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Effect of substitution on deep-blue Ir(III) N-heterocyclic carbene (NHC) emitters

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Supporting Information

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Materials, methods and instrumentation

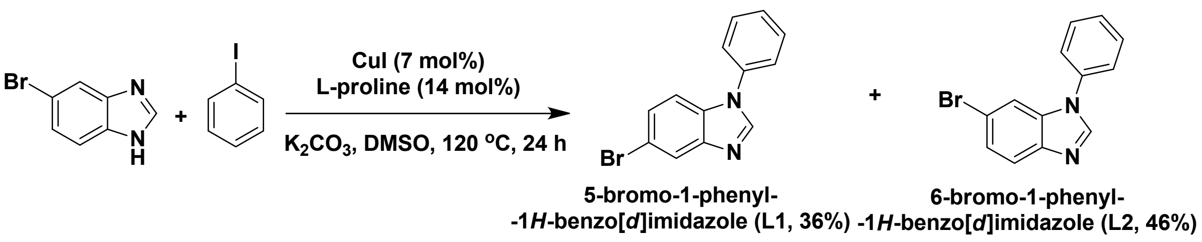
^{1}H and ^{13}C NMR spectra were recorded with a 500 MHz JEOL spectrometer (500 and 126 MHz for ^{1}H and ^{13}C, respectively) in the deuterated solvents as mentioned in the experimental section. The following abbreviations have been used for multiplicity assignments: “s” for singlet, “d” for doublet, “t” for triplet, “m” for multiplet, and “br” for broad. Chemical shifts are reported in parts per million (ppm) relative to respective residual solvent protons and coupling constants (J) are reported in Hertz (Hz). Chromatography was performed on columns with an i.d. of 25−30 mm on silica gel (Silica gel, 100−200 μm). The progress of the reactions and the elution of the products were followed by TLC (silica gel on plastic sheets, 250 μm with indicator F-254). Compounds were visualized under UV light. High-resolution mass spectra were recorded by Xevo, G2-XS QT in ESI$^+$ mode.

Photophysical measurements

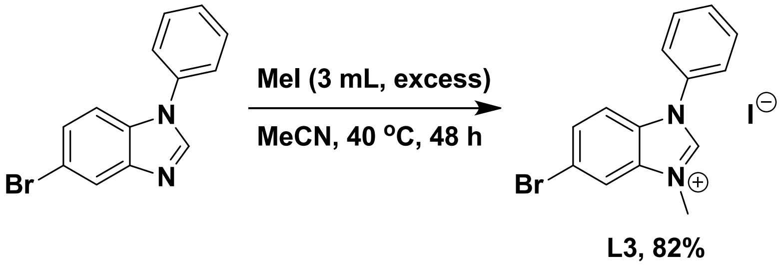
All photophysical measurements were carried out in deaerated acetonitrile at RT in septa-sealed quartz cells. UV−vis spectroscopy (UV) was completed at room temperature using a Cary 5000 UV−vis spectrophotometer. All samples were prepared in HPLC grade MeCN, with varying concentrations in the order of 10^{-5}−10^{-6} μM. Molar absorptivity determination was verified by a linear least-squares fit of values obtained from at least four independent solutions at varying concentrations. For steady state luminescence spectra at 298 K and 77 K, measurements in HPLC grade solvents containing the samples were excited at 360 nm using Shimadzu corp. spectrofluorimeter RF 6000. Excited state lifetimes were measured by time correlated single photon counting (TCSPC) with a Horiba DeltaFlex (light pulse:Hamamatsu PL2 laser diode, pulse width at 360 nm:2 ns). The PL decays were fitted to a bi-exponetial decay function where the normalized pre-exponential factors are quoted. Emission quantum yields were determined using the optical dilution method.[1] A stock solution with an absorbance of *ca.* 1.0 was prepared and then four dilutions were prepared to obtain solutions with absorbance of *ca.* 0.100, 0.075, 0.05 and 0.025, respectively. The Beer-Lambert law was found to be linear at the concentrations of the solutions. The steady-state emission spectra (λ_{exc} = 360 nm) were then measured after the solutions were degassed in the N_2 atmosphere. For each sample, linearity between absorption and emission intensity was verified through linear regression analysis and additional measurements were acquired until the Pearson regression factor (R^2) for the linear fit of the data set surpassed 0.9. Individual relative quantum yield values were calculated for each solution and the values reported represent the slope value. The equation $\Phi_s = \Phi_r(A_r/A_s)(I_s/I_r)(n_s/n_r)^2$ was used to calculate the relative quantum yield of each of the samples, where Φ_r is the absolute quantum yield of the reference, n is the refractive index of the solvent, A is the absorbance at the excitation wavelength and I is the integrated area under the corrected emission curve. The subscripts s and r refer to the sample and reference, respectively. Acetonitrile solution of quinine sulphate in 0.5 M H_2SO_4 (Φ_r = 54.6%) was used as the external reference.[2] Thin film PLQY measurements on quartz plates were performed using an integrating sphere in a Hammamatsu C9920-02 system.[3] Samples were excited by a xenon lamp coupled to a monochromator, which enabled selectivity of the excitation wavelength, chosen here to be 330 nm. The output was then fed into the integrating sphere via a fiber, exciting the sample. PL was collected with a multimode fibre and detected with a back-thinned CCD. The thin film PLQY were then measured in N_2 filled sphere.

Electrochemical measurements

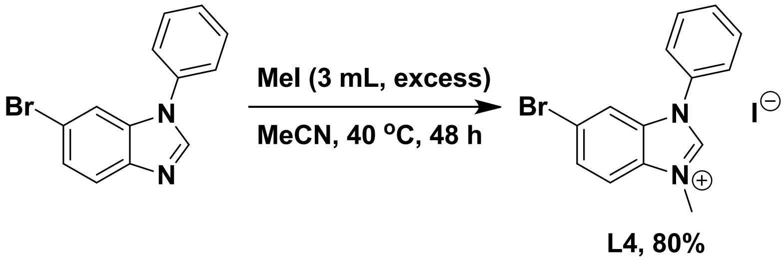
Cyclic voltammetry (CV) measurements were performed on an Electrochemical Analyzer with potentiostat/Galvanostat (model no. CH660E) at a sweep rate of 100 mV/s. Solutions for CV were prepared in MeCN and degassed by purging nitrogen through the solutions for about 6 min before scanning. For supporting electrolytes Tetra(*n*-butyl)ammoniumhexafluorophosphate ($TBAPF_6$; *ca.* 0.1 M in MeCN) was used. For working, counter and reference electrodes Glassy carbon, platinum and silver electrodes, were used. As an internal reference, ferrocene/ferrocenium (Fc/Fc^+) redox couple was used corresponding to a saturated calomel electrode (0.38 V *vs* SCE) [4] and the redox potentials were calibrated to this.



Scheme S1. Synthesis of 5-bromo-1-phenyl-1*H*-benzo[*d*]imidazole (**L1**) and 6-bromo-1-phenyl-1*H*-benzo[*d*]imidazole (**L2**).



Scheme S2. Synthesis of 5-bromo-1-phenyl-3-methyl-1*H*-benzo[*d*]imidazole-3-ium iodide (**L3**).



Scheme S3. Synthesis of 6-bromo-1-phenyl-3-methyl-1*H*-benzo[*d*]imidazole-3-ium iodide (**L4**).

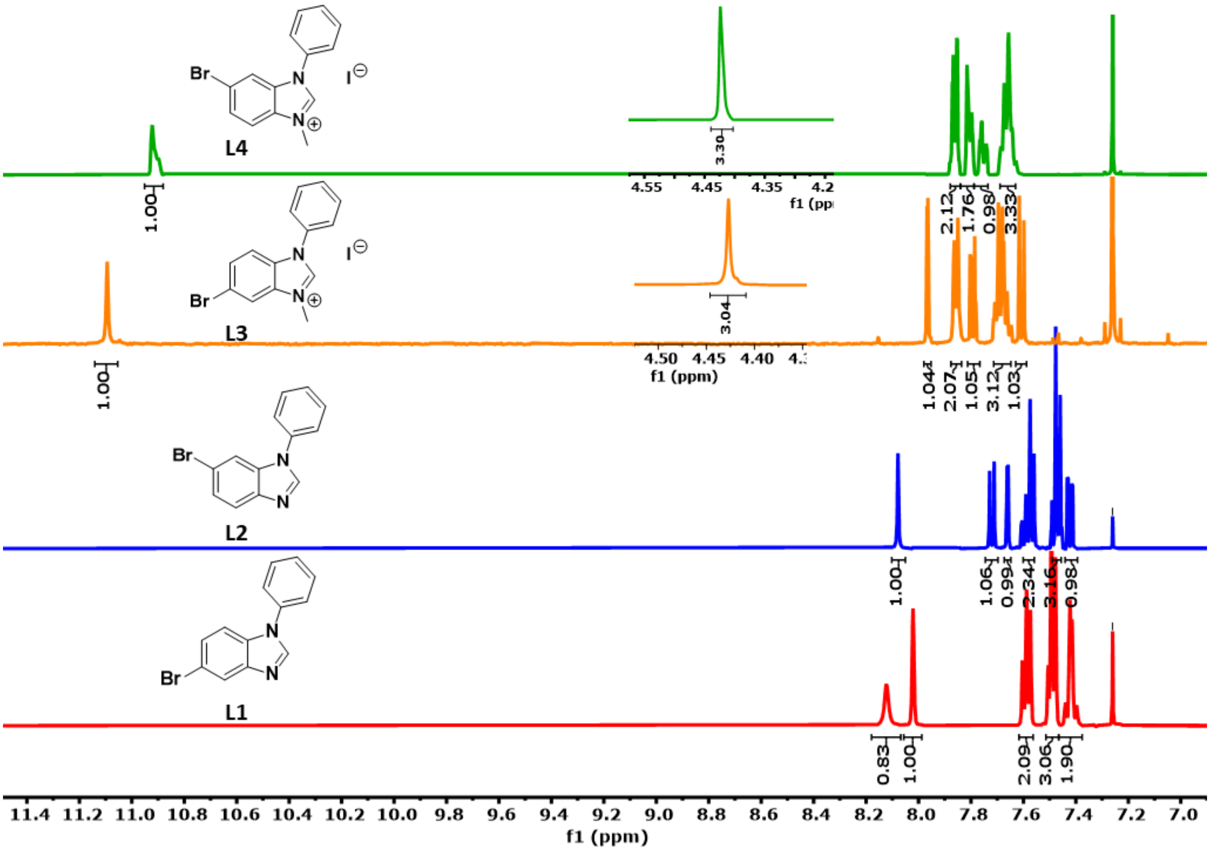


Fig S1. Stacked ^{1}H NMR spectra of **L1**, **L2**, **L3** and **L4** in $CDCl_3$ at 500 MHz at RT (peak at 7.26 ppm corresponds to the solvent residual peak for $CDCl_3$).

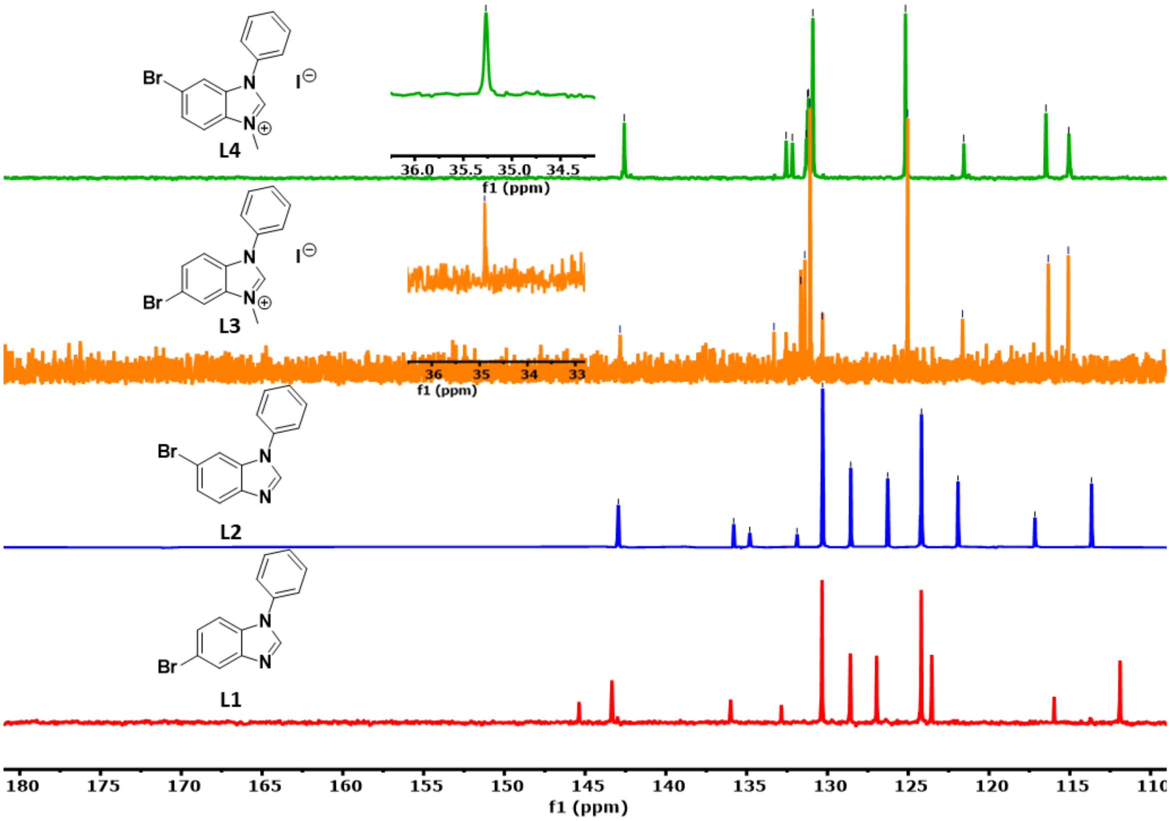


Fig S2. Stacked ^{13}C NMR spectra of **L1**, **L2**, **L3** and **L4** in $CDCl_3$ at 125 MHz at RT.

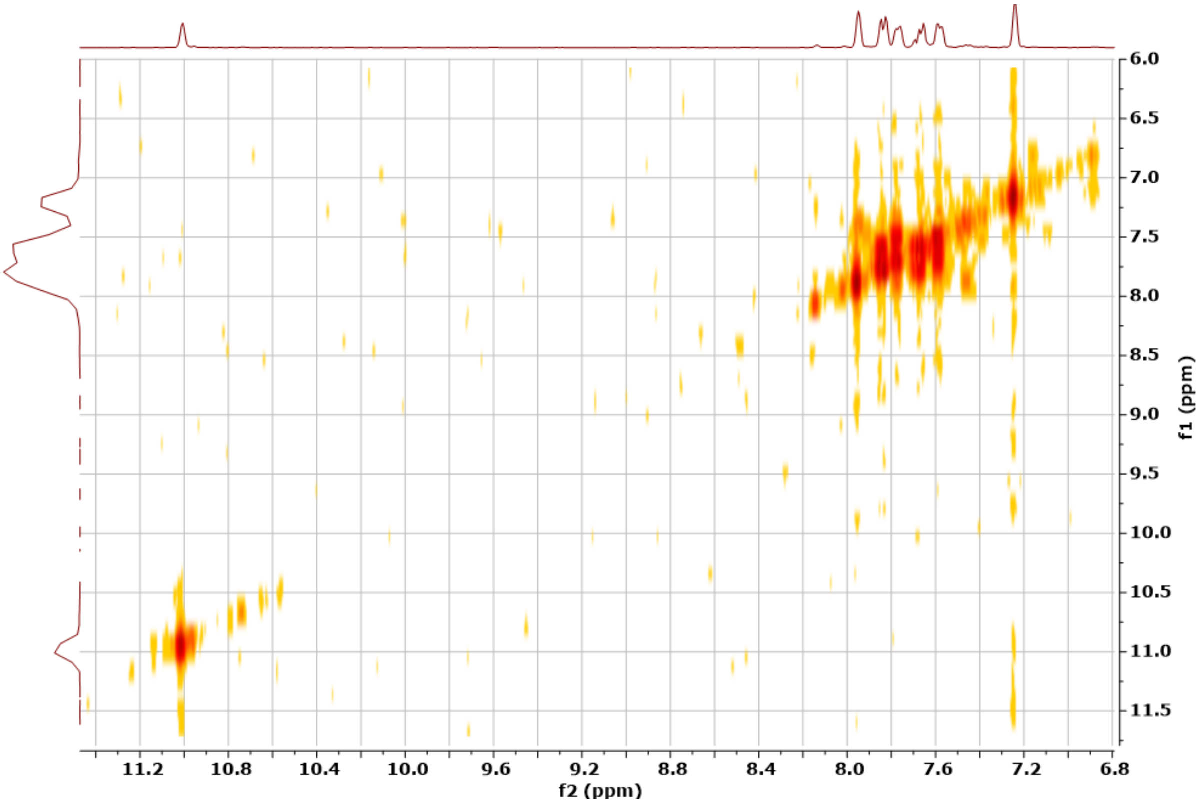


Fig S3. ^{1}H-^{1}H COSY NMR of **L3** at RT in $CDCl_3$ at 500 MHz.

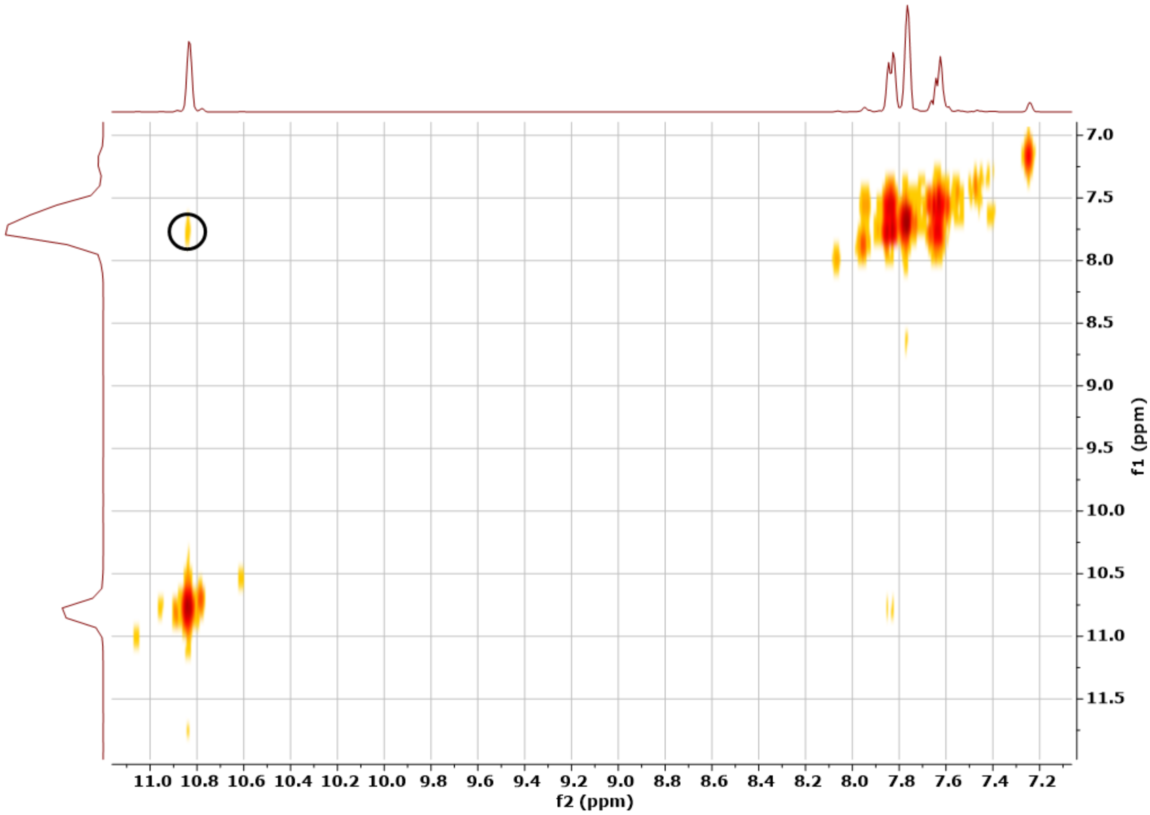


Fig S4. ^{1}H-^{1}H COSY NMR of **L4** at RT in CDCl$_3$ at 500 MHz. The interaction between the carbenic proton and the *ortho* proton of the *N*-Ph moiety is shown in circle.

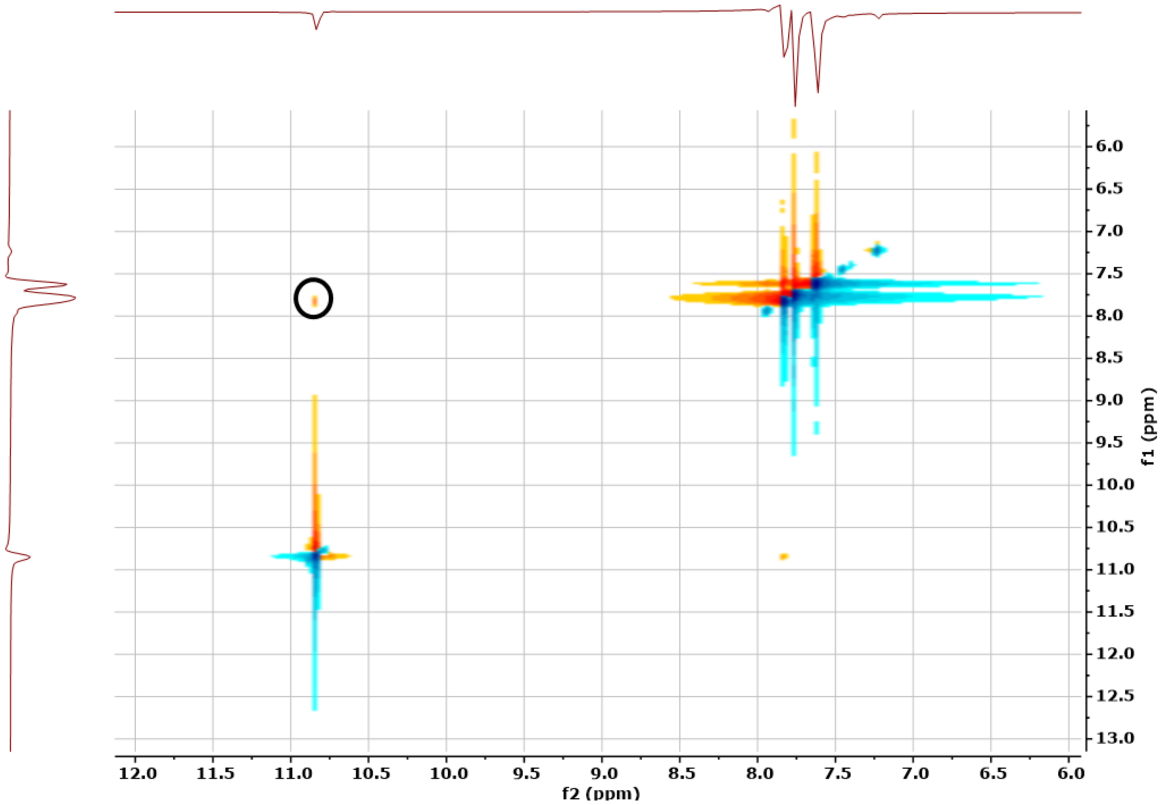
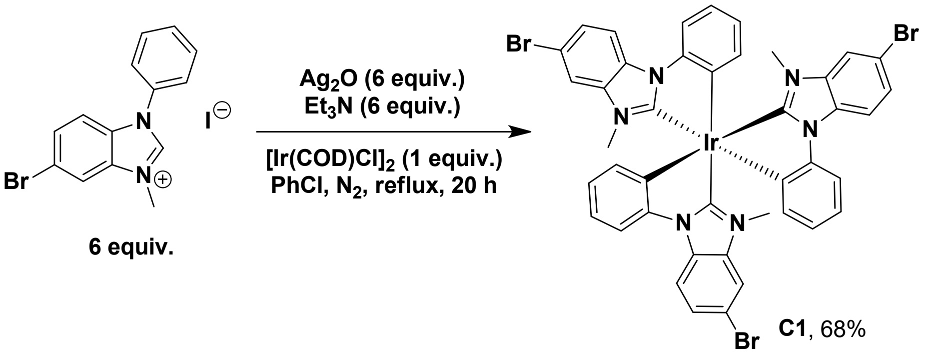
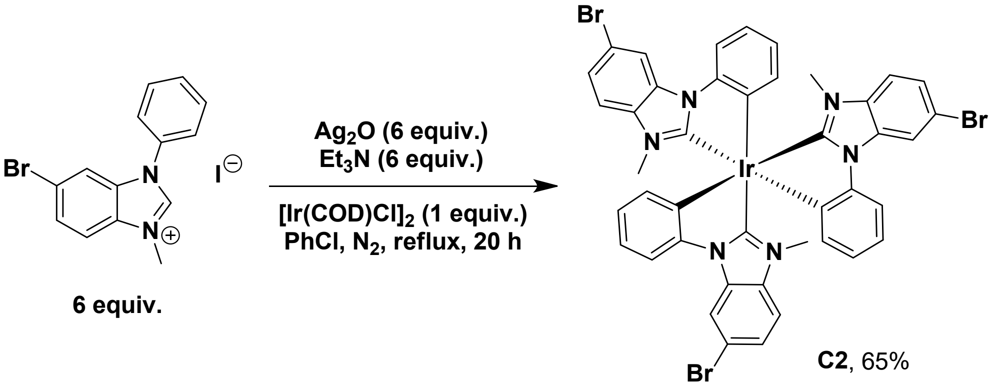


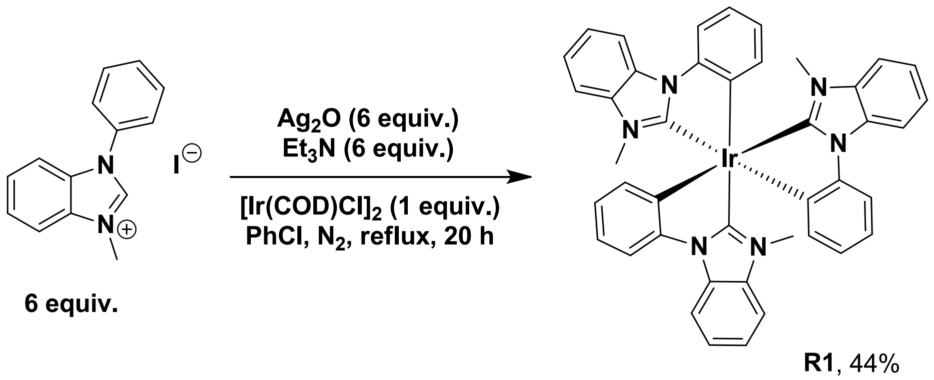
Fig S5. ^{1}H-^{1}H NOESY NMR of **L4** at RT in CDCl$_3$ at 500 MHz. The interaction between the carbenic proton and the *ortho* proton of the *N*-Ph moiety is shown in circle.



Scheme S4. Synthesis of *mer*-[tris(5-bromo-1-phenyl-3-methyl-1*H*-benzo[*d*]imidazoline-2-ylidine-*C*,*C2′*)iridium(III)], (**C1**).



Scheme S5. Synthesis of *mer*-[tris(6-bromo-1-phenyl-3-methyl-1*H*-benzo[*d*]imidazoline-2-ylidine-*C*,*C2′*)iridium(III)], (**C2**).



Scheme S6. Synthesis of *mer*-[tris(1-phenyl-3-methyl-1*H*-benzo[*d*]imidazoline-2-ylidine-*C*,*C2′*)iridium(III)], (**R1**).

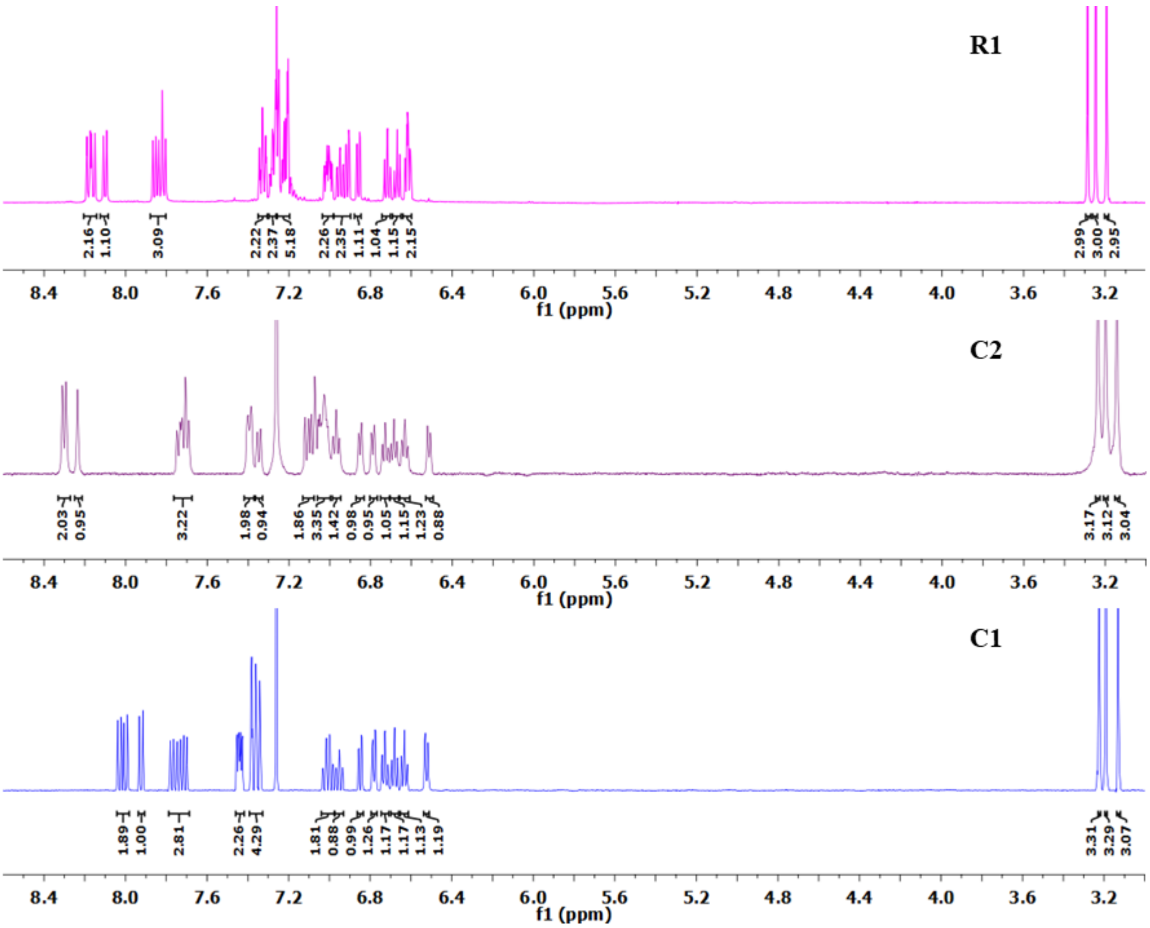


Fig S6. Stacked ^{1}H NMR spectra of **C1** (bottom) and **C2** (middle) and **R1**(top) in CDCl$_3$ at 500 MHz at RT (peak at 7.26 ppm corresponds to the solvent residual peak for CDCl$_3$.

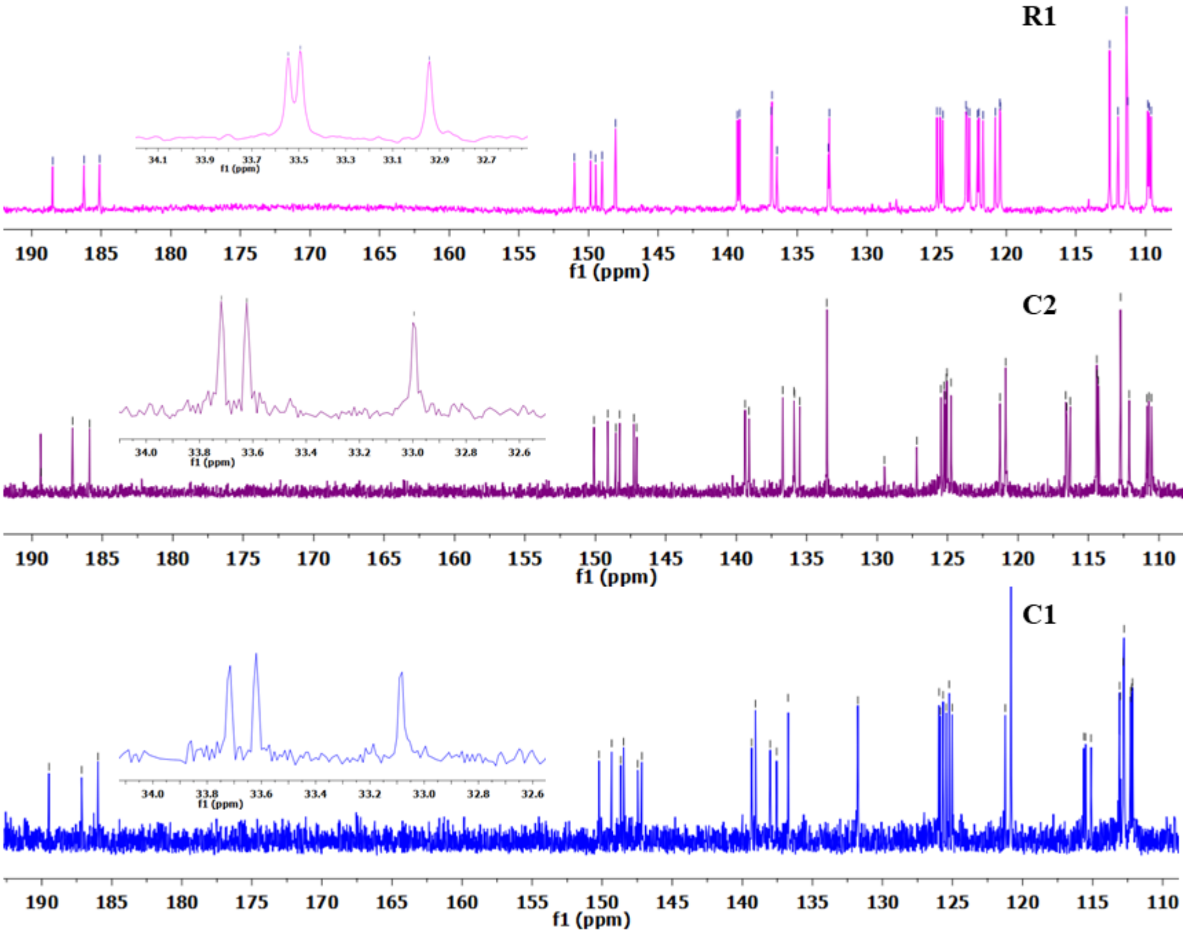


Fig S7. Stacked ^{13}C NMR spectra of **C1** (bottom) and **C2** (middle) and **R1**(top)in $CDCl_3$ at 125 MHz at RT (peak at 77.16 ppm corresponds to the solvent residual peak for $CDCl_3$).

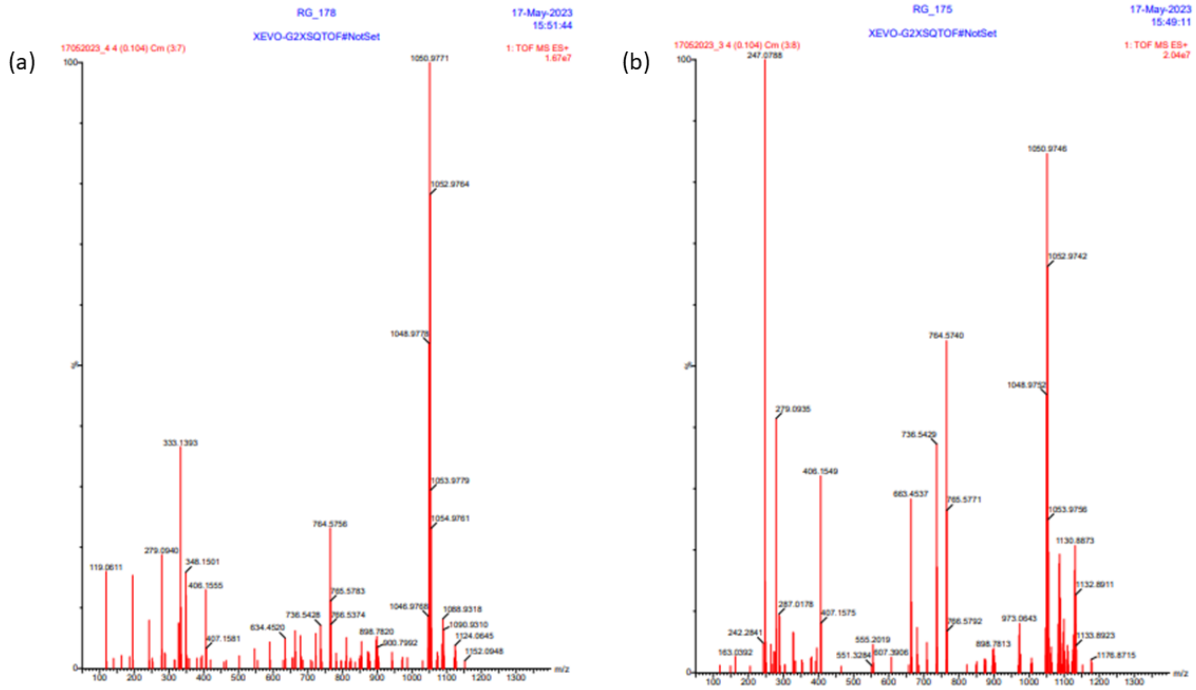


Fig S8. Stacked HRMS images of (a) **C1** and (b) **C2** recorded at a ESI+ mode.

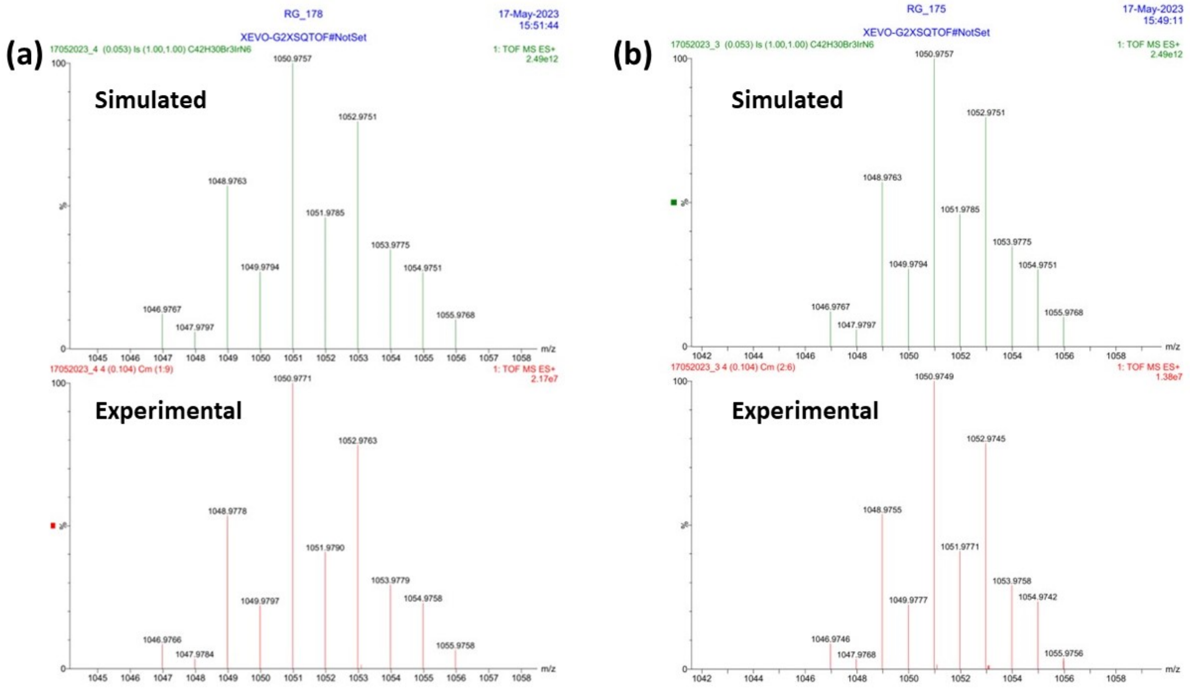
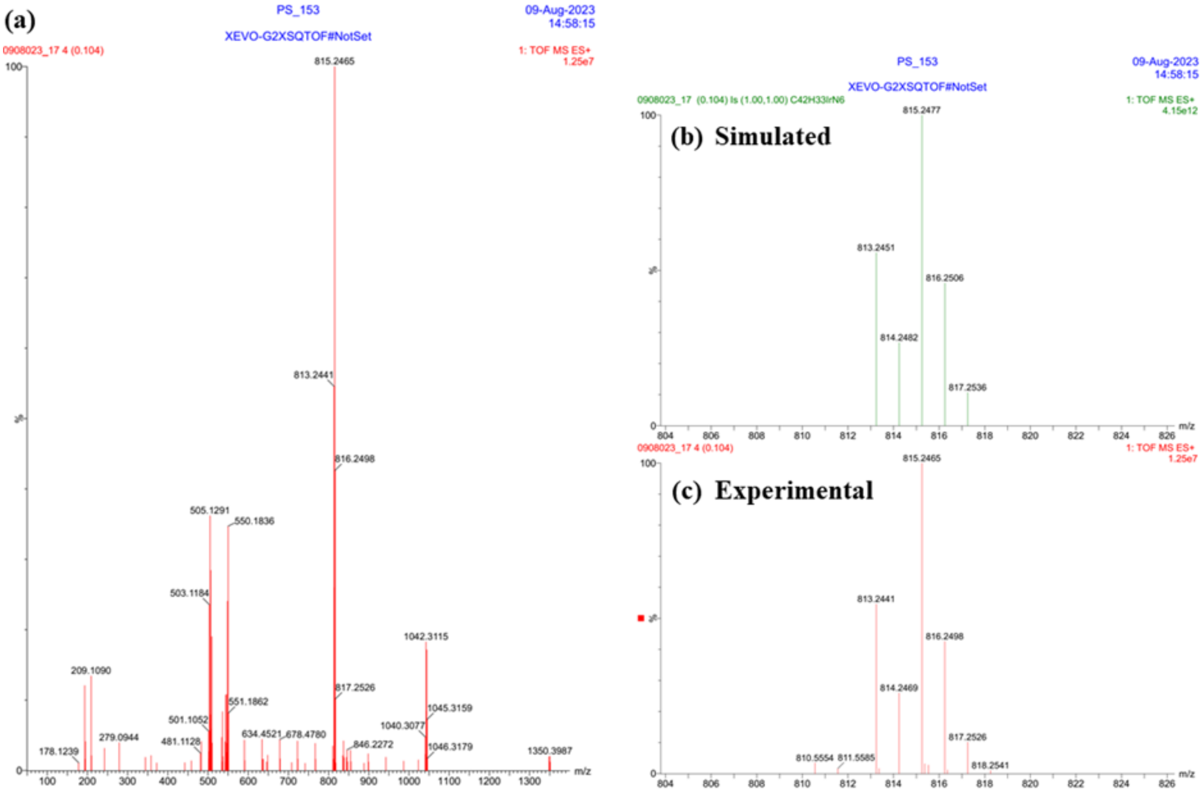


Fig S9. Stacked HRMS images of (a) **C1**, top – simulated and bottom – experimental, (b) **C2**, top – simulated and bottom – experimental.



X-ray diffraction studies

Single crystal suitable for X-ray analysis were grown by slow evaporation of ethylacetate for **L1** and **L2** whereas the single crystals for **L3** were obtained by slow evaporation of acetone. However the crystals for **L4** were obtained by the vapour diffusion of hexanes in the concentrated solution of the **L4** in ethylacetate. X-ray crystallographic data were collected from a single crystal sample, which was mounted on a loop fiber. Data were collected using a Bruker diffractometer equipped with a Bruker APEX-II CCD detector, a Kappa goniometer and a Mo-K_{α} source (λ = 0.71073 Å) at 100(2) K for **L1**, 103(2) K for **L2**, 100(2) K for **L3** and 100(2) for **L4**. The crystal-to-detector distance was 4.0 cm and the data collection was carried out in 1024 x 1024 pixel mode. The initial unit cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 180.0 degree scan in 180 frames over three different parts of the reciprocal space.

The diffraction quality of the crystals were checked, revealing in some cases poor diffraction with a large amount of diffuse scattering, signaling extensive crystal disorder. Data collection, cell refinement and data reduction were done using APEX2[5] and SAINT[6]. Absorption corrections were applied using SADABS[7]. Structures were solved by direct methods using SHELXS2012 and refined on F^2 by full-matrix least squares using SHELXL2012[8]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on calculated positions using a riding model. The minor positional disorders associated with the phosphorus atom and some of the fluorine atoms in the PF_6 anion or carbon atoms of the cosolvated acetonitrile molecule in **L4** were not taken into account for modeling.

Table S1. Crystallographic data of complexes ligands **L1**, **L2, L3** and **L4**.

Compound	**L1**	**L2**	**L3**	**L4**
CCDC numbers	2271386	2271385	2271387	2271388
empirical formula	$C_{13}H_9BrN_2$	$C_{13}H_9BrN_2$	$C_{14}H_{12}BrIN_2$	$C_{14}H_{12}BrIN_2$
fw	273.13	273.13	415.073	415.067
cryst syst	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	P121/n1	P121/c1	P121/c1	P121/c1
a [Å]	16.718(3)	9.4258(5)	10.6109(18)	8.811(3)
b [Å]	3.9640(8)	16.5006(11)	10.0029(16)	22.538(7)
c [Å]	16.793(4)	7.3773(4)	14.313(2)	7.398(2)
α [°]	90	90	90	90
β [°]	101.542(7)	108.406(2)	107.058(5)	106.91(1)
γ [°]	90	90	90	90
vol [Å]^3	1090.4(4)	1088.70(11)	1452.4(4)	1405.6(8)
Z	4	4	4	4
ρ (calc) [mg/m^3]	1.664	1.666	1.898	1.980
μ [cm^{-1}]	3.740	3.745	4.940	5.107
F(000)	544	543.361	792.00	792.0
cryst	colourless, plate	colourless, block	colourless, block	colourless, block
cryst size [mm^3]	0.07 × 0.15 × 0.2	0.20 × 0.18 × 0.16	0.16 × 0.16 × 0.2	0.16 × 0.16 × 0.2
θ range	1.922 – 28.362°	2.28 – 28.25°	2.01 – 28.36°	2.42 – 28.38°
reflns collected	20489	6754	40011	37947
indep reflns (R_{int})	2708 (0.0355)	2058 (0.0587)	3563 (0.0307)	3491(0.0339)
max/min transm	0.7457/ 0.4131	0.7457/0.4651	0.7457/ 0.5532	0.7457/0.4910
data/restraints/params	2708 / 0 / 145	2058/0/145	3563 / 0/ 164	3491 / 0/ 164
final R indices [$I > 2\sigma(I)$]	R1 = 0.0429, wR2 = 0.0960	R1 = 0.0408, wR2 = 0.1093	R1 = 0.0356, wR2 = 0.1042	R1 = 0.0431, wR2 = 0.1145
R indices (all data)	R1 = 0.0479, wR2 = 0.1037	R1 = 0.0456, wR2 = 0.1124	R1 = 0.0388, wR2 = 0.1063	R1 = 0.0483, wR2 = 0.1184

[a] R1(F) based on observed reflections with I>2σ(I) for **L1**, **L2**, **L3** and **L4**; wR(F^2) and GoF(F^2) based on all data for all compounds.

Table S2. Comparison of bond distances and angles in ligands **L1**, **L2**, **L3** and **L4**.

	Bond Length			Angle		
		Obs. (X-ray)	Calc. (DFT)		Obs. (X-ray)	Calc. (DFT)
L1	Br1-C1	1.909(3)	1.923	N1-C4-N2	113.7(3)	114.360
	N1-C4	1.308(5)	1.305	C3-N1-C4	104.6(3)	104.517
	N2-C4	1.378(4)	1.385	C4-N2-C5	106.1(3)	105.627
	N2-C8	1.431(4)	1.421			
L2	Br1-C1	1.935(3)	1.923	N1-C13-N2	114.4(3)	114.322
	N1-C13	1.363(4)	1.387	C4-N2-C13	104.3(3)	104.593
	N2-C13	1.312(4)	1.305	C3-N1-C13	106.4(2)	105.590
	N1-C7	1.427(3)	1.422			
L3	C1-Br1	1.912(4)	1.923	N2-C13-N1	110.0(3)	105.379
	N1-C13	1.326(5)	1.415	C8-C7-N1	119.7(3)	119.286
	N2-C13	1.328(5)	1.408	C14-N2-C13	125.3(3)	123.164
	N1-C7	1.443(5)	1.406	C12-C7-N1	118.5(3)	121.304
	N2-C14	1.462(5)	1.446			
L4	Br1-C1	1.913(6)	1.923	N2-C13-N1	109.4(5)	105.362
	N1-C13	1.352(6)	1.416	C8-C7-N1	119.3(4)	121.301
	N2-C13	1.322(7)	1.407	C14-N2-C13	125.1(6)	123.114
	N1-C7	1.441(6)	1.407	C12-C7-N1	118.6(4)	119.245
	N2-C14	1.471(7)	1.445			

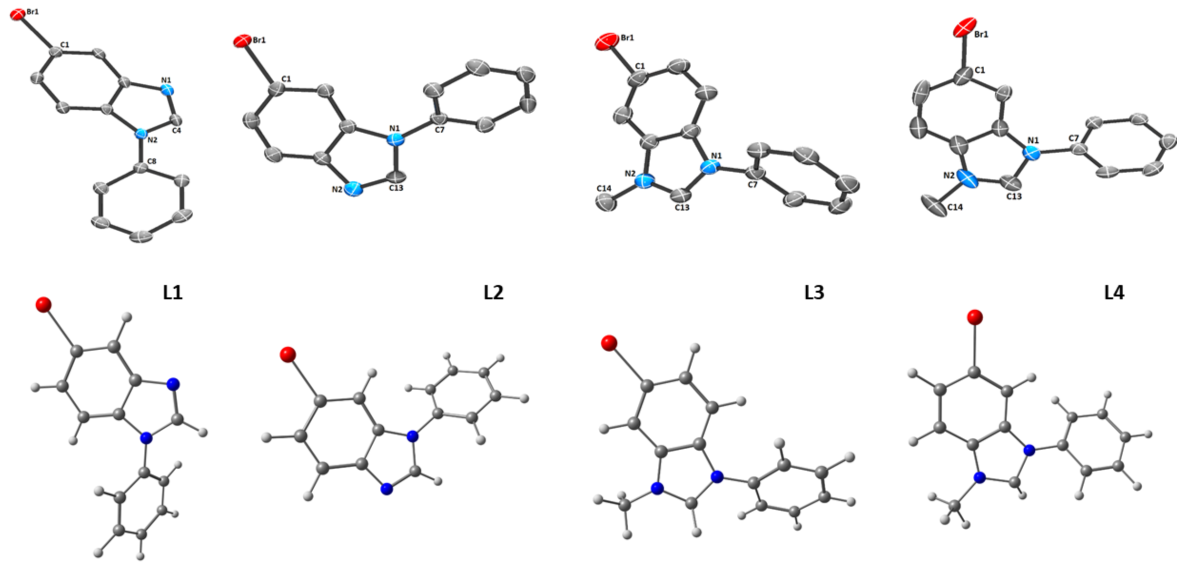


Fig S10. ORTEP (drawn at a 50% probability level) and ball-and-stick views of DFT optimized structures of ligands **L1**-**L4** [[B3LYP/6-31g** for C,H,N,Br]. Counter anions and any cosolvated molecules are removed for clarity.

Table S3. Selected Transitions from TD-DFT calculations of **C1** in the Singlet Ground State (B3LYP/6-31G**[C, H, N], SBKJC-VDZ [Ir], CPCM (MeCN)).

state	λ/nm (TD-DFT)	λ/nm (ε x 10^3 M^{-1}cm^{-1} [expt.]	f	Major transition(s)	character
57	246	245 (4.17)	0.2088	H-4->L+5 (25%), H-7->L+2 (24%), H-1->L+9 (11%) H-5->L+3 (10%),	phenyl(π) to 5-Brbenzimidazole(π^*) (major) + 5-Brbenzimidazole(π) to 5-Brbenzimidazole(π^*) (minor) + Ir(dπ) to 5-Brbenzimidazole(π^*) (minor)
7	307	308 (2.27)	0.3434	H-2->L (79%)	5-Brbenzimidazole(π) to 5-Brbenzimidazole(π^*) (minor) + phenyl(π) to 5-Brbenzimidazole(π^*) (major)+ + Ir(dπ) to 5-Brbenzimidazole(π^*) (minor)
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Table S4. Selected Transitions from TD-DFT calculations of **C2** in the Singlet Ground State (B3LYP/6-31G**[C, H, N], SBKJC-VDZ [Ir], CPCM (MeCN)).

state	λ/nm (TD-DFT)	λ/nm (ε x 10^3 M^{-1}cm^{-1}) [expt.]	f	Major transition(s)	character
58	254	240 (77.31)	0.2336	H-4->L+5 (38%), H-9->L+2 (15%)	6-Brbenzimidazole(π) to 6-Brbenzimidazole(π^*) (major) + phenyl(π) to 6-Brbenzimidazole(π^*) (minor)
7	305	310 (3.21)	0.3687	H-2->L (77%), H-5->L+1 (34%), H-2->L (40%)	phenyl(π) to 6-Brbenzimidazole(π^*) (major) + Brbenzimidazole(π) to 6-Brbenzimidazole(π^*) (minor) + Ir(dπ) to 5-Brbenzimidazole(π^*) (minor)
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Table S5. Comparison of active modes of vibration for **C2** and **R1**.

C2 (C34-Br66)	**R1 (C34-H66)**
Active Modes of Vibration	**Active Modes of Vibration**
Mode 70 (bending)	Mode 74 (bending)
Mode 71 (bending)	Mode 78 (bending)
Mode 73 (stretching)	Mode 85 (bending)
Mode 75 (stretching)	Mode 86 (bending)
Mode 78 (stretching)	Mode 88 (bending)
Mode 80 (stretching)	Mode 89 (bending)

Mode 81 (stretching)	Mode 100 (bending)
Mode 85 (stretching)	Mode 101 (bending)
Mode 86 (stretching)	Mode 104 (bending)
Mode 87 (bending)	Mode 105 (bending)
Mode 92 (bending)	Mode 106 (bending)
Mode 100 (stretching)	Mode 107 (bending)
Mode 103 (bending)	Mode 114 (bending)
Mode 105 (bending)	Mode 118 (bending)
Mode 106 (stretching)	Mode 135 (bending)
Mode 109 (bending)	Mode 136 (bending)
Mode 119 (Stretching)	Mode 139 (bending)
Mode 120 (Stretching)	Mode 140 (bending)
Mode 126 (Stretching)	Mode 142 (bending)
Mode 130 (Stretching)	Mode 144 (bending)
Mode 132 (Stretching)	Mode 146 (bending)
Mode 133 (Stretching)	Mode 150 (bending)
Mode 135 (Stretching)	Mode 151 (bending)
Mode 137 (Stretching)	Mode 152 (bending)
Mode 138 (Stretching)	Mode 153 (bending)
Mode 154 (Stretching)	Mode 155 (bending)
Mode 165 (bending)	Mode 156 (bending)
Mode 171 (Stretching)	Mode 157 (bending)
Mode 172 (bending)	Mode 158 (bending)
Mode 183 (bending)	Mode 159 (bending)
Mode 195 (Stretching)	Mode 160 (bending)
Mode 197 (Stretching)	Mode 163 (bending)
Mode 206 (Stretching)	Mode 164 (bending)
Mode 209 (bending)	Mode 166 (bending)
----	Mode 171 (bending + stretching)
----	Mode 183 (bending)
----	Mode 189 (bending)
----	Mode 190 (bending)
----	Mode 192 (bending)
----	Mode 193 (bending + stretching)
----	Mode 194 (bending + stretching)
----	Mode 224 (stretching)
----	Mode 226 (stretching)
----	Mode 230 (stretching)
----	Mode 231 (stretching)
----	Mode 234 (stretching)
----	Mode 237 (stretching)
----	Mode 240 (stretching)

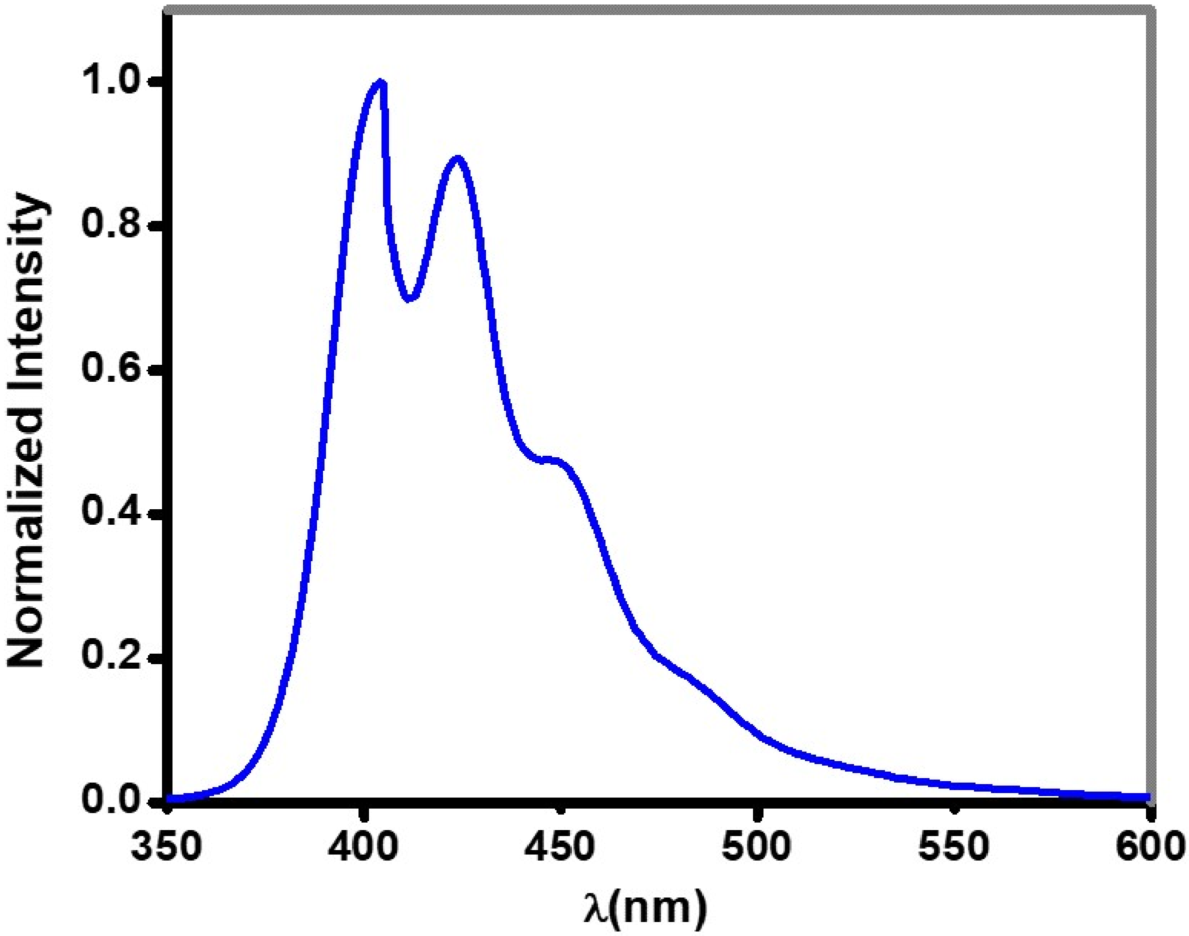

Fig S11. Normalized emission spectra of **R1** in toluene at RT.

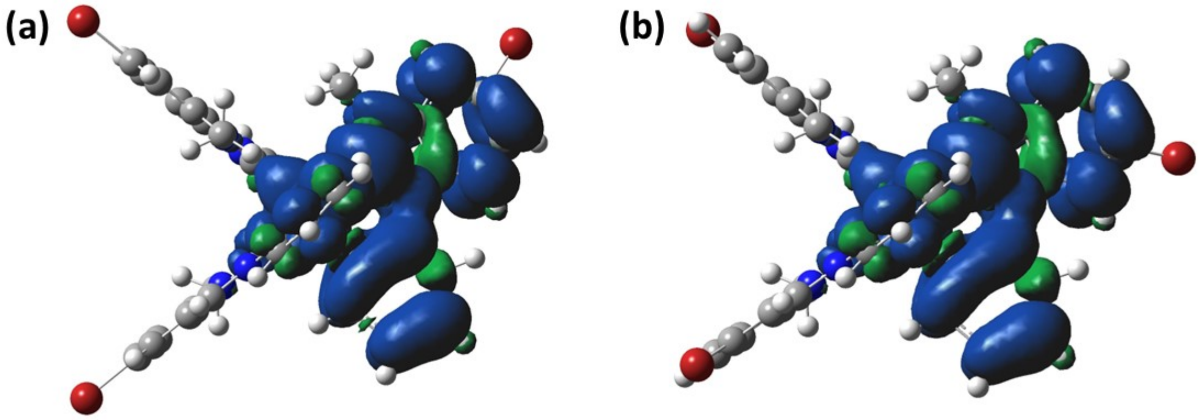

Fig S12. Triplet spin density diagrams of (a) **C1** and (b) **C2** in ethyl acetate (B3LYP/6-31G**[C, H, N], SBKJC-VDZ [Ir], CPCM (MeCN)).

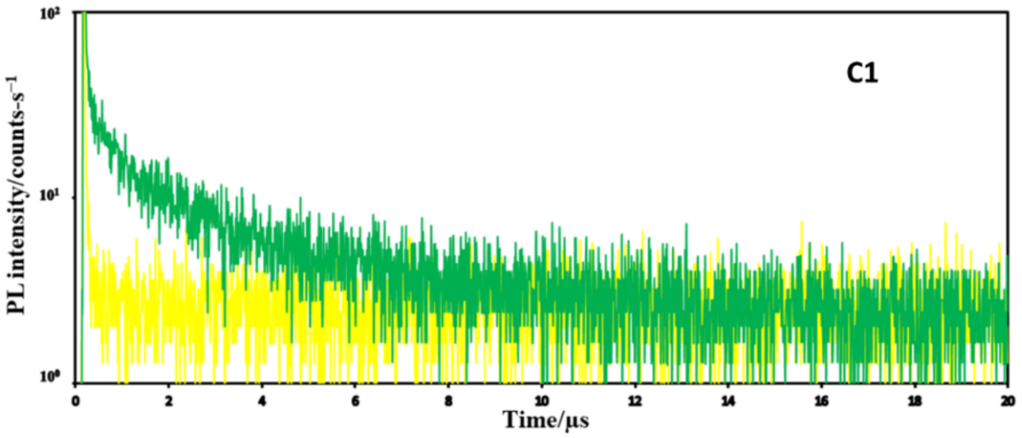

Fig S13. Photoluminescence decay of **C1** in non-degassed (yellow) and degassed (green) conditions in toluene (τ_1 = 508.3 ns (18%), τ_2 = 3584.16 ns (82%), χ^2 = 1.18 for the degassed sample).

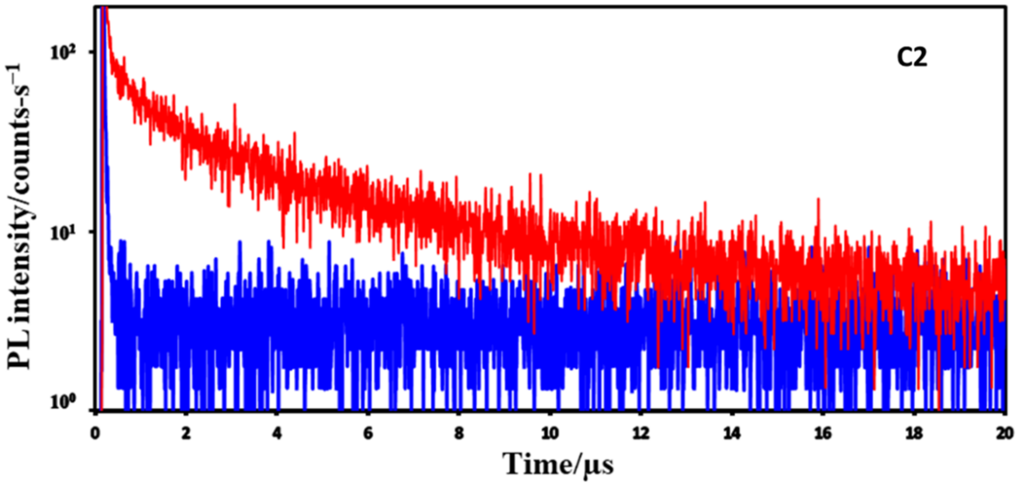

Fig S14. Photoluminescence decay of **C2** in non-degassed (blue) and degassed (red) conditions in toluene (τ_1 = 657.08 ns (13%), τ_2 = 4942.23 ns (87%), χ^2 = 1.16 for the degassed sample).

Table S6. Optimized atomic coordinates obtained from DFT calculations of **L1**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	-0.587304	3.667870	18.984640
2	7	0	-0.847615	3.553072	12.962936
3	6	0	-1.943677	5.062422	9.751573
4	7	0	0.920859	2.537570	13.942861
5	6	0	-1.027249	3.704980	14.336377
6	6	0	-2.000566	4.348526	15.103882
7	6	0	0.091391	3.065091	14.922232
8	6	0	0.336300	2.847496	12.817043
9	6	0	0.243303	3.040180	16.314800

10	6	0	-3.070075	3.783971	11.966471
11	6	0	-1.843225	4.321034	16.486871
12	6	0	-1.688365	4.002504	11.908051
13	6	0	-0.737913	3.670616	17.066973
14	6	0	-3.323200	4.856519	9.809641
15	6	0	-1.124524	4.647872	10.801427
16	6	0	-3.882046	4.221350	10.920668
17	1	0	0.692508	2.576835	11.831415
18	1	0	-3.495921	3.259386	12.815135
19	1	0	-4.953397	4.051156	10.969552
20	1	0	-3.958940	5.189425	8.995050
21	1	0	-1.501962	5.561173	8.894161
22	1	0	-2.844770	4.859018	14.653749
23	1	0	-2.574052	4.805284	17.123901
24	1	0	1.095931	2.551614	16.770548
25	1	0	-0.056036	4.837021	10.776766

Table S7. Optimized atomic coordinates obtained from DFT calculations of **L2**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	-0.539388	3.370012	12.731050
2	6	0	-1.639387	4.867528	9.515555
3	7	0	1.231719	2.360366	13.712683
4	6	0	-0.714796	3.529959	14.103240
5	6	0	-1.694135	4.181071	14.857923
6	6	0	0.405114	2.893739	14.691504
7	6	0	0.645436	2.662865	12.586522
8	6	0	0.547648	2.884512	16.084012
9	6	0	-2.762969	3.592927	11.734267
10	6	0	-1.515123	4.149044	16.236371
11	6	0	-1.381836	3.814526	11.674996
12	6	0	-0.422749	3.513942	16.855877
13	6	0	-3.018468	4.658915	9.574516
14	6	0	-0.819292	4.457764	10.566530
15	6	0	-3.575953	4.025839	10.687375
16	1	0	0.998322	2.386772	11.601236
17	1	0	-3.188179	3.070405	12.584523
18	1	0	-4.646974	3.854157	10.737338
19	1	0	-3.655050	4.988445	8.759209
20	1	0	-1.198873	5.364768	8.656649
21	1	0	-2.537889	4.688250	14.407186
22	35	0	-2.821745	5.016269	17.348922
23	1	0	1.401908	2.398216	16.543096

24	1	0	0.248817	4.648994	10.541341
25	1	0	-0.342933	3.523413	17.936556

Table S8. Optimized atomic coordinates obtained from DFT calculations of [**L3**]$^+$.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	35	0	-1.759857	1.904474	4.906909
2	7	0	-0.193370	4.444123	10.178708
3	7	0	0.337211	5.531689	8.286445
4	6	0	-1.288353	2.631576	6.623745
5	6	0	-0.617698	3.862168	6.661441
6	1	0	-0.383026	4.402201	5.752947
7	6	0	-0.283676	4.355116	7.921436
8	6	0	-0.613388	3.651556	9.106771
9	6	0	-0.309698	4.177651	11.555325
10	6	0	-0.179140	2.872687	12.060004
11	1	0	0.033318	2.050199	11.387250
12	6	0	-0.274372	2.645555	13.431409
13	1	0	-0.168629	1.632319	13.808611
14	6	0	-0.481389	3.704347	14.318690
15	1	0	-0.550557	3.520135	15.386245
16	6	0	-1.635684	1.930838	7.773632
17	1	0	-2.170728	0.991847	7.698498
18	6	0	-1.303887	2.444921	9.040085
19	1	0	-1.606760	1.914370	9.933622
20	6	0	-0.510468	5.244885	12.447695
21	1	0	-0.625280	6.248344	12.051500
22	6	0	-0.591838	5.003192	13.816816
23	1	0	-0.754295	5.836682	14.494429
24	6	0	0.294605	5.678623	9.686247
25	1	0	1.163346	6.110014	10.186051
26	6	0	0.640588	6.621375	7.385519
27	1	0	1.320439	7.316982	7.882504
28	1	0	1.137653	6.237592	6.490020
29	1	0	-0.261165	7.170741	7.082445

Table S9. atomic coordinates obtained from DFT calculations of [**L4**]$^+$.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	35	0	2.706229	4.565696	2.008302

2	7	0	5.646904	9.104552	1.782415
3	7	0	7.629664	8.049206	1.766838
4	6	0	2.928775	12.326665	1.778261
5	1	0	2.234880	13.161465	1.775947
6	6	0	2.616299	11.147261	1.098309
7	1	0	1.680605	11.064978	0.552734
8	6	0	3.502772	10.072209	1.091206
9	1	0	3.271186	9.182370	0.517750
10	6	0	4.718399	10.162824	1.789776
11	6	0	5.391865	7.731754	1.789100
12	6	0	6.649042	7.077462	1.793098
13	6	0	6.739169	5.689232	1.855651
14	1	0	7.699317	5.185406	1.874676
15	6	0	5.547752	4.946802	1.904454
16	1	0	5.585436	3.864781	1.946141
17	6	0	7.042532	9.322523	1.891229
18	1	0	7.467049	10.145305	1.313535
19	6	0	9.039144	7.805414	1.977036
20	1	0	9.267583	7.573725	3.026509
21	1	0	9.370654	6.971438	1.351693
22	1	0	9.602950	8.695049	1.687561
23	6	0	4.207344	7.003015	1.864921
24	1	0	3.239197	7.481151	1.911910
25	6	0	4.322473	5.604620	1.912738
26	6	0	5.037478	11.351407	2.468205
27	1	0	5.971266	11.410094	3.017434
28	6	0	4.146450	12.421742	2.455884
29	1	0	4.402587	13.332253	2.990288

Table S10. Optimized atomic coordinates obtained from DFT calculations of **C1**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.823399	-2.645338	-1.493655
2	6	0	6.150345	-2.365434	-0.161395
3	6	0	5.212046	-1.878203	0.744618
4	6	0	3.921513	-1.687502	0.256695
5	6	0	3.559125	-1.968083	-1.075205
6	6	0	4.524467	-2.448415	-1.965066
7	7	0	2.784049	-1.208976	0.897224
8	6	0	1.726795	-1.169053	0.035798
9	7	0	2.201297	-1.645791	-1.170061
10	6	0	1.261029	-1.740380	-2.247163
11	6	0	-0.027937	-1.266442	-1.909586
12	6	0	-0.981622	-1.335952	-2.939303

13	6	0	-0.681794	-1.834818	-4.211559
14	6	0	0.601601	-2.299322	-4.493380
15	6	0	1.585424	-2.256070	-3.503182
16	77	0	-0.262508	-0.642912	0.106913
17	6	0	-6.761388	-1.741830	0.050591
18	6	0	-6.879635	-0.394545	-0.309197
19	6	0	-5.768648	0.430383	-0.467192
20	6	0	-4.525459	-0.156799	-0.246873
21	6	0	-4.373962	-1.506864	0.125478
22	6	0	-5.506575	-2.312535	0.270981
23	7	0	-3.247696	0.385863	-0.335105
24	6	0	-2.303883	-0.550837	-0.021252
25	7	0	-2.996957	-1.708059	0.256847
26	6	0	-2.215199	-2.855348	0.604436
27	6	0	-0.823968	-2.609187	0.587845
28	6	0	-0.013599	-3.704595	0.923893
29	6	0	-0.543312	-4.954984	1.258721
30	6	0	-1.922929	-5.149200	1.268856
31	6	0	-2.771296	-4.090389	0.940295
32	6	0	-3.002749	1.770016	-0.700229
33	6	0	1.874200	5.669807	-0.111148
34	6	0	1.600940	5.600425	1.260469
35	6	0	1.043240	4.448381	1.817821
36	6	0	0.759698	3.372333	0.971995
37	6	0	1.070629	3.461488	-0.398939
38	6	0	1.624445	4.603771	-0.972322
39	7	0	0.231577	2.090821	1.155285
40	6	0	0.241585	1.377892	-0.027747
41	7	0	0.739260	2.237219	-0.970005
42	6	0	-0.236775	1.411239	2.327435
43	6	0	-0.480977	2.069230	3.535577
44	6	0	-0.917427	1.324044	4.632765
45	6	0	-1.113935	-0.050248	4.499573
46	6	0	-0.900201	-0.675022	3.265826
47	6	0	-0.456686	0.028445	2.133018
48	6	0	2.770476	-0.828501	2.302251
49	6	0	0.935273	1.940586	-2.381804
50	35	0	-8.627752	0.343657	-0.594855
51	35	0	2.632510	7.279756	-0.827980
52	35	0	7.950735	-2.654402	0.435250
53	1	0	6.585967	-3.017282	-2.167607
54	1	0	5.476270	-1.657106	1.771209
55	1	0	4.306858	-2.663254	-3.000930
56	1	0	-1.996290	-0.995263	-2.746075
57	1	0	-1.453066	-1.868946	-4.977109
58	1	0	0.844254	-2.699643	-5.473245

59	1	0	2.570015	-2.642307	-3.728210
60	1	0	-7.651711	-2.349624	0.159778
61	1	0	-5.872974	1.472228	-0.743406
62	1	0	-5.447731	-3.356109	0.542778
63	1	0	1.066857	-3.588299	0.928071
64	1	0	0.123644	-5.775456	1.511334
65	1	0	-2.345926	-6.114459	1.530756
66	1	0	-3.840313	-4.250976	0.959235
67	1	0	-3.278800	2.443356	0.117709
68	1	0	-3.588569	2.024812	-1.588160
69	1	0	-1.946518	1.886010	-0.924406
70	1	0	1.829078	6.446787	1.897432
71	1	0	0.868016	4.408130	2.883307
72	1	0	1.859664	4.661021	-2.027886
73	1	0	-0.378658	3.142459	3.632388
74	1	0	-1.107782	1.822609	5.578681
75	1	0	-1.450801	-0.635173	5.351959
76	1	0	-1.085868	-1.742218	3.180154
77	1	0	1.749424	-0.587985	2.586978
78	1	0	3.416386	0.040212	2.466387
79	1	0	3.131173	-1.662017	2.912489
80	1	0	0.427913	2.693701	-2.993084
81	1	0	0.519869	0.957702	-2.591871
82	1	0	2.002192	1.945535	-2.627184

Table S11. Optimized atomic coordinates obtained from DFT calculations of **C2**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-5.455525	3.550967	0.253820
2	6	0	-5.739292	2.878850	1.448841
3	6	0	-4.809561	1.981502	1.972720
4	6	0	-3.619090	1.797556	1.275377
5	6	0	-3.332061	2.486919	0.081002
6	6	0	-4.267164	3.378257	-0.454807
7	7	0	-2.533398	0.968491	1.537321
8	6	0	-1.583476	1.096580	0.568021
9	7	0	-2.068028	2.041697	-0.316343
10	6	0	-1.224157	2.392696	-1.420405
11	6	0	-0.026092	1.643015	-1.470352
12	6	0	0.828127	1.947947	-2.543628
13	6	0	0.520419	2.923997	-3.497542
14	6	0	-0.665718	3.648565	-3.395862
15	6	0	-1.548508	3.386082	-2.346083

16	77	0	0.267051	0.298357	0.147594
17	6	0	6.798735	0.404901	-0.565632
18	6	0	6.663618	-0.727899	-1.376520
19	6	0	5.396363	-1.261566	-1.609654
20	6	0	4.306925	-0.634078	-1.013358
21	6	0	4.449309	0.498539	-0.188004
22	6	0	5.716930	1.042065	0.041256
23	7	0	2.946828	-0.921970	-1.073788
24	6	0	2.232238	-0.037677	-0.318209
25	7	0	3.156152	0.830645	0.223413
26	6	0	2.643425	1.870371	1.063390
27	6	0	1.235532	1.850385	1.179596
28	6	0	0.682932	2.850513	1.994365
29	6	0	1.469664	3.799892	2.654451
30	6	0	2.856022	3.774187	2.518922
31	6	0	3.453373	2.799730	1.717476
32	6	0	2.412607	-2.034406	-1.838945
33	6	0	-3.091750	-5.114673	-1.885130
34	6	0	-2.666251	-5.558409	-0.626950
35	6	0	-1.844362	-4.803516	0.209348
36	6	0	-1.437518	-3.552179	-0.263880
37	6	0	-1.883831	-3.089144	-1.517259
38	6	0	-2.702674	-3.855468	-2.341926
39	7	0	-0.651625	-2.523175	0.261216
40	6	0	-0.629149	-1.434882	-0.591649
41	7	0	-1.369762	-1.806404	-1.679802
42	6	0	0.045945	-2.394957	1.507614
43	6	0	0.269829	-3.476372	2.363623
44	6	0	0.941809	-3.254976	3.567415
45	6	0	1.386913	-1.971698	3.883824
46	6	0	1.184837	-0.916262	2.987544
47	6	0	0.510562	-1.085180	1.766229
48	6	0	-2.464325	0.107119	2.708813
49	6	0	-1.631097	-0.990146	-2.856537
50	1	0	-5.016385	1.444144	2.891700
51	1	0	-4.110827	3.911524	-1.379164
52	1	0	1.770465	1.413350	-2.639563
53	1	0	1.213005	3.125647	-4.311034
54	1	0	-0.908932	4.420021	-4.120339
55	1	0	-2.449475	3.978058	-2.262174
56	35	0	8.556912	1.120103	-0.272852
57	1	0	5.274035	-2.138960	-2.235294
58	1	0	5.881726	1.917254	0.649481
59	1	0	-0.394831	2.897659	2.125365
60	1	0	0.997440	4.557665	3.274615
61	1	0	3.477839	4.502411	3.030934

62	1	0	4.530809	2.783933	1.630544
63	1	0	2.662331	-2.988339	-1.363193
64	1	0	2.827957	-2.018698	-2.850974
65	1	0	1.333197	-1.929026	-1.893943
66	35	0	-3.247183	-7.283946	-0.016499
67	1	0	-1.569374	-5.178686	1.182993
68	1	0	-3.039685	-3.488601	-3.305319
69	1	0	-0.026814	-4.484074	2.102553
70	1	0	1.119122	-4.086291	4.243397
71	1	0	1.908219	-1.794102	4.821302
72	1	0	1.565246	0.068799	3.243771
73	1	0	-3.237222	-0.666725	2.657418
74	1	0	-2.616695	0.704196	3.612973
75	1	0	-1.328639	-1.531330	-3.758788
76	1	0	-1.060847	-0.067706	-2.773888
77	1	0	-2.697896	-0.754265	-2.926394
78	1	0	-6.678987	3.052950	1.958968
79	35	0	-6.766468	4.764799	-0.450962
80	1	0	7.539713	-1.185412	-1.819982
81	1	0	-3.728373	-5.744417	-2.494858
82	1	0	-1.481456	-0.355773	2.743053

References

1. G. A. Crosby and J. N. Demas, *The Journal of Physical Chemistry*, 1971, **75**, 991-1024.
2. W. H. Melhuish, *The Journal of Physical Chemistry*, 1961, **65**, 229-235.
3. N. C. Greenham, I. D. W. Samuel, G. R. Hayes, R. T. Phillips, Y. A. R. R. Kessener, S. C. Moratti, A. B. Holmes and R. H. Friend, *Chemical Physics Letters*, 1995, **241**, 89-96.
4. N. G. Connelly and W. E. Geiger, *Chemical Reviews*, 1996, **96**, 877-910.
5. APEX2 (2013); Bruker Molecular Analysis Research Tool. Bruker AXS Inc., Madison, WI 53719-1173.
6. SAINT (2013) V8.34A; Integration Software for Single Crystal Data. Bruker AXS Inc., Madison, WI 53719-1173.
7. G.M. Sheldrick, SADABS, Bruker Area Detector Absorption Corrections. Bruker AXS Inc., Madison, WI 53719-1173, 1996.
8. B.A.X.-r.S. Inc., Bruker Analytical X-ray Systems Inc., Madison, WI 53719-1173, 2012.