

A Nitrogen Doped Asymmetric Phenalenyl with Zwitterionic Ground State

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1. Methods and Materials

All reagents were purchased from Sigma-Aldrich, Alfa, Acros and Adamas and used as received. Flash column chromatography was performed with Haiyang silica gel (200-300 mesh). Solvent toluene was freshly distilled from CaH₂ under N₂. Anhydrous Na₂SO₄ was used for drying organic extracts, and all volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by TLC using commercial Huanghai glass plates (HSGF 254, 2.5 x 8 cm). The plates were visualized under UV radiation at 254 and 365 nm. UV absorption spectra were recorded on a Shimadzu UV-2600 UV-VIS spectrophotometer in spectroscopy grade dichloromethane (DCM). ¹H and ¹³C NMR spectra were recorded on a Varian Unity Inova 800 MHz spectrometer. Cyclic voltammograms were measured on a Shanghai Chenhua CHI 660E electrochemical workstation in dry DCM with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte at a scan rate of 100 mV/s at room temperature under the protection of nitrogen. A gold disk was used as working electrode, platinum wire was used as counter electrode, and Ag/AgCl (3 M KCl solution) was used as reference electrode. The potential was externally calibrated after each experiment, against the ferrocene/ferrocenium couple. Thermogravimetric analysis (TGA) measurements were performed on NETZSCH TG 209F1 Iris thermal gravimetric analyzer.

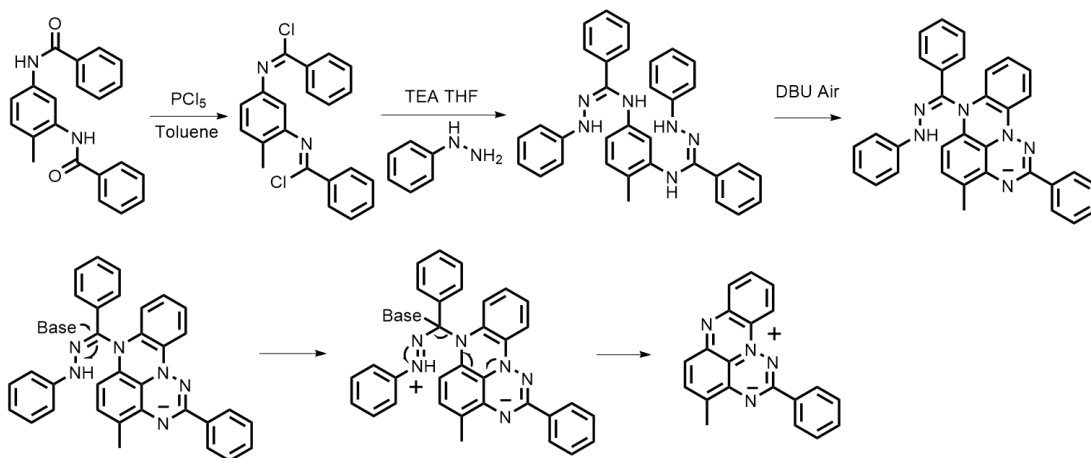
All calculations were performed with the Gaussian 16 program suite¹ using the density functional theory (DFT) with M06-2X exchange-correlational functionals² and employing the 6-311G(d,p) basis set³⁻⁵ for all atoms. Full geometry optimizations were carried out at the M06-2X/6-311G(d,p) level, and the obtained stationary points were characterized by frequency calculations. The ground state absorption was calculated by time-dependent (TD) DFT with M06-2X/6-311G(d,p) level. The NICS(1)zz value were calculated by standard gauge independent atomic orbital (GIAO) method⁶ based on the optimized geometries. The frontier molecular orbital profiles were illustrated using Multiwfn⁷ and VMD⁸. The ACID plots was calculated by using the method developed by Herges⁹.

2. Detailed synthetic procedures

BTAP: N,N'-(4-methyl-1,3-phenylene)dibenzamide (1.50 g, 4.5 mmol) and PCl₅ (1.97 g, 9.5 mmol) were added to a 100 mL two-neck round bottom flask with 30 ml toluene and refluxed for 2 h. POCl₃ was removed by vacuum distillation. Yellow oil was obtained and dissolved into 50 ml of THF following by addition of NEt₃ (1 mL). The solution was cooled to 0 °C, following by slow addition of phenylhydrazine (1 mL), followed by precipitation of triethylammonium chloride salt. The mixture was stirred at room temperature for 24 h. The salt was removed by suction filtration. Then, a yellow oil was obtained by removing THF and was stirred in 250 ml of methanol and treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.1 mL). Air was bubbled through the reaction mixture for 48 h. The work up was to filter off the greenish solid and recrystallized from methanol/DCM mixture. The overall yield was 11 %. Mp: 220-221 °C. ¹H NMR (800 MHz, CDCl₃): 8.44 (ddd, *J* = 9.0, 1.3, 0.6 Hz, 1H), 8.36 – 8.31 (m, 2H), 7.68 (ddd, *J* = 8.7, 1.2, 0.6 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.56 – 7.51 (m, 1H), 7.53 – 7.47 (m, 2H), 7.39 (ddd, *J* = 9.0, 6.6, 1.3 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 1H), 2.43 (s, 3H). ¹³C NMR (201 MHz, CDCl₃): 162.33 , 147.40 , 145.17, 142.23, 136.30, 135.54 , 131.72, 131.01, 129.38, 128.22, 127.64, 127.43, 125.30, 124.86, 120.40, 118.12, 116.19, 16.16. High resolution MS: (M)⁺: 310.1225 (calcd: 310.1218). UV-Vis-NIR (DCM) λ_{max} nm (ε): 247 (23485), 314 (33573), 344 (18780), 390 (3340), 462 (1719), 493 (1115), 665 (2796), 741 (2432) and 817 (1360).

Br-BTAP: **BTAP** (31 mg, 0.1 mmol) were dissolved in 5 mL DMF in a two-neck round bottom flask under Nitrogen, then N-bromosuccinimide (17.8 mg, 0.1 mmol) was added slowly in three times at 0 degree. After 2 h, water was added to quench the reaction and extracted with DCM. The organic phases were dried and concentrated under reduced pressure. The organic solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (DCM) and give compound **Br-BTAP** as a greenish solid (35 mg, 90% yield). ¹H NMR (800 MHz, CDCl₃): 8.53 (d, *J* = 9.06 Hz, 1H), 8.37 (d, *J* = 8.37 Hz, 2H), 8.01 (s, 1H), 7.96 (d, *J* = 8.67 Hz, 1H), 7.72 (t, *J* = 7.75 Hz, 1H), 7.57-7.52 (m, 4H), 2.48 (s, 3H). The ¹³C NMR was not able to be obtained due to low solubility. HR-MS: (M)⁺: 389.0402 (calcd: 389.0397).

3. Proposed Reaction Mechanism



Scheme S1. Proposed reaction mechanism.

4. Figures and Tables

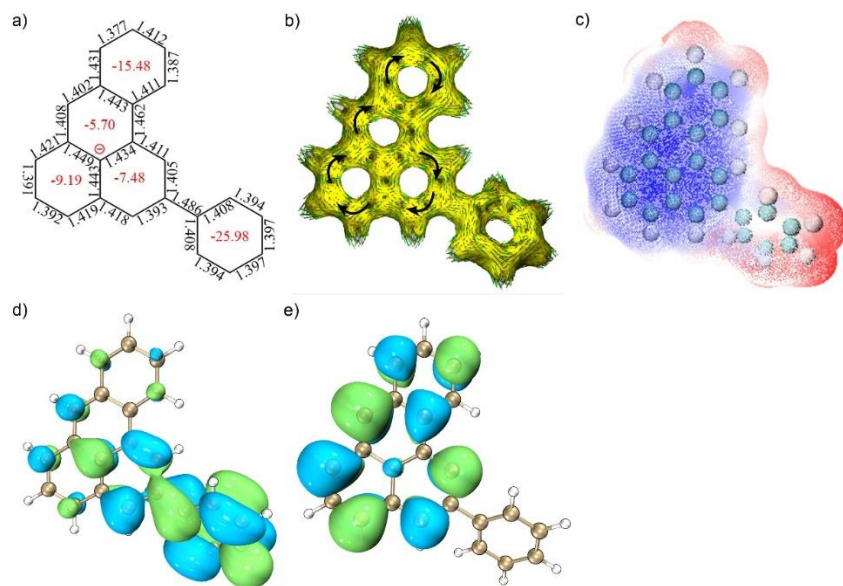


Figure S1 Calculated NICS (1) zz value (a), ACID plot (b), calculated electrostatic potential surface (c), LUMO orbital (d) and HOMO orbital (e) of benzene fused phenalenyl anion.

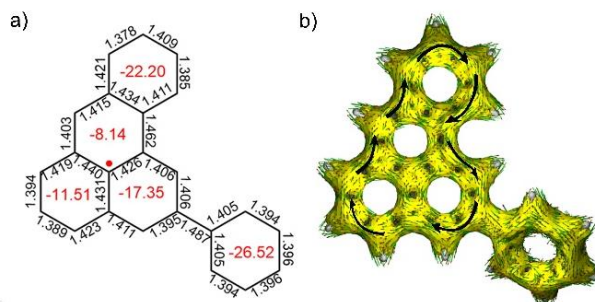


Figure S2 a) Calculated NICS (1) zz value of benzene fused phenalenyl; b) ACID plot of benzene fused phenalenyl.

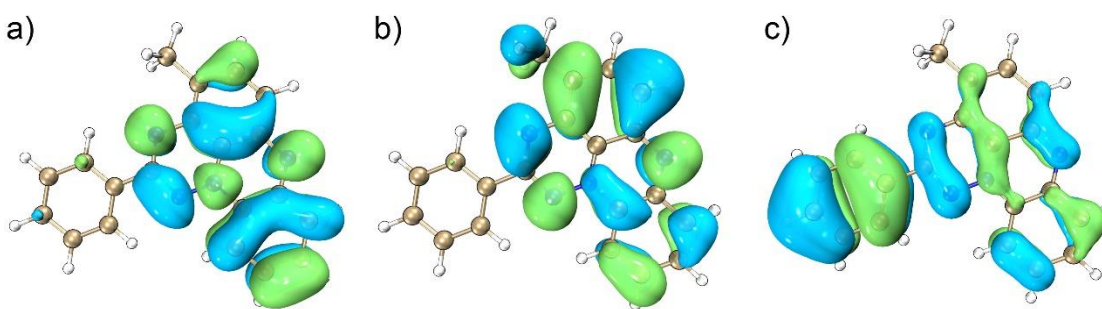


Figure S3 a) Calculated LUMO (a), HOMO (b) and HOMO-1 (c) orbitals of TABP.

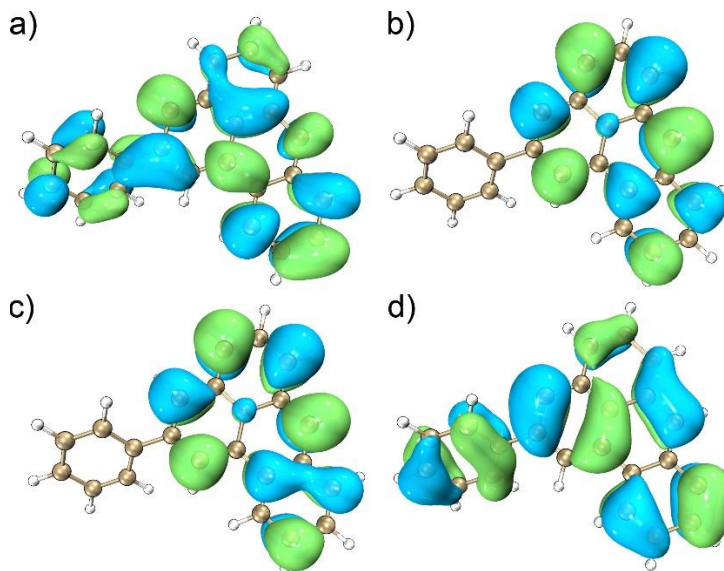


Figure S4 a) Calculated α -LUMO (a), β -LUMO (b), α -SOMO (c) and β -SOMO (d) orbitals of benzene fused phenalenyl.

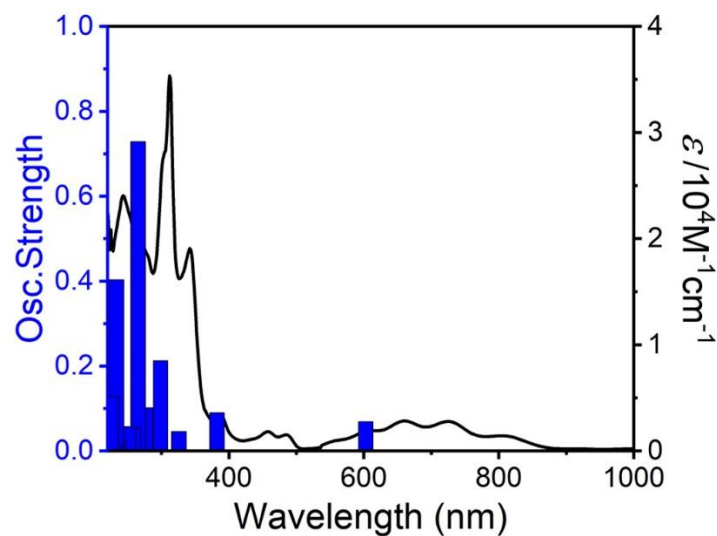


Figure S5. TD-DFT simulated spectrum of **BTAP** along with experimental spectrum.

Table S1 Selected TD-DFT calculated energies, oscillator strength and compositions of major electronic transitions of **BTAP**.

Wavelength (nm)	Energy (eV)	Osc.Strength (<i>f</i>)	Major Contribution
602.8196	2.057	0.0691	HOMO→LUMO (94.48%) HOMO→LUMO+1 (3.84%)
382.2441	3.244	0.0899	HOMO→LUMO+1 (75.64%) HOMO→LUMO+2 (12.01%) HOMO→LUMO (4.32%)
325.7158	3.807	0.0462	HOMO→LUMO+2 (50.17%) HOMO-3→LUMO (30.46%) HOMO→LUMO+1 (10.64%) HOMO-4→LUMO (4.48%)
298.4356	4.155	0.2126	HOMO-1→LUMO (77.46%) HOMO-4→LUMO (7.30%) HOMO-3→LUMO (5.73%)
296.7217	4.179	0.0019	HOMO-6→LUMO (90.80%)
275.8621	4.495	0.1019	HOMO-4→LUMO (47.59%) HOMO-3→LUMO (27.58%) HOMO-1→LUMO (11.81%) HOMO-2→LUMO (4.13%)

265.3542	4.673	0.7288	HOMO-3→LUMO (30.27%) HOMO-4→LUMO (28.65%) HOMO→LUMO+2 (28.24%)
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5. Methods to grow single crystals of BTAP

Three major methods have been used to grow single crystals for x-ray diffraction. Method a: slow evaporation of **BTAP** in pure or mixed solutions (DCM, toluene, THF, DCM/toluene, DCM/hexane, DCM/MeOH, DCM/EtOH, DCM/EA, DCM/acetone, DCM/acetonitrile) in 4 mL glass vials (with cap). Method b: slow diffusion of poor solvents e.g. hexane, toluene, MeOH, EtOH and acetonitrile to saturated DCM solution of **BTAP** in NMR tubes (with cap) and 4 mL glass vials (with cap) at room temperature and -20 °C (in refrigerator). Method c: slow cooling the hot solutions of **BTAP** in pure or mixed solvents (e.g. toluene, THF, EA, acetone, DCM/toluene, DCM/hexane, DCM/MeOH, DCM/EtOH, DCM/EA, DCM/acetone, DCM/acetonitrile).

6. NMR spectra analyst

The carbon peak at 162.45 ppm was assigned to carbon n, therefore based on the HMBC spectrum the proton at 8.32 ppm should be assigned to proton h. Then, based on the HSQC spectrum, the carbon p' can be assigned. And according to the COSEY spectrum, the proton i and j can be assigned. Then, the carbon q' and r' can be assigned on the basis of the HSQC spectrum, the carbon o' can be assigned on the basis of the HMBC spectrum.

And the doublet of doublets proton signal at 8.43 ppm was assigned to proton g, therefore in the light of the HSQC spectrum the proton l can be assigned. Then, based on the HMBC spectrum, the proton f can be assigned. Next, the carbon k' can be assigned according to the HSQC spectrum. And the proton e and d can be assigned based on the COSEY spectrum. Afterwards, the carbon i', j', h' and m can be assigned on the basis of the HSQC spectrum.

According to the NOSEY spectrum, the methyl position was confirmed. And the carbon b was also assigned based on the NOSEY spectrum. Next, according to the COSEY and HMBC spectrum, the carbon c', d' and proton b, c can be assigned. Finally, in the light of the HMBC and ^{13}C APT spectrum, carbon g', e' and f' can be identified.

Finally, the NOSEY spectrum reveals NOEs between protons a and b are visible, which means these protons are spatially close. The structure of **BTAP** was confirmed.

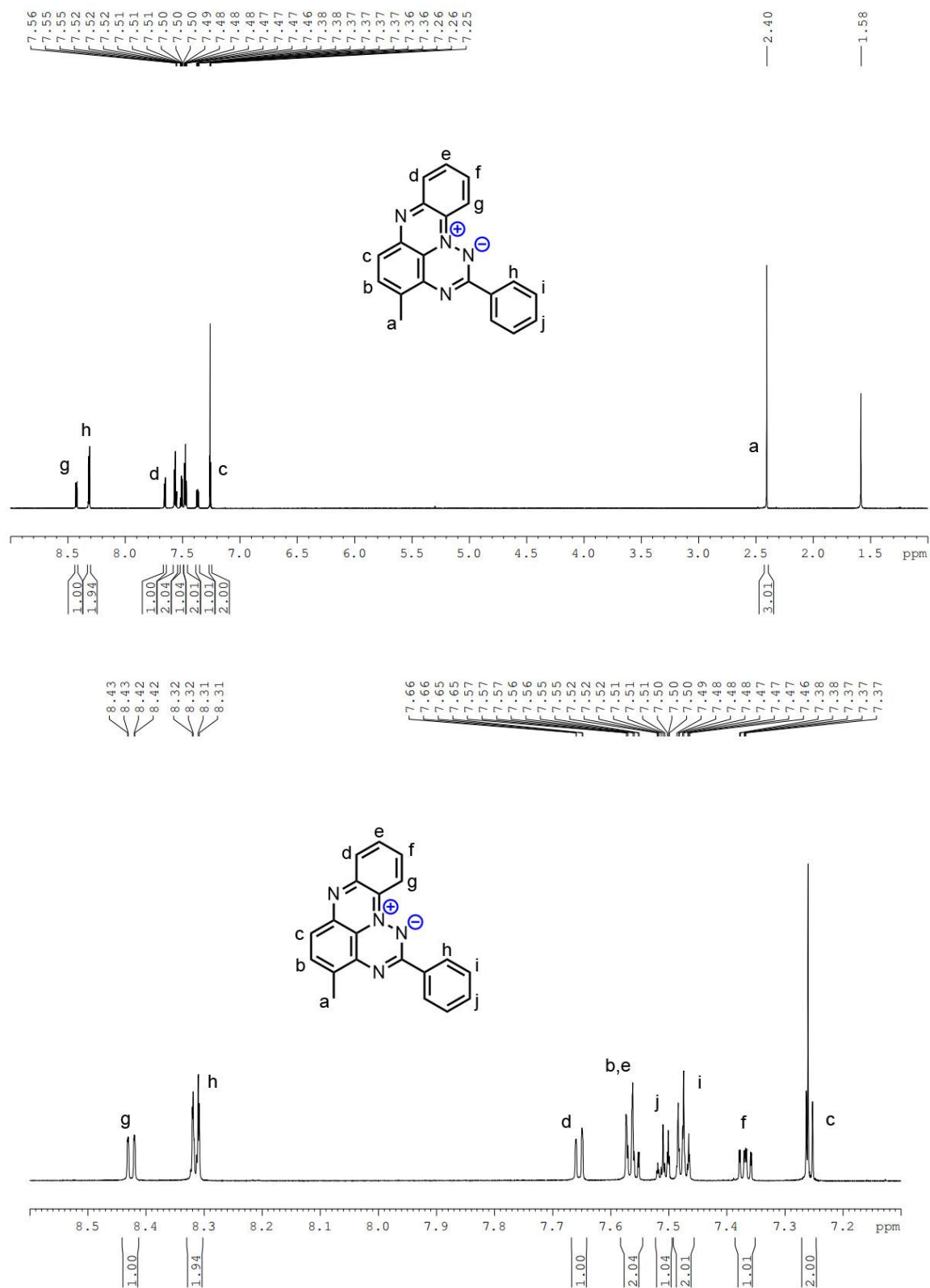


Figure S6. ^1H NMR spectrum of BTAP (800 MHz, CDCl_3).

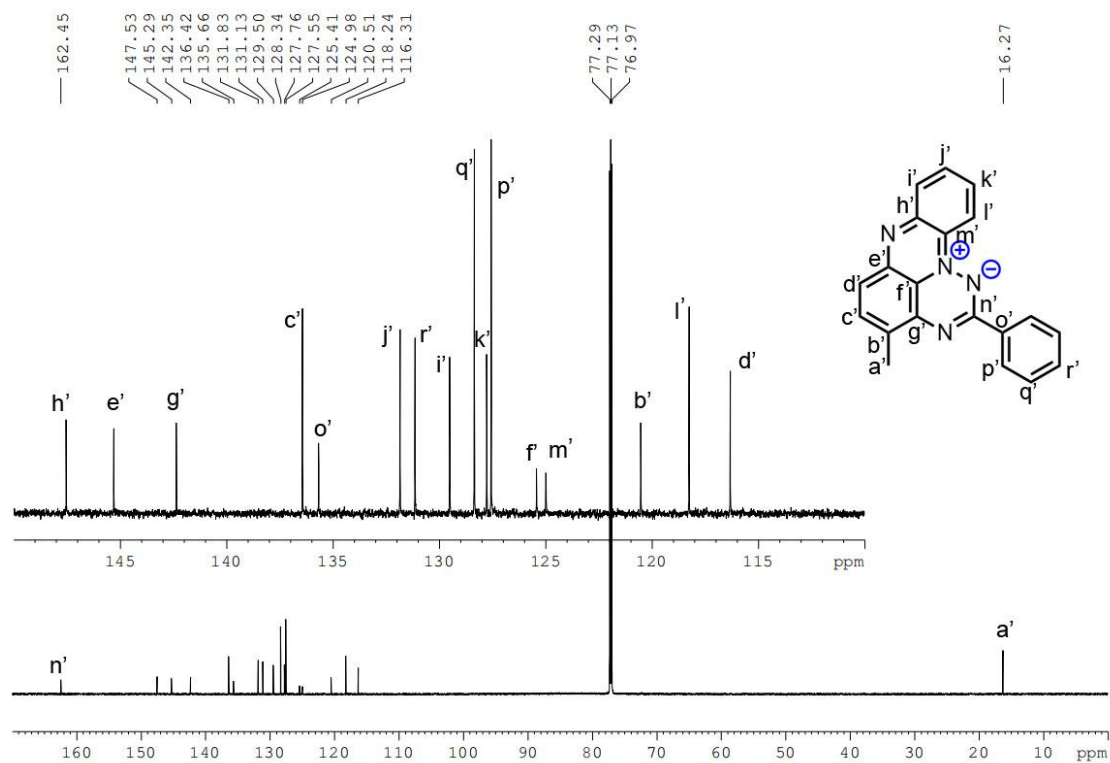


Figure S7. ^{13}C NMR spectrum of **BTAP** (200 MHz, CDCl_3).

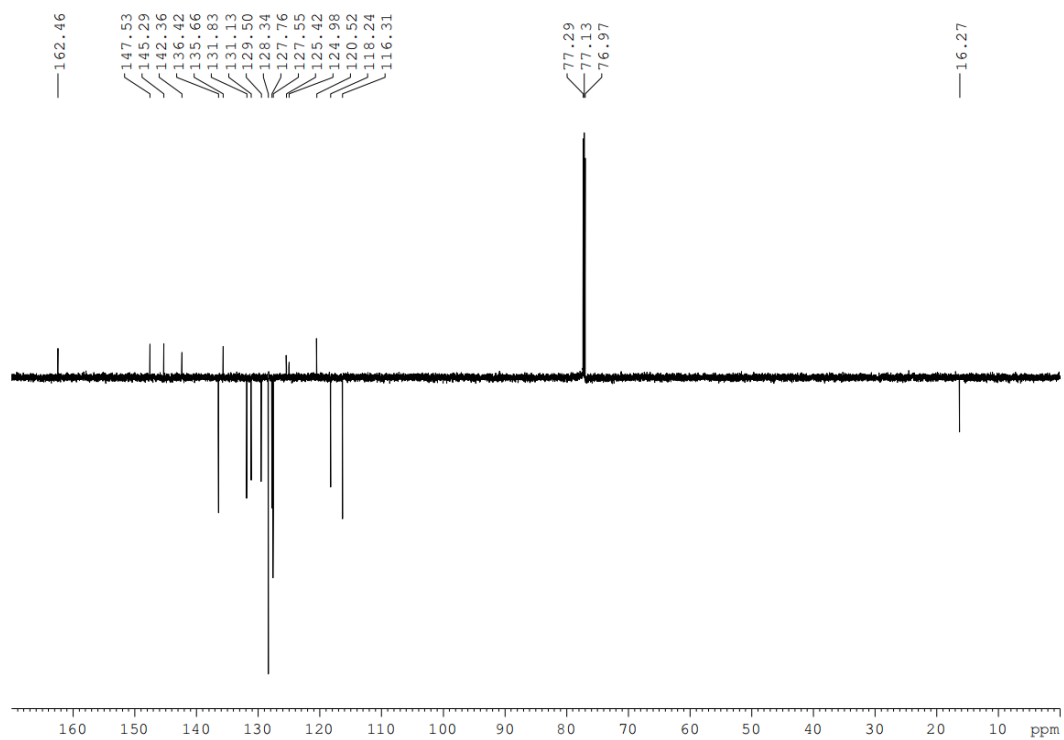


Figure S8. ^{13}C APT NMR spectrum of **BTAP** (200 MHz, CDCl_3).

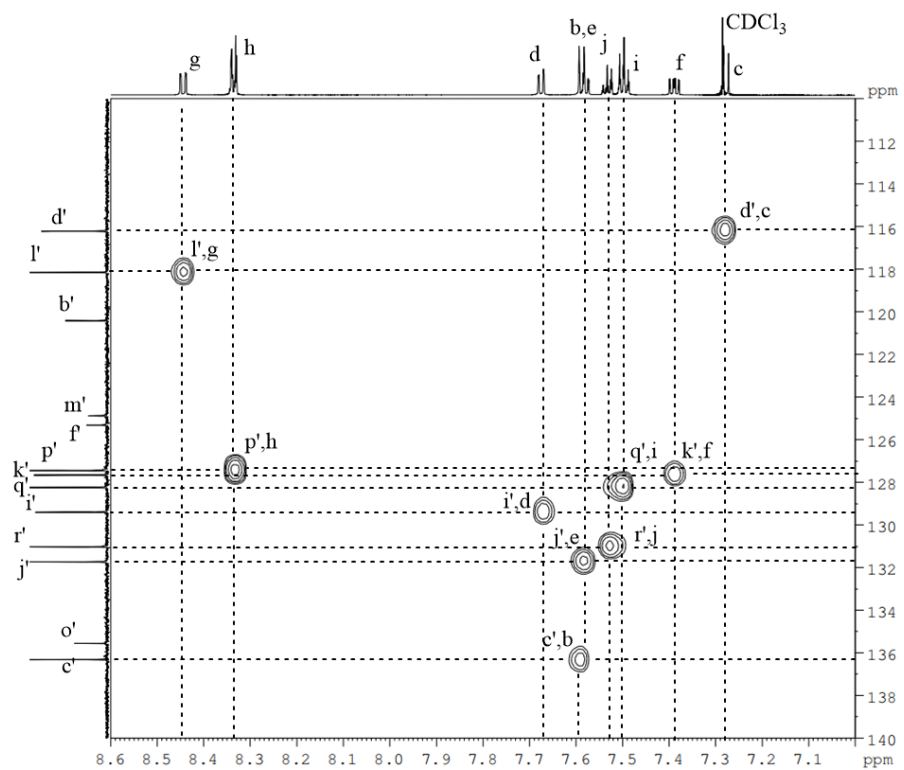
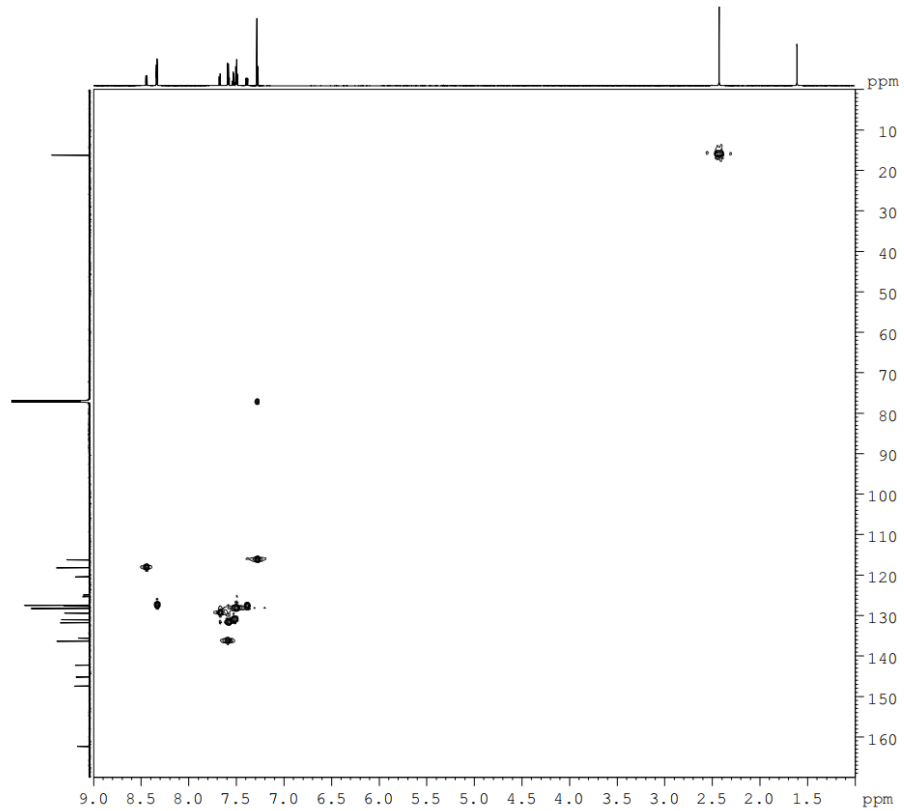


Figure S9. HSQC NMR spectrum of **BTAP**.

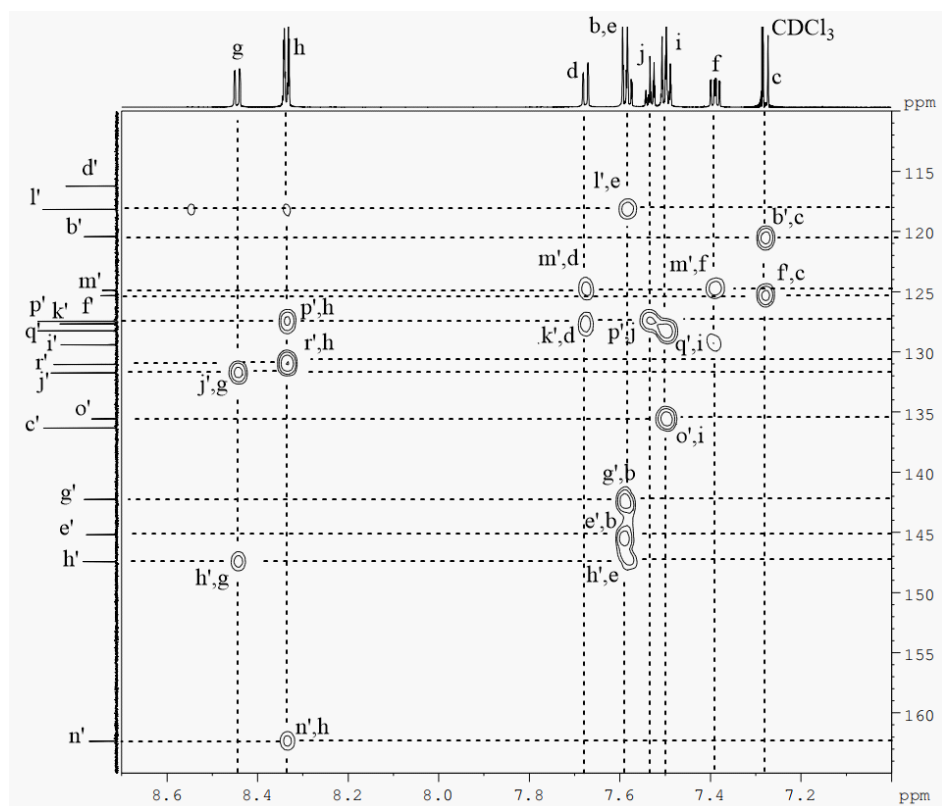
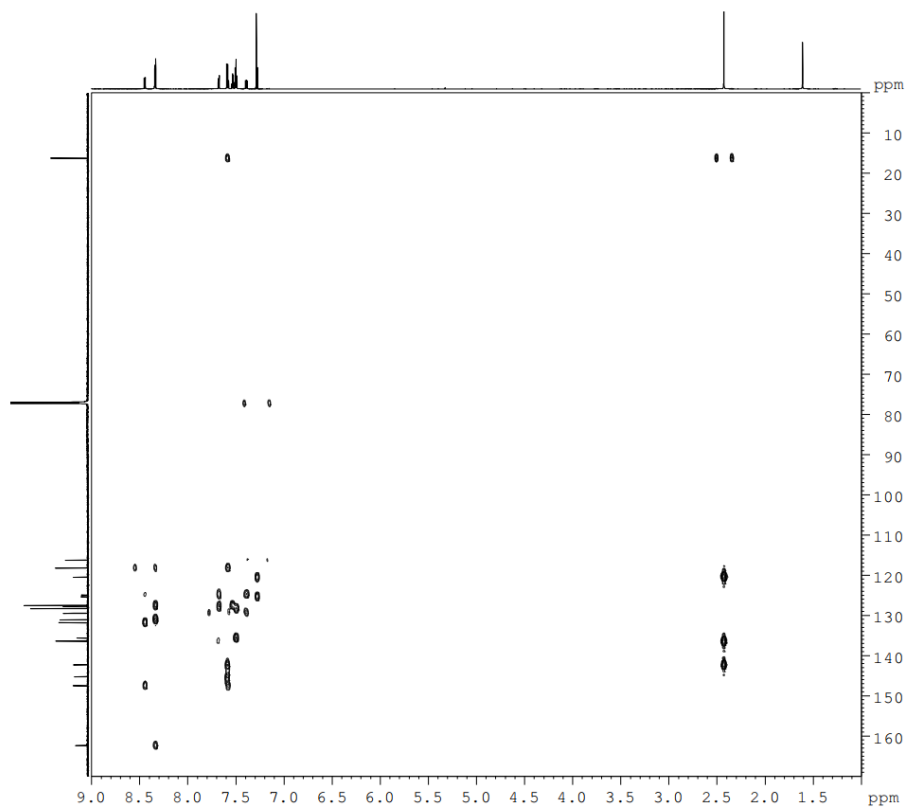


Figure S10. HMBC NMR spectrum of **BTAP**.

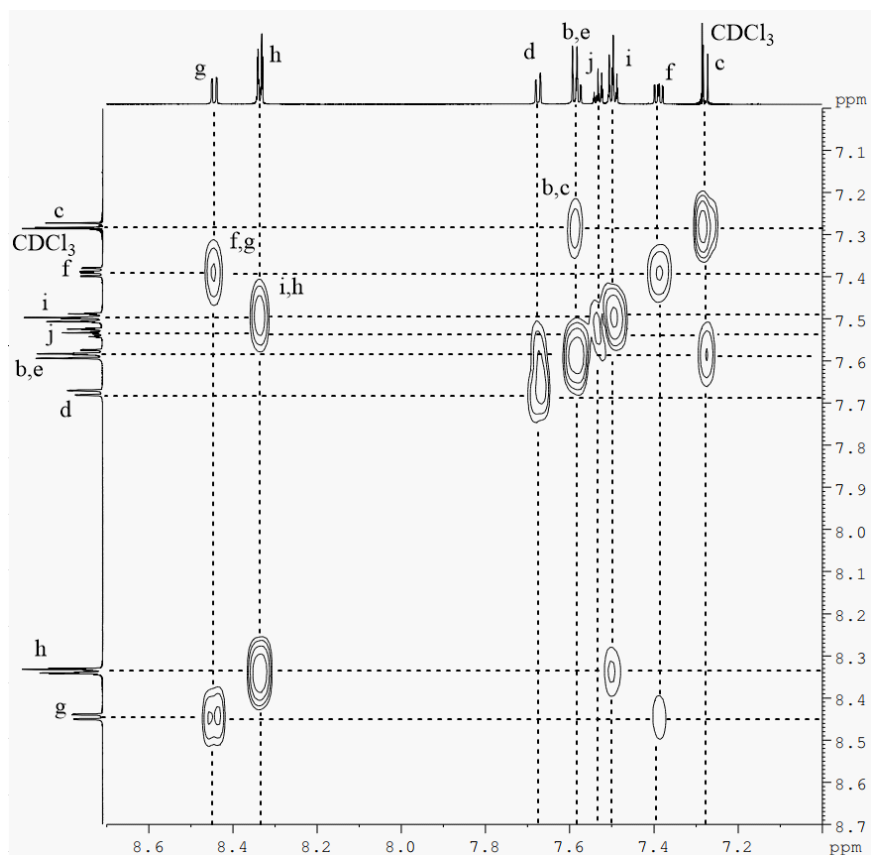
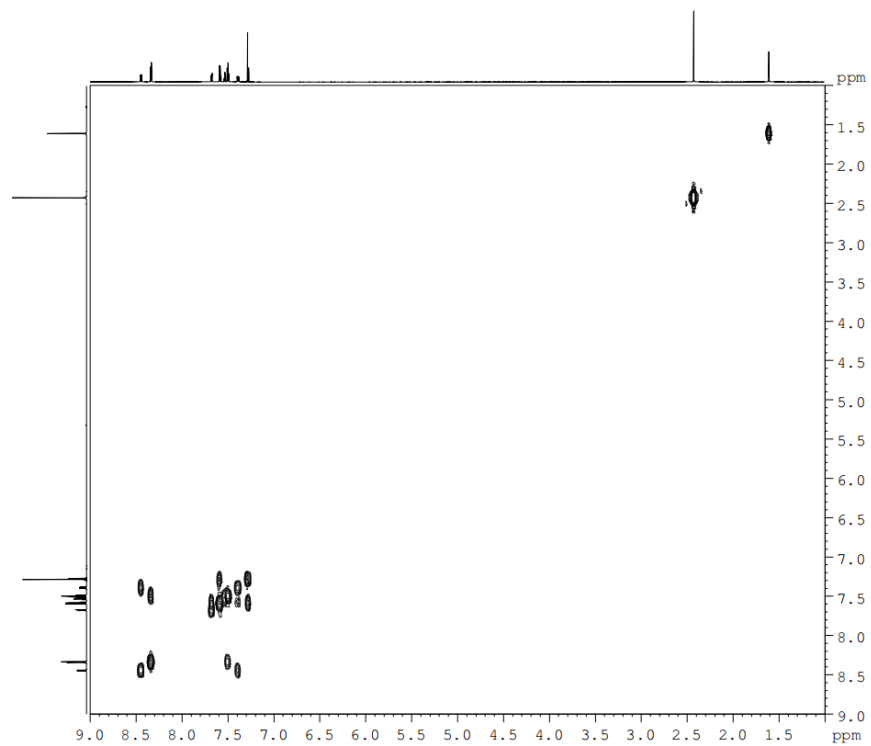


Figure S11. COSEY NMR spectrum of **BTAP**.

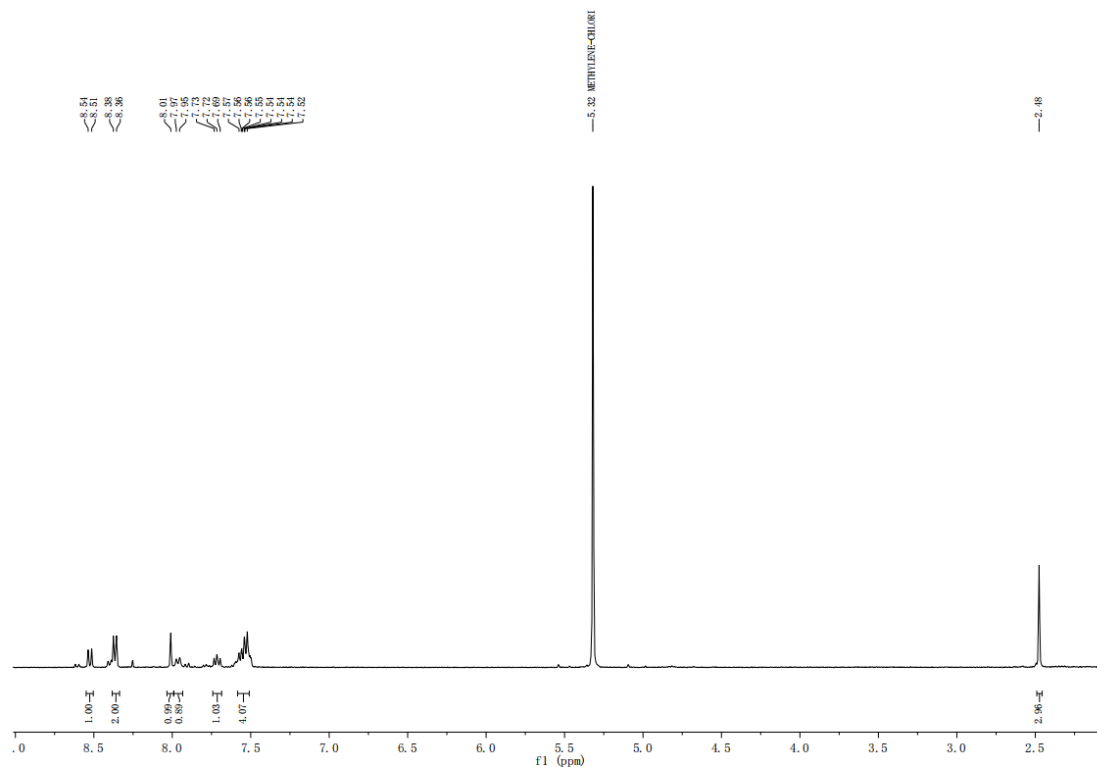


Figure S12. ^1H NMR spectrum of **Br-BTAP**.

7. Single Crystal Data (Deposition Number: 2072332)

Table S2. Crystal data and structure refinement for **Br-BTAP**.

Identification code	Br-BTAP	
Empirical formula	$\text{C}_{20}\text{H}_{13}\text{BrN}_4$	
Formula weight	389.25	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 11.4145(5)$ Å	$a = 90^\circ$.
	$b = 17.9367(8)$ Å	$b = 108.893(2)^\circ$.
	$c = 8.0609(3)$ Å	$g = 90^\circ$.
Volume	$1561.46(11)$ Å ³	
Z	4	
Density (calculated)	1.656 Mg/m ³	

Absorption coefficient	3.663 mm ⁻¹
F(000)	784
Crystal size	0.200 x 0.100 x 0.020 mm ³
Theta range for data collection	4.093 to 68.274°.
Index ranges	-13 ≤ h ≤ 13, -21 ≤ k ≤ 21, -9 ≤ l ≤ 9
Reflections collected	11658
Independent reflections	2837 [R(int) = 0.0341]
Completeness to theta = 67.679°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7531 and 0.4984
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2837 / 0 / 227
Goodness-of-fit on F ²	1.038
Final R indices [I > 2σ(I)]	R1 = 0.0273, wR2 = 0.0771
R indices (all data)	R1 = 0.0283, wR2 = 0.0780
Extinction coefficient	n/a
Largest diff. peak and hole	0.375 and -0.476 e.Å ⁻³

8. Electrochemical data

Table S3. Photophysical and electrochemical data of **BTAP**.

λ_{abs} (nm)	ϵ_{max} (M ⁻¹ cm ⁻¹)	$E_{1/2}^{\text{ox}}$ (V)	$E_{1/2}^{\text{red}}$ (V)	HOMO (eV)	LUMO (eV)	E_{g}^{EC} (eV)	$E_{\text{g}}^{\text{opt}}$ (eV)
312	35346	0.25	-1.42	-4.98	-3.29	1.69	1.38

Definitions: λ_{abs} , absorption maxima measured in DCM; ϵ_{max} is molar extinction coefficient measured at absorption maximum; $E_{1/2}^{\text{ox}}$ and $E_{1/2}^{\text{red}}$ are the half-wave potentials for

respective oxidation and reduction waves with Fc/Fc^+ as reference; HOMO and LUMO energy levels were calculated according to the equations $\text{HOMO} = -(4.8 + E_{\text{ox}}^{\text{onset}})$ and $\text{LUMO} = -(4.8 + E_{\text{red}}^{\text{onset}})$, where $E_{\text{ox}}^{\text{onset}}$ and $E_{\text{red}}^{\text{onset}}$ are the onset potentials of the first oxidative and reductive redox wave, respectively; E_{g}^{EC} is the electrochemical energy gap derived from LUMO–HOMO, and $E_{\text{g}}^{\text{opt}}$ is the optical energy gap derived from the lowest energy absorption onset in the absorption spectrum.

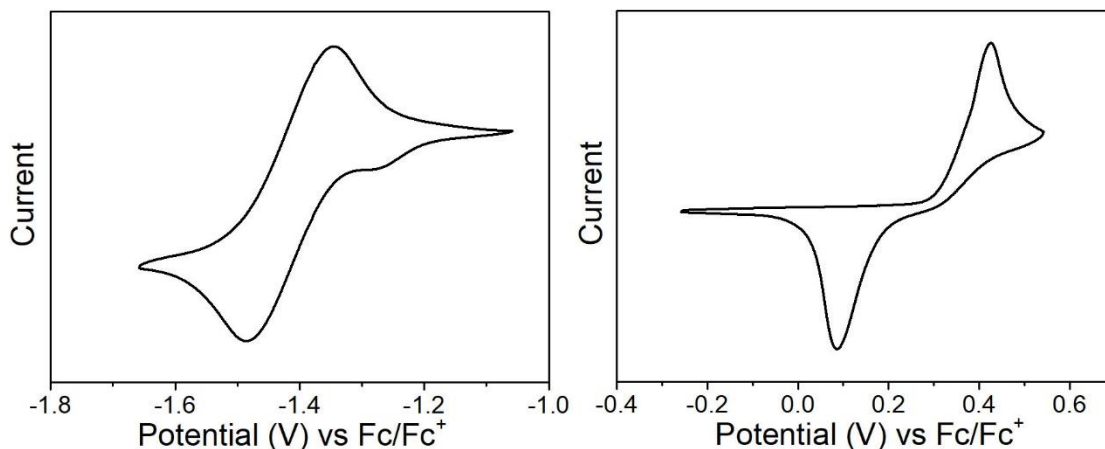


Figure S13. Cyclic voltammogram of **BTAP** in DCM.

9. References

1. R. A. Gaussian 16, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman,

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- and D. J. Fox, Gaussian, Inc. Wallingford CT. 2016.
2. Y. Zhao and D. G. Truhlar, *Theoretical Chemistry Accounts*, 2008, **119**, 525-525.
 3. W. J. Hehre, R. Ditchfield and J. A. Pople, *Journal of Chemical Physics*, 1972, **56**, 2257-2261..
 4. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees and J. A. Pople, *Journal of Chemical Physics*, 1982, **77**, 3654-3665.
 5. M. J. Frisch, J. A. Pople and J. S. Binkley, *Journal of Chemical Physics*, 1984, **80**, 3265-3269.
 6. F. B. S. Hossein, C. S. Wannere, C. Clémence, P. Ralph and P. V. R. Schleyer, *Organic Letters*, 2006, **8**, 863-866.
 7. T. Lu and F. Chen, *J Comput Chem*, 2012, **33**, 580-592.
 8. W. Humphrey, A. Dalke and K. Schulten, *J Mol Graph*, 1996, **14**, 33-38.
 9. D. Geuenich, K. Hess, F. Kohler and R. Herges, *Chemical Reviews*, 2005, **105**, 3758-3772.

10. Coordinates for calculated geometries (Å)

BTAP

C	4.22832400	-1.73878300	-0.00020300
C	3.16570300	-0.78300300	-0.00012100
C	1.83618800	-1.29513300	0.00006700
C	1.57866200	-2.68500700	0.00018000
C	2.63048900	-3.55563100	0.00009900
C	3.96909700	-3.07519000	-0.00009600
N	3.46899300	0.51587400	-0.00023200
C	2.44487000	1.38071400	-0.00014200
C	1.08074800	0.94484200	0.00005600
N	0.79679000	-0.38337200	0.00014500
C	2.65495500	2.77715000	-0.00026600
C	1.58408200	3.64073100	-0.00019500
C	0.24127900	3.21839100	-0.00000600
C	-0.01889700	1.85379100	0.00012900
N	-1.29956300	1.36470600	0.00035000
C	-1.43307700	0.06181400	0.00060300
N	-0.44933700	-0.86299200	0.00037400
C	-2.81035000	-0.50274900	0.00021600
C	-3.02494200	-1.88192500	-0.00003400
C	-4.31906600	-2.38615700	-0.00034100
C	-5.40684900	-1.51956700	-0.00042100
C	-5.19617500	-0.14392900	-0.00019000

C	-3.90463000	0.36399500	0.00011600
H	5.23486700	-1.34082200	-0.00035100
H	0.55315500	-3.02256600	0.00032800
H	2.44445000	-4.62205100	0.00018300
H	4.78748000	-3.78485000	-0.00016100
H	3.67793000	3.12774200	-0.00042500
H	1.77769700	4.70860500	-0.00029900
H	-2.17462300	-2.55058200	0.00003900
H	-4.47870500	-3.45767100	-0.00051900
H	-6.41579000	-1.91476000	-0.00066400
H	-6.04093700	0.53431300	-0.00024800
H	-3.72161700	1.43057300	0.00030700
C	-0.90624500	4.18638100	0.00006500
H	-1.54136800	4.03654300	-0.87640100
H	-1.54113700	4.03668800	0.87672400
H	-0.54457100	5.21490800	-0.00006600

Benzene Fused Phenalenyl

C	1.87501400	-2.32581400	-0.00013100
C	3.18375300	-1.85329400	-0.00030100
C	3.46688100	-0.49182900	-0.00028100
C	2.40943000	0.45599800	-0.00010900
C	1.04089600	-0.00573700	-0.00000400
C	0.77195800	-1.43063200	0.00005700
C	-0.04008000	0.93886900	0.00014400
C	-1.41640100	0.44431300	-0.00002600
C	-1.64602300	-0.98145800	0.00026800
C	-0.56549900	-1.87419600	0.00036500
C	-2.53744300	1.30005900	-0.00055900
C	-3.84267900	0.82687800	-0.00054400
C	-4.06795600	-0.56684400	0.00001300
C	-3.00187600	-1.43910900	0.00038700
C	2.65369200	1.85474100	-0.00001300
C	1.59977900	2.75299000	0.00033400
C	0.27354000	2.31630300	0.00045300
H	1.67553200	-3.39631100	-0.00014200
H	4.00686300	-2.56975200	-0.00043900
H	4.49506200	-0.13413300	-0.00035100
H	-0.76487500	-2.94541200	0.00057200
H	-2.38266200	2.37580600	-0.00112200
H	-4.67915000	1.52274700	-0.00100500
H	-5.08684300	-0.95399700	0.00009000
H	-3.17545700	-2.51495500	0.00072900
H	3.68421700	2.20739000	-0.00013200
H	1.80494800	3.82410800	0.00054800
H	-0.51954100	3.05708700	0.00092900

Benzene Fused Phenalenyl anion

C	3.49932737	0.66269631	-0.00261831
C	3.24704528	-0.71549579	-0.05120890
C	4.30948509	-1.67277874	-0.09853838
C	2.45941719	1.61099748	0.04615133
C	1.08666412	1.14789968	0.03819260
C	0.78877978	-0.25405071	-0.01003954
C	1.89182413	-1.21239779	-0.05192209
C	2.69763242	3.01098319	0.10164557
C	1.64365888	3.91691022	0.14608065
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C	0.01229767	2.11088215	0.07769050
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C	2.74340702	-3.51333523	-0.13382401
C	4.06968225	-3.02801637	-0.13953291
C	-1.32508259	1.63934197	0.06437394
C	-1.61437040	0.27737494	0.01604447
C	-0.56388918	-0.65500368	-0.02001788
C	-3.02450669	-0.19018520	0.00549029
C	-3.41037148	-1.36954050	0.66994954
C	-4.73370821	-1.80891782	0.66071180
C	-5.71678559	-1.07861520	-0.01077951
C	-5.35412142	0.09565742	-0.67451726
C	-4.02911848	0.52964599	-0.66821967
H	4.53131357	1.01167570	-0.00204840
H	5.33240896	-1.29758055	-0.10030559
H	3.72787331	3.36286877	0.11111620
H	1.86296840	4.98464843	0.18936360
H	-0.49853640	4.21438640	0.16898548
H	0.67912487	-3.00050369	-0.08186280
H	2.54596424	-4.58272129	-0.16285516
H	4.90496689	-3.72699446	-0.17430205
H	-2.13079186	2.36673341	0.13907568
H	-0.81371156	-1.70574610	-0.11316838
H	-2.65822309	-1.93097640	1.21666538
H	-4.99987556	-2.72217879	1.18944874
H	-6.74970608	-1.41974395	-0.01738089
H	-6.10574225	0.67250472	-1.21014107
H	-3.75231978	1.42991211	-1.20940541