One-step assembly of Re(I) tricarbonyl 2-pyridyltetrazolato metallacalix[3]arene with aqua emission and reversible three-electron oxidation

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Supplementary Information

General Remarks

All reagents and solvents were purchased from Sigma Aldrich and used as received without further purification. 2-(1H-tetrazol-5-yl)pyridine was synthesised according to previously published procedures.[1, 2] Acidic alumina for column chromatography was of Brockmann I activity. Nuclear magnetic resonance spectra, consisting of ^{1}H, ^{13}C, HSQC, and HMBC were recorded using a Bruker Avance 400 spectrometer (400.1 MHz for ^{1}H, 100 MHz for ^{13}C) at 300 K. ^{1}H and ^{13}C chemical shifts were referenced to residual solvent signals. Infrared spectra were recorded in the solid state, using an attenuated total reflectance Perkin-Elmer Spectrum 100 FT-IR, equipped with a diamond stage. Compounds were scanned from 4000 to 650 cm^{-1}. The intensities of the IR bands are reported as strong (s), medium (m), or weak (w). Melting points were determined Using a BI Barnstead Electrothermal 9100 apparatus. Elemental analyses were obtained at the Central Science Laboratory, University of Tasmania, using a Thermo Finnigan EA 1112 Series Flash.

Photophysical Measurements

Absorption spectra were recorded at room temperature using a Perkin Elmer Lambda 35 UV/Vis spectrometer. Uncorrected steady state emission and excitation spectra were recorded on an Edinburgh FLSP920 spectrometer equipped with a 450 W Xenon arc lamp, double excitation and single emission monochromators and a peltier cooled Hamamatsu R928P photomultiplier tube (185-850 nm). Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by a calibration curve supplied with the instrument. According to the approach described by Demas and Crosby,[3] luminescence quantum yields (Φ_{em}) were measured in optically dilute solutions (O.D. < 0.1 at excitation wavelength) obtained from absorption spectra on a wavelength scale [nm] and compared to the reference emitter by the following equation:

$$\Phi_x = \Phi_r \left[\frac{A_r(\lambda_r)}{A_x(\lambda_x)}\right]\left[\frac{I_r(\lambda_r)}{I_x(\lambda_x)}\right]\left[\frac{n_x^2}{n_r^2}\right]\left[\frac{D_x}{D_r}\right]$$

where A is the absorbance at the excitation wavelength (λ), I is the intensity of the excitation light at the excitation wavelength (λ), n is the refractive index of the solvent, D is the integrated intensity of the luminescence and Φ is the quantum yield. The subscripts r and x refer to the reference and the sample, respectively. The quantum yield determinations were performed at identical excitation wavelength for the sample and the reference, therefore cancelling the $I(\lambda_r)/I(\lambda_x)$ term in the equation. All the Re complexes were measured against an air-equilibrated water solution of Ru(bpy)$_3$Cl$_2$ used as reference ($\Phi_r = 0.028$).[4] Emission lifetimes (τ) were determined with the single photon counting technique (TCSPC) with the same Edinburgh FLSP920 spectrometer using pulsed picosecond LEDs (EPLED 295 or EPLED 360, FHWM < 800 ps) as the excitation source, with repetition rates between 10 kHz and 1 MHz, and the above-mentioned R928P PMT as detector. The goodness of fit was assessed by minimising the reduced χ^2 function and by visual inspection of the weighted residuals. To record the 77 K luminescence spectra, the samples were put in glass tubes (2 mm diameter) and inserted in a special quartz dewar filled up with liquid nitrogen. The solvent (dichloromethane) used for the preparation of the solutions for the photophysical investigations was of spectrometric grade. The prepared solution was filtered through a 0.2 μm syringe filter before measurement. Deaerated samples were prepared by the freeze-pump-thaw technique. Experimental uncertainties are estimated to be ±8% for lifetime determinations, ±20% for quantum yields, ±2 nm and ±5 nm for absorption and emission peaks, respectively.

X-ray Diffraction

Crystallographic data for the structure of **1** were collected at 100(2) K on an Oxford Diffraction Gemini diffractometer fitted with Cu Kα radiation. Following analytical absorption corrections and solution by direct methods, the structure was refined against F^2 with full-matrix least-squares using the program SHELXL-97.[5] The data were collected at 180 K since the crystal appeared to deteriorate at lower temperatures. The solvent was modelled as two molecules of dichloromethane, one of which was found to be disordered over two sets of sites with occupancies constrained to 0.5 after trial refinement. Geometries of the disordered atoms were restrained to ideal values. Anisotropic displacement parameters were employed for the non-hydrogen atoms. All hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atom.

Cyclic Voltammetry in Ionic liquid

A gold microelectrode (made in house and kindly donated by the group of Professor Richard Compton at Oxford University, UK) was polished and modified with a section of disposable micropipette tip into which microlitre quantities of the ionic liquid solvent can be placed. The electrode was then inserted into a "T-cell" apparatus as described elsewhere.[6] A silver wire (0.5 mm diameter) was inserted from the top and acted as a combined counter and reference electrode. The T-cell was placed inside an aluminium Faraday cage and connected to a vacuum pump (Edwards ES50). The samples for electrochemistry were prepared by dissolving the required amount of rhenium complex in a minimal amount of dichloromethane and then adding this solution to the ionic liquid (1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate) in order to obtain a final concentration of the order of 10 mM. The solution was left in an open container to allow the dichloromethane to evaporate. 40 µL of this sample were transferred into the T-cell with the use of a micropipette. Experiments requiring the use of ferrocene followed the above procedure, however 10 µL of a 10 mM solution of ferrocene in acetonitrile was added into the T-cell apparatus along with the ionic liquid containing the rhenium complex. Cyclic voltammetry experiments were performed using a PGSTAT302N potentiostat (Eco-Chemie, Netherlands) interfaced to a PC with GPES (General Purpose Electrochemical System) software. The step potential was fixed at 0.01 V. The potentials are referenced to an internal reference Ferrocene/Ferrocenium redox couple according to IUPAC recommendations,[7] and established in ionic liquids.[8, 9] Scans were performed using a potential window within the range of -1.7 – 2.5 V reliant on the compound investigated. Reported potentials were obtained from a scan rate of 100 mVs^{-1}.

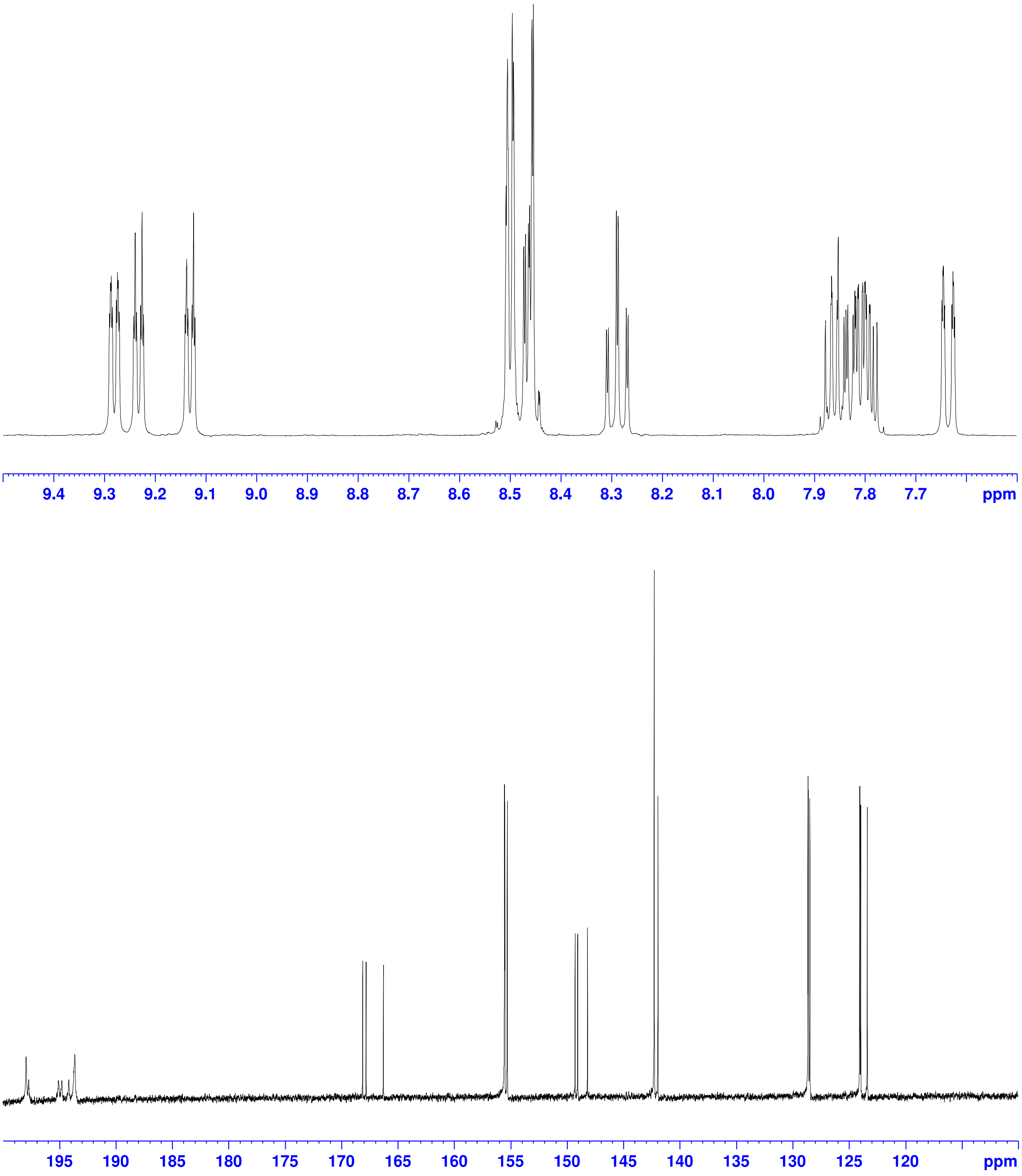
Computational Calculations.

Time-dependent density functional theory calculations were performed with GAUSSIAN 09[10] in order to calculate the absorption spectra for the title compound. Prior to these calculations, the structures were relaxed at the B3LYP level of theory. The Re atoms were treated with the Stuttgart-Dresden (SDD) effective core potential,[11] the Pople 6-311G** basis set was used for C, H, and N atoms and the effect of the solvent was mimicked with the PCM solvation model.[12] The low-lying singlet-singlet excitation energies were calculated at the same level of theory, and the spectra were reproduced as the superposition of Gaussian functions with heights proportional to calculated intensities and a variance of 11nm. Because of the large number of atoms, the computational cost of the TDDFT calculations for **1** became excessive and therefore we limited the calculations to lower-energy transitions up to 295 nm.

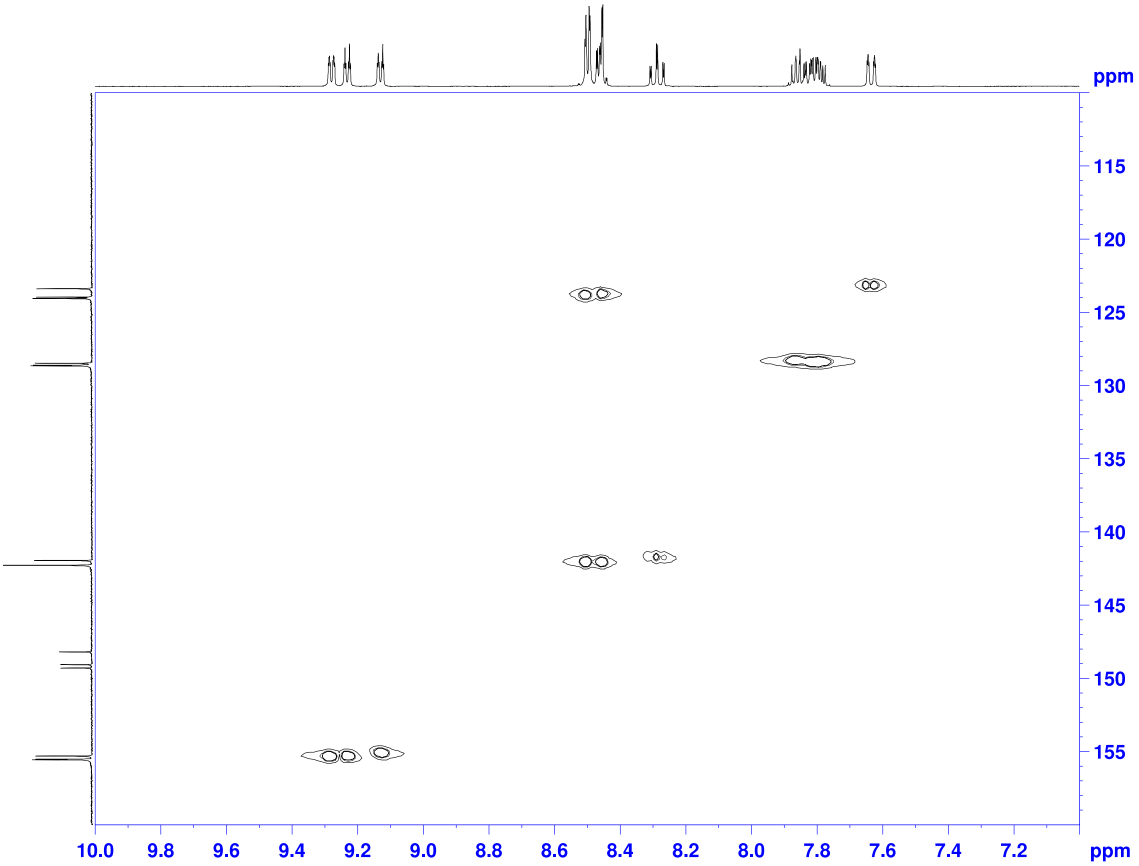
Synthesis of 1

[Re(CO)$_5$Cl] (300 mg, 0.83 mmol) and 2-(1H-tetrazol-5-yl)pyridine (120 mg, 0.83 mmol) were combined in toluene (25 mL). Triethylamine (114 μL, 0.83 mmol) was added and the mixture was stirred at reflux for 12 hours. The mixture was then cooled to room temperature and the solvent was removed under reduced pressure. The resulting solid was dissolved in dichloromethane (50 mL) and sequentially washed with 25 mL of saturated sodium carbonate solution, water, and eventually brine. The organic phase was collected, dried over MgSO$_4$ and the solvent was reduced to a minimal amount (ca. 2-3 mL). The solution was then charged on an alumina-packed column and dichloromethane was used as the eluent. The first fraction was collected and the solvent was removed to yield a white powder. Single crystals suitable for X-ray diffraction were grown by layering hexanes on a dichloromethane solution of **1**. Similar results were obtained starting from [Re(CO)$_5$Br]. Yield: 123 mg (36 %). M.p. > 350 °C. ^{1}H NMR (d$_6$-acetone): δ 9.28 (d, J = 5.8 Hz, 1H; H6(py)), 9.23 (d, J = 5.6 Hz, 1H; H6(py)), 9.13 (d, J = 5.2 Hz, 1H; H6(py)), 8.53-8.43 (m, 4H; H(py)), 8.32-8.25 (m, 1H; H(py)), 7.9-7.76 (m, 3H; H(py)), 7.63 (d, J = 8.1 Hz, 1H; H(py)) ppm. ^{13}C NMR (d$_6$-acetone): nine CO peaks expected but due to low intensity and overlapping nature only six could be clearly distinguished; some signals belonging to the tertiary C atoms in the pyridine ring are also overlapping: δ 198.0 ($\underline{C}$O), 197.7 ($\underline{C}$O), 195.1 ($\underline{C}$O), 194.8 ($\underline{C}$O), 194.2 ($\underline{C}$O), 193.6 ($\underline{C}$O), 168.1 ($\underline{C}N_4$), 167.8 ($\underline{C}N_4$), 166.3 ($\underline{C}N_4$), 155.53, 155.50, 155.3, 149.3, 149.0, 148.2, 142.3, 141.9, 128.62, 128.58, 128.5, 124.0, 123.9, 123.4. IR: ν_{max} 2027 s (CO), 1917 s (CO) 1898 s (CO), 1621 m, 1568 w, 1449 m, 1288 w, 1254 w, 1158 w, 1105 w, 1047 w, 792 w, 754 w, 724 w cm^{-1}. Anal. Calcd (%) for **1**: C 25.96, H 0.97, N 16.82. Found: C 26.12, H 0.96, N 16.74.

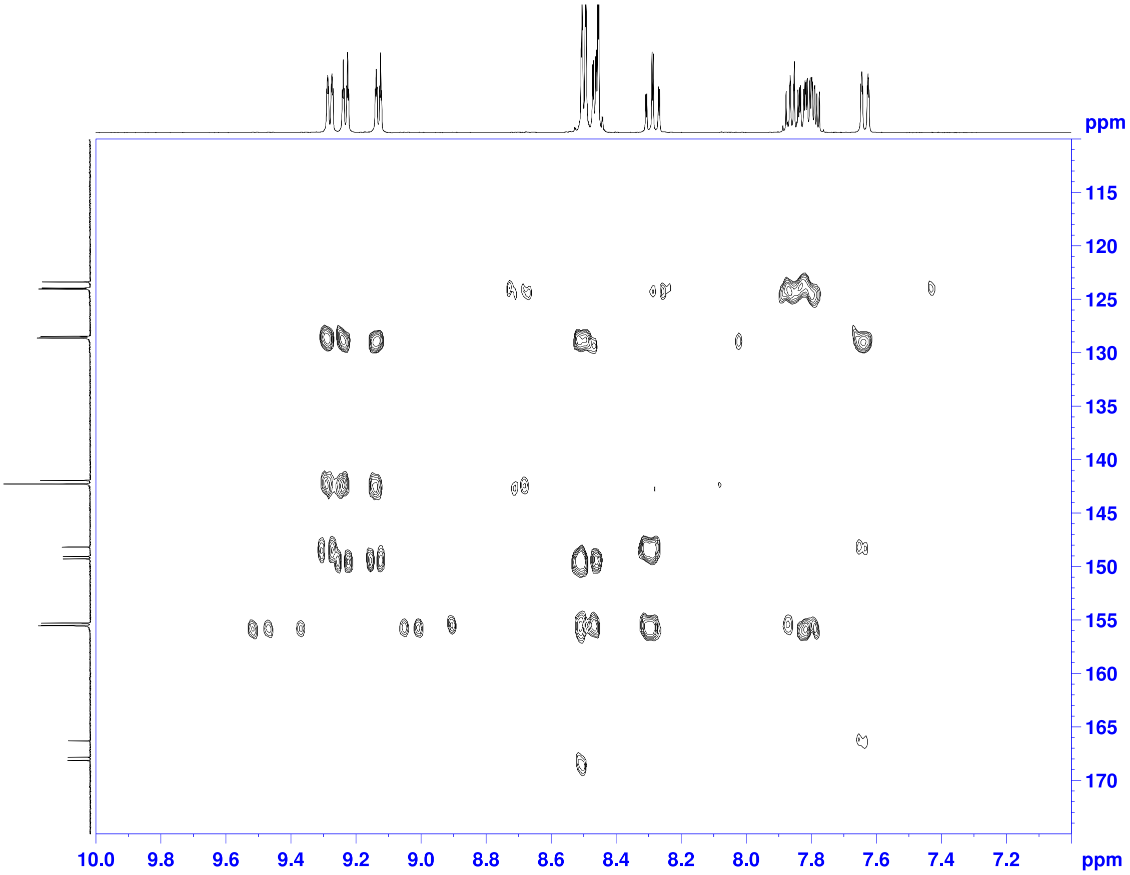
^{1}H and ^{13}C NMR spectra of 1 from a d_6-acetone solution



HSQC spectra of 1 from a d_6-acetone solution



HMBC spectra of 1 from a d_6-acetone solution



X-ray structural characterisation

The metallacalix[3]arene 1 crystallises in the monoclinic space group $P2_1/n$. Each 2**PyTz** links two adjacent rhenium centres with a μ_2-η^2:η^1 binding mode, involving the pyridine N atom and the tetrazole N1 atom for one rhenium centre and the tetrazole N3 atom to bridge the adjacent rhenium. The three **2PyTz** are arranged in a slightly concave equilateral triangle, with sides averaging 6.3 Å. The triangular disposition of the metallacalix[3]arene leaves a cavity of about 4 Å, estimated by the diameter of the circle inscribed within the triangle (Figure S1). However, the likelihood of molecular inclusion in the cavity is slim as evidenced by the visualised void spaces using *CrystalExplorer* (Figure S2).[13] Individual triangular units of 1 do not seem to be involved in hydrogen bonding or π-stacking throughout the lattice. Three molecules of dichloromethane are also present in the lattice. The high R-factor could be attributed to poor crystal quality and problems modelling the solvent molecules.

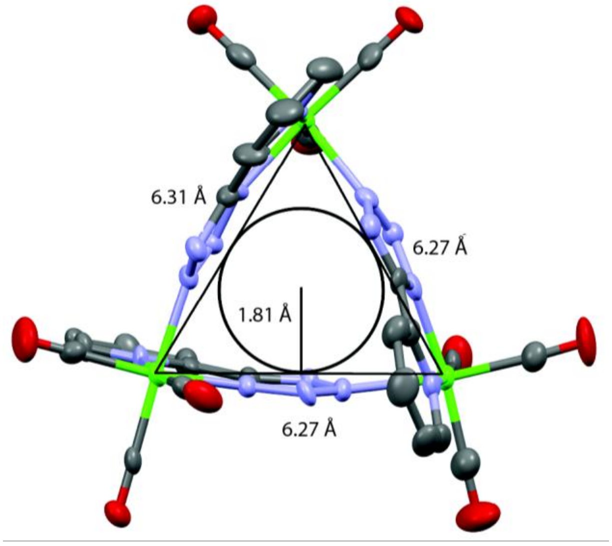


Figure S1. Calculated dimensions of the triangular cavity formed by the metallaclix[3]arene complex.

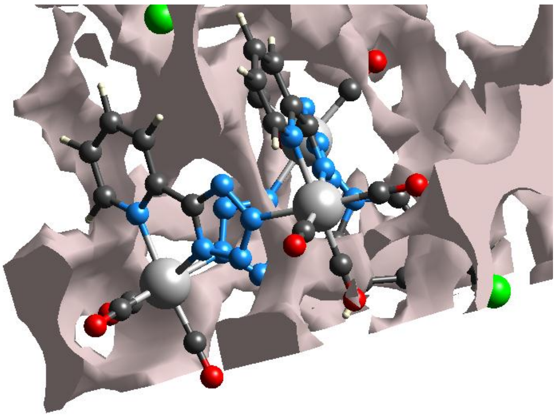


Figure S2. Representation of the void space (grey area) within the cavity of **1**.

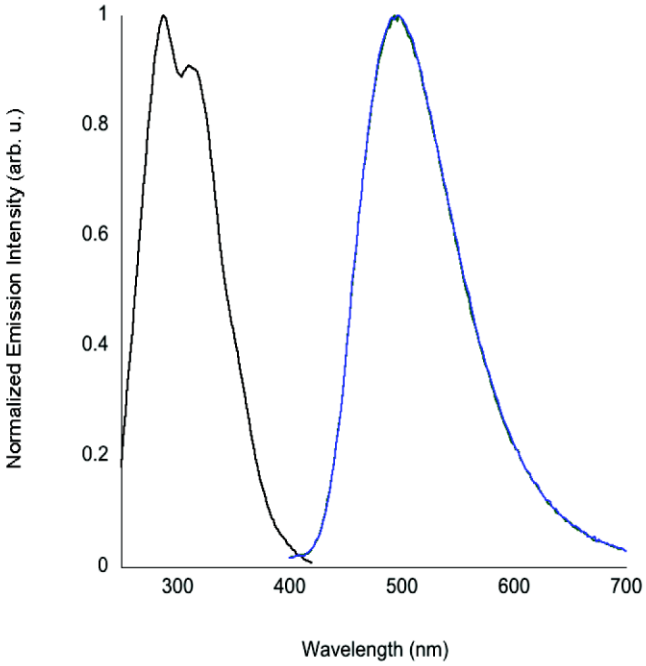
Selected bond lengths [Å] and angles [°] for 1

Re(1)-C(12)	1.887(13)
Re(1)-C(11)	1.915(13)
Re(1)-C(13)	1.959(13)
Re(1)-N(34)	2.145(10)
Re(1)-N(12)	2.181(10)
Re(1)-N(352)	2.199(11)
Re(2)-C(21)	1.905(13)
Re(2)-C(22)	1.908(16)
Re(2)-C(23)	1.929(15)
Re(2)-N(14)	2.171(10)
Re(2)-N(22)	2.176(11)
Re(2)-N(152)	2.213(12)
Re(3)-C(33)	1.890(18)
Re(3)-C(31)	1.924(15)
Re(3)-C(32)	1.930(14)
Re(3)-N(24)	2.145(12)
Re(3)-N(252)	2.190(12)
Re(3)-N(32)	2.195(10)
C(12)-Re(1)-C(11)	90.0(5)
C(12)-Re(1)-C(13)	90.7(5)
C(11)-Re(1)-C(13)	89.2(6)
C(12)-Re(1)-N(34)	95.6(4)
C(11)-Re(1)-N(34)	96.6(5)
C(13)-Re(1)-N(34)	171.4(5)
C(12)-Re(1)-N(12)	177.3(4)
C(11)-Re(1)-N(12)	89.4(5)
C(13)-Re(1)-N(12)	92.0(5)
N(34)-Re(1)-N(12)	81.8(4)
C(12)-Re(1)-N(352)	92.4(5)
C(11)-Re(1)-N(352)	170.5(5)
C(13)-Re(1)-N(352)	100.0(5)
N(34)-Re(1)-N(352)	74.0(4)
N(12)-Re(1)-N(352)	87.6(4)
C(21)-Re(2)-C(22)	87.3(6)
C(21)-Re(2)-C(23)	89.3(6)
C(22)-Re(2)-C(23)	90.9(5)

C(21)-Re(2)-N(14)	100.5(5)
C(22)-Re(2)-N(14)	95.4(5)
C(23)-Re(2)-N(14)	168.6(5)
C(21)-Re(2)-N(22)	92.0(5)
C(22)-Re(2)-N(22)	173.1(5)
C(23)-Re(2)-N(22)	95.9(5)
N(14)-Re(2)-N(22)	78.0(4)
C(21)-Re(2)-N(152)	174.3(5)
C(22)-Re(2)-N(152)	94.8(5)
C(23)-Re(2)-N(152)	95.9(5)
N(14)-Re(2)-N(152)	74.1(4)
N(22)-Re(2)-N(152)	85.3(4)
C(33)-Re(3)-C(31)	89.1(7)
C(33)-Re(3)-C(32)	90.6(7)
C(31)-Re(3)-C(32)	86.9(5)
C(33)-Re(3)-N(24)	169.4(6)
C(31)-Re(3)-N(24)	100.2(5)
C(32)-Re(3)-N(24)	95.0(5)
C(33)-Re(3)-N(252)	96.1(6)
C(31)-Re(3)-N(252)	174.5(5)
C(32)-Re(3)-N(252)	95.0(5)
N(24)-Re(3)-N(252)	74.5(4)
C(33)-Re(3)-N(32)	95.9(6)
C(31)-Re(3)-N(32)	92.4(5)
C(32)-Re(3)-N(32)	173.5(5)
N(24)-Re(3)-N(32)	78.8(4)
N(252)-Re(3)-N(32)	85.1(4)

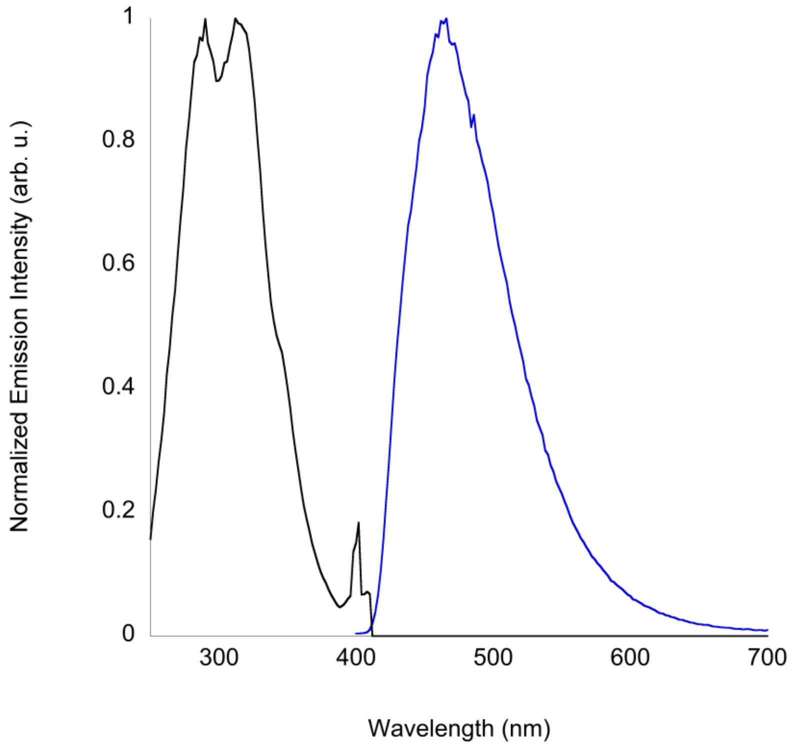
Photophysical studies

Excitation and emission spectra of a 10^{-5} M solution of 1 at room temperature

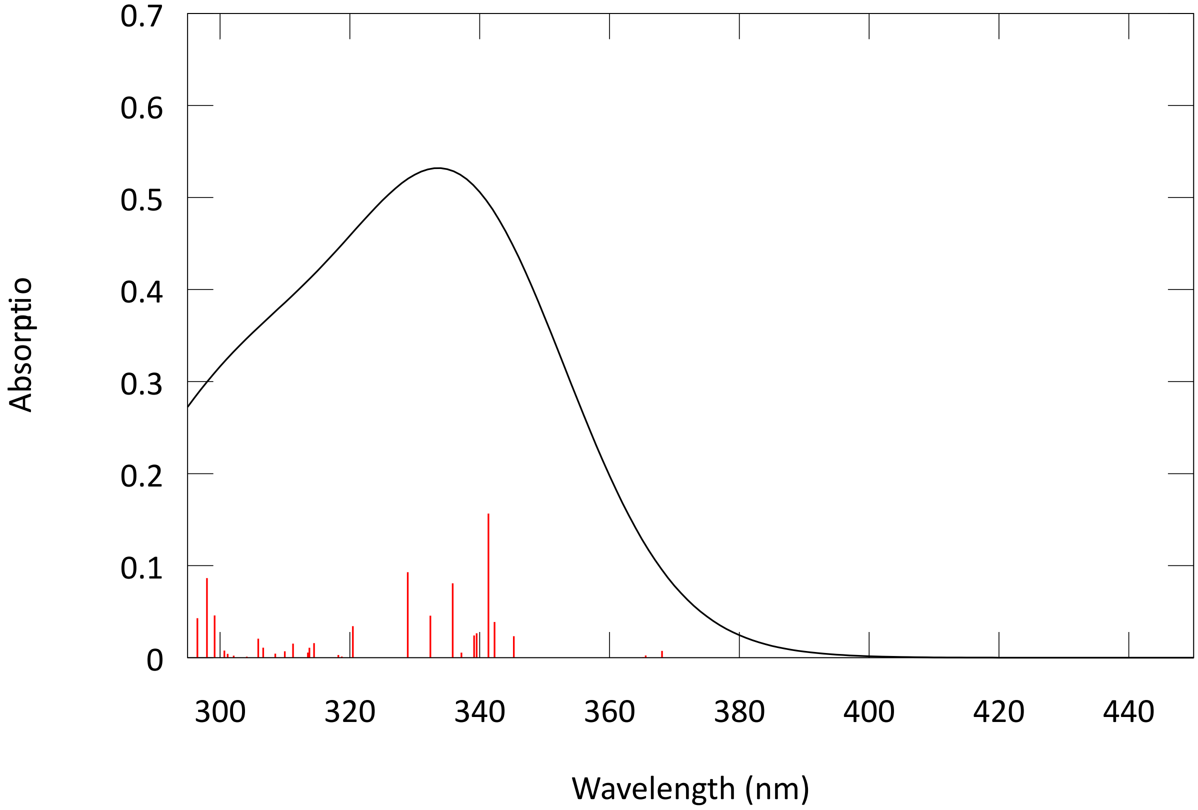


The broad and structureless profile of the emission spectrum indicates the almost exclusive charge transfer (CT) nature of the emissive state and negligible mixing with excited states of LC nature, despite the marked blue-shifted emission maximum on comparing **1** with neutral rhenium tricarbonyl complexes. This is likely to be due to the fact that the LC transition is raised in energy as a consequence of the coordination of the tetrazole ring to two metal centres, a behavior we have previously observed in complexes of Pt(II) bound to the same **2PyTz** ligand.[14]

Excitation and emission spectra of a 10^{-5} M solution of 1 at 77K



Simulated TDDFT absorption spectrum



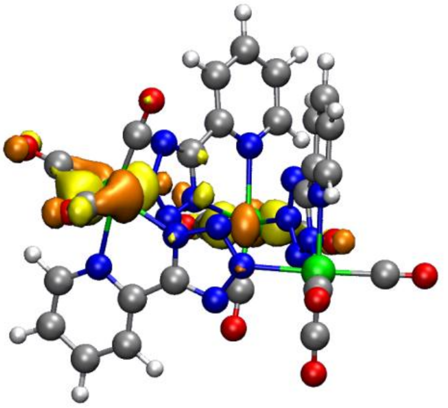
List of calculated transitions

Wavelength	Intensity	Levels	Character
368.09 nm	0.0074	HOMO-1 -> LUMO	42.70%
		HOMO -> LUMO	26.00%
		HOMO -> LUMO+1	14.40%
365.58 nm	0.0024	HOMO-1 -> LUMO+1	24.30%
		HOMO -> LUMO	11.40%
		HOMO -> LUMO+1	21.00%
		HOMO -> LUMO+2	23.80%
365.18 nm	0.0006	HOMO-1 -> LUMO	16.70%
		HOMO-1 -> LUMO+2	29.60%
		HOMO -> LUMO+1	27.60%
345.25 nm	0.0234	HOMO-2 -> LUMO	21.40%
		HOMO -> LUMO	26.10%
		HOMO -> LUMO+2	11.30%
342.28 nm	0.0388	HOMO-4 -> LUMO	25.10%
		HOMO-2 -> LUMO	10.40%

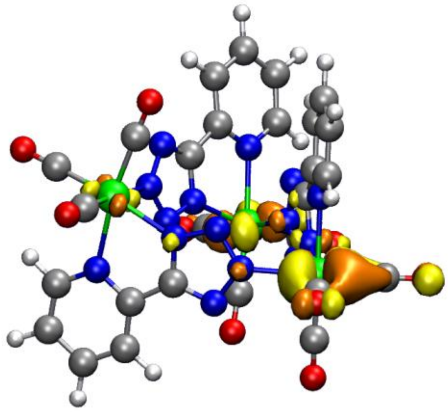
341.35 nm	0.1566	HOMO-1 -> LUMO+1	19.60%
		HOMO -> LUMO	25.90%
339.53 nm	0.0265	HOMO-4 -> LUMO+1	10.30%
		HOMO-3 -> LUMO+1	10.60%
		HOMO-1 -> LUMO+1	18.80%
		HOMO-1 -> LUMO+2	14.90%
		HOMO -> LUMO+2	12.80%
339.14 nm	0.0241	HOMO-1 -> LUMO	15.40%
		HOMO-1 -> LUMO+2	14.90%
		HOMO -> LUMO+1	15.50%
		HOMO -> LUMO+2	18.40%
337.19 nm	0.0055	HOMO-7 -> LUMO+1	12.90%
		HOMO-5 -> LUMO+1	11.70%
		HOMO-1 -> LUMO+1	21.00%
		HOMO-1 -> LUMO+2	14.20%
335.84 nm	0.0808	HOMO-6 -> LUMO	35.60%
		HOMO-6 -> LUMO+2	13.20%
332.40 nm	0.0456	HOMO-8 -> LUMO	14.70%
		HOMO-3 -> LUMO	14.30%
328.92 nm	0.0929	HOMO-7 -> LUMO+1	32.30%
		HOMO-7 -> LUMO+2	15.80%
		HOMO-3 -> LUMO+1	14.30%
320.46 nm	0.0343	HOMO-4 -> LUMO	15.40%
		HOMO-3 -> LUMO	50.40%
318.75 nm	0.0012	HOMO-4 -> LUMO	26.00%
		HOMO-3 -> LUMO+2	15.40%
		HOMO-2 -> LUMO+1	34.80%
318.23 nm	0.0029	HOMO-3 -> LUMO+1	13.20%
		HOMO-2 -> LUMO+1	29.20%
		HOMO-2 -> LUMO+2	36.20%
314.47 nm	0.0158	HOMO-4 -> LUMO+1	35.40%
		HOMO-4 -> LUMO+2	18.10%
		HOMO-3 -> LUMO+2	20.30%
313.76 nm	0.0108	HOMO-5 -> LUMO	12.40%
		HOMO-2 -> LUMO	24.20%
		HOMO-2 -> LUMO+2	26.80%
313.52 nm	0.0056	HOMO-4 -> LUMO+2	36.70%
		HOMO-3 -> LUMO+1	23.60%
		HOMO-3 -> LUMO+2	13.20%
311.24 nm	0.0153	HOMO-5 -> LUMO	32.90%

		HOMO-5 -> LUMO+1	11.20%
		HOMO-3 -> LUMO+2	14.80%
309.97 nm	0.007	HOMO-5 -> LUMO+1	30.60%
		HOMO-5 -> LUMO+2	12.10%
		HOMO-4 -> LUMO+2	11.30%
308.51 nm	0.0044	HOMO-7 -> LUMO	50.70%
		HOMO-5 -> LUMO+2	26.10%
306.64 nm	0.0109	HOMO-8 -> LUMO	39.60%
		HOMO-7 -> LUMO	22.30%
		HOMO-5 -> LUMO+2	13.40%
305.88 nm	0.0207	HOMO-6 -> LUMO+1	52.70%
		HOMO-6 -> LUMO+2	31.50%
304.13 nm	0.0011	HOMO-8 -> LUMO+1	37.30%
		HOMO-8 -> LUMO+2	17.80%
		HOMO-7 -> LUMO	11.20%
302.10 nm	0.0022	HOMO-7 -> LUMO+1	24.40%
		HOMO-7 -> LUMO+2	55.10%
301.16 nm	0.0042	HOMO-8 -> LUMO+1	28.80%
		HOMO-8 -> LUMO+2	23.90%
		HOMO-6 -> LUMO+2	15.80%
300.67 nm	0.0077	HOMO-8 -> LUMO+2	24.90%
		HOMO-6 -> LUMO	23.90%
		HOMO-6 -> LUMO+2	12.00%
299.16 nm	0.0459	HOMO -> LUMO+3	27.60%
		HOMO -> LUMO+4	20.90%
297.99 nm	0.0865	HOMO-1 -> LUMO+3	41.90%
		HOMO-1 -> LUMO+4	19.90%
		HOMO -> LUMO+6	11.80%
296.50 nm	0.0429	HOMO-1 -> LUMO+4	26.90%
		HOMO -> LUMO+3	13.60%
		HOMO -> LUMO+5	24.20%
		HOMO -> LUMO+6	11.30%

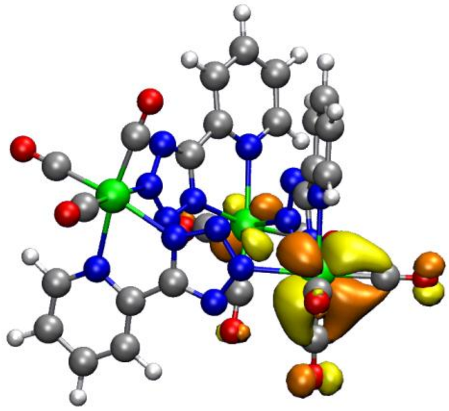
Selected occupied orbitals for 1



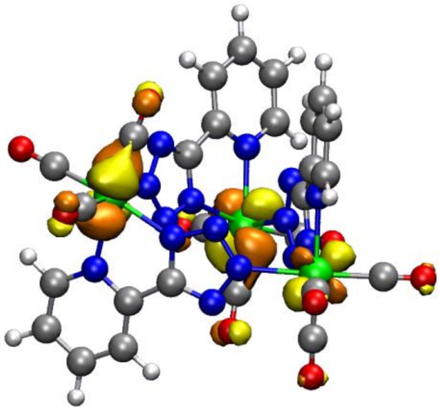
HOMO



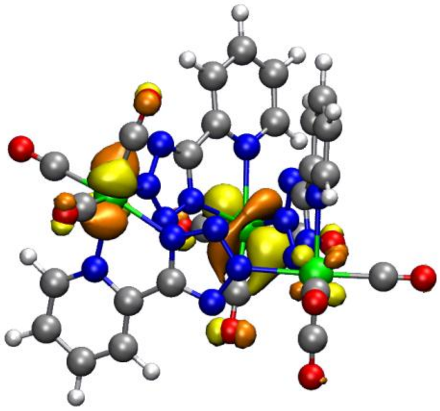
HOMO-1



HOMO-2



HOMO-3



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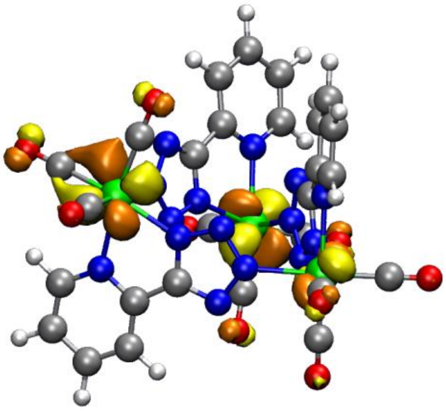

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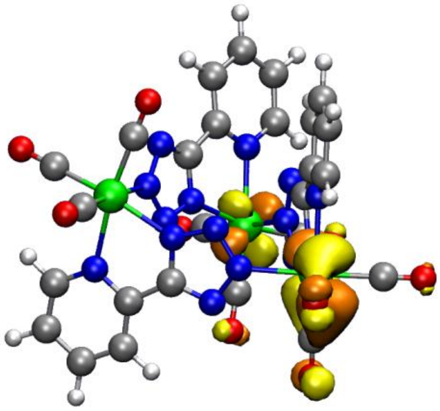
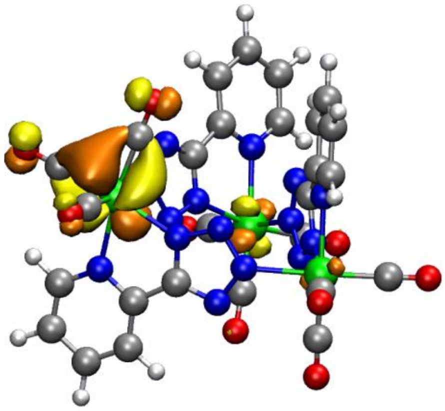
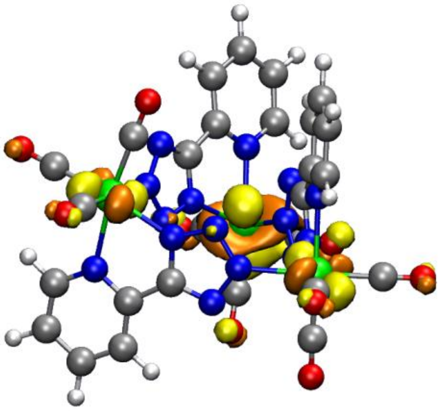


HOMO-6

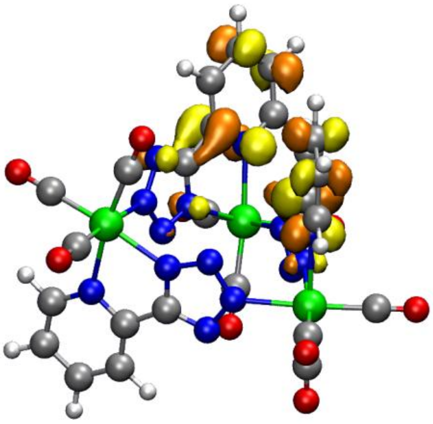


HOMO-7

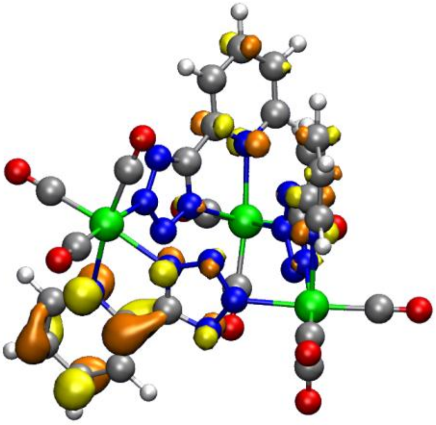


HOMO-8

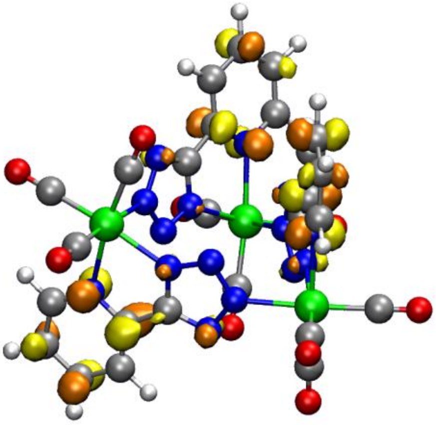
Selected unoccupied orbitals for 1



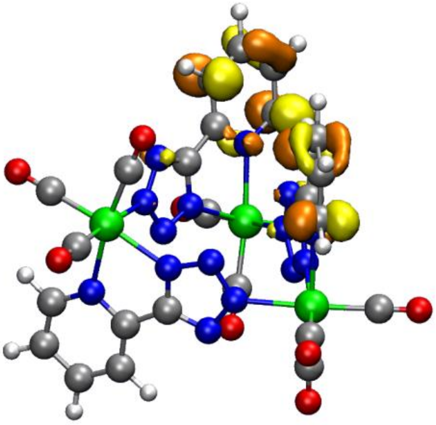
LUMO



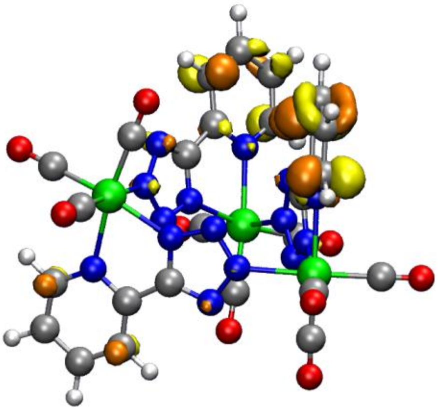
LUMO+1



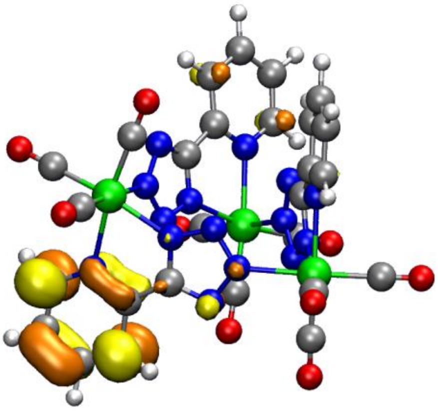
LUMO+2



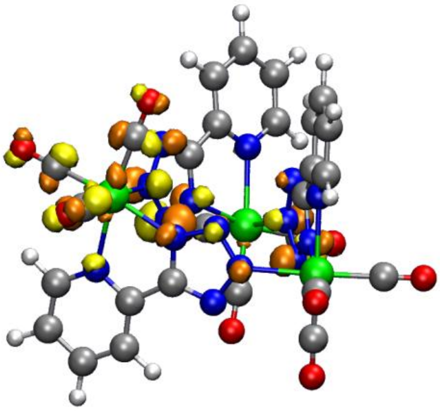
LUMO+3



LUMO+4



LUMO+5



LUMO+6

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