Electronic Supporting Information

Water-soluble Ir(III) complexes of deprotonated *N*-methylbipyridinium ligands: Fluorine-free blue emitters

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1. Experimental Details

Materials and Procedures. 1-Methyl-3-(2′-pyridyl)pyridinium hexafluorophosphate was synthesised via its iodide counterpart, by using an approach similar to that of Koizumi *et al.*[1] All other reagents were obtained commercially and used as supplied. Products were dried overnight in a vacuum desiccator (silica gel) prior to characterisation.

General Physical Measurements. ^{1}H NMR spectra were recorded on a Bruker UltraShield AV-400 spectrometer, with all shifts referenced to residual solvent signals and quoted with respect to TMS. Elemental analyses were performed by the Microanalytical Laboratory, University of Manchester, and UV–vis spectra were obtained by using a Shimadzu UV-2401 PC spectrophotometer. Mass spectra were recorded by using MALDI on a Micromass Tof Spec 2e or +electrospray on a Micromass Platform II spectrometer. Cyclic voltammetric measurements were performed by using an Ivium CompactStat. A single-compartment BASi VC-2 cell was used with a silver/silver chloride reference electrode (3 M NaCl, saturated AgCl) separated by a salt bridge from a 2 mm disc platinum working electrode and platinum wire auxiliary electrode. MeCN was used as supplied from Sigma-Aldrich (HPLC grade), and $[N^nBu_4]PF_6$ (Fluka, electrochemical grade) was used as the supporting electrolyte. Solutions containing ca. 10^{-3} M analyte (0.1 M $[N^nBu_4]PF_6$) were deaerated by purging with dry N_2. All $E_{1/2}$ values were calculated from $(E_{pa} + E_{pc})/2$ at a scan rate of 100 mV s^{-1}. Steady state emission and excitation spectra were recorded on an Edinburgh Instruments FP920 Phosphorescence Lifetime Spectrometer equipped with a 5 W microsecond pulsed xenon flashlamp. Lifetime data were recorded following excitation with an EPL 375 picosecond pulsed diode laser (Edinburgh Instruments), using time-correlated single photon counting (PCS900 plug-in PC card for fast photon counting). Lifetimes were obtained by tail fitting on the data obtained, or by a reconvolution fit using a solution of Ludox® in the scatterer, and the quality of fit judged by minimisation of reduced chi-squared and residuals squared. Quantum yields were measured upon excitation at 370 nm by using a SM4 Integrating Sphere mounted on an Edinburgh Instruments FP920 Phosphorescence Lifetime Spectrometer.

Synthesis of 1-methyl-3-(2′-pyridyl)pyridinium iodide. Methyl iodide (2 mL, 32.1 mmol) was added to a solution of 2,3′-bipyridyl (500 mg, 3.20 mmol) in *tert*-butyl methyl ether (20 mL), and the mixture heated at reflux for 36 h. After cooling to room temperature, the solid was filtered off, washed with *tert*-butyl methyl ether then *n*-pentane and dried to give an off-white powder: 798 mg (84%). δ_H (400 MHz, CD_3OD) 9.66 (1 H, s), 9.21 (1 H, d, J = 8.2 Hz), 8.96 (1 H, d, J = 6.1 Hz), 8.80 (1 H, dd, J = 4.7, 0.6 Hz), 8.22–8.19 (2 H), 8.05 (1 H, td, J = 7.8, 1.7 Hz), 7.56 (1 H, ddd, J = 7.6, 4.8, 0.7 Hz), 4.54 (3 H, s). ES-MS: m/z = 171 $[M - I]^+$.

Synthesis of 1-methyl-3-(2′-pyridyl)pyridinium hexafluorophosphate. 1-methyl-3-(2′-pyridyl)pyridinium iodide was dissolved in a minimum of water and filtered, giving a pale yellow solution to which NH_4PF_6 was added. The precipitate was filtered off, washed extensively with cold water and dried to afford a near quantitative yield. δ_H (400 MHz, CD_3CN) 9.33 (1 H, s), 9.04 (1 H, dt, J = 8.3, 1.2 Hz), 8.78 (1 H, dt, J = 5.0, 1.4 Hz), 8.63 (1

H, d, J = 6.0 Hz), 8.09 (1 H, t, J = 7.1 Hz), 8.04–7.99 (2 H), 7.54 (1 H, ddd, J = 6.4, 4.9, 2.3 Hz), 4.39 (3 H, s). ES-MS: m/z = 171 [M – PF_6]$^+$. Anal. Calcd (%) for $C_{11}H_{11}F_6N_2P$: C, 41.8; H, 3.5; N, 8.9. Found: C, 42.0; H, 3.0; N, 8.9.

Synthesis of [{Ir^{III}(C^N)$_2$Cl}$_2$][PF$_6$]$_4$ [C^N = cyclometalated anion derived from 1-methyl-2-(2′-pyridyl)pyridinium]. Ir^{III}Cl$_3$•2.9H$_2$O (200 mg, 0.570 mmol) and 1-methyl-2-(2′-pyridyl)pyridinium hexafluorophosphate (377 mg, 1.19 mmol) were added to argon-sparged 2-methoxyethanol (22 mL) and water (8 mL), and the mixture heated at 120 °C for 48 h under argon. After cooling to room temperature, the mixture was filtered. An excess of NH_4PF_6 was added to the filtrate, and the solvents evaporated. The residue was suspended in ice-cold water and the solid filtered off, rinsed with a small volume of cold water, then acetone/diethyl ether (1:3, 4 × 5 mL), and dried to give a bright yellow powder: 351 mg (72%). δ_H (400 MHz, CD_3CN) 9.85 (2 H, ddd, J = 5.8, 1.5, 0.8 Hz), 8.59 (2 H, d, J = 1.3 Hz), 8.18–8.10 (4 H), 7.68 (2 H, ddd, J = 7.3, 7.8, 1.7 Hz), 7.44 (2 H, dd, J = 6.5, 1.4 Hz), 6.75 (2 H, d, J = 6.4 Hz), 3.91 (6 H, s). This material was treated as an intermediate, so was not subjected to further purification or analysis.

Synthesis of [Ir^{III}(C^N)$_2$(bpy)][PF$_6$]$_3$, 1P. Argon-sparged 2-methoxyethanol/water (8:2, 15 mL) was added to [{Ir^{III}(C^N)$_2$Cl}$_2$][PF$_6$]$_4$ (100 mg, 0.058 mmol), 2,2′-bipyridyl (30 mg, 0.192 mmol) and $AgPF_6$ (37 mg, 0.146 mmol) under argon, and the mixture heated at 100 °C for 36 h under argon. After cooling to room temperature, the solution was filtered through Celite to remove AgCl and the solvents evaporated. The residue was disolved in a minimum volume of acetone and an excess of [N^{n}Bu$_4$]Cl added. The precipitate was filtered off, washed with acetone and purified by column chromatography on Sephadex SP C-25, eluting with 0.025–0.075 M NaCl in acetone/water (1:1). The main yellow band was evaporated to dryness, cold methanol was added and NaCl removed by filtration. The filtrate was evaporated to dryness, and the residue dissolved in cold water. NH_4PF_6 was added and the precipitate filtered off, washed with ice-cold water and dried to give a yellow-cream powder: 54 mg (41%). δ_H (400 MHz, CD_3CN) 8.84 (2 H, s), 8.60 (2 H, d, J = 8.3 Hz), 8.29–8.24 (4 H), 8.17 (2 H, t, J = 8.5 Hz), 7.88 (2 H, d, J = 5.5 Hz), 7.77–7.73 (4 H), 7.58 (2 H, t, J = 6.6 Hz), 7.41 (2 H, t, J = 7.3 Hz), 6.87 (2 H, d, J = 6.4 Hz), 4.12 (6 H, s). ES-MS: m/z = 979 [M – PF_6]$^+$, 417 [M – 2PF_6]$^{2+}$, 230 [M – 3PF_6]$^{3+}$. Anal. Calcd (%) for $C_{32}H_{28}F_{18}IrN_6P_3$: C, 34.2; H, 2.5; N, 7.5. Found: C, 33.9; H, 2.1; N, 7.4.

Synthesis of [Ir^{III}(C^N)$_2${4,4′-(CF$_3$)$_2$bpy}][PF$_6$]$_3$, 2P. This compound was prepared and purified in a manner identical to **1P** by using 4,4′-di-(trifluoromethyl)-2,2′-bipyridyl (57 mg, 0.195 mmol) in place of 2,2′-bipyridyl. A yellow-cream powder was obtained: 42 mg (29%). δ_H (400 MHz, CD_3CN) 9.04 (2 H, d, J = 0.6 Hz), 8.86 (2 H, d, J = 0.6 Hz), 8.28 (2 H, ddd, J = 8.1, 1.4, 0.7 Hz), 8.19 (2 H, td, J = 7.9, 1.4 Hz), 8.13 (2 H, d, J = 5.8 Hz), 7.89 (2 H, dd, J = 5.8, 1.2 Hz), 7.79 (2 H, dd, J = 6.4, 1.3 Hz), 7.74 (2 H, ddd, J = 5.8, 1.4, 0.7 Hz), 7.42 (2 H, ddd, J = 7.5, 5.9, 1.5 Hz), 6.84 (2 H, d, J = 6.3 Hz), 4.14 (6 H, s). ES-MS: m/z = 1115 [M – PF_6]$^+$, 485 [M – 2PF_6]$^{2+}$, 275 [M – 3PF_6]$^{3+}$. Anal. Calcd (%) for $C_{34}H_{26}F_{24}IrN_6P_3$: C, 32.4; H, 2.1; N, 6.7. Found: C, 32.2; H, 1.7; N, 6.5.

Synthesis of [Ir^{III}(C^N)$_2${4,4′-(^{t}Bu)$_2$bpy}][PF$_6$]$_3$, 3P. This compound was prepared and purified in a manner identical to **1P** by using 4,4′-di-(*tert*-butyl)-2,2′-bipyridyl (52 mg, 0.194 mmol) in place of 2,2′-bipyridyl. A yellow-cream powder was obtained: 41 mg (29%).

δ_H (400 MHz, CD_3CN) 8.85 (2 H, s), 8.54 (2 H, d, J = 1.8 Hz), 8.29 (2 H, d, J = 8.2 Hz), 8.17 (2 H, td, J = 7.9, 1.5 Hz), 7.79–7.69 (6 H), 7.51 (2 H, d, J = 5.9, 2.0 Hz), 7.43 (2 H, ddd, J = 7.5, 5.9, 1.5 Hz), 6.86 (2 H, d, J = 6.3 Hz), 4.12 (6 H, s), 1.42 (18 H, s). ES-MS: m/z = 1091 $[M - PF_6]^+$, 472 $[M - 2PF_6]^{2+}$, 267 $[M - 3PF_6]^{3+}$. Anal. Calcd (%) for $C_{40}H_{44}F_{18}IrN_6P_3$: C, 38.9; H, 3.6; N, 6.8. Found: C, 38.4; H, 3.4; N, 6.7.

Synthesis of $[Ir^{III}(C\string^N)_2(bpy)]Cl_3$, 1C. To a solution of **1P** in acetone was added an excess of $[N^nBu_4]Cl$. The precipitate was filtered off, washed with acetone then diethyl ether and dried to give a near quantitative yield of a pale yellow powder. δ_H (400 MHz, $(CD_3)_2SO$) 9.85 (2 H, s), 9.01 (2 H, d, J = 8.2 Hz), 8.76 (2 H, d, J = 7.9 Hz), 8.39 (2 H, t, J = 7.8 Hz), 8.32 (2 H, t, J = 7.9 Hz), 8.17 (2 H, d, J = 6.9 Hz), 7.98 (2 H, d, J = 4.7 Hz), 7.84 (2 H, d, J = 5.5 Hz), 7.68 (2 H, t, J = 6.5 Hz), 7.52 (2 H, t, J = 6.5 Hz), 6.83 (2 H, d, J = 6.3 Hz), 4.19 (6 H, s). ES-MS: m/z = 362 $[M - 2Cl]^{2+}$, 344 $[M - 3Cl]^{2+}$, 230 $[M - 3Cl]^{3+}$. Anal. Calcd (%) for $C_{32}H_{28}Cl_3IrN_6$•$2.5H_2O$: C, 45.7; H, 4.0; N, 10.0. Found: C, 45.6; H, 4.0; N, 9.9.

Synthesis of $[Ir^{III}(C\string^N)_2\{4,4'\text{-}(CF_3)_2bpy\}]Cl_3$, 2C. This compound was prepared in a manner identical to **1C** by using **2P** instead of **1P** to give a pale yellow powder. δ_H (400 MHz, $(CD_3)_2SO$) 9.85 (2 H, s), 9.69 (2 H, s), 8.75 (2 H, d, J = 8.1 Hz), 8.33 (2 H, t, J = 7.6 Hz), 8.27 (2 H, d, J = 5.6 Hz), 8.20 (2 H, d, J = 6.2 Hz), 8.01 (2 H, d, J = 5.6 Hz), 7.95 (2 H, d, J = 5.6 Hz), 7.50 (2 H, t, J = 6.5 Hz), 6.77 (2 H, d, J = 6.3 Hz), 4.20 (6 H, s). ES-MS: m/z = 895 $[M - Cl]^+$, 430 $[M - 2Cl]^{2+}$, 275 $[M - 3Cl]^{3+}$. Anal. Calcd (%) for $C_{34}H_{26}Cl_3F_6IrN_6$ •$2.5H_2O$: C, 41.8; H, 3.2; N, 8.6. Found: C, 42.0; H, 3.1; N, 8.5.

Synthesis of $[Ir^{III}(C\string^N)_2\{4,4'\text{-}(^tBu)_2bpy\}]Cl_3$, 3C. This compound was prepared in a manner identical to **1C** by using **3P** instead of **1P** to give a pale yellow powder. δ_H (400 MHz, $(CD_3)_2SO$) 9.78 (2 H, s), 8.99 (2 H, d, J = 1.9 Hz), 8.73 (2 H, d, J = 8.2 Hz), 8.33 (2 H, td, J = 7.9, 1.3 Hz), 8.15 (2 H, dd, J = 6.5, 0.9 Hz), 7.86 (2 H, d, J = 5.9 Hz), 7.82 (2 H, d, J = 5.7 Hz), 7.56–7.53 (4 H), 6.80 (2 H, d, J = 6.3 Hz), 4.18 (6 H, s), 1.41 (18 H, s). ES-MS: m/z = 418 $[M - 2Cl]^{2+}$, 400 $[M - 3Cl]^{2+}$, 267 $[M - 3Cl]^{3+}$. Anal. Calcd (%) for $C_{40}H_{44}Cl_3IrN_6$ •$2.5H_2O$: C, 50.4; H, 5.2; N, 8.8. Found: C, 50.2; H, 5.3; N, 8.6.

X-Ray Crystallography. Single crystals were obtained by slow diffusion of diethyl ether vapour into an MeCN (**1P**) or acetone (**3P**) solution of the complex salt. Crystallographic data and refinement details for **1P**·2MeCN and **3P**·$3Me_2CO$ are presented in Table S1. Data were collected on Oxford Diffraction XCalibur 2 or Bruker APEX CCD X-ray diffractometers by using MoKα radiation (λ = 0.71073 Å), and the data were processed by using the Oxford Diffraction CrysAlis Pro and Bruker SMART software packages. The structures were solved by direct methods by using SIR-2004[2] or SHELXS-97,[3] and refined by full-matrix least-squares on all data by using SHELXL-97. All other calculations were carried out by using the SHELXTL package.[4] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in idealised positions by using the riding model, with thermal parameters 1.2 times those of aromatic parent carbon atoms, and 1.5 times those of methyl parent carbons. The crystal of **1P**·2MeCN was pseudo-merohedrally twinned; the twin matrix (–1 0 0 / 0 –1 0 / 1 0 1) was included in the instruction file to account for this and the scale factor refined to 0.314(9). Each twin component was also a racemic twin and the refined scale factors were 0.264(9) and 0.208(9). A problem regarding the pseudo-symmetry is also apparent which appears as an A alert on applying checkCIF. Although most of the structure obeys the lattice halving, one PF_6^- anion could not be refined satisfactorily, and the R value in the halved lattice was 10.0% versus 6.4% for the larger unit cell. In the structure of **3P**·3Me_2CO, one PF_6^- anion, one of the rings and C38–C40 were disordered, so restraints were applied to the geometries of these groups.

Theoretical Studies. DFT and TD-DFT calculations were undertaken on the complex cations **1**–**3** by using Gaussian 09.[5] Geometry optimisations of the singlet ground (S_0) and first triplet excited (T_1) states and subsequent TD-DFT calculations were carried out by using the M06 functional[6] with the Def2-QZVP[7,8] basis set on Ir and Def2-SVP[9] on all other atoms. MeCN was used as CPCM solvent model.[10,11] Using these parameters, the first 100 excited singlet states were calculated and simulated UV–vis absorption spectra were convoluted with Gaussian curves of fwhm of 3000 cm^{-1} by using GaussSum.[12]

1. T. Koizumi, T. Tomon and K. Tanaka, *J. Organomet. Chem.*, 2005, **690**, 1258–1264.
2. M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 2005, **32**, 381–388.
3. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
4. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2015, **C71**, 3–8.
5. Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, J. C. A. Rendell, Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.
6. Y. Zhao and D. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241.
7. F. Weigend, F. Furche and R. Ahlrichs, *J. Chem. Phys.*, 2003, **119**, 12753–12762.
8. D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta*, 1990, **77**, 123–141.
9. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
10. V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995–2001.
11. M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.*, 2003, **24**, 669–681.
12. N. M. O'Boyle, A. L. Tenderholt and K. M. Langner, *J. Comput. Chem.*, 2008, **29**, 839–845.

2. X-Ray Crystallographic Studies

Table S1. Crystallographic data and refinement details for complex salts **1P**·MeCN and **3P**·3Me$_2$CO

	1P·2MeCN	**3P**·3Me$_2$CO
empirical formula	$C_{36}H_{34}F_{18}IrN_8P_3$	$C_{49}H_{62}F_{18}IrN_6O_3P_3$
FW	1205.82	1410.16
crystal appearance	pale yellow plate	yellow rod
crystal system	monoclinic	monoclinic
space group	$P2_1$	$P2_1/n$
a/Å	16.815(5)	10.5238(2)
b/Å	11.822(3)	43.9969(15)
c/Å	22.655(12)	12.3994(3)
α/°	90.00	90.00
β/°	111.57(5)	99.663(2)
γ/°	90.00	90.00
U/Å^3	4188(3)	5659.6(3)
Z	4	4
T/K	100(2)	100(2)
μ/mm^{-1}	3.424	2.550
cryst size/mm	0.30 × 0.22 × 0.10	0.45 × 0.2 × 0.2
reflns collected	30758	111160
independent reflns (R_{int})	15102 (0.0841)	9978 (0.0641)
θ_{max}/° (completeness)	25.35 (99.7)	25.03 (99.8)
reflns with $I > 2\sigma(I)$	8919	8845
GOF on F^2	0.993	1.142
final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0641, 0.1346	0.0793, 0.1556
(all data)	0.1112, 0.1641	0.0883, 0.1610
peak and hole/eÅ^{-3}	2.620, –2.499	2.648, –4.096

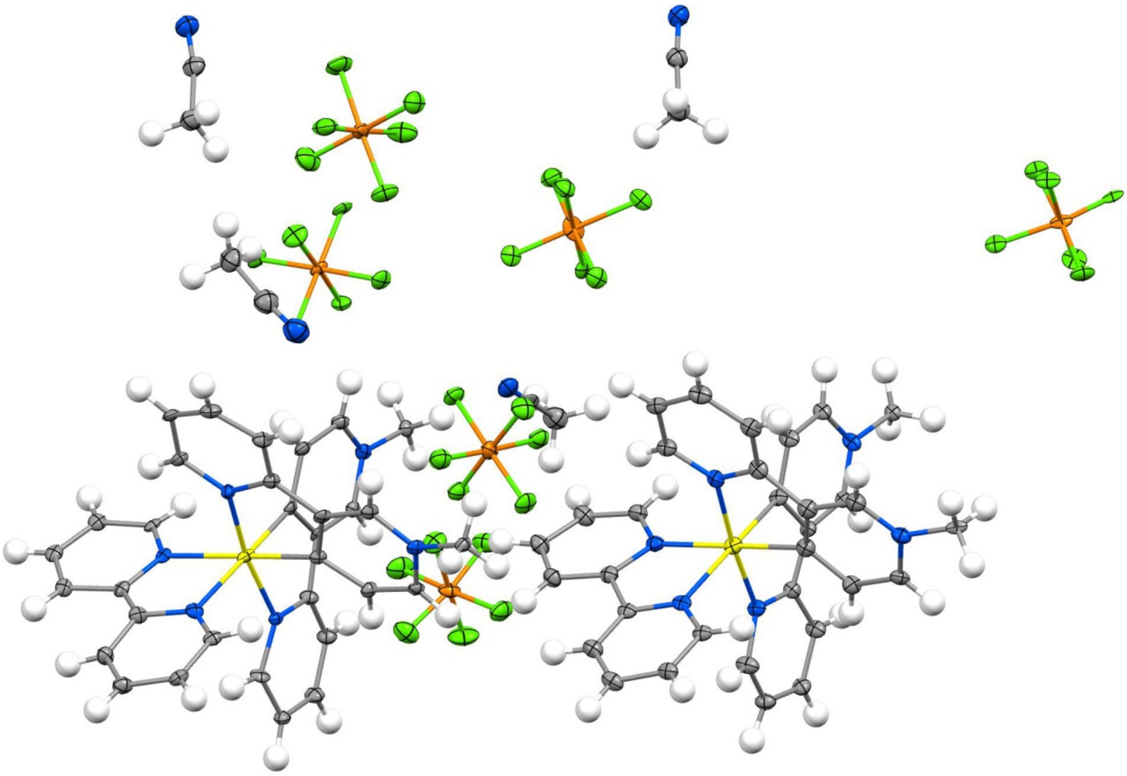

Fig. S1. Representation of the molecular structure of **1P**·2MeCN (30% probability ellipsoids). Element colours: H = white; C = grey; N = blue; Ir = yellow; P = orange; F = green.

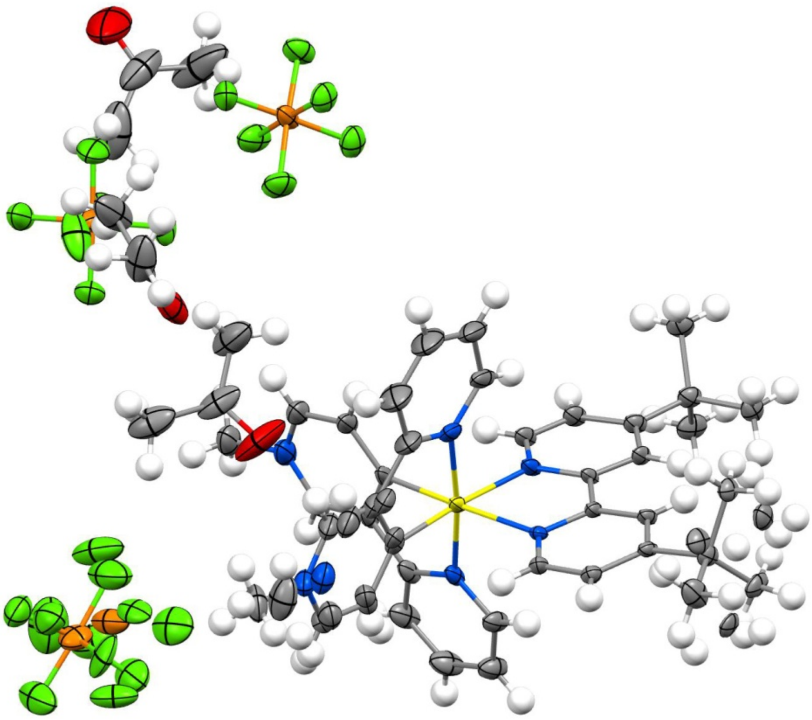

Fig. S2. Representation of the molecular structure of **3P**·3Me_2CO (30% probability ellipsoids). Element colours: H = white; C = grey; N = blue; Ir = yellow; P = orange; F = green; O = red.

3. UV–Vis Spectroscopic and Electrochemical Studies

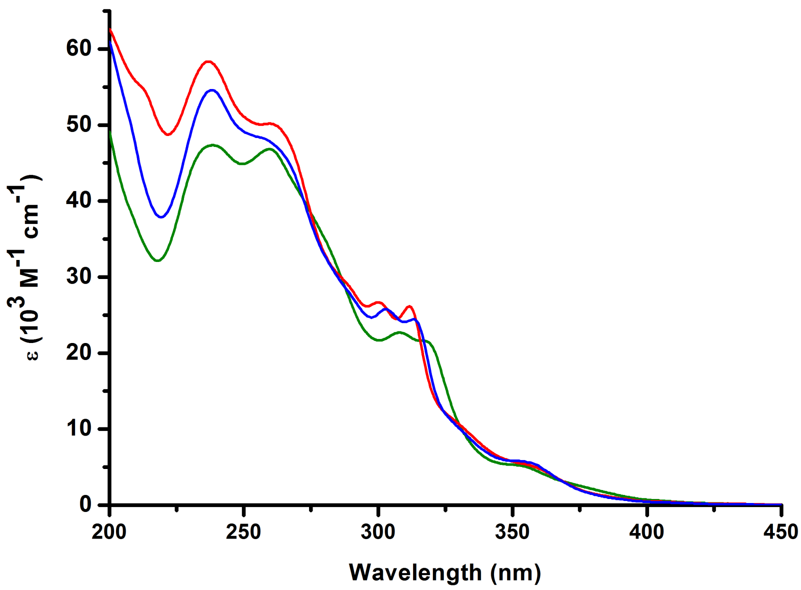

Fig. S3. UV–vis absorption spectra of complex salts **1P** (blue), **2P** (green) and **3P** (red) recorded in MeCN at 295 K.

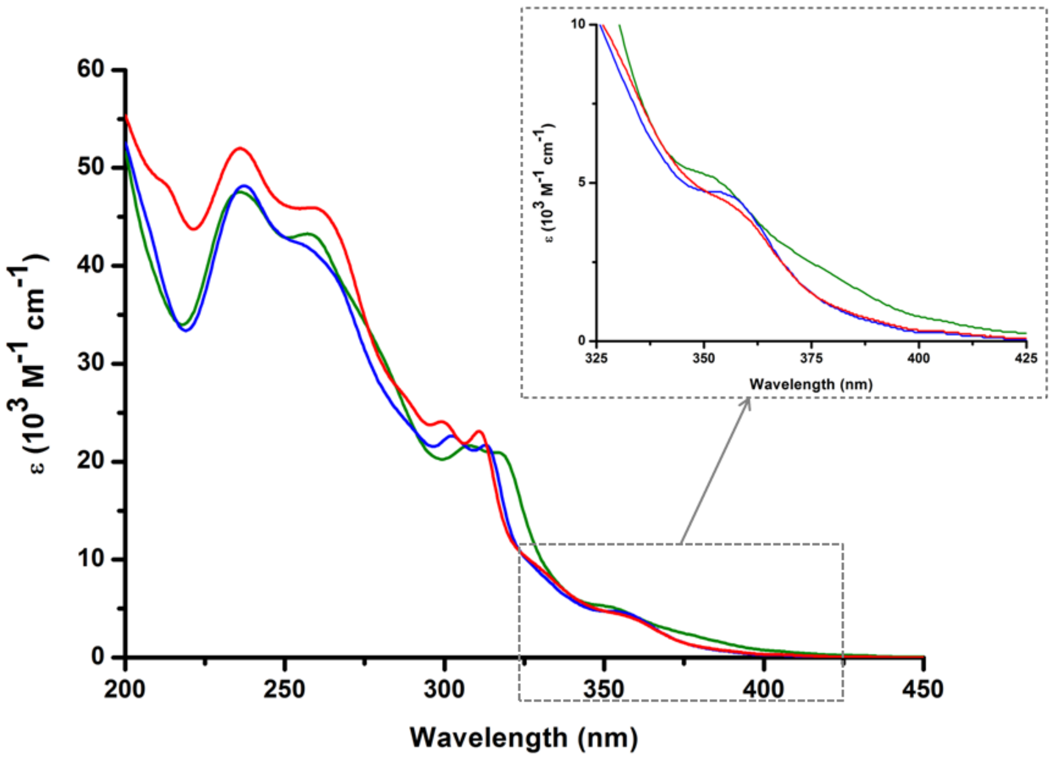

Fig. S4. UV–vis absorption spectra of complex salts **1C** (blue), **2C** (green) and **3C** (red) recorded in water at 295 K, with an expansion of the low energy region.

Table S2. Electrochemical data for complex salts **1P**–**3P**.[a]

	E, V *vs* Ag–AgCl (ΔE_p, mV)				
complex salt	Ir(III/IV)	E(3+/2+)	E(2+/1+)	E(1+/0)	E(0/1–)
1P	2.36[b]	–1.13[c]	–1.26 (60)	–1.52[c]	
2P	2.53[b]	–0.72 (70)	–1.26[c]	–1.44[c]	–1.65 (br)
3P	2.34[b]	–1.18[c]	–1.36[c]	–1.56[c]	

[a] MeCN solutions ca. 1.5 × 10^{-4} M in analyte and 0.1 M in $[N^nBu_4]PF_6$, with a scan rate of 100 mV s^{-1} at 295 K. Fc/Fc^+ internal reference; E = 0.44 V (ΔE_p = 70–90 mV). [b] E_{pa} for an irreversible oxidation process. [c] E_{pc} for an irreversible reduction process.

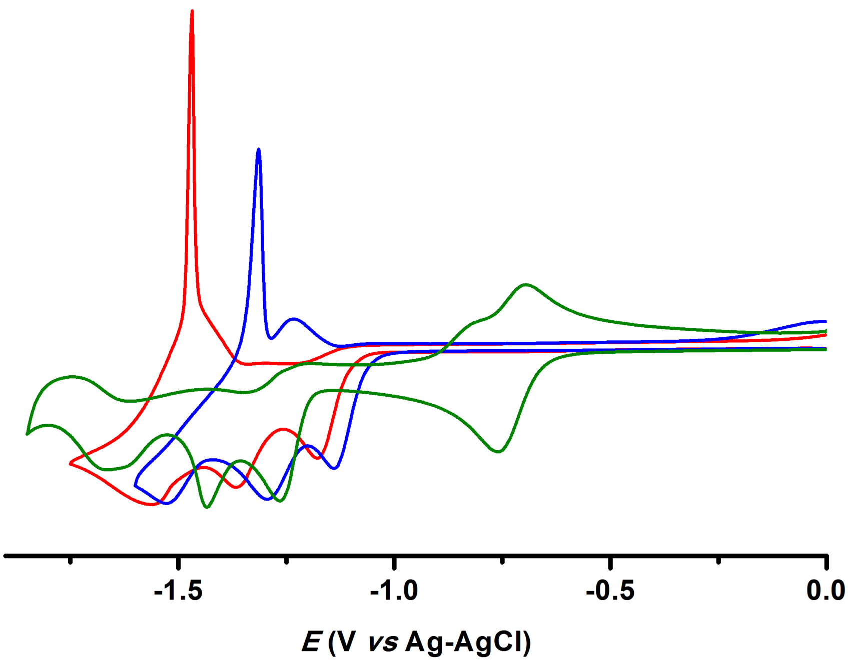

Fig. S5. Cyclic voltammograms depicting the reduction processes of complex salts **1P** (blue), **2P** (green) and **3P** (red) recorded at 100 mV s^{-1} in MeCN 0.1 M in $[N^nBu_4]PF_6$ at 295 K.

4. Theoretical Studies

Table S3. Structural parameters obtained from the X-ray crystallographic studies on **1P**·2MeCN and **3P**·3Me$_2$CO, and the geometries in the ground (S_0) and triplet excited (T_1) states optimised by M06/Def2-QZVP/SVP calculations on the cations **1**–**3** ([Ir^{III}(C^N)$_2$(N^N)]$^{3+}$).

	1				**2**		**3**		
	X-ray[a]		S_0	T_1	S_0	T_1	X-ray	S_0	T_1
	Distances (Å)								
Ir–C	1.99(2)	1.88(2)	2.007	2.000	2.006	2.010	1.93(2)	2.006	2.000
Ir–C	2.01(2)	1.96(2)	2.007	2.007	2.006	2.010	2.006(9)	2.006	2.007
Ir–$N_{C^{\wedge}N}$	2.04(2)	2.05(2)	2.078	2.054	2.080	2.080	2.06(1)	2.078	2.049
Ir–$N_{C^{\wedge}N}$	2.07(2)	2.05(2)	2.078	2.081	2.081	2.080	2.044(9)	2.078	2.082
Ir–$N_{N^{\wedge}N}$	2.14(2)	2.14(2)	2.178	2.183	2.179	2.159	2.127(7)	2.164	2.172
Ir–$N_{N^{\wedge}N}$	2.00(2)	2.10(2)	2.178	2.180	2.179	2.159	2.128(8)	2.164	2.167
N–Me	1.47(1)	1.47(1)	1.474	1.474	1.474	1.474	1.50(2)	1.473	1.472
	1.46(1)	1.46(1)					1.50(1)		
	Angles (˚)								
C–Ir–C	85.8(9)	82.2(8)	87.70	87.81	87.32	87.57	84.4(7)	87.62	87.55
C–Ir–$N_{N^{\wedge}N}$	174.4(8)	177.4(8)	173.37	172.71	173.59	173.87	175.4(7)	173.29	172.85
C–Ir–$N_{N^{\wedge}N}$	100.1(9)	101.8(8)	98.41	97.54	98.59	97.93	99.6(7)	99.38	97.54
C–Ir–$N_{N^{\wedge}N}$	172.8(8)	175.4(8)	173.36	174.09	173.52	173.81	175.8(4)	173.28	174.09
C–Ir–$N_{N^{\wedge}N}$	97.9(8)	99.8(8)	98.40	99.23	98.51	97.93	99.5(4)	98.37	97.54
C–Ir–$N_{C^{\wedge}N}$	80.5(8)	81.3(6)	80.21	81.68	80.20	80.19	80.6(4)	80.28	81.80
C–Ir–$N_{C^{\wedge}N}$	95.5(8)	95.1(7)	96.20	95.07	96.31	96.38	94.5(4)	96.48	95.28
C–Ir–$N_{C^{\wedge}N}$	97.3(8)	92.1(7)	96.21	95.85	96.33	96.38	91.8(6)	96.48	96.03
C–Ir–$N_{C^{\wedge}N}$	79.8(8)	80.2(6)	80.22	80.25	80.22	80.21	84.9(7)	80.28	80.29
$N_{C^{\wedge}N}$–Ir–$N_{C^{\wedge}N}$	175.3(7)	171.9(6)	175.09	175.06	175.26	175.29	174.3(3)	175.57	175.43
$N_{C^{\wedge}N}$–Ir–$N_{N^{\wedge}N}$	94.8(6)	97.1(6)	96.46	96.71	96.42	96.31	97.7(3)	95.97	95.33
$N_{C^{\wedge}N}$–Ir–$N_{N^{\wedge}N}$	87.8(8)	86.8(7)	87.42	87.98	87.34	87.39	86.4(3)	87.55	87.69
$N_{C^{\wedge}N}$–Ir–$N_{N^{\wedge}N}$	89.4(7)	90.7(6)	87.44	87.44	87.33	87.41	87.3(3)	87.56	87.96
$N_{C^{\wedge}N}$–Ir–$N_{N^{\wedge}N}$	95.4(7)	97.0(7)	94.46	95.68	96.40	96.29	97.3(4)	95.96	96.19
$N_{N^{\wedge}N}$–Ir–$N_{N^{\wedge}N}$	76.6(6)	76.2(6)	75.62	75.50	75.72	76.80	76.5(3)	75.81	75.74

[a] For the two independent complex cations in the asymmetric unit.

Table S4. Contributions (%) in terms of metal and ligands to the frontier MOs computed by M06/Def2-QZVP/SVP for complexes **1**–**3**.

	1			**2**			**3**		
MO	Ir	C^N	N^N	Ir	C^N	N^N	Ir	C^N	N^N
LUMO+10	35	62	3	17	80	3	42	56	3
LUMO+9	17	76	7	36	58	6	11	84	5
LUMO+8	1	1	98	3	74	23	1	1	98
LUMO+7	3	49	48	3	97	0	3	49	48
LUMO+6	2	97	0	1	1	98	2	98	0
LUMO+5	2	52	46	2	26	71	2	52	46
LUMO+4	6	93	1	5	94	1	6	93	1
LUMO+3	2	95	4	2	95	4	2	94	4
LUMO+2	5	94	1	6	93	1	3	5	92
LUMO+1	4	25	71	4	17	79	5	94	1
LUMO	3	69	27	4	77	19	4	90	6
HOMO	52	44	4	50	46	4	55	40	5
HOMO–1	68	21	11	66	23	11	66	18	16
HOMO–2	58	28	13	55	31	14	56	30	14
HOMO–3	6	3	91	6	3	91	5	2	93
HOMO–4	3	96	1	3	96	1	1	98	1
HOMO–5	15	84	1	18	80	1	13	86	1
HOMO–6	7	67	27	7	60	33	3	11	86
HOMO–7	2	70	28	0	68	32	5	49	46
HOMO–8	1	36	63	0	38	62	4	46	50
HOMO–9	2	17	81	4	46	50	4	48	47
HOMO–10	13	55	32	0	4	96	11	34	55

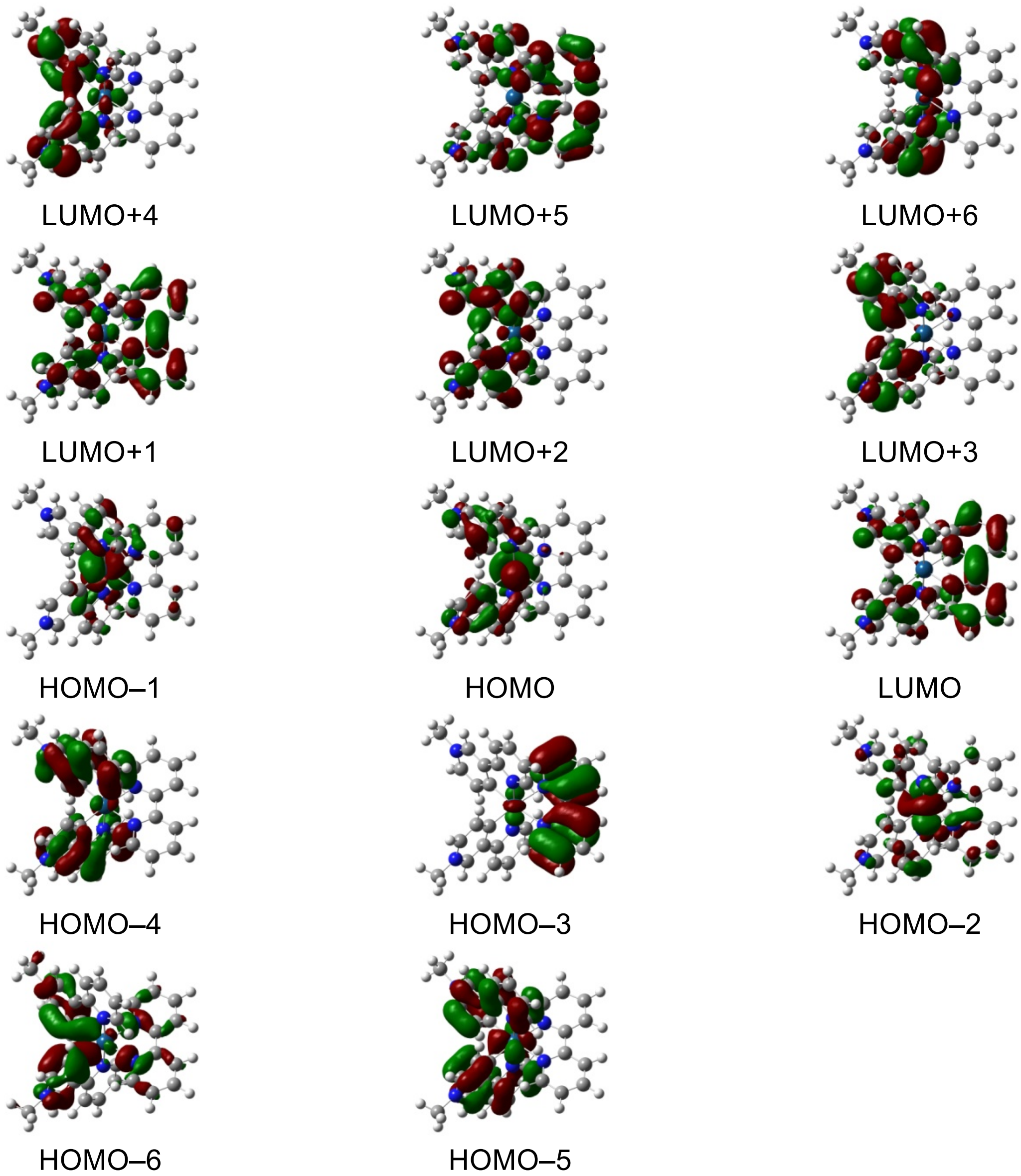

Fig. S6. M06/Def2-QZVP/SVP-derived contour surface diagrams of the frontier MOs for complex **1**.

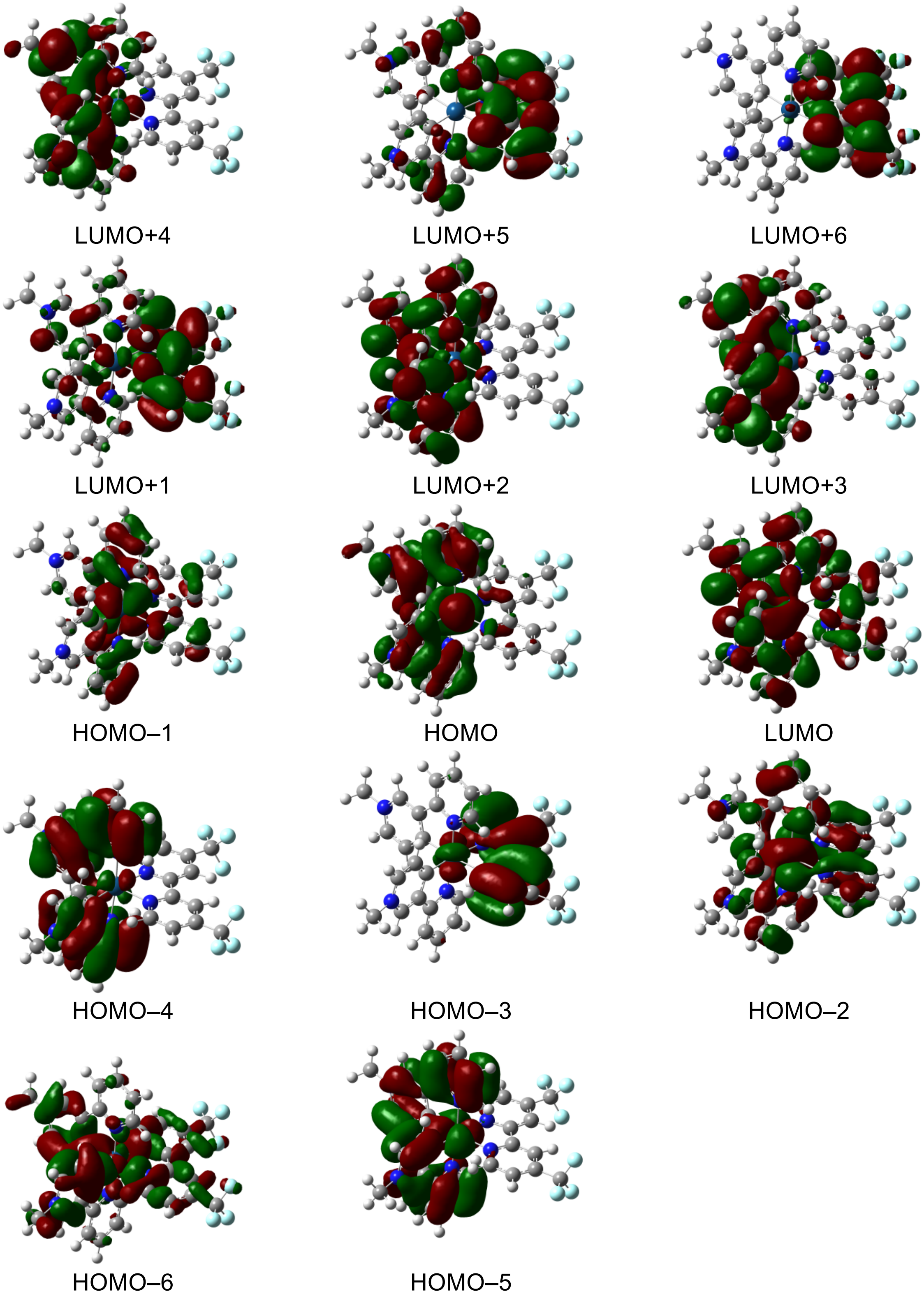

Fig. S7. M06/Def2-QZVP/SVP-derived contour surface diagrams of the frontier MOs for complex **2**.

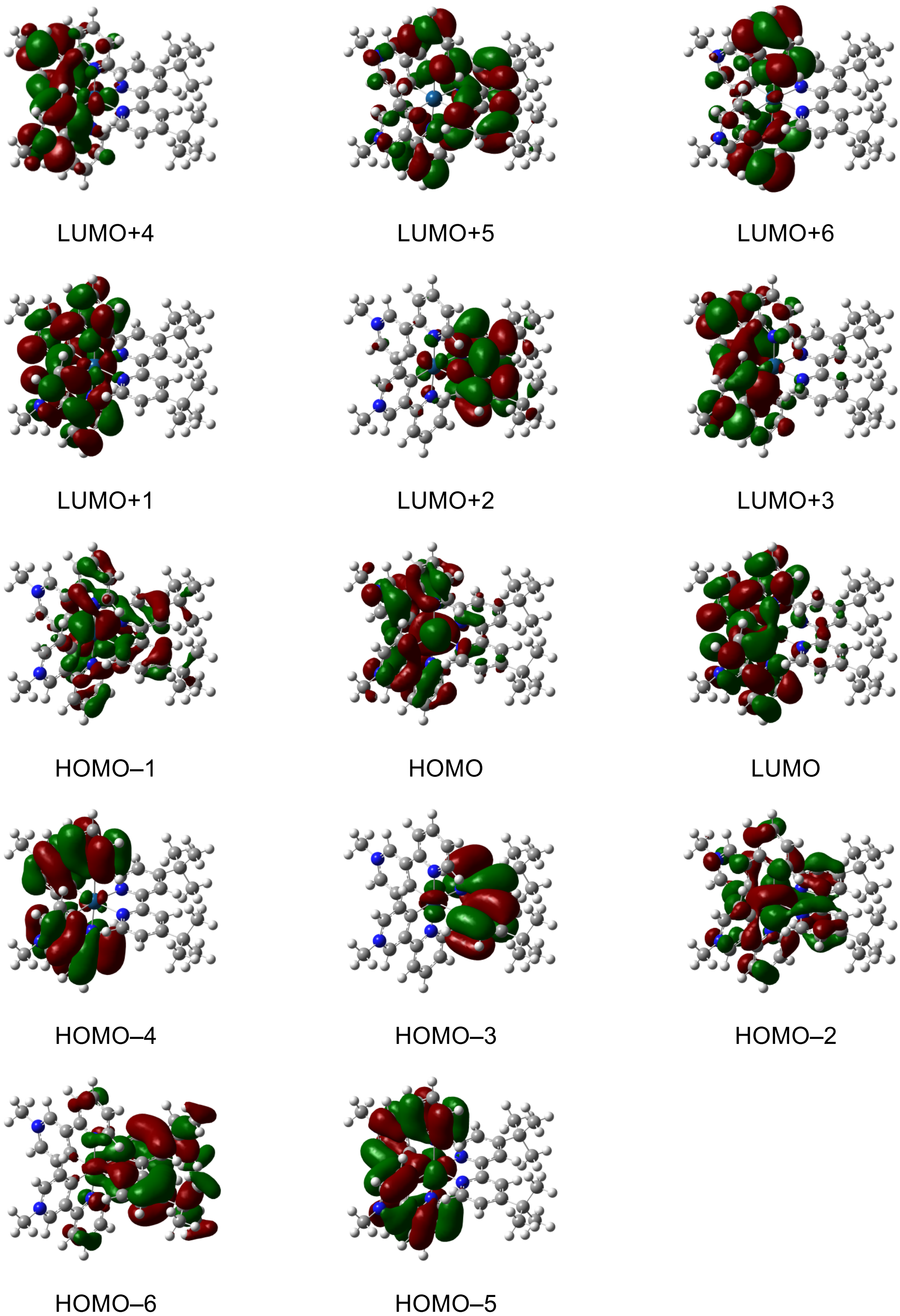

Fig. S8. M06/Def2-QZVP/SVP-derived contour surface diagrams of the frontier MOs for complex **3**.

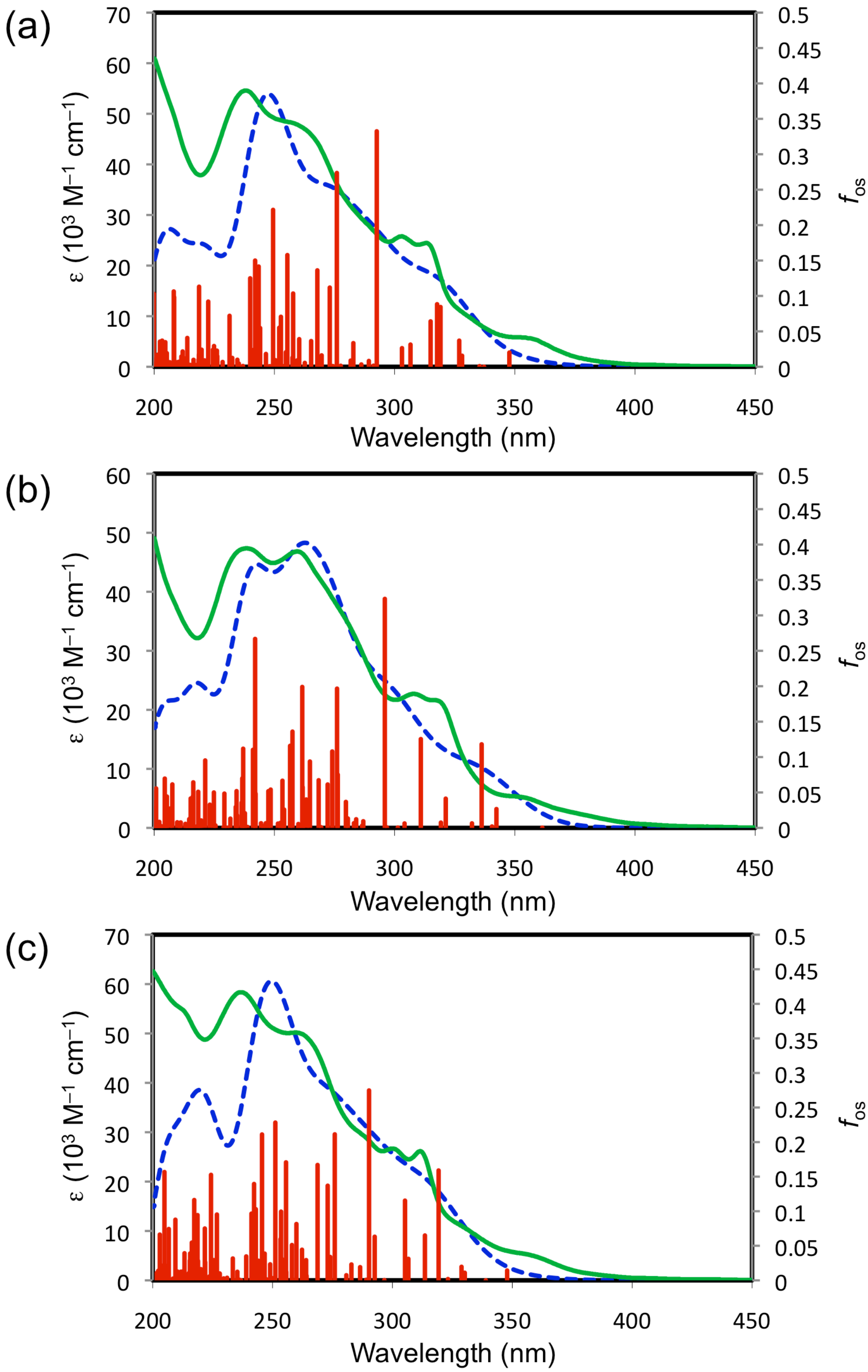

Fig. S9. Experimental (green) and the M06/Def2-QZVP/SVP-calculated (blue dash) UV–vis spectra of (a) **1**, (b) **2** and (c) **3** in MeCN. Experimental data is for the PF_6^- salts and plotted against the ε-axes, with calculated spectra scaled to allow comparison of absorption bands. Individual calculated vertical transitions (red) are plotted versus the oscillator strength (f_{os}) axes.

Table S5. Selected TD-DFT-Calculated data for complex **1**.[a]

λ (nm)	Major contributions	f_{os}
347	H → L (37%), H → L+1 (53%)	0.02
328	H–1 → L (56%), H–1 → L+1 (28%)	0.02
327	H–2 → L (26%), H–2 → L+1 (27%), H–1 → L+2 (29%)	0.04
319	H–2 → L (57%), H–1 → L+2 (23%)	0.08
318	H–2 → L+2 (19%), H–1 → L (30%), H–1 → L+1 (42%)	0.09
315	H–2 → L+1 (55%), H–1 → L+2 (28%)	0.06
307	H–2 → L+2 (41%), H–1 → L+1 (15%), H → L+2 (12%), H → L+4 (14%)	0.03
303	H → L+3 (82%)	0.03
293	H–3 → L (51%), H–3 → L+1 (35%)	0.33
283	H–4 → L (30%), H–4 → L+1 (19%), H–2 → L+4 (27%)	0.03
276	H–4 → L+2 (58%)	0.27
273	H–4 → L+1 (13%), H–2 → L+4 (37%), H → L+4 (23%)	0.11
270	H–3 → L+2 (94%)	0.02
268	H → L+5 (81%)	0.14
265	H–5 → L (56%), H–5 → L+1 (10%), H–4 → L+2 (22%)	0.04
260	H–5 → L+2 (14%), H–1 → L+5 (36%)	0.04
258	H–2 → L+5 (47%)	0.10
258	H → L+6 (50%)	0.01
255	H–5 → L+2 (53%)	0.16
255	H–3 → L+3 (15%), H–2 → L+5 (12%), H → L+7 (40%)	0.02
253	H–1 → L+9 (12%), H–1 → L+10 (27%), H → L+7 (23%)	0.07
252	H–5 → L+3 (13%), H–4 → L+4 (22%), H–1 → L+9 (11%), H–1 → L+10 (19%)	0.06
249	H–2 → L+5 (11%), H–1 → L+6 (55%)	0.22
246	H–6 → L (21%), H–6 → L+1 (22%), H–2 → L+6 (16%), H–2 → L+8 (10%)	0.02
244	H–3 → L+5 (15%), H–2 → L+7 (28%), H–1 → L+8 (13%)	0.05
243	H–6 → L+1 (13%), H–5 → L+3 (18%), H–4 → L+4 (14%), H–1 → L+7 (15%)	0.14
243	H–5 → L+3 (17%), H–4 → L+4 (21%), H–3 → L+4 (33%)	0.06
243	H–3 → L+4 (52%)	0.09
242	H–2 → L+7 (20%), H–1 → L+8 (61%)	0.15
241	H–6 → L+1 (13%), H–2 → L+8 (42%), H–1 → L+7 (18%)	0.02
240	H–6 → L+2 (19%), H–3 → L+5 (21%), H–2 → L+7 (23%)	0.12
232	H–3 → L+8 (48%), H–1 → L+7 (11%)	0.01
231	H–5 → L+5 (22%), H–4 → L+6 (41%)	0.07
226	H–3 → L+6 (46%), H–3 → L+7 (27%)	0.01
226	H–3 → L+6 (31%), H–3 → L+7 (38%)	0.01
226	H–6 → L+3 (28%), H–3 → L+6 (17%)	0.02
225	H–7 → L (16%), H–7 → L+1 (10%), H–4 → L+5 (12%), H–4 → L+7 (18%), H → L+13 (12%)	0.03
224	H–8 → L+1 (10%), H–6 → L+2 (24%)	0.02
222	H–6 → L+3 (24%), H–4 → L+7 (21%)	0.09
220	H–6 → L+4 (47%)	0.02
219	H–11 → L+2 (12%), H–10 → L+2 (13%), H–8 → L+2 (20%), H–7 → L+1 (20%)	0.02
219	H–7 → L+2 (43%)	0.11
219	H–7 → L (25%), H–7 → L+1 (23%), H–6 → L+1 (11%)	0.02
218	H–1 → L+13 (64%)	0.01
214	H–11 → L (26%), H–8 → L (11%)	0.04
213	H–11 → L+1 (13%), H–10 → L (29%), H–8 → L (32%)	0.01
212	H–7 → L+3 (28%), H → L+9 (22%), H → L+10 (11%)	0.02
211	H–11 → L+2 (14%), H–10 → L+2 (18%), H–7 → L+3 (26%)	0.01
208	H–10 → L+3 (16%), H–8 → L+3 (11%), H–6 → L+4 (22%)	0.10
208	H–12 → L (42%), H–12 → L+1 (15%)	0.11
205	H–16 → L (13%), H–16 → L+1 (12%), H–10 → L+2 (11%), H → L+9 (15%)	0.02
205	H–16 → L (21%), H–16 → L+1 (19%), H–10 → L+2 (14%), H–8 → L+2 (12%)	0.01
205	H–9 → L+2 (25%), H–7 → L+4 (17%), H → L+11 (25%)	0.03
203	H–16 → L+2 (13%), H–7 → L+4 (11%), H–1 → L+9 (24%), H–1 → L+10 (13%), H → L+11 (11%)	0.04
203	H–16 → L+2 (33%), H–1 → L+9 (23%), H–1 → L+10 (12%)	0.03

202	H–16 → L+2 (17%), H–12 → L+2 (35%)	0.04
202	H–2 → L+9 (41%), H–2 → L+10 (23%)	0.02

[a] Geometry optimisations and TD-DFT calculations used the M06 functional with the Def2-QZVP/SVP mixed basis set, and a CPCM MeCN solvent model was included for TD-DFT. H = HOMO, L = LUMO.

Table S6. Selected TD-DFT-Calculated data for complex **2**.[a]

λ (nm)	Major contributions	f_{os}
342	H → L+1 (87%)	0.03
336	H–2 → L (87%)	0.12
321	H–2 → L+2 (26%), H–1 → L+1 (55%)	0.04
311	H–2 → L+2 (58%), H–1 → L+1 (30%)	0.13
296	H–5 → L (17%), H–4 → L (54%)	0.32
284	H–3 → L+1 (48%), H → L+5 (17%)	0.01
281	H → L+4 (72%)	0.01
280	H–3 → L+1 (17%), H–1 → L+5 (31%), H → L+5 (25%)	0.04
276	H–3 → L+2 (14%), H–2 → L+5 (56%)	0.08
276	H–3 → L+2 (49%), H–2 → L+5 (18%)	0.20
274	H–1 → L+5 (10%), H → L+6 (78%)	0.11
272	H–2 → L+4 (16%), H–1 → L+5 (29%), H → L+5 (17%)	0.06
268	H–1 → L+4 (60%)	0.07
265	H–5 → L+1 (35%), H–4 → L+1 (26%), H–3 → L+2 (14%)	0.09
263	H–3 → L+3 (25%), H–1 → L+6 (42%)	0.04
262	H–3 → L+3 (26%), H–2 → L+6 (17%), H–1 → L+6 (34%)	0.06
262	H–2 → L+6 (59%)	0.20
258	H → L+7 (75%)	0.14
257	H–5 → L+2 (27%), H–4 → L+2 (24%), H → L+8 (23%)	0.12
254	H–6 → L (11%), H–5 → L+2 (22%), H → L+8 (34%)	0.03
254	H–5 → L+2 (18%), H–4 → L+2 (58%), H → L+8 (14%)	0.02
253	H–5 → L+3 (17%), H–3 → L+5 (32%), H–1 → L+7 (10%)	0.07
248	H–5 → L+3 (12%), H–4 → L+3 (40%), H–4 → L+4 (20%)	0.05
247	H–3 → L+5 (10%), H–2 → L+8 (50%), H–1 → L+7 (26%)	0.05
242	H–5 → L+6 (12%), H–4 → L+6 (36%), H–1 → L+8 (14%)	0.05
242	H–2 → L+8 (34%), H–1 → L+7 (33%)	0.27
241	H–2 → L+7 (30%), H–1 → L+8 (25%)	0.11
238	H–1 → L+10 (26%), H → L+10 (29%)	0.02
237	H–7 → L+1 (10%), H–6 → L+1 (19%), H–6 → L+2 (14%)	0.11
237	H–6 → L+1 (11%), H–6 → L+2 (10%), H–4 → L+3 (11%), H–4 → L+4 (17%)	0.07
236	H–6 → L+2 (13%), H–5 → L+3 (11%), H–4 → L+3 (12%), H–4 → L+4 (25%)	0.04
235	H–5 → L+4 (24%), H–5 → L+5 (13%), H–4 → L+4 (10%)	0.02
234	H–11 → L (23%), H–8 → L (35%)	0.05
234	H–5 → L+4 (36%), H–5 → L+5 (20%), H–3 → L+6 (11%)	0.03
232	H–7 → L (49%), H–6 → L (39%)	0.01
229	H–5 → L+7 (12%), H–3 → L+8 (52%)	0.05
225	H–7 → L+1 (24%), H–6 → L+1 (28%), H–6 → L+3 (10%)	0.05
223	H–11 → L+1 (11%), H–8 → L+1 (20%), H–6 → L+2 (31%)	0.03
221	H–7 → L+1 (14%), H–6 → L+3 (41%)	0.10
220	H–12 → L (31%), H–10 → L (25%)	0.01
218	H–11 → L (36%), H–8 → L (11%), H–1 → L+13 (14%)	0.05
216	H–6 → L+5 (20%)	0.06
216	H–8 → L+2 (10%), H–6 → L+5 (15%), H–3 → L+7 (10%)	0.04
216	H–4 → L+7 (61%), H–3 → L+8 (16%)	0.03
215	H–8 → L+1 (12%), H–7 → L+2 (27%), H–5 → L+7 (17%), H–3 → L+8 (10%)	0.04
215	H–12 → L (16%), H–10 → L (19%), H–4 → L+8 (28%)	0.04
215	H–12 → L (13%), H–10 → L (24%), H–4 → L+8 (27%)	0.01
208	H–8 → L+3 (16%), H–7 → L+5 (12%), H–6 → L+5 (15%), H–6 → L+6 (10%)	0.06
207	H–9 → L+2 (10%), H → L+9 (48%), H → L+10 (10%)	0.03

205	H–14 → L (37%), H–11 → L+1 (11%), H–9 → L+1 (13%)	0.04
205	H–15 → L (20%), H–14 → L (13%), H–10 → L+1 (19%)	0.03
204	H–15 → L (11%), H–14 → L (15%), H–11 → L+1 (18%), H–10 → L+1 (10%), H–9 → L+1 (11%)	0.07
201	H–9 → L+3 (38%)	0.06
200	H–10 → L+2 (44%), H–7 → L+5 (12%)	0.03

[a] Geometry optimisations and TD-DFT calculations used the M06 functional with the Def2-QZVP/SVP mixed basis set, and a CPCM MeCN solvent model was included for TD-DFT. H = HOMO, L = LUMO.

Table S7. Selected TD-DFT-Calculated data for complex **3**.[a]

λ (nm)	Major contributions	f_{os}
348	H → L (87%)	0.01
330	H–1 → L (88%)	0.01
329	H–2 → L (39%), H–1 → L+1 (49%)	0.02
319	H–2 → L (47%), H–1 → L+1 (39%)	0.16
314	H–2 → L+1 (48%), H–1 → L+2 (35%)	0.06
307	H → L+3 (82%)	0.03
305	H–2 → L+2 (81%), H → L+2 (10%)	0.01
305	H–2 → L+1 (18%), H–1 → L+2 (53%), H → L+4 (17%)	0.12
293	H–2 → L+3 (83%)	0.06
290	H–3 → L (10%), H–3 → L+2 (73%)	0.27
287	H–1 → L+4 (85%)	0.02
283	H–5 → L+1 (10%), H–4 → L (55%), H–2 → L+4 (20%)	0.02
276	H–5 → L (14%), H–4 → L+1 (53%), H → L+5 (11%)	0.21
274	H–3 → L+1 (60%), H–2 → L+4 (15%)	0.03
273	H–4 → L (16%), H–3 → L+1 (36%), H–2 → L+4 (21%), H → L+4 (15%)	0.14
269	H → L+5 (78%)	0.17
264	H–5 → L (62%), H–4 → L+1 (25%)	0.03
262	H–4 → L+3 (22%), H–1 → L+5 (49%)	0.04
260	H–3 → L+3 (60%), H–2 → L+5 (22%)	0.08
258	H–3 → L+3 (29%), H–2 → L+5 (44%)	0.05
256	H–5 → L+2 (11%), H–1 → L+6 (11%), H → L+7 (48%)	0.01
256	H–5 → L+1 (60%)	0.17
254	H–5 → L+2 (51%), H–1 → L+10 (15%)	0.03
254	H–4 → L+4 (10%), H–1 → L+6 (17%), H–1 → L+10 (26%), H → L+7 (13%)	0.10
253	H–5 → L+2 (24%), H–5 → L+3 (12%), H–4 → L+4 (18%), H–1 → L+10 (16%)	0.06
251	H–2 → L+5 (16%), H–1 → L+6 (36%), H–1 → L+10 (11%)	0.23
249	H–2 → L+6 (12%), H–1 → L+7 (17%), H → L+8 (59%)	0.02
247	H–6 → L+2 (13%), H–3 → L+5 (35%), H–2 → L+7 (12%)	0.04
246	H–7 → L (13%), H–2 → L+6 (26%), H–1 → L+7 (23%)	0.21
244	H–5 → L+3 (42%), H–4 → L+4 (45%)	0.03
243	H–2 → L+7 (49%), H–1 → L+8 (23%)	0.10
243	H–7 → L+2 (40%), H–2 → L+8 (17%)	0.06
242	H–3 → L+5 (16%), H–1 → L+8 (62%)	0.14
242	H–7 → L (26%), H–2 → L+8 (13%), H–1 → L+7 (21%)	0.02
241	H–10 → L (10%), H–7 → L+1 (40%), H–2 → L+7 (14%)	0.10
239	H–7 → L+2 (23%), H–2 → L+8 (42%)	0.03
235	H–5 → L+6 (10%), H–4 → L+5 (42%)	0.01
233	H–6 → L (22%), H–5 → L+5 (15%), H–4 → L+6 (26%)	0.03
227	H–6 → L (48%), H–5 → L+5 (10%), H–4 → L+6 (18%)	0.10
226	H–9 → L (13%), H–8 → L (38%), H–6 → L+1 (11%), H–4 → L+5 (18%)	0.02
225	H–10 → L+2 (26%), H–6 → L (10%), H–6 → L+2 (12%), H–3 → L+7 (30%)	0.03
224	H–10 → L+1 (14%), H–9 → L (11%), H–7 → L+3 (13%), H–6 → L+1 (35%)	0.15
222	H–10 → L+2 (19%), H–6 → L+2 (11%), H → L+13 (24%)	0.03
222	H–9 → L+1 (15%), H–8 → L+1 (10%), H–7 → L+4 (20%), H–5 → L+5 (13%)	0.08
220	H–5 → L+5 (48%), H–4 → L+6 (22%)	0.02

219	H–10 → L (14%), H–9 → L+1 (10%), H–8 → L+1 (30%), H–6 → L+2 (10%)	0.03
219	H–10 → L+1 (25%), H–9 → L (17%), H–1 → L+13 (13%)	0.09
217	H–8 → L+2 (14%), H–1 → L+13 (47%)	0.12
216	H–10 → L+1 (17%), H–9 → L (10%), H–8 → L+2 (16%), H–1 → L+13 (13%)	0.05
216	H–9 → L+1 (19%), H–8 → L+1 (20%), H–4 → L+8 (13%), H–2 → L+13 (14%)	0.04
216	H–11 → L+2 (29%), H–9 → L+2 (11%), H–8 → L+2 (21%), H–3 → L+8 (11%)	0.03
215	H–9 → L+1 (10%), H–4 → L+8 (68%)	0.01
213	H–9 → L+3 (38%), H–8 → L+3 (29%)	0.04
212	H–12 → L (51%)	0.01
212	H–12 → L (11%), H–5 → L+7 (71%)	0.01
210	H–11 → L (44%), H–8 → L+3 (13%)	0.01
209	H–10 → L+3 (30%), H–8 → L+4 (14%), H–7 → L+4 (13%)	0.09
207	H–11 → L+1 (21%), H–10 → L+3 (15%), H–9 → L+4 (13%)	0.07
206	H–11 → L+1 (68%), H → L+11 (11%)	0.02
206	H–22 → L (13%), H–12 → L+1 (29%), H → L+9 (19%)	0.02
205	H–7 → L+8 (14%), H–6 → L+5 (41%)	0.16
204	H–1 → L+9 (62%), H–1 → L+10 (15%)	0.02
203	H–22 → L+1 (35%), H → L+11 (10%)	0.07
203	H–22 → L+1 (19%), H → L+11 (25%)	0.01
202	H–10 → L+4 (22%), H–6 → L+4 (17%), H–2 → L+9 (29%)	0.01

[a] Geometry optimisations and TD-DFT calculations used the M06 functional with the Def2-QZVP/SVP mixed basis set, and a CPCM MeCN solvent model was included for TD-DFT. H = HOMO, L = LUMO.

Table S8. Coordinates of the M06/Def2-QZVP/SVP-optimised geometries of the S_0 and T_1 states of complexes **1–3**.

S_0 state of **1** (charge = 3, multiplicity = 1)			
	x	y	z
C	1.8104	–2.2194	1.4871
C	2.933	–2.9064	1.9289
C	4.1888	–2.416	1.5837
C	4.2728	–1.26	0.8155
C	3.1052	–0.6149	0.4066
C	3.1046	0.6204	–0.4018
C	4.2716	1.2685	–0.8079
C	4.1866	2.424	–1.5768
C	2.9304	2.9108	–1.9256
C	1.8085	2.2212	–1.4862
C	0.8343	1.3189	2.6627
C	0.7442	2.2686	3.671
C	–0.1647	3.3134	3.5264
C	–0.9518	3.3692	2.3806
C	–0.8178	2.3868	1.4027
C	–1.5808	2.3102	0.1514
C	–2.5376	3.2375	–0.2222
C	–2.9475	2.0785	–2.2172
C	–2.0055	1.1229	–1.8956
C	–1.2792	1.2043	–0.6938
C	–4.1813	4.1467	–1.7923
C	0.8398	–1.3182	–2.6627
C	0.7534	–2.2688	–3.6705

C	–0.1521	–3.3165	–3.5258
C	–0.9397	–3.3741	–2.3805
C	–0.8095	–2.3908	–1.403
C	–1.5745	–2.3149	–0.1531
C	–2.5247	–3.2494	0.223
C	–2.9392	–2.0898	2.2167
C	–2.0047	–1.1286	1.8936
C	–1.2782	–1.2077	0.6908
C	–4.2136	–4.1198	1.7803
H	0.8049	–2.5714	1.7395
H	2.8201	–3.8087	2.5334
H	5.0979	–2.9281	1.9092
H	5.2527	–0.8683	0.5371
H	5.2518	0.8794	–0.5268
H	5.0952	2.9383	–1.9002
H	2.8168	3.8123	–2.531
H	0.8026	2.5702	–1.7415
H	1.532	0.4798	2.7365
H	1.3812	2.1863	4.5539
H	–0.262	4.0796	4.2997
H	–1.6706	4.1824	2.2552
H	–2.802	4.1055	0.389
H	–3.5274	2.0484	–3.144
H	–1.8442	0.3073	–2.6075
H	1.5348	–0.4768	–2.7366
H	1.3906	–2.1849	–4.5531
H	–0.2466	–4.0834	–4.2988
H	–1.6564	–4.1893	–2.2552
H	–2.7825	–4.1193	–0.388
H	–3.5204	–2.0653	3.1433
H	–1.8443	–0.3136	2.6064
H	–4.9811	3.6789	–2.3795
H	–3.6837	4.9169	–2.3996
H	–4.6181	4.6092	–0.899
H	–4.0096	–4.4753	2.7992
H	–4.1874	–4.9712	1.0909
H	–5.2088	–3.6539	1.7462
Ir	0.1688	–0.0004	–0.0003
N	1.8881	–1.1036	0.7478
N	1.8871	1.106	–0.7461
N	0.0772	1.3735	1.556
N	–3.2047	3.1185	–1.3899
N	0.0823	–1.3746	–1.5564
N	–3.1905	–3.133	1.3903

T_1 state of **1** (charge = 3, multiplicity = 3)

	x	y	z
C	–1.82523	2.18052	1.5122
C	–2.94809	2.8683	1.95244
C	–4.20343	2.38807	1.59148
C	–4.28798	1.23946	0.81175
C	–3.12055	0.59263	0.40521
C	–3.12076	–0.63892	–0.41039

C	–4.2881	–1.2905	–0.81017
C	–4.20334	–2.44597	–1.57953
C	–2.94786	–2.92974	–1.93532
C	–1.82555	–2.23611	–1.50273
C	–0.82641	–1.37975	2.64153
C	–0.70854	–2.32945	3.64689
C	0.237	–3.34119	3.50281
C	1.03034	–3.36675	2.36033
C	0.8673	–2.38596	1.38519
C	1.62601	–2.28341	0.13336
C	2.61237	–3.17947	–0.24138
C	2.9731	–2.0166	–2.24366
C	2.0003	–1.09238	–1.92232
C	1.28808	–1.19049	–0.71383
C	4.28781	–4.02886	–1.81654
C	–0.86639	1.35411	–2.63311
C	–0.76945	2.34165	–3.63534
C	0.18249	3.38804	–3.48897
C	0.96824	3.41359	–2.37632
C	0.83406	2.39041	–1.35559
C	1.53858	2.31256	–0.16649
C	2.52458	3.27365	0.24281
C	2.88652	2.10177	2.25451
C	1.94562	1.12442	1.91703
C	1.23982	1.18574	0.72529
C	4.15207	4.13643	1.83673
H	–0.81842	2.51893	1.77917
H	–2.83602	3.76266	2.56867
H	–5.11245	2.90155	1.91512
H	–5.26782	0.85534	0.5228
H	–5.26795	–0.90608	–0.52165
H	–5.11217	–2.96376	–1.89676
H	–2.83523	–3.83186	–2.54005
H	–0.81927	–2.58169	–1.76167
H	–1.55162	–0.56425	2.71577
H	–1.35157	–2.27215	4.52747
H	0.35723	–4.10606	4.2743
H	1.77611	–4.15556	2.23618
H	2.90788	–4.03581	0.3719
H	3.54838	–1.97213	–3.17288
H	1.80738	–0.28546	–2.63589
H	–1.58832	0.53711	–2.74293
H	–1.42365	2.28482	–4.50796
H	0.27805	4.1567	–4.25926
H	1.70723	4.20759	–2.24414
H	2.7961	4.13991	–0.36687

H	3.45551	2.09489	3.1872
H	1.7851	0.31451	2.636
H	5.1139	–3.51244	–2.32165
H	3.84199	–4.7644	–2.50193
H	4.67651	–4.54343	–0.92988
H	3.82361	4.59745	2.77888
H	4.26768	4.91016	1.06942
H	5.11397	3.62928	1.99639
Ir	–0.17922	–0.01728	–0.00772
N	–1.90408	1.07441	0.75905
N	–1.90456	–1.12106	–0.76299
N	–0.06173	–1.40447	1.53937
N	3.27046	–3.04203	–1.41139
N	–0.11857	1.34268	–1.5462
N	3.14883	3.14757	1.40669

S_0 state of **2** (charge = 3, multiplicity = 1)

	x	y	z
C	–0.89318	–2.60361	–0.61274
C	–2.01834	–3.39882	–0.79591
C	–3.26805	–2.80914	–0.65383
C	–3.35117	–1.45668	–0.33432
C	–2.18254	–0.71918	–0.16693
C	–2.1823	0.71826	0.16527
C	–3.35065	1.45654	0.3315
C	–3.26697	2.80885	0.65147
C	–2.01701	3.39762	0.79516
C	–0.89223	2.60169	0.61306
C	0.08194	0.30134	–2.95857
C	0.16672	0.84201	–4.23413
C	1.0716	1.87496	–4.46434
C	1.8607	2.32742	–3.41147
C	1.73179	1.74551	–2.15295
C	2.50025	2.10926	–0.95645
C	3.46164	3.10414	–0.93471
C	3.89277	2.70332	1.33301
C	2.94498	1.70012	1.36963
C	2.2046	1.36672	0.22253
C	5.11926	4.49663	0.19823
C	0.07763	–0.30582	2.95894
C	0.1595	–0.84827	4.23386
C	1.06317	–1.88229	4.46429
C	1.85413	–2.33374	3.41244
C	1.72821	–1.75002	2.15439
C	2.49973	–2.1112	0.95923
C	3.4601	–3.10899	0.93806

C	3.8927	–2.70531	–1.32901
C	2.94721	–1.70193	–1.36665
C	2.20593	–1.36841	–0.21851
C	5.17201	–4.44921	–0.20528
H	0.1102	–3.02847	–0.71901
H	–1.92014	–4.45776	–1.0456
H	–4.3345	–0.99322	–0.21854
H	–4.33417	0.9938	0.21454
H	–1.91842	4.4564	1.04538
H	0.11132	3.02577	0.72077
H	–0.61431	–0.51253	–2.73565
H	–0.47145	0.45517	–5.03132
H	1.16409	2.32467	–5.45637
H	2.57712	3.13543	–3.57704
H	3.72211	3.70594	–1.81069
H	4.48217	2.98927	2.20877
H	2.79247	1.18001	2.32027
H	–0.61761	0.50883	2.73571
H	–0.47986	–0.46205	5.03038
H	1.15341	–2.33346	5.45585
H	2.56979	–3.14233	3.5785
H	3.71718	–3.71052	1.81475
H	4.48544	–2.99482	–2.20192
H	2.7926	–1.18381	–2.31804
H	5.86754	4.32166	0.98041
H	4.60525	5.44972	0.39106
H	5.62396	4.54166	–0.7748
H	4.9691	–5.14978	–1.02635
H	5.15517	–4.99506	0.74494
H	6.1626	–3.99384	–0.34632
Ir	0.75376	–0.0014	0.0008
N	–0.96682	–1.30134	–0.31171
N	–0.96638	1.29958	0.31151
N	0.84121	0.73881	–1.94164
N	4.14144	3.39297	0.19581
N	0.83852	–0.74253	1.94283
N	4.14009	–3.39626	–0.19072
C	–4.55713	–3.59066	–0.84199
C	–4.55564	3.59126	0.83868
F	–4.30672	4.85677	1.10751
F	–5.2783	3.50975	–0.26582
F	–5.24448	3.05799	1.8344
F	–5.2453	–3.05637	–1.83765
F	–5.28013	–3.50926	0.2623
F	–4.30894	–4.85616	–1.11141

T$_1$ state of **2** (charge = 3, multiplicity = 3)			
	x	y	z
C	–0.89318	–2.60361	–0.61274
C	–2.01834	–3.39882	–0.79591
C	–3.26805	–2.80914	–0.65383
C	–3.35117	–1.45668	–0.33432
C	–2.18254	–0.71918	–0.16693
C	–2.1823	0.71826	0.16527
C	–3.35065	1.45654	0.3315
C	–3.26697	2.80885	0.65147
C	–2.01701	3.39762	0.79516
C	–0.89223	2.60169	0.61306
C	0.08194	0.30134	–2.95857
C	0.16672	0.84201	–4.23413
C	1.0716	1.87496	–4.46434
C	1.8607	2.32742	–3.41147
C	1.73179	1.74551	–2.15295
C	2.50025	2.10926	–0.95645
C	3.46164	3.10414	–0.93471
C	3.89277	2.70332	1.33301
C	2.94498	1.70012	1.36963
C	2.2046	1.36672	0.22253
C	5.11926	4.49663	0.19823
C	0.07763	–0.30582	2.95894
C	0.1595	–0.84827	4.23386
C	1.06317	–1.88229	4.46429
C	1.85413	–2.33374	3.41244
C	1.72821	–1.75002	2.15439
C	2.49973	–2.1112	0.95923
C	3.4601	–3.10899	0.93806
C	3.8927	–2.70531	–1.32901
C	2.94721	–1.70193	–1.36665
C	2.20593	–1.36841	–0.21851
C	5.17201	–4.44921	–0.20528
H	0.1102	–3.02847	–0.71901
H	–1.92014	–4.45776	–1.0456
H	–4.3345	–0.99322	–0.21854
H	–4.33417	0.9938	0.21454
H	–1.91842	4.4564	1.04538
H	0.11132	3.02577	0.72077
H	–0.61431	–0.51253	–2.73565
H	–0.47145	0.45517	–5.03132
H	1.16409	2.32467	–5.45637
H	2.57712	3.13543	–3.57704
H	3.72211	3.70594	–1.81069

H	4.48217	2.98927	2.20877
H	2.79247	1.18001	2.32027
H	–0.61761	0.50883	2.73571
H	–0.47986	–0.46205	5.03038
H	1.15341	–2.33346	5.45585
H	2.56979	–3.14233	3.5785
H	3.71718	–3.71052	1.81475
H	4.48544	–2.99482	–2.20192
H	2.7926	–1.18381	–2.31804
H	5.86754	4.32166	0.98041
H	4.60525	5.44972	0.39106
H	5.62396	4.54166	–0.7748
H	4.9691	–5.14978	–1.02635
H	5.15517	–4.99506	0.74494
H	6.1626	–3.99384	–0.34632
Ir	0.75376	–0.0014	0.0008
N	–0.96682	–1.30134	–0.31171
N	–0.96638	1.29958	0.31151
N	0.84121	0.73881	–1.94164
N	4.14144	3.39297	0.19581
N	0.83852	–0.74253	1.94283
N	4.14009	–3.39626	–0.19072
C	–4.55713	–3.59066	–0.84199
C	–4.55564	3.59126	0.83868
F	–4.30672	4.85677	1.10751
F	–5.2783	3.50975	–0.26582
F	–5.24448	3.05799	1.8344
F	–5.2453	–3.05637	–1.83765
F	–5.28013	–3.50926	0.2623
F	–4.30894	–4.85616	–1.11141

S_1 state of **3** (charge = 3, multiplicity = 1)

	x	y	z
C	0.87165	–2.60228	0.58649
C	1.99667	–3.3906	0.77359
C	3.27429	–2.83023	0.65113
C	3.31659	–1.46314	0.33588
C	2.15495	–0.72072	0.16207
C	2.15494	0.72076	–0.16175
C	3.31657	1.46318	–0.33556
C	3.27427	2.83023	–0.65096
C	1.99664	3.39057	–0.77348
C	0.87163	2.60225	–0.58634
C	–0.09309	0.23238	2.95915
C	–0.17027	0.74684	4.24606
C	–1.06831	1.77934	4.50223

C	–1.85976	2.25788	3.46322
C	–1.73962	1.70115	2.19241
C	–2.51287	2.09335	1.00793
C	–3.47315	3.08836	1.0135
C	–3.91456	2.73955	–1.26147
C	–2.96819	1.73786	–1.32486
C	–2.22232	1.37588	–0.18885
C	–5.13508	4.50572	–0.07967
C	–0.09274	–0.23263	–2.95894
C	–0.16981	–0.74709	–4.24585
C	–1.06796	–1.77946	–4.50214
C	–1.85964	–2.25788	–3.46324
C	–1.73958	–1.70116	–2.19242
C	–2.51304	–2.09325	–1.00803
C	–3.47349	–3.08809	–1.01373
C	–3.91508	–2.73925	1.2612
C	–2.96854	–1.73773	1.32471
C	–2.22248	–1.37585	0.18878
C	–5.13578	–4.50518	0.07922
H	–0.12954	–3.03588	0.68374
H	1.86527	–4.44689	1.01535
H	4.28493	–0.97075	0.22338
H	4.2849	0.97078	–0.22298
H	1.86521	4.44683	–1.01534
H	–0.12956	3.03585	–0.68365
H	0.59787	–0.57947	2.71336
H	0.46903	0.33983	5.03201
H	–1.15401	2.20853	5.50375
H	–2.57098	3.06624	3.64787
H	–3.73027	3.67071	1.90339
H	–4.50775	3.04608	–2.12752
H	–2.81854	1.23971	–2.28782
H	0.5983	0.57913	–2.71307
H	0.46967	–0.34019	–5.03171
H	–1.15359	–2.20865	–5.50368
H	–2.57094	–3.06614	–3.64798
H	–3.73062	–3.67038	–1.90365
H	–4.5084	–3.04569	2.12719
H	–2.8189	–1.23963	2.28771
H	–5.88872	4.34802	–0.86042
H	–4.62361	5.46359	–0.2547
H	–5.63426	4.52969	0.89694
H	–4.62446	–5.46317	0.25404
H	–5.63502	–4.52889	–0.89737
H	–5.88935	–4.3475	0.86004
Ir	–0.7747	–0.00007	0.00005

N	0.93319	–1.29705	0.2927
N	0.93316	1.29704	–0.29246
N	–0.8553	0.69513	1.95628
N	–4.15858	3.40324	–0.10719
N	–0.85516	–0.69526	–1.95618
N	–4.15909	–3.40288	0.10689
C	4.55625	–3.62234	0.83861
C	4.55627	3.62229	–0.83865
C	5.36023	–2.99201	1.98332
H	6.28765	–3.56552	2.13956
H	5.6559	–1.95094	1.77463
H	4.79572	–3.00868	2.93031
C	4.275	–5.08201	1.17846
H	3.7237	–5.59905	0.37538
H	5.22663	–5.61904	1.30975
H	3.71377	–5.18998	2.12166
C	5.36444	–3.56146	–0.46407
H	6.29194	–4.14423	–0.34737
H	4.80332	–3.99502	–1.30832
H	5.66024	–2.53486	–0.73489
C	5.35975	2.9921	–1.9838
H	6.28717	3.56555	–2.1403
H	5.65538	1.95095	–1.7754
H	4.79485	3.00899	–2.93055
C	4.27513	5.08207	–1.1781
H	3.72404	5.59898	–0.3748
H	5.2268	5.61903	–1.30942
H	3.71376	5.19034	–2.12118
C	5.36494	3.56106	0.4637
H	4.80423	3.99466	1.30821
H	5.66063	2.53437	0.73429
H	6.29252	4.14364	0.3467

T_1 state of **3** (charge = 3, multiplicity = 3)

	x	y	z
C	0.8638	2.58883	–0.60649
C	1.98237	3.38776	–0.78613
C	3.26463	2.84131	–0.64771
C	3.31886	1.47569	–0.32578
C	2.16377	0.722	–0.15877
C	2.17622	–0.71872	0.17151
C	3.34405	–1.45442	0.33135
C	3.3128	–2.8219	0.6474
C	2.0402	–3.39001	0.78665
C	0.90848	–2.60806	0.61338
C	–0.0789	–0.30652	–2.95202

C	–0.17894	–0.82269	–4.23663
C	–1.11424	–1.82354	–4.48526
C	–1.91566	–2.27305	–3.44091
C	–1.77001	–1.71738	–2.1724
C	–2.54052	–2.08945	–0.97974
C	–3.52064	–3.06641	–0.97495
C	–3.92285	–2.71691	1.30723
C	–2.95507	–1.7359	1.3619
C	–2.22309	–1.38203	0.21462
C	–5.20437	–4.44469	0.151
C	–0.07661	0.29601	2.94692
C	–0.17991	0.84599	4.23898
C	–1.15151	1.85626	4.49037
C	–1.94582	2.27632	3.46767
C	–1.80088	1.70584	2.14214
C	–2.50484	2.06899	1.00569
C	–3.50291	3.09965	0.97847
C	–3.87478	2.73314	–1.31933
C	–2.91629	1.71761	–1.36532
C	–2.19708	1.35342	–0.23691
C	–5.15501	4.46055	–0.18194
H	–0.14237	3.00741	–0.71974
H	1.8424	4.44102	–1.03599
H	4.29144	0.99455	–0.20106
H	4.30837	–0.95779	0.204
H	1.91888	–4.44713	1.03012
H	–0.09001	–3.04584	0.72148
H	0.63869	0.484	–2.7128
H	0.47006	–0.44037	–5.02701
H	–1.22022	–2.25165	–5.48536
H	–2.65415	–3.05783	–3.6203
H	–3.79804	–3.64071	–1.86364
H	–4.51219	–3.01603	2.17878
H	–2.7796	–1.24494	2.32389
H	0.6586	–0.49127	2.74492
H	0.48193	0.48421	5.02865
H	–1.25329	2.28371	5.49054
H	–2.69946	3.04924	3.6361
H	–3.77743	3.68303	1.86155
H	–4.45405	3.05552	–2.18773
H	–2.75216	1.22671	–2.32991
H	–6.04499	–4.15765	0.79523
H	–4.75702	–5.37677	0.52613
H	–5.57412	–4.60109	–0.86929
H	–4.83563	5.24313	–0.88438
H	–5.27543	4.89212	0.81817

H	–6.11237	4.03891	–0.5187
Ir	–0.76341	–0.0199	0.00675
N	0.93744	1.28647	–0.30343
N	0.96022	–1.30301	0.3181
N	–0.8532	–0.73926	–1.94544
N	–4.1969	–3.36983	0.15302
N	–0.83734	0.67075	1.9345
N	–4.13971	3.39511	–0.14891
C	4.53998	3.64552	–0.82727
C	4.60125	–3.6072	0.81822
C	5.35598	3.02236	–1.96756
H	6.27993	3.60321	–2.11712
H	5.65804	1.9833	–1.7579
H	4.79731	3.03584	–2.91801
C	4.24757	5.10274	–1.16819
H	3.68651	5.61409	–0.36827
H	5.1951	5.64845	–1.29309
H	3.69151	5.20646	–2.11487
C	5.34132	3.59176	0.48008
H	6.26268	4.18529	0.36936
H	4.77054	4.01804	1.32157
H	5.64763	2.56839	0.75143
C	5.41434	–2.97497	1.95546
H	6.34703	–3.54315	2.09924
H	5.701	–1.93148	1.74619
H	4.86093	–2.99785	2.90882
C	4.33202	–5.06933	1.15734
H	3.77516	–5.58744	0.3588
H	5.2881	–5.60115	1.27687
H	3.78156	–5.18314	2.10618
C	5.3945	–3.53888	–0.4933
H	4.82525	–3.97117	–1.33277
H	5.6845	–2.51052	–0.76372
H	6.325	–4.11928	–0.38933