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Boron templated synthesis of a BODIPY analogue from a phthalocyanine precursor

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Supporting Information

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General Information

All reagents and starting materials were purchased from commercial vendors and used without further purification. 1,3-diiminoisoindoline was synthesized according to a previously published procedure.[S1] Chlorobenzene was stored over 3 Å molecular sieves. Column chromatography was performed on silica gel (Dynamic Adsorbents, Inc, 63-200 μm). Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received.

NMR spectra were recorded on 300 or 500 MHz spectrometers, Chemical shifts were given in ppm relative to residual solvent resonances (^{1}H, ^{13}C NMR spectra). High resolution mass spectrometry experiments were performed on a Bruker MicroTOF-III instrument. Infrared spectra were collected on Thermo Scientific Nicolet iS5 which was equipped with an iD5 ATR.

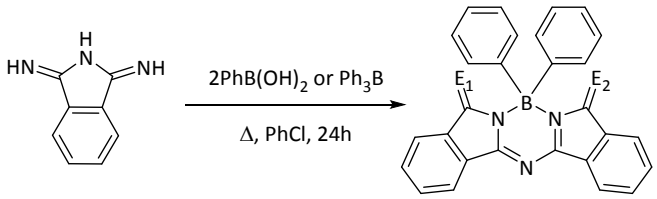
X-ray intensity data were measured on a Bruker CCD-based diffractometer with dual Cu/Mo ImuS microfocus optics (Cu Kα radiation, λ = 1.54178 Å, Mo Kα radiation, λ =0.71073 Å). Crystals were mounted on a cryoloop using Paratone oil and placed under a steam of nitrogen at 100 K (Oxford Cryosystems). The detector was placed at a distance of 5.00 cm from the crystal. The data were corrected for absorption with the SADABS program. The structures were refined using the Bruker SHELXTL Software Package (Version 6.1), and were solved using direct methods until the final anisotropic full-matrix, least squares refinement of F2 converged.

UV-Vis spectra were recorded on a Hitachi UV-Vis spectrophotometer (U-3010). Fluorescence excitation and emission data in solution were recorded on a Horiba Jobin-Yvon FluoroMax-4 fluorescence spectrophotometer using Coumarin 540 in methanol as a standard. All slit widths were held constant at 5 nm. The quantum yields in solution were calculated using the following equation: $\Phi_x = \Phi_{st}\frac{Grad_x\,\eta_x^2}{Grad_{st}\eta_{st}^2}$; η_x = 1.324, η_{st} = 1.329; Φ_{st} = 0.46 and *Grad* the gradient from the plot of integrated fluorescence intensity vs absorbance[S2]

Cyclic voltammograms were obtained using a standard three electrode cell and Electrochemical analyser BAS 100B from Bioanalytical systems and were recorded at 298 K under the following conditions: 10^{-3} M samples in dried acetonitrile in the presence of 0.1 M tetrabu-tylammonium hexafluorophosphate ($TBAPF_6$) as

a supporting electrolyte, Ag/Ag^+ reference electrode, 0.79 mm^2 gold working electrode, and platinum wire auxiliary electrode. The working electrode was polished first with 3 μm fine diamond, then 0.05 μm alumina. The electrode was rinsed with ethanol and deionized water after each polishing and wiped with a Kimwipe. The non-aqueous Ag/Ag^+ reference was prepared by soaking the silver wire in the degassed and dried THF solution of 5% Acetonitrile: 0.01M $AgClO_4$: 0.1M $TBAPF_6$. At a 0.10 V/s sweep rate, the Fc/Fc^+ occurs at 0.060 ±0.005 V (ΔE_p = 119mV; i_{pa}/i_{pc} = 0.99).

All DFT calculations were conducted using the Gaussian 09 software.[S3] All of the geometries were optimized at the DFT level using the TPSSh exchange-correlation functional and the 6-31G(d) basis set was used for all atoms.[S4,S5] The PCM method was used to calculate the solvent effects for all the DFT and TDDFT calculations using DCM as a solvent.[S6] The first 40 states were calculated for the TDDFT calculations. Molecular orbital contributions were compiled from single-point calculations using the QMForge program.[S7]



1 E_1=E_2=NH
2 E_1=NH, E_2=O
3 E_1=E_2=O

Synthesis of **1** and **2:**

Ph_3B (0.097 g ,0.401 mmol) and 1,3-diiminoisoindoline (DII) (0.111 g, 0.765 mmol) were refluxed in dry chlorobenzene for 12 hours with the solution turning from clear to yellow-green. The chlorobenzene was removed, and the remaining solid purified via column chromatography on silica using CH_2Cl_2 as the eluting solvent.

1: Yield: 77 mg, 46%. $\boldsymbol{\lambda}_{max}$= 333 nm, **ε**= 23,000, $\boldsymbol{\lambda}_{max}$= 426 nm, **ε**= 6,700 $M^{-1}cm^{-1}$, excitation at 426 nm ,λ_{em}= 482 nm, 512 nm Φ= 2.5×10^{-2}. IR: ν C=N 1657 cm^{-1}. ^{1}H NMR (300MHz, $CDCl_3$) δ= 9.06 (s, 2H), 8.15-8.12 (m, 2H), 7.96-7.93 (m, 2H), 7.76-7.68 (m, 5H), 7.54-7.52 (m, 4H), δ = 7.36-7.26 (m, 6H). ^{13}C NMR (300MHz, $CDCl_3$) δ= 184.54, 180.37, 169.38, 161.10, 136.10, 134.23, 133.68, 132.15, 132.36, 127.55, 123.99, 123.16. ESI MS calcd for $C_{28}H_{22}BN_5$ m/z 439.1963, found 439.1968.

2: Yield: 23 mg, 13.7%, $\boldsymbol{\lambda}_{max}$= 340 nm, **ε**= 25,000, $\boldsymbol{\lambda}_{max}$= 433 nm, **ε**= 5,300 $M^{-1}cm^{-1}$. Excitation at 433 nm, λ_{em}= 481 nm, 511 nm, Φ= 5.8×10^{-2}. IR: ν C=O 1760 cm^{-1}, C=N 1659 cm^{-1}, ^{1}H NMR (300MHz, d6-DMSO) δ= 11.69(s, 1H), 8.17 (t, J=5.40 Hz, 2H), 8.08 (d, J=6.90 Hz, 1H), 7.90-7.77 (m, 5H), 7.52 (d, J = 7.5Hz, 4H), 7.28-7.06 (m, 6H). ^{13}C NMR (300MHz, $CDCl_3$) δ= 134.86, 133.68, 133.77, 133.7, 132.31, 127.65, 126.93, 124.46, 124.38, 124.20. ESI MS calcd for $C_{28}H_{20}BN_4O$ m/z 439.1725, found m/z 439.1730.

Synthesis of **3**:

$PhB(OH)_2$ (0.241g, 1.98 mmol) and DII (0.274g, 1.89 mmol) were refluxed in chlorobenzene that had not been dried over molecular sieves for 72 hours. The chlorobenzene was removed and the residue was purified by column chromatography on silica, using CH_2Cl_2 as the elution solvent. This reaction also produces compounds

1 and **2**, but in lower yield. Yield: 3.0 mg, 0.36%, λ_{max}= 348 nm, **ε**= 25,000, λ_{max}= 440 nm, **ε**= 5,100 $M^{-1}cm^{-1}$. Excitation at 440 nm, λ_{em}= 492 nm, 515nm Φ= 5.6×10^{-3} IR: ν C=O 1759 cm^{-1}, ^{1}H NMR (300MHz, $CDCl_3$) δ= 8.18-8.15 (m, 2H), 7.81-7.77 (m, 6H), 7.61 (dd, J= 4.50, 7.80, 4H), 7.31-7.19 (m, 6 H).). ^{13}C NMR (500MHz, $CDCl_3$) δ= 164.39, 164.15, 164.08, 164.02, 134.46, 134.22, 134.12, 133.77, 133.53, 133.29, 133.26, 133.15, 132.65. ESI MS calcd for $C_{28}H_{18}BN_3O_2$ m/z 440.1565, found m/z 440.1570.

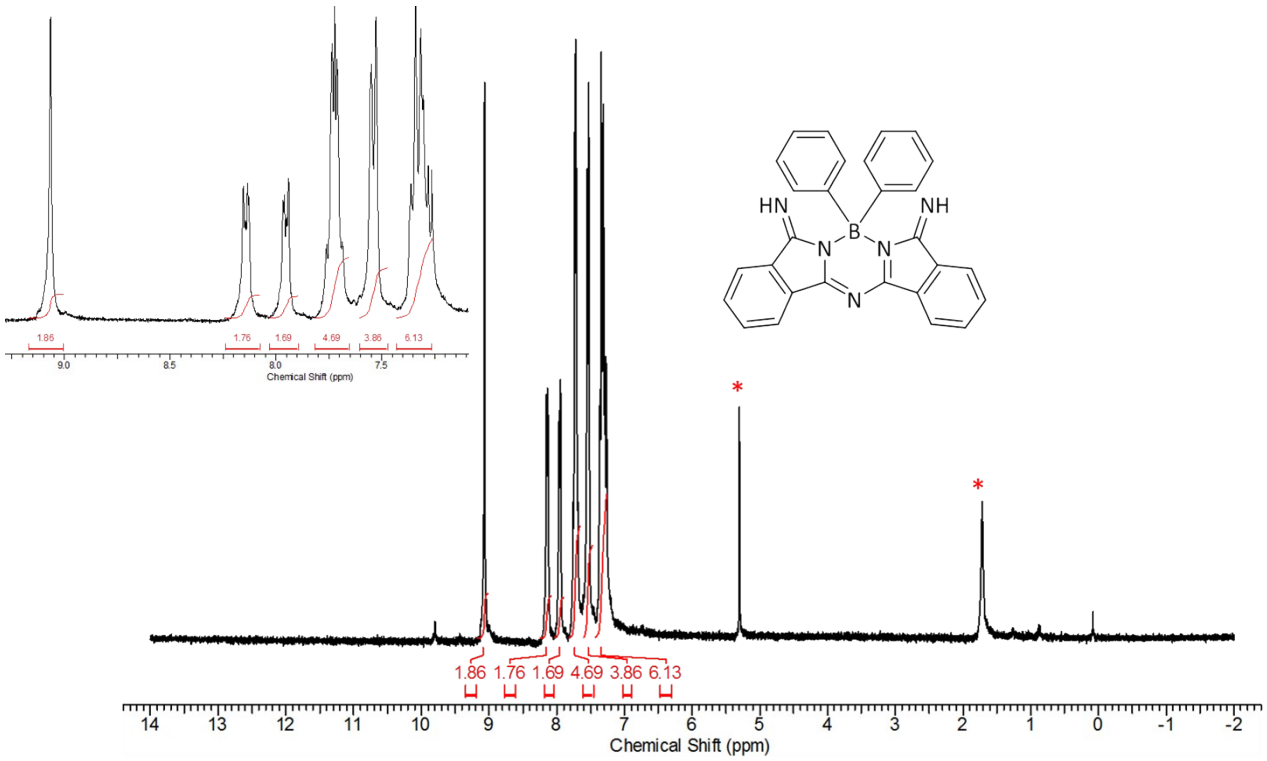


Figure S1: ^{1}H NMR (300 MHz) of **1** in $CDCl_3$. * represents residual CH_2Cl_2 and H_2O

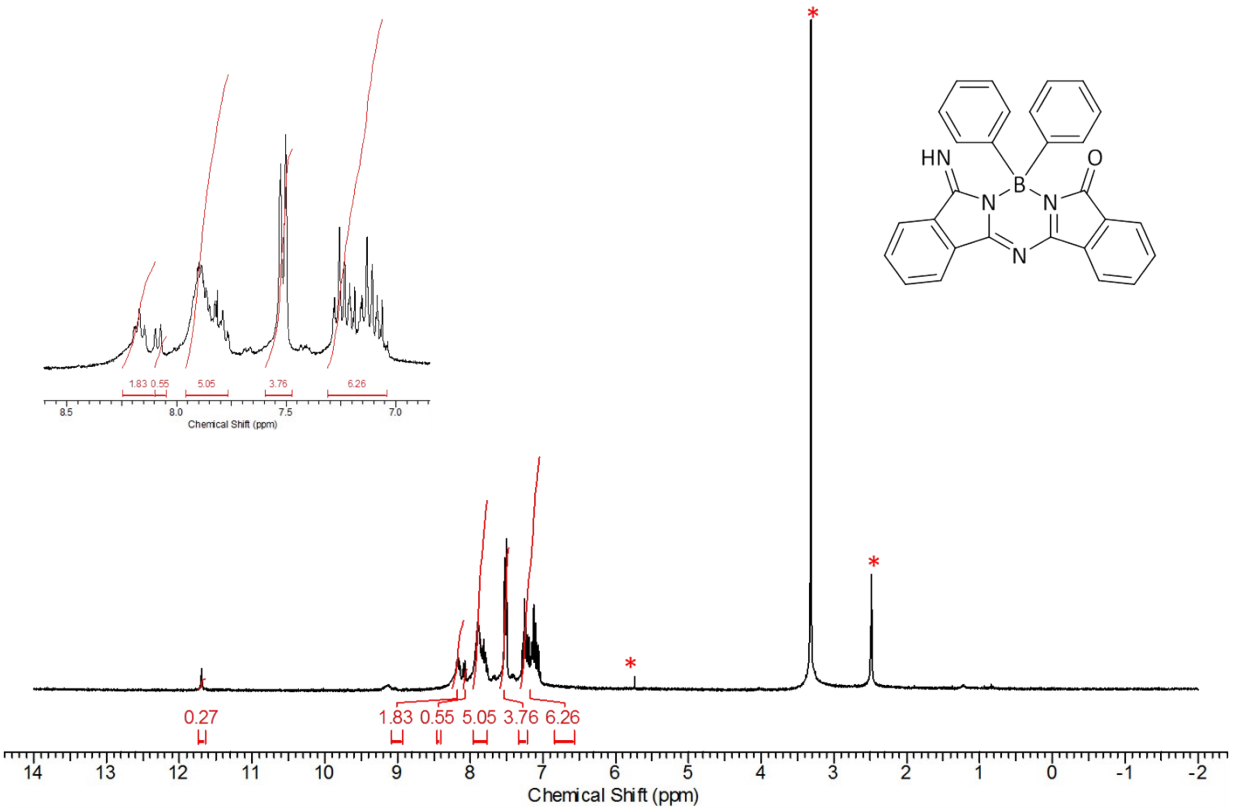


Figure S2: ^{1}H NMR (300 MHz) of **2** in d6-DMSO, * represents H_2O, DMSO, and CH_2Cl_2 peaks

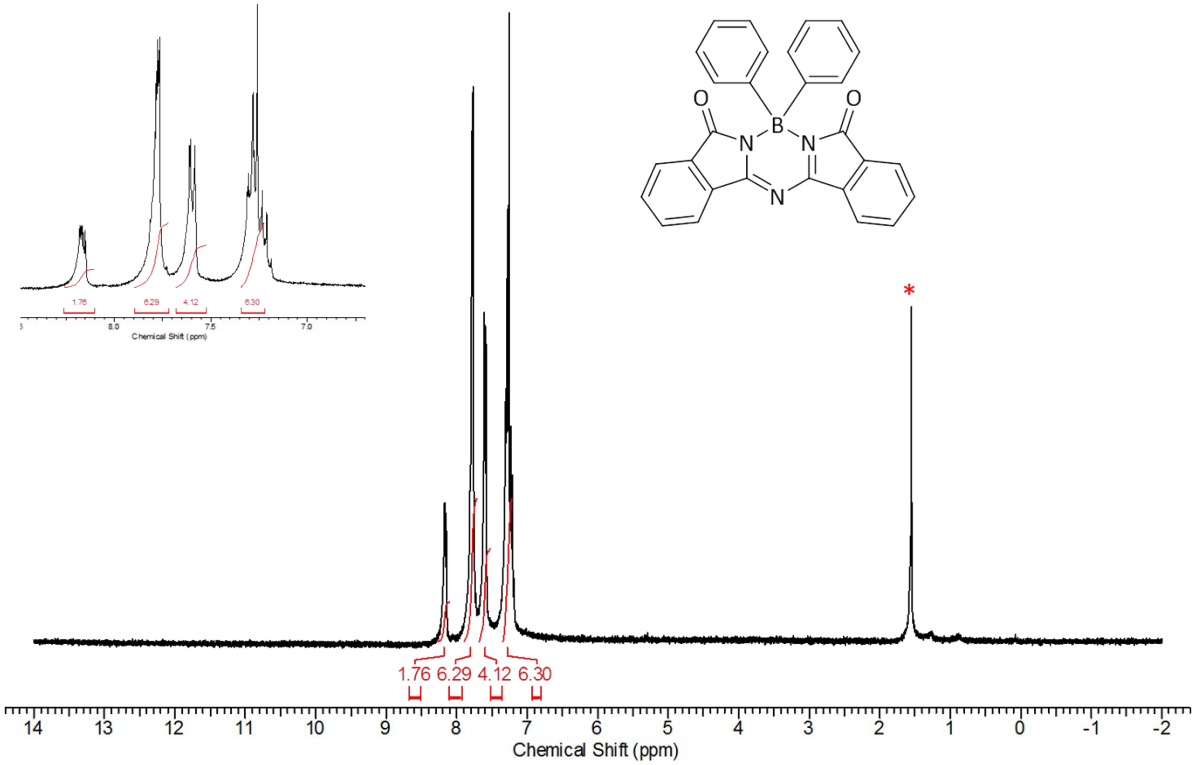


Figure S3:^{1}H NMR (300 MHz) of **3** in $CDCl_3$, * represents H_2O

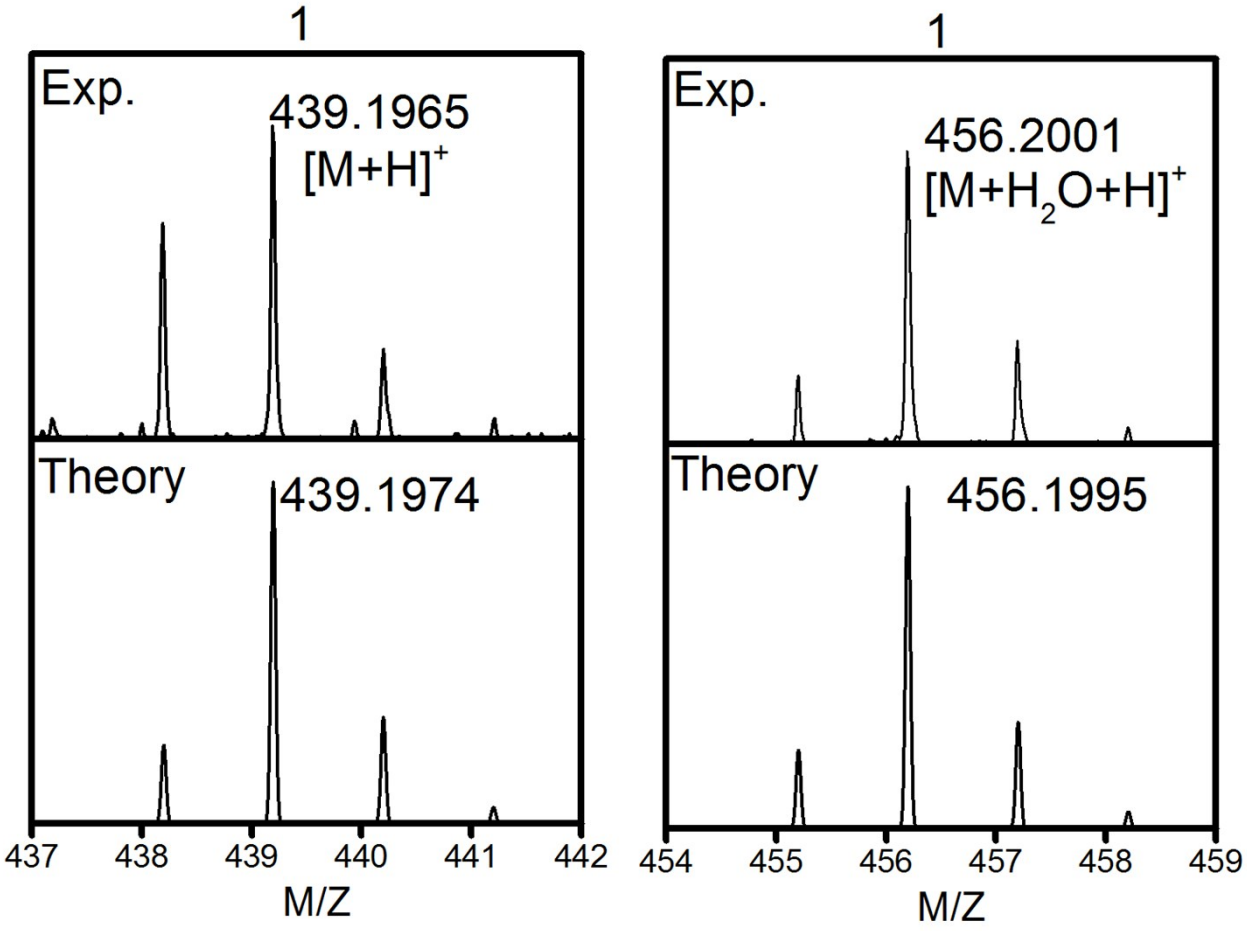


Figure S4: High-resolution ESI mass spectra of **1**

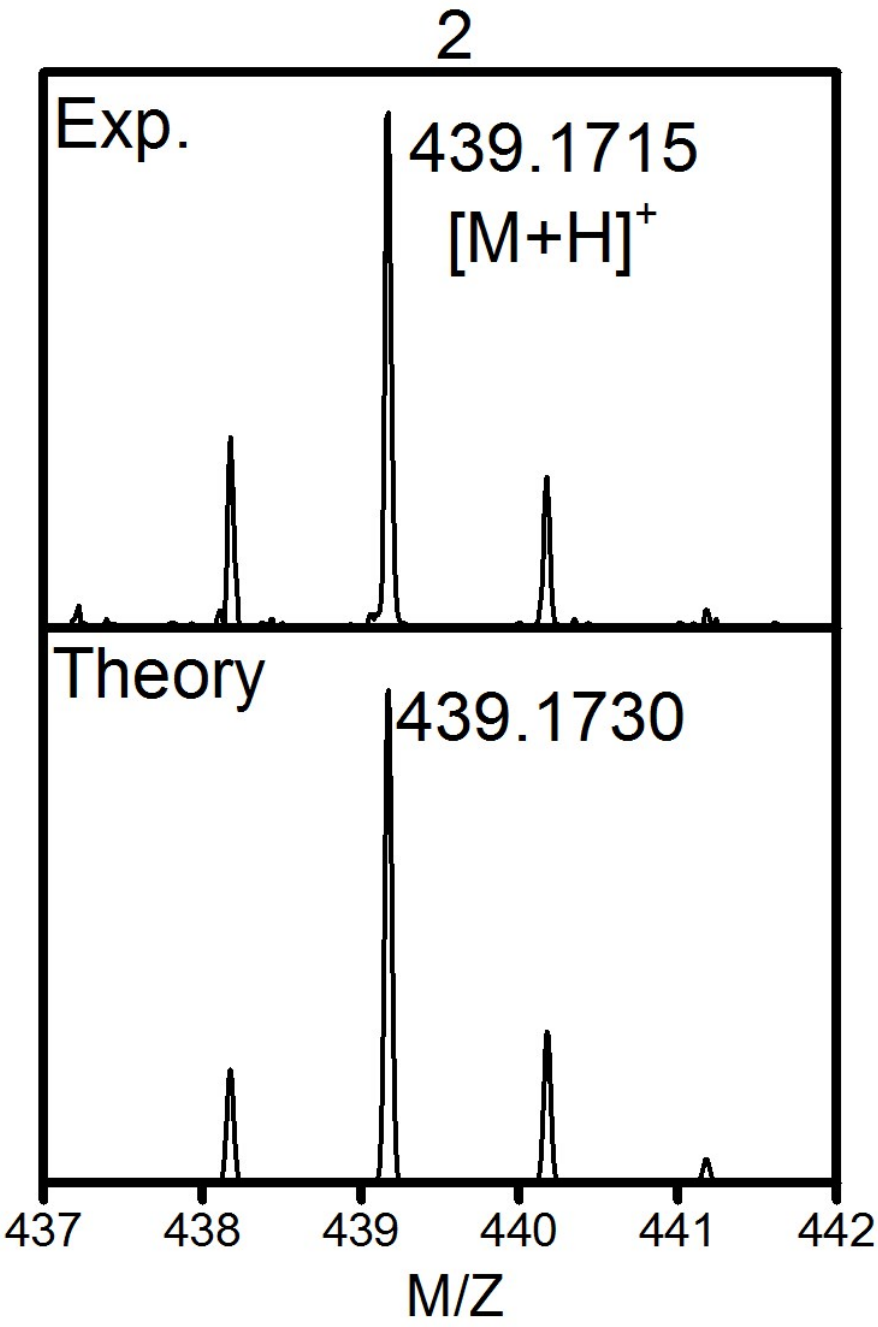


Figure S5: High-resolution ESI mass spectrum of **2**

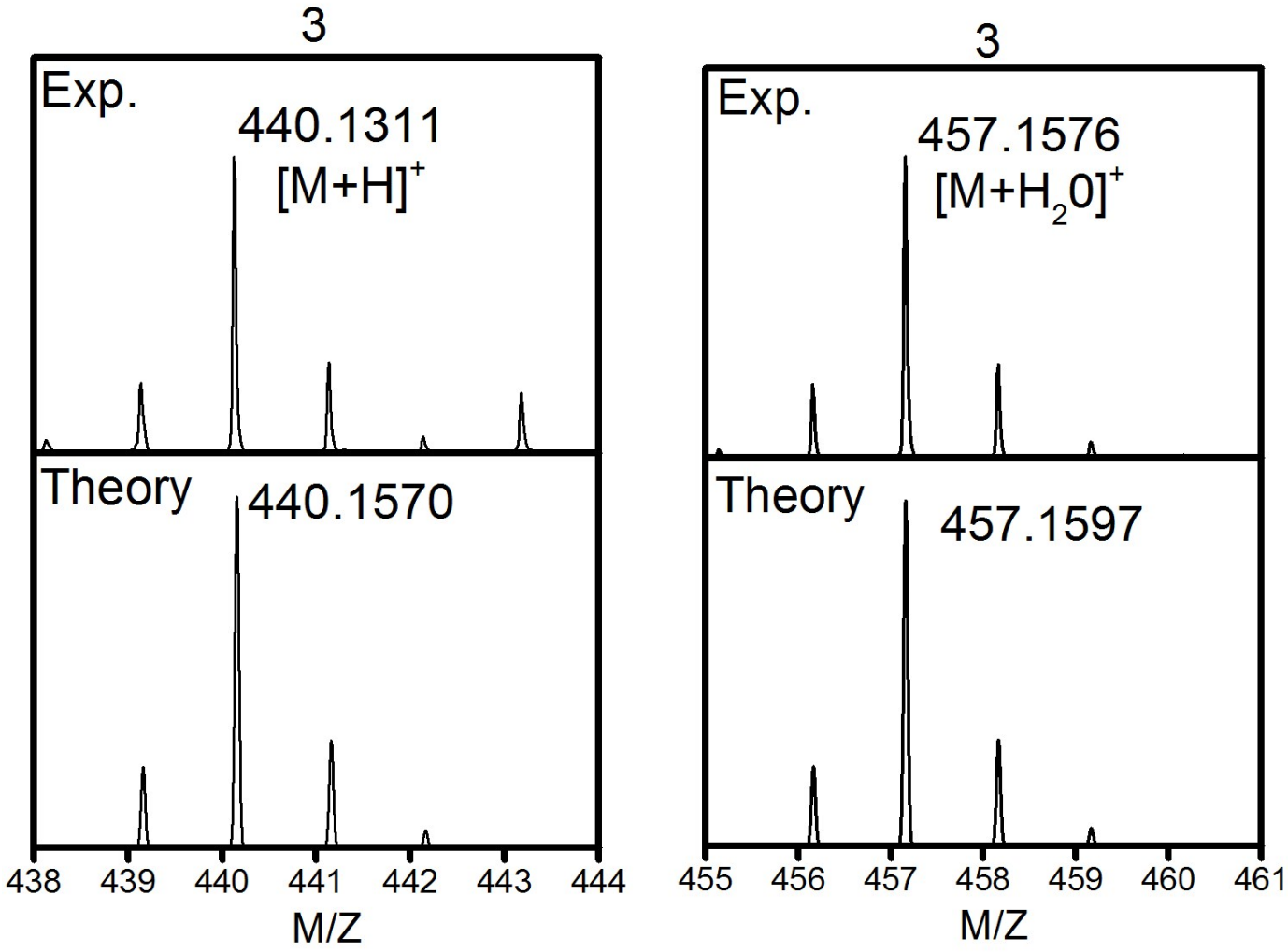


Figure S6: High-resolution ESI mass spectra of **3**

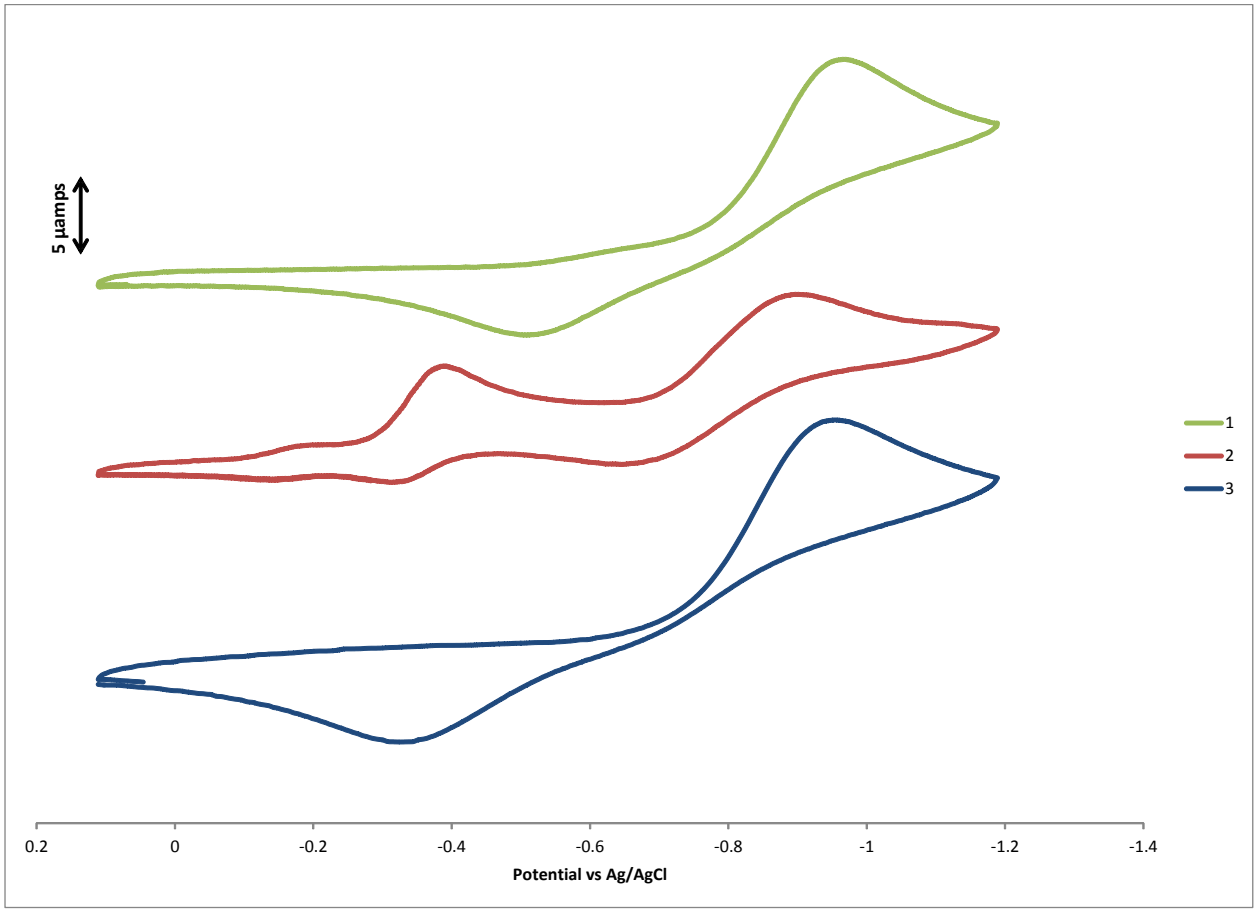


Figure S7: Cyclic voltammongrams of **1**, **2**, and **3** in 0.1 M $TBAPF_6$/acetonitrile at 0.25 V/s and 10.0 µA V^{-1} versus AgCl.

Table S1: Electrochemical data for **1**, **2**, and **3**.

Compound	E_1^c, V	E_1^a, V	E_2^0, V (ΔE_p, mV)
1	-0.967	-0.506	-
2	-0.899	-0.670	-0.388 (70)
3	-0.955	-0.326	-

Compound	**1**	**2**	**3**
Empirical formula	C28 H20 B N5	C29 H21 B Cl2 N4 O	C29 H20 B Cl2 N3 O2
Formula weight	437.30	523.21	524.19
Temperature	100(2) K	100(2) K	100 (2) K
Wavelength	1.54718 Å	0.71073 Å	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P2(1)/c	P-1	P-1
Unit cell dimensions	a = 16.5717(10) Å	a = 8.8161(5)Å	a = 8.7931(11) Å
	b = 22.3081(13) Å	b = 10.6099(6) Å	b = 10.5963(13) Å
	c =11.7698(7) Å	c =13.5285(8) Å	c = 13.5308(18) Å
	α=90°	α=78.972(2)°	α= 78.771(5)°
	β= 99.701(4)°	β= 86.357(3)°	β= 86.503(6)°
	γ = 90°	γ = 84.254(4)°	γ = 84.592(6)°
Volume	4288.9(4) $Å^3$	1235.06(12) $Å^3$	1229.9(3) $Å^3$
Z	8	2	2
Density (calculated)	1.354 Mg/m^3	1.407 Mg/m^3	1.415 Mg/m^3
Absorption coefficient	0.641 mm^{-1}	0.295 mm^{-1}	0.298 mm^{-1}
F(000)	1824	540	540
Crystal size	0.27× 0.18 × 0.11 mm^3	0.29 × 0.18 × 0.09 mm^3	0.27 × 0.24 × 0.21 mm^3
Theta range for data collection	2.70 to 62.99°	1.53 to 26.167°	1.99 to 26.376°
Index ranges	-17<=h<=19, -12<=k<=25,	-10<=h<=10, -13<=k<=12,	-10<=h<=10, -13<=k<=11,
	-13<=l<=13	-16<=l<=16	-15<=l<=16
Reflections collected	25267	14690	16216
Independent reflections	6842 [R(int) = 0.0337]	4687 [R(int) = 0.0833]	4790 [R(int) = 0.0355]
Completeness to theta	98.6 %	97.9 %	97.4 %
Absorption correction	SADABS	SADABS	SADABS
Max. and min. transmission	0.7527 and 0.6871	0.7452 and 0.5357	0.7454 and 0.6416
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data / restraints / parameters	6842 / 0 / 613	4687 / 12 / 374	4790 / 0 / 334
Goodness-of-fit on F2	0.962	1.125	1.080
Final R indices [I>2sigma(I)]	R1 = 0.0403, wR2 = 0.0898	R1 = 0.0509, wR2 = 0.1268	R1 = 0.0572, wR2 = 0.1466
R indices (all data)	R1 = 0.0563, wR2 = 0.0993	R1 = 0.1833, wR2 = 0.1401	R1 = 0.0734, wR2 = 0.1611
Largest diff. peak and hole	0.514 and -0.392 $e.Å^{-3}$	0.286 and -0.418 $e.Å^{-3}$	1.033 and -0.910 e.Å-3

Table S2: Crystallographic data for **1**, **2**, and **3**.

Table S3: Selected bond lengths for **1**, **2**, and **3**.

Compound	C=N	C=O	B-N
1	1.260(2)	--	1.582(2)
	1.264(2)	--	1.597(3)
2	1.251(4)	1.229(4)	1.581(4)
	--	--	1.592(4)
3	--	1.220(3)	1.594(3)
	--	1.244(3)	1.583(3)

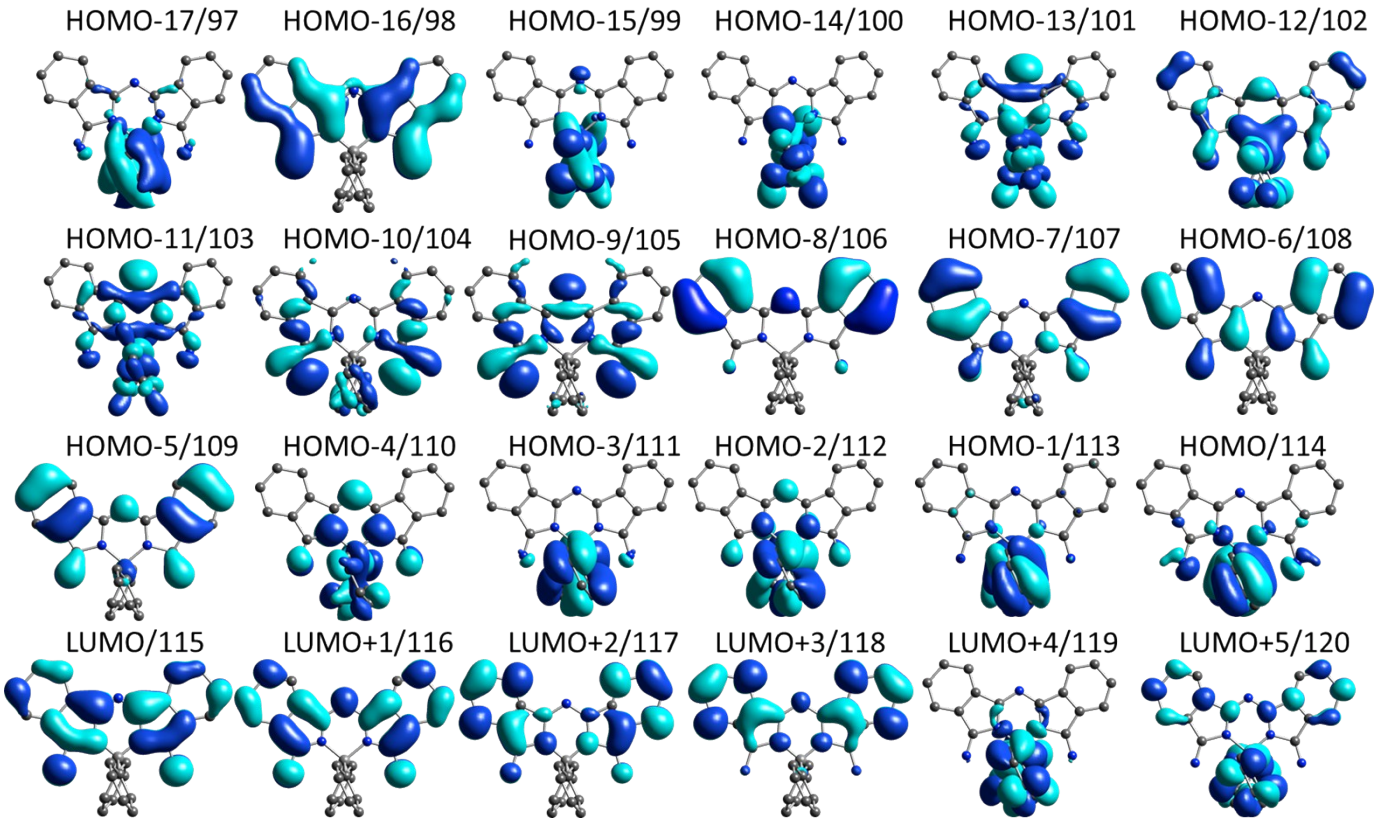


Figure S8: Frontier orbital diagrams for **1**

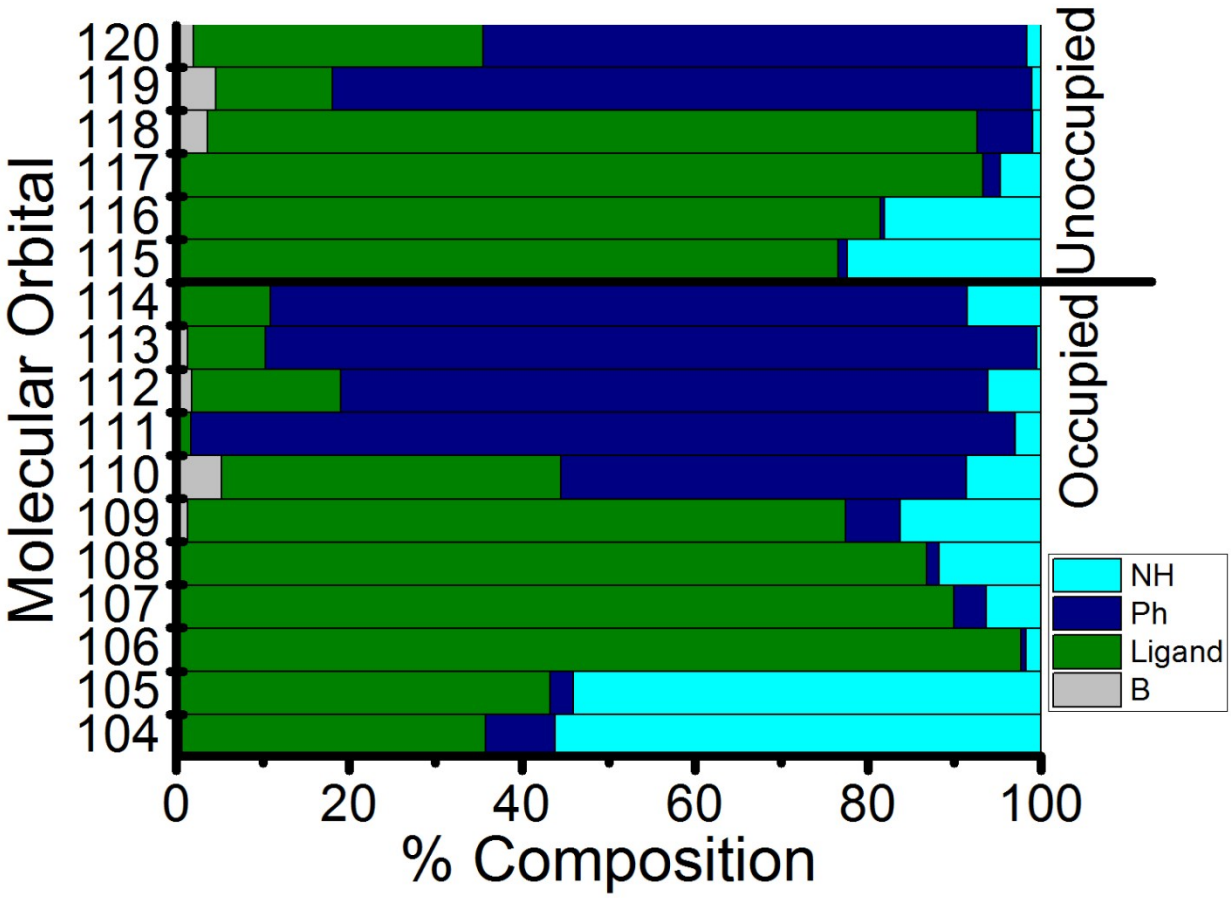


Figure S9 **:** Orbital compositions for **1**

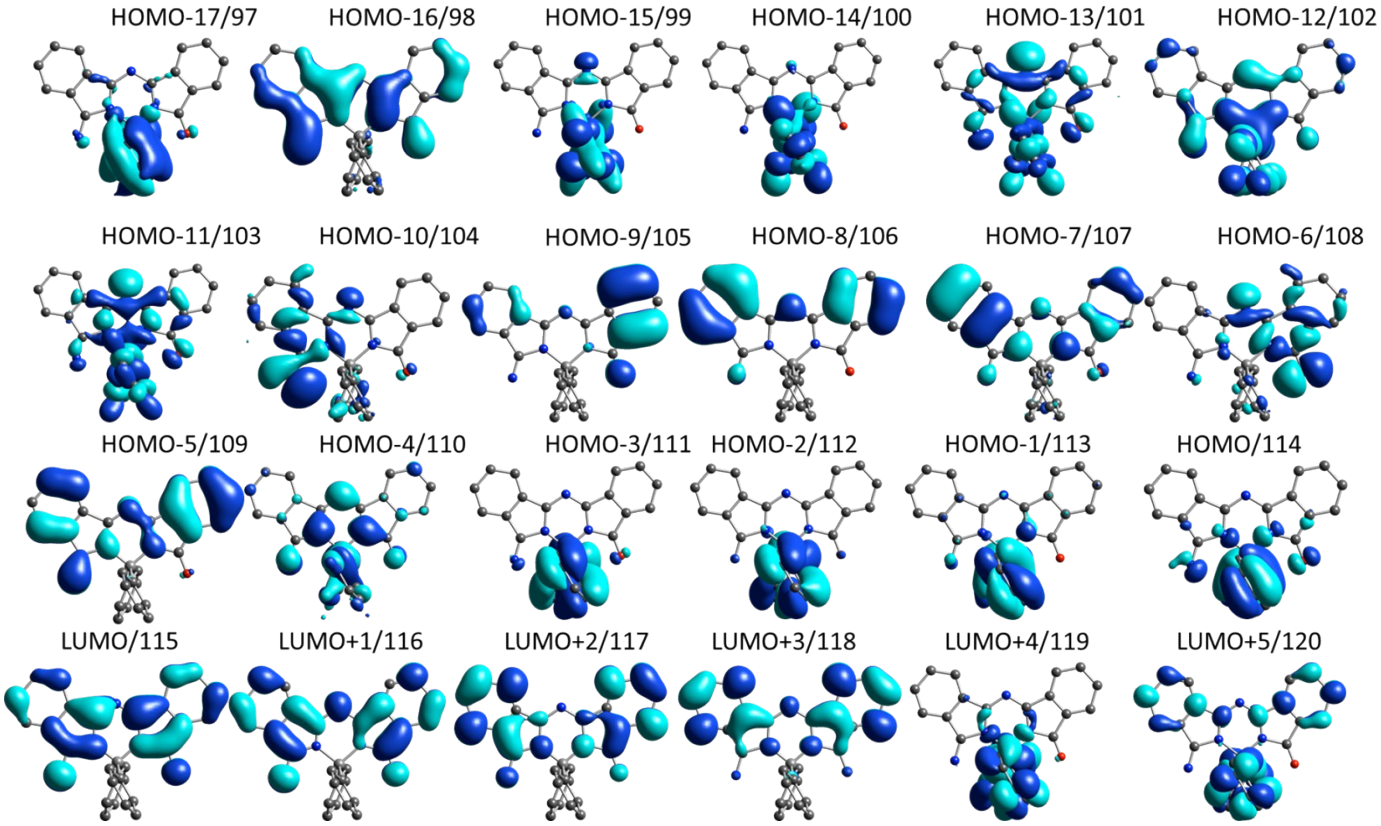


Figure S10: Frontier orbital diagrams for **2**

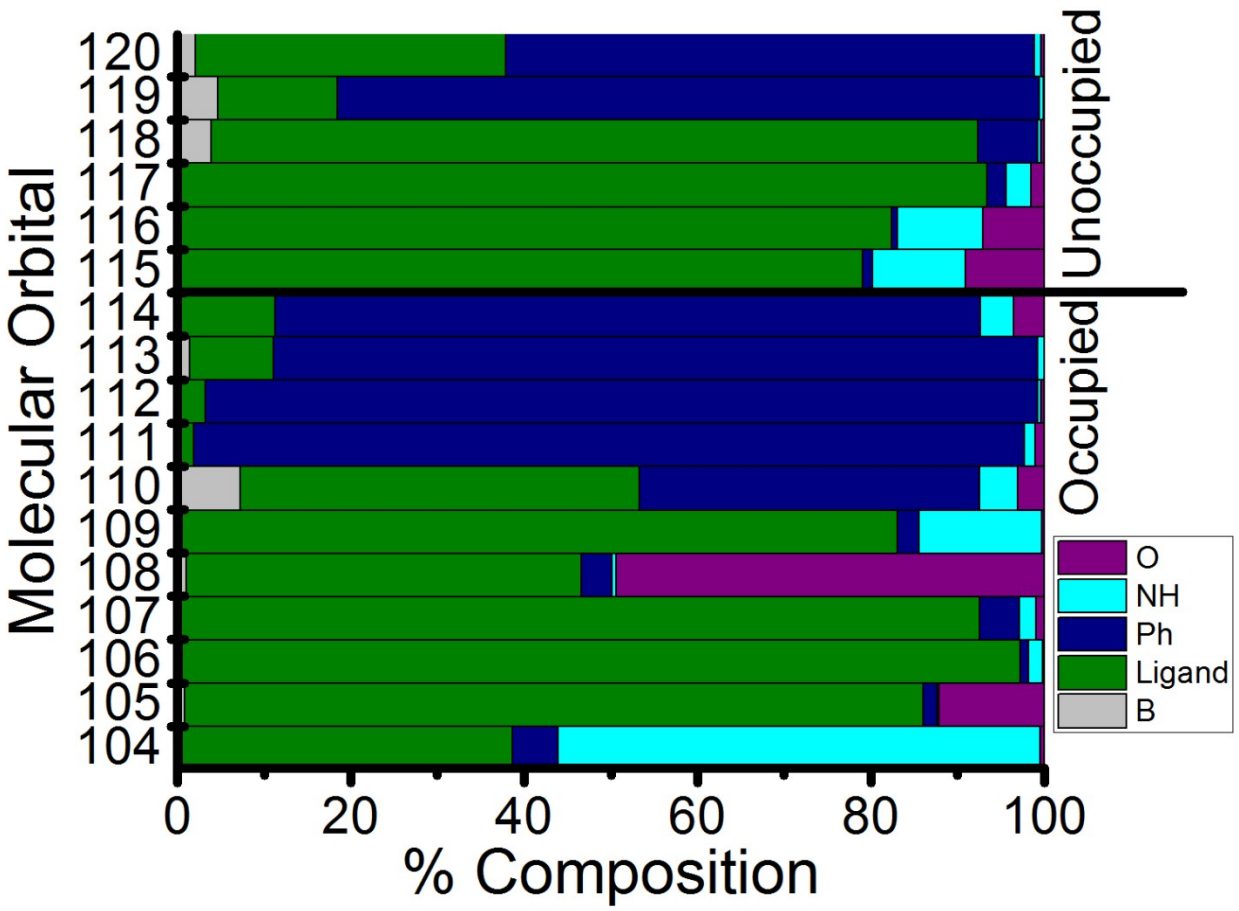


Figure S11: Orbital compositions for **2**

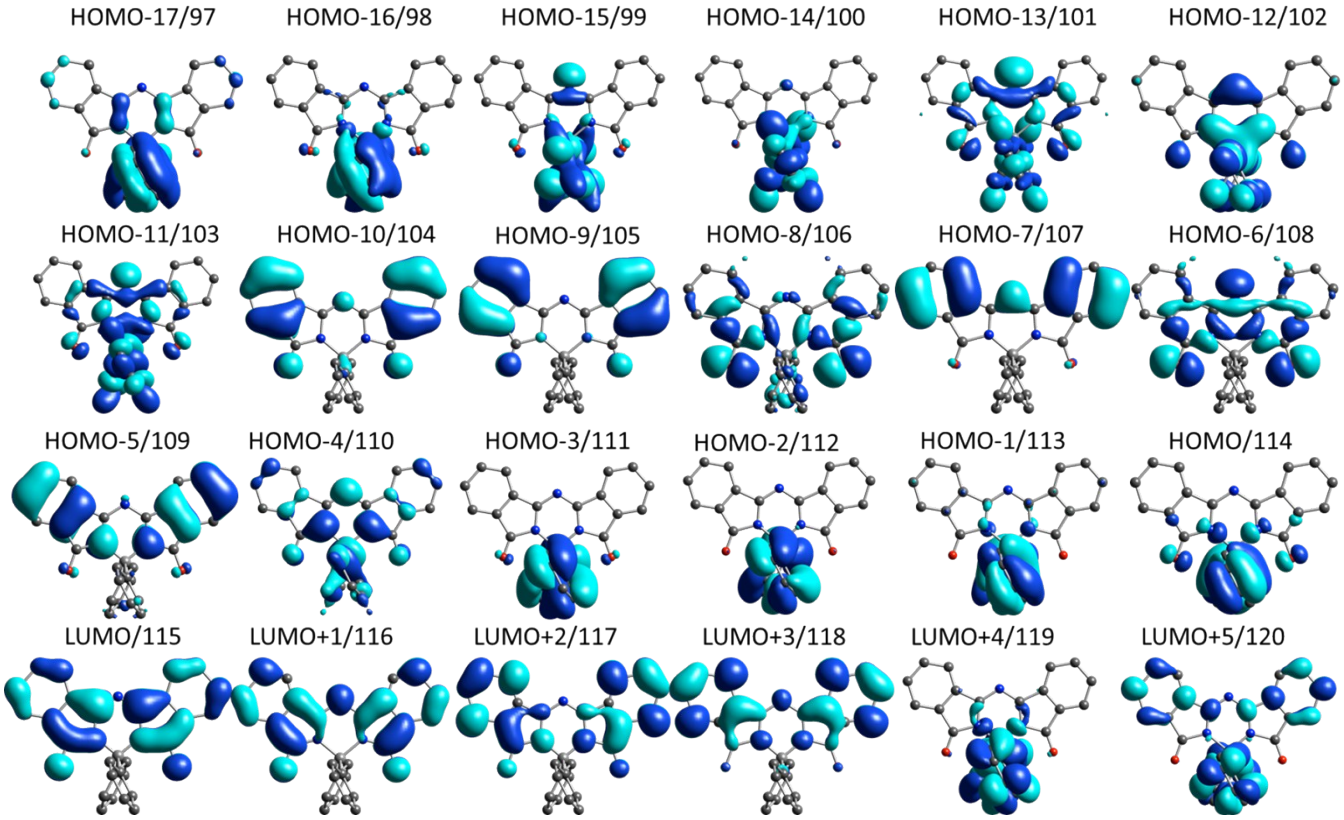


Figure S12: Frontier orbital diagrams for **3**

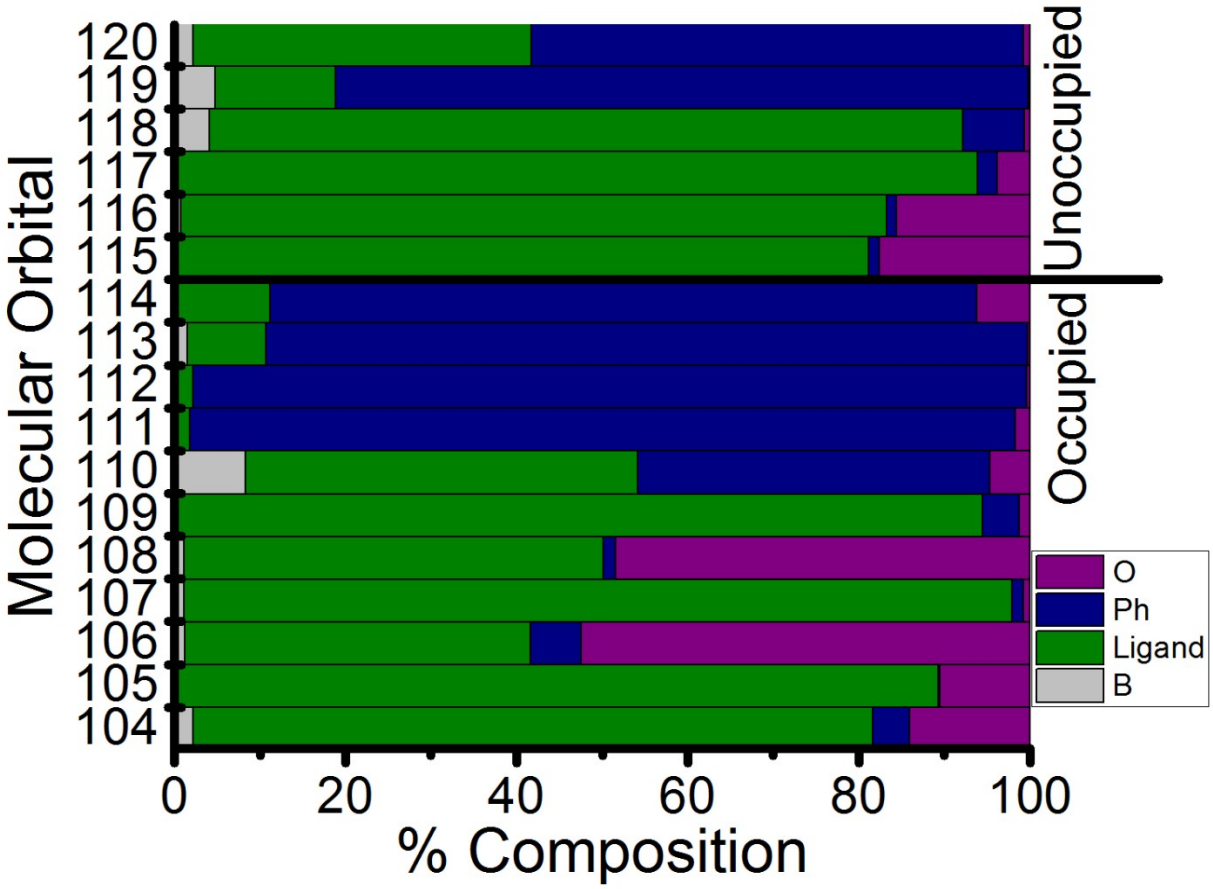


Figure S13: Orbital compositions for **3**

Compound **1**:

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.1886 eV 566.50 nm f=0.0013 <S**2>=0.000
114 ->115 0.70587
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1377.76055600
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.3155 eV 535.46 nm f=0.0063 <S**2>=0.000
113 ->115 0.70668

Excited State 3: Singlet-A 2.4129 eV 513.84 nm f=0.0061 <S**2>=0.000
110 ->115 -0.24869
112 ->115 0.66094

Excited State 4: Singlet-A 2.4576 eV 504.49 nm f=0.0028 <S**2>=0.000
111 ->115 0.70679

Excited State 5: Singlet-A 2.5839 eV 479.83 nm f=0.0563 <S**2>=0.000
109 ->115 -0.13287
110 ->115 0.64819
112 ->115 0.23812

Excited State 6: Singlet-A 3.4241 eV 362.10 nm f=0.0190 <S**2>=0.000
107 ->115 -0.47824
108 ->115 0.51091

Excited State 7: Singlet-A 3.4830 eV 355.97 nm f=0.3320 <S**2>=0.000
109 ->115 0.67992
110 ->115 0.10400

Excited State 8: Singlet-A 3.5193 eV 352.29 nm f=0.0750 <S**2>=0.000
105 ->115 -0.18159
107 ->115 0.44829
108 ->115 0.43174
112 ->116 -0.11585
114 ->116 0.21337

Excited State 9: Singlet-A 3.5307 eV 351.16 nm f=0.0118 <S**2>=0.000
105 ->115 -0.32590
107 ->115 -0.20458
108 ->115 -0.16479
114 ->116 0.56022

Excited State 10: Singlet-A 3.5608 eV 348.19 nm f=0.1834 <S**2>=0.000
106 ->115 0.69302

Excited State 11: Singlet-A 3.5761 eV 346.70 nm f=0.0009 <S**2>=0.000
103 ->115 -0.11186

105 ->115 0.58748
114 ->116 0.36947

Excited State 12: Singlet-A 3.6525 eV 339.45 nm f=0.0043 <S**2>=0.000
104 ->115 0.67697
113 ->116 0.18361

Excited State 13: Singlet-A 3.6672 eV 338.09 nm f=0.0001 <S**2>=0.000
104 ->115 -0.17556
113 ->116 0.67549

Excited State 14: Singlet-A 3.7590 eV 329.84 nm f=0.0112 <S**2>=0.000
110 ->116 -0.21953
112 ->116 0.66330

Excited State 15: Singlet-A 3.8056 eV 325.80 nm f=0.0048 <S**2>=0.000
111 ->116 0.70377

Excited State 16: Singlet-A 3.8334 eV 323.43 nm f=0.0000 <S**2>=0.000
103 ->115 0.68803
105 ->115 0.10948

Excited State 17: Singlet-A 3.9015 eV 317.79 nm f=0.0091 <S**2>=0.000
107 ->115 0.11381
109 ->116 -0.11086
110 ->116 0.64964
112 ->116 0.18776

Excited State 18: Singlet-A 4.1730 eV 297.11 nm f=0.0908 <S**2>=0.000
102 ->115 0.69190

Excited State 19: Singlet-A 4.2100 eV 294.50 nm f=0.0082 <S**2>=0.000
114 ->117 0.70579

Excited State 20: Singlet-A 4.3068 eV 287.88 nm f=0.0018 <S**2>=0.000
114 ->118 0.70551

Excited State 21: Singlet-A 4.3348 eV 286.02 nm f=0.0304 <S**2>=0.000
113 ->117 0.69967

Excited State 22: Singlet-A 4.3637 eV 284.12 nm f=0.0001 <S**2>=0.000
101 ->115 0.69272
103 ->115 -0.10401

Excited State 23: Singlet-A 4.3911 eV 282.35 nm f=0.0042 <S**2>=0.000
112 ->117 0.69066
113 ->118 -0.12585

Excited State 24: Singlet-A 4.4281 eV 280.00 nm f=0.0314 <S**2>=0.000
112 ->117 0.13321
113 ->118 0.68535

Excited State 25: Singlet-A 4.4636 eV 277.77 nm f=0.0001 <S**2>=0.000
111 ->117 0.70480

Excited State 26: Singlet-A 4.4876 eV 276.28 nm f=0.0087 <S**2>=0.000
112 ->118 0.70124

Excited State 27: Singlet-A 4.4886 eV 276.22 nm f=0.0488 <S**2>=0.000
110 ->117 0.69694

Excited State 28: Singlet-A 4.5614 eV 271.81 nm f=0.0007 <S**2>=0.000
111 ->118 0.70633

Excited State 29: Singlet-A 4.5905 eV 270.09 nm f=0.0282 <S**2>=0.000
110 ->118 0.69602

Excited State 30: Singlet-A 4.6089 eV 269.01 nm f=0.0051 <S**2>=0.000
100 ->115 0.70364

Excited State 31: Singlet-A 4.6704 eV 265.47 nm f=0.0194 <S**2>=0.000
107 ->118 0.11301
108 ->116 0.66516
109 ->117 -0.13300

Excited State 32: Singlet-A 4.7106 eV 263.20 nm f=0.0003 <S**2>=0.000
99 ->115 0.70511

Excited State 33: Singlet-A 4.7598 eV 260.48 nm f=0.0465 <S**2>=0.000
98 ->115 -0.36726
109 ->116 0.57131

Excited State 34: Singlet-A 4.8260 eV 256.91 nm f=0.0077 <S**2>=0.000
98 ->115 0.10283
106 ->116 0.63916
107 ->117 -0.14811
109 ->118 0.20674

Excited State 35: Singlet-A 4.8576 eV 255.24 nm f=0.0029 <S**2>=0.000
107 ->116 0.65286
109 ->117 -0.19220

Excited State 36: Singlet-A 4.9343 eV 251.27 nm f=0.0005 <S**2>=0.000
105 ->116 0.69921

Excited State 37: Singlet-A 5.0066 eV 247.64 nm f=0.0000 <S**2>=0.000
104 ->116 0.69929

Excited State 38: Singlet-A 5.2363 eV 236.78 nm f=0.1729 <S**2>=0.000
96 ->115 -0.23071
98 ->115 0.48713
102 ->116 -0.19908
109 ->116 0.30116
109 ->118 -0.12648

Excited State 39: Singlet-A 5.2454 eV 236.37 nm f=0.0034 <S**2>=0.000
103 ->116 0.69915

Excited State 40: Singlet-A 5.3267 eV 232.76 nm f=0.0012 <S**2>=0.000
97 ->115 0.70063

Compound **2**:

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.0167 eV 614.78 nm f=0.0024 <S**2>=0.000
114 ->115 0.70563
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1397.65034324
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.1468 eV 577.53 nm f=0.0099 <S**2>=0.000
113 ->115 0.70632

Excited State 3: Singlet-A 2.2332 eV 555.18 nm f=0.0050 <S**2>=0.000
112 ->115 0.70239

Excited State 4: Singlet-A 2.2802 eV 543.74 nm f=0.0033 <S**2>=0.000
111 ->115 0.70481

Excited State 5: Singlet-A 2.4766 eV 500.63 nm f=0.0420 <S**2>=0.000
109 ->115 0.10529
110 ->115 0.69186

Excited State 6: Singlet-A 3.0242 eV 409.97 nm f=0.0001 <S**2>=0.000
108 ->115 0.69577

Excited State 7: Singlet-A 3.2468 eV 381.87 nm f=0.0076 <S**2>=0.000
106 ->115 0.11591
107 ->115 0.57776
109 ->115 0.36026

Excited State 8: Singlet-A 3.3518 eV 369.90 nm f=0.1930 <S**2>=0.000
106 ->115 -0.10365
107 ->115 -0.34493
109 ->115 0.58074

Excited State 9: Singlet-A 3.3989 eV 364.77 nm f=0.3396 <S**2>=0.000
106 ->115 0.67851
107 ->115 -0.15518

Excited State 10: Singlet-A 3.4302 eV 361.45 nm f=0.0003 <S**2>=0.000
104 ->115 0.12152
114 ->116 0.69102

Excited State 11: Singlet-A 3.4983 eV 354.41 nm f=0.0042 <S**2>=0.000
104 ->115 0.67790
105 ->115 -0.11666
114 ->116 -0.12231

Excited State 12: Singlet-A 3.5432 eV 349.92 nm f=0.0387 <S**2>=0.000
105 ->115 0.53462
113 ->116 0.42695

Excited State 13: Singlet-A 3.5604 eV 348.23 nm f=0.0165 <S**2>=0.000
105 ->115 -0.40258
113 ->116 0.55505

Excited State 14: Singlet-A 3.6400 eV 340.61 nm f=0.0055 <S**2>=0.000
112 ->116 0.70009

Excited State 15: Singlet-A 3.6884 eV 336.14 nm f=0.0037 <S**2>=0.000
111 ->116 0.70430

Excited State 16: Singlet-A 3.7614 eV 329.62 nm f=0.0004 <S**2>=0.000
101 ->115 0.12822
103 ->115 0.68690

Excited State 17: Singlet-A 3.8740 eV 320.04 nm f=0.0090 <S**2>=0.000
110 ->116 0.68868

Excited State 18: Singlet-A 4.1098 eV 301.68 nm f=0.1287 <S**2>=0.000
102 ->115 0.68288

Excited State 19: Singlet-A 4.1879 eV 296.06 nm f=0.0068 <S**2>=0.000
114 ->117 0.70125

Excited State 20: Singlet-A 4.2299 eV 293.11 nm f=0.0008 <S**2>=0.000
101 ->115 0.67745
103 ->115 -0.13691

Excited State 21: Singlet-A 4.3005 eV 288.30 nm f=0.0019 <S**2>=0.000
114 ->118 0.70428

Excited State 22: Singlet-A 4.3103 eV 287.65 nm f=0.0278 <S**2>=0.000
113 ->117 0.70034

Excited State 23: Singlet-A 4.3862 eV 282.67 nm f=0.0020 <S**2>=0.000
112 ->117 0.70324

Excited State 24: Singlet-A 4.4189 eV 280.58 nm f=0.0278 <S**2>=0.000
113 ->118 0.69546

Excited State 25: Singlet-A 4.4354 eV 279.53 nm f=0.0103 <S**2>=0.000
100 ->115 0.56560
108 ->116 0.10151
111 ->117 -0.39725

Excited State 26: Singlet-A 4.4368 eV 279.44 nm f=0.0042 <S**2>=0.000
100 ->115 0.40796
111 ->117 0.56966

Excited State 27: Singlet-A 4.4790 eV 276.82 nm f=0.0004 <S**2>=0.000
108 ->116 0.67358
111 ->117 0.12013

Excited State 28: Singlet-A 4.4972 eV 275.69 nm f=0.0008 <S**2>=0.000
112 ->118 0.70548

Excited State 29: Singlet-A 4.5251 eV 273.99 nm f=0.0002 <S**2>=0.000
99 ->115 0.70240

Excited State 30: Singlet-A 4.5490 eV 272.55 nm f=0.0000 <S**2>=0.000
111 ->118 0.70268

Excited State 31: Singlet-A 4.5634 eV 271.69 nm f=0.0480 <S**2>=0.000
109 ->116 0.25498
110 ->117 0.63347

Excited State 32: Singlet-A 4.6110 eV 268.89 nm f=0.0467 <S**2>=0.000
107 ->116 0.33536
109 ->116 0.50684
110 ->117 -0.28668

Excited State 33: Singlet-A 4.6767 eV 265.11 nm f=0.0289 <S**2>=0.000
105 ->116 0.11467
106 ->116 -0.25789
110 ->118 0.63481

Excited State 34: Singlet-A 4.7477 eV 261.15 nm f=0.0012 <S**2>=0.000
98 ->115 0.20863
106 ->116 -0.34104
107 ->116 0.47088
109 ->116 -0.23118
109 ->118 0.10694
110 ->118 -0.12351

Excited State 35: Singlet-A 4.7599 eV 260.48 nm f=0.0566 <S**2>=0.000
106 ->116 0.48706
107 ->116 0.31647
107 ->117 0.19012
107 ->118 0.11765
109 ->116 -0.16256
110 ->118 0.23705

Excited State 36: Singlet-A 4.8838 eV 253.87 nm f=0.0147 <S**2>=0.000
98 ->115 -0.23673
104 ->116 -0.12608
105 ->116 0.59010

109 ->117 -0.16011

Excited State 37: Singlet-A 4.9108 eV 252.47 nm f=0.0013 <S**2>=0.000
104 ->116 0.68793

Excited State 38: Singlet-A 5.1348 eV 241.46 nm f=0.0010 <S**2>=0.000
97 ->115 0.69911

Excited State 39: Singlet-A 5.1802 eV 239.34 nm f=0.0070 <S**2>=0.000
96 ->115 0.64890
98 ->115 -0.20621

Excited State 40: Singlet-A 5.1999 eV 238.44 nm f=0.0006 <S**2>=0.000
96 ->115 0.10033
103 ->116 -0.35778
108 ->117 0.49859
108 ->118 -0.30695

Compound **3**:

Excitation energies and oscillator strengths:
Excited State 1: Singlet-A 1.8475 eV 671.09 nm f=0.0039 <S**2>=0.000
114 ->115 0.70564
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1417.53896925
Copying the excited state density for this state as the 1-particle RhoCI density.
Excited State 2: Singlet-A 1.9905 eV 622.89 nm f=0.0172 <S**2>=0.000
113 ->115 0.70604
Excited State 3: Singlet-A 2.0477 eV 605.49 nm f=0.0047 <S**2>=0.000
112 ->115 0.70601
Excited State 4: Singlet-A 2.1010 eV 590.12 nm f=0.0020 <S**2>=0.000
111 ->115 0.70605
Excited State 5: Singlet-A 2.3433 eV 529.09 nm f=0.0282 <S**2>=0.000
110 ->115 0.70116
Excited State 6: Singlet-A 2.8745 eV 431.33 nm f=0.0000 <S**2>=0.000
108 ->115 0.69480
Excited State 7: Singlet-A 2.9850 eV 415.35 nm f=0.0004 <S**2>=0.000
106 ->115 0.69844
Excited State 8: Singlet-A 3.0709 eV 403.73 nm f=0.0009 <S**2>=0.000
105 ->115 0.10532
109 ->115 0.68809
Excited State 9: Singlet-A 3.2535 eV 381.07 nm f=0.4560 <S**2>=0.000
107 ->115 0.69493
Excited State 10: Singlet-A 3.3059 eV 375.04 nm f=0.0000 <S**2>=0.000
114 ->116 0.70105
Excited State 11: Singlet-A 3.3766 eV 367.19 nm f=0.0206 <S**2>=0.000
102 ->115 0.10969
104 ->115 0.66309
113 ->116 -0.18996
Excited State 12: Singlet-A 3.3995 eV 364.71 nm f=0.0894 <S**2>=0.000

105 ->115 0.68564
109 ->115 -0.10034
Excited State 13: Singlet-A 3.4341 eV 361.04 nm f=0.0095 <S**2>=0.000
104 ->115 0.17648
113 ->116 0.67951
Excited State 14: Singlet-A 3.4994 eV 354.30 nm f=0.0013 <S**2>=0.000
112 ->116 0.70400
Excited State 15: Singlet-A 3.5557 eV 348.70 nm f=0.0026 <S**2>=0.000
111 ->116 0.70592
Excited State 16: Singlet-A 3.6722 eV 337.63 nm f=0.0001 <S**2>=0.000
101 ->115 -0.12606
103 ->115 0.69003
Excited State 17: Singlet-A 3.8122 eV 325.23 nm f=0.0023 <S**2>=0.000
110 ->116 0.69767
Excited State 18: Singlet-A 4.0701 eV 304.62 nm f=0.1547 <S**2>=0.000
100 ->115 -0.11140
102 ->115 0.67572
104 ->115 -0.10173
Excited State 19: Singlet-A 4.1150 eV 301.29 nm f=0.0002 <S**2>=0.000
99 ->115 0.20735
101 ->115 0.64953
103 ->115 0.14120
106 ->116 0.10635
Excited State 20: Singlet-A 4.1548 eV 298.41 nm f=0.0054 <S**2>=0.000
114 ->117 0.70093
Excited State 21: Singlet-A 4.2695 eV 290.39 nm f=0.0297 <S**2>=0.000
100 ->115 0.69479
Excited State 22: Singlet-A 4.2847 eV 289.36 nm f=0.0310 <S**2>=0.000
113 ->117 0.68875
114 ->118 0.13547
Excited State 23: Singlet-A 4.2880 eV 289.14 nm f=0.0001 <S**2>=0.000
113 ->117 -0.13585
114 ->118 0.69050
Excited State 24: Singlet-A 4.3378 eV 285.82 nm f=0.0002 <S**2>=0.000
99 ->115 0.67097
101 ->115 -0.22034
Excited State 25: Singlet-A 4.3421 eV 285.54 nm f=0.0012 <S**2>=0.000
112 ->117 0.69973
Excited State 26: Singlet-A 4.3654 eV 284.02 nm f=0.0013 <S**2>=0.000
108 ->116 0.68408
Excited State 27: Singlet-A 4.3984 eV 281.88 nm f=0.0002 <S**2>=0.000
106 ->116 0.10121
111 ->117 0.69638
Excited State 28: Singlet-A 4.4130 eV 280.95 nm f=0.0330 <S**2>=0.000
113 ->118 0.70178
Excited State 29: Singlet-A 4.4634 eV 277.78 nm f=0.0000 <S**2>=0.000
106 ->116 0.67483
111 ->117 -0.10930
Excited State 30: Singlet-A 4.4719 eV 277.25 nm f=0.0000 <S**2>=0.000
112 ->118 0.70456
Excited State 31: Singlet-A 4.5261 eV 273.93 nm f=0.0017 <S**2>=0.000
109 ->116 0.52446

111 ->118 0.44683
Excited State 32: Singlet-A 4.5315 eV 273.60 nm f=0.0004 <S**2>=0.000
109 ->116 -0.42464
111 ->118 0.54722
Excited State 33: Singlet-A 4.6233 eV 268.17 nm f=0.0934 <S**2>=0.000
105 ->116 0.17164
109 ->116 0.10592
110 ->117 0.67350
Excited State 34: Singlet-A 4.6295 eV 267.81 nm f=0.0001 <S**2>=0.000
104 ->116 -0.19954
107 ->116 0.59553
109 ->117 0.11511
110 ->118 0.24237
Excited State 35: Singlet-A 4.7714 eV 259.85 nm f=0.0382 <S**2>=0.000
104 ->116 -0.16438
107 ->116 -0.25849
110 ->118 0.61594
Excited State 36: Singlet-A 4.7889 eV 258.90 nm f=0.0130 <S**2>=0.000
104 ->117 -0.13547
105 ->116 0.61337
107 ->117 -0.13251
109 ->118 0.17225
110 ->117 -0.17241
Excited State 37: Singlet-A 4.8567 eV 255.28 nm f=0.0823 <S**2>=0.000
96 ->115 -0.20666
104 ->116 0.58585
107 ->116 0.11887
109 ->117 -0.14790
110 ->118 0.21776
Excited State 38: Singlet-A 4.9425 eV 250.85 nm f=0.0005 <S**2>=0.000
98 ->115 0.70417
Excited State 39: Singlet-A 5.0116 eV 247.39 nm f=0.0013 <S**2>=0.000
96 ->115 -0.17890
97 ->115 0.68172
Excited State 40: Singlet-A 5.1705 eV 239.79 nm f=0.0027 <S**2>=0.000
95 ->115 -0.10690
103 ->116 0.67016
106 ->117 -0.13792

Optimized Geometries:

Compound **1**:

5	0	0.000119	0.884207	-0.000030
6	0	-2.609554	0.214281	-0.099481
6	0	-3.386482	-1.050462	-0.066376

6	0	-4.753994	-1.303725	-0.077989
1	0	-5.485748	-0.501586	-0.110757
6	0	-5.165922	-2.643828	-0.043589
1	0	-6.226831	-2.874652	-0.049572
6	0	-4.234703	-3.692796	-0.001515
1	0	-4.589063	-4.718631	0.023756
6	0	-2.858618	-3.434290	0.008496
1	0	-2.129598	-4.237215	0.040578
6	0	-2.461109	-2.100607	-0.023251
6	0	-1.129655	-1.490158	-0.021221
6	0	1.128948	-1.490577	0.021172
6	0	2.460148	-2.101525	0.023191
6	0	2.857194	-3.435345	-0.008550
1	0	2.127917	-4.238029	-0.040800
6	0	4.233183	-3.694354	0.001625
1	0	4.587144	-4.720326	-0.023705
6	0	5.164786	-2.645744	0.043908
1	0	6.225605	-2.876965	0.050016
6	0	4.753333	-1.305490	0.078372
1	0	5.485356	-0.503606	0.111366
6	0	3.385920	-1.051725	0.066562
6	0	2.609513	0.213333	0.099680
6	0	-0.075266	1.720921	1.392011
6	0	0.405735	1.167664	2.595111
1	0	0.870983	0.182823	2.581393
6	0	0.311870	1.841652	3.817270
1	0	0.699682	1.380691	4.723264
6	0	-0.278964	3.107446	3.872606
1	0	-0.353842	3.638852	4.818438
6	0	-0.774765	3.679949	2.697079
1	0	-1.242285	4.661991	2.726177
6	0	-0.673742	2.993035	1.482671
1	0	-1.081423	3.448121	0.585017
6	0	0.075962	1.720812	-1.392065
6	0	-0.405795	1.167886	-2.595068
1	0	-0.872018	0.183541	-2.581169
6	0	-0.311417	1.841639	-3.817289
1	0	-0.699798	1.380968	-4.723187
6	0	0.280710	3.106852	-3.872862
1	0	0.356013	3.638032	-4.818788
6	0	0.777181	3.679008	-2.697481
1	0	1.245661	4.660580	-2.726673
6	0	0.675620	2.992331	-1.482969
1	0	1.083838	3.447159	-0.585399
7	0	-1.233064	-0.147020	-0.055840
7	0	-0.000507	-2.203287	-0.000118
7	0	1.232827	-0.147527	0.056049
7	0	-2.977539	1.436702	-0.170570
1	0	-4.001975	1.484817	-0.195750
7	0	2.977825	1.435665	0.170489
1	0	4.002293	1.483561	0.195585

Compound **2**:

5	0	-0.005447	-0.880668	-0.001799
6	0	-2.595990	-0.166390	0.084833
6	0	-3.352191	1.118488	0.056358
6	0	-4.715555	1.376251	0.078602
1	0	-5.442249	0.571304	0.120726
6	0	-5.115836	2.722216	0.043710
1	0	-6.173794	2.965590	0.058386
6	0	-4.173911	3.759294	-0.009433
1	0	-4.517295	4.788837	-0.034837
6	0	-2.796935	3.489613	-0.030049
1	0	-2.063669	4.288185	-0.070316
6	0	-2.413395	2.153958	0.002730
6	0	-1.086663	1.521823	-0.003083
6	0	1.171447	1.467088	-0.043571
6	0	2.511649	2.054339	-0.042923
6	0	2.931899	3.381363	-0.019453
1	0	2.217139	4.197242	0.000752
6	0	4.312555	3.615150	-0.021669
1	0	4.684747	4.634658	-0.002356
6	0	5.225285	2.549757	-0.047977
1	0	6.290015	2.761889	-0.047919
6	0	4.790576	1.216257	-0.074192
1	0	5.508270	0.401234	-0.094399
6	0	3.419292	0.987551	-0.070598
6	0	2.620384	-0.262482	-0.097928
6	0	-0.108476	-1.736983	-1.376858
6	0	0.408643	-1.238863	-2.589029
1	0	0.931254	-0.283182	-2.594422
6	0	0.278827	-1.933272	-3.796006
1	0	0.696912	-1.517198	-4.710108
6	0	-0.388274	-3.161684	-3.826138
1	0	-0.492589	-3.707934	-4.760548
6	0	-0.922155	-3.677630	-2.641365
1	0	-1.448408	-4.629673	-2.651626
6	0	-0.782382	-2.972504	-1.441300
1	0	-1.214570	-3.386910	-0.534645
6	0	0.040732	-1.702447	1.398817
6	0	-0.443383	-1.128887	2.591007
1	0	-0.882282	-0.132369	2.566322
6	0	-0.383732	-1.797799	3.818372
1	0	-0.772513	-1.321821	4.715954
6	0	0.173817	-3.077499	3.888876
1	0	0.221421	-3.605009	4.838536
6	0	0.671576	-3.670373	2.723910
1	0	1.112086	-4.664233	2.765553
6	0	0.605035	-2.989229	1.504386
1	0	1.010276	-3.460701	0.613878
7	0	-1.211865	0.174980	0.038391
7	0	0.050234	2.207242	-0.030743

7	0	1.247476	0.125646	-0.066953
7	0	2.959536	-1.492655	-0.155530
1	0	3.982591	-1.567268	-0.173878
8	0	-3.029349	-1.302302	0.143452

Compound **3**:

5	0	0.000000	-0.877049	0.000000
6	0	-2.609831	-0.214818	0.084710
6	0	-3.387294	1.056282	0.061572
6	0	-4.754314	1.290790	0.075832
1	0	-5.468077	0.473976	0.106537
6	0	-5.176374	2.630955	0.047834
1	0	-6.238252	2.856446	0.056467
6	0	-4.251851	3.683642	0.009168
1	0	-4.612028	4.707412	-0.011362
6	0	-2.870024	3.437224	-0.003496
1	0	-2.150012	4.248085	-0.032848
6	0	-2.465116	2.107870	0.022222
6	0	-1.128988	1.498776	0.019225
6	0	1.128990	1.498775	-0.019224
6	0	2.465119	2.107868	-0.022221
6	0	2.870028	3.437221	0.003497
1	0	2.150016	4.248083	0.032850
6	0	4.251855	3.683638	-0.009168
1	0	4.612033	4.707408	0.011362
6	0	5.176377	2.630950	-0.047835
1	0	6.238255	2.856440	-0.056470
6	0	4.754316	1.290786	-0.075834
1	0	5.468078	0.473971	-0.106541
6	0	3.387296	1.056278	-0.061573
6	0	2.609831	-0.214820	-0.084712
6	0	-0.072114	-1.719662	-1.384175
6	0	0.451625	-1.202334	-2.585295
1	0	0.950324	-0.234032	-2.579703
6	0	0.355840	-1.893721	-3.797551
1	0	0.777912	-1.463635	-4.703108
6	0	-0.282695	-3.136320	-3.843348
1	0	-0.360413	-3.679780	-4.781861
6	0	-0.821721	-3.671801	-2.669221
1	0	-1.324356	-4.636161	-2.692301
6	0	-0.715184	-2.970915	-1.463879
1	0	-1.147156	-3.401002	-0.564414
6	0	0.072112	-1.719662	1.384177
6	0	-0.451626	-1.202332	2.585296
1	0	-0.950324	-0.234029	2.579704
6	0	-0.355842	-1.893718	3.797552
1	0	-0.777914	-1.463631	4.703109
6	0	0.282691	-3.136319	3.843349
1	0	0.360407	-3.679778	4.781863
6	0	0.821715	-3.671801	2.669223
1	0	1.324348	-4.636162	2.692303
6	0	0.715180	-2.970915	1.463881

1	0	1.147150	-3.401003	0.564415
7	0	-1.226674	0.153896	0.049934
7	0	0.000001	2.212125	0.000001
7	0	1.226674	0.153895	-0.049934
8	0	-3.016677	-1.359265	0.131456
8	0	3.016677	-1.359268	-0.131459

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