

Unravelling the Intramolecular $n \rightarrow \sigma^*$ Interaction in Ultra-Electron Deficient Naphthalenediimides and their Radical Ions

Sharvan Kumar, Kalyanashis Mandal, Ajayakumar M.R., Geeta Hundal and Pritam Mukhopadhyay*

*Supramolecular and Material Chemistry Lab, School of Physical Sciences,
Jawaharlal Nehru University, New Delhi 110067*

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Experimental Section

General: Chemicals were sourced either from Sigma-Aldrich, Spectrochem (India), Loba Chemie (India) or Thomas Baker (India) and were used as received. The reactions for the synthesis of **2²⁺** was carried out in heavy-wall borosilicate glass tubes (L x OD: 17.8 cm x 25.4 mm) sourced from Sigma Aldrich (Cat. No. Z181072). NMR (¹H, ¹³C, DEPT-135 and APT) spectra were recorded on a Bruker 500 MHz spectrometer in CDCl₃ with TMS as a standard. ³¹P NMR was performed in Bruker 500 MHz spectrometer in CDCl₃ with H₃PO₄ (70% aqueous solution) as an external standard. Spin multiplicities are reported as a singlet (s), doublet (d), and triplet (t) with coupling constants (*J*) given in Hz, or multiplet (m). MALDI-TOF mass spectral data were obtained using a Bruker made Autoflex TOF/TOF instrument with laser repetition rate of 50 psec. 1,8,9-Anthracenetriol was used as the matrix for MALDI-TOF mass spectrometry.

Theoretical Calculations: The ground-state geometry optimization was carried out applying the density functional theory (DFT) with the Becke three-parameter¹ hybrid exchange functional in concurrence with the Lee-Yang-Parr gradient-corrected correlation function (B3LYP functional)² with the 6-311++ G(d,p) basis set as implemented in Gaussian 09W.³ For finding the HOMO-LUMO energy levels in gas phase, single point energy calculations with B3LYP/6-311++G(d,p) ground-state geometry optimization was calculated with DFT level of theory. Radical ions ground state energy optimization and spin density distribution was calculated using UB3LYP/6-311++G(d,p). The electrostatic potentials (ESP) mapped on the electronic density surfaces are based on the DFT calculations and plotted with the GaussView 5.0.9 program. NBO⁴ and AIM⁵ calculations were done by using same basis set. For visualization of interacting NBOs we have used Jmol and for contour plot NBO view. Multiwfn 3.3.7 (dev) package⁶ is used for AIM calculation.

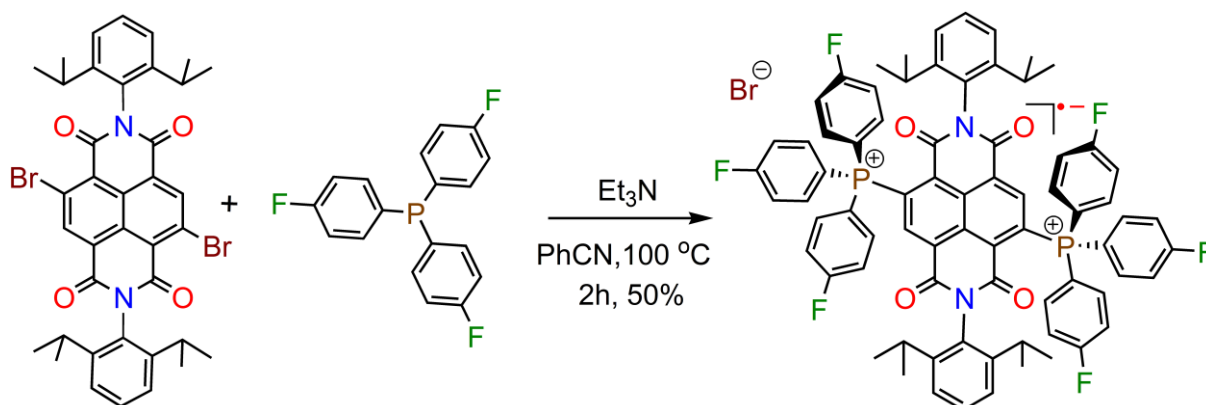
UV-vis-NIR Spectroscopy: UV-vis-NIR spectra were recorded on a JASCO V-670 UV-vis NIR Spectrophotometer. All UV-vis-NIR spectroscopic experiments were performed in a quartz cuvette with 1.0 mm optical pathlength. UV-Grade chloroform was used for the spectroscopic experiments.

Cyclic and Differential Pulse Voltammetry (CV/DPV): CV and DPV were carried out using a computer controlled potentiostat (CHI 650C) and a standard three electrode arrangement that consisted of both platinum working and auxiliary electrodes and Ag/AgCl as reference electrode. All the electrochemical measurements were carried out in Ar-purged solvents with n-Bu₄NPF₆ as the supporting electrolyte. CV studies of themolecules **2²⁺** and **1a²⁺** were performed in degassed DCM under Ar atmosphere at 0.5 mM and the scan rate for the measurements were typically 200-300 mV/s. 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: X-ray data of **1b²⁺** was collected on a Bruker's Apex-II CCD diffractometer using Mo K α ($\lambda = 0.71069 \text{ \AA}$). The data were corrected for Lorentz and polarization effects and empirical absorption corrections were applied using SADABS from Bruker. The number of total, independent and observed reflections ($[I > 2 \sigma(I)]$ for theta 29°) were 15341, 7902 and 4725. The structures were solved by direct methods using SIR-92⁷ and refined by full-matrix least squares refinement methods based on F², using SHELX-97.⁸ Refinement showed a highly disordered BF₄ group and also there was disorder in the terminal methyl and methylene groups of the hexyl chain. The disorder in the methyl (C13) and methylene (C12) group was resolved by splitting these atoms into two positions and refining their *s*ofs and Uiso values as free variables over fixed C-C distances. Two hydrogens attached to the adjacent methylene C11 were also split over two positions so as to correctly define the tetrahedral disposition around it. The disorder in the BF₄ was also resolved in a similar manner by splitting all five atoms with SADI restraints over B-F bonding and F-F non-bonding distances. Similar ADP (SIMU) and rigid bond (DELU) restraints had to be used for the B atom which tends to be NPD on anisotropic refinement. Apart from that there was some much diffused electron

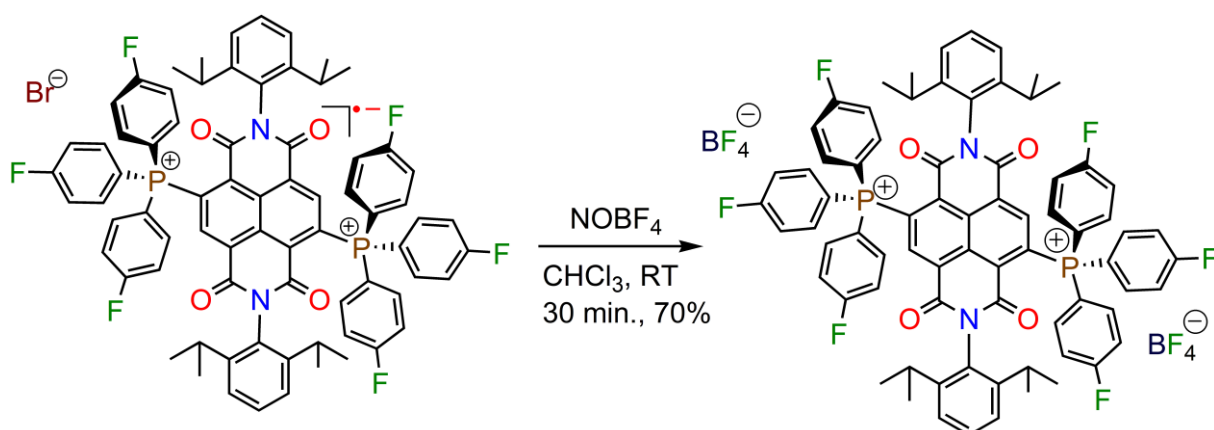
density with maxima around $1.4 \text{ e}\text{\AA}^3$ which could not be modelled, but could be due to some solvent molecule. Therefore, it was removed by using the SQUEEZE routine with PLATON.⁹ The subsequent model refined well with much improved R value. It also showed SAV of the 100\AA^3 which matches well with the volume of the void created (99\AA^3) on removing the solvent. The number of electron recovered (16) from the site indicate that it could be a methanol molecule or 1.5 water molecules in the asymmetric unit. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed geometrically with their U_{iso} values 1.2, 1.2 and 1.5 times of the phenylene, methylene and methyl carbons, respectively. All calculations were performed using Wingx package.¹⁰

1. Synthesis of 2^{2+} :



In a pressure tube (for details, see General Experimental Section) containing 2 mL dry benzonitrile, N,N-bis-(diisopropyl)-2,3-dibromo-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (200 mg, 0.27 mmol), Tris(4-fluorophenyl)phosphine (340 mg, 1.07 mmol) and $(\text{C}_2\text{H}_5)_3\text{N}$ ($56 \mu\text{L}$, 0.40 mmol) were added. The reaction mixture was allowed to heat at 100°C on a magnetic stirrer. The colour of the solution became dark green with the progress of the reaction. After 2 h, the reaction mixture was gradually brought to room temperature and the solution was purified by silica-gel column chromatography (100-200 mesh) with $\text{CHCl}_3/\text{MeOH}$ (100:1) as the eluent. The obtained dark-green colored solid was dissolved in CHCl_3 and layered with hexane ($\text{CHCl}_3/\text{hexane} \sim 1:2.5$) under ambient condition, which produced crystals within 2-3 days. Yield = 50%. $R_f = 0.50$ ($\text{CHCl}_3/\text{MeOH}$ 8.5:1.5). Melting point: 170°C .

2. Synthesis of 2^{2+} :



The compound 2^{2+} (100 mg, 0.07 mmol) was transferred to a 50 mL RB containing 3 mL CHCl_3 and NOBF_4 (12.0 mg, 0.10 mmol) was added to it. The reaction mixture was allowed to stir at room temperature. After 30 min, the dark-green coloured solution gradually turned to yellow. The reaction mixture was dried under vacuum and purified by silica-gel column chromatography (100-200 mesh) with $\text{CHCl}_3/\text{MeOH}$ (100:1.5) as the eluent. The obtained product was recrystallized from toluene/ CHCl_3 (1:0.4) by slow evaporation under ambient condition. Yield = 70%. $R_f = 0.58$ (9:1 $\text{CHCl}_3/\text{MeOH}$). Melting point: $> 300^\circ\text{C}$. $^1\text{H NMR}$ (500 MHz, CDCl_3 , 298 K): $\delta = 8.33$ (d, $J = 14.5$ Hz, 2H), 7.84-7.25 (m, 24H, PPh_3), 7.12-7.0 (m, $J = 7.0$ Hz, 4H, Isopropyl Bz), 2.45 (t, $J = 6.5$ Hz, 4H, Isopropyl H), 0.94 (t, $J = 6.5$ Hz, 12H, Isopropyl CH_3), 0.62 (t, 12H, Isopropyl CH_3). $^{13}\text{C NMR}$ (125 MHz, CDCl_3 , 300K): $\delta = 162.55, 161.29, 145.93, 130.17, 129.05, 128.56, 128.24, 124.05, 118.52, 118.40, 118.22, 28.48, 23.97, 23.92$. ^{31}P (202 MHz, CDCl_3 , 298 K, H_3PO_4): $\delta = 30.13$. Calculated for MS (MALDI-TOF matrix: 1,8,9-Anthracenetriol): Calculated for : $\text{C}_{77}\text{H}_{66}\text{F}_6\text{N}_2\text{O}_4\text{P}_2[\text{M}-2\text{BF}_4]^{2+}$: 1216.39, found 1216.43.

Table S1: Reduction potentials (CV/DPV) against Fc/Fc^+ in DCM.

Entry	E_1^R (V vs Fc/Fc^+)	E_2^R (V vs Fc/Fc^+)	LUMO (eV) ^a
2^{2+}	-0.192 / -0.187	-0.552 / 0.539	-4.91 / -4.92
$1a^{2+}$	-0.199 / -0.203	-0.679 / -0.679	-4.90 / -4.89

^aLUMO = $[-5.1(\text{Fc}) - E_1^R]$ eV against vacuum, [10] LUMO was determined applying the CV/DPV experiments respectively, Ag/AgCl , 0.1 M Bu_4NPF_6 , Fc (external standard), 298 K. All potentials are represented as: $E_R (= (E_{pa} + E_{pc})/2)$, with E_{pa} and E_{pc} determined from the CV experiments.

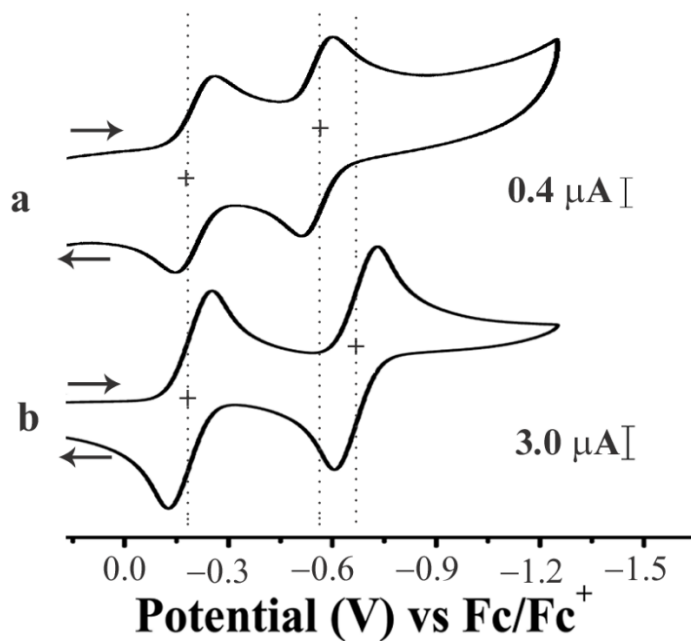


Figure S1: CV results of (a) 2^{2+} and (b) $1a^{2+}$, Conditions: 5×10^{-4} M in CH_2Cl_2 ; reference electrode, Ag/AgCl; working and auxiliary electrodes, Pt with 0.1 M Bu_4NPF_6 and ferrocene/ferrocenium (Fc/Fc^+); 298 K; scan rate, 200 mV/s.

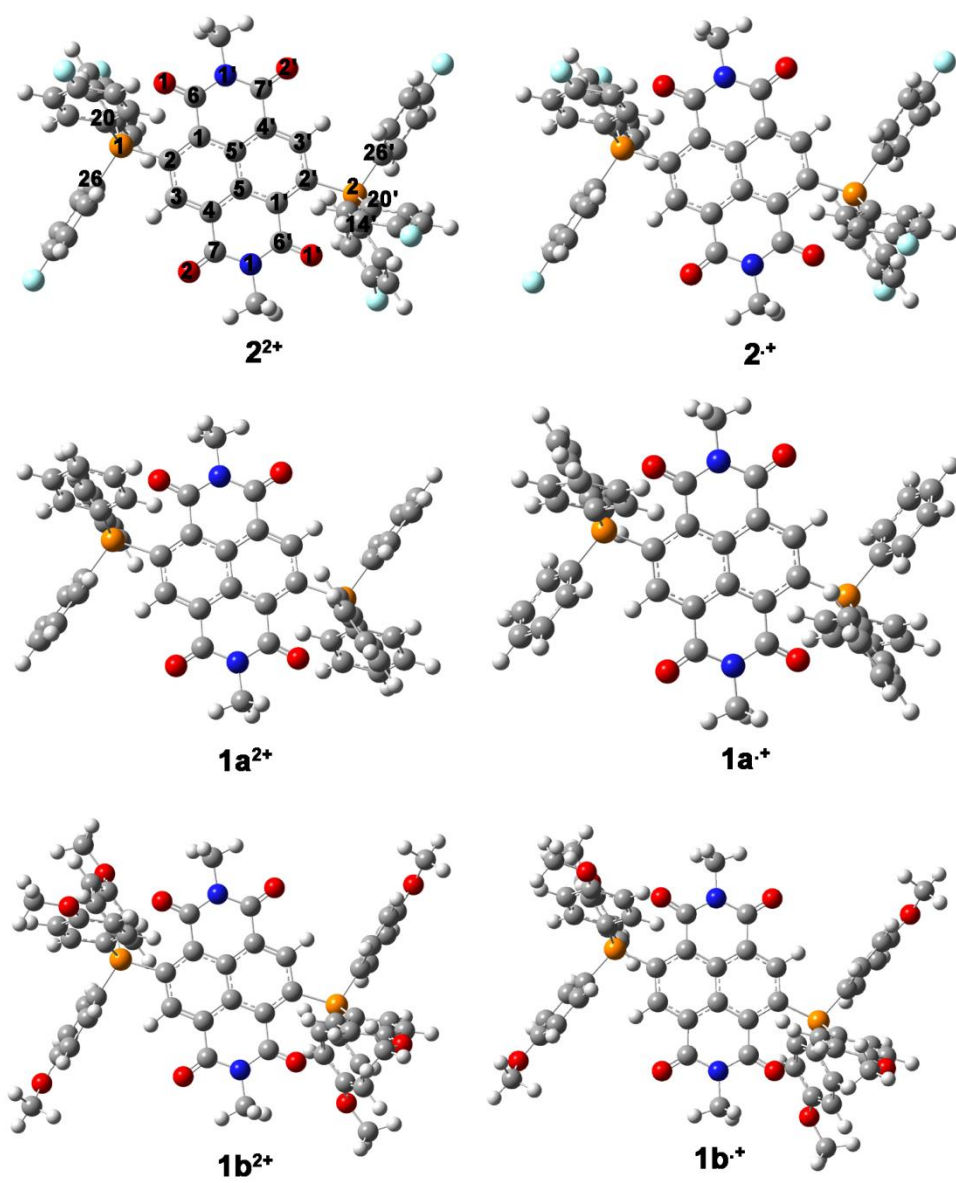


Figure S2: Geometry optimized structures of 2^{2+} , 2^{+} , $1a^{2+}$, $1a^{+}$, $1b^{2+}$ and $1b^{+}$ with atom numbering scheme.

Table S2: Comparison of the selected bond lengths and of the crystal structure and geometry optimized structures of 2^{2+} , 2^{*+} , $1a^{2+}$, $1a^{*+}$, $1b^{2+}$ and $1b^{*+}$.

Atoms	Selected Bond length [Å]						
	B3LYP 6-311++G(d,p)						Crystal data
	2^{2+}	2^{*+}	$1a^{2+}$	$1a^{*+}$	$1b^{2+}$	$1b^{*+}$	$1b^{2+}$
C1-C2, C1'-C2'	1.397	1.428	1.398	1.428	1.399	1.429	1.401 (4)
C2-C3, C2'-C3'	1.412	1.394	1.414	1.393	1.414	1.392	1.409 (4)
C1-C5', C1'-C5	1.416	1.411	1.418	1.411	1.419	1.413	1.408 (4)
C5-C5'	1.417	1.429	1.419	1.429	1.419	1.431	1.410 (4)
C4-C5, C4'-C5'	1.409	1.415	1.411	1.415	1.411	1.415	1.407 (4)
C3-C4, C3'-C4'	1.379	1.397	1.380	1.397	1.379	1.398	1.378 (4)
C1-C6, C1'-C6'	1.488	1.459	1.491	1.459	1.492	1.460	1.482 (4)
C6-N1, C6'-N1'	1.386	1.389	1.387	1.389	1.391	1.393	1.395 (4)
C7-N1', C7'-N1	1.398	1.409	1.403	1.409	1.401	1.407	1.395 (4)
C4-C7, C4'-C7'	1.489	1.467	1.492	1.468	1.491	1.467	1.466 (4)
C6-O1, C6'-O1'	1.219	1.233	1.218	1.233	1.217	1.232	1.220 (3)
C7-O2, C7'-O2'	1.215	1.220	1.210	1.221	1.212	1.223	1.210 (3)
C2-P1, C2'-P1'	1.859	1.827	1.867	1.827	1.873	1.832	1.823 (3)
O1...P1, O1'..P1'	2.805	2.759	2.810	2.751	2.876	2.800	2.755 (2)
P1-C26, P1'-	1.823	1.830	1.825	1.834	1.813	1.824	1.800 (3)
P1-C20, P1'-	1.815	1.819	1.815	1.822	1.803	1.817	1.786 (3)
P1-C14, P1'-	1.813	1.819	1.817	1.823	1.807	1.814	1.780 (3)
F---Ct (centroid of naphthalene ring)							2.821-3.174
Selected bond angles [°]							
C2-P1-C14	111.9	110.5	108.9	110.6	108.7	110.2	108.9 (1)
C2-P1-C20	109.3	114.1	112.3	114.1	111.3	113.6	111.8 (1)
C2-P1-C26	107.2	107.0	106.9	106.9	106.9	107.2	106.9 (1)

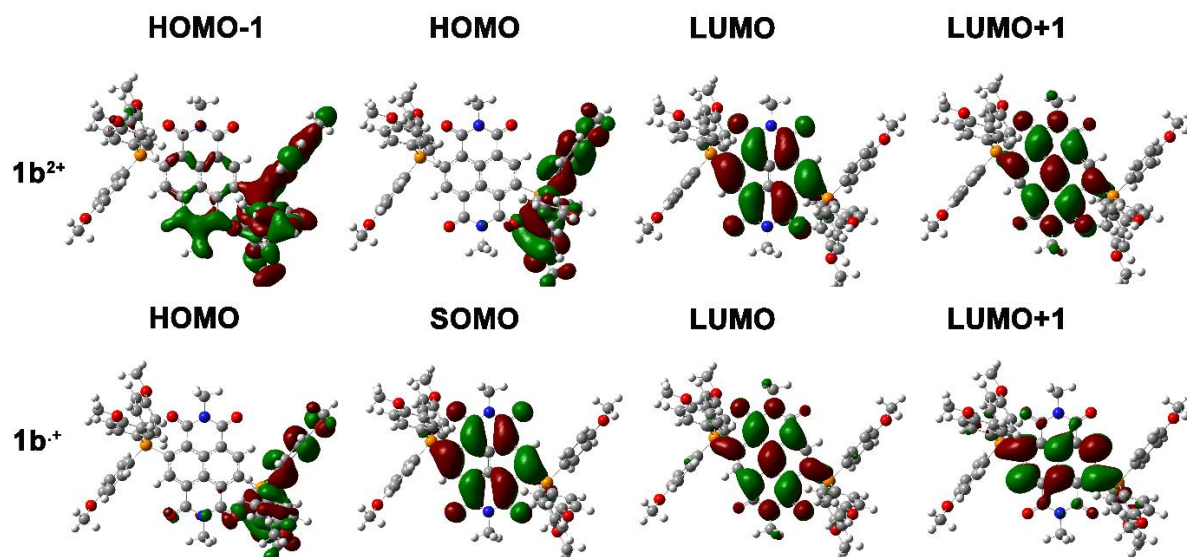


Figure S3: HOMO-1, HOMO, LUMO and LUMO+1 of $1b^{2+}$ and HOMO, SOMO, LUMO and LUMO+1 of $1b^{+}$ optimized at DFT level with B3LYP/6-311++G(d,p) basis set.

Table S3: NPA charge distributions of 2^{2+} , 2^{+} , $1a^{2+}$, $1a^{+}$, $1b^{2+}$ and $1b^{+}$ (selected atoms).

Atom	2^{2+}	2^{+}	$1a^{2+}$	$1a^{+}$	$1b^{2+}$	$1b^{+}$
C1, C1'	-0.085	-0.148	-0.023	-0.161	-0.079	-0.158
C2, C2'	-0.312	-0.401	-0.301	-0.378	-0.287	-0.374
C3, C3'	-0.164	-0.156	-0.131	-0.133	-0.133	-0.158
C4, C4'	-0.093	-0.165	-0.078	-0.164	-0.099	-0.063
C5, C5'	0.036	0.058	-0.018	0.078	0.069	-0.026
C6, C6'	0.683	0.661	0.668	0.659	0.680	0.658
C7, C7'	0.686	0.670	0.692	0.676	0.691	0.649
O1, O1'	-0.571	-0.636	-0.568	-0.636	-0.566	-0.636
O2, O2'	-0.538	-0.598	-0.542	-0.605	-0.552	-0.613
P1, P1'	1.686	1.691	1.631	1.638	1.642	1.647
N1, N1'	-0.482	-0.479	-0.486	-0.485	-0.488	-0.487
C14, C14'	-0.437	-0.416	-0.390	-0.373	-0.437	-0.413
C20, C20'	-0.402	-0.382	-0.390	-0.370	-0.441	-0.417
C26, C26'	-0.471	-0.447	-0.427	-0.403	-0.466	-0.439

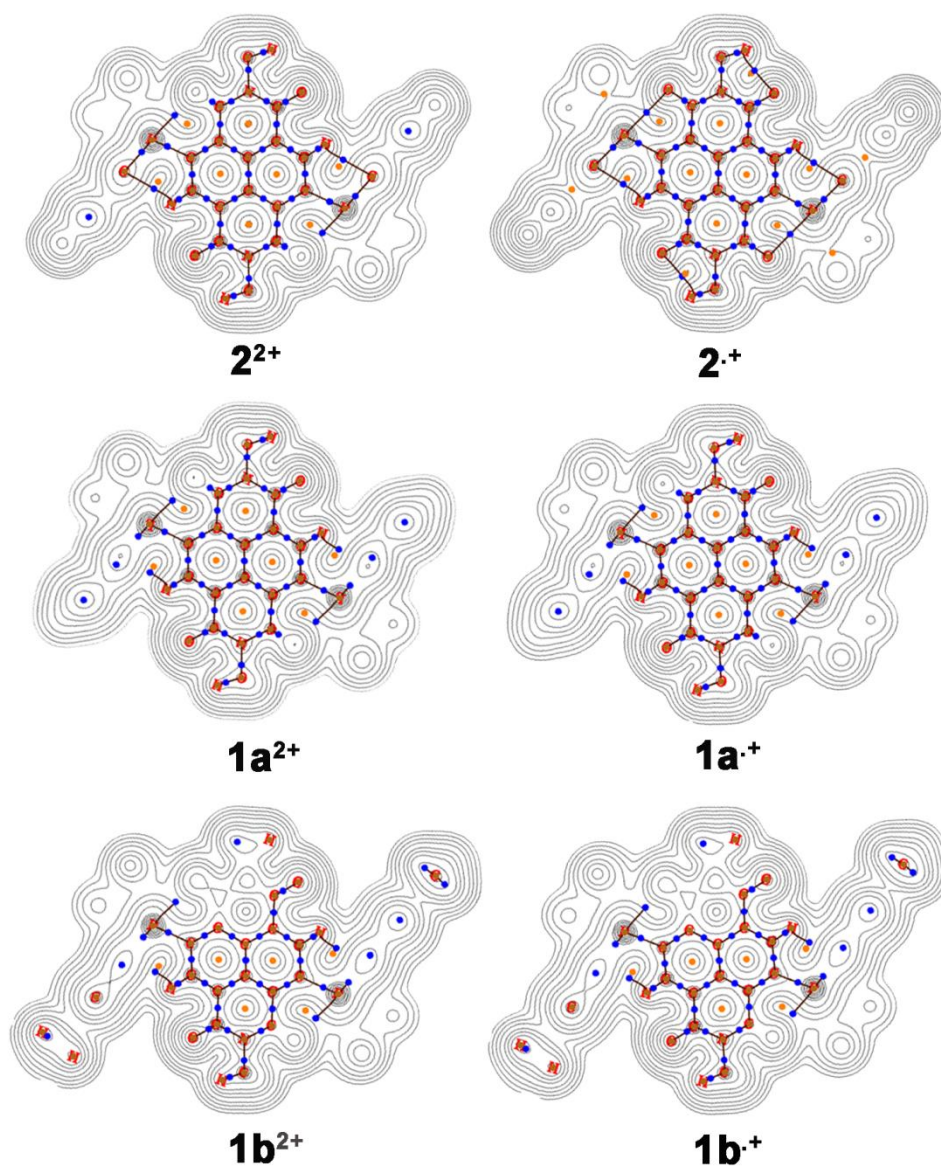


Figure S4: Contour Diagram of 2^{2+} , 2^{+} , $1a^{2+}$, $1a^{+}$, $1b^{2+}$ and $1b^{+}$ obtained by Multiwfn 3.3.7 (dev) package using optimized structure at DFT level.

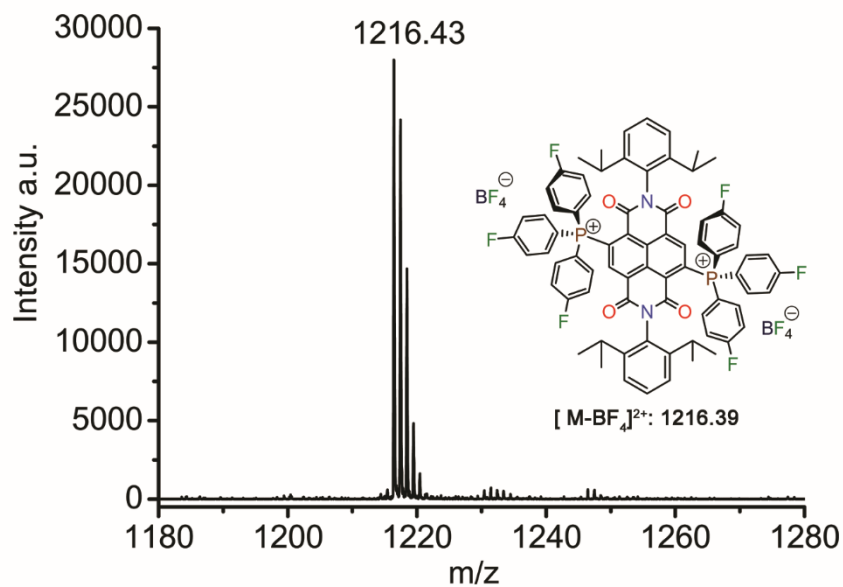


Figure S5: MALDI-TOF mass spectrometry of 2^{2+} .

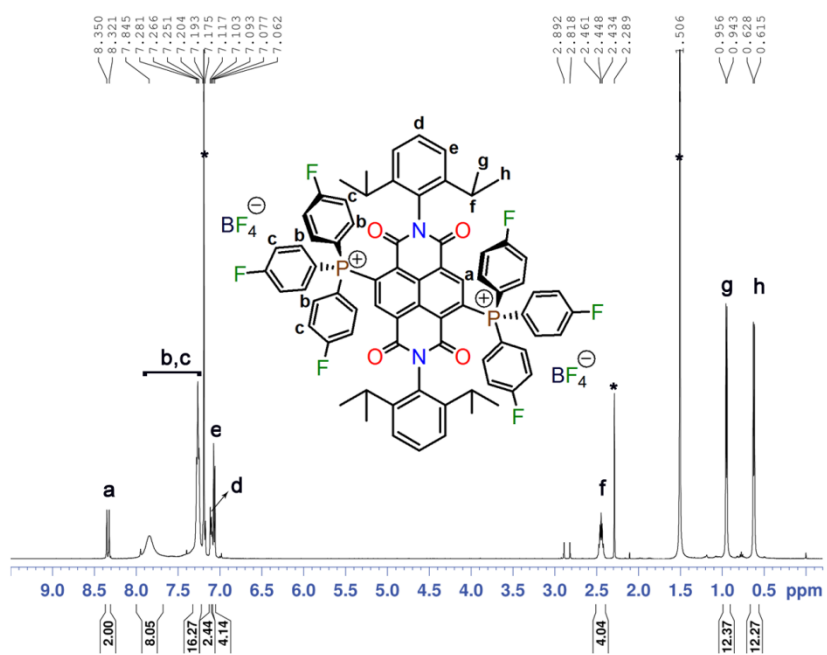


Figure S6: 500 MHz 1H NMR spectrum of 2^{2+} in $CDCl_3$ at room temperature.

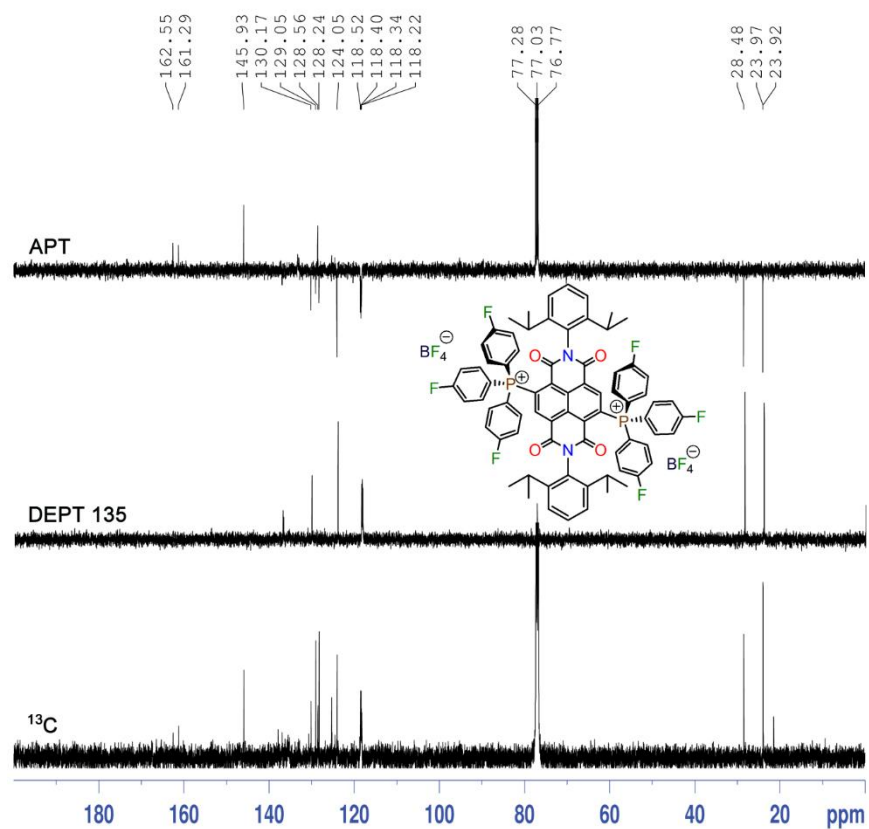


Figure S7: 125 MHz ^{13}C , APT and DEPT-135 spectra of 2^{2+} in CDCl_3 at room temperature.

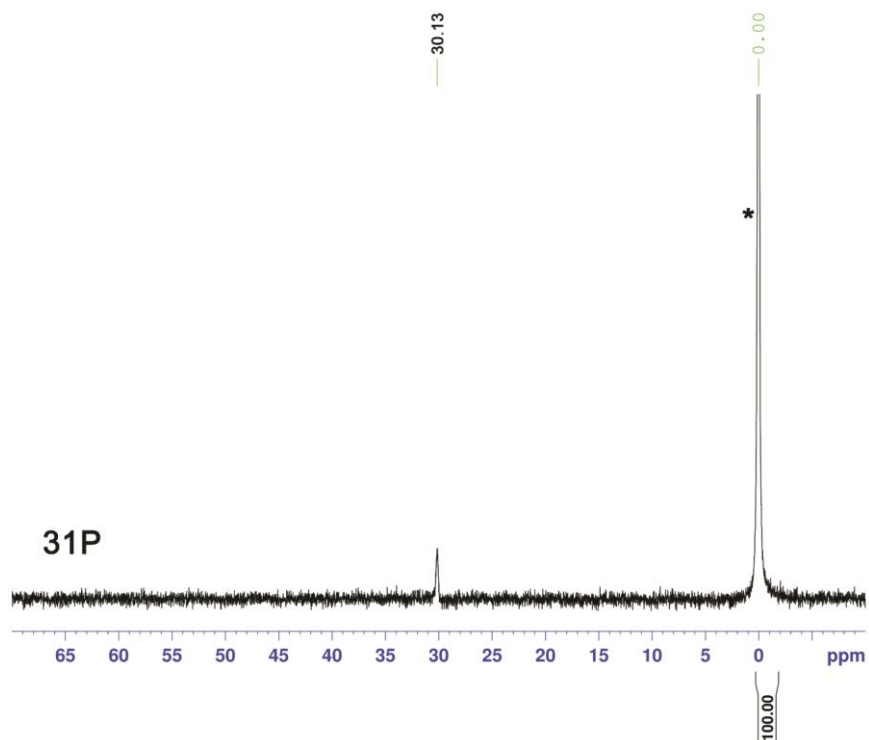


Figure S8: 202 MHz ^{31}P NMR spectrum of 2^{2+} in CDCl_3 at room temperature.

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