Ground- and excited-state electronic structure of an emissive pyrazine-bridged Ruthenium(II) dinuclear complex

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Supporting information

Synthesis

2,5-bis(5'-methyl-4'H-[1,2,4]triaz-3'-yl)-pyrazine ($H_2(Metr)_2pz$). 0.6 g (4.6 mmol) of 2,5-dicyanopyrazine was dissolved in 5 cm^3 of ethanol. 3 cm^3 of hydrazine hydrate was added and the solution stirred for 3 h at room temperature. The yellow precipitate was filtered and air-dried. The *bis*-amidrazone was then added to a 10 cm^3 acetic acid/acetic anhydride (50/50 v/v) solution at 0 ^oC. The temperature was raised slowly to 30 ^oC and the solution stirred for 2 h. The solution was then evaporated to near dryness and 2 cm^3 of ethylene glycol added and boiled for 15 min. On cooling 10 cm^3 of water was added and the precipitate collected by vacuum filtration and washed with 10 cm^3 of methanol and the product allowed to air-dry. Yield 320 mg (1.32 mmol, 29 %). ^1H NMR in [D_6]-DMSO; 9.41 (2H, s), 2.79 (6H, s).

$[(Ru(bpy)_2)_2((Metr)_2Pz)](PF_6)_2.3H_2O$ (**1**).350 mg (0.67 mmol) of *cis*-$[Ru(bpy)_2Cl_2]$ was heated at reflux with 50 mg (0.21 mmol) of $H_2(metr)_2pz$ ligand in ethanol/water for 24 h. The cooled reaction mixture was reduced *in vacuo,* diluted with water and filtered. A few drops of conc. ammonia solution, followed by a saturated aqueous solution of ammonium hexafluorophosphate was added to the purple filtrate and the precipitate which formed was filtered, washed with 20 cm^3 of diethylether and air-dried. The complex was purified by column chromatography on neutral alumina using acetonitrile as eluent. Yield 120 mg (0.089 mmol, 24 %).

$[(Ru([D_8-]bpy)_2)_2(H_2(Metr)_2Pz)](PF_6)_4$ **2.** As for **1** except 200 mg (0.37 mmol) of *cis*-$[Ru([D_8]\text{-}bpy)_2Cl_2]$ and 30 mg (0.124 mmol) of $H_2(metr)_2pz$. After column chromatography the complex was dissolved in acidic aqueous solution and

precipitated with saturated aqueous NH_4PF_6 solution. The complex was recrystallised by slow evaporation of an acetonitrile solution. Yield 41 mg (0.027 mmol, 22 %)

Physical measurements

^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) NMR Spectrometer. All measurements were carried out in [D_6]-DMSO for ligands [D_6]-acetonitrile for complexes. Peak positions are relative to residual solvent peaks – Mass spectra were obtained using a Bruker-Esquire LC_00050 electrospray ionization mass spectrometer at positive polarity with cap-exit voltage of 167 V. Spectra were recorded in the scan range of 50-2200 m/z with an acquisition time of between 300 and 900 μs and a potential of between 30 and 70 V. Each spectrum was recorded by summation of 20 scans – Elemental analysis was carried out at the Micro-analytical Laboratory at University College Dublin.

UV/Vis absorption spectra (accuracy ± 2 nm) were recorded in 10 mm quartz cuvettes on a Shimadzu UV/Vis-NIR 3100 spectrophotometer interfaced with an Elonex PC466 using UV/Vis data manager. Molar absorption coefficients are +/- 10%.

Emission spectra (accuracy ± 5 nm) were recorded at 298 K using a LS50B luminescence spectrophotometer, equipped with a red sensitive Hamamatsu R928 PMT detector, interfaced with an Elonex PC466 employing Perkin-Elmer FL WinLab custom built software. Emission and excitation slit widths were 10 nm. Emission spectra are uncorrected for photomultiplier response.

pH titrations of **1** and **2** were carried out in Britton-Robinson buffer (0.04 M H_3BO_3, 0.04 M H_3PO_4, 0.04 M CH_3CO_2H) (pH was adjusted using concentrated sulfuric acid or sodium hydroxide solution) and followed by monitoring the pH dependence of absorption and emission spectra. pH_i refers to the inflection point of the emission titration curve. The appropriate isosbestic point from the absorption spectra was used as the excitation wavelength for emission titrations.

Luminescence lifetime measurements were made using an Edinburgh Analytical Instruments (EAI) Time-Correlated Single-Photon Counting apparatus (TCSPC) as described previously.[1] Samples were deoxygenated by bubbling argon for 20 min using Ar gas before measurements were carried out, followed by periodic deaeration to maintain oxygen exclusion. Emission lifetimes were calculated using a single exponential fitting function, involving a Levenberg-Marquardt algorithm with iterative reconvolution (Edinburgh instruments F900 software) and are $\underline{+}$ 10%. The χ^2 and residual plots were used to judge the quality of the fits.

Electrochemical measurements were carried out on either a Model 600A or 660 Electrochemical Workstation (CH Instruments). Typical complex concentrations were 0.5 to 1 mM in anhydrous acetonitrile containing 0.1 M TEAP. A Teflon shrouded glassy carbon working electrode, a Pt wire auxiliary electrode and SCE reference electrode were employed. Solutions for reduction measurements were deoxygenated by purging with N_2 or Ar gas for 15 min prior to the measurement. Measurements were made in the range of –2.0 to 1.8 V (vs SCE electrode). Protonation of complexes was achieved by addition of trifluoroacetic acid (0.1 M in acetonitrile) to the electrolyte solution. Cyclic voltammograms were obtained at sweep rates of 100 mV s^{-1}; differential pulse voltammetry (DPV) experiments were performed with a scan rate of 20 mV s^{-1}, a pulse height of 75 mV, and a duration of 40 ms. For reversible processes the half-wave potential values are reported; identical values are obtained from DPV and CV measurements. Redox potentials are +/- 10 mV. Spectroelectrochemistry was carried out using an OTTLE setup comprising of a homemade Pyrex glass, thin layer cell (2 mm). The optically transparent working electrode was made from platinum-rhodium gauze, a platinum wire counter electrode, and the reference electrode was a *pseudo*-Ag/AgCl reference electrode. The working electrode was held at the required potential throughout the measurement using an EG&G PAR Model 362 potentiostat. Absorption spectra were recorded as described above. Protonation of complexes under bulk electrolysis was achieved by addition of anhydrous trifluoroacetic acid (1 M in acetonitrile).

Transient differential absorption spectra were recorded following pulsed irradiation of the samples with a Coherent Infinity Nd:YAG-XPO laser (1 ns pulses, FWHM), using a low pressure, high-power EG&G FX-504 Xe lamp as the probe source. The transmitted light was dispersed by an Acton SpectraPro-150s imaging spectrograph equipped with 150 or 600 g mm^{-1} grating and tunable slit (1-500 μm) resulting in 6 or 1.2 nm maximum resolution respectively. The data were collected with a gated intensified CCD detector (Princeton Instruments ICCD-576G/RB-EM) and an EG&G Princeton Applied Research Model 9650 digital delay generator. I and I_o were measured simultaneously using a double 8 Kernel 200 μm optical fibre with OMA-4 Setup, controlled by Microsoft Windows based WINSPEC (version 1.6.1, Princeton Instruments).

Ground state resonance Raman spectra of the complexes were recorded at 457.9, 488 and 514 nm using an Argon ion laser (Spectra Physics model 2050) as the excitation source.[2] The laser power at the sample was typically 30-40 mW. The Raman backscatter was focused onto the entrance slit of a single stage spectrograph (JY Horiba HR640), which was coupled to a CCD detector (Andor Technology DV420-OE). Spectra generated at an excitation wavelength of 532 nm were recorded using an Andor Technology Raman Station. The spectra were run in quartz cuvettes and were not corrected for detector response. Transient resonance Raman spectra were recorded using the single-colour pump and probe method in which the leading edge of the pulse excites the molecules and the trailing edge probes the resultant Raman scattering.[3] The excitation source was a pulsed laser (Spectra Physics Q-switched ND:YAG, GCR-3) at 354.7nm with a typical pulse energy of approx 3 mJ at the sample. The Raman backscatter was focused onto the entrance slit of a double-stage spectrograph (Spex 1870), which was coupled to an ICCD (Andor Technology DH501). Typically, spectra were collected as a summation of 6000 accumulations. Time resolved resonance Raman spectra were recorded as for TR^2 spectra, except that a separate pump pulse at 532 nm was employed and spectra recorded at a series of pump-probe delays.

Photolysis experiments were carried out at room temperature in acetonitrile using visible light with a 400 W Tungsten filament light source. A 400 nm filter was employed to eliminate UV light. Samples for photolysis were held in quartz cuvettes or NMR tubes. The photochemistry in acetonitrile was followed by ^1H NMR spectroscopy and mass spectrometry. For NMR experiments, thermal reversibility of the samples following photolysis was checked by removal of [D_3]-acetonitrile *in vacuo* followed by refluxing of the residue in acetone for 4 h. The acetone was then removed *in vacuo* and the residue redissolved in [D_3]-acetonitrile.

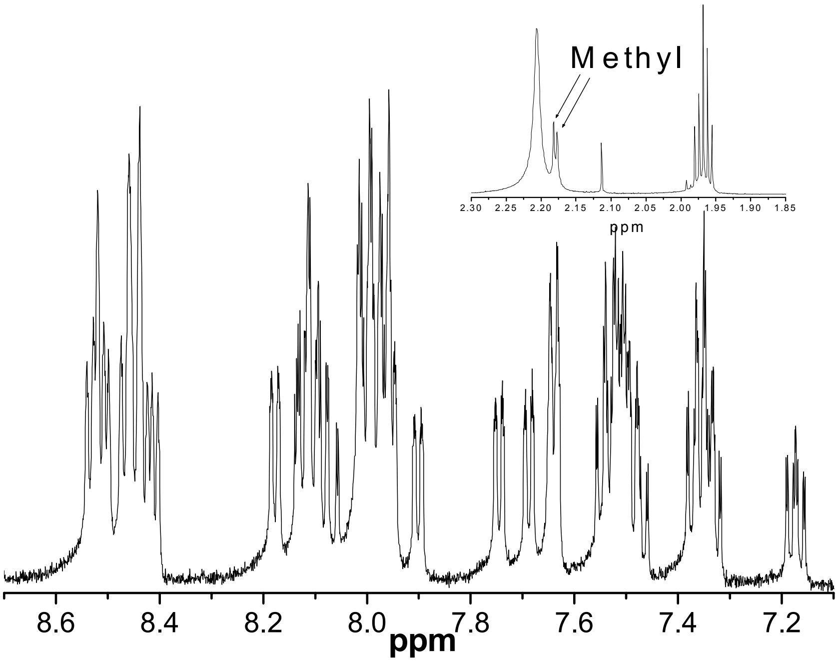

Figure S1 ^{1}H NMR spectrum (400 MHz) in CD_3CN of **1**

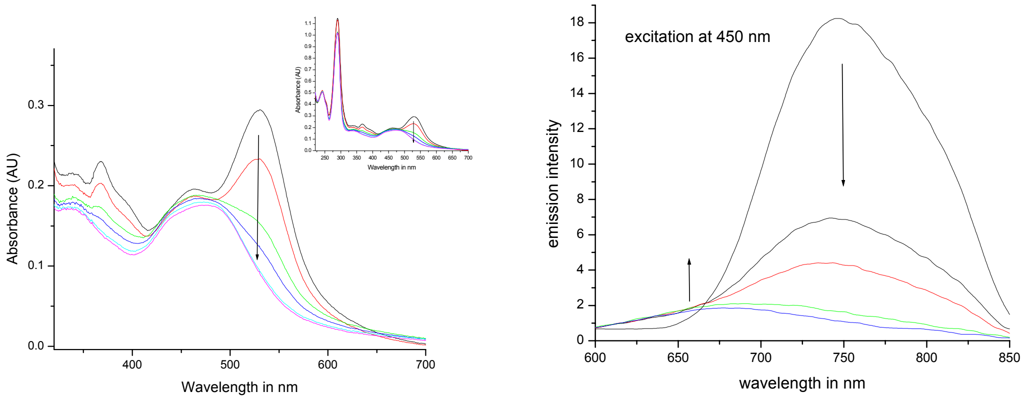

Figure S2 Changes observed in the UV.Vis absorption (left) and emission at λ_{exc} = 450 nm (right) spectra of **1** upon photolysis in acetonitrile (inset: full spectrum)

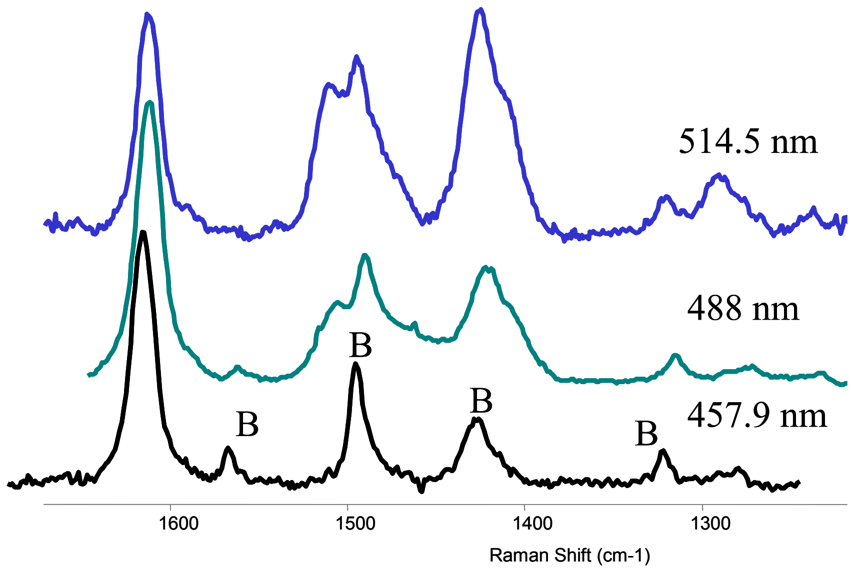

Figure S3 Resonance Raman spectrum of **$H_2$1** in H_2O at several probe wavelengths, B = bpy vibrational modes.

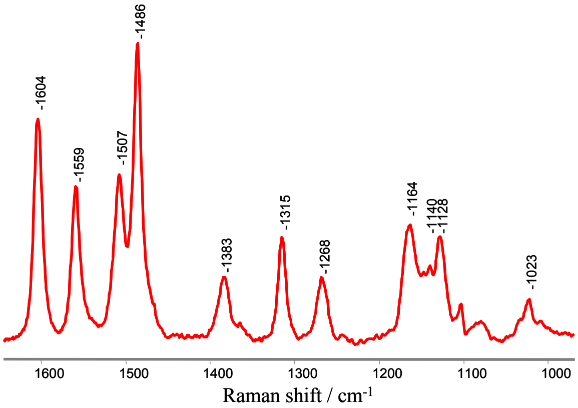

Figure S4 Resonance Raman spectrum of **1** in CH_3CN at 457.9 nm probe wavelength.

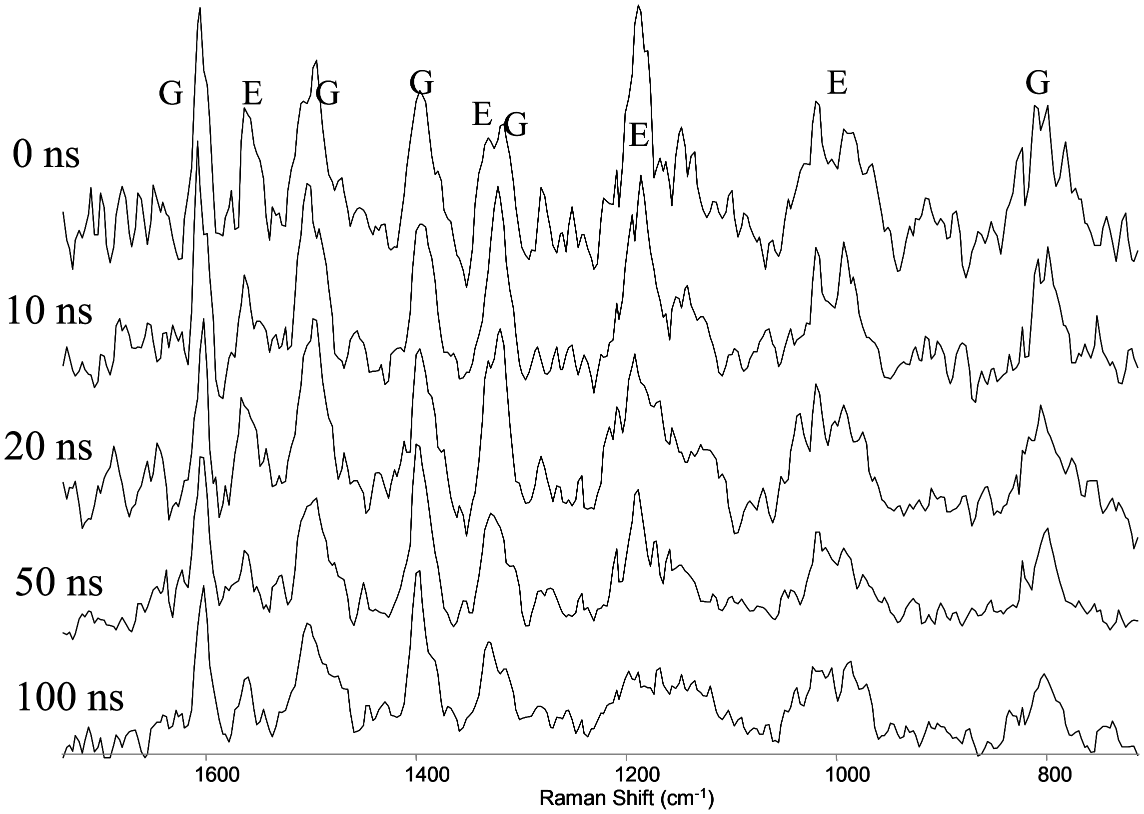

Figure S5 TR^3 spectra of **1** in H_2O (ca. 10^{-3} M). Pump λ = 532 nm (10 mJ), probe λ = 354.67 nm (0.6 mJ). Spectra are normalized to 1398 cm^{-1} feature (ground state vibrational mode), G: ground state feature; E: excited state feature.

Table S1 – The eigenvalues, symmetry and percent contribution of various groups (see text) for the frontier molecular orbitals of (a) **1** and (b) **H$_2$1**.

(a)

MO		eV	Symmetry	Ru	flatbpy	orthobpy	Metrz	pz
252	L+10	-5.49	AG	2	47	51	0	0
251	L+9	-5.58	AU	1	31	57	3	8
250	L+8	-5.59	AG	2	38	60	0	0
249	L+7	-5.64	AU	2	7	55	6	29
248	L+6	-5.77	AG	2	18	80	0	0
247	L+5	-5.89	AU	2	13	37	12	36
246	L+4	-6.38	AU	6	87	1	1	5
245	L+3	-6.4	AG	5	92	2	0	0
244	L+2	-6.53	AU	10	3	49	5	33
243	**L+1**	**-6.61**	**AG**	**5**	**3**	**92**	**0**	**0**
242	**LUMO**	**-6.7**	**AU**	**2**	**6**	**47**	**8**	**37**
241	**HOMO**	**-9.34**	**AG**	**37**	**3**	**1**	**49**	**9**
240	**H-1**	**-9.6**	**AU**	**63**	**6**	**3**	**26**	**3**
239	H-2	-9.81	AG	80	7	6	3	4
238	H-3	-9.89	AU	76	11	8	4	2
237	H-4	-9.9	AG	69	6	11	10	4
236	H-5	-10.12	AG	42	5	3	40	9
235	H-6	-10.21	AU	72	3	11	7	7
234	H-7	-10.62	AU	0	1	0	99	0
233	H-8	-10.63	AG	1	0	0	98	0
232	H-9	-10.73	AU	15	3	1	70	10
231	H-10	-11.24	AG	3	68	1	28	1

(b)

MO		eV	Symmetry	Ru	flatbpy	orthobpy	MeHtrz	pz
252	L+10	-9.75	AG	5	16	5	64	10
251	L+9	-9.79	AU	1	52	46	0	0
250	L+8	-9.8	AG	1	39	45	12	2
249	L+7	-9.93	AU	2	31	65	1	1
248	L+6	-9.96	AG	1	29	63	5	1
247	L+5	-10.7	AU	4	85	11	0	0
246	L+4	-10.7	AG	4	83	12	0	0
245	L+3	-10.8	AU	3	12	85	0	0
244	L+2	-10.81	AG	2	13	84	0	0
243	**L+1**	**-11.05**	**AU**	**2**	**1**	**2**	**14**	**81**
242	**LUMO**	**-11.91**	**AU**	**14**	**1**	**2**	**21**	**61**
241	**HOMO**	**-14.54**	**AG**	**78**	**7**	**4**	**8**	**2**
240	**H-1**	**-14.59**	**AG**	**79**	**5**	**8**	**5**	**4**
239	H-2	-14.62	AU	79	8	4	8	1
238	H-3	-14.73	AG	74	11	11	2	1
237	H-4	-14.74	AU	74	12	10	3	1
236	H-5	-15.05	AU	67	3	13	4	14
235	H-6	-15.51	AG	1	92	7	0	0
234	H-7	-15.52	AU	1	92	6	0	0
233	H-8	-15.61	AG	1	6	92	0	0
232	H-9	-15.62	AU	2	6	91	0	0
231	H-10	-16.22	AG	5	8	1	55	32

Table S2 – The calculated wavelengths and oscillator strength of the electronic transitions of (a) **1** and (b) **H$_2$1**. Major singly-excited contributions are shown along with the change in the percent contribution of each of the listed groups to the molecular orbitals associated with the transition.

(a) **No.**	**λ (nm)**	**Osc. Strength**	**Symmetry**	**Major contribs**	***Ru***	***flatbpy***	***orthobpy***	***Metrz***	***pz***
1	621.42	0.0358	Singlet-AU	HOMO->LUMO (83%)	40-->2 (-38)	3-->7 (4)	2-->50 (48)	47-->7 (-40)	8-->34 (26)
2	606.52	0	Singlet-AG	H-1->LUMO (15%), H-1->L+2 (-13%), HOMO->L+1 (66%)	45-->5 (-40)	4-->4 (0)	2-->78 (76)	42-->2 (-40)	7-->10 (3)
3	598.99	0.0129	Singlet-AU	H-1->L+1 (-21%), HOMO->L+2 (68%)	44-->9 (-35)	4-->4 (0)	2-->58 (56)	43-->4 (-39)	7-->25 (18)
4	569.61	0	Singlet-AG	H-1->LUMO (60%), H-1->L+2 (31%)	62-->5 (-57)	6-->7 (1)	3-->47 (44)	26-->7 (-19)	3-->34 (31)
5	543.31	0	Singlet-AG	H-1->L+4 (26%), HOMO->L+3 (60%)	47-->5 (-42)	4-->88 (84)	2-->5 (3)	40-->0 (-40)	7-->2 (-5)
6	542.57	0.0214	Singlet-AU	H-1->L+3 (25%), HOMO->L+4 (61%)	48-->6 (-42)	4-->86 (82)	2-->3 (1)	39-->1 (-38)	7-->4 (-3)
7	521.47	0.0099	Singlet-AU	H-3->L+1 (25%), H-2->LUMO (40%), H-2->L+2 (-20%)	76-->5 (-71)	8-->5 (-3)	7-->62 (55)	6-->4 (-2)	3-->24 (21)
8	521.1	0	Singlet-AG	H-3->LUMO (10%), H-3->L+2 (-18%), H-2->L+1 (54%)	76-->6 (-70)	8-->4 (-4)	7-->75 (68)	6-->2 (-4)	3-->13 (10)
9	515.12	0.0543	Singlet-AU	H-4->LUMO (14%), H-4->L+2 (17%), H-2->LUMO (29%), H-2->L+2 (27%)	74-->7 (-67)	7-->7 (0)	8-->48 (40)	8-->6 (-2)	4-->33 (29)
10	505.76	0	Singlet-AG	H-3->LUMO (65%), H-3->L+2 (25%)	75-->5 (-70)	10-->7 (-3)	8-->47 (39)	5-->7 (2)	2-->35 (33)
11	500.05	0.0157	Singlet-AU	H-1->L+1 (54%), HOMO->L+2 (19%)	57-->5 (-52)	5-->4 (-1)	3-->72 (69)	30-->3 (-27)	5-->15 (10)
12	497.91	0	Singlet-AG	H-1->LUMO (-16%), H-1->L+2 (43%), HOMO->L+1 (25%)	57-->7 (-50)	5-->5 (0)	3-->62 (59)	30-->4 (-26)	5-->22 (17)
13	487.76	0.2226	Singlet-AU	H-4->LUMO (53%), H-2->LUMO (-10%)	68-->3 (-65)	6-->8 (2)	9-->53 (44)	13-->6 (-7)	4-->30 (26)
14	468.43	0	Singlet-AG	H-4->L+1 (18%), H-3->L+4 (17%), H-2->L+3 (20%), HOMO->L+3 (15%)	67-->6 (-61)	7-->63 (56)	7-->26 (19)	16-->1 (-15)	4-->5 (1)
15	467.06	0.0881	Singlet-AU	H-3->L+3 (16%), H-2->L+4 (26%), H-1->L+3 (-11%), HOMO->L+4 (20%)	65-->6 (-59)	7-->75 (68)	6-->11 (5)	18-->1 (-17)	4-->6 (2)
16	460.56	0	Singlet-AG	H-6->L+4 (-14%), H-4->L+3 (-22%), H-2->L+3 (31%)	72-->5 (-67)	6-->69 (63)	9-->20 (11)	9-->1 (-8)	5-->4 (-1)
17	458.4	0.0131	Singlet-AU	H-6->L+3 (17%), H-4->L+4 (33%), H-2->L+4 (-22%), H-1->L+3 (-11%)	70-->6 (-64)	6-->81 (75)	8-->6 (-2)	12-->1 (-11)	5-->5 (0)
18	456.16	0	Singlet-AG	H-4->L+1 (17%), H-4->L+3 (-12%), H-1->L+4 (30%), HOMO->L+3 (-16%)	63-->6 (-57)	6-->61 (55)	6-->27 (21)	21-->1 (-20)	4-->6 (2)
19	450.12	0.0999	Singlet-AU	H-4->L+2 (-13%), H-4->L+4 (11%), H-1->L+3 (25%), HOMO->L+4 (-10%)	63-->6 (-57)	6-->58 (52)	6-->22 (16)	21-->2 (-19)	5-->11 (6)
20	441.7	0.0389	Singlet-AU	H-1->L+3 (11%), HOMO->L+5 (43%)	51-->4 (-47)	5-->31 (26)	4-->32 (28)	34-->7 (-27)	7-->25 (18)
21	439.07	0	Singlet-AG	H-4->L+3 (16%), H-3->L+4 (18%), H-1->L+4 (24%)	67-->6 (-61)	7-->69 (62)	7-->16 (9)	15-->2 (-13)	4-->8 (4)
22	430.18	0.0436	Singlet-AU	H-5->LUMO (54%)	54-->3 (-51)	6-->15 (9)	5-->47 (42)	29-->6 (-23)	7-->28 (21)
23	426.94	0	Singlet-AG	H-6->LUMO (14%), H-4->L+1 (11%), H-3->LUMO (-10%), H-3->L+2 (18%), H-2->L+1 (15%), H-1->L+5 (12%)	68-->5 (-63)	7-->7 (0)	7-->62 (55)	14-->5 (-9)	4-->22 (18)
24	424.16	0.0086	Singlet-AU	H-4->L+2 (32%), H-3->L+1 (33%)	69-->7 (-62)	7-->6 (-1)	8-->63 (55)	12-->4 (-8)	4-->21 (17)
25	423.36	0	Singlet-AG	H-6->LUMO (23%), H-4->L+1 (-24%), H-1->L+5 (17%)	66-->4 (-62)	5-->9 (4)	8-->61 (53)	16-->5 (-11)	5-->21 (16)
26	419.29	0	Singlet-AG	H-6->LUMO (11%), H-5->L+1 (30%), HOMO->L+6 (23%)	54-->4 (-50)	5-->9 (4)	4-->72 (68)	30-->3 (-27)	7-->12 (5)
27	419.14	0.0399	Singlet-AU	H-5->LUMO (-10%), H-5->L+2 (12%), H-2->L+2 (11%), HOMO->L+5 (19%)	55-->5 (-50)	6-->16 (10)	4-->51 (47)	29-->5 (-24)	6-->23 (17)
28	411.14	0	Singlet-AG	H-5->L+1 (36%), HOMO->L+6 (-33%)	47-->4 (-43)	4-->13 (9)	3-->76 (73)	38-->1 (-37)	8-->6 (-2)
29	408.22	0.0511	Singlet-AU	H-5->L+2 (48%), HOMO->L+7 (14%)	47-->7 (-40)	5-->10 (5)	4-->52 (48)	36-->5 (-31)	8-->27 (19)
30	399.19	0.1895	Singlet-AU	H-1->L+6 (11%), HOMO->L+7 (40%)	49-->4 (-45)	4-->22 (18)	4-->49 (45)	36-->5 (-31)	7-->21 (14)
31	397.13	0	Singlet-AG	H-6->LUMO (-17%), H-6->L+2 (12%), H-1->L+5 (23%)	61-->4 (-57)	5-->17 (12)	6-->51 (45)	23-->5 (-18)	6-->22 (16)
32	394.96	0	Singlet-AG	H-5->L+3 (11%), H-4->L+3 (-12%), H-3->L+4 (12%), H-1->L+9 (-10%), HOMO->L+8 (28%)	55-->3 (-52)	5-->56 (51)	5-->34 (29)	30-->1 (-29)	6-->5 (-1)
33	394.86	0.0055	Singlet-AU	H-6->L+1 (43%), H-4->L+4 (-11%)	66-->5 (-61)	5-->33 (28)	8-->53 (45)	15-->1 (-14)	6-->7 (1)
34	394.03	0.0272	Singlet-AU	H-6->L+1 (16%), H-1->L+8 (-10%), HOMO->L+9 (43%)	52-->3 (-49)	4-->32 (28)	4-->56 (52)	32-->2 (-30)	7-->7 (0)
35	393.09	0	Singlet-AG	H-4->L+3 (10%), H-3->L+4 (-21%), HOMO->L+8 (24%)	58-->4 (-54)	6-->55 (49)	5-->34 (29)	25-->1 (-24)	5-->6 (1)

(b) No.	λ (nm)	Osc. Strength	Symmetry	Major contribs	*Ru*	*flatbpy*	*orthobpy*	*MeHtrz*	*pz*
1	707.56	0.0001	Singlet-AU	HOMO->LUMO (93%)	78-->14 (-64)	7-->1 (-6)	4-->2 (-2)	8-->22 (14)	2-->61 (59)
2	682.09	0	Singlet-AG	H-2->LUMO (93%)	78-->14 (-64)	8-->1 (-7)	5-->2 (-3)	7-->22 (15)	1-->61 (60)
3	632.98	0.0035	Singlet-AU	H-3->LUMO (90%)	75-->15 (-60)	10-->1 (-9)	11-->2 (-9)	2-->21 (19)	2-->61 (59)
4	626.95	0	Singlet-AG	H-4->LUMO (93%)	74-->15 (-59)	11-->1 (-10)	10-->2 (-8)	3-->21 (18)	1-->61 (60)
5	561.32	0.3784	Singlet-AU	H-1->LUMO (74%)	78-->13 (-65)	6-->4 (-2)	8-->3 (-5)	5-->20 (15)	4-->60 (56)
6	469.97	0	Singlet-AG	H-5->LUMO (67%), H-2->L+1 (20%)	69-->12 (-57)	5-->2 (-3)	11-->2 (-9)	5-->20 (15)	11-->64 (53)
7	444	0.0842	Singlet-AU	H-1->L+1 (-18%), HOMO->L+1 (72%)	77-->3 (-74)	7-->2 (-5)	5-->3 (-2)	8-->14 (6)	3-->79 (76)
8	439	0.1372	Singlet-AU	H-1->L+1 (75%), HOMO->L+1 (14%)	77-->3 (-74)	6-->3 (-3)	7-->3 (-4)	6-->14 (8)	4-->78 (74)
9	432.47	0	Singlet-AG	H-2->L+1 (60%)	76-->4 (-72)	8-->4 (-4)	6-->15 (9)	7-->12 (5)	3-->64 (61)
10	429.29	0.0023	Singlet-AU	H-2->L+2 (37%), HOMO->L+3 (49%)	78-->3 (-75)	8-->18 (10)	4-->76 (72)	8-->1 (-7)	2-->2 (0)
11	428.8	0	Singlet-AG	H-2->L+1 (-13%), H-2->L+3 (31%), HOMO->L+2 (42%)	78-->3 (-75)	8-->16 (8)	5-->65 (60)	8-->3 (-5)	2-->13 (11)
12	420.52	0.0516	Singlet-AU	H-3->L+1 (88%)	75-->2 (-73)	10-->5 (-5)	11-->5 (-6)	3-->13 (10)	2-->75 (73)
13	420.24	0	Singlet-AG	H-4->L+1 (87%)	74-->3 (-71)	11-->4 (-7)	9-->3 (-6)	4-->13 (9)	2-->76 (74)
14	414.23	0.0057	Singlet-AU	H-2->L+4 (34%), HOMO->L+5 (45%)	78-->4 (-74)	8-->73 (65)	5-->17 (12)	7-->1 (-6)	2-->4 (2)
15	414.21	0	Singlet-AG	H-2->L+5 (34%), HOMO->L+4 (44%)	78-->4 (-74)	8-->72 (64)	5-->18 (13)	7-->1 (-6)	2-->4 (2)
16	406.09	0	Singlet-AG	H-4->L+3 (-21%), H-3->L+2 (-11%), H-1->L+2 (51%)	76-->3 (-73)	7-->19 (12)	9-->76 (67)	4-->0 (-4)	4-->1 (-3)
17	405.85	0.0048	Singlet-AU	H-4->L+2 (-22%), H-3->L+3 (-11%), H-1->L+3 (49%)	76-->3 (-73)	7-->19 (12)	9-->76 (67)	4-->0 (-4)	4-->1 (-3)
18	398.99	0.0068	Singlet-AU	H-6->LUMO (96%)	1-->14 (13)	89-->1 (-88)	9-->2 (-7)	0-->21 (21)	0-->61 (61)
19	398.21	0	Singlet-AG	H-7->LUMO (96%)	2-->14 (12)	89-->1 (-88)	8-->2 (-6)	0-->21 (21)	0-->61 (61)
20	391.71	0	Singlet-AG	H-5->L+5 (12%), H-1->L+2 (14%), H-1->L+4 (52%)	75-->4 (-71)	6-->65 (59)	10-->28 (18)	4-->1 (-3)	5-->2 (-3)
21	391.11	0.0013	Singlet-AU	H-8->LUMO (53%), H-1->L+5 (23%)	34-->10 (-24)	8-->30 (22)	54-->13 (-41)	2-->12 (10)	2-->35 (33)
22	390.68	0.0038	Singlet-AU	H-8->LUMO (-42%), H-1->L+5 (35%)	44-->9 (-35)	6-->44 (38)	44-->11 (-33)	3-->9 (6)	3-->27 (24)
23	390.49	0	Singlet-AG	H-9->LUMO (91%)	6-->14 (8)	8-->4 (-4)	85-->3 (-82)	0-->20 (20)	1-->59 (58)
24	386.26	0	Singlet-AG	H-4->L+3 (20%), H-3->L+2 (29%), H-1->L+4 (-17%)	73-->4 (-69)	9-->34 (25)	12-->58 (46)	3-->1 (-2)	3-->3 (0)
25	385.14	0.1888	Singlet-AU	H-4->L+2 (21%), H-3->L+3 (28%), H-1->L+3 (11%), H-1->L+5 (-12%)	74-->4 (-70)	9-->33 (24)	11-->61 (50)	3-->1 (-2)	3-->1 (-2)
26	375.57	0	Singlet-AG	H-5->L+1 (77%)	67-->3 (-64)	5-->13 (8)	13-->4 (-9)	4-->12 (8)	12-->68 (56)
27	364.82	0	Singlet-AG	H-4->L+5 (25%), H-3->L+4 (27%)	72-->5 (-67)	10-->56 (46)	11-->24 (13)	4-->5 (1)	3-->11 (8)
28	364.37	0.0123	Singlet-AU	H-4->L+4 (26%), H-3->L+5 (27%)	73-->5 (-68)	10-->58 (48)	10-->30 (20)	5-->3 (-2)	2-->4 (2)
29	362.22	0	Singlet-AG	H-2->L+3 (55%), HOMO->L+2 (-41%)	78-->3 (-75)	8-->14 (6)	4-->83 (79)	8-->0 (-8)	2-->0 (-2)
30	362.13	0.0008	Singlet-AU	H-2->L+2 (48%), HOMO->L+3 (-39%)	78-->3 (-75)	8-->16 (8)	5-->80 (75)	7-->0 (-7)	2-->1 (-1)
31	347.91	0.0007	Singlet-AU	H-2->L+4 (54%), HOMO->L+5 (-41%)	78-->4 (-74)	8-->83 (75)	4-->13 (9)	8-->0 (-8)	2-->0 (-2)
32	347.86	0	Singlet-AG	H-2->L+5 (54%), HOMO->L+4 (-41%)	78-->4 (-74)	8-->83 (75)	5-->13 (8)	8-->0 (-8)	2-->0 (-2)
33	345.75	0.0006	Singlet-AU	H-4->L+2 (48%), H-3->L+3 (-46%)	74-->3 (-71)	11-->13 (2)	10-->84 (74)	3-->0 (-3)	2-->0 (-2)
34	345.67	0	Singlet-AG	H-4->L+3 (49%), H-3->L+2 (-45%)	75-->3 (-72)	11-->14 (3)	10-->83 (73)	3-->0 (-3)	2-->0 (-2)
35	338.54	0.0005	Singlet-AU	H-2->L+18 (32%), HOMO->L+19 (30%)	76-->62 (-14)	9-->12 (3)	6-->16 (10)	7-->7 (0)	2-->3 (1)

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