TUNING THE ELECTRONICS OF BIS(TRIDENTATE)RUTHENIUM(II) COMPLEXES WITH LONG-LIVED EXCITED STATES: MODIFICATIONS TO THE LIGAND SKELETON BEYOND CLASSICAL EDG- OR EWG DECORATIONS.

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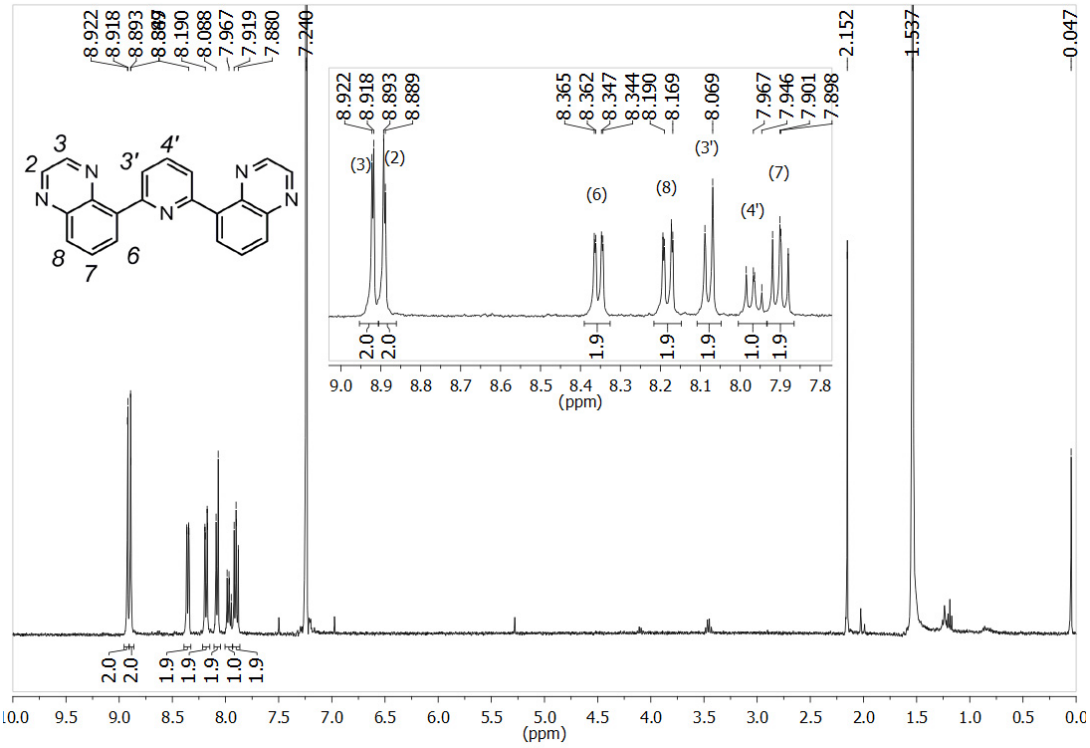


Figure S1. ^{1}H-NMR (400MHz, $CDCl_3$): 2,6-bis(quinoxalin-5-yl)pyridine (**dqxp**).

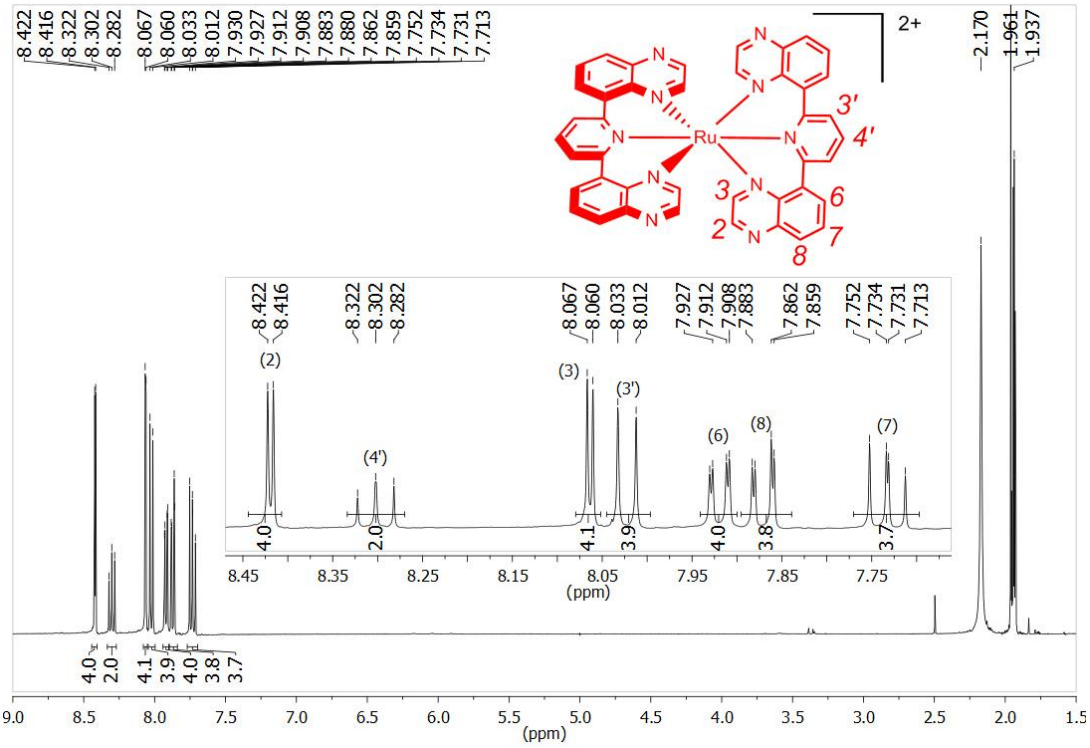


Figure S2. ^{1}H-NMR (400MHz, CD_3CN): Complex **1** $[Ru(dqxp)_2](PF_6)_2$.

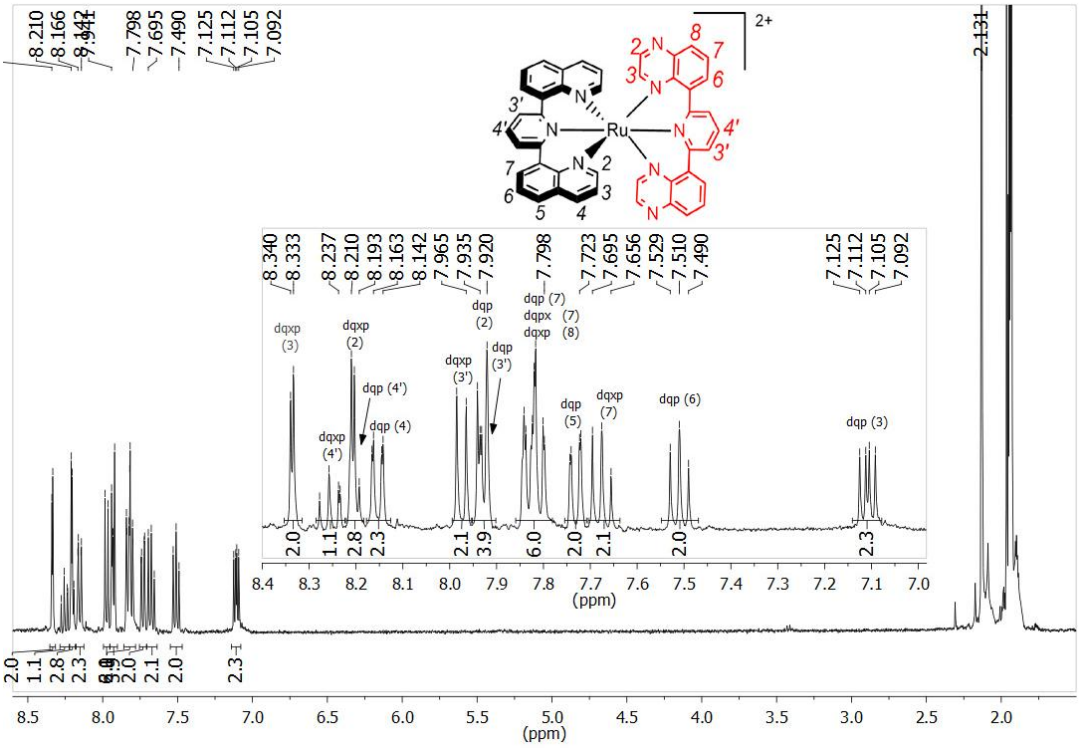


Figure S3. ^{1}H-NMR (400MHz, CD_3CN): Complex **2** $[Ru(dqp)(dqxp)](PF_6)_2$.

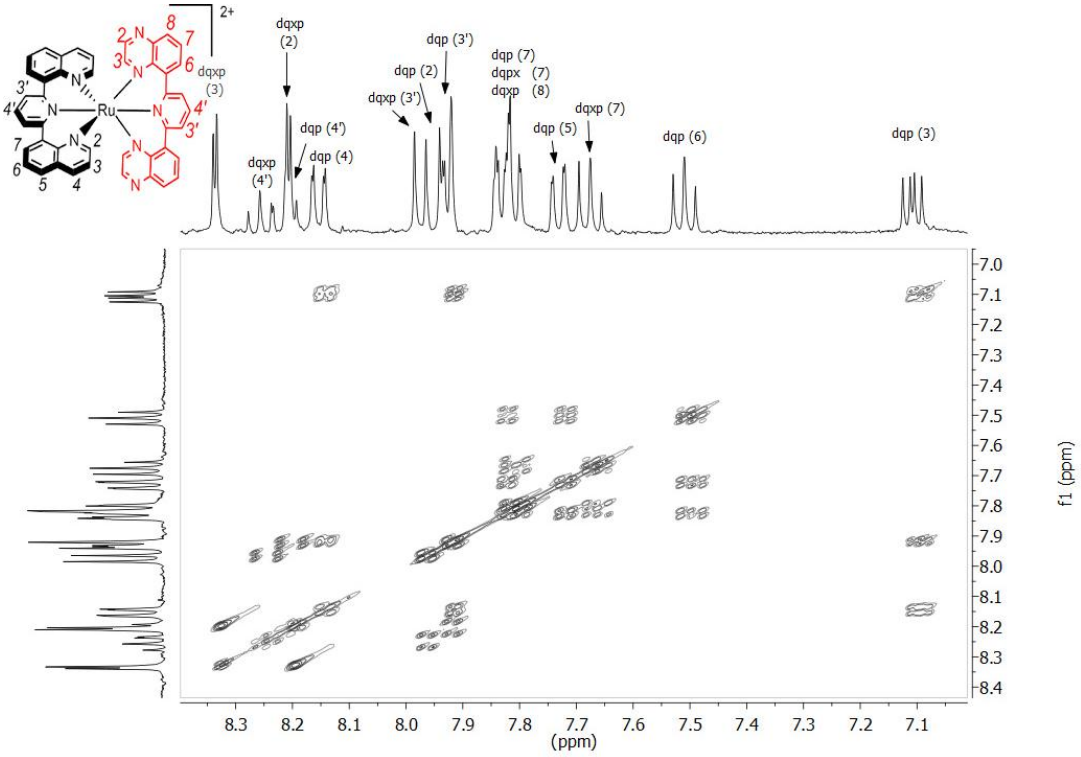


Figure S4. COSY ^{1}H-^{1}H NMR (CD_3CN): Complex **2** $[Ru(dqp)(dqxp)](PF_6)_2$.

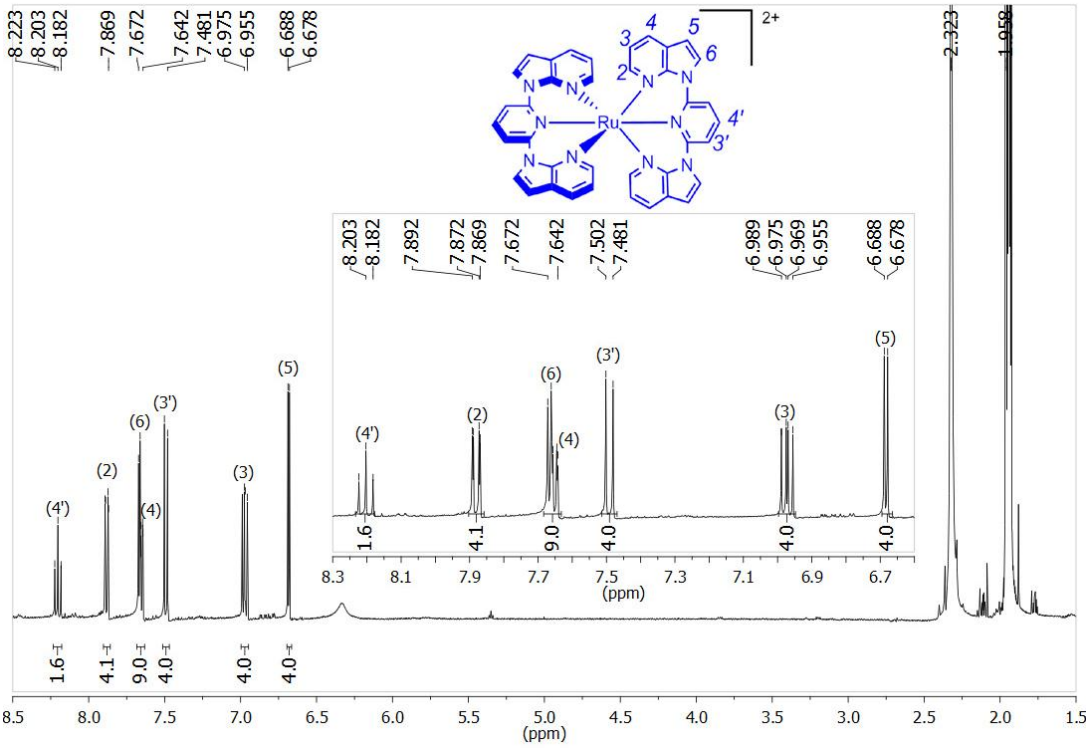


Figure S5. ^{1}H-NMR (400MHz, CD_3CN): Complex **3** $[Ru(dNinp)_2](PF_6)_2$.

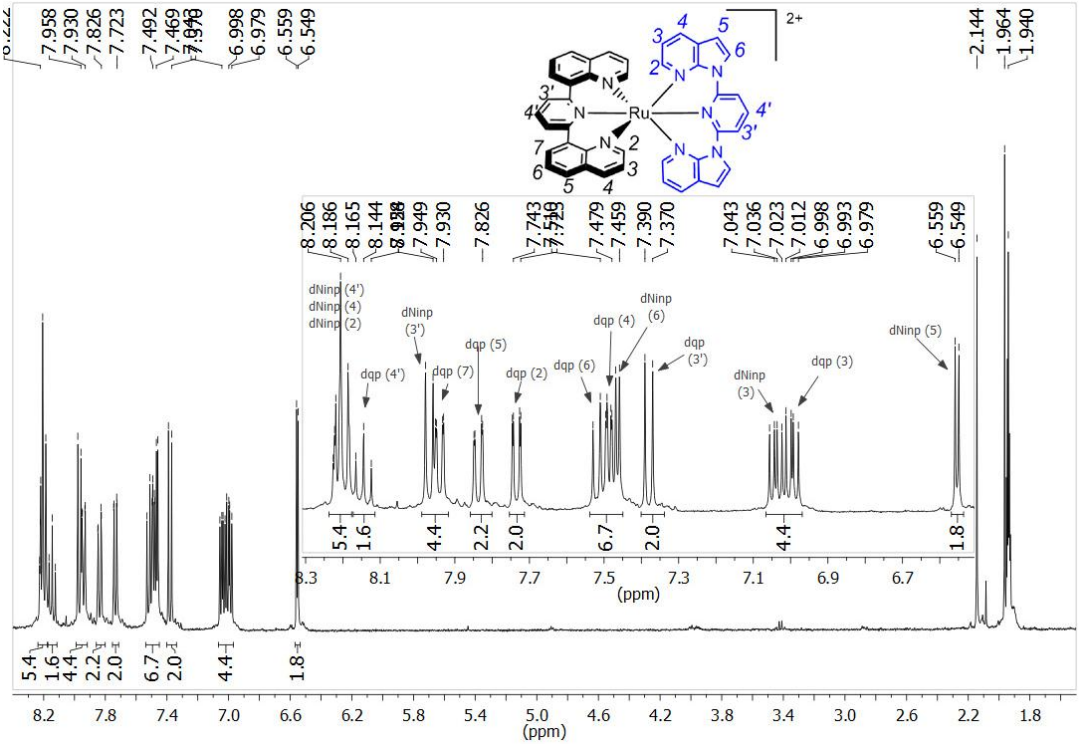


Figure S6. ^{1}H-NMR (400MHz, CD_3CN): Complex **4** $[Ru(dqp)(dNinp)](PF_6)_2$.

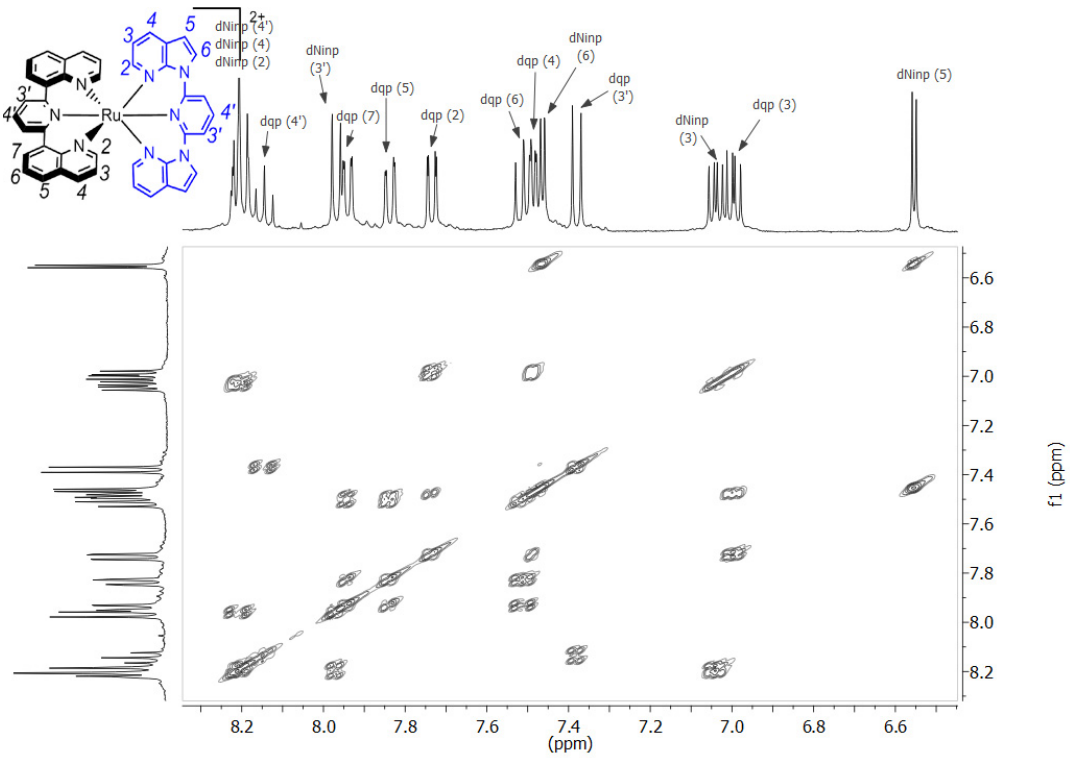


Figure S7. COSY ^{1}H-^{1}H NMR (CD_3CN): Complex **4** [Ru(dqp)(dqNinp)]$(PF_6)_2$.

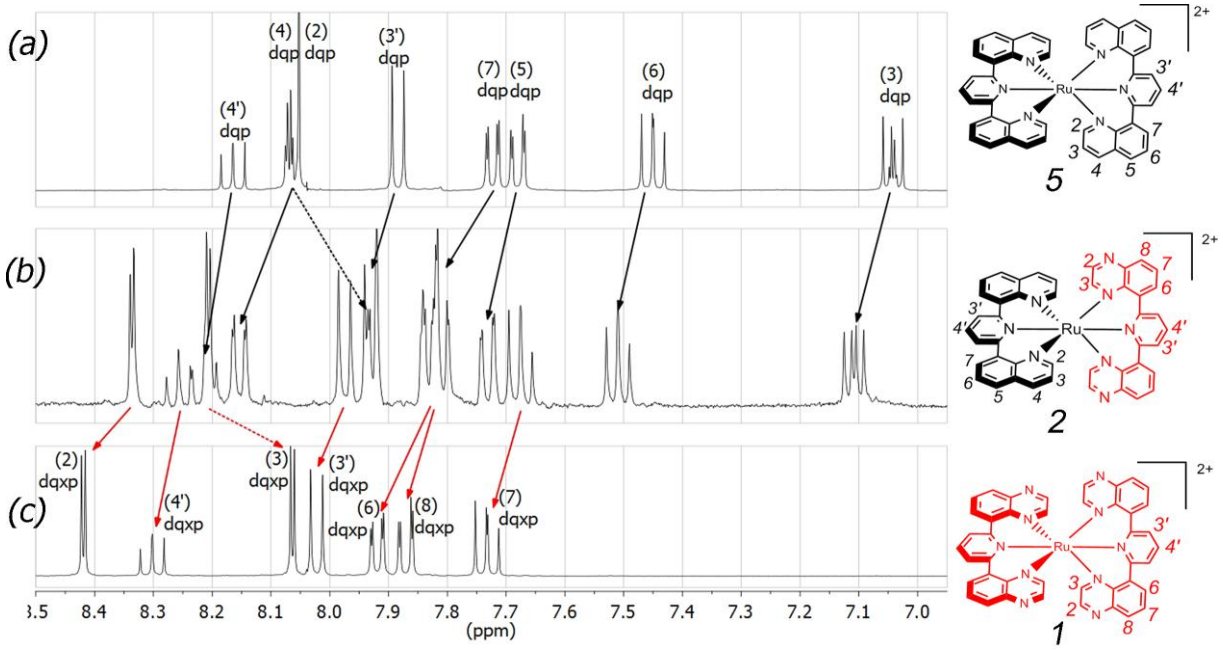


Figure S8. Comparison of the ^{1}H-NMR (400 MHz) chemical shift for the complexes with dqxp in CD_3CN as PF_6^- salts. Panel (a): Reference complex **5,** panel (b): complex **2** panel (c): complex **1**. Arrows between panels (a) and (b) point the shifts of the proton signals on **dqp** in **2** *versus* **5**. Arrows between panels (b) and (c) point the shifts on the proton signals on **dqxp** in **1** *versus* **2**.

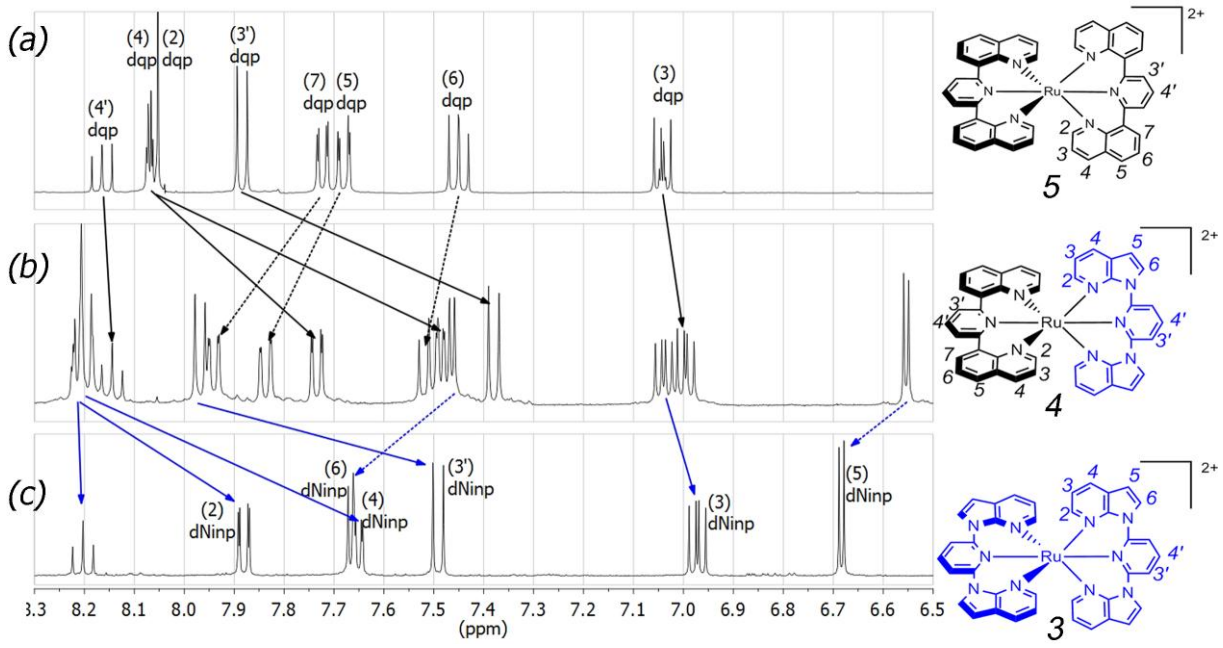


Figure S9. Comparison of the ^{1}H-NMR (400 MHz) chemical shift for the complexes with dNinp in CD_3CN as PF_6- salts. Panel (a): Reference complex **5**, panel (b): complex **4** panel (c): complex **3**. Arrows between panels (a) and (b) point the shifts of the proton signals on

dqp in **4** *versus* **5**. Arrows between panels (b) and (c) point the shifts on the proton signals on **dNinp** in **3** *versus* **4**.

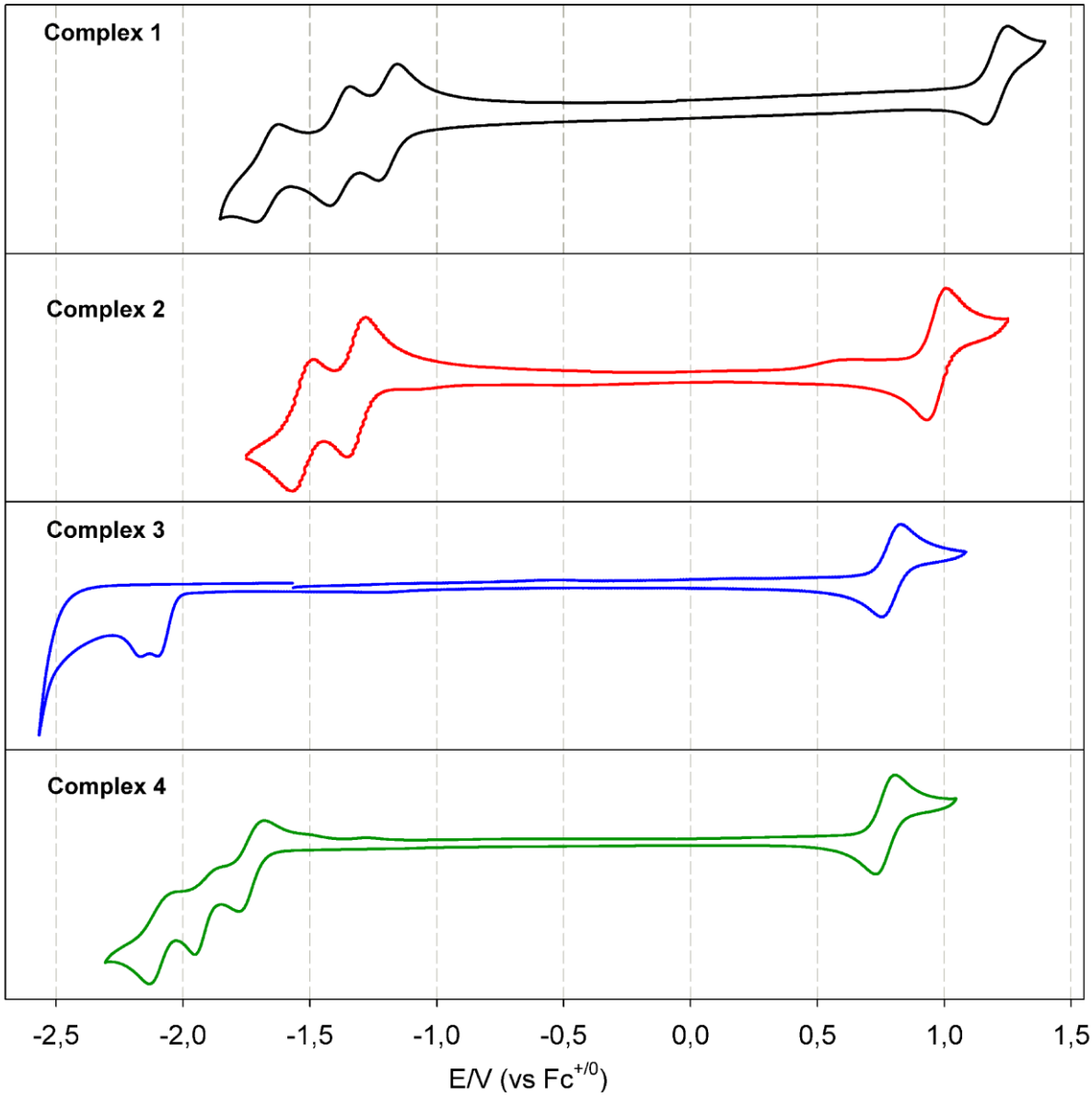


Figure S10. Cyclic Voltammetry of the complexes **1** (black), **2** (red), **3** (blue) and 4 (green) *vs*. $Fc^{+/0}$ at 0.1 Vs^{-1} (CH_3CN, $TBAPF_6$ (0.1M), 293 K). Second scan for complexes **1**,**2** and **4**, start potential 0.0 volts. First scan for **3**, stat potential -1.5 volts.

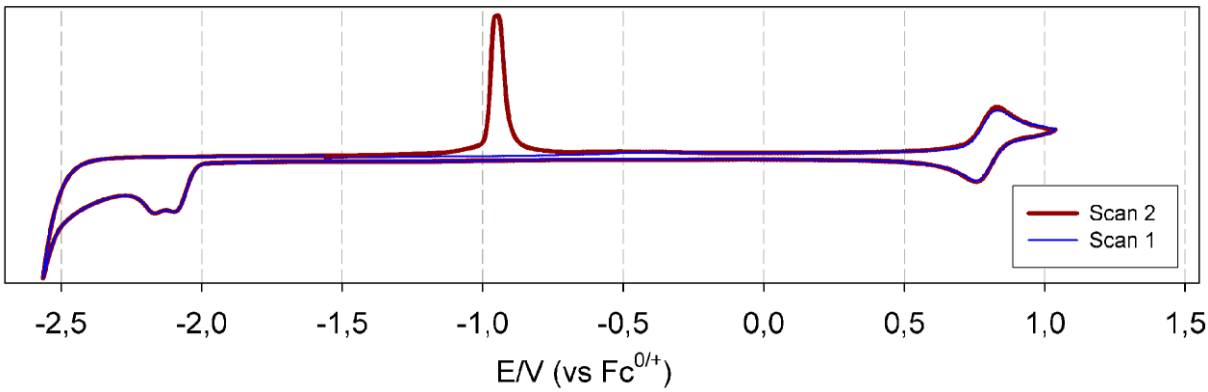


Figure S11. Cyclic Voltammetry of the complex **3** *vs*. $Fc^{+/0}$ at 0.1 Vs^{-1} (CH_3CN, $TBAPF_6$ (0.1M), 293 K). First and second scans. Start potential -1.5volts.

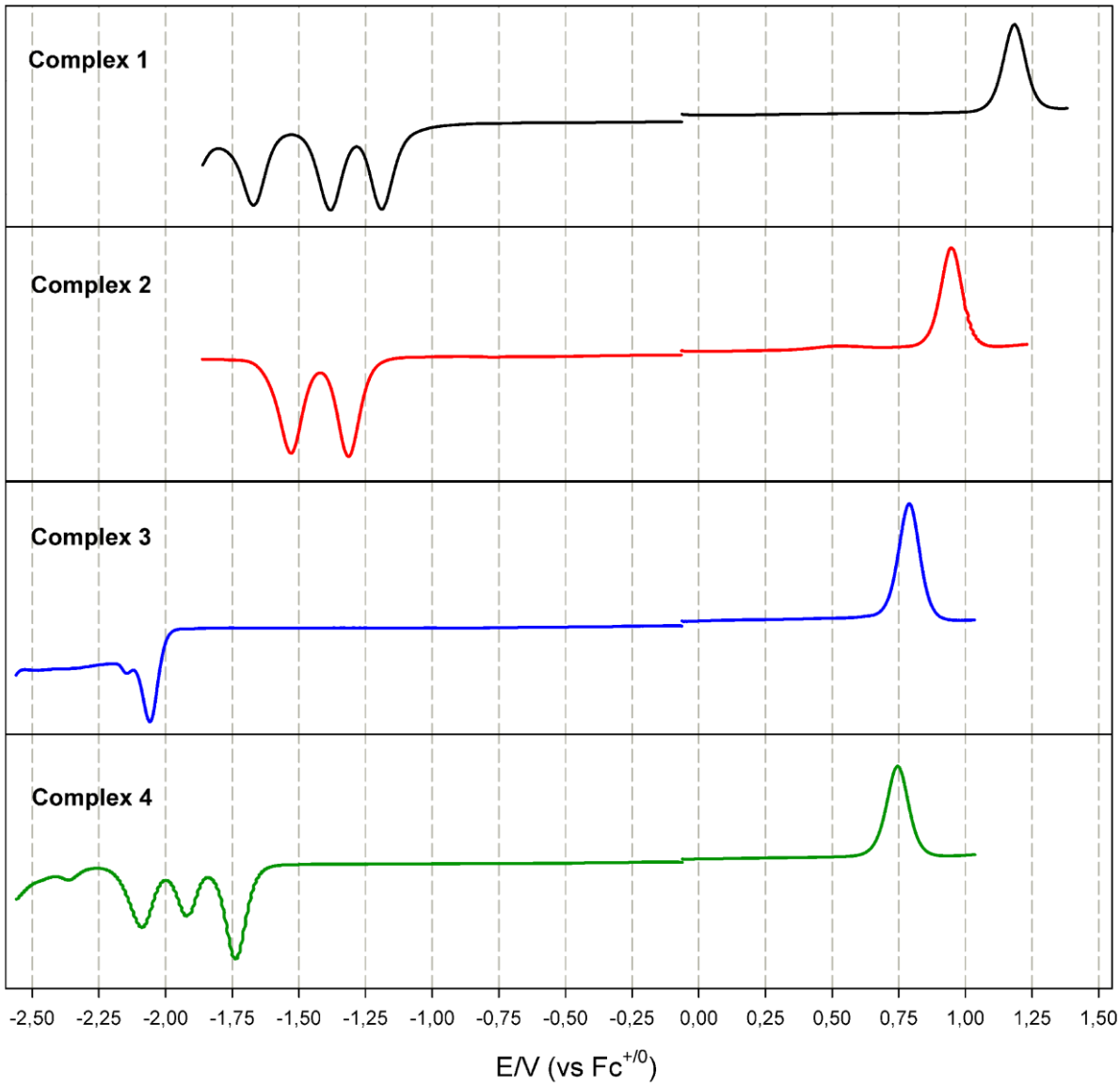


Figure S12. Differential Pulse Voltammetry of the complexes **1** (black), **2** (red), **3** (blue) and 4 (green) *vs*. $Fc^{+/0}$ (CH_3CN, $TBAPF_6$ (0.1M), 293 K).

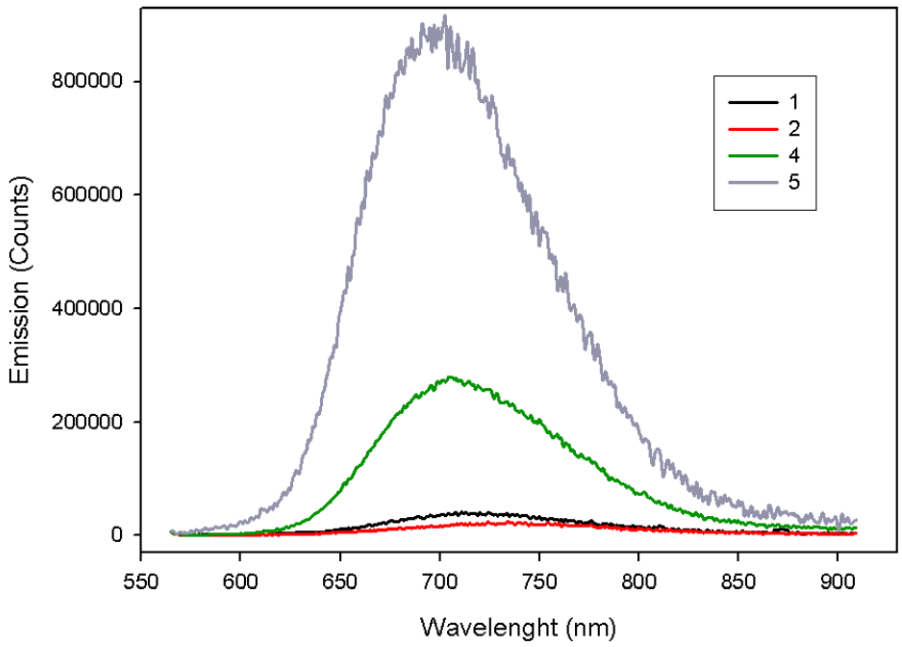


Figure S13. Steady state emission spectra at room temperature (CH_3CN), argon purged samples of **1** (black), **2** (red), **4** (green) and 5 (gray). All the samples adjusted to $OD_{(480\ nm)}$ = 0.15 Excitation and emission slits at 5 nm. Integration time = 1 second.

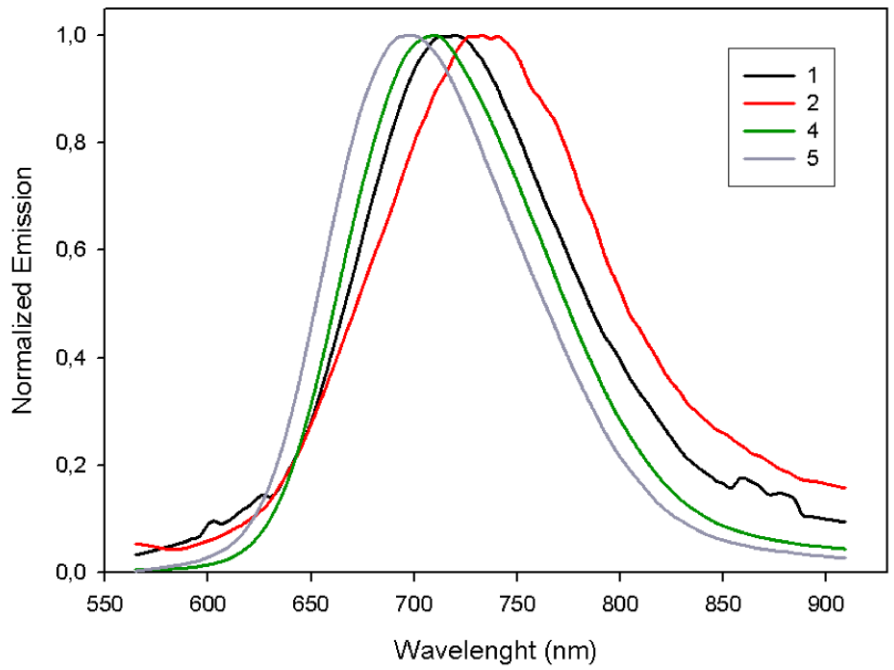


Figure S14. Normalized steady state emission spectra at room temperature (CH_3CN), argon purged samples of **1** (black), **2** (red), **4** (green) and 5 (gray).

Table S1. Crystallographic data for **2** and **4**

Compound	**2**	**4**
Formula	C44 H28 N10 P2 Ru, 2(P F6), 2(C2 H3 N)	$C_{42}H_{28}N_8Ru\cdot(H_2KN_3O_{10})\cdot C_2H_3N$
M_w (g/mol); F(000)	1141.86; 2296	1029.99; 2096
T (K); wavelength (Å)	100; 0.71073	100; 0.71073
Crystal System	Orthorhombic	Monoclinic
Space Group	Pbcn	P21/n
Unit Cell: a (Å)	16.7445(16)	11.9736(11)
b (Å)	13.7792(13)	26.443(3)
c (Å)	19.4056(19)	14.2001(14)
β (°)	90	112.189(1)
V (Å^3); Z; $d_{calcd.}$ (g/cm^3)	4477.4(7); 4; 1.694	4163.0(7); 4; 1.643
θ range (°); completeness	1.91 to 31.18; 0.969	1.54 to 30.51; 98.4
collected reflections; R_σ	86187; 0.0388	78795; 0.0606
unique reflections; R_{int}	7026; 0.091	12504; 0.063
μ (mm^{-1}); Abs. Corr.	0.522; Semi-empirical from equivalents	0.555; Semi-empirical from equivalents
$R_1(F)$; w$R(F^2)$ [$I > 2\sigma(I)$]	0.0570; 0.1478	0.0667; 0.1826
$R_{1a}(F)$; w$R(F^2)$ (all data)	0.0694; 0.1553	0.0913; 0.1925
GoF(F^2)	1.032	1.106
Residual electron density (e$^-$/Å^3)	2.843; -1.678	1.075; -2.402

TableS2. Selected bond lengths (Å) and angles (˚) for **2**.

	Complex 2
Ru1-N1	2.067(2)
Ru1-N2	2.033(4)
Ru1-N3	2.050(3)
Ru1-N5	2.021(4)
C9-C10	1.495(4)
C19-C21	1.493(5)
C20-C19-C21-N5	-36.4(4)
C6-C9-C10-N2	-37.4(4)

Table S3. Selected bond lengths (Å) and angles (˚) for **4**.

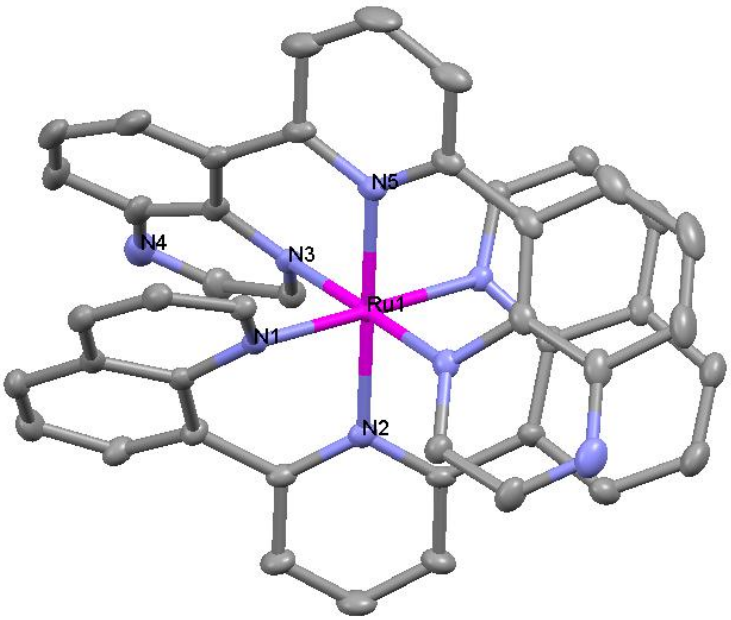
	Complex 4
Ru1-N1	2.029(3)
Ru1-N2	2.068(3)
Ru1-N3	2.071(3)
Ru1-N4	2.083(3)
Ru1-N6	2.064(3)
Ru1-N8	2.065(3)
C1-C6	1.486(6)
C5-C15	1.492(5)
C28-N5	1.427(6)
C24-N7	1.405(6)
N1-C5-C15-C23	-40.3 (6)
N1-C1-C6-C14	-36.8 (6)
C42-N7-C24-N4	-39.7 (6)
C35-N5-C28-N4	-39.9 (6)

X-ray crystallography

Crystallographic data sets were collected from single crystal samples mounted on a loop fiber and coated with N-paratone oil (Hampton Research). Collection was performed using a Bruker SMART APEX diffractometer equiped with an APEXII CCD detector, a graphite monochromator and a 3-circles goniometer. The crystal-to-detector distance was 5.0 cm, and the data collection was carried out in 512 x 512 pixel mode. The initial unit cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 10.0 degrees scan in 33 frames over three different parts of the reciprocal space (99 frames total). Cell refinement and data reduction were performed with SAINT V7.68A (Bruker AXS). Absorption correction was done by multi-scan methods using SADABS96 (Sheldrick).

The structure was solved by direct methods and refined using SHELXL97 (Sheldrick). All non-H atoms were refined by full-matrix least-squares with anisotropic displacement parameters while hydrogen atoms were placed in idealized positions. Refinement of F^2 was performed against all reflections. The weighted R-factor *w*R and goodness of fit S are based on F^2. Crystal structures data were deposited at the Cambridge Crystallographic Data Centre, and allocated the respective deposition numbers CCDC 848070 (**4**) CCDC 849360 (**2**).

COMPLEX 2



COMPLEX **2**; no noticeable effect in the packing, each complex is isolated by surrounding counterions and solvent molecules.

There are pi-pi stacking between the aromatic rings of the coordinated ligands (Calculations made by Platon routine):

- Centroid Cg5: ring N1/C1/C2/C3/C4/C6

  Centroid Cg11: ring C19/C18/C17/C16/C15/C20

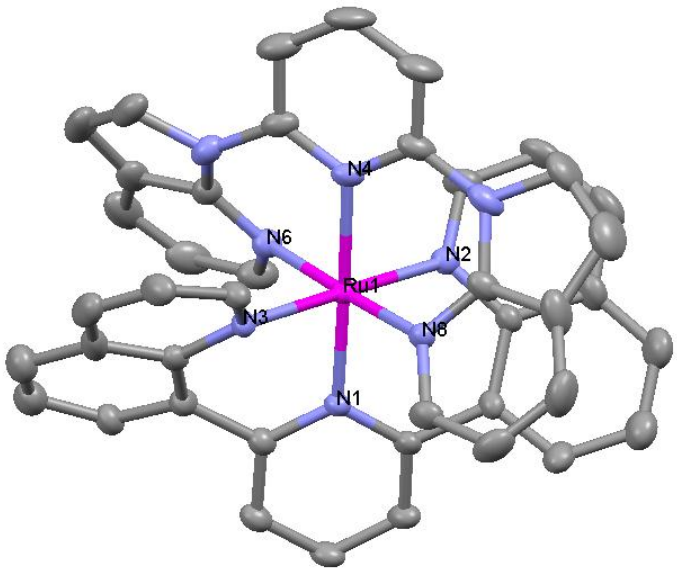
  Distance cg5-cg11 = 3.5002(18)

- Centroid Cg7: ring C20/C15/N4/C14/C13/N3

  Centroid Cg9: ring C6/C4/C5/C7/C8/C9

  Distance cg7-cg9 = 3.5062(18)

COMPLEX 4



COMPLEX 4; no noticeable effect in the packing, each complex is isolated by surrounding counterions and solvent molecules.

There are pi-pi stacking between the aromatic rings of the coordinated ligands (Calculations made by Platon routine):

- Centroid Cg1: ring N5/C35/C31/C30/C29

  Centroid Cg9: ring N3/C13/C12/C11/C10/C14

  Distance cg1-cg9 = 3.660 (3)

- Centroid Cg11: ring N6/C34/C33/C32/C31/C35

  Centroid Cg13: ring C14/C10/C9/C8/C7/C6

  Distance cg11-cg13 = 3.610 (3)

- Centroid Cg2: ring N7/C42/C38/C37/C36

  Centroid Cg8: ring N2/C22/C21/C20/C19/C23

  Distance cg2-cg8 = 3.627 (3)

- Centroid Cg12: ring N8/C41/C40/C39/C38/C42

  Centroid Cg14: ring C15/C16/C17/C18/C19/C23

  Distance cg12-cg14 = 3.658 (3)

Table S4. Calculated centroid-centroid distances for stacking ligands in **2**, **4** and **5** (using Platon). Abbreviations for the aromatic rings: pyridine = py, pyrazine = pz, benzene = bz, azaindole = aza.

Compound	**Centroid-Centroid distance Cgi-Cgj (Å)**	**Centroid-Centroid distance Cgi-Cgj (Å)**	**Average centroid-centroid distance (Å)**
2	cg5-cg11(py-bz)= 3.5002(18)	cg7-cg9(pz-bz)= 3.5062(18)	3.5032(18)
4	cg11-cg13 (py-bz) = 3.610 (3)	cg12-cg14 (py-bz) = 3.658 (3)	3.634 (3)
	cg2-cg8(aza-py) = 3.627 (3)	cg1-cg9 (aza-py) = 3.660 (3)	3.643 (3)
5	Less than 3.5 and 3.6		

Definition of the centroids in **2**: (i) Cg5: ring N1/C1/C2/C3/C4/C6 and Cg11: ring C19/C18/C17/C16/C15/C20; (ii) Cg7: ring C20/C15/N4/C14/C13/N3 and Cg9: ring C6/C4/C5/C7/C8/C9.

Definition of the centroids in **4**: (i) Cg1: ring N5/C35/C31/C30/C29 and Cg9: ring N3/C13/C12/C11/C10/C14; (ii) Cg11: ring N6/C34/C33/C32/C31/C35 and Cg13: ring C14/C10/C9/C8/C7/C6; (iii) Cg2: ring N7/C42/C38/C37/C36 and Cg8: ring N2/C22/C21/C20/C19/C23; (iv) Cg12: ring N8/C41/C40/C39/C38/C42 and Cg14: ring C15/C16/C17/C18/C19/C23.

Table S5. Calculated optimized geometries. Gas phase, PBE0/SDD[Ru],6-31G(d,p)[H,C,N].

5 (Å)				**1** (Å)				**3** (Å)			
	X	Y	Z		X	Y	Z		X	Y	Z
Ru	0.000184	-7.9E-07	1.14E-05	Ru	0	2.3E-05	0	Ru	-1E-06	5.08E-06	-1E-06
C	-0.00139	4.910965	0.001233	C	-4.85197	-2.28894	-0.86136	C	4.853448	2.308963	-0.81166
C	-1.11252	4.209099	0.431066	C	-3.61283	-2.71578	-0.34512	C	3.606805	2.708461	-0.2978
C	-1.10041	2.81555	0.369017	C	-2.41807	-2.06132	-0.61706	C	2.423265	2.04665	-0.59849
C	1.099216	2.816392	-0.36617	C	-3.72681	-0.51074	-2.02662	C	3.754872	0.530983	-2.01385
C	1.110329	4.209906	-0.42846	C	-4.90722	-1.23308	-1.73479	C	4.920211	1.272122	-1.70647
H	-0.00183	5.996189	0.001141	H	-5.751	-2.83804	-0.60165	H	5.745583	2.863164	-0.53918
H	-1.97242	4.731812	0.826441	H	-3.59977	-3.60349	0.279238	H	3.572994	3.584461	0.342056
H	1.969924	4.73312	-0.82387	H	-5.82517	-0.92274	-2.22282	H	5.857612	1.002156	-2.18386
N	-0.00032	2.107211	0.001426	C	-1.14162	-2.749	-0.28505	C	1.143136	2.733638	-0.27796
C	2.373383	0.963754	-1.44996	C	-1.14135	-4.14733	-0.33658	C	1.142602	4.132243	-0.33176
C	3.51311	2.792689	-0.85693	C	7.93E-06	-4.8537	-7E-06	C	-7.4E-05	4.838738	-8.8E-05
C	3.628365	0.922986	-2.09139	H	-2.03245	-4.67366	-0.65407	H	2.035166	4.657884	-0.64624
C	4.34412	2.090532	-1.66424	C	1.141628	-2.749	0.285043	C	-1.14322	2.733616	0.277902
H	3.702545	3.709824	-0.32078	C	1.141368	-4.14733	0.33657	C	-1.14273	4.132224	0.331625
C	3.885723	-0.15355	-2.93879	H	9.91E-06	-5.9391	-1E-05	H	-9.2E-05	5.9241	-0.00012
C	1.703699	-1.0044	-2.35225	H	2.032463	-4.67366	0.654057	H	-2.0353	4.657858	0.64608
H	5.359923	2.360626	-1.91544	N	2.97E-06	-2.06582	0	N	-3E-05	2.051997	-1.1E-05
C	2.880617	-1.10253	-3.09121	C	-2.50275	-0.85774	-1.37847	C	2.52116	0.849503	-1.37349
H	4.827969	-0.2423	-3.47038	C	-1.51751	0.956615	-2.4057	C	3.772441	-0.52909	-2.94902
H	0.935826	-1.76579	-2.42207	C	-2.69261	1.17367	-3.15209	C	1.489955	-0.95413	-2.4189
H	3.008271	-1.94356	-3.76372	H	-0.65985	1.612402	-2.5061	C	2.620151	-1.23086	-3.20014
C	-2.37322	0.96108	1.451576	H	-2.72	1.955427	-3.90743	H	4.697711	-0.76354	-3.46791
C	-3.51403	2.790234	0.861293	N	-1.44254	-0.00147	-1.49142	H	0.597433	-1.5649	-2.50185
C	-3.62793	0.918968	2.093468	C	2.418074	-2.06131	0.617065	H	2.581107	-2.02392	-3.93844
C	-4.3444	2.086687	1.668032	C	3.612836	-2.71577	0.345125	N	1.447671	0.009158	-1.50327
H	-3.70425	3.707896	0.326352	C	3.726811	-0.51073	2.026625	C	-2.42332	2.046598	0.598483
C	-3.88454	-0.15871	2.939626	C	4.85198	-2.28893	0.861369	C	-3.60689	2.708366	0.297802
C	-1.70248	-1.00802	2.351081	H	3.599784	-3.60348	-0.27923	C	-3.75485	0.530932	2.013909
H	-5.36022	2.356014	1.919964	C	4.907215	-1.23307	1.734805	C	-4.85351	2.308852	0.811705
C	-2.87902	-1.10751	3.090444	H	5.751009	-2.83802	0.601662	H	-3.57312	3.584346	-0.34208
H	-4.82654	-0.24847	3.471481	H	5.825168	-0.92273	2.222837	C	-4.92022	1.272036	1.706548
H	-0.93425	-1.76918	2.419557	C	2.502752	-0.85773	1.378475	H	-5.74566	2.863023	0.539242
H	-3.00607	-1.94941	3.761986	C	1.517507	0.956621	2.405694	H	-5.8576	1.002059	2.183976
N	1.455825	0.001051	-1.49101	C	2.692601	1.173678	3.152094	C	-2.52117	0.849463	1.373508
N	-1.45537	-0.00142	1.490947	H	0.659838	1.612408	2.506091	C	-1.4899	-0.95413	2.418922
N	-2.2768	2.136686	0.723303	H	2.719986	1.955436	3.907435	C	-3.77237	-0.52912	2.949111
N	2.276179	2.138347	-0.72019	N	1.442539	-0.00147	1.491415	C	-2.62006	-1.23086	3.20021
C	-1.10018	-2.81561	-0.36909	H	-2.71992	-1.9554	3.907463	H	-0.59736	-1.56488	2.50186
C	1.099446	-2.81633	0.366106	C	-2.69254	-1.17363	3.152134	H	-4.69762	-0.76358	3.468033
C	-1.11216	-4.20915	-0.4313	C	-1.51744	-0.95655	2.405741	H	-2.58098	-2.02391	3.938518
C	1.11068	-4.20986	0.428231	H	-0.65976	-1.61232	2.506145	N	-1.44766	0.00914	1.503274
C	-0.00096	-4.91097	-0.00155	C	-3.72679	0.51072	2.026623	H	2.581115	2.023978	3.938393
H	-1.97202	-4.73189	-0.82674	N	-1.44249	0.001527	1.491451	C	2.620167	1.230911	3.200108
H	1.970315	-4.73305	0.823591	C	-2.50273	0.857755	1.378486	C	1.489987	0.954193	2.418839
H	-0.00131	-5.99619	-0.00159	C	-2.41808	2.061319	0.617048	C	3.772454	0.52913	2.949025
N	-0.00015	-2.10721	-0.00143	C	-4.90722	1.232973	1.734725	H	0.597468	1.564964	2.501767
C	-2.37316	-0.96121	-1.45154	C	-3.61289	2.715676	0.345007	C	3.754896	-0.53095	2.013857
C	-3.51383	-2.79043	-0.86122	C	-4.85202	2.288776	0.861223	H	4.697713	0.763573	3.467936
C	-3.62788	-0.91918	-2.0934	H	-5.82518	0.922596	2.222729	N	1.44771	-0.00912	1.503229
C	-4.34427	-2.08694	-1.66795	H	-3.59988	3.603317	-0.27944	C	2.521194	-0.84947	1.373476
H	-3.70397	-3.7081	-0.32627	H	-5.75108	2.837787	0.601434	C	2.423323	-2.04661	0.598459
C	-3.88457	0.158486	-2.93957	C	-1.14164	2.749036	0.285024	C	4.920242	-1.27209	1.706505
C	-1.70254	1.007926	-2.35107	C	-1.14136	4.147368	0.336581	C	3.606869	-2.70842	0.297798
H	-5.36008	-2.35633	-1.91985	C	1.14163	2.749038	-0.28504	C	4.8535	-2.30893	0.811693
C	-2.8791	1.107337	-3.09041	C	-7.9E-06	4.853745	-1.3E-05	H	5.85763	-1.00213	2.183926
H	-4.82658	0.248189	-3.47141	H	-2.03244	4.673703	0.654101	H	3.573072	-3.58443	-0.34205
H	-0.93435	1.769118	-2.41956	C	1.141349	4.147369	-0.3366	H	5.745641	-2.86313	0.539243
H	-3.00621	1.949221	-3.76196	H	-9.9E-06	5.939145	-1.7E-05	C	1.143212	-2.73361	0.27789
C	2.373439	-0.96363	1.450001	H	2.032424	4.673705	-0.65413	C	1.142722	-4.13222	0.331608
C	3.513312	-2.79248	0.856987	N	-3E-06	2.065866	-4E-06	C	-1.14314	-2.73363	-0.27795
C	3.628406	-0.92277	2.091455	C	2.418076	2.061324	-0.61705	C	6.41E-05	-4.83873	-7.7E-05
C	4.344252	-2.09027	1.664322	C	2.502731	0.857757	-1.37849	H	2.03531	-4.65785	0.646034
H	3.702832	-3.7096	0.320846	C	3.612876	2.715685	-0.34501	C	-1.14261	-4.13223	-0.33173
C	3.885686	0.153774	2.938863	C	4.852017	2.288785	-0.86122	H	7.92E-05	-5.92409	-0.0001
C	1.703622	1.004492	2.352281	H	3.599868	3.603328	0.279433	H	-2.03519	-4.65788	-0.64618
H	5.360065	-2.3603	1.915555	C	4.907224	1.232978	-1.73472	N	2.6E-05	-2.05199	-1.6E-05
C	2.880521	1.102693	3.091256	H	5.751071	2.837799	-0.60143	C	-2.42327	-2.04666	-0.59849
H	4.827918	0.242579	3.470472	H	5.825182	0.922602	-2.22272	C	-2.52119	-0.8495	-1.37347
H	0.935703	1.76583	2.42209	C	3.72679	0.510722	-2.02662	C	-3.6068	-2.70851	-0.29783
H	3.00811	1.943737	3.763767	C	2.692548	-1.17363	-3.15213	C	-4.85345	-2.30903	-0.81169
N	-2.27665	-2.1368	-0.72327	C	1.51745	-0.95655	-2.40574	H	-3.57297	-3.58453	0.341996
N	-1.45537	0.001341	-1.49093	H	2.71993	-1.9554	-3.90746	C	-4.92023	-1.27217	-1.70647
N	2.276336	-2.13823	0.720228	H	0.659768	-1.61232	-2.50615	H	-5.74557	-2.86326	-0.53924
N	1.455821	-0.00098	1.491035	N	1.442495	0.001527	-1.49145	H	-5.85763	-1.00222	-2.18386
				N	3.797082	0.508609	2.915292	C	-3.75491	-0.53099	-2.01382
				N	-3.79709	0.5086	-2.91528	C	-3.7725	0.529112	-2.94896
				N	3.797045	-0.5086	-2.9153	C	-2.62024	1.23092	-3.20005
				N	-3.79704	-0.5086	2.915308	H	-4.69778	0.76355	-3.46785
								C	-1.49003	0.954205	-2.41881
								H	-2.58121	2.024005	-3.93832
								H	-0.59753	1.564998	-2.50174
								N	-1.44772	-0.00912	-1.50323

Table S6. Calculated metal (Ru) orbital contribution to Molecular orbitals for complexes **1**, **3**, and **5**.

Complex 5			Complex 1			Complex 3		
MO	**E / eV**	**Ru / %**	**MO**	**E / eV**	**Ru / %**	**MO**	**E / eV**	**Ru / %**
162	-14.07	5.40	162	-14.41	3.50	150	-14.49	5.77
163	-13.92	2.76	163	-14.33	8.25	151	-14.32	3.41
164	-13.92	5.30	164	-14.19	1.98	152	-14.22	4.03
165	-13.84	3.64	165	-13.88	3.24	153	-14.16	1.30
166	-13.68	2.53	166	-13.81	0.43	154	-14.14	2.10
167	-13.68	3.84	167	-12.99	2.08	155	-14.08	3.16
168	-13.46	2.50	168	-12.97	3.95	156	-13.82	2.41
169	-13.24	5.86	169	-12.97	2.05	157	-13.60	5.12
170	-13.12	0.56	170	-12.94	2.26	158	-13.37	0.21
171	-12.46	1.54	171	-12.82	2.42	159	-12.67	10.60
172	-12.46	2.74	172	-12.80	0.98	160	-12.35	3.07
173	-12.29	0.43	173	-12.77	0.75	161	-12.11	4.36
174	-12.26	0.29	174	-12.76	0.16	162	-11.93	0.50
175	-12.12	14.71	175	-12.69	12.79	163	-11.91	17.76
176	-12.03	10.81	176	-12.59	10.79	164	-11.84	11.81
177	-11.62	15.25	177	-12.12	24.13	165	-11.75	19.24
178	-11.46	0.48	178	-11.97	0.42	166	-11.66	0.28
179	-11.03	78.01	179	-11.81	78.61	167	-11.38	74.13
180	-10.76	71.11	180	-11.58	64.75	168	-10.97	66.15
181 (HOMO)	-10.58	65.61	181 (HOMO)	-11.34	64.32	169 (HOMO)	-10.85	64.36
182 (LUMO)	-7.14	3.08	182 (LUMO)	-7.83	4.42	170 (LUMO)	-6.80	4.08
183	-7.01	2.97	183	-7.83	3.74	171	-6.55	4.81
184	-6.98	6.56	184	-7.67	7.65	172	-6.54	4.41
185	-6.94	7.83	185	-7.60	9.10	173	-6.46	6.17
186	-6.19	3.27	186	-6.85	2.89	174	-6.37	2.12
187	-6.10	2.96	187	-6.74	3.27	175	-6.35	4.72
188	-6.04	5.38	188	-6.58	5.11	176	-6.17	0.55
189	-5.93	5.78	189	-6.58	4.42	177	-6.00	10.90
190	-5.61	10.09	190	-6.14	10.27	178	-5.14	5.15
191	-5.55	2.31	191	-6.08	2.90	179	-4.87	3.93
192	-5.51	2.07	192	-6.01	1.73	180	-4.86	31.74
193	-5.47	4.96	193	-6.00	5.46	181	-4.78	10.98
194	-4.63	5.55	194	-5.13	5.40	182	-4.56	42.38
195	-4.55	18.51	195	-5.05	16.88	183	-4.53	59.32
196	-4.43	37.05	196	-5.01	39.56	184	-4.32	92.12
197	-4.28	83.54	197	-4.75	62.76	185	-3.96	52.00
198	-4.07	78.06	198	-4.48	64.83	186	-3.88	26.01
199	-3.85	66.75	199	-4.46	81.49	187	-3.88	74.08
200	-3.77	44.44	200	-4.34	50.54	188	-3.65	11.23
201	-3.55	80.34	201	-3.96	72.62	189	-3.52	62.26
202	-3.46	62.41	202	-3.93	83.20	190	-3.46	84.10
203	-3.17	82.61	203	-3.53	84.87	191	-3.35	21.01
204	-2.75	2.10	204	-3.28	3.13	192	-2.22	28.01
205	-2.71	3.53	205	-3.25	5.74	193	-2.13	3.41

Figure S15. Calculated molecular orbitals for absorption spectra of complex **5**:

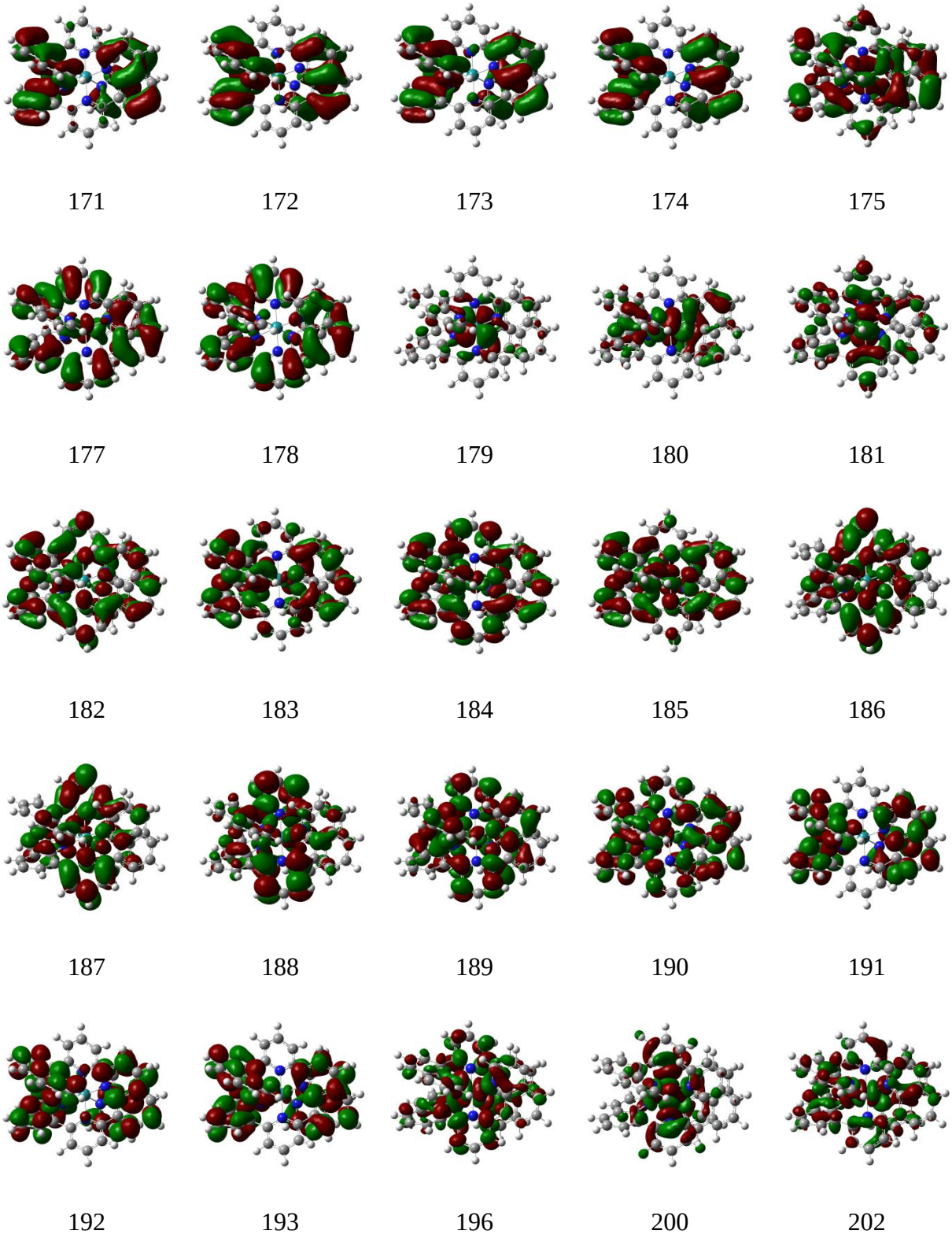


Table S6. Transitions for complex **5**:

Excited State	Excition Energy (eV)	Wavelength (nm)	f	Transistion	
1	2.594	477.96	0.0322	181 → 182	97.82%
2	2.6724	463.94	0.0211	181 → 184 180 → 185	84.64% 12.31%
3	2.6943	460.17	0.0022	181 → 183 180 → 182	62.22% 34.50%
4	2.7541	450.18	0.0652	180 → 182 181 → 183	62.57% 33.91%
6	2.8053	441.97	0.0673	180 → 185 181 → 184 179 → 183	77.10% 10.95% 6.75%
7	2.8321	437.78	0.0052	180 → 183 180 → 188 180 → 196	89.35% 2.40% 2.35%
9	2.9856	415.27	0.0004	179 → 185	94.83%
10	3.0631	404.76	0.009	179 → 184	95.33%
12	3.1012	399.8	0.0737	179 → 183 180 → 185	87.79% 5.33%
13	3.3987	364.8	0.0152	181 → 186	93.99%
14	3.4976	354.49	0.0008	181 → 188 180 → 186 181 → 196	48.03% 41.69% 2.84%
16	3.5618	348.09	0.0033	180 → 186 181 → 188 177 → 182 178 → 185	49.56% 37.36% 5.43% 2.73%
17	3.5804	346.28	0.0006	180 → 188 180 → 196 180 → 183 180 → 193 180 → 202	63.23% 13.98% 6.29% 4.38% 4.23%
18	3.5947	344.91	0.0535	178 → 182 180 → 187	52.41% 41.83%
19	3.6505	339.63	0.0304	181 → 189 178 → 182	87.30% 5.24%
20	3.7107	334.13	0.1973	180 → 187 178 → 182 181 → 189	54.42% 36.38% 4.59%
21	3.7278	332.6	0.0943	177 → 182 178 → 185 180 → 186	54.36% 30.44% 5.73%
24	3.812	325.25	0.0001	178 → 185 177 → 182	62.75% 33.69%
25	3.8224	324.36	0.0092	178 → 184 179 → 187	49.74% 45.74%
26	3.8676	320.57	0.0075	179 → 188 179 → 196 181 → 200 179 → 183 179 → 193 179 → 202	72.09% 7.50% 3.57% 3.09% 2.78% 2.41%
27	3.8814	319.43	0.0206	177 → 183 179 → 187 178 → 184 175 → 182	39.37% 31.35% 21.89% 2.60%
28	3.912	316.94	0.0412	177 → 183	51.60%

				178 → 184 179 → 187	21.36% 19.98%
Excited State	Excition Energy (eV)	Wavelength (nm)	f	Transistion	
29	3.9168	316.54	0.0738	177 → 185 181 → 190 175 → 184 180 → 185	87.22% 2.86% 2.30% 2.24%
32	4.0256	307.99	0.0039	179 → 189 181 → 193 181 → 196 181 → 188 179 → 200	54.17% 17.92% 5.29% 4.47% 3.18%
33	4.0333	307.4	0.0038	181 → 190 174 → 182 173 → 183 180 → 191 179 → 188 175 → 184	69.36% 7.33% 5.20% 4.61% 3.91% 2.14%
34	4.1003	302.38	0.0036	181 → 192 180 → 193 180 → 188 180 → 196 174 → 184 173 → 185 171 → 183 172 → 182 175 → 182 180 → 202	26.51% 23.26% 14.41% 10.23% 3.99% 3.82% 3.16% 3.14% 3.12% 2.38%
36	4.1255	300.53	0.0059	181 → 193 179 → 189 179 → 190 180 → 192 181 → 196 174 → 185 173 → 184 171 → 182	37.46% 35.70% 3.88% 3.50% 3.16% 2.77% 2.63% 2.09%

Figure S16. Calculated molecular orbitals for absorption spectra of complex **1**:

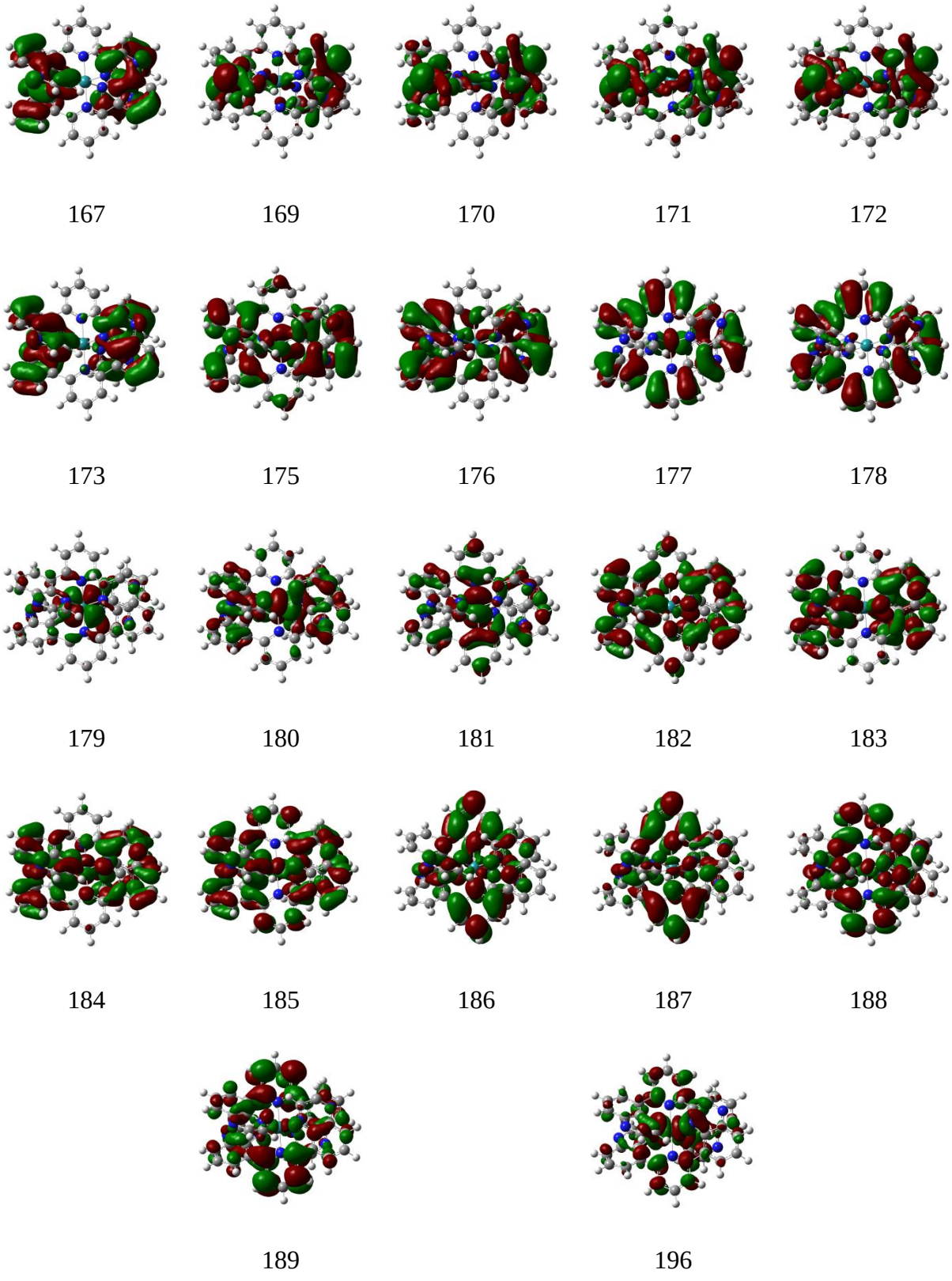
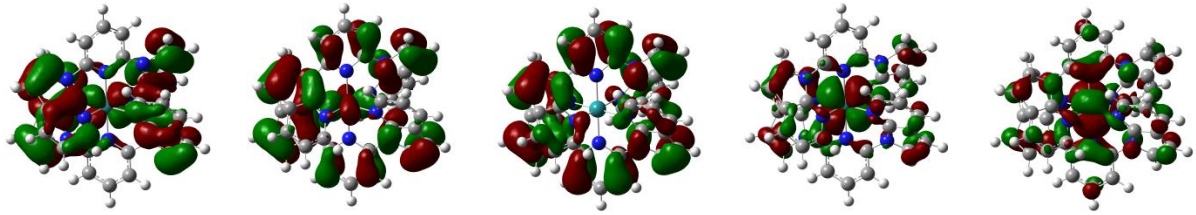


Table S7. Transitions for complex **1**:

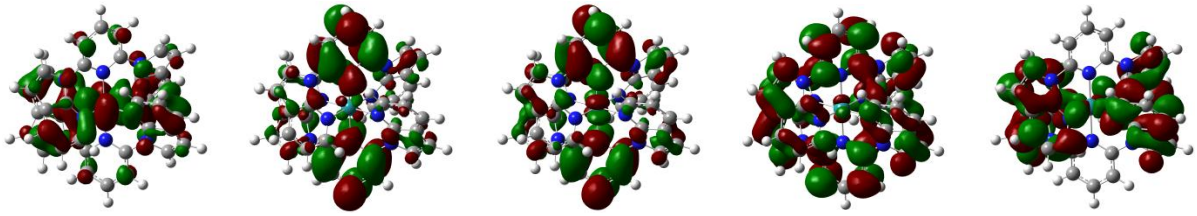
Excited State	Excition Energy (eV)	Wavelength (nm)	f	Transistion	
1	2.6047	476	0.0217	181 → 182	95.45%
2	2.6242	472.47	0.0188	181 → 182	96.51%
3	2.7377	452.88	0.0174	181 → 185	85.65%
5	2.8126	440.82	0.0074	180 → 183 177 → 183	88.77% 3.78%
6	2.8629	433.07	0.0421	180 → 182 177 → 182 179 → 185	90.29% 4.80% 2.37%
7	2.8878	429.34	0.0243	180 → 184 179 → 183 181 → 185 177 → 184	51.79% 36.88% 4.61% 3.02%
9	3.0398	407.87	0.0001	179 → 184	95.39%
10	3.0707	403.77	0.1366	179 → 183 180 → 184 181 → 185 178 → 182 177 → 184	57.59% 28.73% 4.70% 2.55% 2.25%
11	3.158	392.61	0.0163	179 → 185 180 → 182	92.04% 2.06%
14	3.432	361.26	0.1726	178 → 182 176 → 183 180 → 184	85.28% 3.13% 2.30%
15	3.4723	357.07	0.0189	181 → 186 178 → 185	92.47% 2.54%
16	3.4815	356.13	0.0249	177 → 182 178 → 184 180 → 182 171 → 183	52.37% 33.26% 3.41% 2.87%
17	3.5185	352.38	0.0018	177 → 183 180 → 183	85.21% 4.99%
18	3.5708	347.21	0.0013	178 → 184 177 → 182	54.17% 36.07%
20	3.6279	341.75	0.012	178 → 185 170 → 183 171 → 182 172 → 184 169 → 185 175 → 182 176 → 184 177 → 183 167 → 183	24.78% 17.21% 17.07% 12.16% 7.76% 4.76% 3.87% 2.92% 2.21%
21	3.6388	340.73	0.0005	177 → 184 172 → 183 169 → 182 171 → 185 170 → 184 178 → 182	41.19% 17.00% 9.62% 7.27% 6.72% 6.20%
22	3.6599	338.76	0.013	171 → 183 180 → 186 170 → 182 169 → 184 172 → 185 178 → 184	24.72% 18.88% 14.12% 11.21% 9.62% 7.64%

				175 → 183 167 → 182	4.03% 2.18%
Excited State	Excition Energy (eV)	Wavelength (nm)	f	Transistion	
24	3.6735	337.51	0.0507	177 → 184 172 → 183 169 → 182 170 → 184 171 → 185 180 → 184 175 → 185 173 → 183	46.74% 14.52% 9.57% 7.07% 4.71% 4.17% 3.51% 3.07%
25	3.6916	335.86	0.0098	180 → 186 181 → 189 171 → 183 170 → 182 169 → 184 172 → 185	63.22% 10.76% 5.80% 3.24% 2.58% 2.17%
26	3.7137	333.86	0.0216	178 → 185 171 → 182 170 → 183 172 → 184 169 → 185 181 → 186	64.09% 8.63% 6.56% 5.80% 2.93% 2.37%
27	3.7715	328.74	0.0009	181 → 188 180 → 187	77.31% 15.38%
29	3.7894	327.19	0.0192	181 → 189 180 → 186 181 → 196 175 → 183	71.41% 11.78% 3.16% 2.03%
30	3.8312	323.62	0.0151	180 → 187 181 → 188	76.69% 15.25%

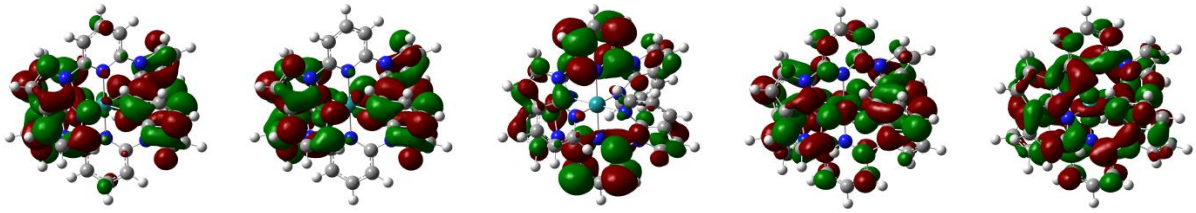
Figure S17. Calculated molecular orbitals for absorption spectra of complex **3**:



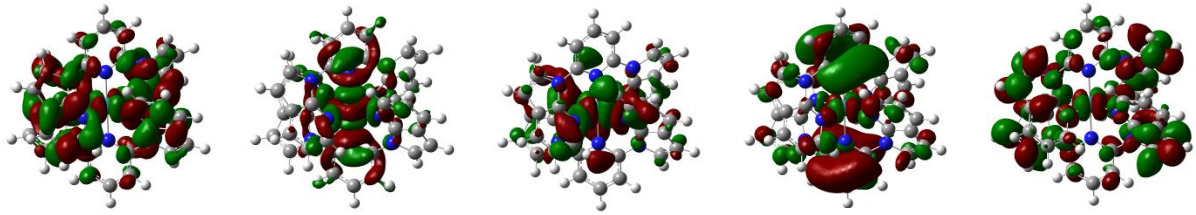
163 165 166 167 168



169 170 171 172 173



174 175 176 177 180



181 182 183 187 191

Table S9. Transitions for complex **3**:

Excited State	Excition Energy (eV)	Wavelength (nm)	f	Transistion	
1	3.0655	404.45	0.0045	169 → 170 169 → 175	95.74% 2.18%
2	3.1804	389.84	0.018	168 → 170 169 → 173	86.51% 6.86%
3	3.2789	378.12	0.0104	169 → 171	94.77%
4	3.3019	375.50	0.0129	169 → 173 169 → 183 168 → 170 169 →181	69.30% 10.26% 8.93% 2.44%
6	3.4337	361.08	0.0159	168 → 173 168 → 183 168 → 176 167 → 182	81.18% 5.18% 3.00% 2.68%
7	3.4422	360.18	0.0161	168 → 172 168 → 182 168 → 177 169 → 174	70.32% 14.60% 4.22% 2.86%
9	3.5807	346.25	0.0808	169 → 174 167 → 173 166 → 170	86.72% 2.77% 2.15%
10	3.586	345.75	0.0001	167 → 170 168 → 174 168 → 171 169 → 177 163 → 170	71.85% 11.70% 6.19% 5.78% 2.05%
11	3.5958	344.80	0.0542	169 → 175 169 → 170	92.18% 2.13%
12	3.6625	338.52	0.0018	168 → 175 168 → 170	94.74% 2.14%
14	3.7284	332.54	0.0009	168 → 182 168 → 172 167 → 173 168 → 177 168 → 180 167 → 183	23.46% 20.77% 20.17% 18.57% 3.47% 3.15%
15	3.7639	329.40	0.0089	167 → 171 169 → 176 163 → 171	84.54% 8.87% 3.24%
16	3.8278	323.91	0.0048	168 → 177 167 → 173 167 → 183 163 → 173	43.10% 40.53% 3.38% 2.05%
17	3.8388	322.98	0.0274	169 → 176 167 → 171 169 → 173	85.72% 7.78% 2.14%
18	3.8452	322.44	0.0047	167 → 172 167 → 182 168 → 173 168 → 176 168 → 183 167 → 180 163 → 182	59.81% 16.29% 5.26% 3.58% 3.03% 2.09% 2.01%
19	3.8896	318.76	0.0065	168 → 176 168 → 173 165 → 170	86.57% 4.08% 2.63%

21	4.0302	307.64	0.0004	167 → 174 169 → 183 163 → 174	84.74% 4.71% 3.16%
Excited State	Excition Energy (eV)	Wavelength (nm)	f	Transistion	
22	4.0529	305.92	0.0467	166 → 170 168 → 177 168 → 182 165 → 171 167 → 173 167 → 176	44.29% 15.99% 14.22% 7.17% 4.46% 3.58%
23	4.0602	305.37	0.0034	169 → 183 169 → 173 169 → 181 167 → 174 165 → 183 169 → 191 169 → 187	39.16% 18.68% 13.69% 9.73% 4.01% 3.69% 3.30%
24	4.0621	305.22	0.0756	165 → 170 166 → 171 167 → 177 167 → 182 167 → 172 168 → 173 168 → 176	47.53% 13.11% 10.83% 7.30% 6.51% 2.72% 2.01%
25	4.1117	301.54	0.1997	166 → 170 167 → 173 168 → 182 168 → 177 165 → 171 168 → 180 169 → 174 168 → 172	29.50% 17.74% 14.97% 12.55% 5.77% 4.34% 3.10% 3.06%
26	4.1209	300.87	0.0135	167 → 172 165 → 170 167 → 182 168 → 183 166 → 171 167 → 180 163 → 182	27.63% 22.53% 20.35% 7.00% 3.74% 3.18% 2.53%

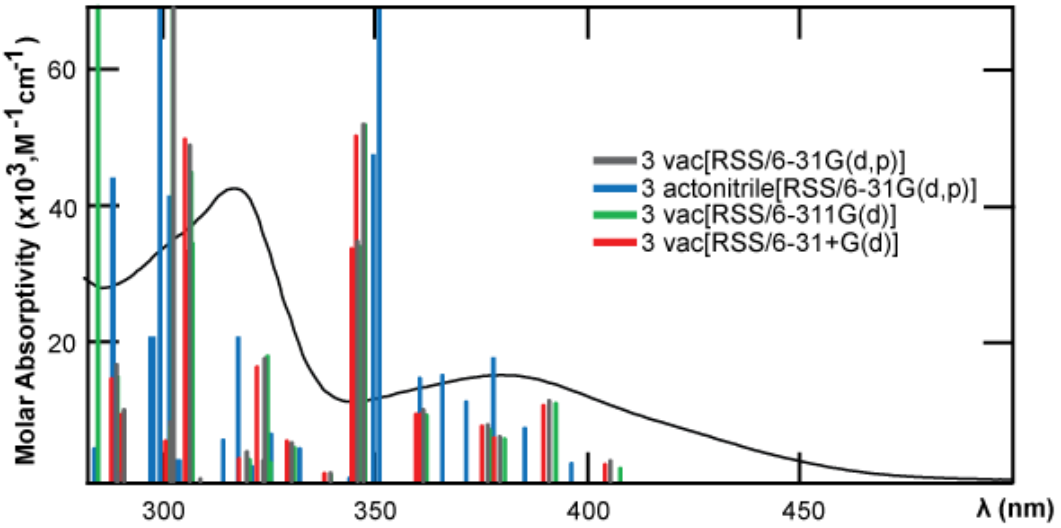


Figure S18. Comparison of basis sets and PCM solvation for calculated DFT spectrum of complex **3**.