Supporting Information

On the Ambiguity of 1,3,2-Benzodiazaboroles as Donor/Acceptor Functionalities in Luminescent Molecules

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Figure S1. Absorption and emission spectra of **1-4**. CyH = cyclohexane, DCM = dichloromethane.

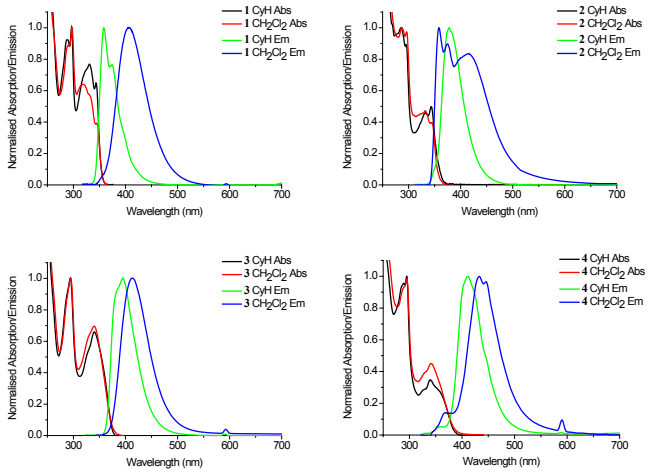


Figure S2. Absorption and emission spectra of **5-10**.

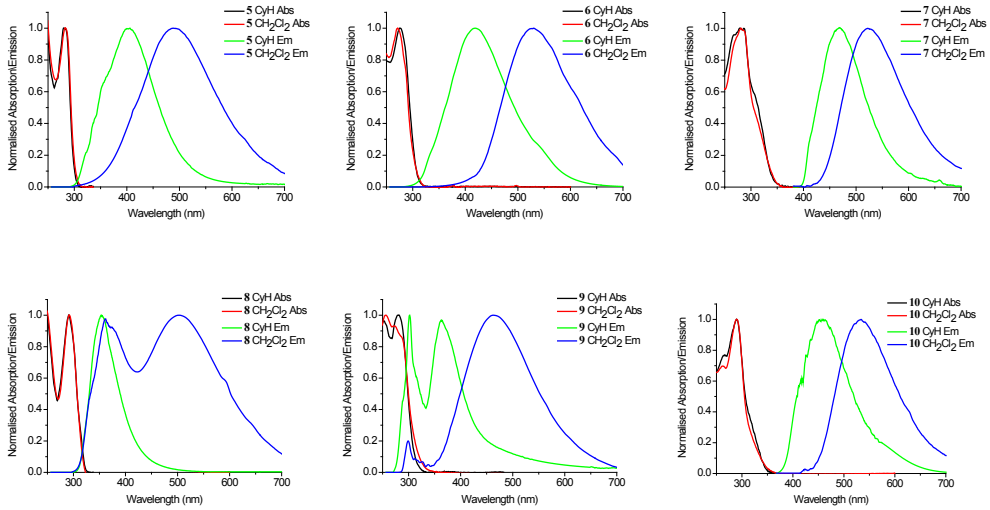


Figure S3. Absorption and emission spectra of **11-14** and **20**

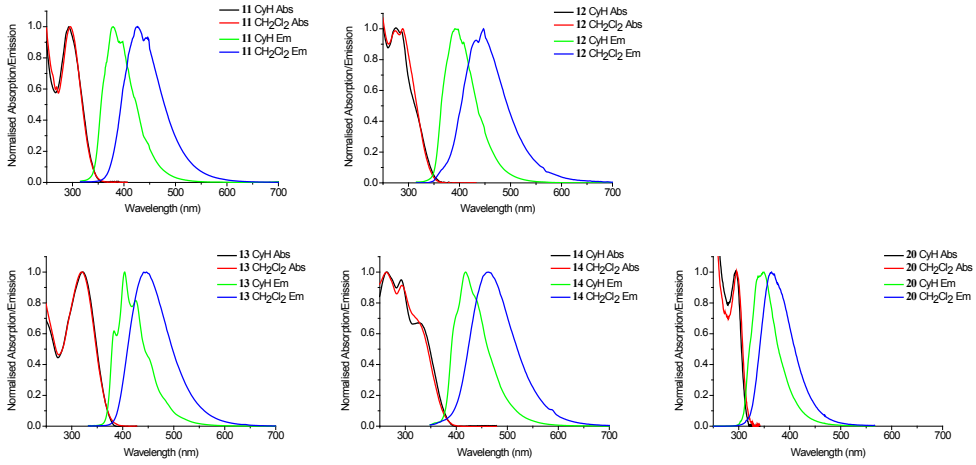


Table S1. Excitation wavelengths (nm) used for emission spectra of **1**-**14** and **20**.

	CyH	DCM
1	331	316
2	343	311
3	340	341
4	340	344
5	280	282
6	273	273
7	282	281
8	290	291
9	276	280
10	288	288
11	293	296
12	282	289
13	323	321
14	330	325
20	294	292

Calculation of the change of the dipole moment using the Lippert-Mataga equation:

$$\nu_A - \nu_F = \frac{2}{hc}\left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right)\frac{(\mu_E - \mu_G)^2}{a^3} + const. = \frac{2\Delta f}{hca^3}(\mu_E - \mu_G)^2 + const.$$

$\nu_A - \nu_F$ is the Stokes shift calculated from the maxima of the excitation and emission in wavenumbers

ε the dielectric constant

n is the refractive index

Δf is the orientation polarisation

$\mu_E - \mu_G$ change of the dipole moment

a is the estimated radius of the fluorophor (Onsager radius)

c the velocity of light

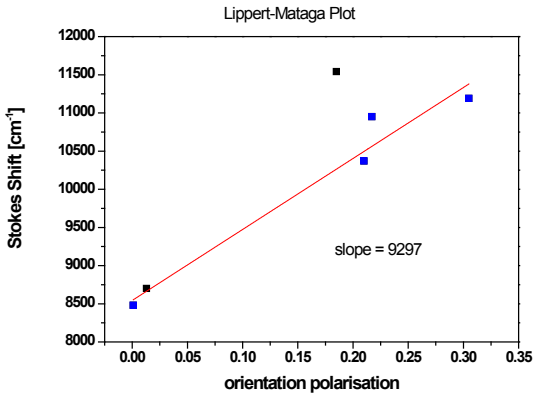
h Planck´s constant

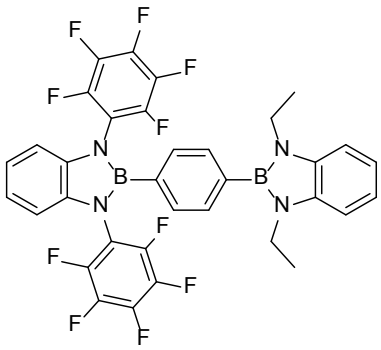
The Stokes shift is plotted against the orientation polarisation to calculate the change in the dipole moment from the slope of the plot.

Table S2. Lippert Mataga data for **11**.

solvent	orientation polarisation	Stokes shift	notes
CyH	0.001	8480	
Toluene	0.013	8700	Not used - solvent π-stacking
$CHCl_3$	0.185	11540	Not used – anomalous excitation spectrum
THF	0.210	10370	
CH_2Cl_2	0.217	10950	
CH_3CN	0.305	11190	

Figure S4. Lippert Mataga plot for **11**.



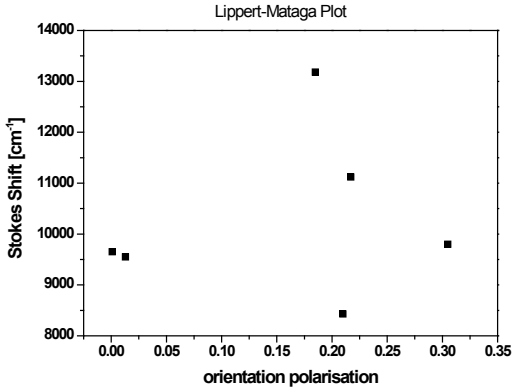


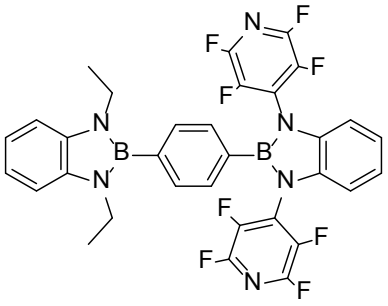
Onsager radius: 6.84 Å Δμ = 15.8 D

Table S3. Lippert Mataga data for **12**.

solvent	orientation polarisation	Stokes shift
CyH	0.001	9650
Toluene	0.013	9550
$CHCl_3$	0.185	13180
THF	0.210	8430
CH_2Cl_2	0.217	11120
CH_3CN	0.305	9800

Figure S5. Lippert Mataga plot for **12**.



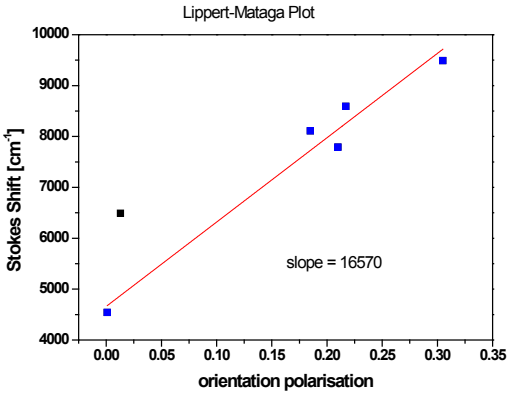


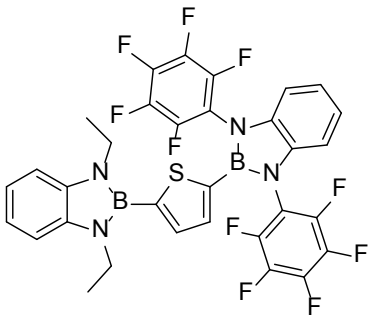
It was not possible to make a linear fit. The excitation spectra show one type of spectral shape for three solvents and another type of spectral shape for three other solvents. This suggests that either LCT or RCT emission takes place for **11** depending on the solvent.

Table S4. Lippert Mataga data for **13**.

solvent	orientation polarisation	Stokes shift	notes
CyH	0.001	4540	
Toluene	0.013	6490	Not used - solvent π-stacking
$CHCl_3$	0.185	8110	
THF	0.210	7790	
CH_2Cl_2	0.217	8590	
CH_3CN	0.305	9490	

Figure S6. Lippert Mataga plot for **13**.



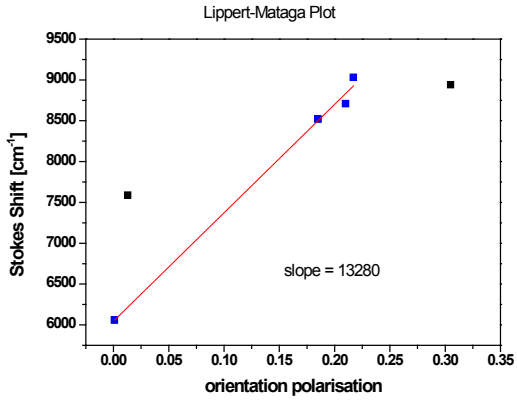


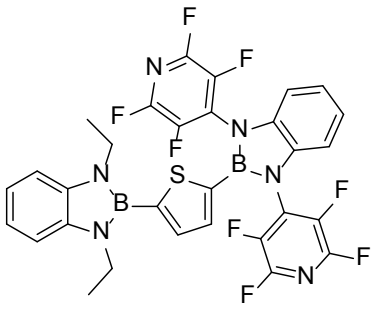
Onsager radius: 6.84 Å Δμ = 23.0 D

Table S5. Lippert Mataga data for **14**.

solvent	orientation polarisation	Stokes shift	notes
CyH	0.001	6060	
Toluene	0.013	7590	Not used - solvent π-stacking
$CHCl_3$	0.185	8520	
THF	0.210	8710	
CH_2Cl_2	0.217	9030	
CH_3CN	0.305	8940	Not used – anomalous excitation spectrum

Figure S7. Lippert Mataga plot for **14**.





Onsager radius: 6.32 Å Δμ = 18.3 D

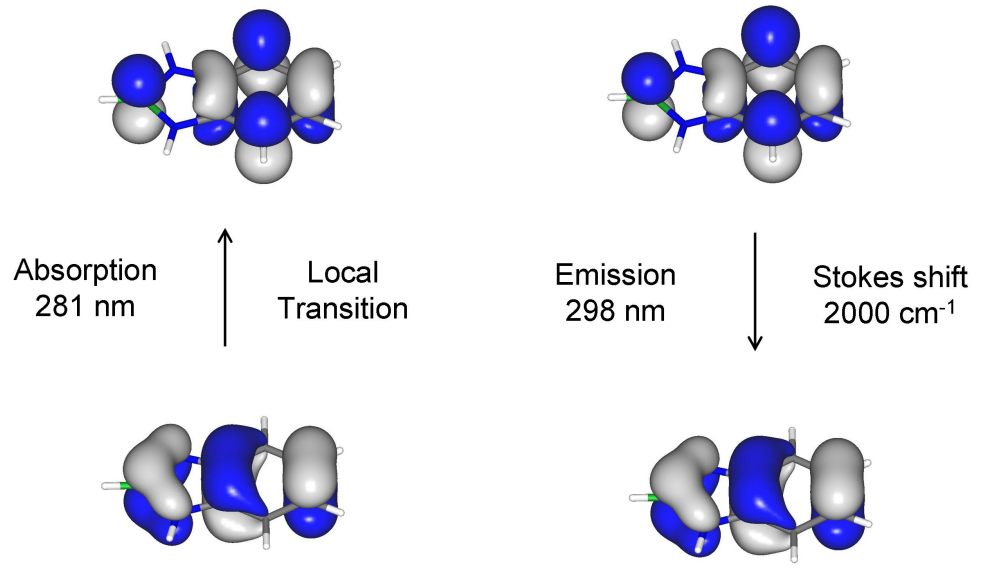


Figure S8. Molecular orbitals involved in the absorption (optimised S_0 geometry, $S_0 > S_1$) and emission (optimised S_1 geometry, $S_0 < S_1$) transitions for the parent benzodiazaborole, 1,3,2-$N_2BC_6H_7$.

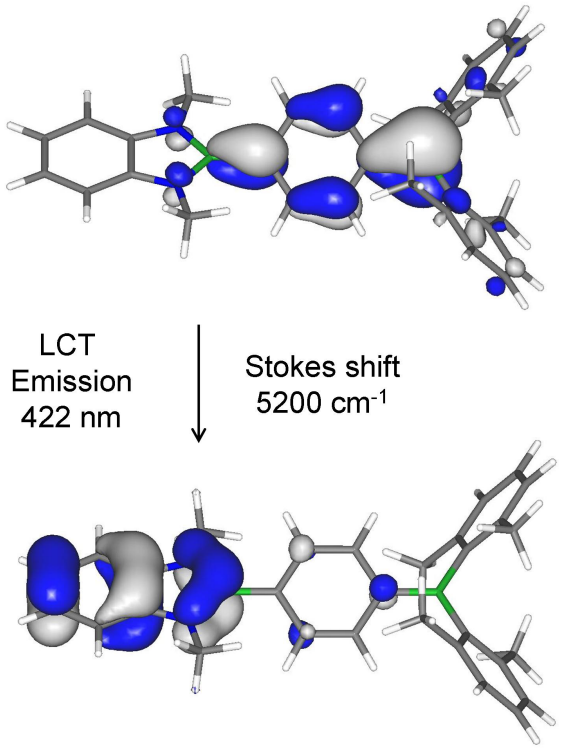


Figure S9. Molecular orbitals involved in the LCT emission of the model excited state geometry of the push-pull system **21** as reported in reference S1.

Table S6. Comparison of selected geometric parameters for computed and optimised geometries, **11-13**. Et_2BDB = 1,3-diethyl-1,3,2-benzodiazaborolyl group, $^{F}Ar_2BDB$ = 1,3-difluoroaryl-1,3,2-benzodiazaborolyl group.

	11 Calc.	**11** Obs.	**12** Calc.	**12A** Obs.	**12B** Obs.	**13** Calc.	**13A** Obs.	**13B** Obs.
B-C bond length								
At Et_2BDB group	1.567 Å	1.565(1) Å	1.568 Å	1.556(2) Å	1.553(2) Å	1.557 Å	1.548(2) Å	1.551(2) Å
At $^{F}Ar_2BDB$ group	1.557 Å	1.551(1) Å	1.557 Å	1.542(2) Å	1.537(2) Å	1.545 Å	1.537(2) Å	1.540(2) Å
Ring orientation								
Et_2BDB – bridge	54.1°	45.3(1)°	54.8°	44.1(2)°	42.5(2)°	41.1°	26.3(2)°	45.8(2)°
$^{F}Ar_2BDB$ – bridge	52.3°	43.5(1)°	53.7°	41.4(2)°	42.9(2)°	40.9°	21.1(2)°	4.9(2)°
^{F}Ar-BDB	79.4°	56.0(1)°	84.3°	60.1(2)°	57.6(2)°	60.1°	67.9(2)°	58.2(2)°
	87.1°	56.1(1)°	85.3°	54.4(2)°	57.2(2)°	77.2°	69.0(2)°	60.5(2)°

Cartesian coordinates for optimised ground and excited state geometries of **5**, **11** and **20**.

Optimised ground state geometry for **5**

```
46
B        0.000000    0.201000    0.000000
N        1.145600   -0.680500   -0.063200
C        0.702700   -2.018700   -0.032700
C       -0.702700   -2.018700    0.032600
N       -1.145600   -0.680500    0.063200
C        1.418300   -3.210300   -0.062900
C        0.698700   -4.409400   -0.030300
C       -0.698800   -4.409400    0.030300
C       -1.418300   -3.210300    0.062800
H       -2.502900   -3.210200    0.113100
H       -1.236900   -5.352400    0.054000
H        1.236800   -5.352400   -0.054100
H        2.502900   -3.210200   -0.113100
C        0.000000    4.582900    0.000000
C        0.681400    3.881900   -0.996700
C        0.684100    2.486900   -0.992500
C        0.000000    1.758600    0.000000
C       -0.684100    2.486900    0.992600
C       -0.681300    3.881900    0.996800
H        1.209900    4.421500   -1.778400
H        1.211500    1.956700   -1.780500
H       -1.211500    1.956700    1.780500
H       -1.209900    4.421600    1.778400
C       -2.518000   -0.350100    0.027000
C       -3.224200   -0.350800   -1.181800
C       -3.220700   -0.022700    1.190700
C       -4.577900   -0.028900   -1.232800
C       -4.571900    0.312900    1.156400
C        2.518000   -0.350100   -0.027000
C        3.224200   -0.350900    1.181800
C        3.220700   -0.022700   -1.190700
C        4.577900   -0.028900    1.232800
C        4.571800    0.312900   -1.156400
F       -2.590400   -0.657800   -2.317100
F       -5.231700   -0.033300   -2.398800
F       -5.218100    0.635100    2.281800
F       -2.582900    0.002800    2.368600
F        2.582900    0.002900   -2.368600
F        5.218100    0.635100   -2.281700
F        5.231700   -0.033400    2.398800
F        2.590400   -0.657900    2.317100
C       -5.252700    0.300700   -0.058900
C        5.252700    0.300700    0.058900
F       -6.549800    0.612900   -0.100500
F        6.549800    0.612900    0.100500
H        0.000000    5.669800    0.000000
```

Optimised LCT excited state geometry for **5**

```
46
B        0.000000    0.347300   -0.000100
N        1.156600   -0.620500   -0.180000
C        0.713600   -1.899200   -0.091700
C       -0.713700   -1.899200    0.091700
N       -1.156600   -0.620400    0.179900
C        1.423800   -3.108000   -0.165000
C        0.703600   -4.285700   -0.078900
C       -0.703700   -4.285700    0.078900
C       -1.423900   -3.108000    0.165000
H       -2.498000   -3.108500    0.303500
H       -1.224800   -5.234900    0.140300
H        1.224700   -5.234900   -0.140300
H        2.498000   -3.108500   -0.303500
C        0.000100    4.692300   -0.000500
C        1.011100    3.976100   -0.658200
C        1.022100    2.600800   -0.659800
C        0.000000    1.828400   -0.000200
C       -1.022000    2.601000    0.659200
C       -1.011000    3.976300    0.657300
H        1.792800    4.514300   -1.188200
H        1.782600    2.091300   -1.238900
H       -1.782600    2.091600    1.238500
H       -1.792600    4.514700    1.187200
C       -2.536500   -0.341900    0.094300
C       -3.200900   -0.464900   -1.124700
C       -3.277500    0.048300    1.204800
C       -4.555800   -0.198600   -1.238700
C       -4.630900    0.330800    1.104900
C        2.536500   -0.341900   -0.094200
C        3.200700   -0.464700    1.124900
C        3.277700    0.047900   -1.204700
C        4.555600   -0.198300    1.239000
C        4.631000    0.330400   -1.104700
F       -2.524400   -0.855000   -2.201800
F       -5.171800   -0.326100   -2.410400
F       -5.318500    0.711800    2.177700
F       -2.678100    0.191100    2.384000
F        2.678400    0.190500   -2.384000
F        5.318800    0.711200   -2.177500
F        5.171400   -0.325600    2.410900
F        2.524100   -0.854500    2.202000
C       -5.271100    0.200200   -0.118900
C        5.271100    0.200100    0.119100
F       -6.569700    0.457800   -0.219100
F        6.569600    0.457700    0.219500
H        0.000100    5.777100   -0.000600
```

Optimised RCT excited state geometry for **5**

```
46
B       -0.106900   -0.014100   -0.104100
N       -1.164700    1.001400   -0.320100
C       -0.599100    2.214000   -0.302100
C        0.823100    2.093800   -0.125000
N        1.125300    0.759500    0.010500
C       -1.204100    3.488100   -0.443800
C       -0.385000    4.584300   -0.435300
```

C	1.018400	4.448800	-0.278300
C	1.635300	3.213700	-0.123700
H	2.708400	3.132200	0.000500
H	1.630800	5.344100	-0.271900
H	-0.806600	5.576600	-0.544700
H	-2.277200	3.551400	-0.547000
C	-0.290300	-4.338400	0.202900
C	-0.938500	-3.695900	-0.846600
C	-0.907200	-2.311600	-0.943400
C	-0.203500	-1.544300	-0.002200
C	0.456900	-2.212900	1.042100
C	0.403300	-3.594900	1.152400
H	-1.481900	-4.273800	-1.587100
H	-1.423800	-1.823600	-1.760900
H	0.992000	-1.643500	1.795900
H	0.900900	-4.092700	1.978700
C	2.460200	0.295500	0.051800
C	3.165400	0.081100	-1.128800
C	3.098900	0.033700	1.258700
C	4.469300	-0.388100	-1.111200
C	4.399700	-0.443900	1.293600
C	-2.622300	0.880200	-0.368200
C	-3.281400	1.011800	0.893000
C	-3.203100	-0.046900	-1.270100
C	-4.370000	0.250700	1.228700
C	-4.295500	-0.792000	-0.945900
F	2.577200	0.327200	-2.295200
F	5.129700	-0.585000	-2.246700
F	4.991100	-0.699500	2.455500
F	2.442200	0.206700	2.404100
F	-2.684900	-0.132400	-2.531100
F	-4.877900	-1.588100	-1.861800
F	-4.999900	0.447400	2.401200
F	-2.942500	2.081500	1.678100
C	5.086200	-0.647200	0.104900
C	-4.882100	-0.684700	0.332500
F	6.333400	-1.096300	0.130800
F	-5.758300	-1.625300	0.745700
H	-0.329400	-5.420400	0.284000

Optimised ground state geometry for **11**

72

C	8.667200	-0.189300	-0.802300
C	7.475100	0.186000	-1.431600
C	6.275000	-0.009900	-0.750500
C	6.266500	-0.566000	0.551800
C	7.457200	-0.942800	1.170800
C	8.658200	-0.747800	0.479700
N	4.954300	0.234600	-1.140100
C	4.627700	0.905200	-2.393000
N	4.941300	-0.658700	0.988500
C	4.587100	-1.229900	2.281900
B	4.086100	-0.168700	-0.062800
B	-1.899900	0.004600	-0.012300
N	-2.749400	1.169200	0.112700
C	-4.099400	0.764700	0.068100
C	-4.138000	-0.635400	-0.065700
N	-2.812600	-1.112300	-0.126400

C	-5.270800	1.510000	0.140200
C	-6.489200	0.825600	0.079700
C	-6.527600	-0.566800	-0.048900
C	-5.348900	-1.316100	-0.123500
H	7.459300	-1.378400	2.165500
H	9.594900	-1.033800	0.950000
H	9.610900	-0.043800	-1.320600
H	7.490700	0.612000	-2.430300
H	5.205200	0.443400	-3.204700
H	3.572600	0.715700	-2.606000
H	5.145500	-2.165300	2.421600
H	3.526600	-1.495000	2.245600
H	-5.378700	-2.396500	-0.226700
H	-7.485100	-1.077400	-0.093300
H	-7.417100	1.387100	0.135300
H	-5.240800	2.590400	0.243500
C	2.519600	-0.115600	-0.047300
C	1.808200	0.526300	0.983700
C	0.414800	0.571500	0.994000
C	-0.343400	-0.038000	-0.023500
C	0.363700	-0.689500	-1.052300
C	1.757000	-0.720700	-1.064900
H	2.354300	1.010400	1.790200
H	-0.090300	1.075700	1.813500
H	-0.182100	-1.167600	-1.861200
H	2.262700	-1.238800	-1.877000
C	4.881000	2.416900	-2.357300
H	5.926700	2.641500	-2.124500
H	4.641700	2.866100	-3.328100
H	4.254700	2.892500	-1.595000
C	4.846300	-0.286700	3.462500
H	4.250200	0.627500	3.368800
H	4.576500	-0.776200	4.405500
H	5.899600	0.005700	3.518700
C	-2.519200	-2.493400	-0.152700
C	-2.534500	-3.251500	1.024100
C	-2.213500	-3.152500	-1.347300
C	-2.248000	-4.614000	1.014900
C	-1.913100	-4.512100	-1.373100
C	-1.939200	-5.245000	-0.188800
C	-2.381500	2.532200	0.138200
C	-2.372500	3.294500	-1.035900
C	-2.024600	3.169500	1.330400
C	-2.013000	4.639600	-1.026700
C	-1.651300	4.510900	1.356100
C	-1.654300	5.248600	0.174400
F	-2.821200	-2.659800	2.187200
F	-2.266000	-5.317700	2.151400
F	-1.660700	-6.550200	-0.205700
F	-1.611100	-5.116800	-2.526700
F	-2.175100	-2.464800	-2.496400
F	-2.007700	2.476500	2.476800
F	-1.301500	5.094400	2.507200
F	-1.305700	6.536800	0.191400
F	-2.008600	5.347500	-2.160700
F	-2.706600	2.723400	-2.196700

Optimised LCT excited state geometry for **11**

```
72
C       -8.636200   -0.860600    0.619500
C       -7.454100   -0.961500    1.323700
C       -6.253200   -0.678400    0.647500
C       -6.276500   -0.265500   -0.735800
C       -7.496200   -0.179300   -1.429800
C       -8.656200   -0.481100   -0.745300
N       -4.976600   -0.716000    1.080000
C       -4.651900   -0.876100    2.490600
N       -5.015200   -0.032600   -1.152900
C       -4.707300    0.281300   -2.540700
B       -4.062300   -0.316600   -0.037700
B        1.849600    0.036900   -0.008000
N        2.668700    1.240400   -0.128800
C        4.023600    0.894800   -0.058800
C        4.123700   -0.498200    0.070200
N        2.832000   -1.036300    0.123800
C        5.157500    1.688400   -0.107000
C        6.402100    1.062900   -0.035600
C        6.501700   -0.320900    0.078400
C        5.359600   -1.119600    0.134100
H       -7.523400    0.123700   -2.469300
H       -9.609700   -0.421100   -1.259100
H       -9.574900   -1.077100    1.117900
H       -7.447900   -1.258900    2.365200
H       -5.261100   -1.686800    2.904600
H       -3.610800   -1.183500    2.562600
H       -5.329900   -0.348100   -3.186800
H       -3.670800   -0.008500   -2.714200
H        5.436400   -2.197600    0.232000
H        7.479900   -0.788200    0.129000
H        7.303200    1.666500   -0.074000
H        5.078900    2.766200   -0.204700
C       -2.570100   -0.246500   -0.047000
C       -1.842400    0.687300   -0.865200
C       -0.477500    0.782000   -0.836900
C        0.332700   -0.066600   -0.023200
C       -0.376000   -1.019800    0.763100
C       -1.743200   -1.101000    0.765900
H       -2.388400    1.376200   -1.503200
H        0.003900    1.500300   -1.493000
H        0.180400   -1.685100    1.415400
H       -2.204700   -1.882900    1.361900
C       -4.859000    0.415600    3.277300
H       -5.898000    0.754700    3.221500
H       -4.604000    0.261300    4.329700
H       -4.216500    1.206200    2.880800
C       -4.917700    1.754700   -2.879100
H       -4.278600    2.392400   -2.262700
H       -4.673100    1.937800   -3.929500
H       -5.955600    2.058100   -2.712200
C        2.629400   -2.422200    0.008300
C        2.751400   -3.056200   -1.227500
C        2.318500   -3.214800    1.108800
C        2.562100   -4.422000   -1.365700
C        2.111500   -4.580600    0.986600
C        2.243600   -5.185900   -0.252900
C        2.264200    2.581000   -0.006800
C        2.242500    3.203400    1.240400
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C	1.887100	3.339500	-1.110500
C	1.853000	4.525200	1.386300
C	1.482200	4.659700	-0.981700
C	1.475100	5.255400	0.269400
F	3.052100	-2.338400	-2.305900
F	2.682800	-5.004700	-2.557700
F	2.056200	-6.497000	-0.377800
F	1.798900	-5.313100	2.055300
F	2.169600	-2.656400	2.309800
F	1.866900	2.785300	-2.322300
F	1.110600	5.358600	-2.054000
F	1.096600	6.524100	0.401300
F	1.839400	5.097900	2.589100
F	2.598200	2.516700	2.322200

Optimised ground state geometry for **20**

46

B	0.000000	0.232000	0.000000
N	1.154100	-0.642000	0.010200
C	0.705700	-1.975600	0.006400
C	-0.705700	-1.975600	-0.006400
N	-1.154100	-0.642000	-0.010200
C	1.417900	-3.172800	0.036000
C	0.699200	-4.371900	0.021800
C	-0.699200	-4.371900	-0.021800
C	-1.417900	-3.172800	-0.036000
H	-2.502400	-3.172600	-0.067600
H	-1.238600	-5.314700	-0.043200
H	1.238600	-5.314700	0.043200
H	2.502400	-3.172600	0.067600
C	-0.000000	4.623200	-0.000000
C	0.888800	3.920900	-0.816200
C	0.890400	2.526100	-0.809600
C	-0.000000	1.794100	0.000000
C	-0.890400	2.526100	0.809500
C	-0.888800	3.920900	0.816200
H	1.583000	4.459700	-1.456400
H	1.594200	1.997000	-1.446800
H	-1.594200	1.997000	1.446800
H	-1.583000	4.459700	1.456400
C	-2.537200	-0.301700	-0.061300
C	-3.031900	0.471900	-1.117700
C	-3.410600	-0.731800	0.946800
C	-4.382600	0.817600	-1.159600
C	-4.763200	-0.394700	0.892100
C	2.537200	-0.301700	0.061300
C	3.031900	0.471900	1.117700
C	3.410600	-0.731800	-0.946800
C	4.382600	0.817600	1.159600
C	4.763200	-0.394700	-0.892100
C	-5.253600	0.382600	-0.159000
C	5.253600	0.382600	0.159000
H	-0.000000	5.710300	-0.000000
H	-6.306500	0.647900	-0.197500
H	-4.755000	1.422300	-1.982000
H	-2.352300	0.798600	-1.898200
H	-3.021900	-1.320800	1.772200

H	-5.432200	-0.733600	1.678600
H	3.021900	-1.320900	-1.772200
H	2.352200	0.798600	1.898200
H	4.755000	1.422300	1.982000
H	6.306500	0.647900	0.197500
H	5.432200	-0.733600	-1.678600

Optimised LCT excited state geometry for **20**

46

B	0.000000	0.301900	-0.000000
N	-1.178600	-0.648200	0.056200
C	-0.719100	-1.926400	0.023800
C	0.719200	-1.926300	-0.023900
N	1.178700	-0.648200	-0.056200
C	-1.424000	-3.143200	-0.016000
C	-0.706600	-4.320500	-0.021300
C	0.706700	-4.320400	0.021200
C	1.424100	-3.143200	0.016000
H	2.505600	-3.147400	0.046600
H	1.235800	-5.266900	0.053100
H	-1.235700	-5.266900	-0.053200
H	-2.505500	-3.147400	-0.046600
C	-0.000100	4.654800	-0.000000
C	-1.085400	3.940000	0.526500
C	-1.098100	2.563400	0.526700
C	-0.000000	1.789400	-0.000000
C	1.098000	2.563500	-0.526700
C	1.085300	3.940000	-0.526600
H	-1.927400	4.478900	0.953800
H	-1.935900	2.052900	0.987100
H	1.935800	2.053000	-0.987100
H	1.927300	4.478900	-0.953900
C	2.552300	-0.323200	0.014500
C	2.996900	0.605600	0.962900
C	3.472500	-0.907400	-0.862600
C	4.347700	0.914400	1.045500
C	4.819100	-0.587400	-0.773100
C	-2.552300	-0.323200	-0.014500
C	-2.996900	0.605500	-0.962900
C	-3.472400	-0.907400	0.862600
C	-4.347800	0.914400	-1.045500
C	-4.819000	-0.587500	0.773100
C	5.264400	0.320800	0.185000
C	-5.264400	0.320700	-0.185000
H	-0.000100	5.739900	-0.000000
H	6.318100	0.571900	0.250600
H	4.683600	1.630900	1.788600
H	2.277700	1.068000	1.627900
H	3.121200	-1.586500	-1.632300
H	5.522700	-1.038500	-1.465800
H	-3.121200	-1.586600	1.632300
H	-2.277700	1.068000	-1.627800
H	-4.683700	1.630900	-1.788500
H	-6.318100	0.571800	-0.250600
H	-5.522700	-1.038700	1.465800

Reference

S1. L. Weber, D. Eickhoff, T. B. Marder, M. A. Fox, P. J. Low, A. D. Dwyer, D. J. Tozer, S. Schwedler, A. Brockhinke, H.-G. Stammler, B. Neumann, *Chem. Eur. J.* 2012, **18**, 1369-1382.