Electronic Supplementary Material (ESI) for Chemical Science.

The Deeper It Goes, The Brighter It Glows: NIR emissive Nitro-Terrylene Diimides with Deep LUMOs

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Table of contents

I. General Information

All the chemicals were purchased either from SIGMA-ALDRICH or SPECTROCHEM and used directly without any further purification unless mentioned. Spectroscopic grade solvents were used for optical and electrochemical measurements. Air-sensitive reactions were carried out in oven-dried glassware and in a dry argon/N_2 atmosphere. The synthesized compounds were purified by silica gel (mesh size 100-200) and neutral alumina column chromatography. ^{1}H and ^{13}C NMR spectra were recorded at 298 K on Bruker Avance 500 MHz instruments using Chloroform-d ($CDCl_3$) and Benzene-d_6 (C_6D_6) as a solvent. Chemical shifts are reported in parts per million (ppm) relative to the residual solvent peaks ($CDCl_3$: δ = 7.26 ppm, C_6D_6: δ = 7.16 ppm for ^{1}H). ^{13}C NMR spectra are referenced to the following solvent peaks: $CDCl_3$: δ = 77.16 ppm. Abbreviations were used to indicate multiplicity: singlet (s), doublet (d), multiplet (m). High resolution mass spectra were measured on electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) on Bruker micro TOF-QII mass spectrometer. Absorption measurements were performed in a Perkin Elmer LAMBDA 950 UV/VIS/NIR spectrophotometer with 10 mm path length quartz cuvette, and emission spectra were recorded on Horiba Fluoromax-4 spectrometer. Low temperature emission experiments were performed using liquid nitrogen Dewar setup. Unless otherwise mentioned, the photophysical measurements were carried out from 10^{-6} M solutions. Electrochemical studies were performed on CHI instrument. Cyclic voltammetry (CV) and differential pulse voltammograms (DPV) measurements were carried out using CH potentiostat. Pt disk as a working, saturated calomel electrode (SCE) as a reference electrode and platinum wire as a counter were used. All the electrochemical measurements were performed using 0.1 M solution of Tetrabutylammonium hexafluorophosphate (TBAP) in dry $CHCl_3$ as supporting electrolyte. Single crystal X-ray diffraction (SCXRD) measurements were collected at 100 K on Bruker Apex diffractometer with a CCD detector with Mo-Kα radiation at 100 K. Density functional theory (DFT) calculations were performed using Gaussian 09 program package.[1]

The relative quantum yield of all nitro-TDIs calculated using following formula:

$$Q = Q_R \frac{I}{I_R} \frac{OD_R}{OD} \frac{n^2}{n_R^2}$$

Where

Q: relative quantum yield

R: reference fluorophre

I: integrated integrated area

OD: optical density

n: refractive index

LUMO energy calculated using following formula:

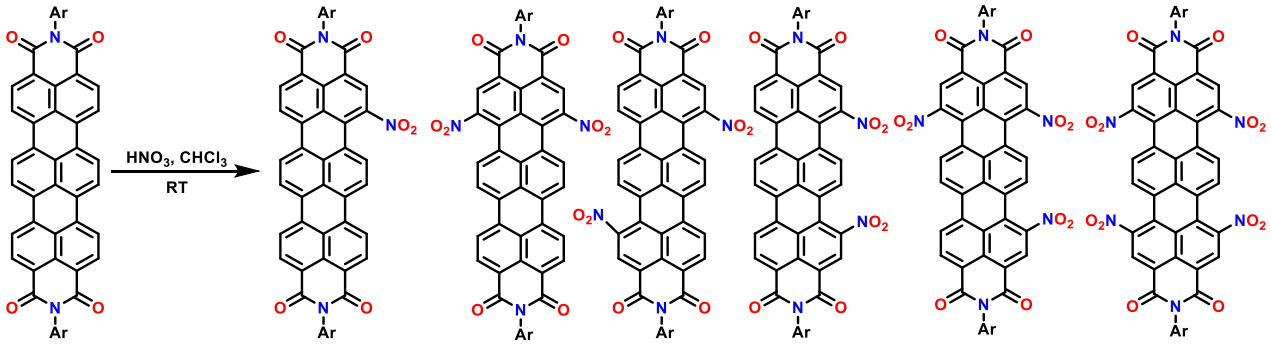
$$E_{LUMO\ vs\ Fc/Fc^+} = -4.8 - E_{1/2}^R$$

E_{LUMO} = energy of lowest unoccupied molecular orbital

$E_{1/2}^R$ = potential of 1st reduction

Experimental Procedures:

General scheme for the nitration:



Ar = 2,6-diisopropylphenyl

Compound	HNO_3 (eqv.)	Time	Yield (%)						
			TDI	T_a	T_{ab}	T_{ac}	T_{ad}	T_{abc}	T_{abcd}
T_a - a = NO_2; b,c,d = H	50	5 min	t	85	t	t	t		
T_{ab} - a,b = NO_2; c,d = H	100	1 hr			30	42	20	t	
T_{ac} - a,c = NO_2; b,d = H	100	1 hr			30	42	20	t	
T_{ad} - a,d = NO_2; b,c = H	100	1 hr			30	42	20	t	
T_{abc} - a,b,c = NO_2; d = H	150	12 hr			12	20	10	50	t
T_{abcd} - a,b,c,d = NO_2	500	36 hr						45	55

Synthesis Procedure for T_a: In a dry and degassed 100 mL round bottom flask, TDI (100 mg, 0.1198 mmol) was dissolved in 50 mL dry $CHCl_3$. Nitric acid (265 μL, 5.99 mmol) was added after 15 minutes. The reaction mixture was stirred at room temperature for 5 minutes. Completion of reaction was monitored by TLC and the remaining acid was quenched by saturated solution of KOH. The organic layer was collected using chloroform, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was subjected to neutral alumina column chromatography using DCM and hexane as eluents. The pure greenish blue product **T_a** was isolated in 85 % yield. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 8.75 (dd, *J* = 7.7, 4.7 Hz, 2H), 8.70 (s, 1H), 8.65 (d, *J* = 7.7 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.87-7.81 (m, 3H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.41-7.37 (m, 2H), 7.30 (d, *J* = 7.9 Hz, 4H), 3.09 (ddt, *J* = 20.4, 13.8, 6.9 Hz, 4H), 1.35-1.29 (m, 24H). ^{13}C {^{1}H} (126 MHz, $CDCl_3$, 298K): δ 163.15, 162.37, 146.73, 145.68, 145.60, 136.93, 136.09, 135.18, 133.35, 133.10, 132.08, 130.23, 129.68, 128.79, 127.55, 127.11, 126.11, 125.59, 124.55, 124.51, 124.30, 124.24, 124.13, 122.93, 122.89, 122.61122.46, 121.91, 121.58, 121.44, 29.30, 29.24, 24.04, 24.01. HRMS (APCI) (m/z): calculated for $C_{58}H_{45}N_3O_6$, 880.3416; found, 880.3381.

Synthesis Procedure for $T_{ab\text{-}ad}$: In a dry and degassed 100 mL round bottom flask, TDI (100 mg, 0.1198 mmol) was dissolved in 50 mL dry $CHCl_3$. Nitric acid (531 μL, 11.98 mmol) was added after 15 minutes. The reaction mixture was stirred at room temperature for 1 hour. Completion of reaction was monitored by TLC and the remaining acid was quenched by saturated solution of KOH. The organic layer was collected using chloroform, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was subjected to neutral alumina column chromatography using DCM and hexane as eluents. The pure greenish blue products **$T_{ab\text{-}ad}$** were isolated in 30%, 42 % and 20 % yield respectively.

^{1}H NMR of **T_{ab}** (500 MHz, $CDCl_3$, 298 K): δ 8.95 (s, 2H), 8.83 (d, *J*= 8.0 Hz, 2H), 8.77 (d, *J*= 8.1, 2H), 8.74 (d, *J*= 8.6 Hz, 2H), 8.40 (d, *J*= 8.4 Hz, 2H), 7.53 (dt, *J*= 12.7, 7.8 Hz, 2H), 7.37 (dd, *J*= 7.8, 5.9 Hz, 4H), 2.77 (dt, *J*= 13.7, 6.9 Hz, 2H), 2.69 (dt, *J*=13.7, 6.9 Hz, 2H), 1.20 (d, *J*=1.42 Hz, 12H), 1.19 (d, *J*=1.4 Hz, 12H). ^{13}C {^{1}H} (126 MHz, $CDCl_3$, 298K): δ163.53,

161. 89, 147.73, 145.83, 145.65, 144.53, 141.70, 141.03, 134.72, 134.27, 132.28, 130.71, 129.36, 128.49, 126.18, 124.78, 124.51, 124.34, 124.31, 124.07, 123.79, 121.53, 115.75, 111.60, 110.94, 29.85, 29.53, 24.18, 24.16. HRMS (APCI) (m/z): calculated for $C_{58}H_{44}N_4O_8$, 925.3232; found, 925.3242.

^{1}H NMR of **T_{ac}** (500 MHz, $CDCl_3$, 298 K): δ 8.89 (d, *J* = 8.0 Hz, 2H), 8.85 (s, 2H), 8.76 (d, *J* = 8.1 Hz, 2H), 8.70 (d, *J* = 8.6 Hz, 2H), 8.36 (d, *J* = 8.4 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 4H), 2.72 (dt, *J* = 13.5, 6.7 Hz, 4H), 1.19 (d, *J* = 6.8 Hz, 24H). ^{13}C {^{1}H} (126 MHz, $CDCl_3$, 298K): δ 162.07, 162.32, 162.32, 157.57, 147.37, 136.23, 133.62, 131.58, 130.24, 130.18, 130.12, 129.50, 128.75, 127.53, 127.24, 127.19, 125.28, 124.41, 124.28, 122.88, 122.58, 29.45, 24.18, 24.15. HRMS (APCI) (m/z): calculated for $C_{58}H_{44}N_4O_8$, 925.3232; found, 925.3222.

^{1}H NMR of **T_{ad}** (500 MHz, $CDCl_3$, 298 K): δ 8.89 (d, *J* = 8.0 Hz, 2H), 8.84 (s, 2H), 8.83 (s, 2H), 8.79 (d, *J* = 8.1 Hz, 2H), 8.22 (s, 2H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 4H), 2.72 (dt, *J* = 13.6, 6.8 Hz, 4H), 1.19 (d, *J* = 6.8 Hz, 24H). ^{13}C {^{1}H} (126 MHz, $CDCl_3$, 298K): δ 162.12, 162.27, 147.56, 145.71, 136.58, 133.58, 130.69, 130.23, 130.17, 130.11, 129.13, 128.60, 128.10, 127.80, 127.49, 127.16, 125.59, 124.41, 123.88, 123.18, 122.26, 29.85, 29.45, 24.18, 24.15. HRMS (APCI) (m/z): calculated for $C_{58}H_{44}N_4O_8$, 925.3232; found, 925.3247.

Synthesis Procedure for T_{abc}: In a dry and degassed 100 mL round bottom flask, TDI (100 mg, 0.1198 mmol) was dissolved in 50 mL dry $CHCl_3$. After 15 minutes nitric acid (800 μL,17.97 mmol) was added. Then the reaction mixture was stirred at room temperature for 12 hours. Completion of reaction was monitored by TLC and the remaining acid was quenched by saturated solution of KOH. The organic layer was collected using chloroform, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was subjected to neutral alumina column chromatography using DCM and hexane as eluents. The pure greenish blue product **T_{abc}** was isolated in 50 % yield. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.96 (s, 1H), 8.94 (s, 1H), 8.91 (d, *J* = 8.0 Hz, 1H), 8.85 (s, 1H), 8.82 (d, *J* = 8.1 Hz, 1H), 8.75 (d, *J* = 8.5 Hz, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 8.28 (s, 2H), 7.54 (dd, *J* = 14.6, 7.5 Hz, 2H), 7.38 (dd, *J* = 7.8, 2.8 Hz, 4H), 2.70 (ddd, *J* = 20.5, 13.7, 6.8 Hz, 4H), 1.19 (d, *J* = 6.8 Hz, 24H). ^{13}C {^{1}H} (126 MHz, $CDCl_3$, 298K): δ 162.89, 162.08, 161.68, 161.63, 148.39, 148.21, 148.01, 145.72, 145.63, 135.67, 133.67, 132.49, 130.31, 130.02, 129.92, 128.74, 128.51, 128.48, 128.37, 128.33, 127.28, 127.11, 127.04, 126.39, 125.60, 125.21, 125.11, 124.54, 124.44, 123.98, 123.25, 122.74, 122.39, 29.85, 29.54, 29.47, 24.19, 24.16. HRMS (APCI) (m/z): calculated for $C_{58}H_{43}N_5O_{10}$, 970.3083; found, 970.3045.

Synthesis Procedure for T_{abcd}: In a dry and degassed 100 mL round bottom flask, TDI (100 mg, 0.1198 mmol) was dissolved in 50 mL dry $CHCl_3$. After 15 minutes nitric acid (2.65 mL, 59.9 mmol) was added. Then the reaction mixture was stirred at room temperature for 36 hours. Completion of reaction was monitored by TLC and the remaining acid was quenched by saturated solution of KOH. The organic layer was collected using chloroform, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was subjected to neutral alumina column chromatography using DCM and hexane as eluent. The pure greenish blue product **T_{abcd}** was isolated in 55 % yield. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.95 (s, 4H), 8.95 (s, 4H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 4H), 2.73 – 2.62 (m, 4H), 1.19 (d, *J* = 6.8 Hz, 12H). ^{13}C {^{1}H} (126 MHz, $CDCl_3$, 298K): δ 161.42, 148.83, 145.62, 130.48, 129.51, 129.43, 128.50, 127.86, 127.22, 124.57, 123.50, 29.56, 24.17. HRMS (APCI) (m/z): calculated for $C_{58}H_{42}N_6O_{12}$, 1015.2933; found, 1015.2932.

III. NMR Spectra:

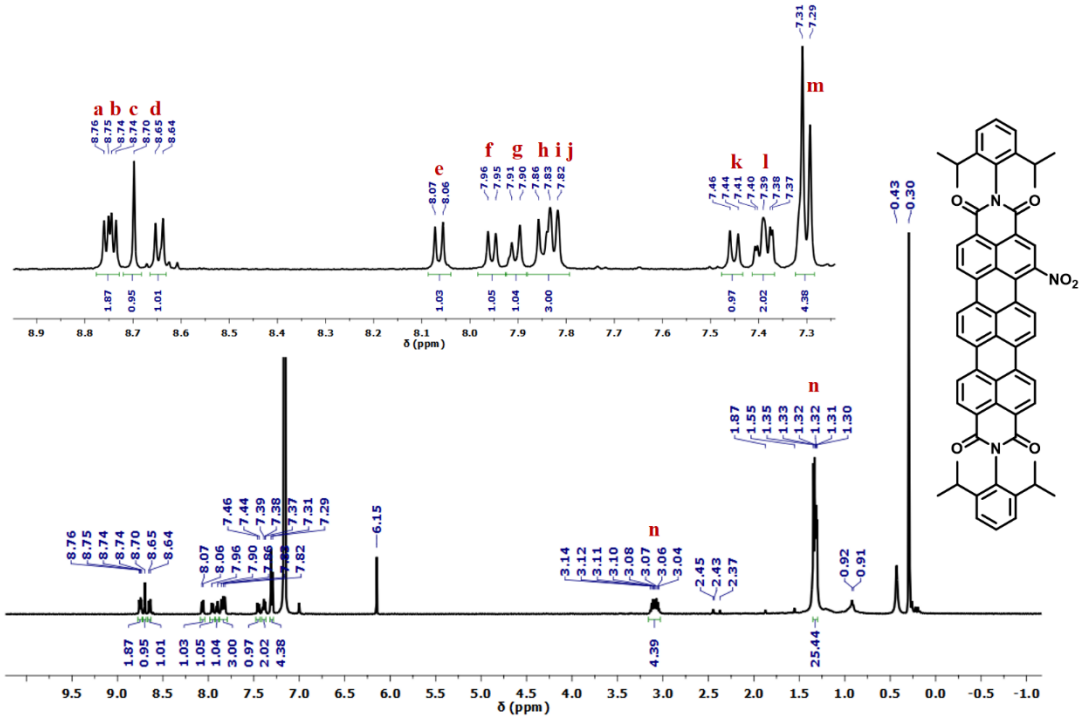


Figure S1: ^{1}H NMR of $\mathbf{T_a}$ (500 MHz, C_6D_6, 298 K)

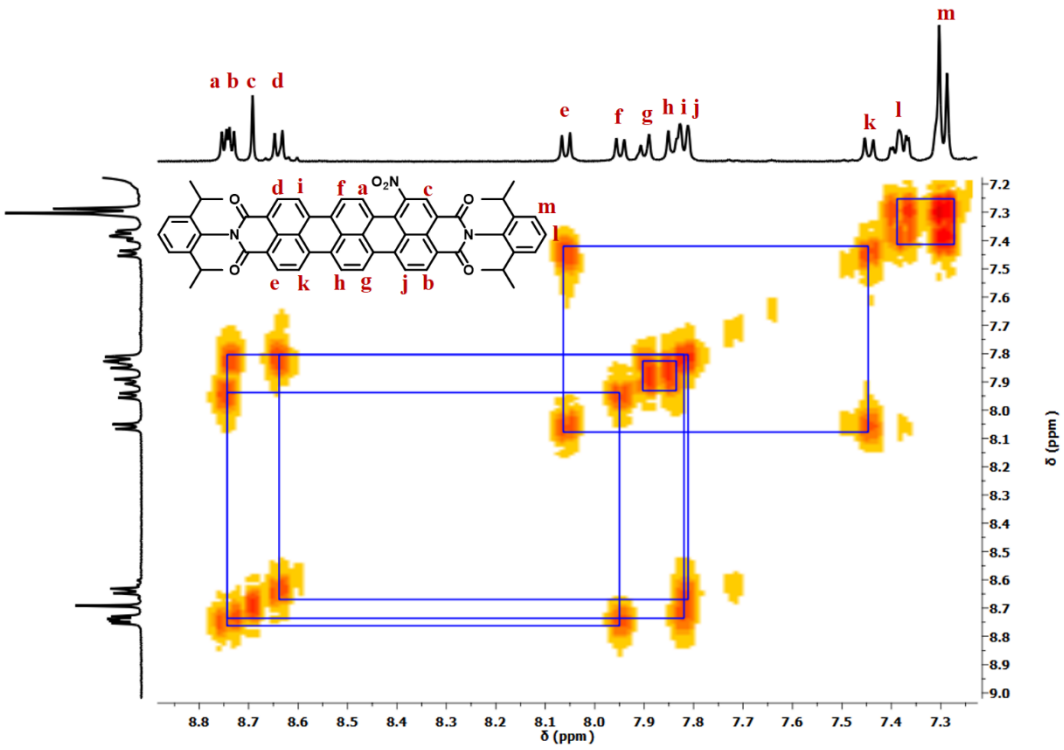


Figure S2: ^{1}H-^{1}H correlation (COSY) NMR of **T_a** (500 MHz, C_6D_6, 298 K)

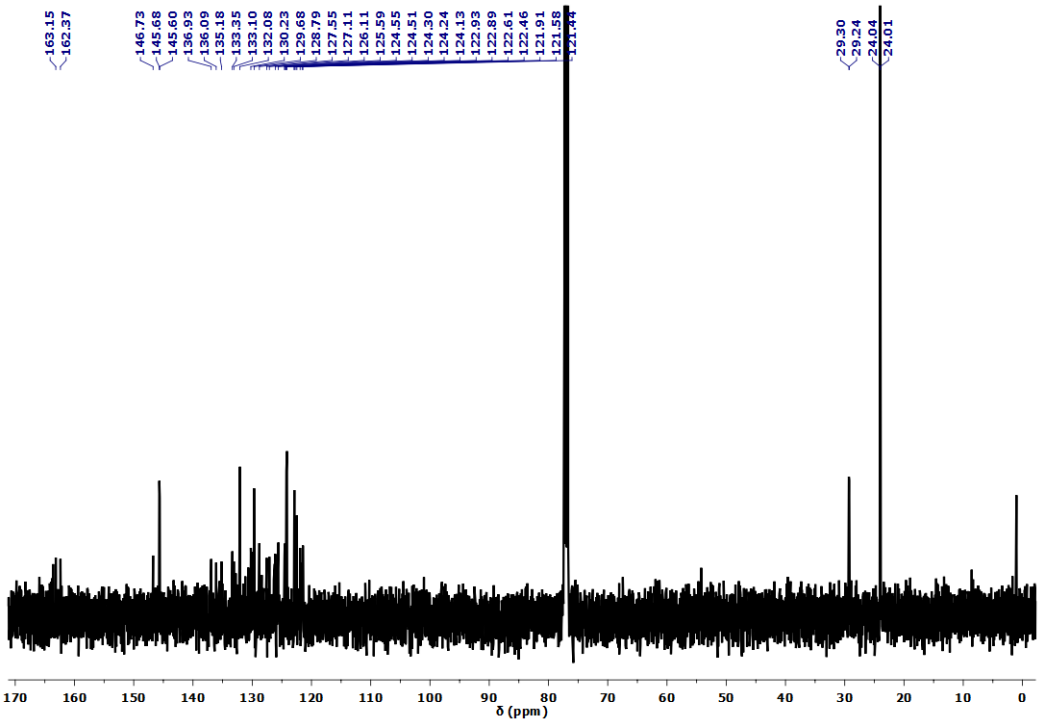


Figure S3: ^{13}C {^{1}H} NMR of **T_a** (126 MHz, $CDCl_3$, 298 K)

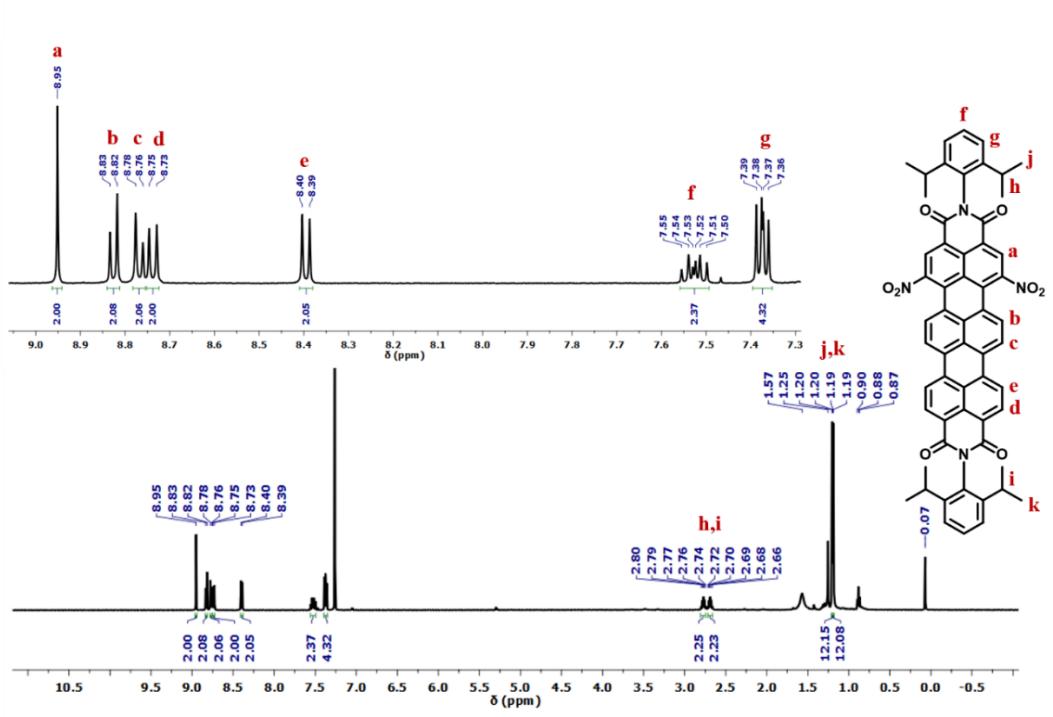


Figure S4: ^{1}H NMR of **T_{ab}** (500 MHz, $CDCl_3$, 298 K)

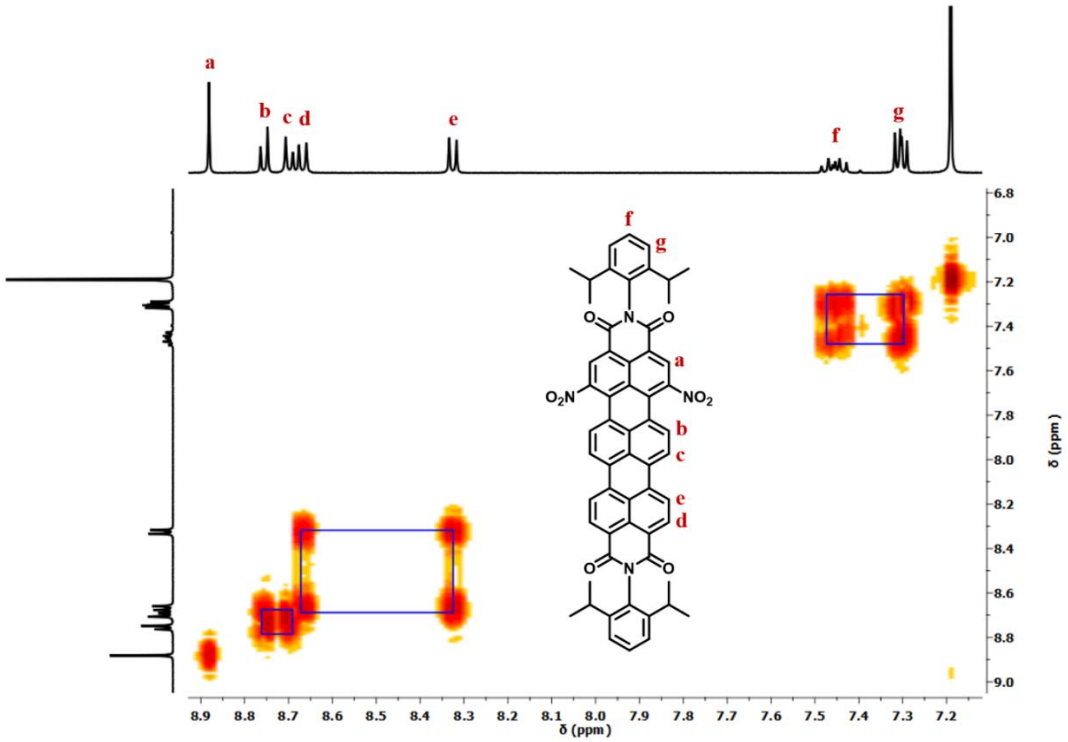


Figure S5: ^{1}H-^{1}H correlation (COSY) NMR of **T_{ab}** (500 MHz, $CDCl_3$, 298 K)

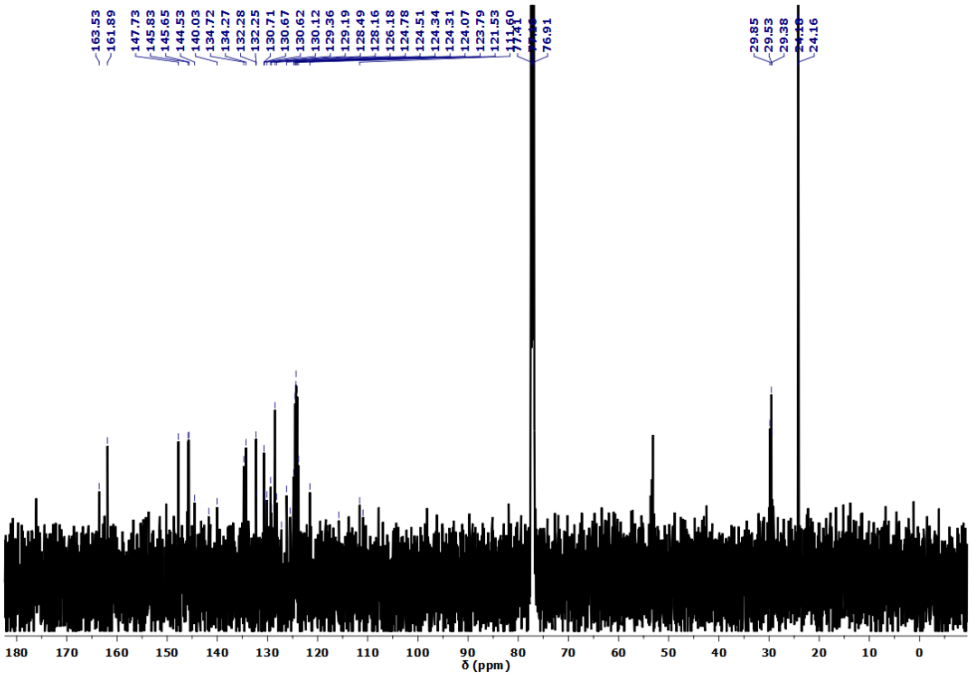


Figure S6: ^{13}C {^{1}H} NMR of **T_{ab}** (126 MHz, $CDCl_3$, 298 K)

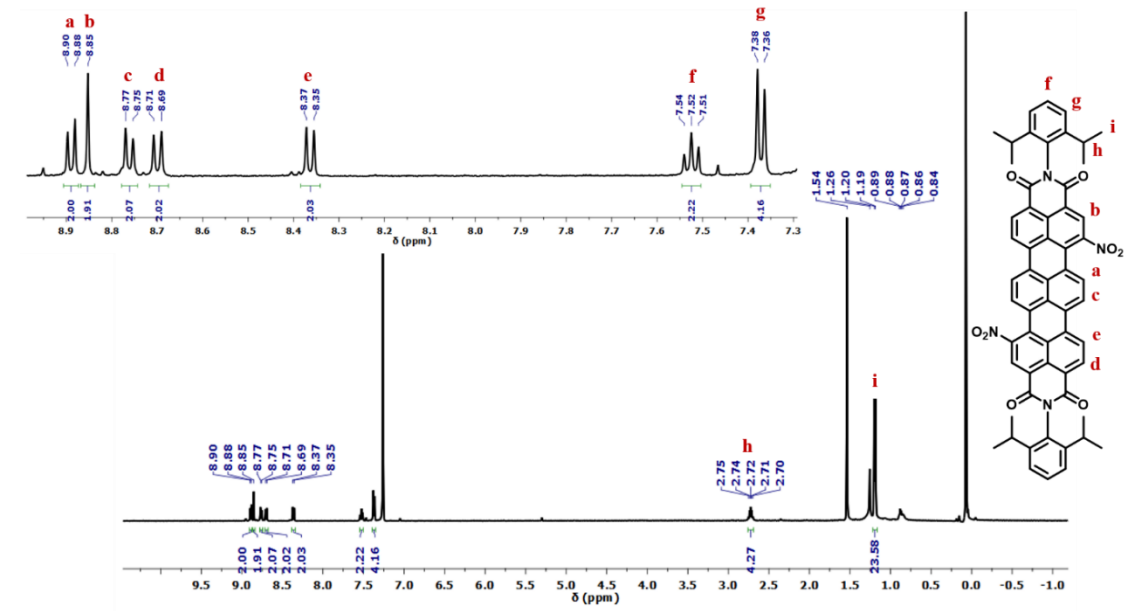


Figure S7: ^{1}H NMR of **T_{ac}** in (500 MHz, $CDCl_3$, 298 K)

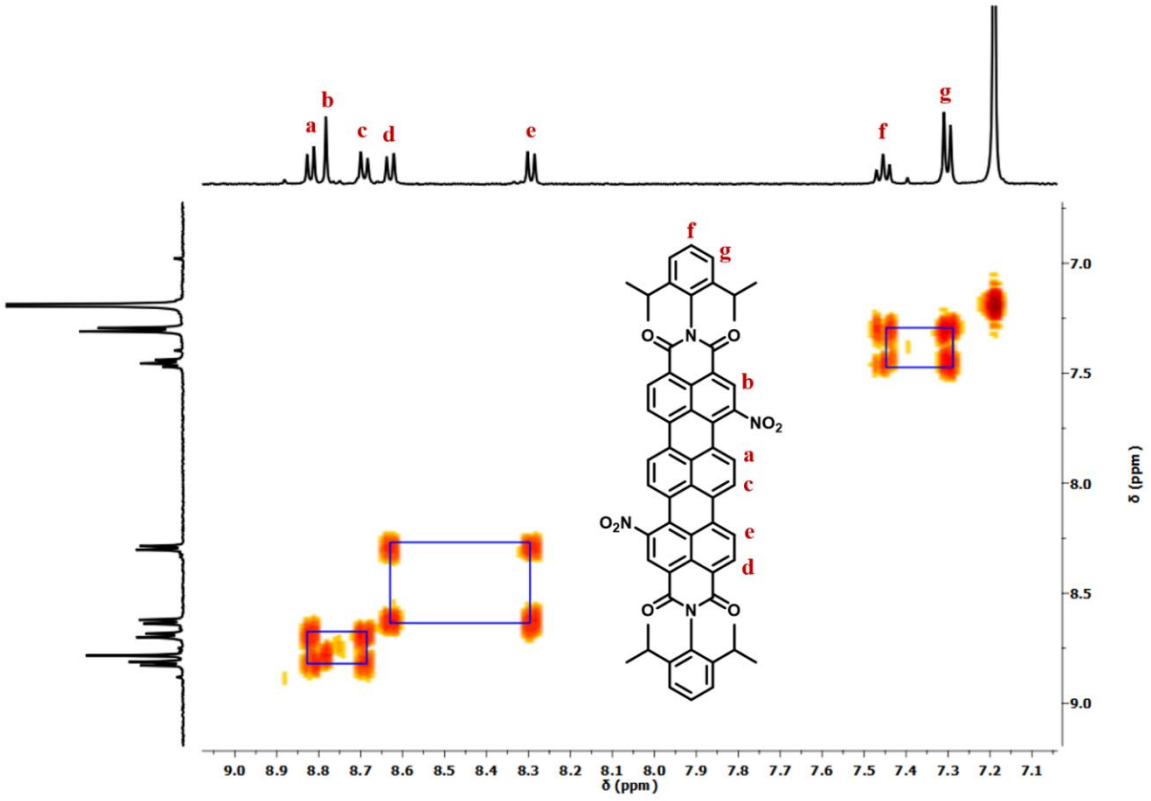


Figure S8: ^{1}H-^{1}H correlation (COSY) NMR of **T_{ac}** (500 MHz, $CDCl_3$, 298 K)

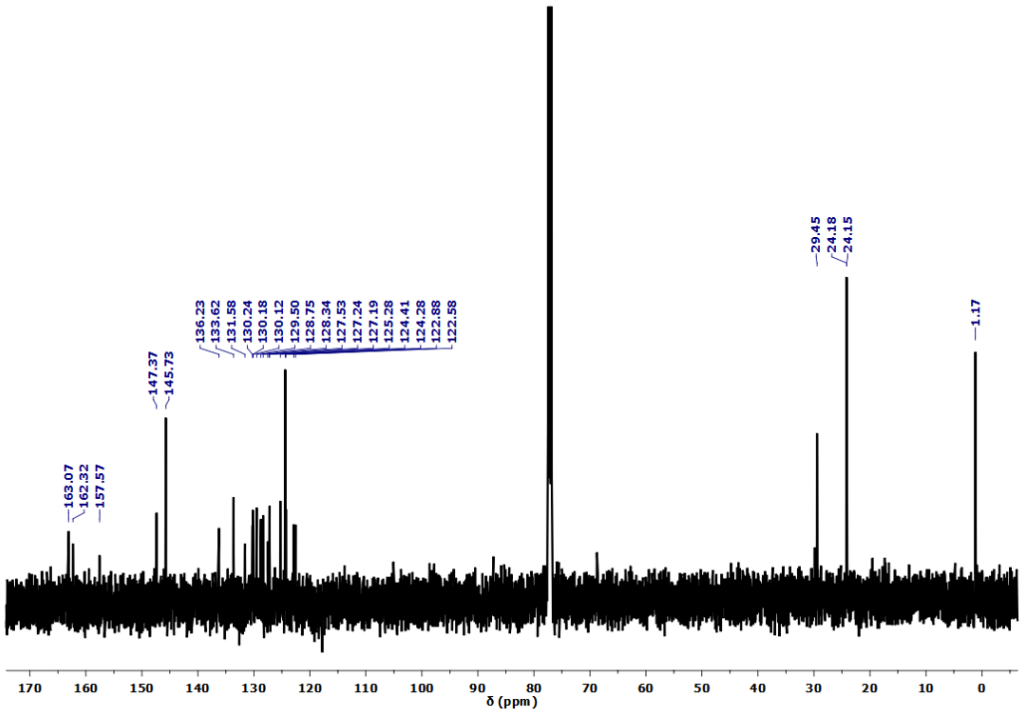


Figure S9: ^{13}C {^{1}H} NMR of $\mathbf{T_{ac}}$ (126 MHz, $CDCl_3$, 298 K)

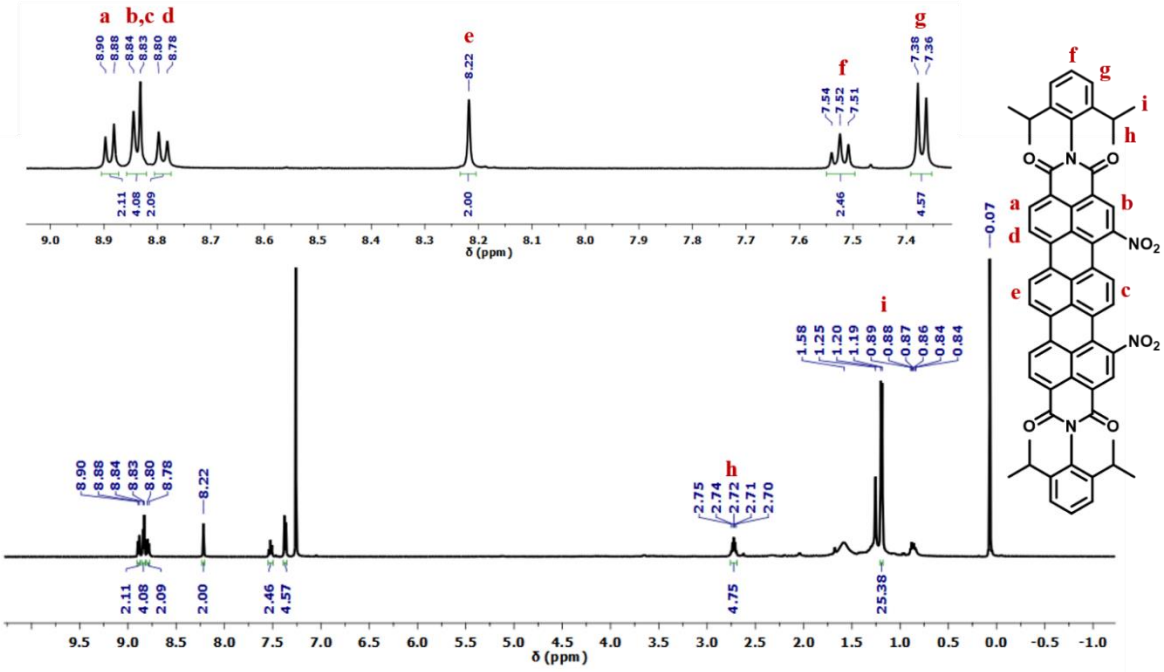


Figure S10: ^{1}H NMR of $\mathbf{T_{ad}}$ (500 MHz, $CDCl_3$, 298 K)

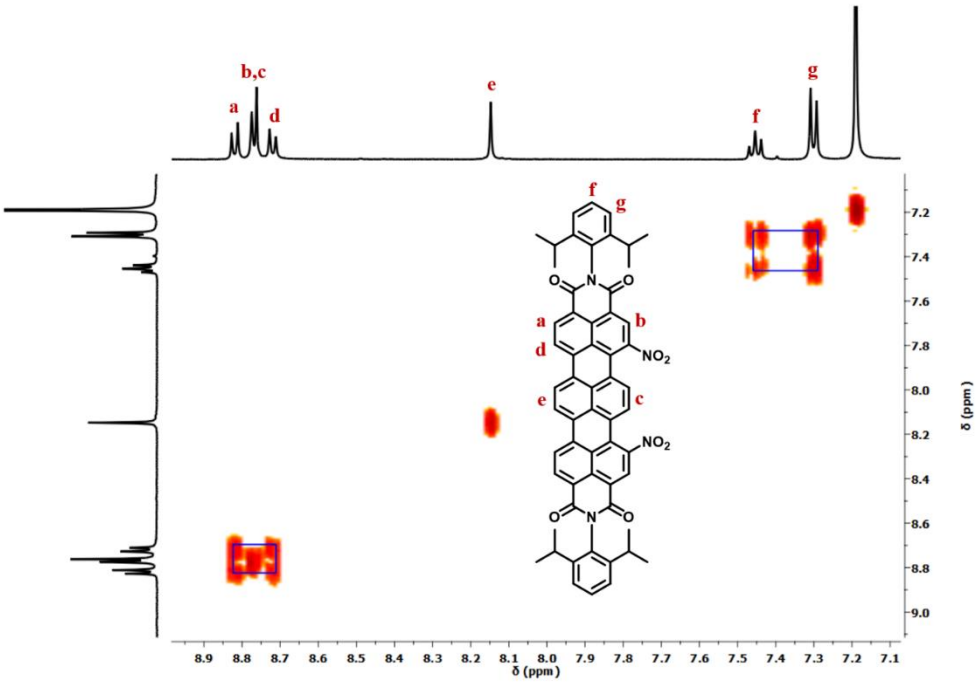


Figure S11: ^{1}H-^{1}H correlation (COSY) NMR of **T_{ad}** (500 MHz, $CDCl_3$, 298 K)

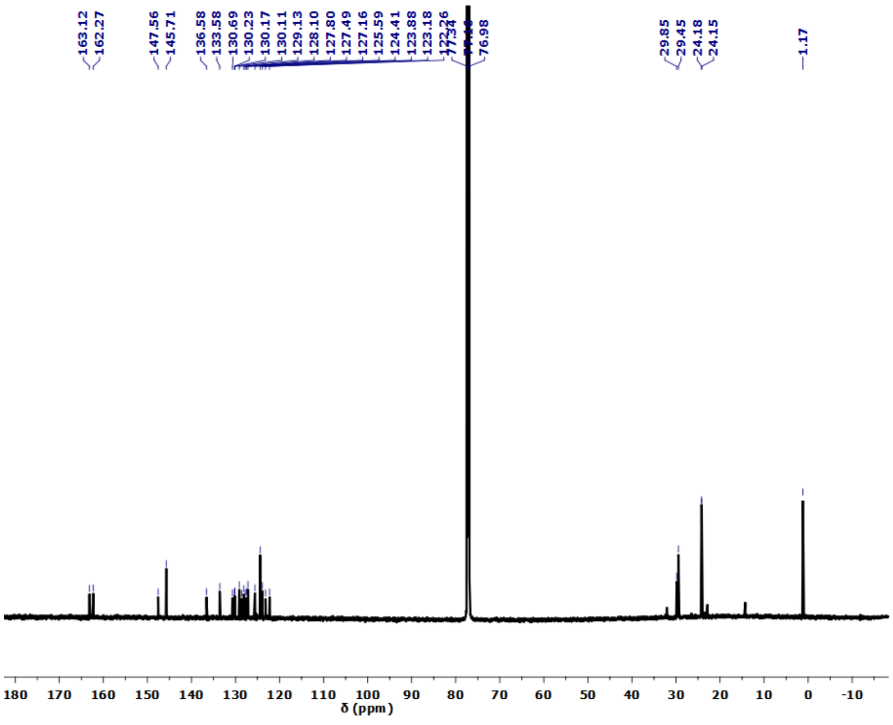


Figure S12: ^{13}C {^{1}H} NMR of **T_{ad}** (126 MHz, $CDCl_3$, 298 K)

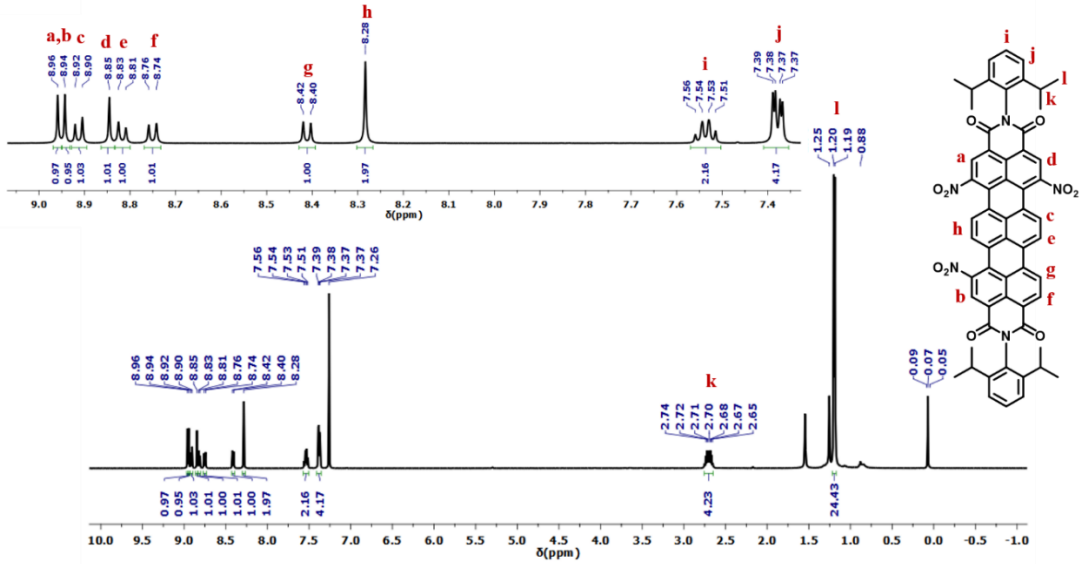


Figure S13: ^{1}H NMR of $\mathbf{T_{abc}}$ (500 MHz, $CDCl_3$, 298 K)

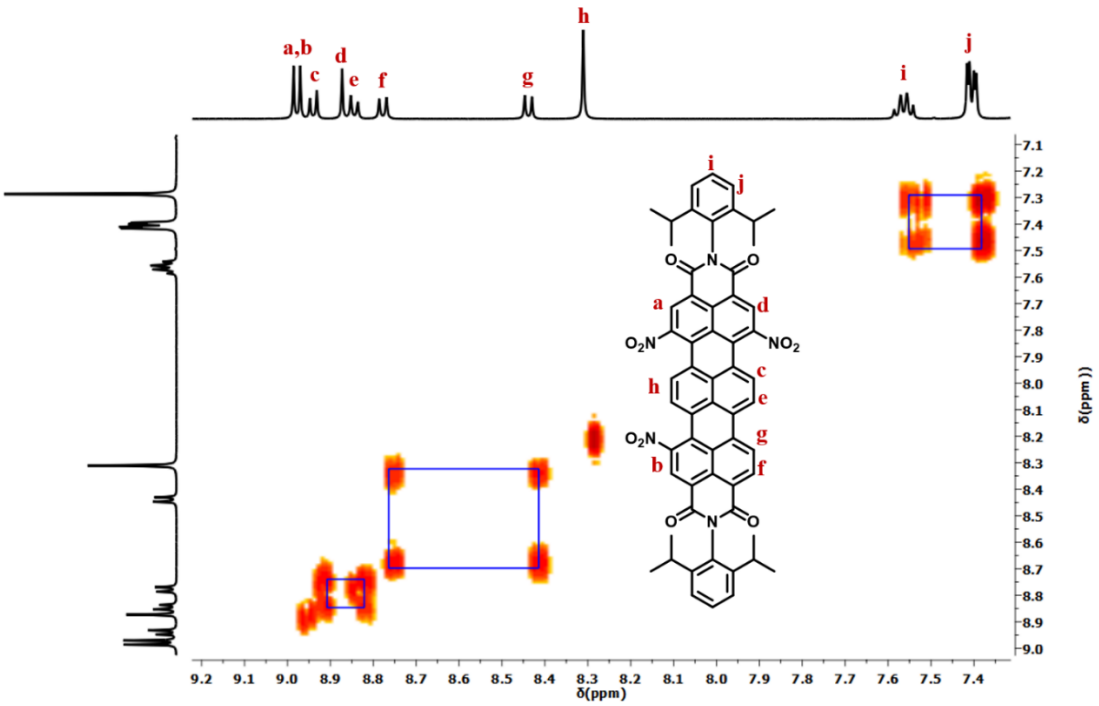


Figure S14: ^{1}H-^{1}H correlation (COSY) NMR of $\mathbf{T_{abc}}$ (500 MHz, $CDCl_3$, 298 K)

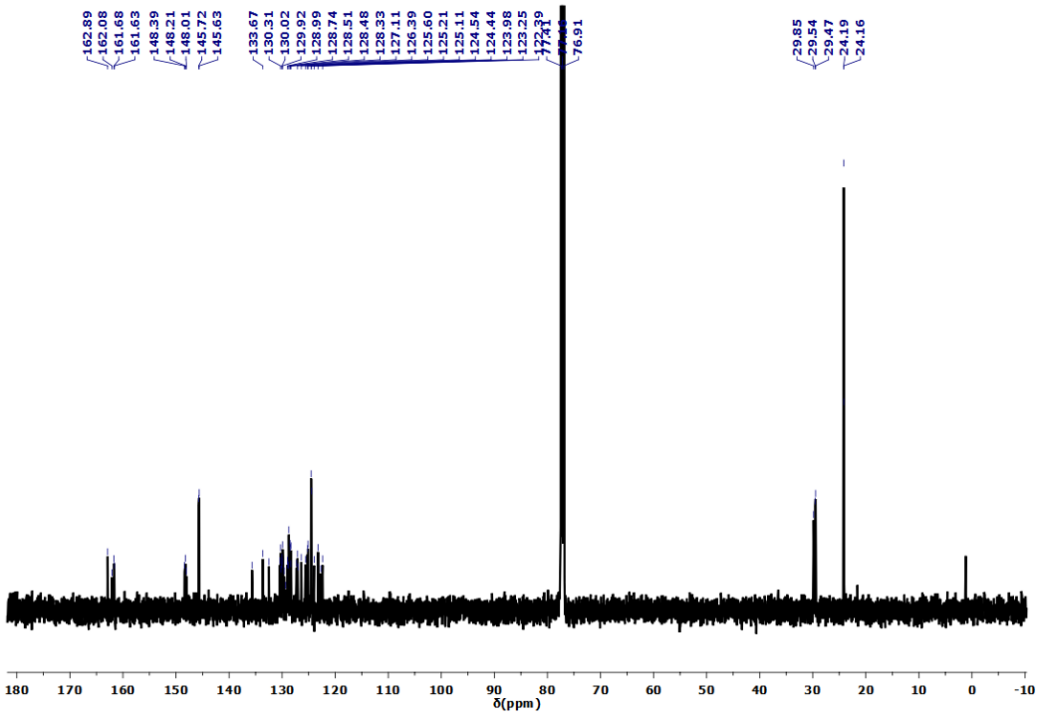


Figure S15: ^{13}C {^{1}H} NMR of **T_{abc}** (126 MHz, $CDCl_3$, 298 K)

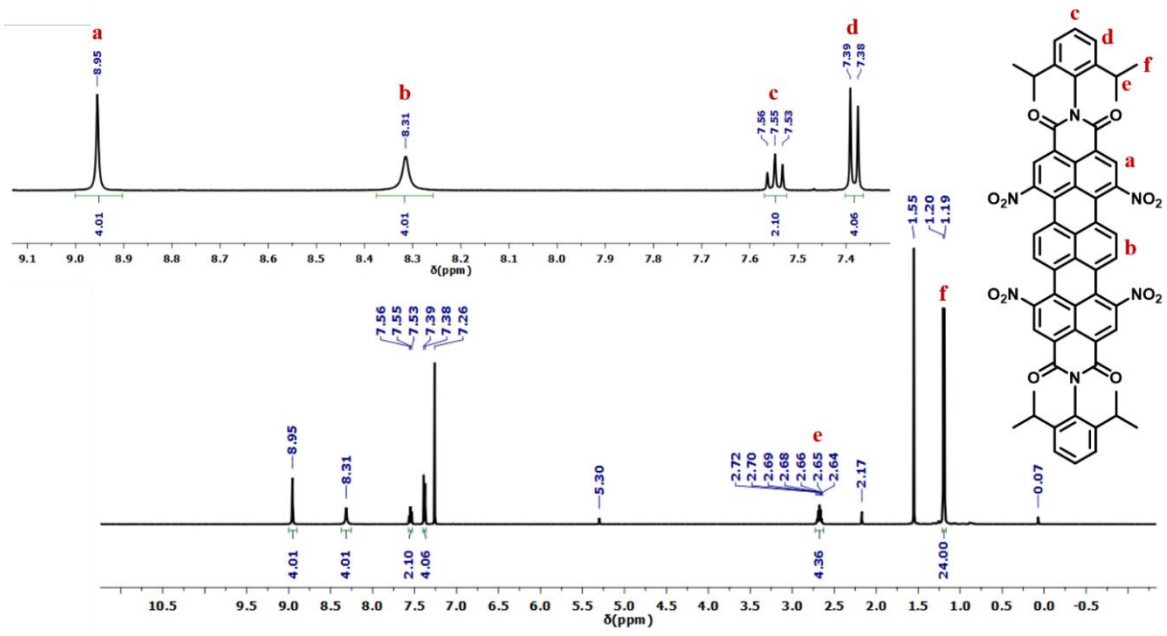


Figure S16: ^{1}H NMR of **T_{abcd}** (500 MHz, $CDCl_3$, 298 K)

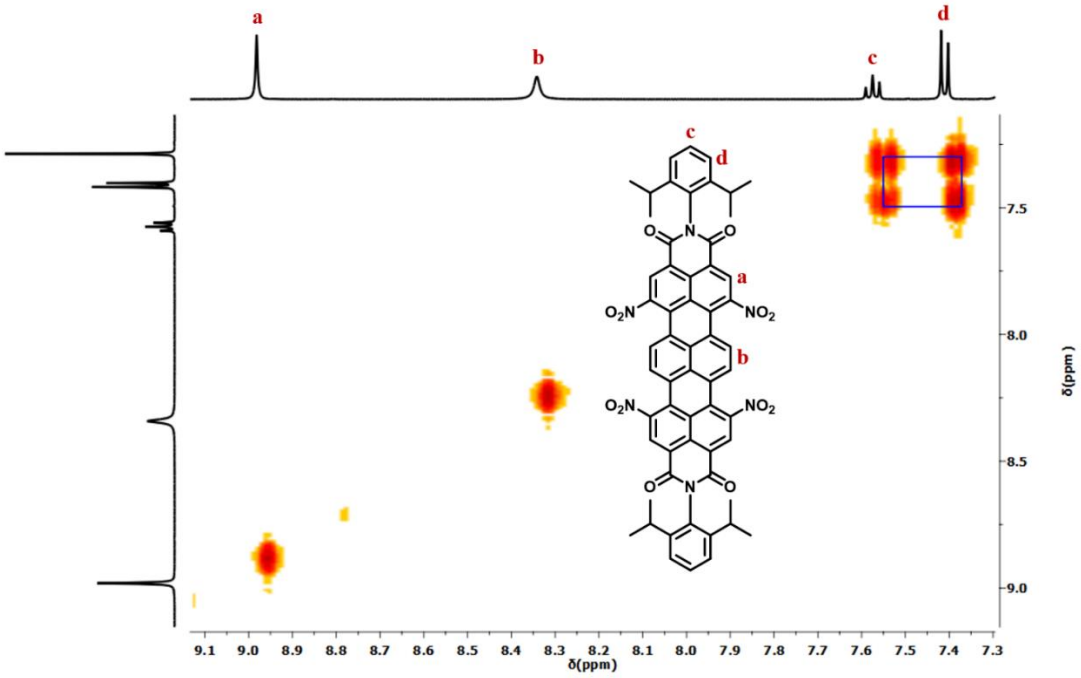


Figure S17: ^{1}H-^{1}H correlation (COSY) NMR of $\mathbf{T_{abcd}}$ (500 MHz, $CDCl_3$, 298 K)

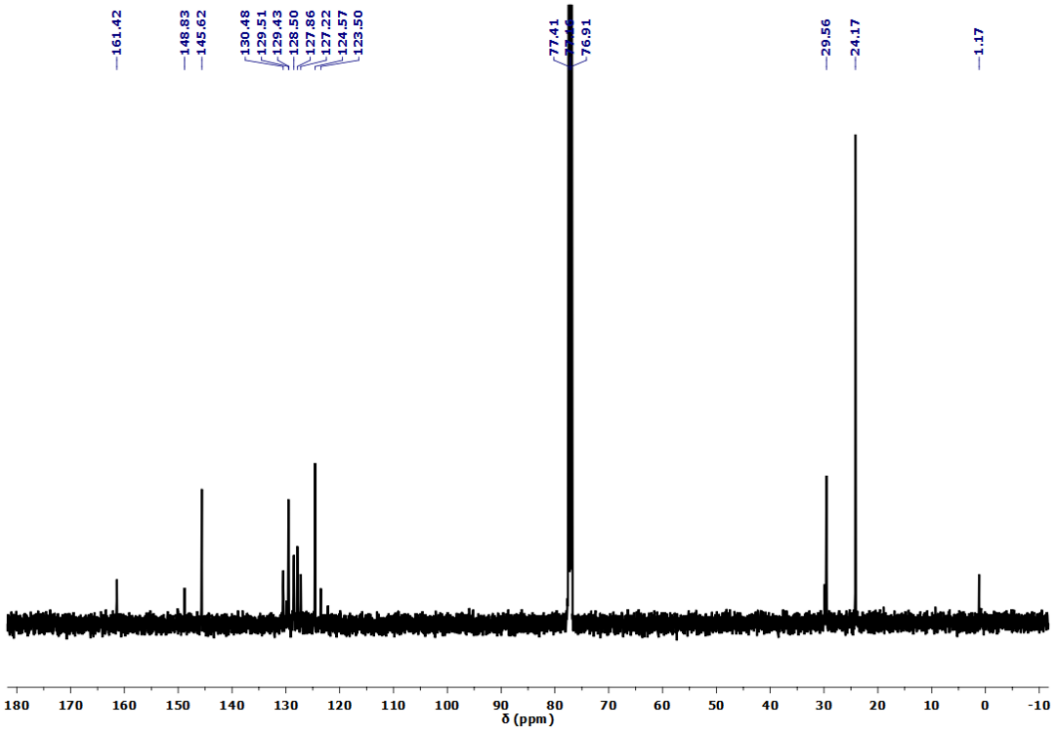


Figure S18: ^{13}C $\{^{1}H\}$ NMR of $\mathbf{T_{abcd}}$ (126 MHz, $CDCl_3$, 298 K)

IV. Mass Spectra:

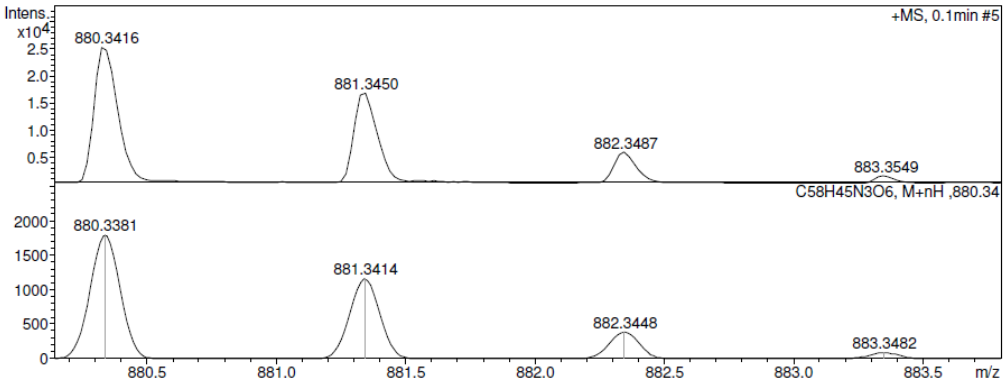


Figure S19: APCI-HRMS of $\mathbf{T_a}$

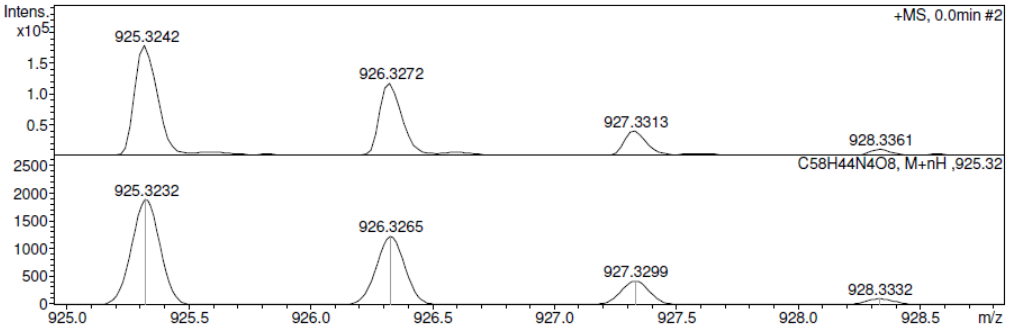


Figure S20: APCI-HRMS of $\mathbf{T_{ab}}$

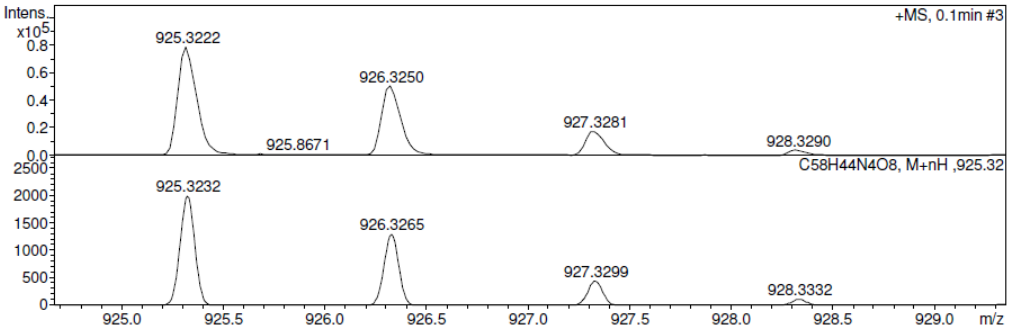


Figure S21: APCI-HRMS of $\mathbf{T_{ac}}$

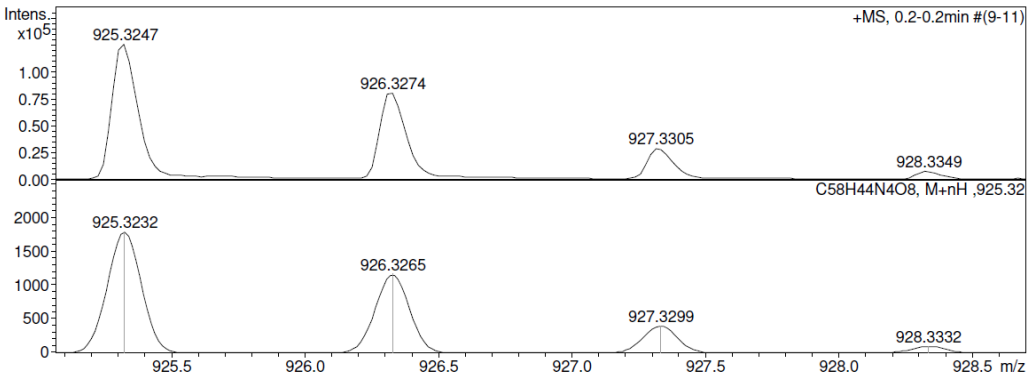


Figure S22: APCI-HRMS of $\mathbf{T_{ad}}$

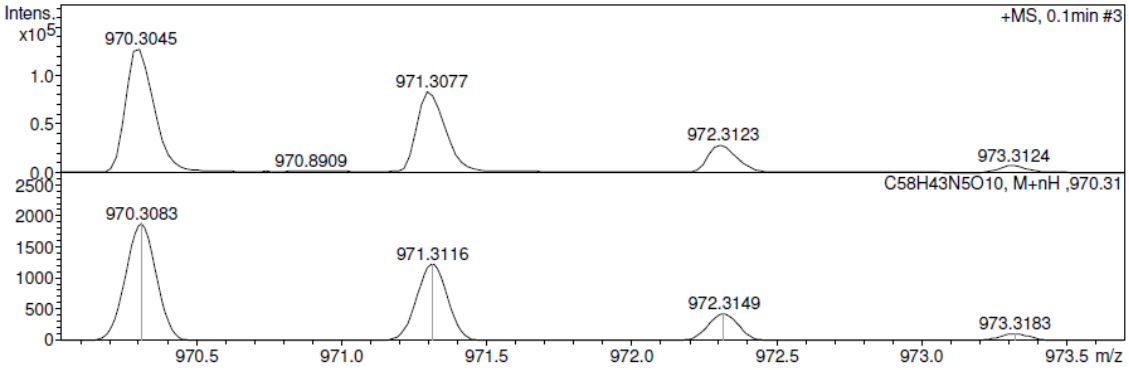


Figure S23: APCI-HRMS of $\mathbf{T_{abc}}$

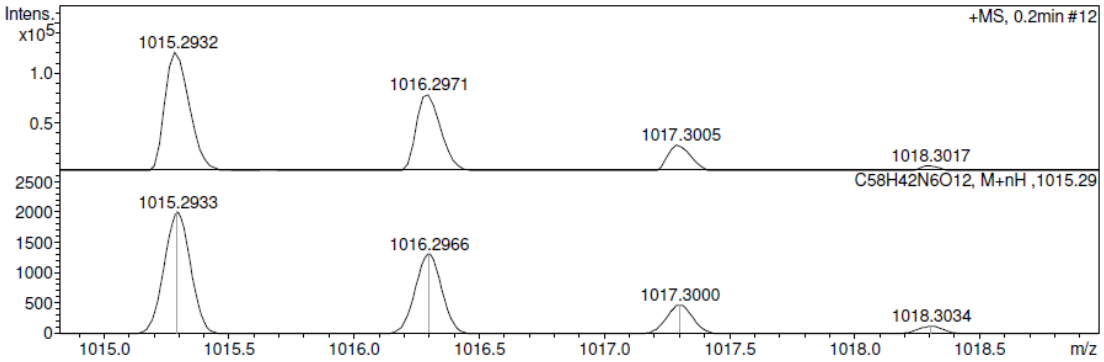


Figure S24: APCI-HRMS of $\mathbf{T_{abcd}}$

V. Photo-physical studies:

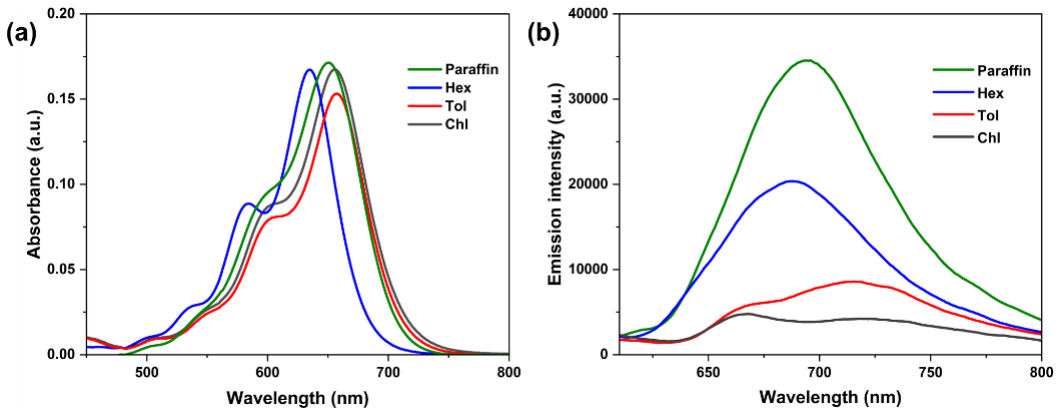


Figure S25: Solvent dependent absorption and emission Spectra of $\mathbf{T_a}$ (λ_{exc} 600 nm)

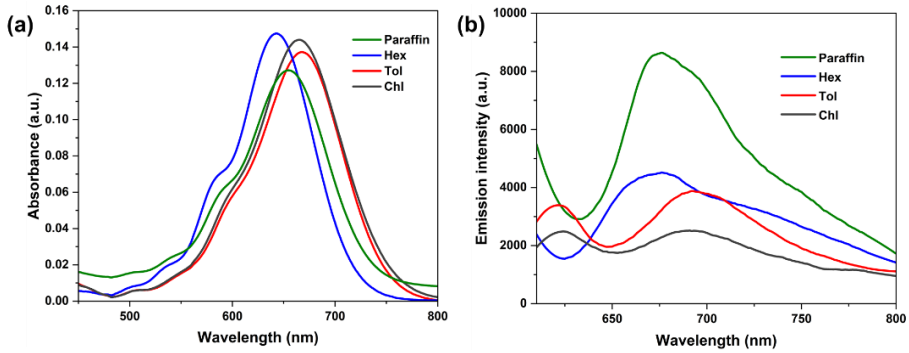


Figure S26: Solvent dependent absorption and emission Spectra of $\mathbf{T_{ab}}$ (λ_{exc} 600 nm)

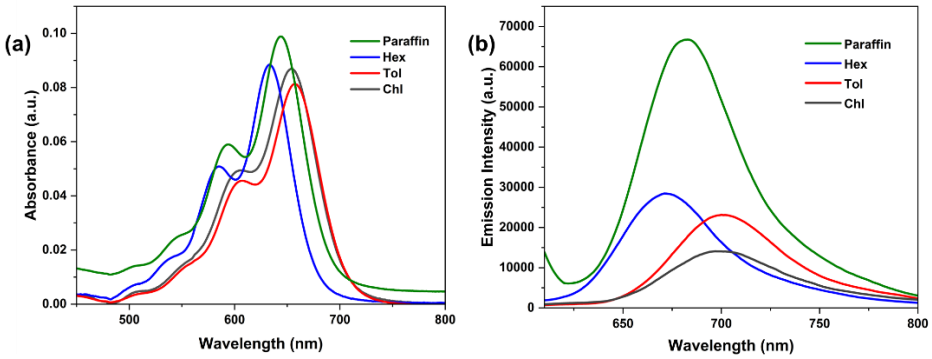


Figure S27: Solvent dependent absorption and emission Spectra of $\mathbf{T_{ac}}$ (λ_{exc} 600 nm)

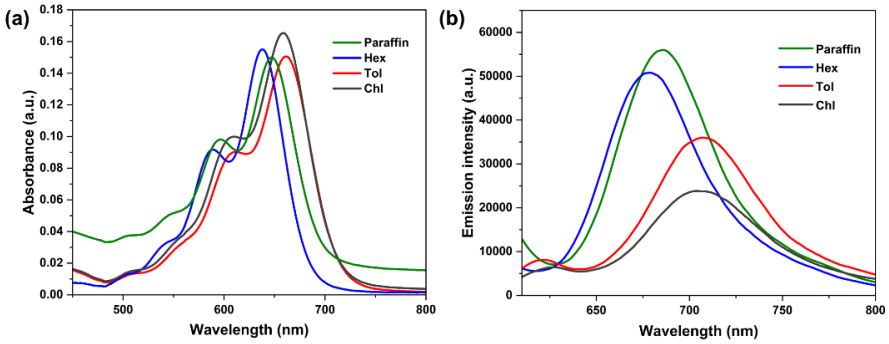


Figure S28: Solvent dependent absorption and emission Spectra of $\mathbf{T_{ad}}$ (λ_{exc} 600 nm)

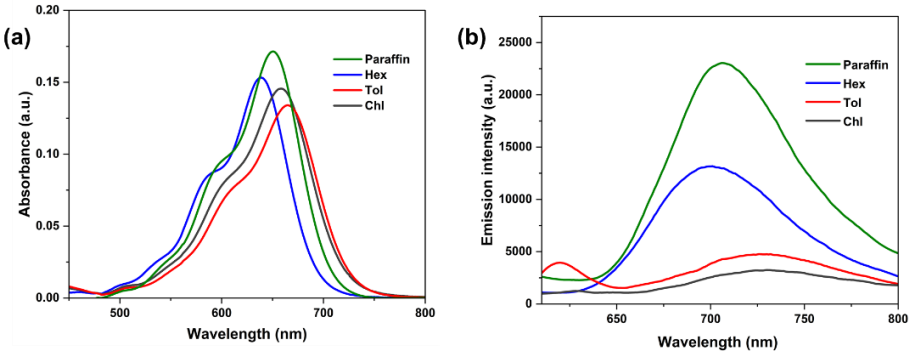


Figure S29: Solvent dependent absorption and emission Spectra of $\mathbf{T_{abc}}$ (λ_{exc} 600 nm)

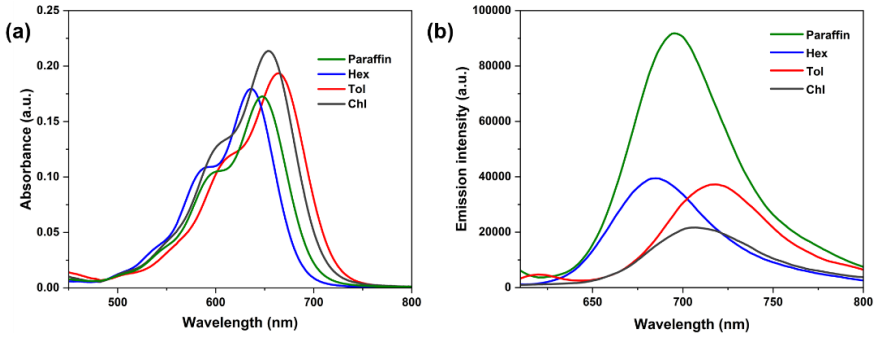


Figure S30: Solvent dependent absorption and emission Spectra of $\mathbf{T_{abcd}}$ (λ_{exc} 600 nm)

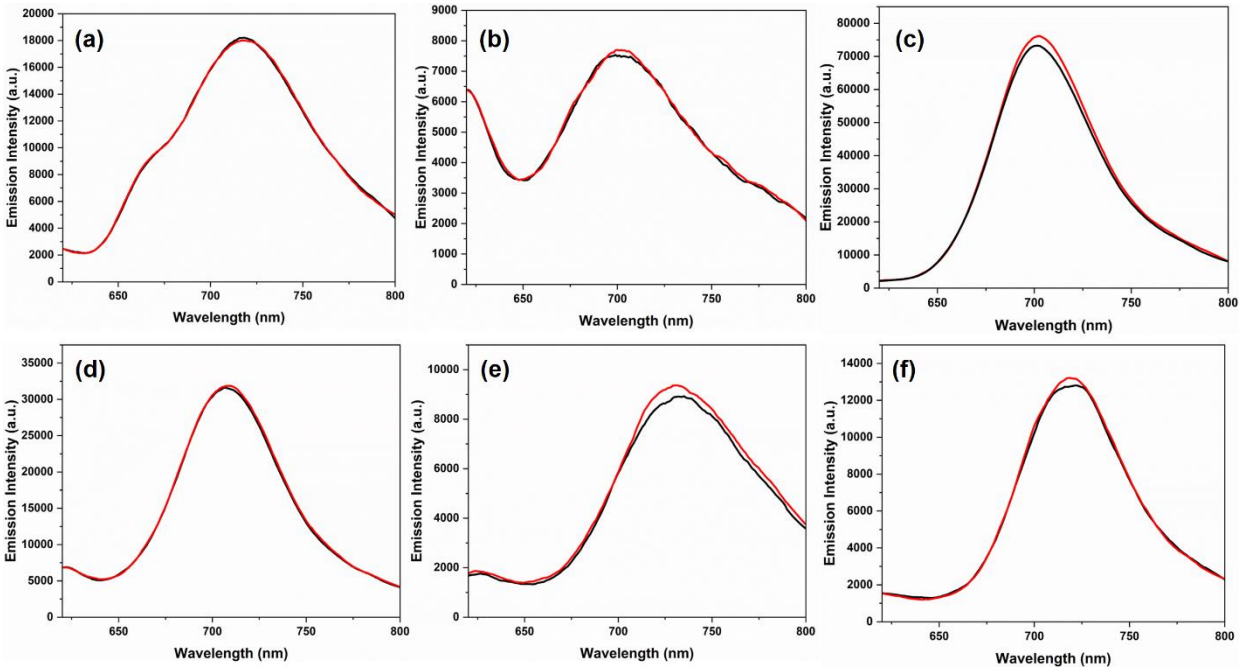


Figure S31: Change in emission spectra of (a) $\mathbf{T_a}$, (b) $\mathbf{T_{ab}}$, (c) $\mathbf{T_{ac}}$, (d) $\mathbf{T_{ad}}$, (e) $\mathbf{T_{abc}}$ and (f) $\mathbf{T_{abcd}}$ under argon (red) and under air (black). (λ_{exc} 600 nm)

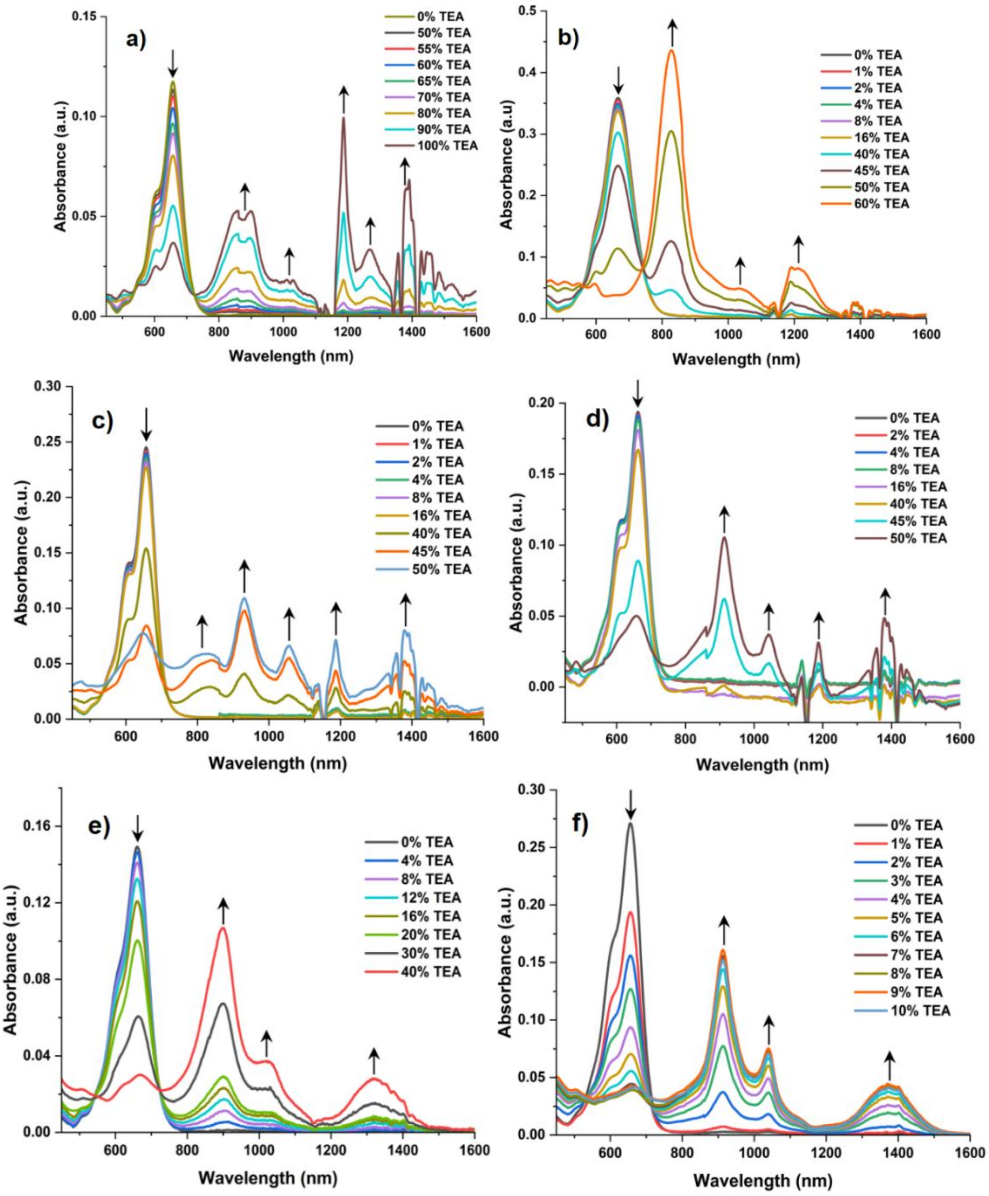


Figure S32: Change in absorption spectra of (a) $\mathbf{T_a}$, (b) $\mathbf{T_{ab}}$, (c) $\mathbf{T_{ac}}$, (d) $\mathbf{T_{ad}}$, (e) $\mathbf{T_{abc}}$ and (f) $\mathbf{T_{abcd}}$ upon addition of successive amount of triethyl amine in chloroform.

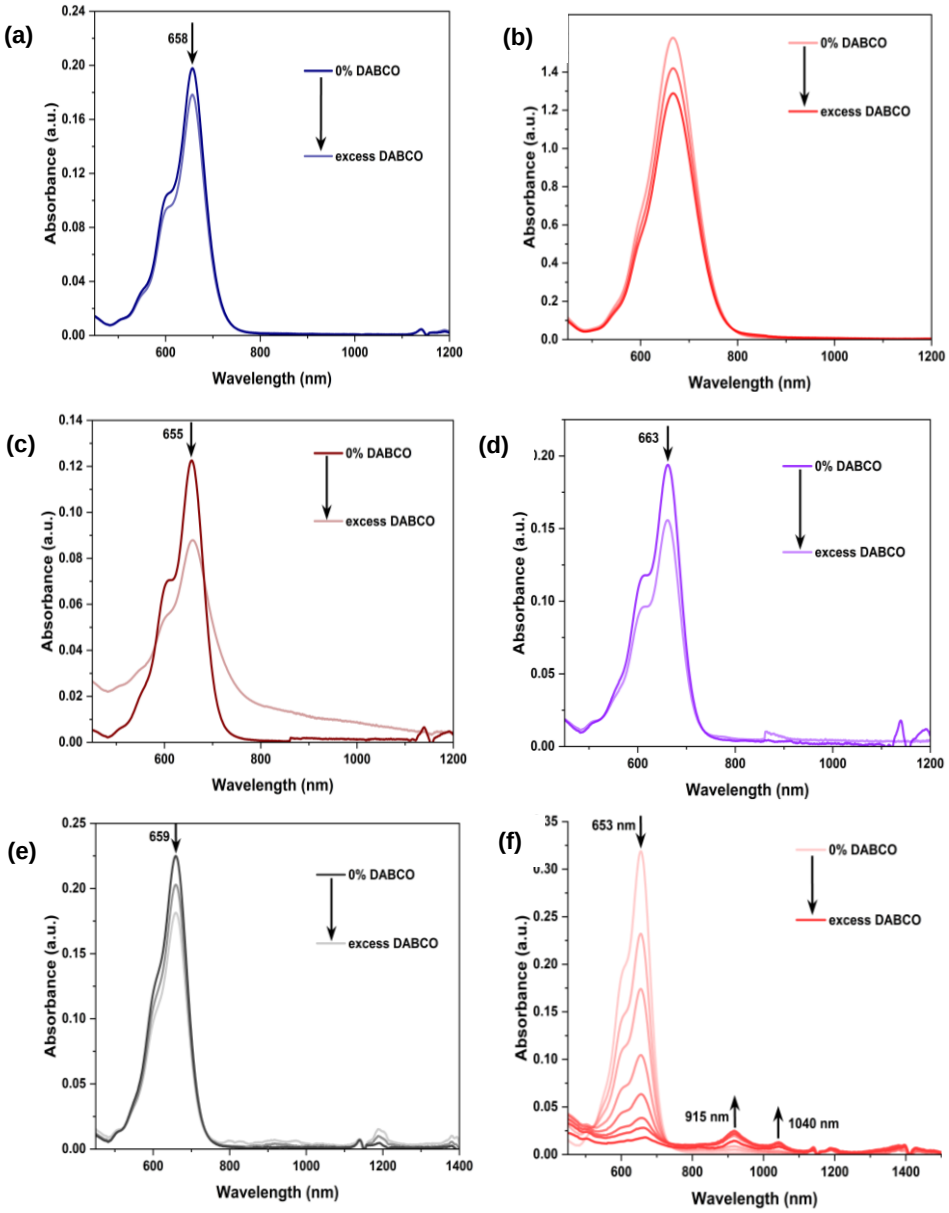


Figure S33: Change in absorption spectra of (a) $\mathbf{T_a}$, (b) $\mathbf{T_{ab}}$, (c) $\mathbf{T_{ac}}$, (d) $\mathbf{T_{ad}}$, (e) $\mathbf{T_{abc}}$ and (f) $\mathbf{T_{abcd}}$ upon addition of successive amount of 1,4-diazabicyclo [2.2.2] octane (DABCO) in chloroform.

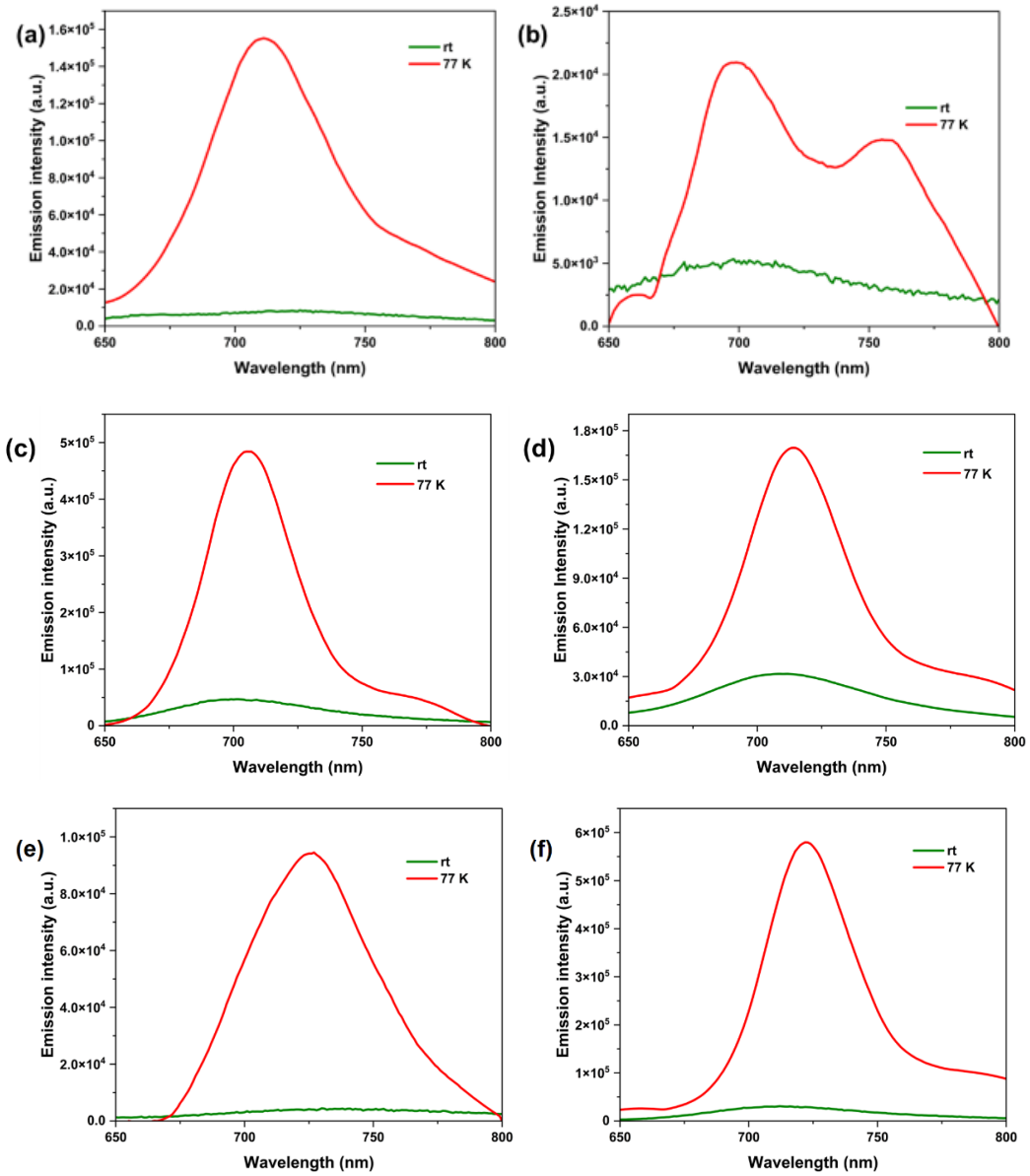


Figure S34: Change in emission spectra of (a) $\mathbf{T_a}$, (b) $\mathbf{T_{ab}}$, (c) $\mathbf{T_{ac}}$, (d) $\mathbf{T_{ad}}$, (e) $\mathbf{T_{abc}}$ and (f) $\mathbf{T_{abcd}}$ at different temperatures. (λ_{exc} 600 nm)

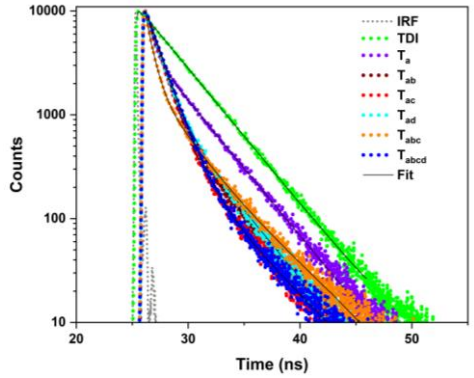


Figure S35: Emission decay profile of **TDI**, $\mathbf{T_a}$, $\mathbf{T_{ab}}$, $\mathbf{T_{ac}}$, $\mathbf{T_{ad}}$, $\mathbf{T_{abc}}$ and $\mathbf{T_{abcd}}$ (λ_{ex} : Absorption maxima).

VI. Electrochemical studies:

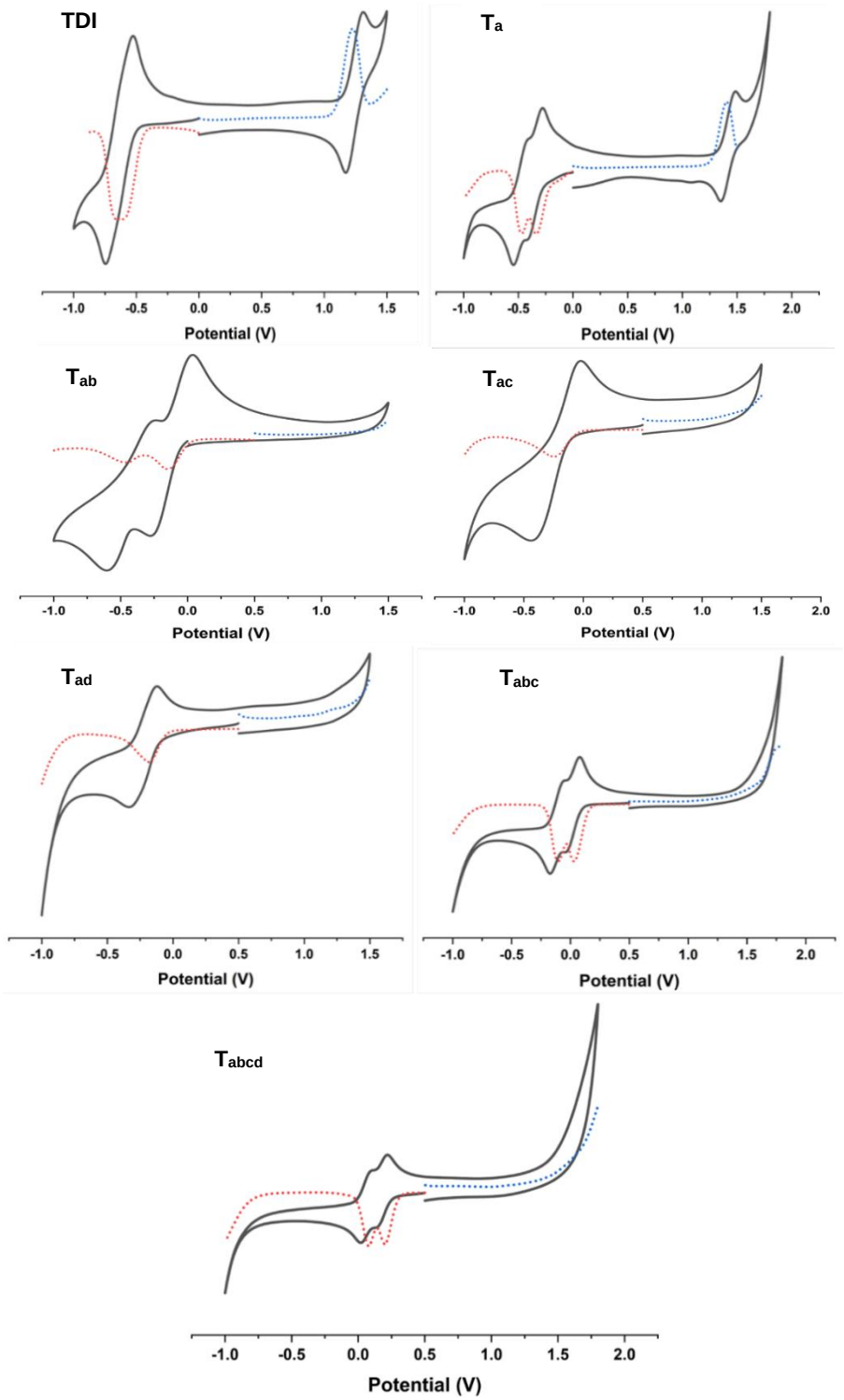


Figure S36: Bold lines and dotted lines showing cyclic and differential pulse voltammetry of nitro TDIs in 0.1 M solution of TBAP in chloroform.

Table S1. LUMO energy for synthesized molecules:

Comp	Vs SCE [eV]	DFT Cal. B3LYP 6-31g(d,p) PCM-DCM [eV]
TDI	-3.80	-3.52
T_a	-4.06	-3.64
T_{ab}	-4.25	-3.87
T_{ac}	-4.16	-3.85
T_{ad}	-4.22	-3.84
T_{abc}	-4.43	-4.08
T_{abcd}	-4.60	-4.23

VII. DFT studies:

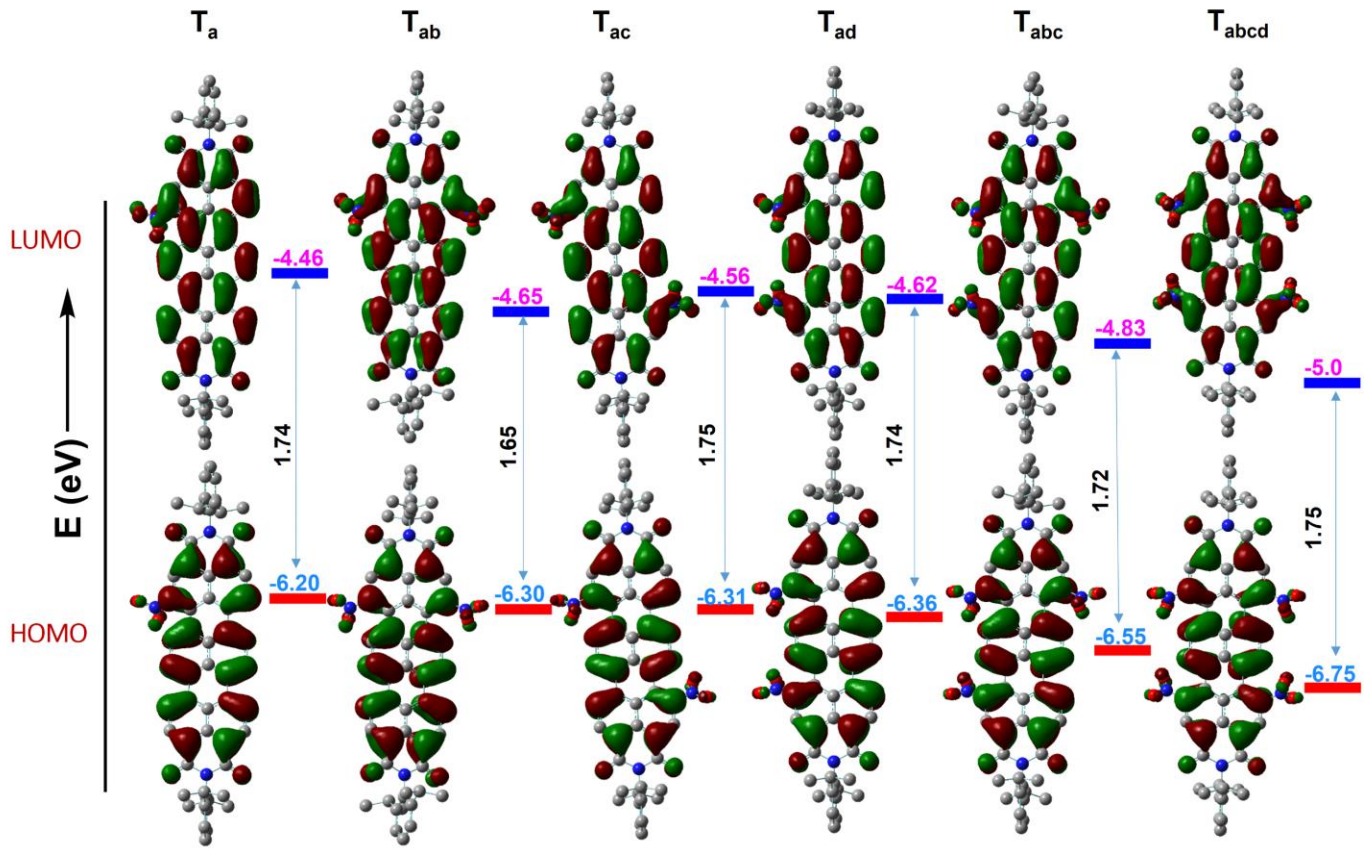


Figure S37. DFT computed frontier molecular orbital diagrams with experimentally calculated optical band gaps (E_g).

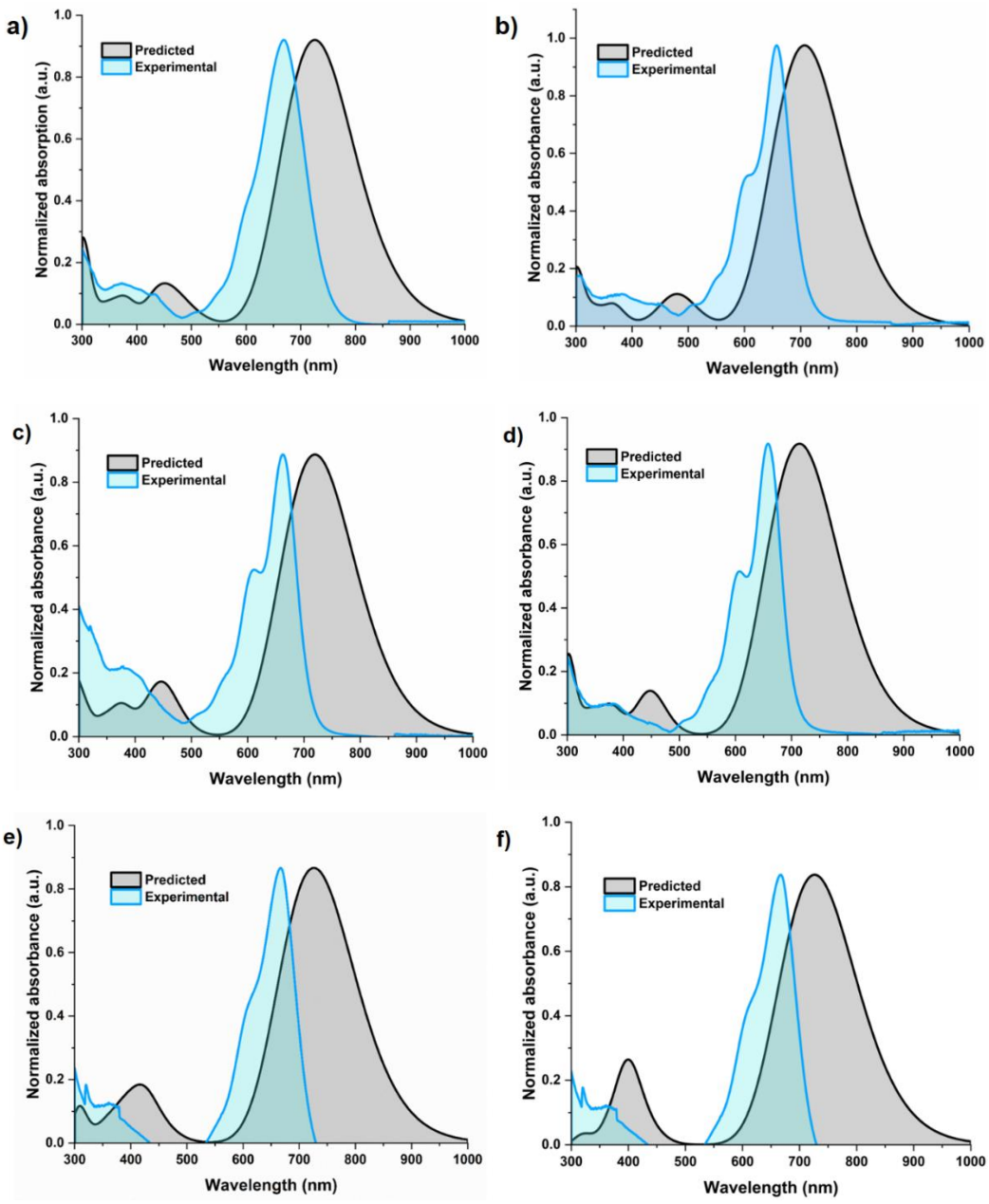


Figure S38: Experimentally observed and TD-DFT predicted absorption spectra of (a) $\mathbf{T_a}$, (b) $\mathbf{T_{ab}}$, (c) $\mathbf{T_{ac}}$, (d) $\mathbf{T_{ad}}$, (e) $\mathbf{T_{abc}}$ and (f) $\mathbf{T_{abcd}}$.

Table S2. Selected TDDFT (RB3LYP/6-31G*) calculated Wavelength, oscillator strength and compositions of major electronic transitions of T_a.

Wavelength (nm)	Osc. Strength (f)	Major contributions
706.58342	1.3459	HOMO->LUMO (100%)
484.69192	0.0578	H-2->LUMO (55%), HOMO->L+1 (38%)
448.4382	0	H-3->LUMO (97%)
395.04283	0.0025	H-7->LUMO (83%)
384.08982	0.0015	HOMO->L+3 (91%)
383.48394	0	H-8->LUMO (91%)
373.1429	0.0066	H-9->LUMO (74%)
367.62199	0.0886	H-11->LUMO (83%)
331.03058	0.0045	H-16->LUMO (65%), HOMO->L+4 (10%)
320.19884	0	H-3->L+1 (85%), H-3->L+2 (11%)
309.55806	0	H-4->L+1 (12%), H-4->L+2 (82%)
301.76015	0.078	H-5->L+2 (30%), HOMO->L+6 (28%)

Table S3. Selected TDDFT (RB3LYP/6-31G*) calculated Wavelength, oscillator strength and compositions of major electronic transitions of T_{ab}.

Wavelength (nm)	Osc. Strength (f)	Major contributions
725.26583	1.2698	HOMO->LUMO (100%)
528.22168	0	H-1->LUMO (99%)
525.13424	0	H-2->LUMO (99%)
485.69825	0.0537	HOMO->L+1 (97%)
480.8198	0	H-3->LUMO (98%)
471.7636	0.0346	H-5->LUMO (32%), HOMO->L+2 (67%)
441.93261	0.1388	H-5->LUMO (44%), HOMO->L+2 (19%), HOMO->L+3 (35%)
411.11544	0.0012	H-9->LUMO (12%), H-7->LUMO (81%)
400.43987	0	H-8->LUMO (92%)
387.42639	0.0063	H-10->LUMO (57%), H-9->LUMO (30%)
380.21464	0.002	HOMO->L+4 (83%)
377.18412	0.0805	H-11->LUMO (75%)
352.70879	0	H-1->L+2 (97%)
350.81261	0.051	H-12->LUMO (90%)
335.27364	0.0232	H-5->L+1 (75%)
309.98373	0.1065	H-15->LUMO (10%), HOMO->L+5 (59%)
302.09101	0.0136	H-6->L+1 (55%), H-5->L+2 (11%), H-5->L+3 (18%)

Table S4. Selected TDDFT (RB3LYP/6-31G*) calculated Wavelength, oscillator strength and compositions of major electronic transitions of $\mathbf{T_{ac}}$.

Wavelength (nm)	Osc. Strength (f)	Major contributions
713.61916	1.2669	HOMO->LUMO (100%)
521.99475	0	H-1->LUMO (99%)
448.27606	0.1893	HOMO->L+2 (96%)
404.12058	0.0125	H-7->LUMO (93%)
391.04331	0	H-10->LUMO (12%), H-8->LUMO (80%)
378.48523	0.1152	H-11->LUMO (89%)
342.02536	0.0023	H-16->LUMO (63%), H-14->LUMO (27%)
335.9459	0.0349	H-5->L+1 (65%)
333.2998	0.0017	H-3->L+1 (94%)
321.43574	0.0022	H-2->L+2 (21%), H-1->L+3 (27%), HOMO->L+5 (14%), HOMO->L+6 (27%)
312.00411	0.0115	HOMO->L+5 (43%), HOMO->L+6 (27%)
306.20942	0.081	H-6->L+1 (42%), H-5->L+3 (15%)
301.92181	0.0495	H-17->LUMO (29%), H-6->L+1 (27%)

Table S5. Selected TDDFT (RB3LYP/6-31G*) calculated Wavelength, oscillator strength and compositions of major electronic transitions of $\mathbf{T_{ad}}$.

Wavelength (nm)	Osc. Strength (f)	Major contributions
719.04073	1.224	HOMO->LUMO (100%)
520.70133	0	H-1->LUMO (99%)
486.95728	0.0139	H-5->LUMO (11%), HOMO->L+1 (86%)
450.14774	0.1751	HOMO->L+2 (95%)
421.38529	0.0591	H-6->LUMO (97%)
377.66668	0.0143	HOMO->L+4 (83%)
376.97769	0.1085	H-11->LUMO (88%)
346.89626	0.0649	H-12->LUMO (92%)
329.72766	0	H-3->L+1 (94%)
321.89473	0.0012	HOMO->L+6 (88%)
312.46016	0.0606	H-14->LUMO (13%), HOMO->L+5 (61%)
309.01028	0.0132	H-5->L+2 (66%)
302.55544	0.0107	H-7->L+1 (64%), HOMO->L+7 (15%)

Table S6. Selected TDDFT (RB3LYP/6-31G*) calculated Wavelength, oscillator strength and compositions of major electronic transitions of **Tabc**.

Wavelength (nm)	Osc. Strength (f)	Major contributions
725.60539	1.1962	HOMO->LUMO (100%)
504.96556	0	H-3->LUMO (98%)
462.24813	0.036	HOMO->L+2 (91%)
423.95005	0.1544	H-7->LUMO (10%), H-6->LUMO (14%), HOMO->L+3 (54%), HOMO->L+4 (13%)
416.33376	0.0305	H-7->LUMO (81%)

400.98381	0.0111	H-5->LUMO (10%), HOMO->L+4 (67%)
386.78582	0.0978	H-11->LUMO (83%)
372.05675	0	H-1->L+1 (97%)
358.75056	0.0685	H-12->LUMO (82%)
354.69659	0.008	H-13->LUMO (78%)
331.99677	0.0176	H-5->L+1 (27%), H-4->L+2 (34%)
316.86011	0.0044	HOMO->L+6 (14%), HOMO->L+7 (68%)
308.05822	0.055	H-18->LUMO (13%), H-7->L+1 (36%), H-6->L+1 (16%), HOMO->L+6 (11%)
304.86917	0.0217	H-25->LUMO (11%)
300.61875	0.0093	H-9->L+1 (14%), HOMO->L+8 (35%)

Table S7. Selected TDDFT (RB3LYP/6-31G*) calculated Wavelength, oscillator strength and compositions of major electronic transitions of $\mathbf{T_{abcd}}$.

Wavelength (nm)	Osc. Strength (f)	Major contributions
725.94527	1.1554	HOMO->LUMO (100%)
604.44712	0	H-1->LUMO (99%)
603.68192	0.0013	H-2->LUMO (99%)
436.1801	0.0554	HOMO->L+3 (90%)
426.42887	0.0075	H-6->LUMO (93%)
412.74408	0.0011	H-8->LUMO (91%)
402.53301	0.1765	HOMO->L+4 (96%)
396.85101	0.15	H-11->LUMO (86%)
367.94929	0.0934	H-12->LUMO (93%)
358.12881	0.002	H-16->LUMO (10%), H-14->LUMO (82%)
348.23108	0.0023	H-16->LUMO (80%)
332.65593	0.0189	H-18->LUMO (34%), H-5->L+1 (21%)
324.4046	0.0091	H-21->LUMO (13%), H-5->L+2 (39%)
314.41735	0.002	H-21->LUMO (29%), HOMO->L+8 (37%)
311.76874	0.0206	H-21->LUMO (14%), H-7->L+1 (14%), H-5->L+2 (20%), HOMO->L+8 (34%)

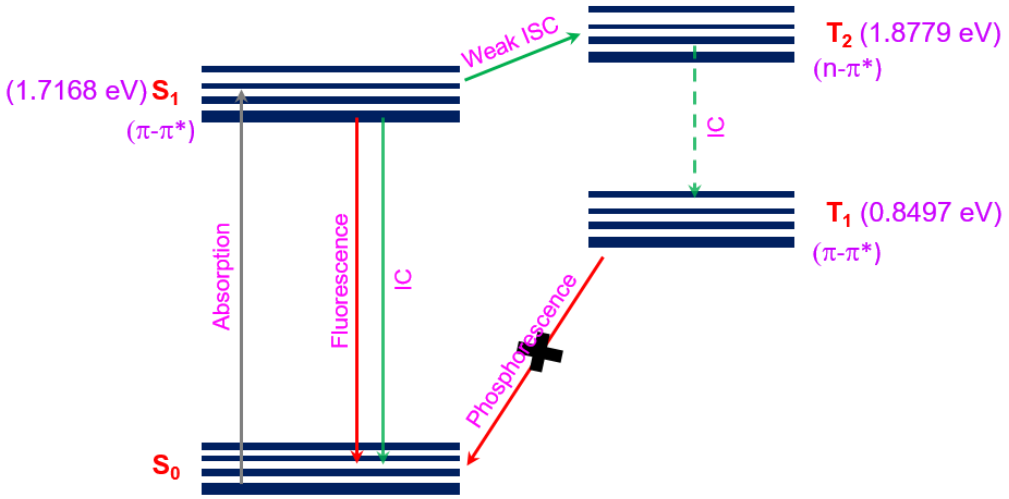


Figure S39: Plausible energy diagram for radiative deactivation of Nitro TDIs with calculated energy of T_{abcd}.

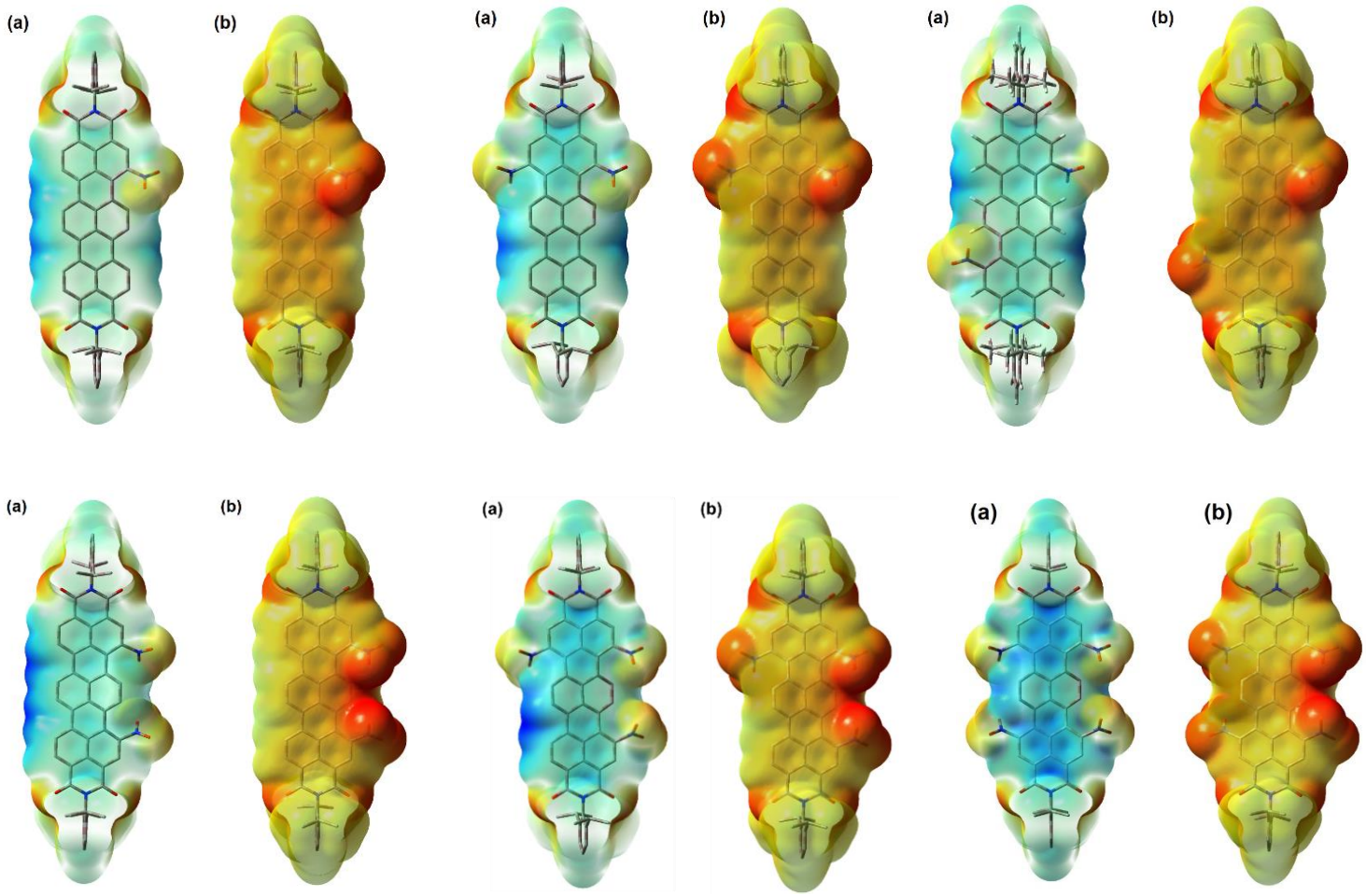


Figure S40: ESP surfaces (a) neutral molecule and (b) respective radical anion for T_a, T_{ab}, T_{ac}, T_{ad}, T_{abc} and T_{abcd} respectively.

Cartesian coordinates of the DFT optimized structures:

T_a:

Symbol	X	Y	Z
O	-7.96548	1.990504	0.915672
O	-8.02479	-2.22606	-0.8718
N	-8.00702	-0.11778	0.022446
C	-0.85751	-0.17081	-0.08571
C	-5.16265	-0.14313	-0.01205
C	-1.55222	0.962282	0.444576
C	-5.88953	-1.26244	-0.48403
C	-3.74806	2.083645	0.914323
C	-3.7337	-0.15642	-0.02848
C	-3.01866	0.982383	0.455633
C	-5.20849	-2.36822	-0.9654
H	-5.78346	-3.21518	-1.32325
C	-3.81111	-2.38653	-0.9891
C	-5.85742	0.99043	0.474448
C	-3.04986	-1.30621	-0.53196
C	-5.14579	2.088897	0.927678
H	-5.69673	2.950435	1.288441
C	-9.45984	-0.10495	0.040749
C	-7.34002	1.025582	0.501443
C	-0.8566	-2.40867	-1.02022
H	-1.36931	-3.28454	-1.39751
C	0.533868	-2.43262	-0.99413
H	1.034592	-3.32459	-1.35101
C	-7.37245	-1.27206	-0.47358
C	-1.58263	-1.31158	-0.55534
C	-10.1463	0.37929	-1.08621
C	-10.1261	-0.57694	1.184899
C	-12.2308	-0.07992	0.076016
H	-13.3169	-0.07	0.089866
C	-9.42682	0.891843	-2.32844
H	-8.34999	0.806462	-2.15615
C	-11.5254	-0.55363	1.177743
H	-12.0681	-0.91152	2.047483
C	-11.5452	0.381195	-1.0434

H	-12.1033	0.749245	-1.89906
C	-9.38452	-1.10218	2.40872
H	-8.3111	-1.03739	2.208408
C	-9.66372	-0.23328	3.649518
H	-9.39979	0.811144	3.459584
H	-9.07845	-0.58805	4.505013
H	-10.7209	-0.26792	3.933898
C	-9.72563	2.382496	-2.57554
H	-10.7874	2.549528	-2.786
H	-9.15539	2.749657	-3.43589
H	-9.45677	2.982746	-1.70147
C	-9.75444	0.029937	-3.56226
H	-9.50543	-1.01955	-3.38011
H	-9.18488	0.374799	-4.43227
H	-10.8177	0.084897	-3.8192
C	-9.7049	-2.58672	2.66531
H	-10.7639	-2.73359	2.903188
H	-9.11982	-2.9639	3.511291
H	-9.46997	-3.19259	1.785337
O	7.674244	-2.5431	-0.36542
O	7.746131	1.980389	0.362477
O	2.218434	3.805476	-0.82497
O	3.320406	4.355081	0.979608
N	7.723201	-0.28359	0.00748
N	2.968459	3.553532	0.114099
C	0.578051	-0.1708	-0.12587
C	4.881713	-0.22453	-0.0955
C	1.277665	-1.3478	-0.53109
C	5.612936	0.968664	0.119992
C	3.461355	-2.58137	-0.58363
C	3.453038	-0.19297	-0.12736
C	2.735693	-1.39762	-0.41345
C	4.941892	2.169266	0.237408
H	5.503347	3.088498	0.355515
C	3.545411	2.196339	0.176378
C	5.572145	-1.44477	-0.27841
C	2.755262	1.037603	0.094401
C	4.855695	-2.60876	-0.51008
H	5.403548	-3.53582	-0.63855
C	9.175056	-0.3171	0.065052
C	7.052311	-1.50085	-0.22283

C	0.59202	2.031863	0.880985
H	1.109308	2.872693	1.323241
C	-0.79614	2.011292	0.966965
H	-1.28122	2.849719	1.450442
C	7.095316	0.962971	0.178595
C	1.302743	0.99555	0.274882
C	9.797197	-0.53931	1.30568
C	9.903418	-0.12555	-1.12177
C	11.94281	-0.37967	0.175483
H	13.02793	-0.40387	0.218809
C	9.009958	-0.7492	2.594017
H	7.944427	-0.68325	2.355308
C	11.29998	-0.16138	-1.03898
H	11.89025	-0.01583	-1.93865
C	11.19617	-0.56669	1.334473
H	11.70578	-0.73665	2.278133
C	9.231364	0.116553	-2.46828
H	8.148367	0.099123	-2.31506
C	9.560825	-1.00542	-3.4708
H	9.274723	-1.98202	-3.06942
H	9.023073	-0.84724	-4.41206
H	10.63097	-1.03603	-3.70193
C	9.254132	-2.15397	3.176836
H	10.30104	-2.2905	3.468288
H	8.638264	-2.31063	4.069256
H	9.004577	-2.92716	2.444377
C	9.30909	0.357503	3.622648
H	9.099987	1.345807	3.20297
H	8.691794	0.224684	4.517868
H	10.35785	0.339978	3.937828
C	9.583968	1.507252	-3.02892
H	10.65549	1.595331	-3.23804
H	9.047	1.689544	-3.96625
H	9.313605	2.292802	-2.31742
H	-3.32451	-3.27236	-1.37795
H	-3.23502	2.970546	1.264834
H	2.941441	-3.51365	-0.76709

T_{ab}:

Symbol	X	Y	Z

O	-7.58376	-2.28833	0.123401
O	-7.58375	2.28841	-0.1237
N	-7.60131	0.000043	-2.7E-05
O	-1.97414	3.910429	0.972838
N	-2.76804	3.747969	0.050583
O	-1.97418	-3.91044	-0.97256
O	-3.13766	4.620143	-0.73504
O	-3.13763	-4.61996	0.735451
O	8.110611	2.110731	-0.88828
N	-2.76804	-3.74788	-0.0503
C	-4.75431	0.000049	0.000014
C	-0.4461	2.244613	-0.90872
H	-0.957	3.112784	-1.30458
C	0.941122	2.211211	-0.99595
H	1.436917	3.062722	-1.44406
C	-5.46725	-1.21949	0.069347
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C	1.684801	1.139044	-0.49865
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C	3.151121	1.145975	-0.4913
C	-1.16692	1.18702	-0.35092
C	-4.77573	-2.41454	0.101896
H	-5.32274	-3.34988	0.116996
C	-0.45665	0.000037	0.000072
C	-9.05553	0.000064	-5.7E-05
C	-6.95131	-1.24534	0.069971
C	-3.32499	0.000048	0.000056
C	-6.9513	1.245442	-0.07011
C	-1.16692	-1.18694	0.35108
C	-5.46725	1.219587	-0.06937
C	-2.6099	-1.23601	0.131074
C	0.977543	0.000029	0.000054
O	8.110609	-2.1108	0.888103
C	3.896347	2.239074	-0.94376
H	3.396229	3.128055	-1.30734
C	-0.44611	-2.24454	0.908863
H	-0.957	-3.1127	1.304747
C	1.684801	-1.139	0.498745
C	-4.77572	2.414644	-0.10185
H	-5.32272	3.34998	-0.11698
C	-3.37901	-2.41117	0.092448

C	-9.73051	0.060227	1.231348
C	-3.379	2.411268	-0.0923
C	-9.00053	-0.12541	-2.56812
H	-7.92481	-0.11821	-2.36876
C	3.15112	-1.14595	0.491343
C	3.849599	0.00001	0.000012
C	11.65358	-0.46914	-1.11
H	12.20417	-0.8335	-1.97204
C	5.278199	-1E-06	-1.2E-05
C	5.294458	2.23238	-0.9387
H	5.857696	3.088139	-1.29401
C	-9.31035	-1.4373	-3.3136
H	-10.3709	-1.50759	-3.57766
H	-9.05883	-2.30493	-2.69668
H	-8.73299	-1.49463	-4.24277
C	9.578446	-0.00001	-3.1E-05
C	0.941123	-2.21115	0.996061
H	1.436916	-3.06267	1.44416
C	10.25434	-0.47981	-1.13522
C	12.34905	-1.8E-05	-2.9E-05
H	13.43528	-2.5E-05	-2.6E-05
C	-9.30476	-1.11142	3.434417
H	-8.72815	-1.07745	4.365216
H	-9.04817	-2.03229	2.902732
H	-10.3653	-1.16144	3.703164
C	-11.1297	0.05865	1.203643
H	-11.6804	0.103971	2.13834
C	5.989473	1.127758	-0.47565
C	-9.30516	1.110825	-3.43512
H	-8.72844	1.076686	-4.36584
H	-9.04904	2.03205	-2.90383
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C	-11.8249	0.000134	-0.00011
H	-12.9111	0.000158	-0.00014
C	7.473888	1.149503	-0.48411
C	-9.73047	-0.06006	-1.23149
C	5.989472	-1.12777	0.475596
C	7.473886	-1.14954	0.484011
C	-11.1297	-0.05842	-1.20384
H	-11.6803	-0.10375	-2.13855
C	11.65359	0.469111	1.109938

H	12.20417	0.833459	1.971987
C	3.896345	-2.23906	0.943771
H	3.396225	-3.12803	1.307374
C	-9.00062	0.125359	2.568013
H	-7.92489	0.118723	2.368655
C	5.294455	-2.23239	0.938665
H	5.857694	-3.08816	1.29395
C	9.524059	1.000836	2.367563
H	8.448595	0.923017	2.183071
C	10.25435	0.479787	1.135163
C	-9.31099	1.436735	3.31413
H	-9.06	2.304791	2.697592
H	-8.73351	1.493928	4.243237
H	-10.3715	1.506389	3.578429
C	9.524057	-1.00086	-2.36762
H	8.448593	-0.92303	-2.18314
C	9.830776	-0.14014	-3.60765
H	10.89119	-0.18857	-3.87731
H	9.57695	0.908266	-3.42585
H	9.253201	-0.49147	-4.4697
C	9.831166	2.4899	2.61436
H	10.89167	2.649248	2.83678
H	9.253838	2.863476	3.467161
H	9.577261	3.09013	1.735821
C	9.830766	0.140119	3.607594
H	9.57679	-0.90826	3.42586
H	9.253308	0.491565	4.469677
H	10.89121	0.188425	3.877157
C	9.83114	-2.48993	-2.61441
H	9.253809	-2.8635	-3.46721
H	9.577215	-3.09015	-1.73587
H	10.89164	-2.64931	-2.83682

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O	3.493275	-4.57501	0.593414

N	7.859457	0.176528	-0.00143
N	3.147153	-3.70834	-0.20861
C	0.716059	0.003178	-0.04023
C	5.015592	0.094682	-0.07721
C	1.451722	-1.19746	0.213008
C	5.691258	1.335185	-0.15054
C	3.708746	-2.35489	-0.02452
C	3.587671	0.049372	-0.09422
C	2.904447	-1.20469	0.015776
C	4.961876	2.50809	-0.26059
H	5.498342	3.449487	-0.30419
C	3.565924	2.471449	-0.3197
C	5.762325	-1.10429	0.012361
C	2.857185	1.26831	-0.2561
C	5.105891	-2.31831	0.021354
H	5.678648	-3.23796	0.04366
C	9.311896	0.220655	0.045207
C	7.24652	-1.08696	0.054031
C	0.639753	2.320167	-0.7429
H	1.12651	3.222432	-1.09284
C	-0.75077	2.307558	-0.68807
H	-1.27398	3.1891	-1.03221
C	7.173063	1.401937	-0.10606
C	1.398655	1.216387	-0.35579
C	10.02892	0.165907	-1.1625
C	9.944463	0.315075	1.296842
C	12.07923	0.302612	0.135275
H	13.1644	0.334592	0.170596
C	9.345477	0.063303	-2.52117
H	8.264119	0.04161	-2.35676
C	11.34329	0.354867	1.31485
H	11.86127	0.427461	2.266363
C	11.42583	0.209185	-1.08953
H	12.00797	0.168666	-2.00522
C	9.16915	0.375086	2.607913
H	8.101543	0.328551	2.373613
C	9.485931	-0.83683	3.504277
H	9.278617	-1.77415	2.979855
H	8.877558	-0.80846	4.414841
H	10.5379	-0.84638	3.808834
C	9.717321	-1.24757	-3.23945

H	10.78768	-1.29027	-3.4674
H	9.173136	-1.33259	-4.18639
H	9.470058	-2.11464	-2.62011
C	9.642558	1.297773	-3.39326
H	9.342618	2.216915	-2.88158
H	9.09785	1.236133	-4.34174
H	10.70944	1.375335	-3.6283
C	9.410265	1.707851	3.341677
H	10.45855	1.817918	3.639169
H	8.800618	1.760011	4.250356
H	9.150702	2.556633	2.702285
O	-7.90774	2.110839	-0.13039
O	-7.78041	-2.46051	0.154395
O	-2.41527	3.885824	1.178418
O	-3.49319	4.575108	-0.59299
N	-7.85945	-0.17655	0.001338
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C	-0.71605	-0.0031	0.040339
C	-5.01558	-0.09466	0.077213
C	-1.45172	1.19754	-0.21289
C	-5.69123	-1.33518	0.150454
C	-3.70878	2.354942	0.024747
C	-3.58766	-0.04932	0.094271
C	-2.90445	1.204758	-0.01564
C	-4.96184	-2.50807	0.26047
H	-5.49829	-3.44948	0.303995
C	-3.56589	-2.47141	0.319634
C	-5.76233	1.104305	-0.01231
C	-2.85717	-1.26826	0.256123
C	-5.10592	2.318338	-0.02119
H	-5.6787	3.237976	-0.04342
C	-9.31188	-0.2207	-0.04534
C	-7.24653	1.086955	-0.05403
C	-0.63975	-2.32012	0.742936
H	-1.12651	-3.2224	1.092819
C	0.750773	-2.30751	0.688134
H	1.273998	-3.18907	1.032217
C	-7.17303	-1.40195	0.105907
C	-1.39864	-1.21632	0.355858
C	-10.0289	-0.166	1.162352
C	-9.94442	-0.31508	-1.29699

C	-12.0792	-0.3027	-0.13548
H	-13.1644	-0.33469	-0.17083
C	-9.34553	-0.06343	2.521045
H	-8.26417	-0.04174	2.356667
C	-11.3432	-0.3549	-1.31504
H	-11.8612	-0.42747	-2.26657
C	-11.4258	-0.2093	1.089344
H	-12.008	-0.16882	2.00502
C	-9.16907	-0.37504	-2.60805
H	-8.10147	-0.32847	-2.37372
C	-9.48587	0.836891	-3.50439
H	-9.27861	1.774202	-2.97995
H	-8.87747	0.808561	-4.41494
H	-10.5378	0.846407	-3.80898
C	-9.71739	1.247424	3.239342
H	-10.7878	1.290128	3.467256
H	-9.17323	1.332422	4.186302
H	-9.47011	2.114506	2.62002
C	-9.64264	-1.29792	3.393103
H	-9.34269	-2.21705	2.881413
H	-9.09796	-1.2363	4.341596
H	-10.7095	-1.37548	3.628118
C	-9.41012	-1.7078	-3.34184
H	-10.4584	-1.81789	-3.63936
H	-8.80045	-1.75991	-4.25051
H	-9.15054	-2.55658	-2.70246
H	3.030981	3.409828	-0.40134
H	-3.03093	-3.40979	0.401249

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Symbol	X	Y	Z
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O	-2.39981	3.653151	-1.06646
O	-3.38704	4.241644	0.793363
N	-7.86192	-0.39172	0.059664
N	-3.09119	3.426058	-0.07927
C	-0.71764	-0.3159	-0.23137
C	-5.01978	-0.35072	-0.10016

C	-1.42796	-1.51687	-0.53456
C	-5.74265	0.853398	0.075717
C	-3.62057	-2.73377	-0.5035
C	-3.59201	-0.32738	-0.16044
C	-2.88581	-1.54876	-0.39882
C	-5.06612	2.055007	0.131362
H	-5.62207	2.980551	0.224184
C	-3.67098	2.072464	0.041778
C	-5.71982	-1.57418	-0.21467
C	-2.88676	0.909972	-0.012
C	-5.01429	-2.75085	-0.40635
H	-5.56825	-3.67985	-0.48411
C	-9.31293	-0.41479	0.147091
C	-7.20023	-1.62027	-0.1289
C	-0.69616	1.936009	0.655432
H	-1.19532	2.787961	1.097111
C	0.696166	1.936006	0.655439
H	1.195335	2.787957	1.097116
C	-7.22523	0.857098	0.163207
C	-1.42764	0.875237	0.121286
C	-9.91086	-0.57762	1.408676
C	-10.0634	-0.27193	-1.0328
C	-12.0776	-0.45601	0.314653
H	-13.1617	-0.47179	0.380365
C	-9.09937	-0.7357	2.689351
H	-8.03837	-0.68144	2.428201
C	-11.4581	-0.2959	-0.92081
H	-12.0655	-0.18699	-1.81423
C	-11.3091	-0.59555	1.46601
H	-11.8007	-0.72021	2.426093
C	-9.41752	-0.09445	-2.40208
H	-8.33163	-0.10855	-2.26992
C	-9.76991	-1.26054	-3.34477
H	-9.47867	-2.21872	-2.90454
H	-9.25073	-1.14794	-4.30282
H	-10.8445	-1.29779	-3.55285
C	-9.33395	-2.11536	3.333203
H	-10.3752	-2.2375	3.650063
H	-8.70115	-2.23705	4.219173
H	-9.09997	-2.91822	2.628025
C	-9.37766	0.41199	3.678117

H	-9.17601	1.382545	3.215561
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H	-10.42	0.408787	4.0141
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H	-10.8531	1.351466	-3.21167
H	-9.25939	1.40603	-3.97531
H	-9.49161	2.087291	-2.35205
O	7.865849	1.885542	0.314706
O	7.826677	-2.66564	-0.21348
O	2.399726	3.653164	-1.06624
O	3.387062	4.241596	0.793544
N	7.861922	-0.39172	0.059647
N	3.09116	3.426041	-0.0791
C	0.717642	-0.3159	-0.23136
C	5.019784	-0.35073	-0.10016
C	1.427646	0.875226	0.121305
C	5.719824	-1.57418	-0.21468
C	3.670977	2.072448	0.041856
C	3.592018	-0.32739	-0.16044
C	2.886762	0.909957	-0.01197
C	5.014294	-2.75086	-0.40638
H	5.568257	-3.67985	-0.48414
C	3.620575	-2.73378	-0.50352
C	5.742654	0.853391	0.075726
C	2.885811	-1.54876	-0.39883
C	5.066122	2.054996	0.131418
H	5.622065	2.98054	0.224262
C	9.312937	-0.41479	0.147072
C	7.22523	0.857096	0.163167
C	0.695304	-2.64146	-0.91594
H	1.204046	-3.55173	-1.20874
C	-0.69531	-2.64146	-0.91593
H	-1.20405	-3.55173	-1.20874
C	7.200227	-1.62028	-0.12889
C	1.427956	-1.51687	-0.53456
C	10.06335	-0.27195	-1.03282
C	9.910869	-0.57761	1.408658
C	12.07762	-0.45602	0.314628
H	13.16173	-0.47181	0.380338
C	9.417515	-0.09447	-2.4021
H	8.331633	-0.10863	-2.26995

C	11.3091	-0.59554	1.465989
H	11.80073	-0.7202	2.426072
C	11.45814	-0.29592	-0.92084
H	12.06551	-0.18703	-1.81426
C	9.099376	-0.73567	2.689338
H	8.038378	-0.68142	2.428188
C	9.377663	0.412044	3.678078
H	9.176009	1.382588	3.215502
H	8.743279	0.314192	4.565767
H	10.42003	0.408852	4.014057
C	9.777793	1.26979	-3.01996
H	10.85301	1.351546	-3.21163
H	9.259327	1.406061	-3.97529
H	9.491501	2.087274	-2.35199
C	9.769975	-1.2605	-3.34484
H	9.478784	-2.21871	-2.90464
H	9.250788	-1.14789	-4.30288
H	10.84459	-1.29769	-3.55292
C	9.333966	-2.11531	3.333219
H	10.37523	-2.23744	3.650081
H	8.701166	-2.23699	4.219193
H	9.09999	-2.91819	2.628059
H	-3.10989	-3.67678	-0.65425
H	3.109895	-3.67679	-0.65428

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Symbol	X	Y	Z
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O	-3.54244	4.368501	0.923388
N	-7.98161	-0.2859	0.023609
N	-3.25264	3.584716	0.020667
C	-0.83727	-0.13801	-0.15085
C	-5.13598	-0.21209	-0.09596

C	-1.55867	1.048688	0.193204
C	-5.82154	-1.44092	-0.24213
C	-3.81681	2.221371	0.107281
C	-3.70837	-0.17205	-0.13611
C	-3.01775	1.069975	0.043897
C	-5.10278	-2.60719	-0.44415
H	-5.64567	-3.54052	-0.54402
C	-3.70737	-2.57341	-0.52224
C	-5.87483	0.980077	0.090463
C	-2.98883	-1.38212	-0.38851
C	-5.2129	2.187792	0.176656
H	-5.78063	3.105287	0.278313
C	-9.4338	-0.32605	0.090439
C	-7.35961	0.966473	0.158054
C	-0.78242	-2.43355	-0.92886
H	-1.27706	-3.32207	-1.30113
C	0.606919	-2.43853	-0.86639
H	1.125843	-3.32262	-1.21268
C	-7.30401	-1.50327	-0.17781
C	-1.53061	-1.33523	-0.50214
C	-10.169	-0.1676	-1.09702
C	-10.0466	-0.52079	1.340285
C	-12.1992	-0.40029	0.218515
H	-13.2839	-0.42909	0.268768
C	-9.5066	0.044334	-2.45347
H	-8.42235	0.037007	-2.3073
C	-11.4452	-0.55485	1.37751
H	-11.9487	-0.70432	2.327838
C	-11.5648	-0.20866	-1.00482
H	-12.1611	-0.0884	-1.90416
C	-9.25141	-0.69588	2.629001
H	-8.18732	-0.62597	2.384321
C	-9.55531	0.429542	3.635742
H	-9.35772	1.411101	3.195116
H	-8.93226	0.320785	4.530113
H	-10.6021	0.409019	3.956969
C	-9.87118	1.418133	-3.04733
H	-10.9444	1.494006	-3.25196
H	-9.34119	1.579225	-3.99238
H	-9.60184	2.224005	-2.3585
C	-9.83586	-1.10437	-3.42543

H	-9.54238	-2.06943	-3.00203
H	-9.30477	-0.9668	-4.3736
H	-10.9071	-1.14626	-3.64908
C	-9.48099	-2.08995	3.242938
H	-10.5252	-2.22828	3.542654
H	-8.85945	-2.22232	4.135251
H	-9.22921	-2.87707	2.526252
O	7.733838	-2.39568	0.011509
O	7.710214	2.187067	0.064612
O	2.142951	-4.00278	1.104478
O	2.147171	3.760412	-1.1885
O	3.288406	-4.76489	-0.59356
O	3.215915	4.498265	0.570691
N	7.742116	-0.10412	0.036759
N	2.892746	3.617954	-0.22548
N	2.925437	-3.86987	0.168442
C	0.595645	-0.1367	-0.11131
C	4.893049	-0.11807	-0.01485
C	1.315747	-1.34079	-0.37367
C	5.600078	1.10634	0.017142
C	3.531212	-2.53602	-0.02348
C	3.464402	-0.1252	-0.04206
C	2.757239	-1.36964	-0.13029
C	4.904394	2.298517	-0.00519
H	5.447255	3.236433	-0.01224
C	3.507531	2.287046	-0.03763
C	5.613218	-1.33528	-0.01721
C	2.743344	1.112157	0.024294
C	4.928478	-2.53382	-0.00806
H	5.479818	-3.46608	0.028385
C	9.196528	-0.09674	0.061896
C	7.098435	-1.35362	0.009085
C	0.554975	2.13821	0.710232
H	1.051138	3.010516	1.115906
C	-0.83715	2.121366	0.721165
H	-1.34237	2.973745	1.153779
C	7.08535	1.139047	0.043226
C	1.292892	1.068052	0.203834
C	9.849656	-0.10521	1.306467
C	9.892103	-0.08121	-1.15939
C	11.96484	-0.08257	0.109702

H	13.05082	-0.07694	0.128461
C	9.097102	-0.12152	2.63204
H	8.024796	-0.12701	2.414599
C	11.29062	-0.07449	-1.1073
H	11.85738	-0.06254	-2.03332
C	11.24911	-0.09768	1.302704
H	11.78359	-0.10367	2.247757
C	9.185647	-0.07155	-2.51017
H	8.106453	-0.07742	-2.32997
C	9.51215	-1.33825	-3.32368
H	9.251739	-2.24036	-2.76246
H	8.95195	-1.34292	-4.265
H	10.57748	-1.39145	-3.57182
C	9.3992	-1.4017	3.433776
H	10.45522	-1.45643	3.718639
H	8.806082	-1.42497	4.354424
H	9.162086	-2.29431	2.847548
C	9.382076	1.149	3.455153
H	9.132212	2.047982	2.88424
H	8.789293	1.14866	4.376302
H	10.43749	1.213294	3.740314
C	9.501999	1.212409	-3.30029
H	10.5667	1.278451	-3.54802
H	8.941127	1.230278	-4.24103
H	9.235178	2.102014	-2.72234
H	-3.18191	-3.50764	-0.67748

T_{abcd}:

Symbol	X	Y	Z
O	-7.84905	2.230894	0.525556
O	-7.84909	-2.23068	-0.52583
O	-2.17805	3.934774	-0.5659
O	-2.17817	-3.93475	0.565767
O	-3.57852	4.670236	0.93748
O	-3.57857	-4.67012	-0.93772
N	-7.82161	0.00006	0.00004
N	-3.0793	-3.75713	-0.25882
N	-3.07922	3.757205	0.25866
C	-0.72247	0.000009	-1.6E-05

C	-5.00654	0.000056	-4.2E-05
C	-1.43246	1.159679	0.434228
C	-5.71662	-1.19306	-0.28165
C	-3.63962	2.417474	0.398353
C	-3.56541	0.000041	-4.2E-05
C	-2.84824	1.217621	0.263327
C	-5.01612	-2.38988	-0.46349
H	-5.57093	-3.31179	-0.58209
C	-3.63967	-2.41738	-0.39848
C	-5.7166	1.193191	0.281545
C	-2.84826	-1.21755	-0.26341
C	-5.01607	2.390004	0.463345
H	-5.57086	3.311933	0.58191
C	-9.26623	0.000071	0.00009
C	-7.17394	1.224942	0.292642
C	-0.68101	-2.20033	-1.06292
H	-1.2009	-2.99494	-1.58304
C	0.680986	-2.20034	-1.06289
H	1.200876	-2.99497	-1.58299
C	-7.17396	-1.22477	-0.29275
C	-1.43247	-1.15964	-0.43428
C	-9.95165	0.381205	-1.16737
C	-9.95158	-0.38104	1.167606
C	-12.0492	0.00013	0.00019
H	-13.1365	0.000155	0.000233
C	-9.21529	0.808638	-2.43104
H	-8.14694	0.65658	-2.25998
C	-11.3511	-0.37725	1.143363
H	-11.8996	-0.6746	2.033156
C	-11.3512	0.377466	-1.14303
H	-11.8997	0.674833	-2.0328
C	-9.21514	-0.80867	2.431164
H	-8.14684	-0.65609	2.260225
C	-9.60319	0.059241	3.641617
H	-9.41997	1.117427	3.43264
H	-9.01168	-0.22468	4.519537
H	-10.6613	-0.05701	3.904445
C	-9.42139	2.309943	-2.70746
H	-10.4759	2.538202	-2.90493
H	-8.84113	2.623733	-3.58306
H	-9.09706	2.8994	-1.84583

C	-9.60293	-0.06003	-3.6411
H	-9.4192	-1.11802	-3.43157
H	-9.01156	0.223741	-4.51916
H	-10.6611	0.055587	-3.90394
C	-9.42067	-2.31019	2.706886
H	-10.4751	-2.53889	2.904184
H	-8.84036	-2.62416	3.582389
H	-9.09609	-2.89914	1.845008
O	7.849048	-2.2309	-0.52556
O	7.84909	2.230678	0.525854
O	2.178019	-3.93476	0.565861
O	2.178169	3.93475	-0.56578
O	3.578538	-4.67023	-0.93747
O	3.578592	4.670131	0.937677
N	7.821604	-6.3E-05	-3.3E-05
N	3.079296	3.757131	0.258812
N	3.079214	-3.7572	-0.25867
C	0.722468	-8E-06	0.000004
C	5.006535	-5.8E-05	0.00004
C	1.432454	-1.15968	-0.43424
C	5.716619	1.193057	0.281647
C	3.639613	-2.41747	-0.39836
C	3.565406	-0.00004	0.000034
C	2.848234	-1.21762	-0.26334
C	5.016118	2.389879	0.463487
H	5.570922	3.311791	0.582092
C	3.639662	2.417384	0.398472
C	5.716594	-1.19319	-0.28154
C	2.848256	1.217554	0.263402
C	5.016069	-2.39001	-0.46335
H	5.570852	-3.31194	-0.58191
C	9.266227	-7.5E-05	-7.9E-05
C	7.173938	-1.22495	-0.29263
C	0.68101	2.200327	1.062901
H	1.200902	2.994943	1.583019
C	-0.68099	2.200343	1.062881
H	-1.20088	2.994972	1.582983
C	7.17396	1.224771	0.292757
C	1.432471	1.159645	0.434269
C	9.951642	-0.38117	1.167398
C	9.951578	0.380994	-1.16761

C	12.04915	-0.00014	-0.00018
H	13.13654	-0.00017	-0.00022
C	9.215288	-0.8085	2.431107
H	8.146932	-0.65657	2.259988
C	11.35109	0.377194	-1.14336
H	11.89959	0.674511	-2.03317
C	11.35116	-0.37743	1.143063
H	11.8997	-0.67476	2.032841
C	9.215145	0.808525	-2.43121
H	8.146839	0.656069	-2.26023
C	9.603108	-0.0596	-3.64154
H	9.419786	-1.11773	-3.43239
H	9.011621	0.224249	-4.5195
H	10.6612	0.056508	-3.90438
C	9.421511	-2.30974	2.707754
H	10.47604	-2.53789	2.905293
H	8.841259	-2.62345	3.583388
H	9.097258	-2.89935	1.846205
C	9.602819	0.060405	3.641028
H	9.418979	1.118338	3.431324
H	9.011472	-0.22328	4.519136
H	10.66098	-0.05506	3.903898
C	9.420796	2.309987	-2.70714
H	10.47526	2.538591	-2.90449
H	8.840491	2.623882	-3.58267
H	9.096276	2.899081	-1.84534

VI. Crystallographic Data:

Crystal System	**T_{ab}**	**T_{ac}**	**T_{ad}**	**T_{abc}**	**T_{abcd}**
Formula	$C_{60}H_{46}Cl_6N_4O_8$	$C_{58}H_{44}N_4O_8$	$C_{117}H_{89}Cl_3N_8O_{16}$	$C_{58}H_{43}N_5O_{10}$	$C_{62}H_{46}Cl_{12}N_6O_{12}$
Formula weight	1163.71	924.97	1969.31	969.97	1492.45
CCDC no.	2204224	2204225	2204226	2204227	2204228
Space Group	$Pca2_1$	$C2/c$	P-1	P-1	P-1
Temperature (K)	120	100	100	120	296.15
a (Å)	14.4750(15)	26.736(3)	9.412(2)	8.7404(11)	10.4617(15)
b (Å)	22.912(2)	16.294(2)	23.109(16)	9.8973(14)	12.3933(19)
c (Å)	31.837(3)	14.3851(17)	30.268(10)	15.641(2)	13.748(2)
α (˚)	90	90	86.235(7)	100.242(6)	67.233(10)
β (˚)	90	114.589(5)	85.355(2)	95.440(6)	88.114(11)
γ (˚)	90	90	89.587(9)	96.856(7)	80.705(10)
Volume [V(Å^3)]	10558.5(18)	5698.4(12)	6548(5)	1312.6(3)	1621.2(5)
Density (g/cm^3)	1.464	1.078	0.999	1.227	1.529
Z', Z	2, 8	0.5, 4	1, 2	0.5, 1	0.5, 1
Size of crystal (mm^3)	0.092 × 0.085 × 0.07	0.403 × 0.08 × 0.059	0.102 × 0.086 × 0.074	0.264 × 0.091 × 0.065	0.102 × 0.056 × 0.048
Treatment of hydrogens	Constrained	Constrained	Constrained	Constrained	Constrained
μ/mm^{-1}	0.388	0.073	0.126	0.085	0.579
F (000)	4800.0	1936.0	2052.0	506.0	760.0
$2\theta_{min,max}$	4.198 to 56.564	3.35 to 57.398	3.532 to 50.382	4.224 to 57.396	3.214 to 60.068
$h_{min,max}$	-19, 19	-36, 36	-11, 11	-9, 11	-14, 14
$k_{min,max}$	-30, 30	-22, 22	-27, 27	-13, 12	-17, 17
$l_{min,max}$	-42, 42	-19, 19	-36, 36	-21, 21	-19, 19
No. of reflections	182532	91148	169920	16099	32219
No. of unique/ observed reflections	26200, 15007	7360, 5386	23329, 4205	6375, 2044	9415, 4922
No. of parameters	1385	350	1332	371	448
R_{all}, R_{obs}	0.1825, 0.1111	0.1030, 0.0835	0.3913, 0.1584	0.2968, 0.1396	0.1294, 0.0597
$wR2_{all}$, $wR2_{obs}$	0.2831, 0.2443	0.2585, 0.2464	0.5390, 0.4012	0.4474, 0.3880	0.1584, 0.1311
$\Delta\rho_{max,min}$ (e·Å^{-3})	0.76/-0.93	0.62/-0.45	0.62/-0.53	0.52/-0.74	0.44/-0.47
G.o.F	1.022	1.050	0.971	1.098	0.973

VII. References:

(1) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision D.01, *Gaussian, Inc*. Wallingford CT, 2013.

(2) F. Nolde, J. Qu, C. Kohl, N. G. Pschirer, E. Reuther and K. Müllen, *Chem. Eur. J*, 2005, **11**, 3959–3967.