}CNMR (125 MHz, $CDCl_3$, 298 K, TMS): δ = 162.50, 161.91, 148.58, 132.11, 131.14, 127.56, 126.94, 126.81, 126.78, 126.58, 125.94, 114.16, 41.16, 31.81, 29.29, 29.20, 28.08, 27.08, 22.65, 14. 11. DEPT 135 (125 MHz, $CDCl_3$, 298 K, TMS): δ = 132.11, 131.14, 126.81, 114.16, 41.16, 31.81, 29.29, 29.20, 28.08, 27.08, 22.65, 14.16. APT (125 MHz, $CDCl_3$, 298 K, TMS): δ = 162.50, 161.91, 148.58, 132.11, 131.14, 127.56, 126.94, 126.80, 126.77, 126.58, 125.94 114.16, 41.16, 31.80, 29.29, 28.08, 27.08, 22.65, 14. 11. MS (MALDI–TOF matrix: α-Cyano-4-hydroxycinnamic acid): calculated for $C_{29}H_{26}F_3N_3O_4$ (m/z) 537.53, found 538.16. FTIR (KBr pellet) $\upsilon = 3340$ (NH_{str}), (2926, 2858) (CH_{str}), (1714, 1691) ($C{=}O_{str}$), 1661, 1330, 1247 cm^{-1}. UV-vis (THF): $\lambda_{max}(\varepsilon)$ = 356 nm (12857 M^{-1}cm^{-1}), 376 nm (14286 M^{-1}cm^{-1}). Anal. calcd. for $C_{29}H_{26}F_3N_3O_4$: C, 64.80; H, 4.88; N, 7.82; found: C 64.76, H 4.78, N 7.76.

Reference:

4. Synthesis of **1a** have been reported in: a) M. R. Ajayakumar and P. Mukhopadhyay, *Chem. Commun.*, 2009, **25**, 3702, and **1b** in b) M. R. Ajayakumar, S. Yadav, S. Ghosh and P. Mukhopadhyay, *Org. Lett.* 2010, **12**, 2646.

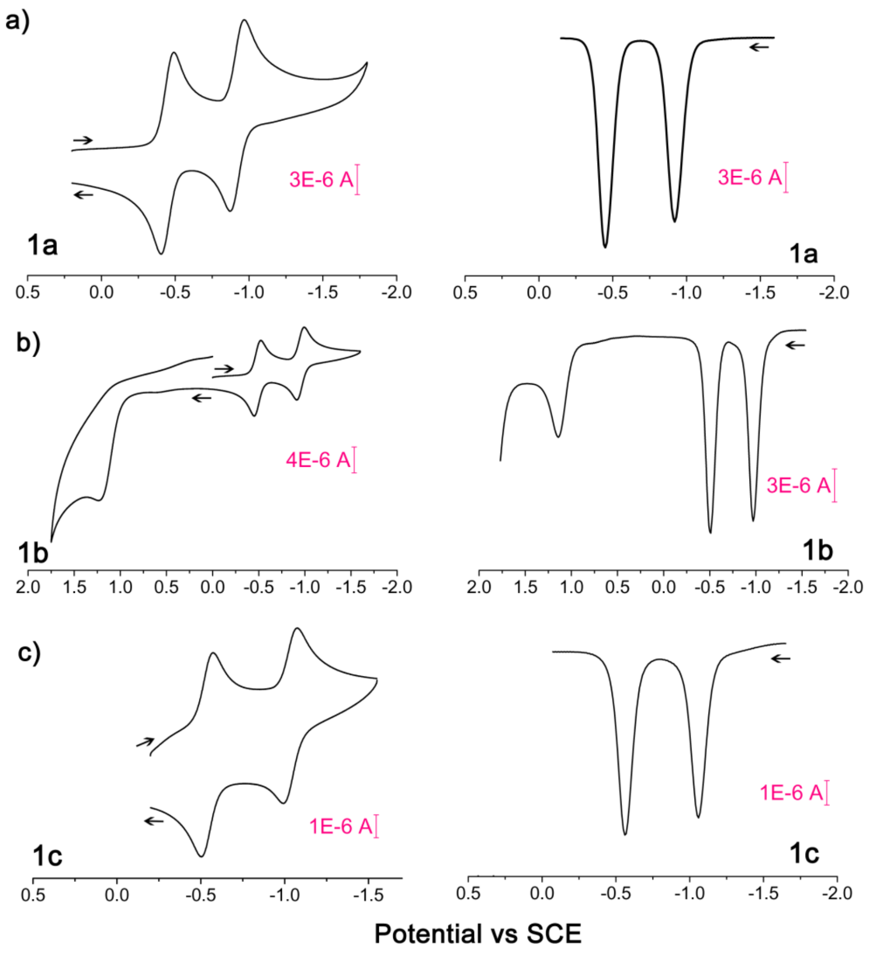


Figure S1: CV and DPV results of **1a-c** in DMF.

Table S1: Redox potentials of **1a-c** in DMF.

	E^1_R (V)	E^2_R (V)	E^1_{Ox} (V)
1a	-0.447/-0.449	-0.920/-0.920	-
1b	-0.490/-0.506	-0.953/-0.972	+1.164/+1.141
1c	-0.538/-0.566	-1.034/-1.059	-

All potentials reported as $E_{1/2} = [(E^a_p + E^c_p)/2]$ in V. CV in DMF with 0.1 M Bu_4NPF_6 as the electrolyte and a saturated calomel reference electrode (SCE).

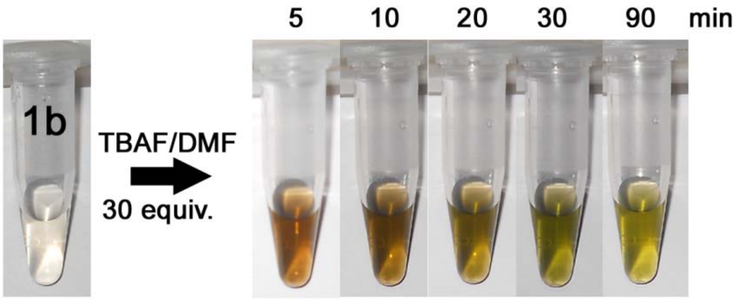


Figure S2: Photographs show the colour change in **1b** after the addition of 30 equiv. TBAF in DMF

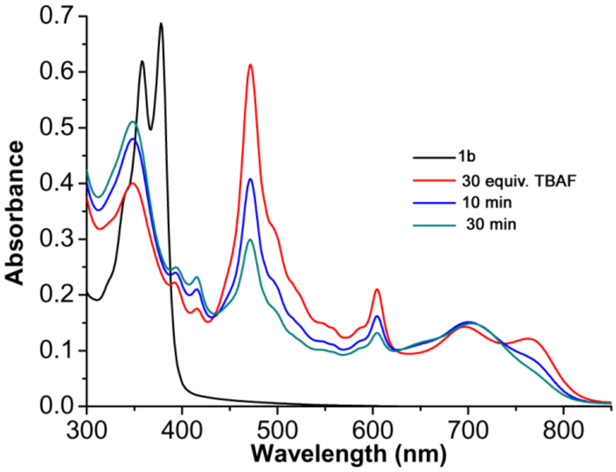


Figure S3: UV-vis-NIR absorption spectra of **1b** (0.3mM) with the addition of 30 equiv. TBAF in DMF. **1b** forms mainly radical anion **1b**$^{\cdot-}$ through SET.

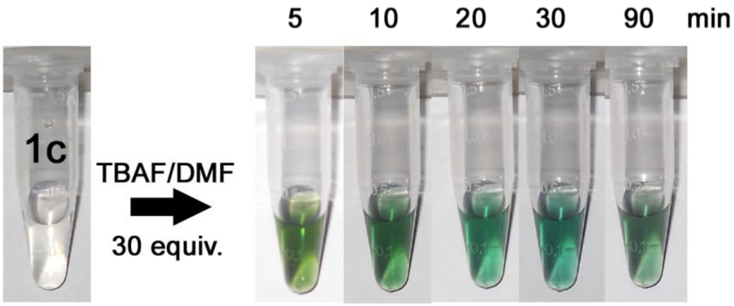


Figure S4: Photographs show the colour change in **1c** after the addition of 30 equiv. TBAF in DMF

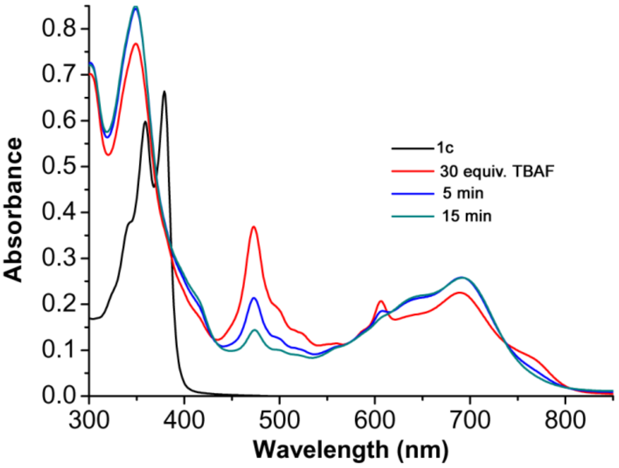


Figure S5: UV-vis-NIR absorption spectra of **1c** (0.3mM) with the addition of 30 equiv. TBAF in DMF. Deprotonation and the formation of the ICT states were observed after 15 min.

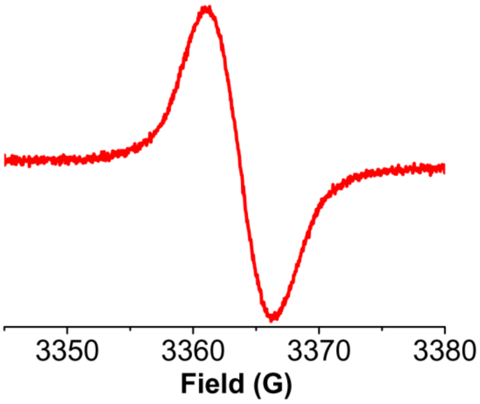


Figure S6: EPR spectrum of **1a** (3×10^{-4} M) with 5.0 equiv. of TBAF in DMF.

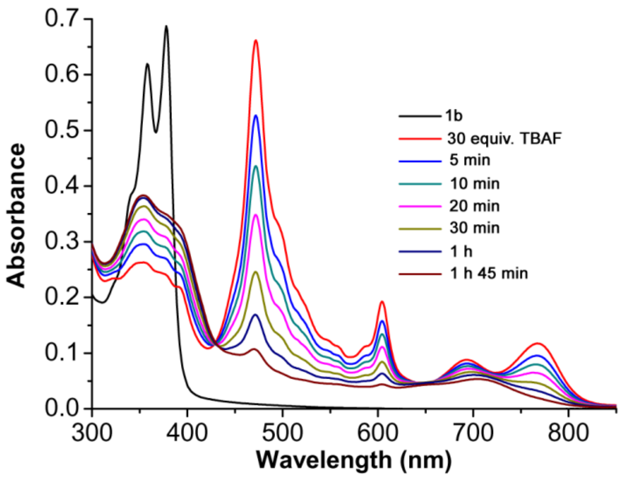


Figure S7: UV-vis-NIR absorption spectra of **1b** (0.3 mM) with 30 equiv. TBAF in DMF/H_2O (99:1 *v/v*). No dianion formation was observed with time.

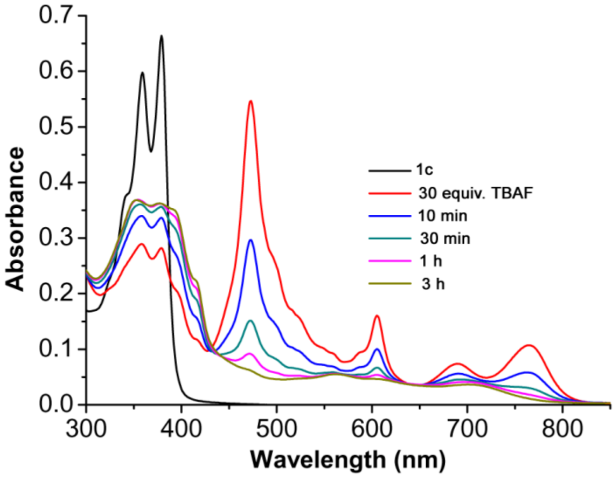


Figure S8: UV-vis-NIR absorption spectra of **1c** (0.3mM) with 30 equiv. TBAF in DMF/H_2O (99:1 *v/v*). No dianion formation was observed with time.

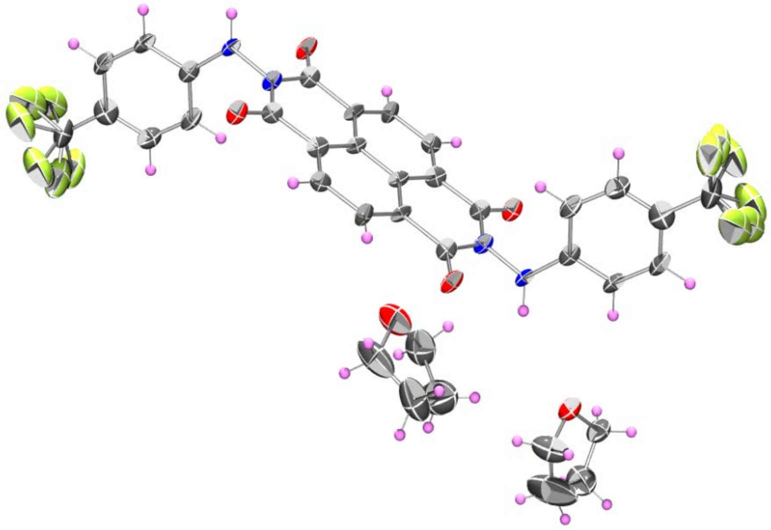


Figure S9: i) Crystal structure of **1a** showing the two THF solvent molecules and the disordered Fluorine atoms. Colour representation: C, Grey; H, Pink; N, Blue; O, Red; Fluorine, Yellow-Green. Structure has been drawn with POV-Ray.

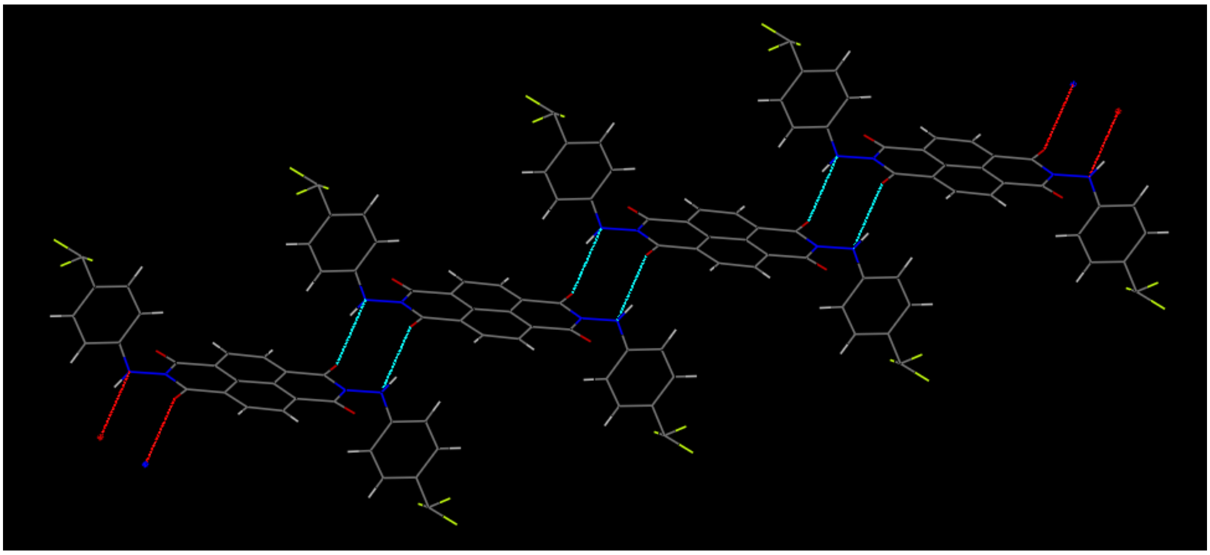


Figure S9: ii) Crystal structure showing the packing of **1a** forming H-bonded ladder-like network, view along the b-axis. Colour representation: C, Grey; H, White; N, Blue; O, Red; Fluorine, Yellow-Green.

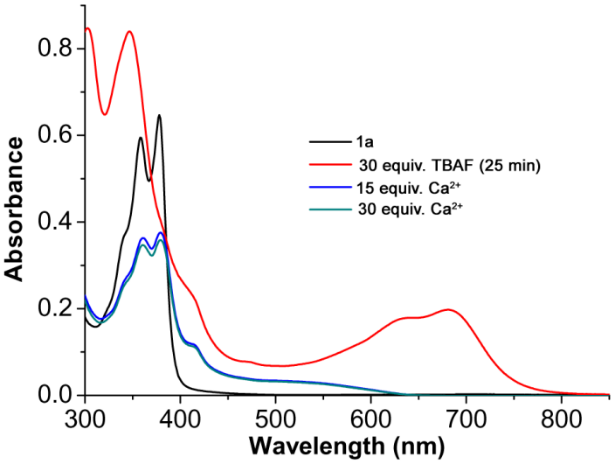


Figure S10: Regeneration of **1a** induced by 15 equiv. of $Ca(ClO_4)_2$.

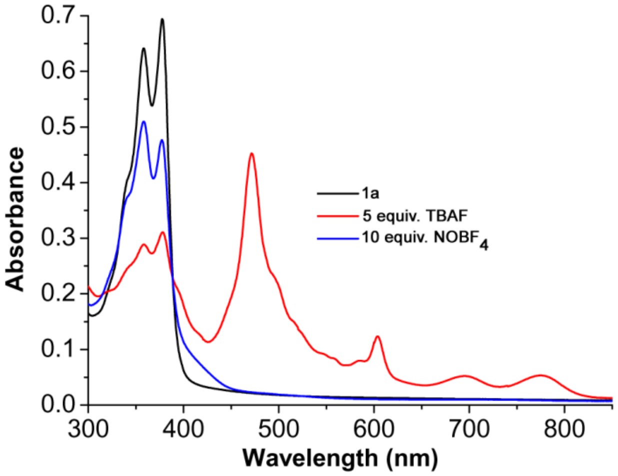


Figure S11: Regeneration of **1a**$^{\bullet-}$ to **1a** induced by 5 equiv. of $NOBF_4$.

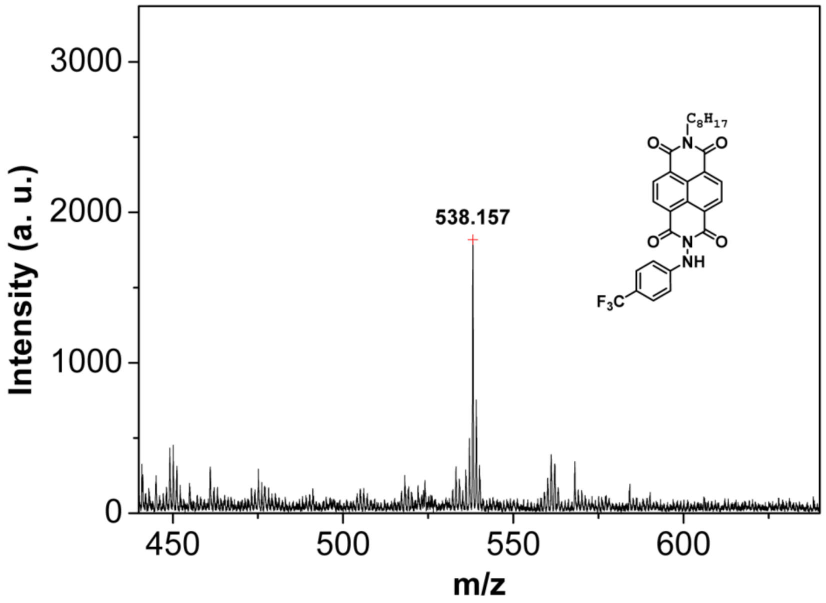


Figure S12: MALDI-TOF Mass spectra of compound **1c**.

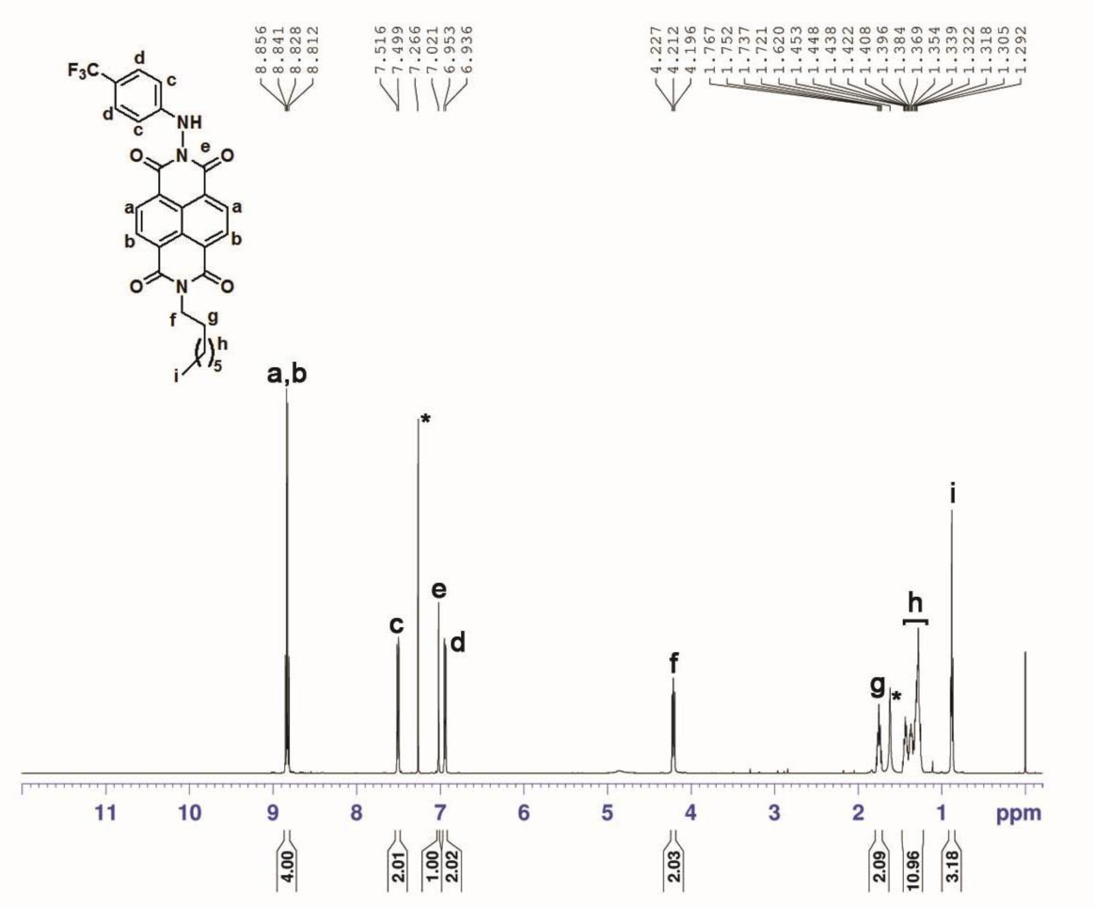


Figure S13: 500 MHz ^{1}H NMR of **1c** in $CDCl_3$.

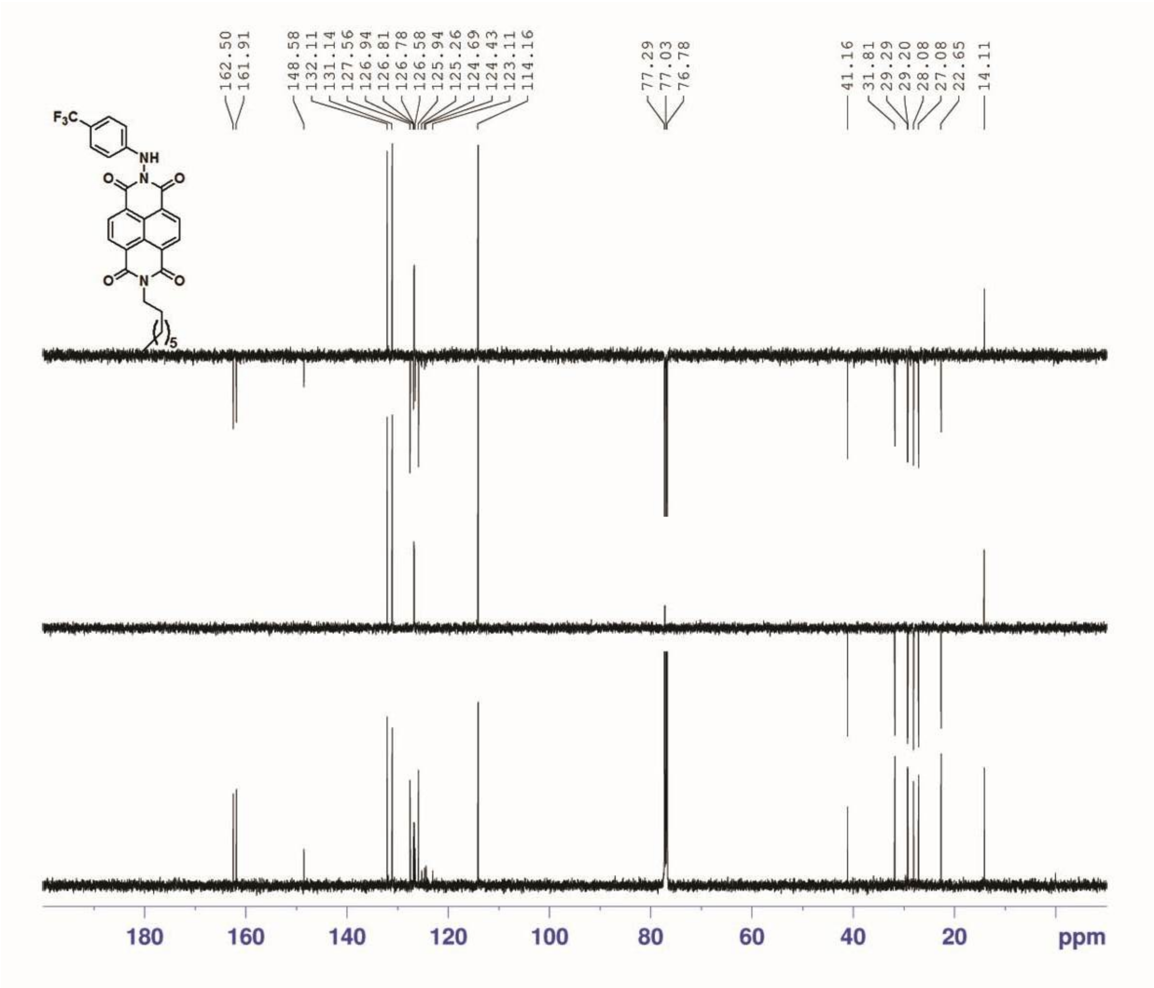


Figure S14: 125 MHz ^{13}C (bottom), DEPT 135 (middle) and APT (top) of **1c** in $CDCl_3$.