The planar cyclooctatetraene bridge in bismetallic macrocycles: isolating or conjugating?

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SI Table of Contents: **Page**

Methods and materials

^{1}H and ^{19}F NMR spectra at room temperature (r.t.) were measured on Bruker AvanceIII400 spectrometer equipped with a 5 mm, automated tuning and matching broad band probe (BBFO) with z-gradients, operating at 400.4 MHz for ^{1}H and 376.7 for ^{19}F, respectively. Chemical shifts are reported in ppm relative to residual hydrogen atoms in deuterated solvents $CDCl_3$ and pyridine-d_5.

Absorption spectra of the samples were measured on HP 8453 diode array spectrometer. Single crystals immersed in Paratone-N oil were quickly fished with a glass rod and mounted on a Kappa CCD diffractometer under a cold stream of nitrogen at 200 K. Data collection was carried out with monochromated Mo Kα radiation using φ and ω scans to cover the Ewald sphere.[1] Accurate cell parameters were obtained with complete collections of intensities, and these were corrected in the usual way.[2] The structure was solved by SHELXS-97 direct methods[3] and refined by the SHELXL-97 program package. The atoms were refined anisotropically. Hydrogen atoms were calculated using the riding model. Software used for molecular graphics: Mercury 3.1.4

Cyclic voltammetry measurements were carried out with dichloroethane (anodic range) and pyridine solutions (cathodic range) containing 0.5 mM of the complex and 0.1 M TBAP (Fluka, for electrochemical analysis) as the electrolyte at scan rate of 100 mv/sec under an argon atmosphere. A conventional three electrode system consisting of a glassy carbon working electrode, a Pt wire as counter electrode and Ag/AgCl reference electrode was used with an EmStat^{3+} electrochemical system. Ferrocene ($E_{1/2}$ = 0.83 V vs. Ag/AgCl in DCE, $E_{1/2}$ = 0.42 V vs. Ag/AgCl in pyridine) was added as an internal standard. All potentials are given with reference to the Ag/AgCl electrode. Spectroelectrochemistry, usually at 0.2 M TBAP and smaller complex concentration, was used in parallel with chemical oxidation to confirm that identical species were obtained.

Sillica gel 60 (230-400 mesh) was used for column chromatography. Reagents (from Aldrich) and solvents were used without further purification.

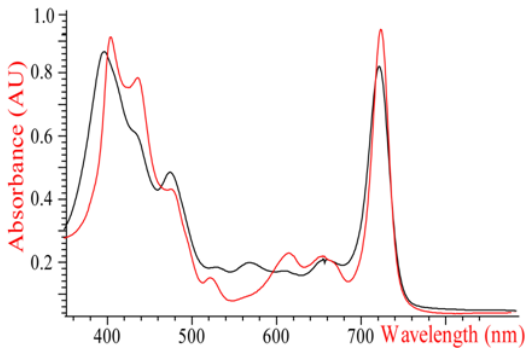

Figure S1. UV-visible spectra (CH_2Cl_2, 298 K) of $(H_3tpfc)_2COT$ (black) and $[(Ga\text{-}tpfc)_2]COT(py)_2$ (red).

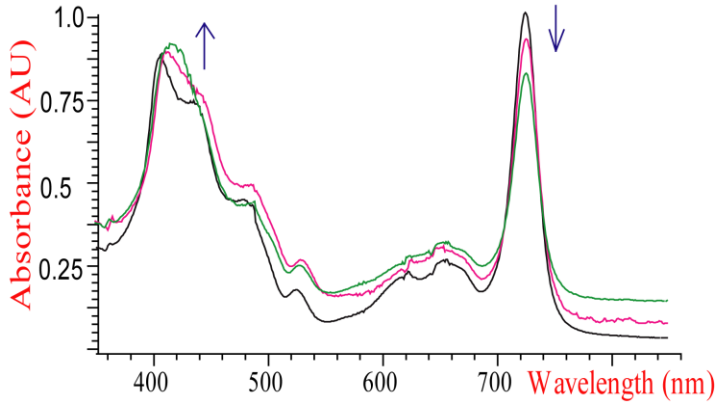

Figure S2. UV-visible spectra (at 298 K) recorded upon dissolving $[(Ga\text{-}tpfc)_2]COT(py)_2$ in: a) CH_2Cl_2 (black); b) CH_2Cl_2 in the presence of a 20% of pyridine (pink); c) in neat pyridine (green).

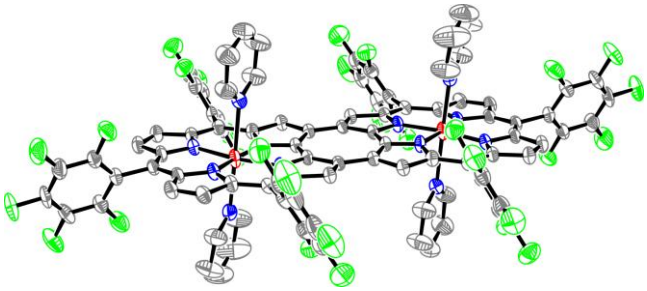

Figure S3. A perspective view of $[(Ga\text{-}tpfc)_2]COT(py)_4$, with 50% thermal contours.

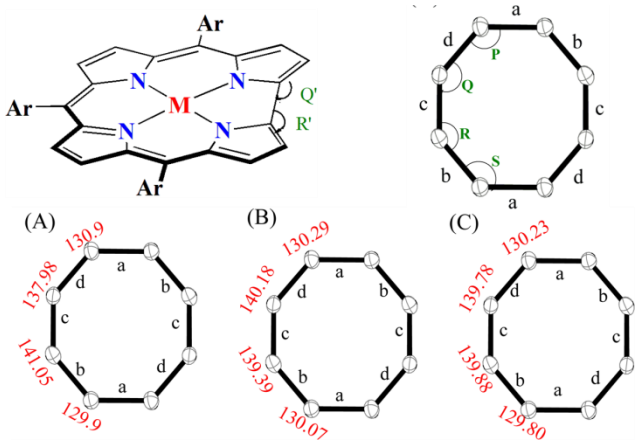

Figure S4. X-ray crystallography determined C-C-C angle within the COT moiety of (A) $(H_3tpfc)_2COT$, (B) $[(Ga\text{-}tpfc)_2]COT(py)_2$, and (C) $[(Ga\text{-}tpfc)_2]COT(py)_4$.

Table S1. The comparison between X-ray crystallography determined C-C-C bond angles (°) within the COT moiety of $(H_3tpfc)_2COT$, $[(Ga\text{-}tpfc)_2]COT(py)_2$, $[(Ga\text{-}tpfc)_2]COT(py)_4$ and Ga(tpfc)Py.

Compound	P	Q	R	S
$(H_3tpfc)_2COT$	130.9	137.98	141.05	129.9
$[(Ga\text{-}tpfc)_2]COT(py)_2$	130.29	140.18	139.39	130.07
$[(Ga\text{-}tpfc)_2]COT(py)_4$	130.23	139.78	139.88	129.80
Ga(tpfc)Py	-	Q′	R′	
		138.37	137.49	

Table S2. The comparison of C-C bond lengths (marked as a-d according to Figure 3) within the COT moiety of $(H_3tpfc)_2COT$, $[(Ga\text{-}tpfc)_2]COT(py)_2$, $[(Ga\text{-}tpfc)_2]COT(py)_4$ and Ga-(tpfc)Py, as determined by X-ray crystallography and DFT calculations (in brackets).

Compound	a	b	c	d
$(H_3tpfc)_2COT$	1.448(6), [1.454]	1.418(6), [1.435]	1.423(6), [1.434]	1.432(6), [1.461]
$[(Ga\text{-}tpfc)_2]COT(py)_2$	1.453(5), [1.454]	1.432(6), [1.440]	1.432(5), [1.435]	1.432(6), [1.439]
$[(Ga\text{-}tpfc)_2]COT(py)_4$	1.445(6), [1.453]	1.423(7), [1.444]	1.423(8), [1.444]	1.422(6), [1.444]
Ga(tpfc)Py	-	1.415, [1.423]	1.428, [1.432]	1.418, [1.423]

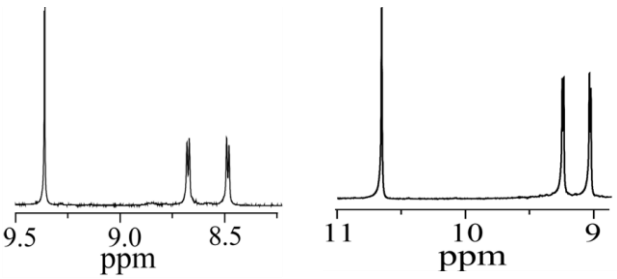

Figure S5. ^1H NMR spectra (400 MHz, 298 K) obtained for $[(Ga\text{-}tpfc)_2]COT(py)_2$ in $CDCl_3$ (left) and in pyridine-d^5 (right), which leads to in situ production of the 6-coordinate complex $[(Ga\text{-}tpfc)_2]COT(py)_4$.

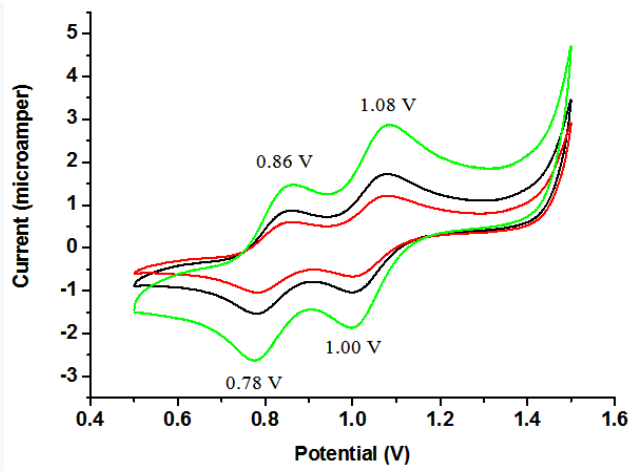

Figure S6. Cyclic voltammogram of $[(Ga\text{-}tpfc)_2]COT(py)_2$ (0.5 mM) in 0.1 M TBAP/dichloroethane solution. 50 mv/sec (red), black – 100 mv/sec, green - 250 mv/sec.

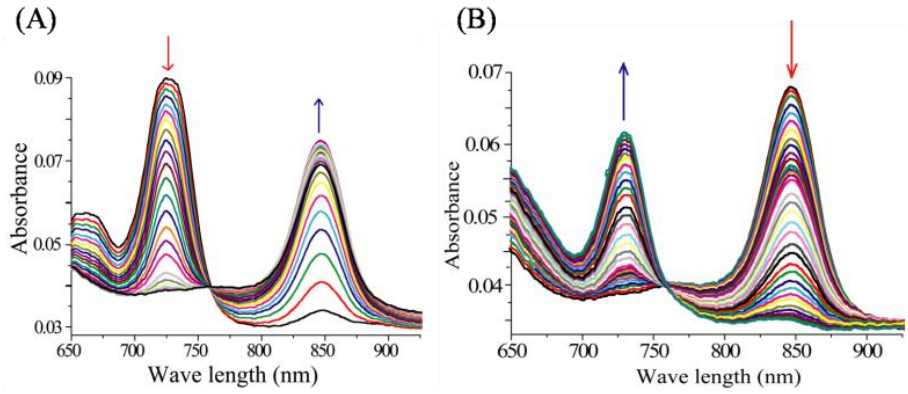

Figure S7. (A) Spectroelectrochemistry of $[(Ga\text{-}tpfc)_2]COT(py)_2$ (0.125 mM) in 0.2 M TBAP/dichloroethane solution at an applied potential of +1.2 V (1440 seconds, scanned every 60 seconds). (B) Reduction of the oxidized solution at an applied potential of +0.6 V (3600 seconds, scanned every 100 seconds).

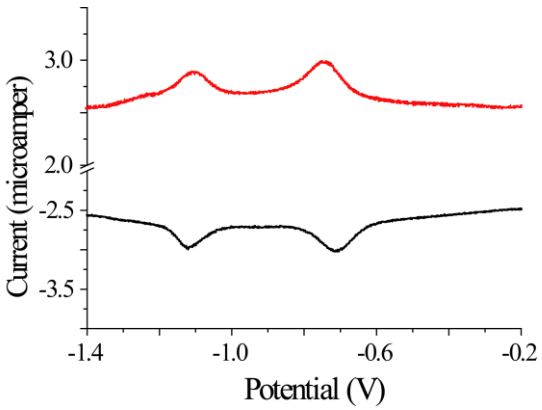

Figure S8. Square wave voltammogram of $[(Ga\text{-}tpfc)_2]COT(py)_2$ (0.5 mM) in 0.1M TBAP/pyridine solution at a scan rate of 250 mV/sec.

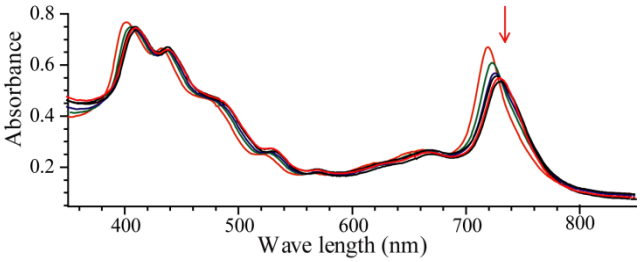

Figure S9. UV-vis changes upon titration of $[(Ga\text{-}tpfc)_2]COT(py)_2$ with $NaBH_4$, in pyridine solution at 298 K.

Table S3. Crystallographic table

	(H_3tpfc)$_2$COT	[(Ga-tpfc)$_2$]COT(py)$_2$	[(Ga-tpfc)$_2$]COT(py)$_4$
Formula	$C_{74}H_{18}F_{30}N_8$	$C_{86}H_{22}F_{30}Ga_2N_{10}Cl_4$	$C_{134}H_{72}F_{30}Ga_2N_{10}$
T (K)	200(2)	200(2)	200(2)
Formula weight	1570.82	2046.38	2671.56
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	*P*-1	*P* 21/c	*P*-1
a, Å	6.33(4)	17.516(11)	9.22(3)
b, Å	15.80(6)	10.025(16)	15.59(6)
c, Å	15.90(9)	25.875(15)	20.27(4)
α, deg	113.36(7)	90.0	96.33(5)
β, deg	94.3(2)	123.847(13)	98.49(3)
γ, deg	97.78(13)	90.0	90.73(12)
V, Å^3	1432(13)	3774(7)	2862(15)
Z	1	2	1
d_{calcd}, g•cm^{-3}	1.822	1.801	1.550
μ, mm^{-1}	0.178	0.989	0.584
F(000)	770	2016	1348
unique data	4311	5627	8717
parameters refined	505	605	838
GOF on F^2	1.044	1.059	1.074
*R*1[a] [$I > 2\sigma(I)$]	0.0678	0.0530	0.0634
*R*1[a] (all data)	0.1018	0.0670	0.0791
*wR*2[b] (all data)	0.1789	0.1426	0.1714

$$a\ R1 = \frac{\sum ||Fo| - |Fc||}{\sum |Fo|} \qquad b\ wR2 = \sqrt{\frac{\sum \left[w\left(Fo^2 - Fc^2\right)^2\right]}{\sum \left[w\left(Fo^2\right)^2\right]}}$$

DFT calculations

Computational Methods

All calculations were performed with the G09 program, revision D.01.[4] Geometries of all models were optimized and verified as minima, ensuring all positive frequencies. The "stable=opt" option was used prior to both geometry optimizations and UV electronic transitions calculations, to ensure lowest possible solution for the wave function. The unrestricted B3LYP functional[5] with 6-31g(d,p) basis set[6] was used for all geometry optimization calculations. The molecular orbitals, NBO charges and the UV spectra were computed with PBE1PBE and the cam-B3LYP[7] and B3LYP functionals.

Optimized geometries, UB3LYP/6-31G(d,p), appear at Scheme 2 in the main text

	1				**2**		
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C	-5.48084900	-0.02228000	-4.47630800
H	-6.74075400	1.67339400	-4.00066300
H	-4.13567700	-1.71712300	-4.56753600
H	-5.71686300	-0.02640700	-5.53602000

4

N	1.29959400	1.42136200	-0.00052600
N	1.30039900	-1.42064700	0.00031400
C	1.00877600	2.78635400	-0.00087000
C	2.26381900	3.48329600	-0.00115100
H	2.36667100	4.56062100	-0.00157300
C	3.27529800	2.55458400	-0.00072800
H	4.34044400	2.74401800	-0.00074200
C	2.67506200	1.25180300	-0.00032600
C	3.30617500	0.00092400	0.00023200
C	2.67580200	-1.25033600	0.00048100
C	3.27674400	-2.55276200	0.00033000
H	4.34198800	-2.74164200	0.00041100
C	2.26577700	-3.48204700	-0.00020000
H	2.36925400	-4.55931300	-0.00063900
C	1.01036100	-2.78582400	-0.00029100
N	-1.42938500	-1.24173700	-0.00018400
C	-1.47204900	-2.61167200	-0.00087800
C	-2.85574500	-2.97929700	-0.00119500
H	-3.24043600	-3.99072100	-0.00188400
C	-3.60744000	-1.80817500	-0.00051900
C	-2.69454200	-0.71680300	0.00019100
N	-1.43009800	1.24097100	0.00157900
C	-0.27469300	-3.34682100	-0.00088100
C	-2.69495800	0.71530200	0.00094100
C	-3.60847200	1.80616000	-0.00011300
C	-2.85745100	2.97771100	-0.00036800
H	-3.24273800	3.98890700	-0.00134200
C	-1.47354800	2.61088700	0.00036400
C	-0.27656900	3.34666700	-0.00050500
H	-0.33502500	-4.43032300	-0.00150500
H	4.39130400	0.00127900	0.00048100
H	-0.33742100	4.43014000	-0.00123600

C	-4.09560100	0.00008100	3.34783200
C	2.88637600	-0.00018900	-2.60681400
C	1.51630600	-0.00017700	-2.99149800
H	1.14940100	-0.00017800	-4.00900300
C	0.72643000	-0.00014000	-1.83037700
C	1.65183600	-0.00014100	-0.72174100
C	-1.65178000	-0.00005400	-0.72172600
C	-0.72638200	-0.00010400	-1.83037100
C	-1.51626100	-0.00011200	-2.99149100
H	-1.14935300	-0.00014900	-4.00899500
C	-2.88632900	-0.00007200	-2.60680000
C	-4.09558500	-0.00005600	-3.34780300
N	2.91222900	0.00002900	1.24469900
N	-2.91219600	0.00001000	1.24470600
C	4.09563300	-0.00019700	-3.34781600
C	-2.88633900	0.00005500	2.60684600
C	-1.51627100	0.00006800	2.99154300
H	-1.14936600	0.00010000	4.00904800
C	-0.72638800	0.00003100	1.83042500
C	-1.65178400	-0.00001400	0.72177800
C	1.65182000	-0.00003600	0.72176600
C	0.72642400	0.00005300	1.83041900
C	1.51630800	0.00017800	2.99153400
H	1.14940200	0.00027900	4.00903900
C	2.88637500	0.00015900	2.60683700
C	4.09563700	0.00026600	3.34782500
H	-4.02578300	-0.00008200	-4.43135300
H	4.02583900	-0.00020300	-4.43136600
H	8.75992000	-0.00006100	0.00000200
H	4.02585500	0.00039900	4.43137600
H	-4.02581800	0.00009800	4.43138300
H	-8.75987400	0.00015700	0.00000500
Ga	-4.39373300	0.00001800	0.00001200
Ga	4.39378100	-0.00005100	0.00001600
N	4.38833700	-2.24059600	0.00022100
C	4.37947300	-2.92447900	1.15312500
C	4.37974200	-2.92450300	-1.15267000
C	4.36531000	-4.31486200	1.19802200
H	4.38077200	-2.33358200	2.06140700
C	4.36559600	-4.31488600	-1.19755000
H	4.38124800	-2.33361800	-2.06095800
C	4.35957300	-5.02675000	0.00024200
H	4.35825300	-4.82533300	2.15494700
H	4.35876300	-4.82537400	-2.15446700
H	4.34891400	-6.11273400	0.00025200
N	-4.38829600	2.24061300	-0.00002200
C	-4.37956500	2.92452500	1.15286700
C	-4.37958200	2.92449300	-1.15292900
C	-4.36540900	4.31490900	1.19773700
H	-4.38097400	2.33364900	2.06115900
C	-4.36542500	4.31487600	-1.19783600
H	-4.38100100	2.33359400	-2.06120500
C	-4.35953400	5.02676800	-0.00005900
H	-4.35846200	4.82540200	2.15465100
H	-4.35849000	4.82534400	-2.15476300
H	-4.34887300	6.11275300	-0.00007400
N	-4.38849500	-2.24055100	0.00001300
C	-4.37992700	-2.92442300	-1.15290300
C	-4.37979300	-2.92448500	1.15289000
C	-4.36594400	-4.31480700	-1.19782800
H	-4.38132100	-2.33351500	-2.06117200
C	-4.36581600	-4.31487100	1.19774200
H	-4.38107000	-2.33362100	2.06118900
C	-4.36008800	-5.02671700	-0.00006200
H	-4.35911900	-4.82526100	-2.15476400
H	-4.35888900	-4.82537400	2.15465000
H	-4.34956500	-6.11270300	-0.00009200
N	4.38839100	2.24054800	-0.00009100
C	4.37962800	2.92457200	1.15272600
C	4.37978100	2.92431200	-1.15307000
C	4.36551600	4.31496100	1.19745800
Ga	0.02847000	0.00000900	0.00109000
H	-4.68762800	1.73250600	-0.00070100
H	-4.68663400	-1.73509500	-0.00041100

H	4.38096500	2.33378100	2.06107000
C	4.36566200	4.31469100	-1.19811600
H	4.38126500	2.33331800	-2.06128800
C	4.35972900	5.02670400	-0.00040900
H	4.35854100	4.82554800	2.15432100
H	4.35880400	4.82506000	-2.15509700
H	4.34910000	6.11268800	-0.00053400

5

N	0.01774700	1.86755900	-0.75108000
N	1.87832100	-0.28818900	-0.70794100
C	-1.09135700	2.69913200	-0.87299100
C	-0.60458400	4.02981300	-1.11960600
H	-1.23390500	4.89813800	-1.26725300
C	0.76514600	3.98082700	-1.16403900
H	1.44707100	4.79896600	-1.35613300
C	1.15908000	2.61521900	-0.94665000
C	2.45637700	2.08490200	-0.98450500
C	2.79348000	0.72530400	-0.91007300
C	4.08845500	0.12636000	-1.07889800
H	5.00420100	0.67227600	-1.26518200
C	3.93068800	-1.23581700	-1.00219100
H	4.69839900	-1.99097800	-1.11338600
C	2.53784100	-1.51357200	-0.78339900
N	-0.30654600	-1.92270200	-0.48103400
C	0.54204200	-2.98449400	-0.61618600
C	-0.26810600	-4.16064900	-0.73165600
H	0.09800700	-5.17147800	-0.85769000
C	-1.59908400	-3.75894500	-0.70544700
C	-1.60464600	-2.34294800	-0.56229500
N	-1.93966300	-0.03492400	-0.51689200
C	1.93001500	-2.77424300	-0.71580800
C	-2.54300100	-1.26099000	-0.58544700
C	-3.93717200	-1.04883300	-0.77154700
C	-4.13764900	0.32748000	-0.83814000
H	-5.07972300	0.83390600	-1.00502700
C	-2.85907200	0.95925400	-0.70546100
C	-2.43215500	2.29654800	-0.82866700
H	2.57844300	-3.63896900	-0.81538000
H	3.26926500	2.78484100	-1.14861900
H	-3.18217700	3.06861200	-0.96776300
Ga	-0.00097000	-0.01086600	-0.26920800
H	-4.69162200	-1.81824100	-0.86798800
H	-2.46997600	-4.39390500	-0.79933000
N	0.10576500	0.13681800	1.76370800
C	1.27550100	-0.03641100	2.40045600
C	-0.99829400	0.41880400	2.47554900
C	1.38235500	0.06141300	3.78179200
H	2.12914900	-0.26096000	1.77164600
C	-0.97087700	0.53569200	3.85920600
H	-1.90911100	0.55134600	1.90294700
C	0.23993900	0.35279600	4.52599600
H	2.34341100	-0.08740600	4.26081700
H	-1.88254300	0.76458100	4.39929900
H	0.29228200	0.43634700	5.60721000

6

N	-0.00004900	1.44501400	-1.31055700
N	0.00019400	-1.44450500	-1.31111600
C	-0.00014200	2.80093600	-1.01717700
C	-0.00009000	3.50152900	-2.27738400
H	-0.00013800	4.57861600	-2.38814700
C	0.00002800	2.56629900	-3.28361000
H	0.00009000	2.75257300	-4.34992300
C	0.00007700	1.26160100	-2.67045900
C	0.00027300	0.00064600	-3.29957300
C	0.00039000	-1.26054600	-2.67094300
C	0.00074500	-2.56500000	-3.28461800
H	0.00092000	-2.75084800	-4.35100500
C	0.00079400	-3.50063300	-2.27876700
H	0.00104400	-4.57767500	-2.38996000
C	0.00046400	-2.80054600	-1.01828100
N	-0.00004100	-1.25456500	1.44493700
C	0.00012300	-2.61510600	1.48577800
C	-0.00004600	-2.98463800	2.87395500
H	0.00002100	-3.99464500	3.26408900
C	-0.00030200	-1.81014900	3.62226500
C	-0.00029100	-0.72159800	2.69945100
N	-0.00021700	1.25399400	1.44542700
C	0.00038300	-3.35669200	0.27716200
C	-0.00041300	0.72053700	2.69973100
C	-0.00068700	1.80872500	3.62297500
C	-0.00067200	2.98350700	2.87512800
H	-0.00085000	3.99336300	3.26564800
C	-0.00038600	2.61451500	1.48680600
C	-0.00032400	3.35657600	0.27848600
H	0.00057000	-4.44060900	0.34209900
H	0.00038000	0.00085500	-4.38510600
H	-0.00043400	4.44046700	0.34383900
Ga	0.00000200	-0.00001100	-0.02712600
H	-0.00088600	1.73148300	4.70225900
H	-0.00047200	-1.73332600	4.70157800
N	2.24545600	0.00020300	-0.02198600
C	2.92981300	-1.15254100	-0.01333300
C	2.92959100	1.15307900	-0.01343400
C	4.32025700	-1.19744000	0.00141300
H	2.33888900	-2.06081100	-0.01456600
C	4.32002800	1.19824300	0.00129600
H	2.33849500	2.06123500	-0.01473000
C	5.03200900	0.00047000	0.00763200
H	4.83077600	-2.15434500	0.00832400
H	4.83036000	2.15524700	0.00810500
H	6.11796400	0.00057400	0.01872600
N	-2.24543400	-0.00014300	-0.02244200
C	-2.92982000	1.15258100	-0.01379400
C	-2.92953600	-1.15304200	-0.01406900
C	-4.32026900	1.19743800	0.00075200
H	-2.33891600	2.06086500	-0.01482800
C	-4.31997300	-1.19824600	0.00044400
H	-2.33842200	-2.06118900	-0.01535400
C	-5.03198800	-0.00049200	0.00675900
H	-4.83081000	2.15433100	0.00766000
H	-4.83027800	-2.15526600	0.00711400
H	-6.11794500	-0.00062900	0.01768200

Optimized geometries, UB3LYP/6-31G(d,p) of charged species

2^+

N	-5.56489400	1.42233000	0.87276100
N	-5.56835300	-1.41104900	0.85921500
C	-5.25108400	2.78096400	0.92909400
C	-6.43228600	3.47909400	1.39034100
H	-6.49297000	4.54879000	1.54144300
C	-7.40480200	2.55219600	1.62765200
H	-8.40270300	2.72559200	2.00739700
C	-6.85445000	1.25046800	1.31683800
C	-7.47561700	0.00630600	1.47943400
C	-6.85570100	-1.23823100	1.29961600
C	-7.41384100	-2.53903900	1.60093900
H	-8.41409300	-2.70983100	1.97548900
C	-6.44577300	-3.46786200	1.35967600
H	-6.51219200	-4.53849100	1.50090900
C	-5.26096800	-2.77034700	0.90573200
N	5.56835300	-1.41104800	-0.85921500
N	5.56489400	1.42233000	-0.87276000
N	2.91196300	-1.24058300	-0.18238400
N	-2.91196200	-1.24058300	0.18238400
C	5.26096800	-2.77034600	-0.90573300
C	6.44577300	-3.46786100	-1.35967900
H	6.51219100	-4.53849000	-1.50091200
C	7.41384100	-2.53903800	-1.60094100
H	8.41409200	-2.70983000	-1.97549300
C	6.85570100	-1.23823000	-1.29961700
C	7.47561700	0.00630700	-1.47943600
C	6.85445000	1.25046900	-1.31683800
C	7.40480200	2.55219700	-1.62765200
H	8.40270200	2.72559300	-2.00739900
C	6.43228500	3.47909400	-1.39034100
H	6.49297000	4.54879000	-1.54144200
C	5.25108400	2.78096500	-0.92909300
C	4.01118800	3.33983500	-0.65279300
C	-2.85023300	-2.59652500	0.33174600
C	-1.49560300	-2.98147500	0.22945600
H	-1.11983300	-3.99058300	0.32179200
C	-0.71695600	-1.81850700	0.06649300
C	-1.65224300	-0.71477300	0.06358200
C	1.65224400	-0.71477300	-0.06358200
C	0.71695600	-1.81850600	-0.06649400
C	1.49560300	-2.98147500	-0.22945700
H	1.11983300	-3.99058300	-0.32179300
C	2.85023300	-2.59652500	-0.33174700
C	4.02412000	-3.33804200	-0.63568100
N	-2.91245600	1.23447600	0.19217100
N	2.91245600	1.23447600	-0.19217100
C	-4.02412000	-3.33804200	0.63568000
C	2.84656200	2.59016600	-0.34141500
C	1.49235700	2.97535100	-0.23493100
H	1.11706200	3.98448800	-0.32754700
C	0.71607400	1.81402200	-0.06806100
C	1.65506300	0.71019600	-0.06907500
C	-1.65506200	0.71019600	0.06907600
C	-0.71607400	1.81402200	0.06806100
C	-1.49235700	2.97535100	0.23493200
H	-1.11706200	3.98448800	0.32754800
C	-2.84656200	2.59016600	0.34141600
C	-4.01118800	3.33983400	0.65279400
H	3.93783800	-4.41472600	-0.73361700
H	-3.93783800	-4.41472700	0.73361500
H	-8.49945000	0.00428400	1.83608800
H	-3.91522300	4.41545900	0.75341000
H	3.91522300	4.41546000	-0.75340800
H	8.49944900	0.00428500	-1.83609000
Ga	4.42530900	0.00087400	-0.17266800
Ga	-4.42530900	0.00087400	0.17266900
N	-4.92903100	0.00108700	-1.78880400
C	-5.81324800	0.89496300	-2.26710900

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N	-5.60333300	1.41885900	0.81894500
N	-5.58758600	-1.42747900	0.87896000
C	-5.30570400	2.77822900	0.81647800
C	-6.50514300	3.47773400	1.18050600
H	-6.58573900	4.55393400	1.27306300
C	-7.49163000	2.54359600	1.41567100
H	-8.51015800	2.73028900	1.73364200
C	-6.92551000	1.24715300	1.20121600
C	-7.53571000	-0.00455400	1.37294700
C	-6.90968700	-1.25173500	1.25013900
C	-7.46468500	-2.54454800	1.52545600
H	-8.48231800	-2.72513200	1.84974200
C	-6.47147600	-3.47661900	1.33521300
H	-6.54199400	-4.54846300	1.47419000
C	-5.27731000	-2.78078900	0.93856800
N	5.60330700	-1.41920900	-0.81842900
N	5.58757600	1.42711300	-0.87924400
N	2.91753100	-1.22985600	-0.22605500
N	-2.89911800	-1.24937500	0.29359800
C	5.30573400	-2.77858200	-0.81563600
C	6.50518100	-3.47814400	-1.17957600
H	6.58577700	-4.55436700	-1.27186600
C	7.49162400	-2.54404700	-1.41498300
H	8.51014800	-2.73075800	-1.73295800
C	6.92545600	-1.24754700	-1.20086400
C	7.53564600	0.00408400	-1.37301100
C	6.90962800	1.25132000	-1.25054700
C	7.46455400	2.54405600	-1.52628400
H	8.48214600	2.72459900	-1.85072200
C	6.47131300	3.47614900	-1.33623700
H	6.54178700	4.54795200	-1.47554400
C	5.27722900	2.78039800	-0.93926200
C	4.01742100	3.34660200	-0.69991700
C	-2.84146600	-2.61106600	0.42533900
C	-1.48133800	-2.98399900	0.29635700
H	-1.09561600	-3.99170600	0.37156600
C	-0.70818000	-1.81509300	0.12227300
C	-1.64199500	-0.72378200	0.13843500
C	1.65482200	-0.71395900	-0.10219500
C	0.73078800	-1.81300000	-0.03766200
C	1.51451100	-2.97858500	-0.15744700
H	1.14208100	-3.99367200	-0.18417500
C	2.87215900	-2.59614000	-0.29784700
C	4.04775200	-3.33808300	-0.54147200
N	-2.91748400	1.22956500	0.22669900
N	2.89901200	1.24905300	-0.29422300
C	-4.01753300	-3.34697600	0.69908300
C	2.84137300	2.61074700	-0.42602800
C	1.48126100	2.98369500	-0.29687000
H	1.09553700	3.99140200	-0.37210300
C	0.70811900	1.81481000	-0.12256300
C	1.64192800	0.72348700	-0.13877300
C	-1.65483400	0.71366900	0.10238600
C	-0.73080500	1.81271200	0.03774100
C	-1.51449100	2.97829400	0.15786700
H	-1.14203800	3.99337300	0.18462900
C	-2.87211900	2.59586000	0.29853200
C	-4.04769500	3.33774800	0.54237200
H	3.97046100	-4.42013100	-0.58734600
H	-3.93625600	-4.42533000	0.79548500
H	-8.57906200	-0.00541000	1.67497800
H	-3.97040200	4.41979000	0.58841700
H	3.93613900	4.42493900	-0.79652100
H	8.57897100	0.00483200	-1.67513300
Ga	4.41512900	0.01775300	-0.23919100
Ga	-4.41513400	-0.01791500	0.23928800
N	-4.83453400	-0.07727800	-1.75153000
C	-5.67546800	0.82004900	-2.30148000

C	-4.38890300	-0.90239100	-2.62698800
C	-6.18462500	0.92049100	-3.60425600
H	-6.21807600	1.59765900	-1.54886100
C	-4.71312200	-0.94126800	-3.97588000
H	-3.68601200	-1.60001200	-2.18769300
C	-5.62629700	-0.01348900	-4.47635400
H	-6.89898300	1.65789600	-3.95180400
H	-4.25696300	-1.68514000	-4.61886500
H	-5.89854100	-0.01891500	-5.52700500
N	4.92903100	0.00108600	1.78880400
C	5.81324500	0.89496500	2.26711100
C	4.38890500	-0.90239500	2.62698600
C	6.18462100	0.92049100	3.60425800
H	6.21807100	1.59766300	1.54886400
C	4.71312500	-0.94127300	3.97587900
H	3.68601700	-1.60001800	2.18769000
C	5.62629600	-0.01349100	4.47635500
H	6.89897600	1.65789800	3.95180800
H	4.25696800	-1.68514800	4.61886300
H	5.89853900	-0.01891800	5.52700600

2^-- singlet

N	5.57365100	1.39918600	-0.95345500
N	5.58759600	-1.44213100	-0.83415400
C	5.26564000	2.75109000	-1.02597300
C	6.44594300	3.43883600	-1.47957900
H	6.51231900	4.50871700	-1.63975400
C	7.42968600	2.50054300	-1.68762800
H	8.43619300	2.67099700	-2.05235500
C	6.87946800	1.21447100	-1.36656200
C	7.49971400	-0.03586200	-1.49127500
C	6.89234900	-1.28208300	-1.27074100
C	7.44714600	-2.58322800	-1.49179100
H	8.45193600	-2.77696700	-1.84960600
C	6.46662400	-3.51019000	-1.20544400
H	6.53741800	-4.58866100	-1.28678700
C	5.28690800	-2.79801000	-0.80132700
N	-5.58273000	-1.39781300	0.95091000
N	-5.59735500	1.44401000	0.82432400
N	-2.91201700	-1.24021100	0.29025400
N	2.91983000	-1.23674900	-0.17391500
C	-5.27421500	-2.74905900	1.03209900
C	-6.45681500	-3.43574500	1.48110300
H	-6.52370100	-4.50492700	1.64556000
C	-7.44239900	-2.49695800	1.67882000
H	-8.45114200	-2.66626000	2.03788600
C	-6.89150600	-1.21209900	1.35498900
C	-7.51307100	0.03797200	1.47126900
C	-6.90498000	1.28387900	1.25167100
C	-7.46155100	2.58445100	1.46825500
H	-8.46910200	2.77798000	1.81827600
C	-6.47942500	3.51208400	1.18796600
H	-6.55109500	4.59053000	1.26902800
C	-5.29615700	2.80011300	0.79420700
C	-4.04177500	3.35274700	0.48930600
C	2.86727800	-2.60199500	-0.23380700
C	1.50684900	-2.97943700	-0.09140700
H	1.12970000	-3.99333000	-0.11428500
C	0.72676700	-1.81054700	0.01174900
C	1.65921500	-0.71727900	-0.06058100
C	-1.65476400	-0.71959900	0.13476500
C	-0.71519800	-1.80742700	0.15925500
C	-1.48890400	-2.97112700	0.36081400
H	-1.10175800	-3.97510900	0.47495900
C	-2.85064600	-2.59511000	0.46639300
C	-4.02147600	-3.32353400	0.78014800
N	2.90711700	1.24100200	-0.27549700
N	-2.92518800	1.23726800	0.18294700
C	4.03456600	-3.35155400	-0.49140200
C	-2.87278900	2.60264600	0.24044700
C	-1.51200700	2.97979500	0.10172300
H	-1.13491700	3.99371000	0.12293800

C	-4.26669400	-1.01251200	-2.53893400
C	-5.97560400	0.81551000	-3.65508700
H	-6.09712100	1.54863500	-1.61875300
C	-4.51995300	-1.08005900	-3.90076900
H	-3.60125200	-1.70813300	-2.04121600
C	-5.38917200	-0.15047900	-4.47784800
H	-6.65557400	1.55868400	-4.05732800
H	-4.03923500	-1.84714600	-4.49794900
H	-5.60233300	-0.17662100	-5.54208300
N	4.83463200	0.07796200	1.75155300
C	4.26565200	1.01269500	2.53874400
C	5.67675100	-0.81813800	2.30167600
C	4.51890400	1.08091900	3.90054500
H	3.59931700	1.70733900	2.04086100
C	5.97699800	-0.81283200	3.65525100
H	6.09928800	-1.54638900	1.61913100
C	5.38936500	0.15261500	4.47780300
H	4.03723600	1.84754300	4.49755500
H	6.65797000	-1.55499900	4.05765500
H	5.60258100	0.17931600	5.54201300

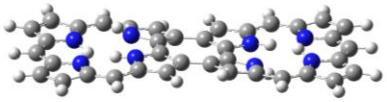
2^-- triplet

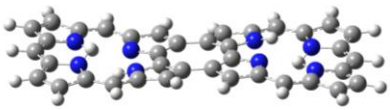
N	5.59132600	1.42890600	-0.84409600
N	5.57385000	-1.41417900	-0.93809600
C	5.29177700	2.78531100	-0.82412200
C	6.47350500	3.49256400	-1.22933200
H	6.54582500	4.57026200	-1.31954300
C	7.45458100	2.56197300	-1.50446400
H	8.46088000	2.75196600	-1.86008300
C	6.89787000	1.26369300	-1.27503100
C	7.50360000	0.01462300	-1.48414900
C	6.88103400	-1.23397000	-1.35230700
C	7.42849700	-2.52201200	-1.66514600
H	8.43474800	-2.69681000	-2.02855000
C	6.44212000	-3.45759900	-1.45118000
H	6.50631300	-4.52848400	-1.60569400
C	5.26385000	-2.76555900	-1.00192300
N	-5.60025900	-1.43235200	0.83275000
N	-5.58241800	1.41151000	0.93502400
N	-2.92539000	-1.23343000	0.19779800
N	2.90623600	-1.24762900	-0.26334300
C	-5.30024500	-2.78901000	0.81612900
C	-6.48629900	-3.49613100	1.20894700
H	-6.55974400	-4.57381500	1.29853400
C	-7.46956800	-2.56500300	1.47533400
H	-8.47932700	-2.75480600	1.82107700
C	-6.91068200	-1.26713800	1.25127500
C	-7.51769600	-0.01846100	1.45806400
C	-6.89356500	1.23014000	1.33654300
C	-7.44232100	2.51692600	1.65166200
H	-8.45168600	2.69054000	2.00693500
C	-6.45333500	3.45297200	1.45149400
H	-6.51827400	4.52306300	1.61103300
C	-5.27171900	2.76217100	1.00923200
C	-4.01688300	3.33411500	0.75437800
C	2.84270700	-2.60474000	-0.42667500
C	1.48130500	-2.97817500	-0.31397800
H	1.09292400	-3.98272500	-0.41808700
C	0.70829500	-1.81067900	-0.12490000
C	1.64886300	-0.72367300	-0.11422200
C	-1.66401200	-0.71553400	0.08193800
C	-0.73217800	-1.80953400	0.02194500
C	-1.51435500	-2.97793400	0.13382400
H	-1.13779600	-3.99175700	0.16679200
C	-2.87401300	-2.59848700	0.26818300
C	-4.04474000	-3.34573300	0.52122600
N	2.92078300	1.23141500	-0.18950600
N	-2.91004500	1.24537600	0.28060500
C	4.01110100	-3.33720400	-0.73791300
C	-2.84693900	2.60228100	0.44578500
C	-1.48507500	2.97574200	0.33549200
H	-1.09655200	3.98007400	0.44137700

C	-0.73197200	1.81050700	0.00183600
C	-1.66451100	0.71743500	0.07221500
C	1.64935400	0.71999900	-0.12104600
C	0.71008900	1.80785800	-0.14364500
C	1.48378100	2.97192100	-0.34415800
H	1.09664300	3.97599200	-0.45728500
C	2.84508100	2.59596000	-0.45149800
C	4.01430200	3.32506100	-0.76803400
H	-3.93816200	-4.39933200	0.90607800
H	3.95255000	-4.43423600	-0.52618500
H	8.53239400	-0.04333000	-1.83017000
H	3.93044200	4.40111100	-0.89131600
H	-3.95967100	4.43550300	0.52230000
H	-8.54783100	0.04595200	1.80374200
Ga	-4.44291800	-0.00892900	0.16661400
Ga	4.43915800	0.00941300	-0.16306900
N	4.94218700	0.11042200	1.74987800
C	4.23256400	0.88587900	2.63184100
C	6.01602800	-0.58289400	2.24500400
C	4.55937800	0.98255600	3.96505800
H	3.38800900	1.41805300	2.21147800
C	6.39695400	-0.52105600	3.56537900
H	6.55232000	-1.18821700	1.52410000
C	5.66835700	0.27450300	4.47884700
H	3.95085700	1.61057800	4.60962800
H	7.25962700	-1.09600800	3.89144000
H	5.94477900	0.33463100	5.52632100
N	-4.92679900	-0.11496000	-1.75120400
C	-5.82347500	0.75588600	-2.31357500
C	-4.37576100	-1.06845100	-2.56919100
C	-6.18083800	0.70076700	-3.64107600
H	-6.23434100	1.50010400	-1.64202600
C	-4.69283400	-1.17402300	-3.90400500
H	-3.66914100	-1.73911100	-2.09570900
C	-5.61838900	-0.28062700	-4.48795300
H	-6.89653900	1.42351800	-4.02372200
H	-4.21733500	-1.95063700	-4.49643100
H	-5.87942100	-0.34079700	-5.53937700

C	-0.71230000	1.80875000	0.14335500
C	-1.65320900	0.72187100	0.12960700
C	1.65954900	0.71392000	-0.07002500
C	0.72797500	1.80813800	-0.00668200
C	1.51016800	2.97616500	-0.12150600
H	1.13353300	3.98997000	-0.15497400
C	2.86939200	2.59635600	-0.26081900
C	4.03854600	3.34290100	-0.52215300
H	-3.96367500	-4.42821800	0.56411300
H	3.92655100	-4.41410400	-0.85287800
H	8.53689500	0.01782100	-1.82135600
H	3.95776600	4.42535600	-0.56581100
H	-3.93257100	4.41061600	0.87329100
H	-8.55389100	-0.02234400	1.78624800
Ga	-4.44117200	0.01405200	0.17059800
Ga	4.43818500	-0.01550800	-0.16701800
N	4.93267900	-0.09033900	1.75441600
C	5.98840800	0.62843800	2.24789200
C	4.23140700	-0.86926900	2.63722400
C	6.35941400	0.59022100	3.57265700
H	6.51919100	1.23421800	1.52329200
C	4.54864300	-0.94515800	3.97459900
H	3.40156800	-1.42276500	2.21490300
C	5.63855200	-0.20867200	4.48814500
H	7.20809900	1.18510000	3.89930500
H	3.94773500	-1.57780400	4.62156900
H	5.90717300	-0.25111000	5.53854700
N	-4.91782000	0.09652800	-1.75524400
C	-4.36342600	1.03959700	-2.58016400
C	-5.81027100	-0.78129800	-2.30959400
C	-4.67239000	1.12836800	-3.91866400
H	-3.66065700	1.71689700	-2.11023600
C	-6.15933000	-0.74503100	-3.64054200
H	-6.22524700	-1.51568600	-1.62975000
C	-5.59248300	0.22573900	-4.49569600
H	-4.19474800	1.89802100	-4.51819000
H	-6.87219200	-1.47302700	-4.01819200
H	-5.84759400	0.27223800	-5.54929400

Optimized geometries of free base bis-corrole, 2-no Ga, UB3LYP/6-31G(d,p)





N	-5.52966000	-1.44672000	-0.05638400
N	-5.65923100	1.45121000	-0.06368800
H	-5.04407600	0.73518500	-0.42216700
C	-5.29091800	-2.80764900	-0.04398300
C	-6.55089200	-3.52854800	-0.10327100
H	-6.65528300	-4.60610000	-0.10530500
C	-7.53709600	-2.59092300	-0.13474300
H	-8.60719800	-2.75024900	-0.17448100
C	-6.88307200	-1.29082700	-0.10196000
C	-7.57718300	-0.06132100	-0.08940400
C	-7.01937400	1.21312700	-0.03639900
C	-7.63982700	2.50079000	0.07897400
H	-8.70626300	2.66188500	0.15876400
C	-6.65352200	3.45934600	0.10011300
H	-6.78527600	4.52746000	0.20800400
C	-5.37626800	2.81151300	0.00071400
N	5.52966000	1.44672100	0.05638100
N	5.65923100	-1.45121000	0.06369100
H	5.04407700	-0.73518400	0.42217100
N	2.87947400	1.30544200	-0.19227800
H	3.80795900	0.88814600	-0.06804500
N	-2.91567400	1.25905400	0.27436900
H	-3.62892500	0.84369000	0.85698800
C	5.29091700	2.80765000	0.04397900

N	-5.59722600	-1.48457900	0.12067700
N	-5.60696200	1.51903100	0.00782600
H	-4.81574400	0.89523900	-0.14939500
C	-5.32455400	-2.85978400	-0.00358200
C	-6.59757100	-3.48990600	-0.15680600
H	-6.73385400	-4.54854300	-0.33248300
C	-7.58303000	-2.52801900	-0.10972500
H	-8.64600300	-2.68225000	-0.23739900
C	-6.97333100	-1.24895600	0.07741900
C	-7.57238600	0.00794700	0.13837100
C	-6.95228400	1.27144300	0.12484300
C	-7.57725900	2.55954200	0.20414200
H	-8.64191100	2.71344700	0.31576500
C	-6.59913400	3.52897000	0.12332400
H	-6.73881700	4.60091300	0.15451700
C	-5.33615700	2.87328400	-0.00787900
N	5.59729900	1.48459600	-0.12035300
N	5.60697400	-1.51895800	-0.00829000
H	4.81575400	-0.89517100	0.14895000
N	2.87254200	1.30948500	0.26342700
H	3.64358800	0.77945000	0.63246800
N	-2.96085000	1.20194800	-0.25375100
C	5.32455700	2.85974300	0.00426100
C	6.59754500	3.48987200	0.15767300

C	6.55089100	3.52854800	0.10326500
H	6.65528300	4.60610100	0.10529800
C	7.53709500	2.59092400	0.13473900
H	8.60719700	2.75025000	0.17447600
C	6.88307200	1.29082800	0.10195700
C	7.57718300	0.06132200	0.08940400
C	7.01937400	-1.21312600	0.03640100
C	7.63982700	-2.50079000	-0.07897100
H	8.70626300	-2.66188400	-0.15876100
C	6.65352300	-3.45934600	-0.10010800
H	6.78527600	-4.52746000	-0.20799700
C	5.37626800	-2.81151300	-0.00070900
C	4.09806000	-3.36870000	-0.01073400
C	-2.90112600	2.62413500	0.05400900
C	-1.55007600	2.95273200	-0.15739900
H	-1.19221800	3.94058500	-0.40802700
C	-0.75777200	1.78841300	-0.06954000
C	-1.64581000	0.70198700	0.18488100
C	1.63915000	0.72192400	-0.18570300
C	0.69651800	1.80786100	-0.16122400
C	1.44749500	2.99487100	-0.14447600
H	1.04828100	3.99698500	-0.08812600
C	2.82345800	2.66965000	-0.14355300
C	4.02330700	3.39965200	-0.04009200
N	-2.87947400	-1.30544200	0.19227500
H	-3.80795800	-0.88814600	0.06804100
N	2.91567400	-1.25905500	-0.27436700
H	3.62892600	-0.84369200	-0.85698600
C	-4.09806000	3.36870000	0.01074000
C	2.90112600	-2.62413500	-0.05400500
C	1.55007600	-2.95273200	0.15740200
H	1.19221800	-3.94058500	0.40803200
C	0.75777200	-1.78841300	0.06954100
C	1.64581000	-0.70198800	-0.18488100
C	-1.63915000	-0.72192500	0.18570100
C	-0.69651800	-1.80786200	0.16122300
C	-1.44749600	-2.99487100	0.14447300
H	-1.04828100	-3.99698500	0.08812300
C	-2.82345800	-2.66965100	0.14354900
C	-4.02330700	-3.39965200	0.04008700
H	3.96437000	4.48263500	-0.01817800
H	-4.02396900	4.44947300	-0.03036700
H	-8.66130100	-0.11319600	-0.09733700
H	-3.96437000	-4.48263500	0.01817200
H	4.02397000	-4.44947300	0.03037500
H	8.66130100	0.11319700	0.09733600
H	6.73378100	4.54846300	0.33366200
C	7.58304900	2.52804300	0.11033500
H	8.64601400	2.68229000	0.23804800
C	6.97340300	1.24901500	-0.07716800
C	7.57244400	-0.00788100	-0.13855400
C	6.95230500	-1.27136300	-0.12528800
C	7.57726500	-2.55946000	-0.20479800
H	8.64191600	-2.71335700	-0.31645000
C	6.59914000	-3.52889200	-0.12407000
H	6.73881800	-4.60083200	-0.15539500
C	5.33616800	-2.87321700	0.00726500
C	4.03260300	-3.37322800	0.11840500
C	-2.88365000	2.56520600	-0.20982600
C	-1.50602400	2.95646900	-0.16805600
H	-1.14565100	3.97416900	-0.10032700
C	-0.73539800	1.80267500	-0.15477900
C	-1.69993700	0.70710100	-0.20873300
C	1.63541700	0.72461400	0.17421100
C	0.71522100	1.80265100	-0.05167200
C	1.48853300	2.98200600	-0.12078400
H	1.11205400	3.97075300	-0.33841700
C	2.84989900	2.66459400	0.06915600
C	4.04659200	3.41457100	0.02706300
N	-2.87263100	-1.30957200	-0.26309300
H	-3.64369400	-0.77973800	-0.63241900
N	2.96084400	-1.20198300	0.25340400
C	-4.03257500	3.37325300	-0.11905100
C	2.88365500	-2.56522900	0.20937900
C	1.50602500	-2.95651100	0.16772600
H	1.14564800	-3.97420800	0.09995400
C	0.73538200	-1.80272000	0.15465000
C	1.69990100	-0.70715200	0.20857200
C	-1.63548400	-0.72467500	-0.17411800
C	-0.71525700	-1.80267700	0.05182100
C	-1.48854800	-2.98202500	0.12123600
H	-1.11202700	-3.97072100	0.33903300
C	-2.84993000	-2.66465300	-0.06861000
C	-4.04660600	-3.41463000	-0.02622800
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H	-3.90745800	4.45109900	-0.09729300
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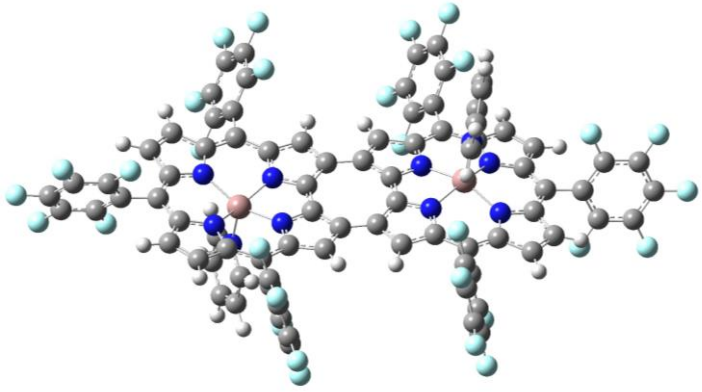
H	-3.97290900	-4.49637500	-0.01520900
H	3.90751800	-4.45107500	0.09649000
H	8.65707100	-0.01665400	-0.16255800
H	5.00503500	0.91305900	-0.70923200
H	-5.00487000	-0.91288200	0.70934600

Optimized geometry of the full model 2, including pentafluoropehnyl groups at the *meso* positions, UB3LYP/6-31G(d,p)



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H	6.68238300	4.52585500	-0.64238400
C	-5.03111900	1.22154400	-4.39076900
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C	7.58787400	2.52815300	-0.56918500
H	8.63130100	2.71293800	-0.77992200
C	6.99868700	1.23646700	-0.35721000
C	7.64703300	-0.01658000	-0.39425800
C	6.99831000	-1.26609200	-0.31153400
C	7.59471000	-2.56788500	-0.42632800
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C	-6.59256900	-3.49498300	0.32719100
H	-6.69947800	-4.56867500	0.38169900
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H	-8.63126900	2.71305700	0.77972700
C	-6.58545000	3.45936400	0.49808300
H	-6.68230500	4.52592800	0.64213000
C	-5.35214200	2.76772600	0.24352100
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C	1.65771800	0.70824700	0.08588600
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C	2.87643300	2.58744200	-0.03213900
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C	9.96890400	0.42326300	0.47824400
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C	11.94253400	0.01862200	-0.83679000
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C	4.17769200	-5.65030700	-1.13392700
C	3.54632100	-5.50169900	1.15881200
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C	3.39185300	-6.88315400	1.22433100
C	3.63965200	-7.65368100	0.09048400
C	3.96698000	4.82901200	-0.15793500
C	4.46535200	5.58855000	0.90756700
C	3.36322700	5.53639500	-1.20351700
C	4.37969000	6.97723700	0.93733800
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C	-3.96693400	4.82902000	0.15779900
C	-4.46523400	5.58857300	-0.90770900
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C	-4.37960400	6.97726600	-0.93740200
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C	-3.77031200	7.64877500	0.12007100
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C	-9.96895800	0.42291800	-0.47832600
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C	-3.94031900	-4.84645900	0.01377900
C	-4.17735200	-5.65024600	1.13410400
C	-3.54669100	-5.50174300	-1.15883300
C	-4.03710900	-7.03606500	1.09290500
C	-3.39224500	-6.88320200	-1.22433700
C	-3.63969800	-7.65367900	-0.09038000
F	12.12489000	0.86666500	1.36320500
F	13.27180700	0.03169900	-0.97015200
F	11.70179600	-0.83031500	-3.02914300
F	9.01618300	-0.85330900	-2.77054700
F	9.44097400	0.83294800	1.64177200
F	-9.01605600	-0.85252200	2.77085400
F	-11.70165100	-0.82959800	3.02953700
F	-13.27179200	0.03166000	0.97031700
F	-12.12500000	0.86591500	-1.36335100
F	-9.44110000	0.83222200	-1.64202200
F	3.31830000	-4.79122000	2.27795600
F	3.01975100	-7.47474500	2.36602800
F	3.49891400	-8.98100200	0.14000700
F	4.27030400	-7.77458600	-2.18384400
F	4.55175200	-5.09292200	-2.29270200
F	-4.26964700	-7.77447500	2.18414900
F	-4.55103600	-5.09281200	2.29297700
F	-3.31900500	-4.79132200	-2.27808100
F	-3.02048500	-7.47484300	-2.36612000
F	-3.49897600	-8.98100100	-0.13988600
F	5.04381700	4.97549400	1.95567000
F	4.86642300	7.66776900	1.97555000
F	3.67796300	8.98119300	-0.10302200
F	2.67605500	7.56875300	-2.21329600
F	2.86653300	4.87938000	-2.26033500
F	-2.86669500	4.87924300	2.26029200
F	-2.67628900	7.56866800	2.21343700
F	-3.67804000	8.98117500	0.10315200
F	-4.86628700	7.66784800	-1.97560400
F	-5.04362200	4.97552400	-1.95585500

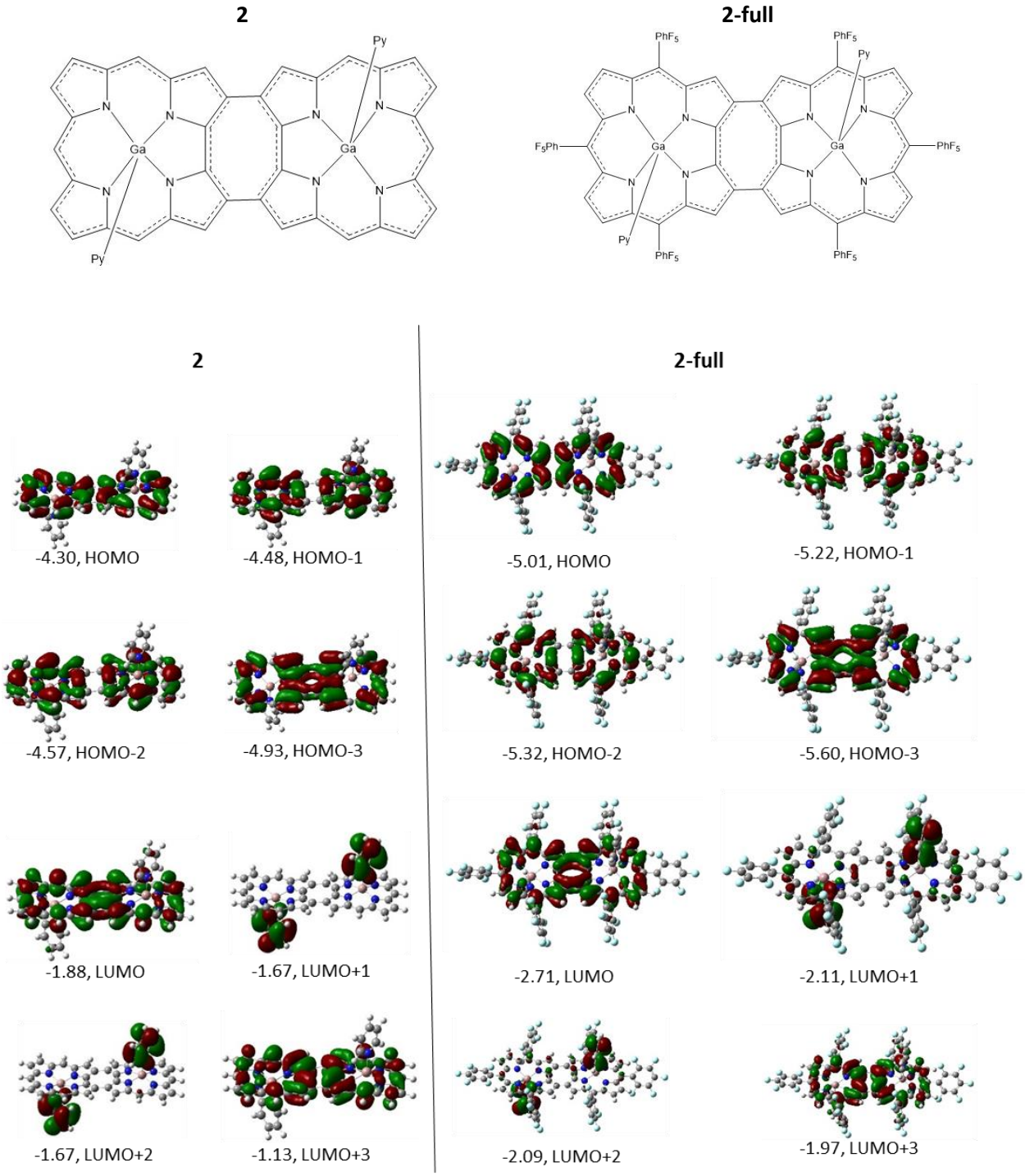

Figure S10. Comparison between the model systems, 2, and the full complex – computed FMOs, UPBE1PBE/6-31G(d,p) //UB3LYP/6-31G(d,p).

The FMOs of **2** and **2-full** have the same shape. The energies of FMOs of **2-full** are lower than those of **2**, due to the electronegative penta-fluoro-phenyl substituent's in **2-full**, which eventually lower the HOMO-LUMO gap.

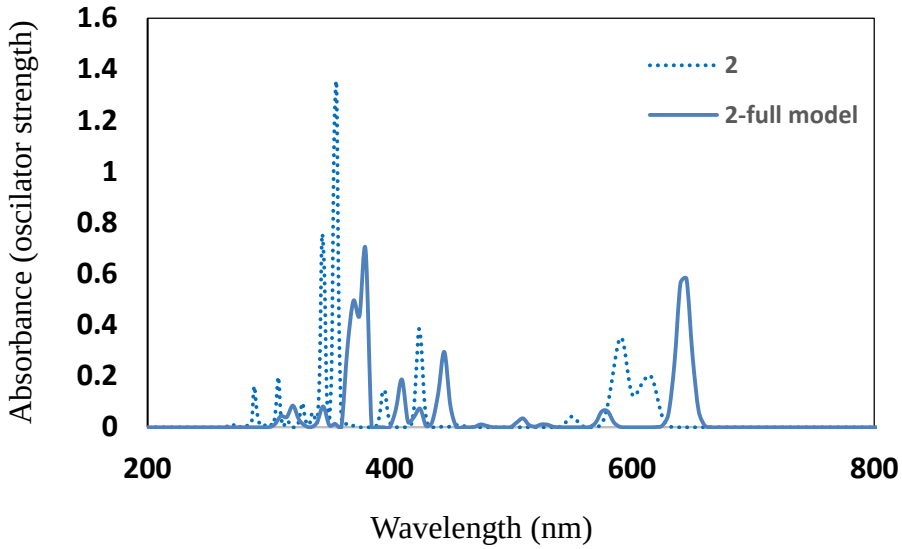

Figure S11. Computed UV spectra of model Ga bis-corrole, **2**, and the full system, **2-full**, with the six penta-fluoro-phenyl substituents at the *meso* positions, UPBE1PBE/6-31G(d,p) //UB3LYP/6-31G(d,p).

The computed UV spectra of **2-full** is shifted to higher wavelength, i.e. lower transition energies, corresponding to the reduced HOMO-LUMO gap in **2-full** compared to **2**.

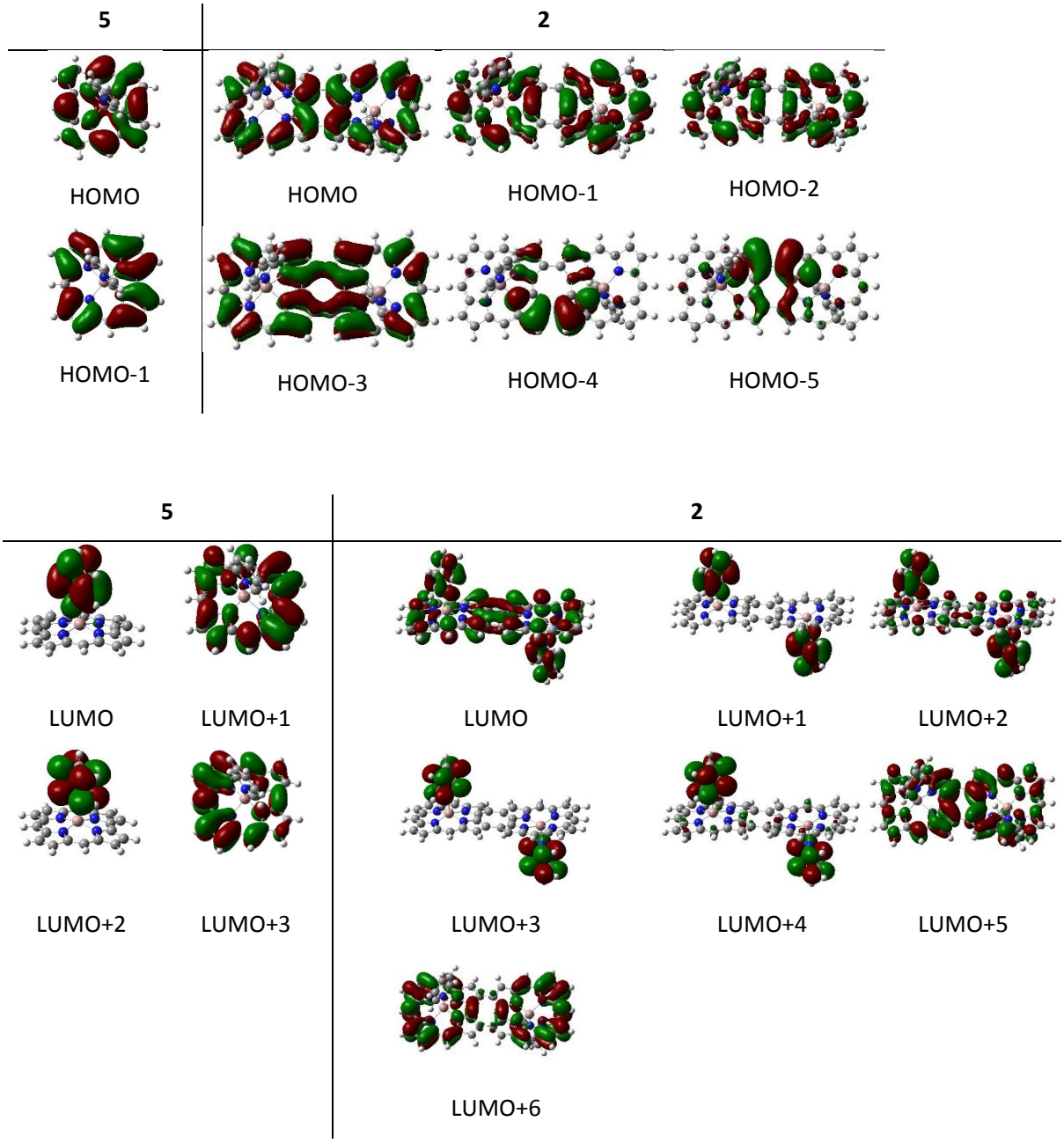

Figure S12: Molecular orbitals computed at the **UB3LYP/6-31G(d,p)**//UB3LYP/6-31G, a.u./Å^3

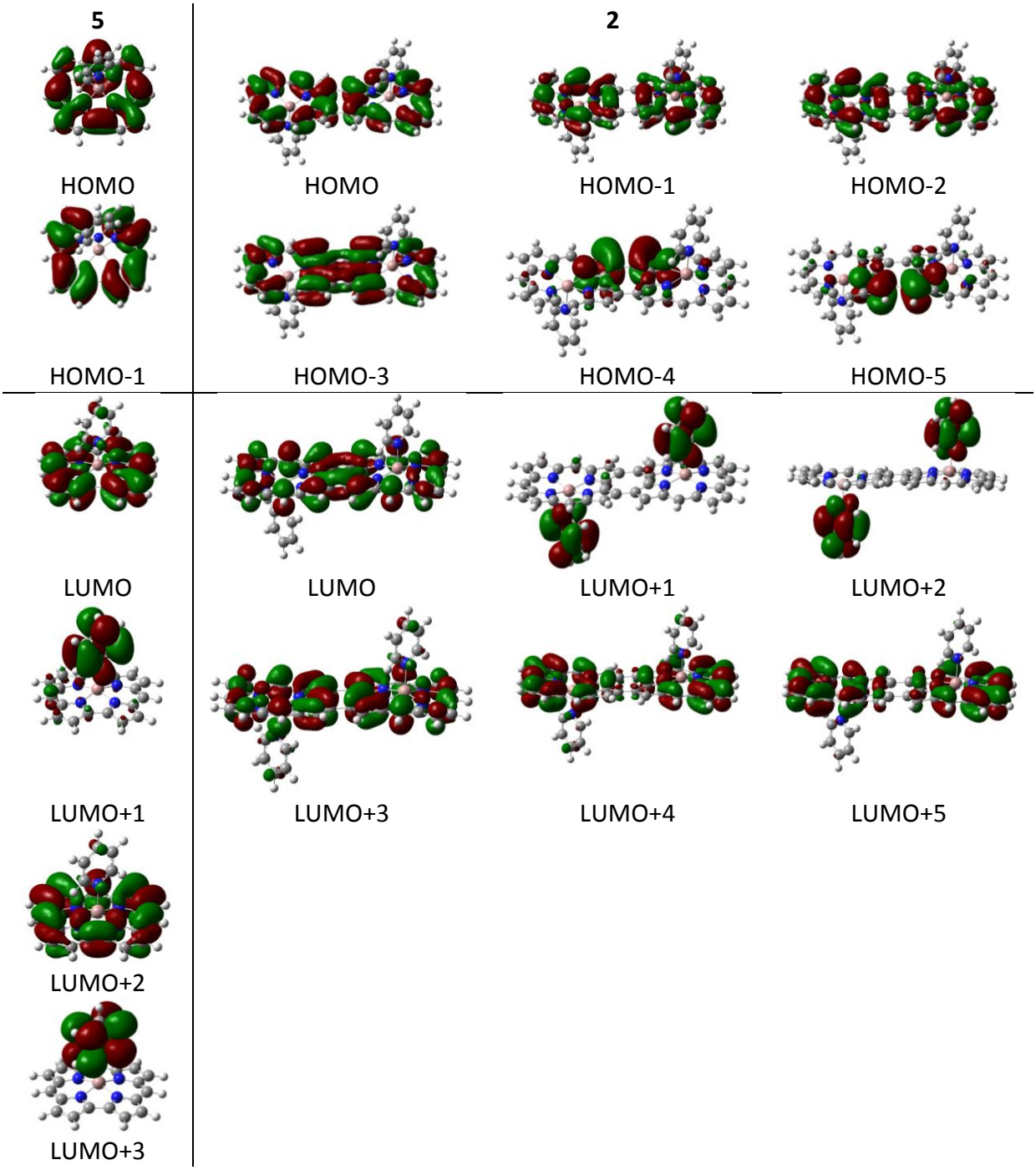

Figure S13: Molecular orbitals computed at the **UCAM-B3LYP/6-31G(d,p)**//UB3LYP/6-31G, a.u./Å^3

Table S4. Computed atomic NBO charges, q_{atom}, of **2**, $\mathbf{2}^{-\cdot}$ and $\mathbf{2}^{+\cdot}$.

atom	q_{atom}(**2**)	$q_{atom}(\mathbf{2}^{-\cdot})$	$\Delta q = q_{atom}(\mathbf{2}^{-\cdot}) - q_{atom}(\mathbf{2})$	$q_{atom}(\mathbf{2}^{+\cdot})$	$\Delta q = q_{atom}(\mathbf{2}^{+\cdot}) - q_{atom}(\mathbf{2})$
N	-0.735	-0.744	-0.009	-0.736	0.000
N	-0.726	-0.735	-0.009	-0.725	0.001
C	0.131	0.135	0.004	0.154	0.023
C	-0.263	-0.293	-0.030	-0.237	0.026
H	0.253	0.240	-0.013	0.267	0.014
C	-0.280	-0.294	-0.014	-0.262	0.018
H	0.253	0.239	-0.014	0.268	0.015
C	0.158	0.132	-0.027	0.200	0.042
C	-0.308	-0.309	-0.001	-0.317	-0.009
C	0.167	0.140	-0.026	0.210	0.043
C	-0.275	-0.287	-0.012	-0.260	0.015
H	0.252	0.238	-0.014	0.267	0.015
C	-0.259	-0.287	-0.028	-0.233	0.027
H	0.252	0.239	-0.013	0.266	0.014
C	0.142	0.146	0.004	0.161	0.019
N	-0.726	-0.744	-0.019	-0.725	0.001
N	-0.735	-0.735	0.000	-0.736	0.000
N	-0.709	-0.701	0.008	-0.707	0.002
N	-0.709	-0.714	-0.005	-0.707	0.002
C	0.142	0.135	-0.007	0.161	0.019
C	-0.259	-0.293	-0.033	-0.233	0.027
H	0.252	0.240	-0.013	0.266	0.014
C	-0.275	-0.294	-0.019	-0.260	0.015
H	0.252	0.239	-0.014	0.267	0.015
C	0.167	0.132	-0.035	0.210	0.043
C	-0.308	-0.309	-0.001	-0.317	-0.009
C	0.158	0.140	-0.018	0.200	0.042
C	-0.280	-0.287	-0.007	-0.262	0.018
H	0.253	0.238	-0.015	0.268	0.015
C	-0.263	-0.287	-0.024	-0.237	0.026
H	0.253	0.239	-0.014	0.267	0.014
C	0.131	0.146	0.015	0.154	0.023
C	-0.268	-0.319	-0.051	-0.258	0.010
C	0.133	0.137	0.005	0.163	0.030
C	-0.259	-0.300	-0.041	-0.259	0.000
H	0.248	0.238	-0.009	0.259	0.011
C	-0.082	-0.086	-0.004	-0.061	0.021
C	0.172	0.170	-0.002	0.184	0.012
C	0.172	0.176	0.004	0.184	0.012
C	-0.082	-0.086	-0.004	-0.061	0.021
C	-0.259	-0.296	-0.037	-0.259	0.000
H	0.248	0.237	-0.011	0.259	0.011
C	0.133	0.151	0.018	0.163	0.030

C	-0.275	-0.315	-0.040	-0.260	0.015
N	-0.696	-0.701	-0.005	-0.696	0.001
N	-0.696	-0.714	-0.018	-0.696	0.001
C	-0.275	-0.319	-0.044	-0.260	0.015
C	0.144	0.137	-0.007	0.175	0.031
C	-0.252	-0.300	-0.048	-0.255	-0.003
H	0.247	0.238	-0.009	0.259	0.011
C	-0.081	-0.086	-0.005	-0.059	0.022
C	0.177	0.170	-0.007	0.194	0.017
C	0.177	0.176	-0.001	0.194	0.017
C	-0.081	-0.086	-0.005	-0.059	0.022
C	-0.252	-0.296	-0.044	-0.255	-0.003
H	0.247	0.237	-0.011	0.259	0.011
C	0.144	0.151	0.007	0.175	0.031
C	-0.268	-0.315	-0.046	-0.258	0.010
H	0.256	0.243	-0.014	0.269	0.013
H	0.256	0.243	-0.013	0.269	0.013
H	0.257	0.243	-0.014	0.270	0.014
H	0.256	0.243	-0.014	0.269	0.013
H	0.256	0.243	-0.013	0.269	0.013
H	0.257	0.243	-0.014	0.270	0.014
Ga	1.794	1.791	-0.003	1.797	0.003
Ga	1.794	1.791	-0.003	1.797	0.003
N	-0.560	-0.556	0.004	-0.577	-0.017
C	0.062	0.061	-0.001	0.059	-0.003
C	0.064	0.065	0.000	0.059	-0.005
C	-0.278	-0.287	-0.009	-0.271	0.007
H	0.270	0.273	0.002	0.267	-0.003
C	-0.277	-0.283	-0.007	-0.271	0.006
H	0.272	0.276	0.004	0.268	-0.005
C	-0.185	-0.200	-0.015	-0.173	0.012
H	0.270	0.261	-0.009	0.279	0.009
H	0.271	0.265	-0.007	0.278	0.007
H	0.266	0.255	-0.010	0.276	0.010
N	-0.560	-0.556	0.004	-0.577	-0.017
C	0.062	0.065	0.003	0.059	-0.003
C	0.064	0.061	-0.003	0.059	-0.005
C	-0.278	-0.283	-0.005	-0.271	0.007
H	0.270	0.276	0.006	0.267	-0.003
C	-0.277	-0.287	-0.010	-0.271	0.006
H	0.272	0.273	0.000	0.268	-0.005
C	-0.185	-0.200	-0.015	-0.173	0.012
H	0.270	0.265	-0.006	0.279	0.009
H	0.271	0.261	-0.010	0.278	0.007
H	0.266	0.255	-0.010	0.276	0.010

Computed UV spectra using several DFT potentials

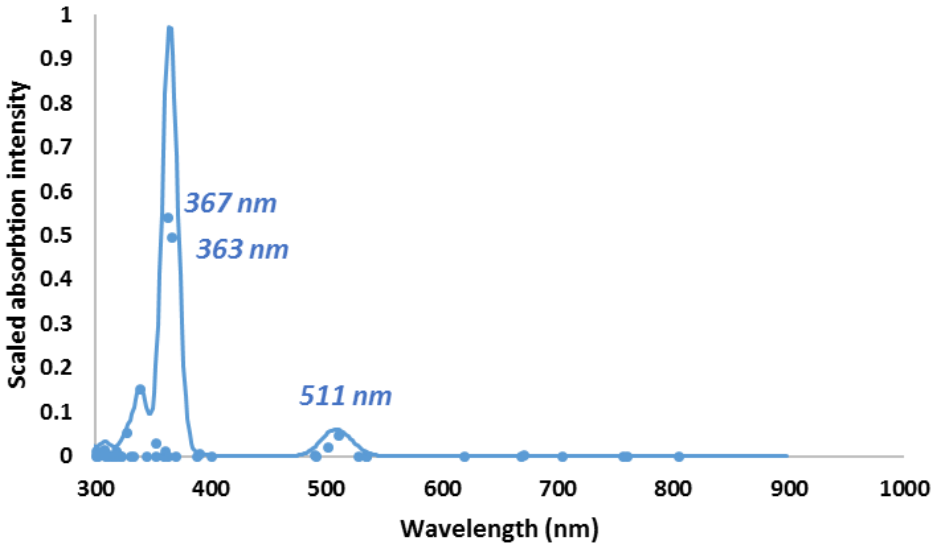

Figure S14: Computed UV/Vis spectrum of **5**, by TPSSH/6-31g(d,p)//B3LYP/6-31g(d,p).

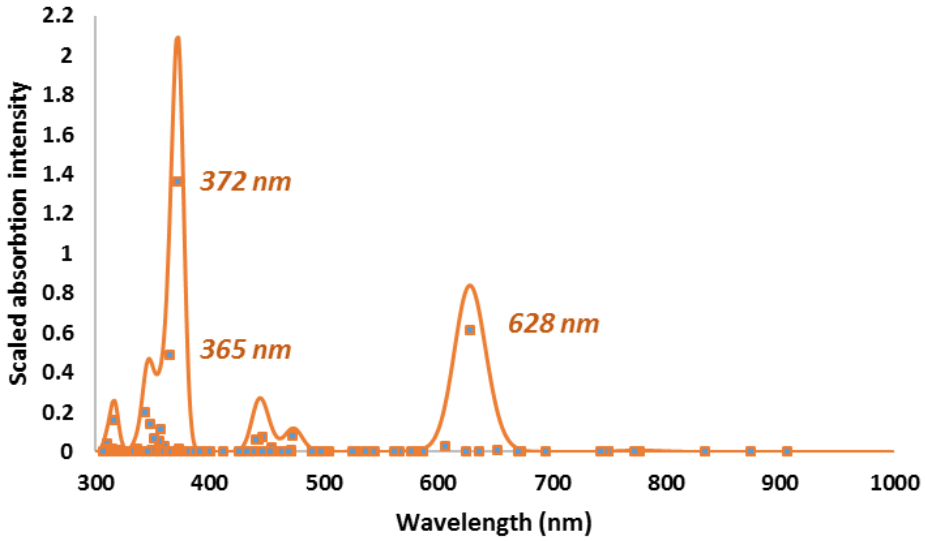

Figure S15: Computed UV/Vis spectrum of **2**, by TPSSH/6-31g(d,p)//B3LYP/6-31g(d,p).

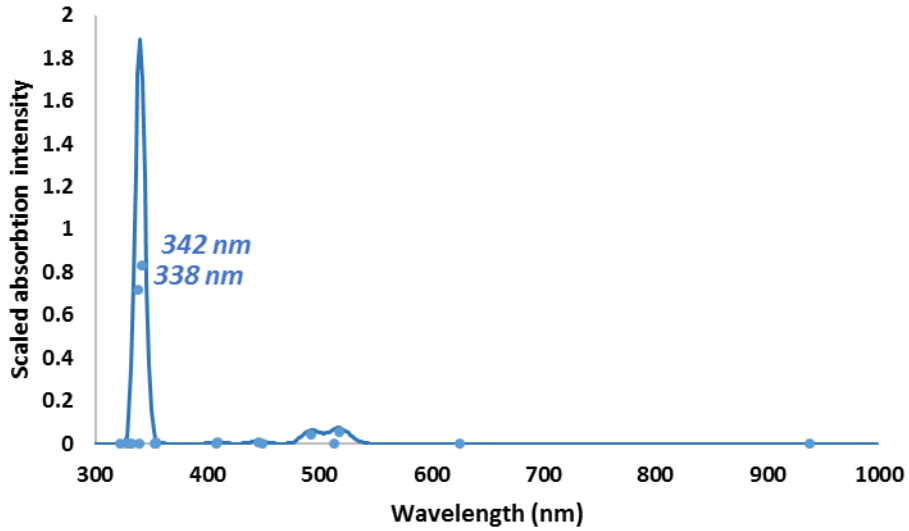

Figure S16: Computed UV/Vis spectrum of **5**, by CAM-B3LYP/6-31g(d,p)//B3LYP/6-31g(d,p).

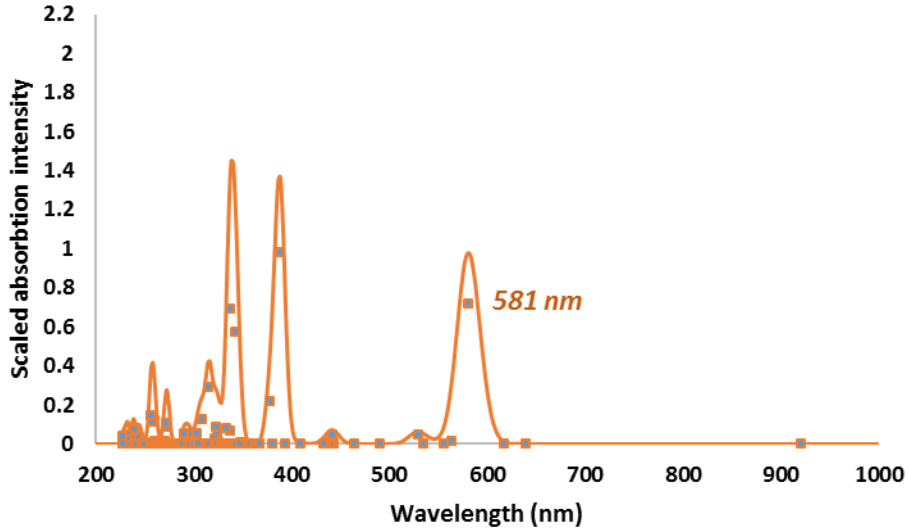

Figure S17: Computed UV/Vis spectrum of **2**, by CAM-B3LYP/6-31g(d,p)//B3LYP/6-31g(d,p).

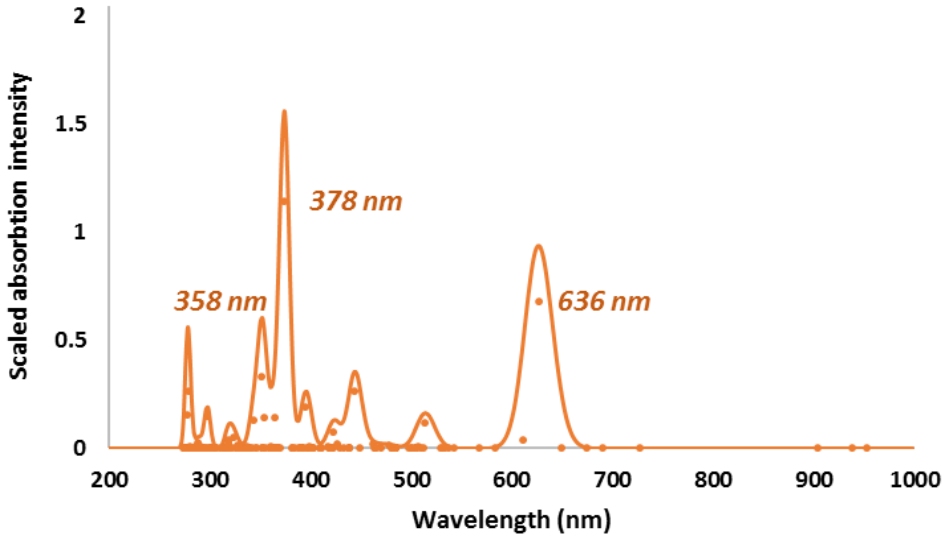

Figure S18: Computed UV/Vis spectrum of **3** (4 pyridine ligands), by B3LYP/6-31g(d,p)//B3LYP/6-31g(d,p).

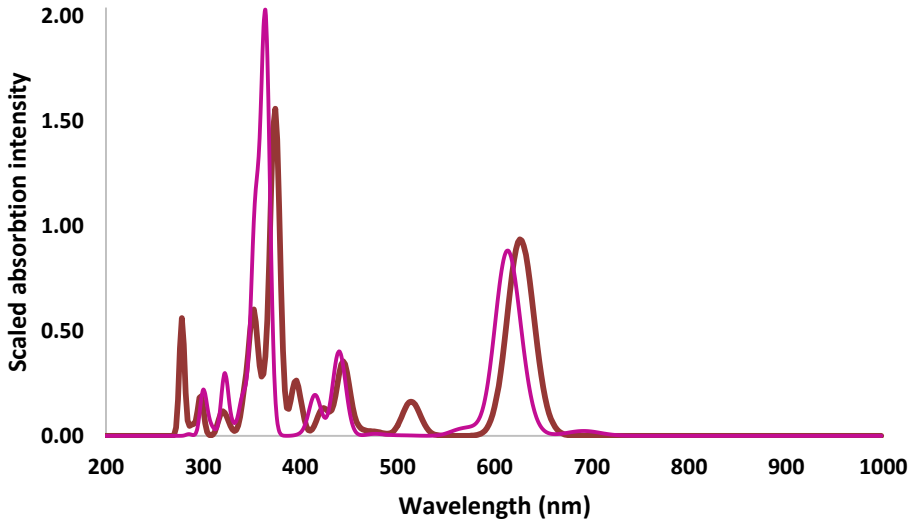

Figure S19: Computed UV/Vis spectrum of **2** (pink) and **3** (brown), by B3LYP/6-31g(d,p)//B3LYP/6-31g(d,p).

Individual transitions of the computed UV spectrum and their orbital assignment, UPBE1PBE/6-31G(d,p) //UB3LYP/6-31G(d,p), **2-full**

2-full, Orbital Numbering: HOMO = 464, LUMO = 465

Excited State 7: 1.000-A 1.9292 eV 642.69 nm f=0.7797
<S**2>=0.000

463A -> 469A	0.11139
464A -> 465A	0.68268
463B -> 469B	0.11139
464B -> 465B	0.68268

Excited State 29: 1.000-A 2.7817 eV 445.72 nm f=0.3540
<S**2>=0.000

460A -> 465A	0.16421
461A -> 467A	-0.12728
461A -> 468A	-0.28264
462A -> 467A	0.27879
462A -> 470A	-0.18411
463A -> 466A	0.29886
463A -> 469A	0.38529
464A -> 465A	-0.11886
460B -> 465B	0.16421
461B -> 467B	-0.12728
461B -> 468B	-0.28264
462B -> 467B	0.27879
462B -> 470B	-0.18411
463B -> 466B	0.29886
463B -> 469B	0.38529
464B -> 465B	-0.11886

Excited State 33: 1.000-A 2.8179 eV 440.00 nm f=0.1257
<S**2>=0.000

459A -> 465A	-0.10666
460A -> 465A	-0.23432
461A -> 468A	0.19599
462A -> 467A	0.45434
462A -> 468A	0.10143
462A -> 470A	0.13552
463A -> 466A	0.27219
463A -> 469A	-0.24904
464A -> 469A	0.10993
459B -> 465B	-0.10666
460B -> 465B	-0.23432
461B -> 468B	0.19599
462B -> 467B	0.45434
462B -> 468B	0.10143
462B -> 470B	0.13552
463B -> 466B	0.27219
463B -> 469B	-0.24904
464B -> 469B	0.10993

Excited State 37: 1.000-A 2.9256 eV 423.80 nm f=0.1011
<S**2>=0.000

461A -> 466A	0.55955
461A -> 469A	0.11302
463A -> 468A	0.21195
464A -> 467A	-0.16767
464A -> 470A	-0.28924
461B -> 466B	0.55955
461B -> 469B	0.11302
463B -> 468B	0.21195
464B -> 467B	-0.16767
464B -> 470B	-0.28924

Excited State 44: 1.000-A 3.0349 eV 408.52 nm f=0.2810
<S**2>=0.000

461A -> 466A	-0.35989
461A -> 469A	0.38012
463A -> 468A	0.26278
464A -> 470A	-0.35887
461B -> 466B	-0.35989
461B -> 469B	0.38012
463B -> 468B	0.26278
464B -> 470B	-0.35887

Excited State 60: 1.000-A 3.2814 eV 377.84 nm f=1.5695
<S**2>=0.000

461A -> 468A	0.50062
462A -> 470A	-0.37605
463A -> 469A	0.22302
461B -> 468B	0.50062
462B -> 470B	-0.37605
463B -> 469B	0.22302

Excited State 64: 1.000-A 3.3709 eV 367.80 nm f=1.2147
<S**2>=0.000

459A -> 468A	0.11657
461A -> 466A	0.12600
461A -> 469A	0.53959
462A -> 465A	-0.16149
463A -> 468A	-0.29678
464A -> 470A	0.16866
459B -> 468B	0.11657
461B -> 466B	0.12600
461B -> 469B	0.53959
462B -> 465B	-0.16149
463B -> 468B	-0.29678
464B -> 470B	0.16866

Excited State 121: 1.000-A 3.8953 eV 318.30 nm f=0.1083
<S**2>=0.000

459A -> 469A	-0.19335
462A -> 474A	-0.37830
463A -> 473A	0.12928
463A -> 475A	0.48403
463A -> 476A	-0.19681
459B -> 469B	-0.19335
462B -> 474B	-0.37830
463B -> 473B	0.12928
463B -> 475B	0.48403
463B -> 476B	-0.19681

Individual transitions of the computed UV spectrum and their orbital assignment, UPBE1PBE/6-31G(d,p)//UB3LYP/6-31G(d,p).

5, Orbital Numbering: HOMO (α,β) = 224, LUMO (α,β) = 225

Excited State 17: 1.000-A 3.5016 eV 354.08 nm f=0.5963
<S**2>=0.000

112A ->116A	0.36649
112A ->117A	0.45640
113A ->115A	-0.34288
112B ->116B	0.36649
112B ->117B	0.45640
113B ->115B	-0.34288

Excited State 18: 1.000-A 3.5282 eV 351.41 nm f=0.7549
<S**2>=0.000

111A ->115A	0.13419
112A ->115A	0.40302
112A ->117A	-0.10252
113A ->116A	0.33434
113A ->117A	0.42101
111B ->115B	0.13419
112B ->115B	0.40302
112B ->117B	-0.10252
113B ->116B	0.33434
113B ->117B	0.42101

2, HOMO (α,β) = 113, LUMO (α,β) = 114

Excited State 7: 1.000-A 2.0125 eV 616.07 nm f=0.1729
<S**2>=0.000

221A -> 226A	0.11032
223A -> 225A	-0.27027
224A -> 225A	0.42760
224A -> 227A	0.46049
221B -> 226B	0.11032
223B -> 225B	-0.27027
224B -> 225B	0.42760
224B -> 227B	0.46049

Excited State 9: 1.000-A 2.0442 eV 606.51 nm f=0.1205
<S**2>=0.000

222A -> 226A	0.26072
223A -> 225A	0.47783
223A -> 227A	0.29992
224A -> 225A	0.29486
224A -> 229A	0.10484
222B -> 226B	0.26072
223B -> 225B	0.47783
223B -> 227B	0.29992
224B -> 225B	0.29486
224B -> 229B	0.10484

Excited State 14: 1.000-A 2.0948 eV 591.87 nm f=0.3011
<S**2>=0.000

223A -> 225A	0.25191
223A -> 229A	0.10143
224A -> 225A	-0.37467
224A -> 227A	0.49904
223B -> 225B	0.25191
223B -> 229B	0.10143
224B -> 225B	-0.37467
224B -> 227B	0.49904

Excited State 16: 1.000-A 2.1209 eV 584.59 nm f=0.1237
<S**2>=0.000

222A -> 226A	0.33106
223A -> 225A	-0.29799
223A -> 227A	0.46154
224A -> 225A	-0.23127
224A -> 227A	0.10340
224A -> 229A	-0.10422

Excited State 54: 1.000-A 3.1377 eV 395.15 nm f=0.1490
<S**2>=0.000

221A -> 229A	0.40778
223A -> 228A	0.27352
223A -> 230A	0.10062
224A -> 230A	0.32342
224A -> 232A	-0.32225
221B -> 229B	0.40778
223B -> 228B	0.27352
223B -> 230B	0.10062
224B -> 230B	0.32342
224B -> 232B	-0.32225

Excited State 78: 1.000-A 3.4899 eV 355.26 nm f=1.4483
<S**2>=0.000

221A -> 228A	0.50536
222A -> 230A	-0.27495
222A -> 232A	0.26668
223A -> 229A	0.24882
224A -> 225A	0.10366
221B -> 228B	0.50536
222B -> 230B	-0.27495
222B -> 232B	0.26668
223B -> 229B	0.24882
224B -> 225B	0.10366

Excited State 83: 1.000-A 3.5969 eV 344.70 nm f=0.8082
<S**2>=0.000

219A -> 228A	0.11339
220A -> 228A	0.19762
221A -> 229A	0.50313
222A -> 225A	-0.17259
223A -> 228A	-0.30645
224A -> 230A	-0.15980
224A -> 232A	0.14413
219B -> 228B	0.11339
220B -> 228B	0.19762
221B -> 229B	0.50313
222B -> 225B	-0.17259
223B -> 228B	-0.30645
224B -> 230B	-0.15980
224B -> 232B	0.14413

Excited State 102: 1.000-A 4.0279 eV 307.82 nm f=0.1846
<S**2>=0.000

217A -> 225A	-0.18073
219A -> 229A	0.62835
220A -> 229A	0.10591
223A -> 233A	-0.18729
217B -> 225B	-0.18073
219B -> 229B	0.62835

222B -> 226B 0.33106
223B -> 225B -0.29799
223B -> 227B 0.46154
224B -> 225B -0.23127
224B -> 227B 0.10340
224B -> 229B -0.10422

Excited State 45: 1.000-A 2.9207 eV 424.50 nm f=0.3859 <S**2>=0.000
220A -> 225A 0.20791
221A -> 228A -0.36244
222A -> 230A -0.11269
222A -> 232A 0.11407
223A -> 229A 0.51108
224A -> 225A 0.15253
220B -> 225B 0.20791
221B -> 228B -0.36244
222B -> 230B -0.11269
222B -> 232B 0.11407
223B -> 229B 0.51108
224B -> 225B 0.15253

220B -> 229B 0.10591
223B -> 233B -0.18729

Excited State 126: 1.000-A 4.2975 eV 288.50 nm f=0.1364 <S**2>=0.000
215A -> 225A 0.50151
216A -> 225A 0.13504
220A -> 230A 0.10765
220A -> 232A -0.10369
221A -> 233A -0.38338
215B -> 225B 0.50151
216B -> 225B 0.13504
220B -> 230B 0.10765
220B -> 232B -0.10369
221B -> 233B -0.38338

$2^{+\cdot}$, Orbital Numbering: (S)HOMO(α) = 224, (S)LUMO(α) = 225; (S)HOMO(β) = 223, (S)LUMO(β) = 224

Excited State 3: 2.015-A 0.8312 eV 1491.58 nm f=0.2097 <S**2>=0.765
224A -> 225A 0.19992
221B -> 224B 0.93295
222B -> 224B 0.28853

Excited State 8: 2.428-A 1.7786 eV 697.09 nm f=0.3684 <S**2>=1.223
221A -> 226A 0.12055
221A -> 228A 0.11112
222A -> 230A 0.25585
223A -> 227A -0.12346
223A -> 229A 0.28028
224A -> 225A 0.83908
221B -> 224B -0.15021
221B -> 228B 0.12488
222B -> 230B -0.11968
223B -> 229B -0.12827

Excited State 77: 2.495-A 3.6590 eV 338.85 nm f=0.5045 <S**2>=1.307
216A -> 225A 0.10884
217A -> 228A 0.11391
217A -> 230A -0.12907
218A -> 225A 0.26662
218A -> 229A 0.11832
219A -> 226A 0.25045
219A -> 228A 0.15258
221A -> 229A 0.39658
222A -> 225A -0.14806
222A -> 231A -0.11095
223A -> 226A 0.15535
223A -> 228A 0.19135
224A -> 230A -0.17713
212B -> 224B -0.13809
214B -> 224B -0.13440
217B -> 224B 0.13304
218B -> 225B -0.15977
220B -> 227B 0.16108
220B -> 228B -0.14064
221B -> 229B -0.35861
221B -> 233B -0.11162
222B -> 225B -0.11921
222B -> 229B -0.11677
223B -> 228B 0.26405

Excited State 78: 2.997-A 3.6684 eV 337.97 nm f=0.1286 <S**2>=1.995
214A -> 225A -0.19539
215A -> 230A 0.11736
216A -> 229A 0.10311
217A -> 226A 0.16549
217A -> 228A 0.18180
218A -> 225A 0.44933
220A -> 226A 0.13492
221A -> 229A -0.18991
222A -> 231A -0.15002
223A -> 228A -0.10155
223A -> 232A 0.10838
212B -> 224B 0.14845
215B -> 225B 0.12243
217B -> 224B 0.23551
217B -> 228B -0.17437
218B -> 225B -0.30799
220B -> 227B -0.25126
220B -> 228B 0.16649

221B -> 229B 0.14903
222B -> 229B 0.10410
223B -> 228B -0.12594
223B -> 230B 0.12145

Excited State 31: 2.452-A 2.6974 eV 459.65 nm f=0.1467
<S**2>=1.253
220A -> 225A 0.30611
224A -> 225A 0.10269
215B -> 224B 0.80183
219B -> 225B -0.12643
220B -> 225B -0.16702
222B -> 230B 0.17132
223B -> 229B 0.27649

Excited State 91: 3.025-A 3.7916 eV 326.99 nm f=0.1292
<S**2>=2.037
211A -> 225A 0.13861
215A -> 226A -0.11516
215A -> 228A -0.10218
216A -> 225A 0.34766
217A -> 230A -0.19653
218A -> 229A 0.18485
219A -> 226A 0.27772
219A -> 228A -0.10094
220A -> 226A -0.10210
220A -> 230A 0.13118
221A -> 229A -0.11000
211B -> 225B -0.15492
212B -> 224B 0.27029
212B -> 228B -0.11312
214B -> 224B -0.18324
214B -> 228B 0.10945
216B -> 225B -0.24166
217B -> 230B 0.17645
218B -> 229B -0.17035
219B -> 227B -0.15457
220B -> 227B 0.17864
221B -> 229B 0.13223
223B -> 228B -0.10378

Excited State 68: 2.303-A 3.4817 eV 356.10 nm f=0.6753
<S**2>=1.076
220A -> 229A 0.11376
221A -> 226A -0.12466
221A -> 228A -0.19072
222A -> 230A 0.45324
223A -> 233A -0.23129
224A -> 233A -0.19896
205B -> 224B -0.22508
206B -> 224B -0.21557
208B -> 224B 0.33472
221B -> 228B 0.29283
221B -> 230B -0.10912
222B -> 230B 0.42892
223B -> 229B 0.10620
223B -> 233B 0.17213

Excited State 92: 2.495-A 3.7970 eV 326.53 nm f=0.3790
<S**2>=1.306
212A -> 225A 0.24183
214A -> 226A 0.13437
214A -> 228A 0.13288
215A -> 225A -0.12080
219A -> 227A -0.10071
221A -> 226A -0.12615
221A -> 228A -0.15651
222A -> 230A 0.14543
223A -> 229A 0.15749
223A -> 233A 0.48809
205B -> 224B 0.42512
206B -> 224B 0.28462
208B -> 224B -0.11720
213B -> 225B 0.11846
219B -> 225B -0.12797
222B -> 230B 0.11791
223B -> 229B 0.11354
223B -> 233B 0.22865

Excited State 70: 2.417-A 3.5197 eV 352.26 nm f=0.1113
<S**2>=1.211
219A -> 227A -0.11558
219A -> 229A 0.14362
221A -> 230A 0.21376
222A -> 230A -0.14451
224A -> 233A -0.19182
205B -> 224B 0.31213
208B -> 224B 0.69672
219B -> 226B 0.12223
219B -> 229B -0.19554
219B -> 233B 0.12264
221B -> 228B -0.11663
222B -> 230B -0.25140

Excited State 112: 2.161-A 4.1019 eV 302.26 nm f=0.2774
<S**2>=0.917
217A -> 225A -0.11652
219A -> 229A 0.66951
213B -> 225B 0.13149
217B -> 225B -0.17013
219B -> 229B 0.49585
220B -> 229B -0.34315
223B -> 233B -0.17099

$2^{-\cdot}$, Orbital Numbering: (S)HOMO(α) = 225, (S)LUMO(α) = 226; (S)HOMO(β) = 224, (S)LUMO(β) = 225

Excited State 5: 2.096-A 0.9015 eV 1375.26 nm f=0.1807
<S**2>=0.848
225A -> 228A 0.71836
225A -> 230A -0.62611
224B -> 227B -0.24669

Excited State 18: 3.017-A 1.8566 eV 667.79 nm f=0.1546
<S**2>=2.025
221A -> 226A -0.13447
222A -> 232A 0.27902
223A -> 231A -0.32758
224A -> 227A 0.42808
225A -> 228A -0.20571
222B -> 231B -0.38585
223B -> 230B 0.46605
224B -> 227B -0.37900

Excited State 23: 2.728-A 2.0477 eV 605.49 nm f=0.2777
<S**2>=1.611
222A -> 232A 0.26032
223A -> 231A -0.33475
224A -> 227A -0.13331
222B -> 226B -0.35110
222B -> 231B -0.19330
223B -> 225B -0.30920
223B -> 230B 0.22357
224B -> 227B 0.67299

Excited State 55: 2.377-A 2.8359 eV 437.20 nm f=0.2044
<S**2>=1.163
220A -> 226A -0.18810
221A -> 228A -0.36697
221A -> 230A 0.16626
222A -> 232A -0.21268
223A -> 231A 0.43248
220B -> 226B 0.26192
220B -> 227B -0.36277
221B -> 232B -0.18773
223B -> 230B 0.53230

Excited State 71: 2.575-A 3.1604 eV 392.30 nm f=0.1559
<S**2>=1.408
219A -> 232A -0.16199
220A -> 228A 0.17858
221A -> 231A 0.49689

Excited State 80: 2.247-A 3.4104 eV 363.54 nm f=0.8872
<S**2>=1.012
220A -> 231A -0.11587
221A -> 228A 0.41042
221A -> 230A -0.21514
222A -> 232A -0.39052
223A -> 231A 0.14169
225A -> 239A 0.12188
219B -> 230B 0.20158
221B -> 232B 0.60461
222B -> 231B -0.26823
223B -> 230B 0.22335

Excited State 88: 2.390-A 3.5400 eV 350.24 nm f=0.4960
<S**2>=1.178
220A -> 228A 0.10377
221A -> 231A 0.59355
223A -> 228A -0.23721
223A -> 230A 0.11905
224A -> 232A 0.10318
225A -> 238A 0.10270
219B -> 228B -0.13553
219B -> 230B 0.12162
219B -> 232B 0.38194
220B -> 231B -0.25776
221B -> 230B 0.28466
221B -> 233B -0.11112
222B -> 227B -0.13632
223B -> 232B -0.24193
224B -> 231B -0.21485

Excited State 91: 2.778-A 3.6041 eV 344.01 nm f=0.2324
<S**2>=1.679
219A -> 232A -0.16070
220A -> 228A -0.35420
220A -> 231A -0.12297
221A -> 231A 0.16255
221A -> 233A -0.18523
223A -> 228A -0.11442
223A -> 233A -0.12193
224A -> 232A 0.11152
225A -> 238A -0.13997
211B -> 227B -0.11600
217B -> 231B -0.10479
219B -> 230B 0.20750
219B -> 232B -0.38213
220B -> 231B 0.41508
221B -> 230B 0.34477
221B -> 233B 0.14919
223B -> 232B -0.16338
223B -> 233B 0.15320

Excited State 111: 2.179-A 3.8842 eV 319.20 nm f=0.1393
<S**2>=0.937
220A -> 231A 0.63968
223A -> 233A -0.31489
217B -> 227B -0.10306
219B -> 230B 0.45945
223B -> 233B -0.45480

222A -> 232A -0.25949
223A -> 228A 0.19574
224A -> 232A -0.46662
219B -> 232B -0.13292
220B -> 227B 0.22497
221B -> 232B -0.25412
222B -> 227B 0.10710
222B -> 231B -0.16376
223B -> 232B 0.26249
224B -> 231B 0.21214

triplet-2^{2-}, Orbital Numbering: (S)HOMO(α) = 226, (S)LUMO(α) = 227; (S)HOMO(β) = 224, (S)LUMO(β) = 225

Excited State 6: 3.084-A 0.9249 eV 1340.49 nm f=0.1630
<S**2>=2.128
225A -> 228A 0.93616
226A -> 227A -0.22860
224B -> 225B -0.26386
226A <- 227A 0.18566

Excited State 58: 3.197-A 3.3684 eV 368.08 nm f=0.6330
<S**2>=2.306
220A -> 229A 0.12263
221A -> 228A 0.44882
222A -> 230A -0.29403
223A -> 229A -0.12808
226A -> 234A 0.10184
219B -> 226B -0.18074
221B -> 228B 0.58827
222B -> 227B -0.18998
222B -> 229B -0.23162
222B -> 230B 0.25791
223B -> 226B -0.18587
223B -> 230B -0.18946

Excited State 19: 3.267-A 2.0173 eV 614.62 nm f=0.4704
<S**2>=2.419
222A -> 230A 0.22963
223A -> 229A 0.30237
224A -> 227A 0.33385
225A -> 228A 0.13895
221B -> 228B 0.10903
222B -> 227B -0.11321
223B -> 226B -0.12856
224B -> 225B 0.81053

Excited State 61: 3.230-A 3.4634 eV 357.98 nm f=0.4591
<S**2>=2.358
220A -> 228A -0.11934
221A -> 229A 0.62194
223A -> 228A 0.25982
226A -> 235A 0.13935
219B -> 228B -0.40470
220B -> 227B -0.24769
221B -> 226B 0.28321
222B -> 225B -0.13322
223B -> 228B 0.22600
224B -> 227B -0.21639

Excited State 35: 3.148-A 2.7645 eV 448.49 nm f=0.3083
<S**2>=2.228
221A -> 228A 0.40605
222A -> 230A 0.22219
223A -> 229A 0.50048
220B -> 225B 0.26081
221B -> 228B 0.12968
223B -> 226B 0.61515
223B -> 230B 0.11100

Excited State 65: 3.458-A 3.5439 eV 349.85 nm f=0.1105
<S**2>=2.740
219A -> 230A -0.12321
220A -> 228A 0.27191
221A -> 230A -0.15744
223A -> 231A -0.12597
224A -> 231A 0.16355
225A -> 236A 0.10370
226A -> 234A 0.11219
219B -> 228B 0.20892
220B -> 227B 0.36241
220B -> 228B -0.11267
221B -> 226B 0.28306
221B -> 229B 0.21541
221B -> 230B 0.12574
222B -> 231B 0.12893
222B -> 232B -0.24816
223B -> 228B 0.11108
223B -> 231B -0.32920
223B -> 233B 0.10511
224B -> 231B -0.31745

Excited State 48: 3.443-A 3.0982 eV 400.18 nm f=0.1977
<S**2>=2.713
221A -> 228A -0.19435
221A -> 229A -0.21270
222A -> 230A 0.50751
223A -> 228A 0.10107
224A -> 230A 0.21175
220B -> 225B -0.42371

Excited State 93: 3.128-A 3.8393 eV 322.93 nm f=0.1142
<S**2>=2.197
220A -> 229A -0.43925
222A -> 232A 0.11940
223A -> 231A 0.16792
223A -> 233A 0.40561
226A -> 238A 0.10191
217B -> 225B -0.10171

221B -> 228B	0.47409	219B -> 226B	-0.31708
222B -> 227B	0.27668	222B -> 232B	-0.22647
223B -> 228B	0.12731	223B -> 231B	0.21318
224B -> 225B	-0.16957	223B -> 233B	0.56902

Excited State 50: 3.387-A 3.1114 eV 398.49 nm f=0.1488
<S**2>=2.617

219A -> 230A	-0.18443
220A -> 228A	-0.16929
221A -> 229A	0.50671
221A -> 230A	0.10263
222A -> 230A	0.24835
223A -> 228A	-0.23670
224A -> 230A	-0.46605
219B -> 228B	0.14608
220B -> 225B	-0.12172
220B -> 227B	0.10530
221B -> 228B	0.15021
222B -> 225B	0.10751
223B -> 228B	-0.26100
223B -> 230B	-0.14152
224B -> 227B	0.22816

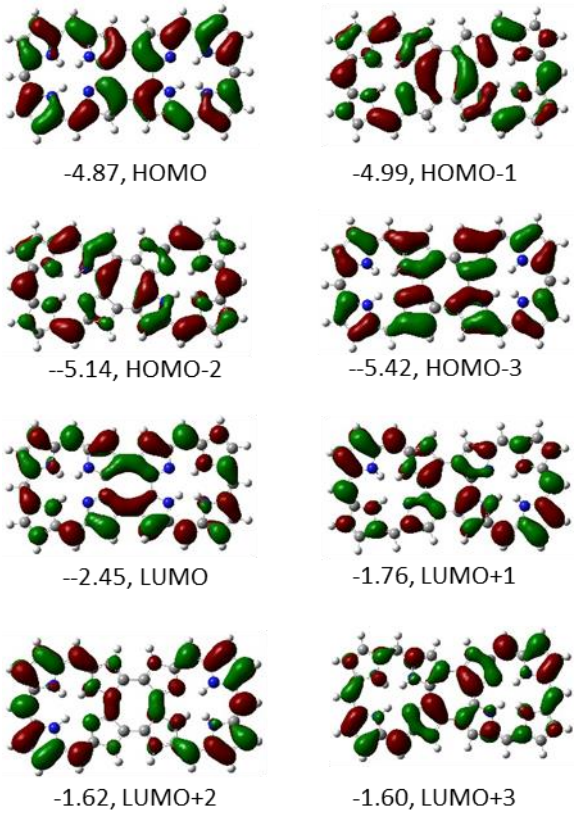

Figure S20: Molecular orbitals of free base bis-corrole, $(H_3tpfc)_2COT$, computed by UPBE1PBE/6-31G(d,p)//UB3LYP/6-31G, a.u./$Å^3$

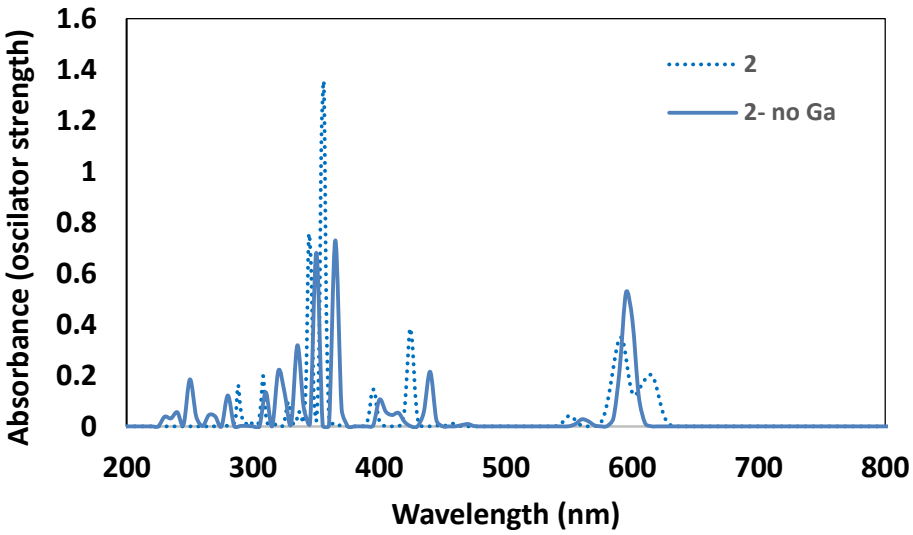

Figure S21: Computed, UPBE1PBE/6-31G(d,p)//UB3LYP/6-31G(d,p), UV/Vis spectrum of free base bis corrole $(H_3tpfc)_2COT$, in bold blue line. The UV of model **2** is presented in dashed blue, for comparison.

Individual transitions of the computed UV spectrum and their orbital assignment, pbe1pbe/6-31g(d,p).

2-no Ga, Orbital Numbering: HOMO = 154, LUMO = 155

Excited State 8: 1.000-A 2.0789 eV 596.38 nm f=0.6771
<S**2>=0.000

152A ->157A	0.11651
153A ->156A	0.10961
153A ->158A	0.10430
154A ->155A	0.67994
152B ->157B	0.11651
153B ->156B	0.10961
153B ->158B	0.10430
154B ->155B	0.67994

Excited State 21: 1.000-A 2.8220 eV 439.35 nm f=0.2733
<S**2>=0.000

150A ->155A	0.39506
151A ->156A	0.23385
151A ->158A	-0.22497
152A ->157A	0.15448
153A ->156A	0.27829
153A ->158A	0.33711
154A ->155A	-0.12479
150B ->155B	0.39506
151B ->156B	0.23385
151B ->158B	-0.22497
152B ->157B	0.15448
153B ->156B	0.27829
153B ->158B	0.33711
154B ->155B	-0.12479

Excited State 31: 1.000-A 3.0954 eV 400.54 nm f=0.1339
<S**2>=0.000

150A ->155A	-0.18149

Excited State 52: 1.000-A 3.7994 eV 326.33 nm f=0.2376
<S**2>=0.000

149A ->156A	0.17531
149A ->158A	0.41577
150A ->157A	0.43919
151A ->156A	0.16191
151A ->158A	0.14059
153A ->159A	-0.15436
149B ->156B	0.17531
149B ->158B	0.41577
150B ->157B	0.43919
151B ->156B	0.16191
151B ->158B	0.14059
153B ->159B	-0.15436

Excited State 55: 1.000-A 3.8654 eV 320.75 nm f=0.3122
<S**2>=0.000

149A ->158A	-0.35990
150A ->157A	0.52068
153A ->156A	-0.10410
153A ->159A	0.18638
154A ->157A	0.11982
149B ->158B	-0.35990
150B ->157B	0.52068
153B ->156B	-0.10410
153B ->159B	0.18638
154B ->157B	0.11982

Excited State 59: 1.000-A 3.9944 eV 310.40 nm f=0.1736
<S**2>=0.000

149A ->156A	0.14733

151A ->158A -0.33262
152A ->157A 0.46483
153A ->158A -0.23635
154A ->157A -0.26568
150B ->155B -0.18149
151B ->158B -0.33262
152B ->157B 0.46483
153B ->158B -0.23635
154B ->157B -0.26568

Excited State 35: 1.000-A 3.3888 eV 365.87 nm f=1.0102
<S**2>=0.000
149A ->156A 0.30841
149A ->158A -0.18774
151A ->156A -0.12149
151A ->158A 0.44005
152A ->157A 0.31843
153A ->156A 0.14536
153A ->158A 0.12216
149B ->156B 0.30841
149B ->158B -0.18774
151B ->156B -0.12149
151B ->158B 0.44005
152B ->157B 0.31843
153B ->156B 0.14536
153B ->158B 0.12216

Excited State 41: 1.000-A 3.5460 eV 349.65 nm f=0.8603
<S**2>=0.000
149A ->156A 0.16831
149A ->158A -0.28697
150A ->155A 0.11015
151A ->156A 0.38283
151A ->159A -0.10757
152A ->155A -0.14238
152A ->157A -0.21188
153A ->158A -0.28821
153A ->159A 0.11765
154A ->157A -0.18715
149B ->156B 0.16831
149B ->158B -0.28697
150B ->155B 0.11015
151B ->156B 0.38283
151B ->159B -0.10757
152B ->155B -0.14238
152B ->157B -0.21188
153B ->158B -0.28821
153B ->159B 0.11765
154B ->157B -0.18715

Excited State 47: 1.000-A 3.6815 eV 336.77 nm f=0.7576
<S**2>=0.000
149A ->156A 0.55880
150A ->157A -0.10672
151A ->158A -0.28971
153A ->156A -0.16786
153A ->159A -0.13995
154A ->157A 0.13223
149B ->156B 0.55880
150B ->157B -0.10672
151B ->158B -0.28971
153B ->156B -0.16786
153B ->159B -0.13995
154B ->157B 0.13223

149A ->158A 0.25117
153A ->159A 0.63001
149B ->156B 0.14733
149B ->158B 0.25117
153B ->159B 0.63001

Excited State 77: 1.000-A 4.4060 eV 281.40 nm f=0.3483
<S**2>=0.000
141A ->155A -0.16616
151A ->159A 0.64518
141B ->155B -0.16616
151B ->159B 0.64518

Excited State 100: 1.000-A 4.9022 eV 252.91 nm f=0.2264
<S**2>=0.000
143A ->155A 0.15139
146A ->158A -0.22437
148A ->156A -0.17903
148A ->158A 0.19869
149A ->159A 0.51667
154A ->160A 0.15535
143B ->155B 0.15139
146B ->158B -0.22437
148B ->156B -0.17903
148B ->158B 0.19869
149B ->159B 0.51667
154B ->160B 0.15535

Excited State 102: 1.000-A 4.9538 eV 250.28 nm f=0.2397
<S**2>=0.000
138A ->155A 0.13249
142A ->158A 0.12108
143A ->155A -0.13467
144A ->157A -0.20034
145A ->156A -0.11522
145A ->158A -0.12483
146A ->156A -0.18059
146A ->158A 0.13285
148A ->156A 0.25069
148A ->158A -0.24230
149A ->159A 0.33477
154A ->160A 0.20873
138B ->155B 0.13249
142B ->158B 0.12108
143B ->155B -0.13467
144B ->157B -0.20034
145B ->156B -0.11522
145B ->158B -0.12483
146B ->156B -0.18059
146B ->158B 0.13285
148B ->156B 0.25069
148B ->158B -0.24230

149B ->159B 0.33477
154B ->160B 0.20873
Excited State 122: 1.000-A 5.2508 eV 236.12 nm f=0.1085
<S**2>=0.000
139A ->156A -0.14682
139A ->158A -0.12941
140A ->157A 0.17557
142A ->156A 0.28843
142A ->158A -0.16927
143A ->155A 0.10107
145A ->156A 0.15185
145A ->158A -0.16296
146A ->156A -0.18674
149A ->159A 0.11323
152A ->160A 0.29524
153A ->161A -0.21833
154A ->160A -0.13443
139B ->156B -0.14682
139B ->158B -0.12941
140B ->157B 0.17557
142B ->156B 0.28843
142B ->158B -0.16927
143B ->155B 0.10107
145B ->156B 0.15185
145B ->158B -0.16296
146B ->156B -0.18674
149B ->159B 0.11323
152B ->160B 0.29524
153B ->161B -0.21833
154B ->160B -0.13443

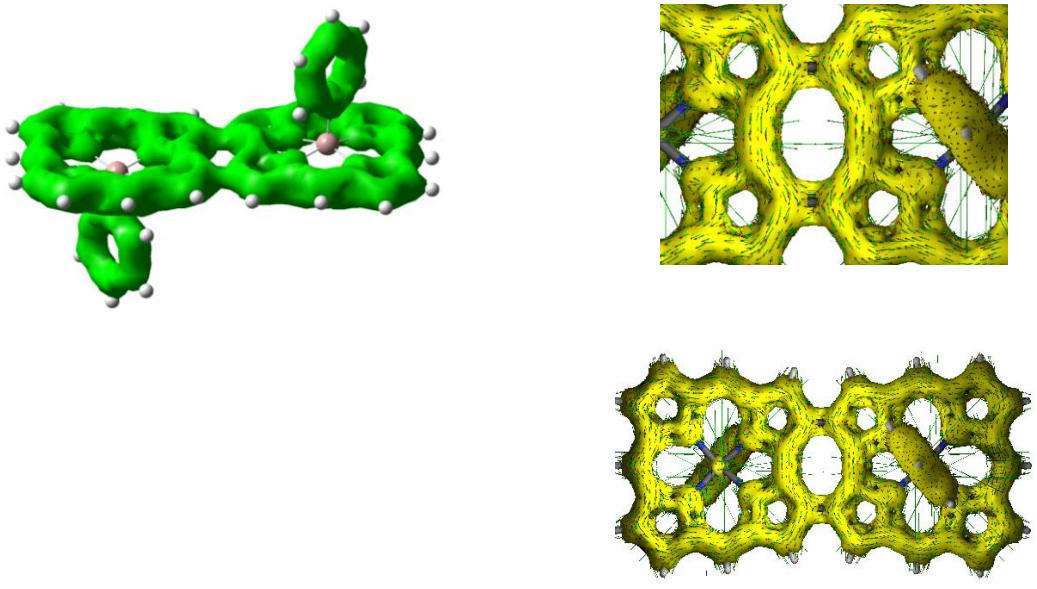

Figure S22: Computed *anisotropy-current-induced-density*, ACID, surface iso density value 0.05.

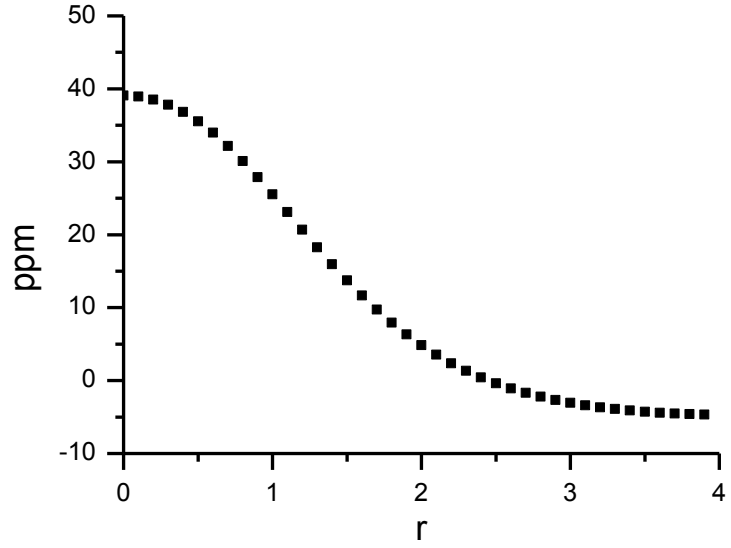

Figure S23: $NICS_{zz}$-scan at the center of the eight membered ring in **AA** (The bis-Ga complex).

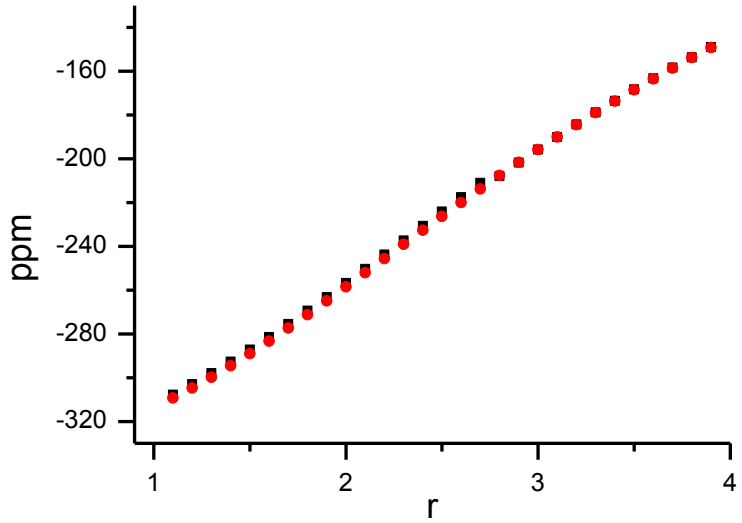

Figure S24: A plot of $NICS_{zz,\pi}$ (from the σ-only model) as a function of distance. Black - Δ(out-of-plane). Red: 3Δ(isotropic).

Explanation: The $NICS_{zz}$ scan (figure S23) shows (relatively small) paratropic values; $NICS(1)_{zz}$=25.5 ppm. The $NICS_{zz,\pi}$ (figure S24) suggests very diatropic values – $NICS(1)_{zz,\pi}$=-314.3±0.4. These results suggest that the eight membered ring is π aromatic and the paratropicity that is observed is a results of a paratropic σ framework.

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