Supporting information (SI)

Ruthenium(II) [3+2+1] Mixed Ligand Complexes: Substituent Effect On Photolability, Photooxidation of Bases, Photocytotoxicity and Photonuclease Activity

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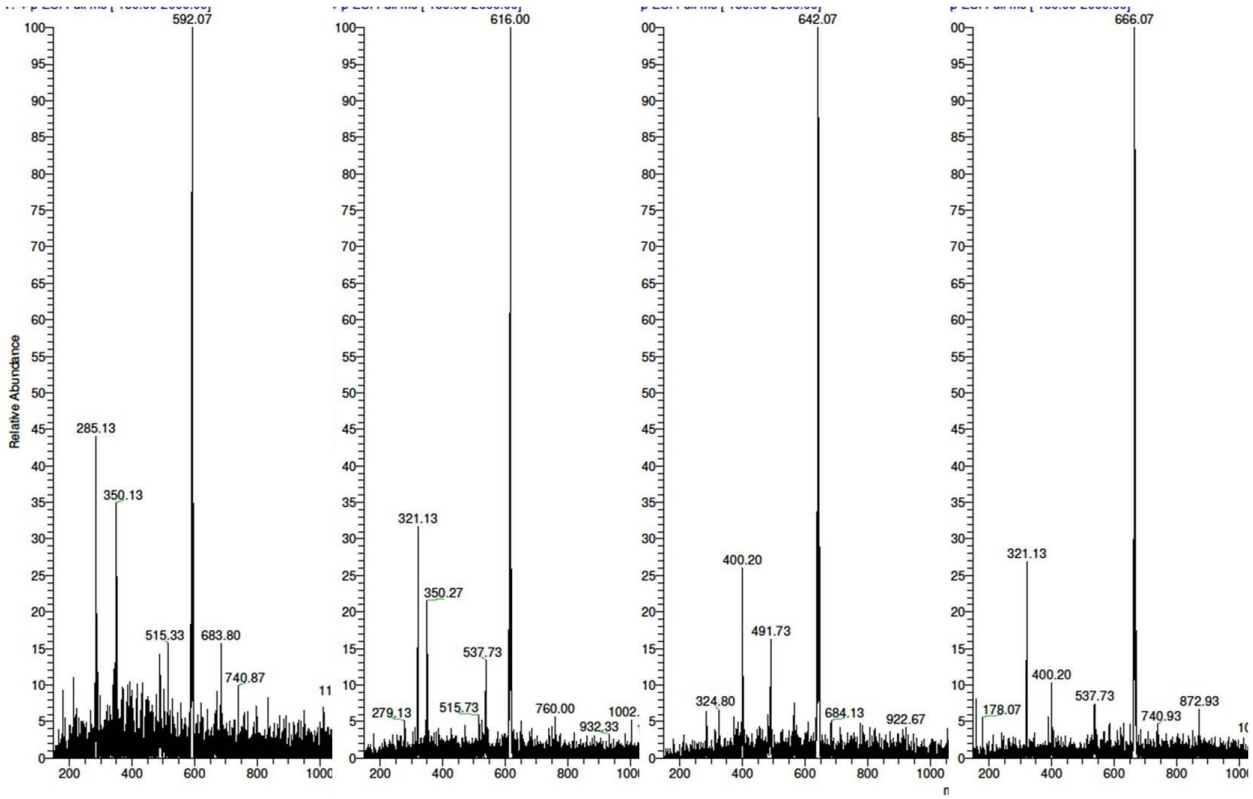

Fig. S1 ESI-MS spectra of complexes **1-4** in acetonitrile.

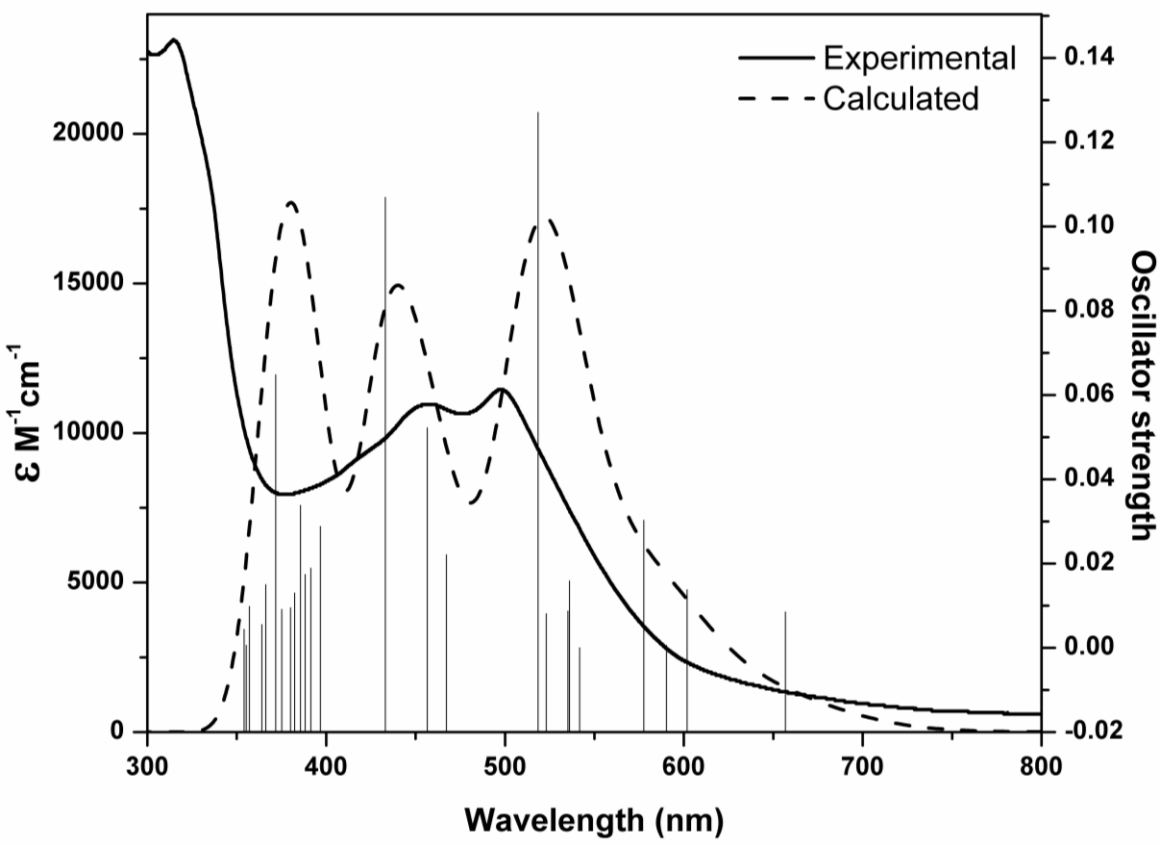

Fig. S2 Experimental (solid line) and calculated (dotted line) absorption spectra with the corresponding stick spectra of $[Ru(itpy)(phen)Cl]^+$. Each stick spectrum is composed of the δ-functions at the excitation energies obtained from TDDFT calculations, with their intensities equal to the calculated oscillator strength (in vaccum).

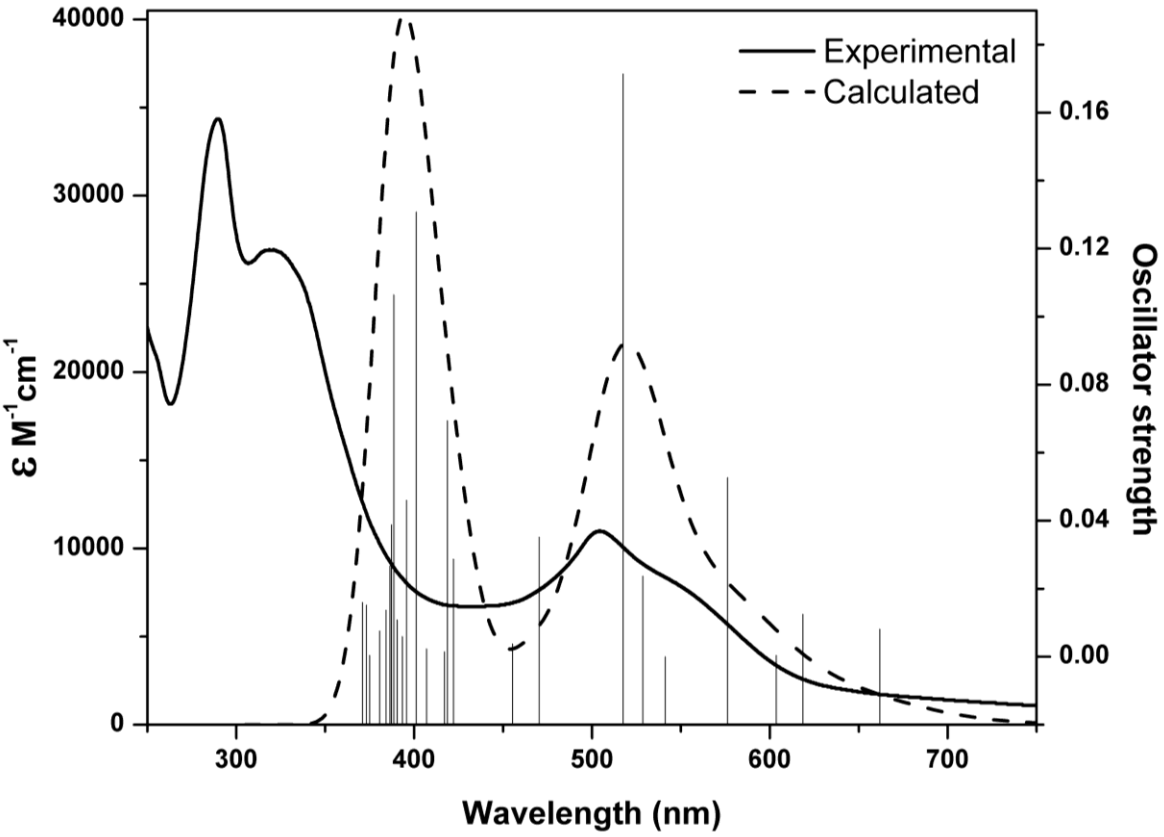

Fig. S3 Experimental (solid line) and calculated (dotted line) absorption spectra with the corresponding stick spectra of $[Ru(bitpy)(bpy)Cl]^+$. Each stick spectrum is composed of the δ-functions at the excitation energies obtained from TDDFT calculations, with their intensities equal to the calculated oscillator strength (in vaccum).

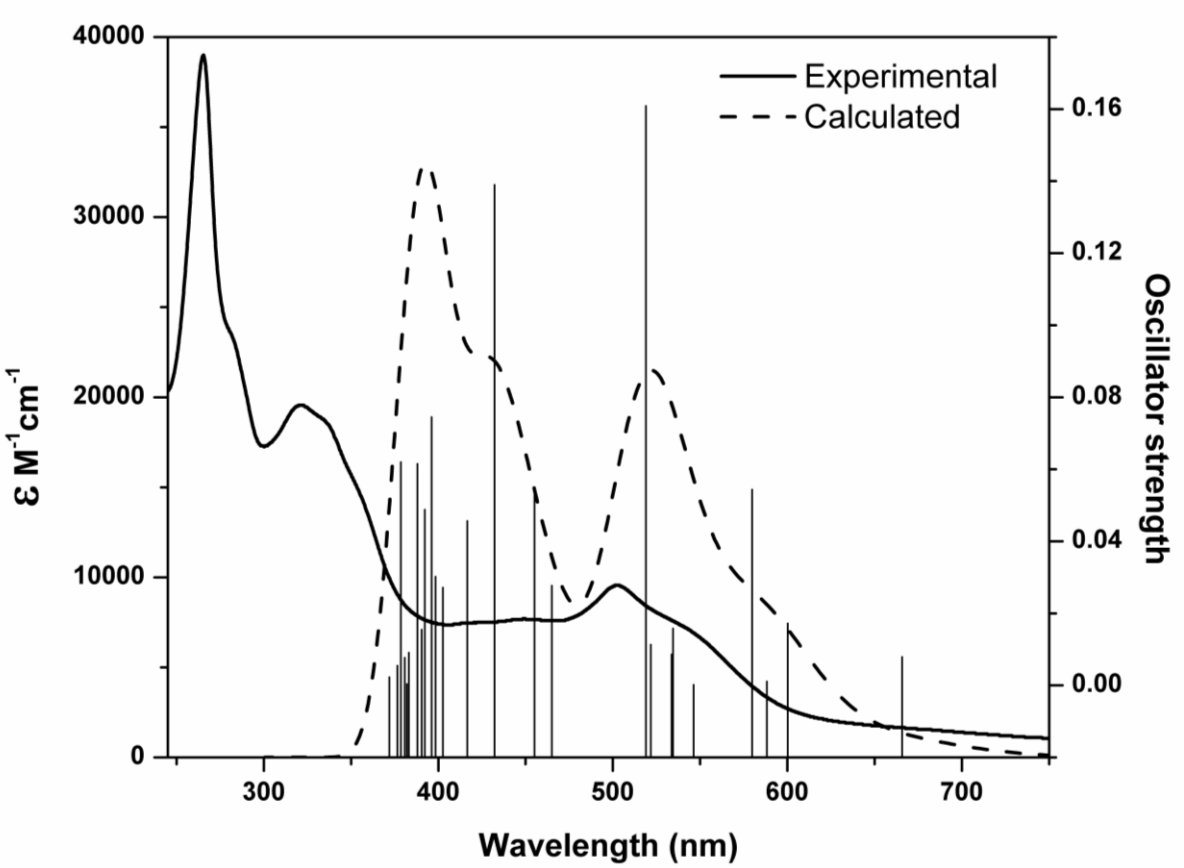

Fig. S4 Experimental (solid line) and calculated (dotted line) absorption spectra with the corresponding stick spectra of $[Ru(bitpy)(phen)Cl]^+$. Each stick spectrum is composed of the δ-functions at the excitation energies obtained from TDDFT calculations, with their intensities equal to the calculated oscillator strength (in vaccum).

Cartesian coordinates in Ångstroms for optimized structures of complexes considered in this work. All calculations used B3LYP functional and LanL2DZ basis set for all atoms.

Cartesian coordinates of complex **1**

Ru	-0.00193	-3.87462	0.65664
Cl	-1.00393	-2.81662	2.58964
N	-1.84393	-4.00662	-0.26636
C	-2.61593	-5.10262	-0.42236
H	-2.35293	-5.91762	-0.00936
C	-3.78993	-5.07162	-1.17336
H	-4.31193	-5.85962	-1.27736
C	-4.19093	-3.89162	-1.76536
H	-4.99493	-3.85462	-2.26936
C	-3.40793	-2.76362	-1.61436
H	-3.66993	-1.94062	-2.00836
C	-2.22993	-2.84662	-0.87636
C	-1.28293	-1.72762	-0.73936
C	-1.50293	-0.40962	-1.09736
H	-2.33193	-0.14762	-1.48136
C	-0.48893	0.53338	-0.88836
C	0.73107	0.11638	-0.32836
H	1.43907	0.73638	-0.19936
C	0.88807	-1.21362	0.03464
N	-0.10893	-2.10662	-0.17436
C	2.05007	-1.81162	0.72164
C	3.25407	-1.14462	0.91964
H	3.36107	-0.24862	0.61864
C	4.30007	-1.80062	1.56264
H	5.12807	-1.35862	1.70764
C	4.11707	-3.11062	1.98664
H	4.82307	-3.58262	2.41464
C	2.88707	-3.71962	1.77564
H	2.76207	-4.60962	2.08064
N	1.86107	-3.10262	1.15664
C	-0.71693	1.95638	-1.16336
N	0.18507	2.91038	-0.99336
C	-0.48093	4.09838	-1.29036
C	-1.80893	3.81538	-1.64136
N	-1.92993	2.44438	-1.56336
H	-2.59993	1.98238	-1.72136
N	0.79407	-4.95662	-0.85936
C	0.98807	-4.49262	-2.11036
H	0.74107	-3.59762	-2.31136
C	1.53807	-5.27862	-3.11536
H	1.65407	-4.92862	-3.99036
C	1.91407	-6.57962	-2.82736
H	2.31307	-7.12462	-3.49436
C	1.70007	-7.07462	-1.55336
H	1.94307	-7.96762	-1.33936
C	1.12207	-6.25062	-0.58236
C	0.80507	-6.69062	0.77864
C	1.10707	-7.96062	1.27364

H	1.52207	-8.60962	0.71564
C	0.79407	-8.25962	2.58064
H	1.02007	-9.10662	2.94364
C	0.14407	-7.31362	3.36364
H	-0.08693	-7.50762	4.26464
C	-0.15893	-6.08862	2.81064
H	-0.62893	-5.45262	3.33864
N	0.18507	-5.75162	1.54664
H	-2.56954	4.51721	-1.91303
H	-0.04606	5.07542	-1.25587

Cartesian coordinates of complex **2**

Ru	0.90563	0.01308	-0.39874
Cl	0.47422	0.07187	-2.83474
N	0.53835	2.07319	-0.3439
C	1.44279	3.07471	-0.4906
H	2.47477	2.77243	-0.62302
C	1.07303	4.42666	-0.49153
H	1.83141	5.1918	-0.61885
C	-0.28506	4.7604	-0.33536
H	-0.60375	5.79814	-0.33537
C	-1.22577	3.72895	-0.18853
H	-2.27789	3.96734	-0.07689
C	-0.80227	2.38906	-0.19825
C	-1.71311	1.22904	-0.0857
C	-3.1123	1.26233	0.02149
H	-3.6227	2.21904	0.05664
C	-3.83795	0.04746	0.07374
C	-3.12623	-1.17782	-0.00287
H	-3.69834	-2.09772	0.01268
C	-1.73428	-1.16274	-0.11377
N	-1.05909	0.03031	-0.1225
C	-0.84641	-2.33453	-0.27103
C	-1.30281	-3.66294	-0.30163
H	-2.35953	-3.87716	-0.18573
C	-0.38644	-4.70867	-0.49588
H	-0.72876	-5.73833	-0.52752
C	0.97674	-4.39964	-0.65861
H	1.7159	-5.17661	-0.82239
C	1.37805	-3.05701	-0.61616
H	2.41516	-2.77418	-0.75184
N	0.49803	-2.04215	-0.42276
C	-5.29154	-0.01795	0.19032
N	-5.98197	-1.16569	0.34682
C	-7.32184	-0.81428	0.41449
C	-7.46045	0.56728	0.29633
N	-6.16868	1.0626	0.15685
H	-5.93282	2.0363	0.02267
N	1.54604	-0.04121	1.57232
C	0.71976	-0.05986	2.65689
H	-0.34363	-0.042	2.45098
C	1.20315	-0.10126	3.96862
H	0.50381	-0.11607	4.79788

C	2.59565	-0.12428	4.18338
H	3.00177	-0.15679	5.18945
C	3.60039	-0.10681	3.06831
C	2.91216	-0.06416	1.77146
C	3.72345	-0.0434	0.54087
C	5.13147	-0.06063	0.5166
C	5.80285	-0.03979	-0.71542
H	6.8879	-0.05297	-0.749
C	5.04645	-0.00213	-1.90371
H	5.52587	0.0143	-2.87682
C	3.64731	0.01402	-1.82581
H	3.009	0.04213	-2.70301
N	2.99244	-0.00586	-0.62823
H	-8.33138	1.20257	0.2967
H	-8.09525	-1.55505	0.54057
C	5.93569	-0.10302	1.82924
H	7.00518	-0.1165	1.79907
C	5.14356	-0.12186	3.02651
H	5.70775	-0.1513	3.9352

Cartesian coordinates of complex **3**

Ru	0.90563	0.01308	-0.39874
Cl	0.47422	0.07187	-2.83474
N	0.53835	2.07319	-0.3439
C	1.44279	3.07471	-0.4906
H	2.47477	2.77243	-0.62302
C	1.07303	4.42666	-0.49153
H	1.83141	5.1918	-0.61885
C	-0.28506	4.7604	-0.33536
H	-0.60375	5.79814	-0.33537
C	-1.22577	3.72895	-0.18853
H	-2.27789	3.96734	-0.07689
C	-0.80227	2.38906	-0.19825
C	-1.71311	1.22904	-0.0857
C	-3.1123	1.26233	0.02149
H	-3.6227	2.21904	0.05664
C	-3.83795	0.04746	0.07374
C	-3.12623	-1.17782	-0.00287
H	-3.69834	-2.09772	0.01268
C	-1.73428	-1.16274	-0.11377
N	-1.05909	0.03031	-0.1225
C	-0.84641	-2.33453	-0.27103
C	-1.30281	-3.66294	-0.30163
H	-2.35953	-3.87716	-0.18573
C	-0.38644	-4.70867	-0.49588
H	-0.72876	-5.73833	-0.52752
C	0.97674	-4.39964	-0.65861
H	1.7159	-5.17661	-0.82239
C	1.37805	-3.05701	-0.61616
H	2.41516	-2.77418	-0.75184
N	0.49803	-2.04215	-0.42276
C	-5.29154	-0.01795	0.19032
N	-5.98197	-1.16569	0.34682

N	-6.16868	1.0626	0.15685
H	-5.93282	2.0363	0.02267
N	1.54604	-0.04121	1.57232
C	0.71976	-0.05986	2.65689
H	-0.34363	-0.042	2.45098
C	1.20315	-0.10126	3.96862
H	0.50381	-0.11607	4.79788
C	2.59565	-0.12428	4.18338
H	3.00177	-0.15679	5.18945
C	3.45045	-0.10535	3.07237
H	4.52466	-0.12313	3.21698
C	2.91216	-0.06416	1.77146
C	3.72345	-0.0434	0.54087
C	5.13147	-0.06063	0.5166
H	5.69766	-0.09048	1.44073
C	5.80285	-0.03979	-0.71542
H	6.8879	-0.05297	-0.749
C	5.04645	-0.00213	-1.90371
H	5.52587	0.0143	-2.87682
C	3.64731	0.01402	-1.82581
H	3.009	0.04213	-2.70301
N	2.99244	-0.00586	-0.62823
C	-7.46045	0.56728	0.29633
C	-8.60427	1.37687	0.30911
H	-8.50533	2.43807	0.40385
C	-9.85791	0.55767	0.25057
H	-10.72756	1.18096	0.26095
C	-7.32184	-0.81428	0.41449
C	-8.43282	-1.65442	0.56885
H	-8.2937	-2.71177	0.65574
C	-9.74469	-0.87078	0.55744
H	-10.58908	-1.51729	0.67548

Cartesian coordinates of complex **4**

Ru	1.66116	0.01443	-0.39727
Cl	1.29773	0.10468	-2.84261
N	1.31976	2.07867	-0.32767
C	2.24085	3.0697	-0.43672
H	3.27204	2.75522	-0.54462
C	1.88876	4.42638	-0.43055
H	2.66017	5.18292	-0.52715
C	0.53129	4.77606	-0.30739
H	0.22612	5.81785	-0.30276
C	-0.42645	3.75555	-0.19957
H	-1.47803	4.00668	-0.11357
C	-0.02014	2.41041	-0.21467
C	-0.94813	1.26125	-0.14137
C	-2.3494	1.31085	-0.07248
H	-2.84906	2.27299	-0.03851
C	-3.09002	0.10506	-0.05301
C	-2.39305	-1.12818	-0.12365
H	-2.97812	-2.04	-0.13256
C	-0.99866	-1.13052	-0.19656

N	-0.30851	0.05433	-0.17369
C	-0.122	-2.31181	-0.34251
C	-0.5943	-3.63382	-0.39968
H	-1.65648	-3.83531	-0.3152
C	0.31373	-4.68929	-0.57954
H	-0.04055	-5.71407	-0.63139
C	1.68474	-4.39631	-0.70118
H	2.41831	-5.18111	-0.85231
C	2.10171	-3.0595	-0.63386
H	3.14581	-2.7891	-0.73753
N	1.22955	-2.03531	-0.45457
C	-4.54987	0.05906	0.0265
N	-5.24181	-1.07931	0.17337
N	-5.39425	1.17328	-0.0343
H	-5.12139	2.134	-0.18315
N	2.24944	-0.06936	1.58925
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H	3.60699	-0.23928	5.24206
C	4.2624	-0.17494	3.1381
C	3.60935	-0.11069	1.8241
C	4.45318	-0.08734	0.61554
C	5.86099	-0.12225	0.62775
C	6.56458	-0.09778	-0.58614
H	7.6499	-0.12426	-0.59146
C	5.84022	-0.03924	-1.79335
H	6.34519	-0.01949	-2.75338
C	4.43976	-0.0061	-1.7517
H	3.82462	0.03847	-2.64464
N	3.7539	-0.02904	-0.57185
C	-6.70993	0.7099	0.07782
C	-7.95357	1.36458	0.07453
H	-8.04398	2.4421	-0.02885
C	-9.0897	0.55276	0.21259
H	-10.07421	1.01299	0.21594
C	-6.59191	-0.70964	0.21025
C	-7.74669	-1.50801	0.34915
H	-7.66226	-2.58537	0.45011
C	-8.98888	-0.86176	0.34846
H	-9.89916	-1.44561	0.45204
C	6.63014	-0.18819	1.96029
H	7.69979	-0.21523	1.95771
C	5.80692	-0.20881	3.13635
H	6.34682	-0.25466	4.05901

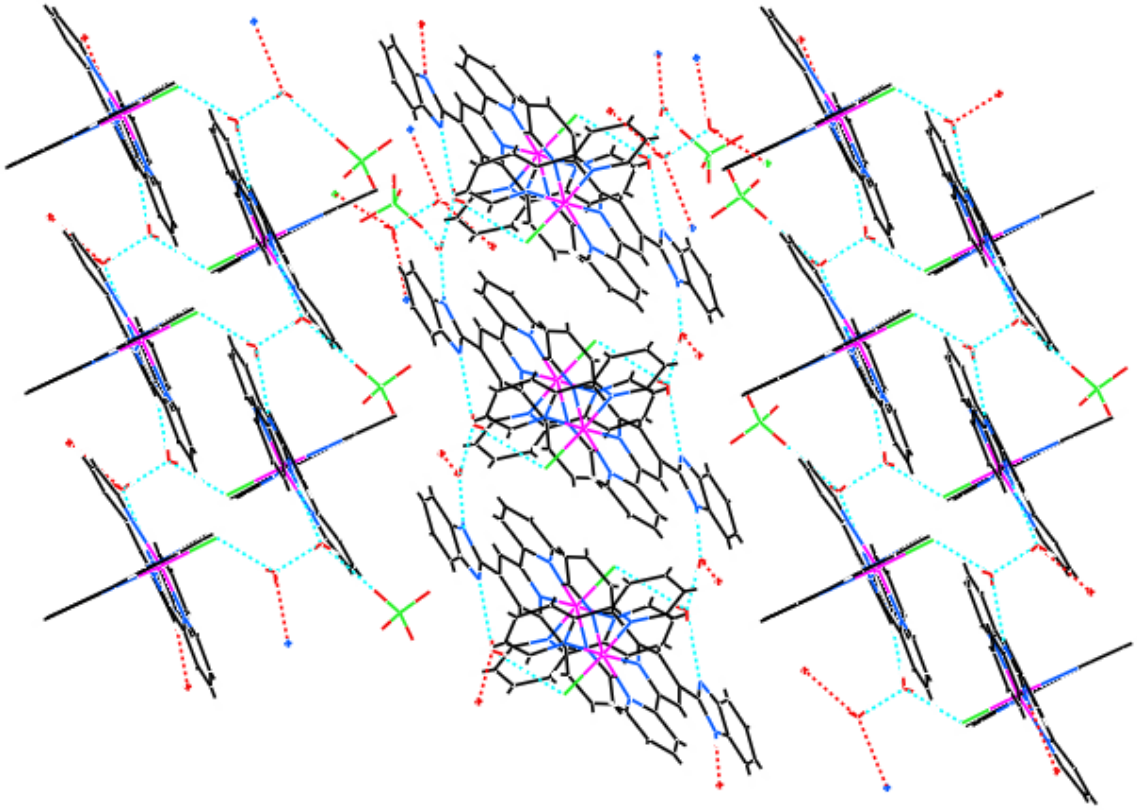

Fig. S5 Crystal Packing of complex **3**

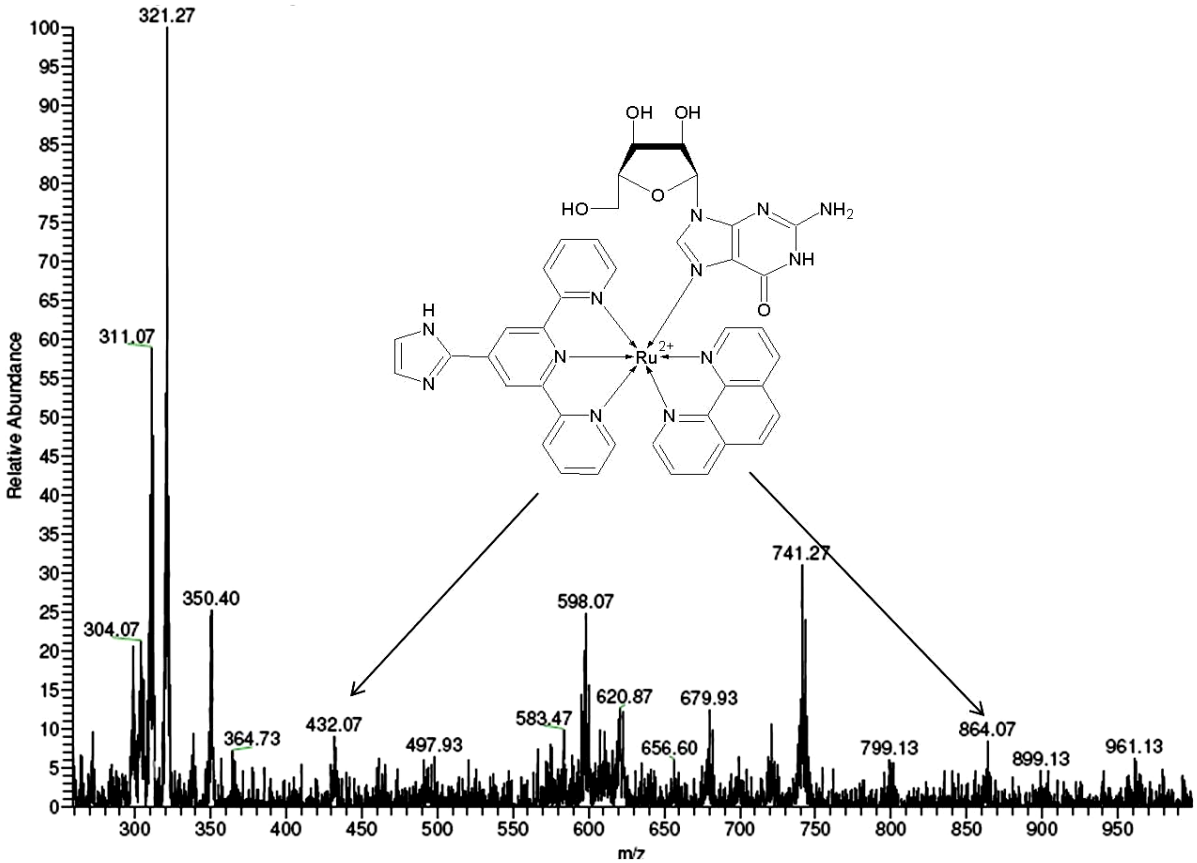

Fig. S6 ESI-MS spectra of acetone-water solution of complex **2** irradiated in the presence of guanosine.

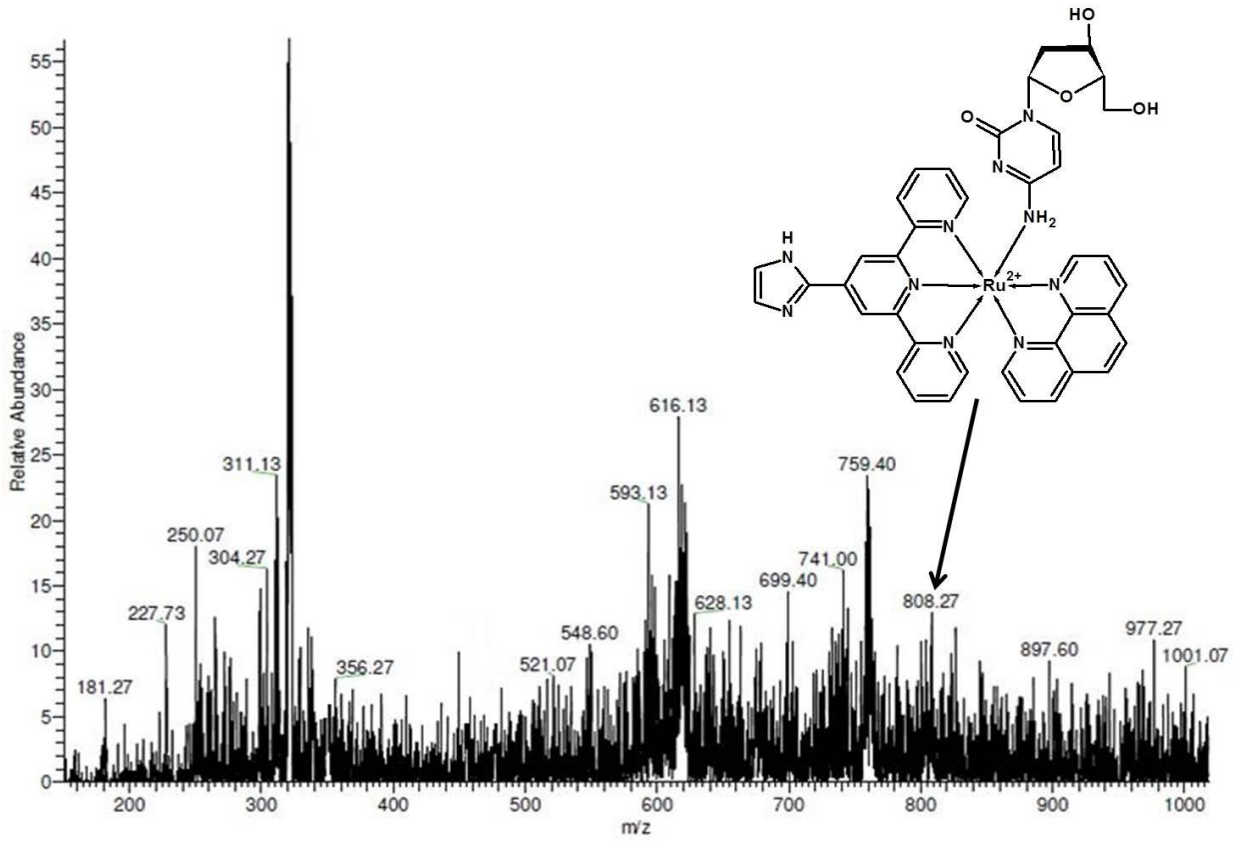

Fig. S7 ESI-MS spectra of acetone-water solution of complex **2** irradiated in the presence of deoxyguanosine.

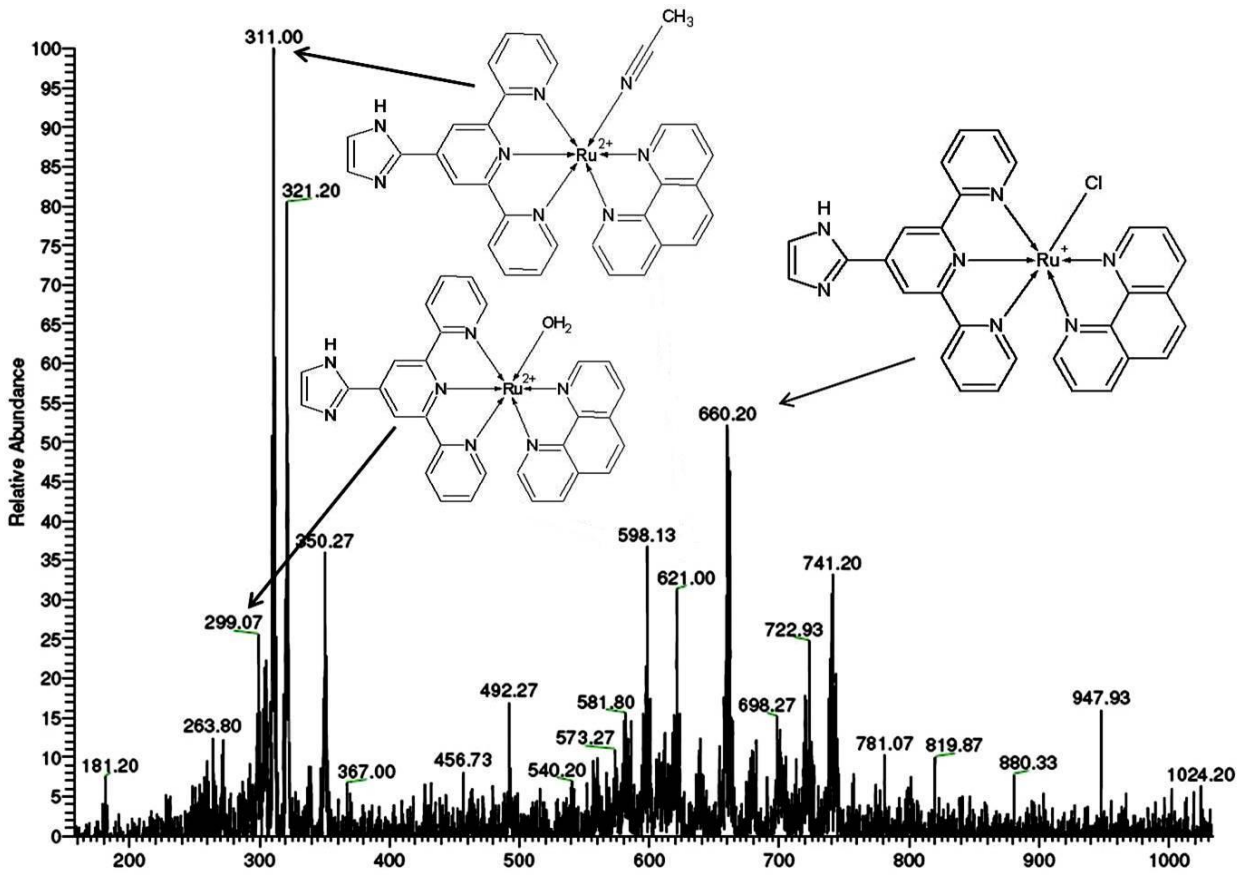

Fig. S8 ESI-MS spectra of complex **2** in acetonitrile-water solution after irradiation at 440 nm for 50 min.

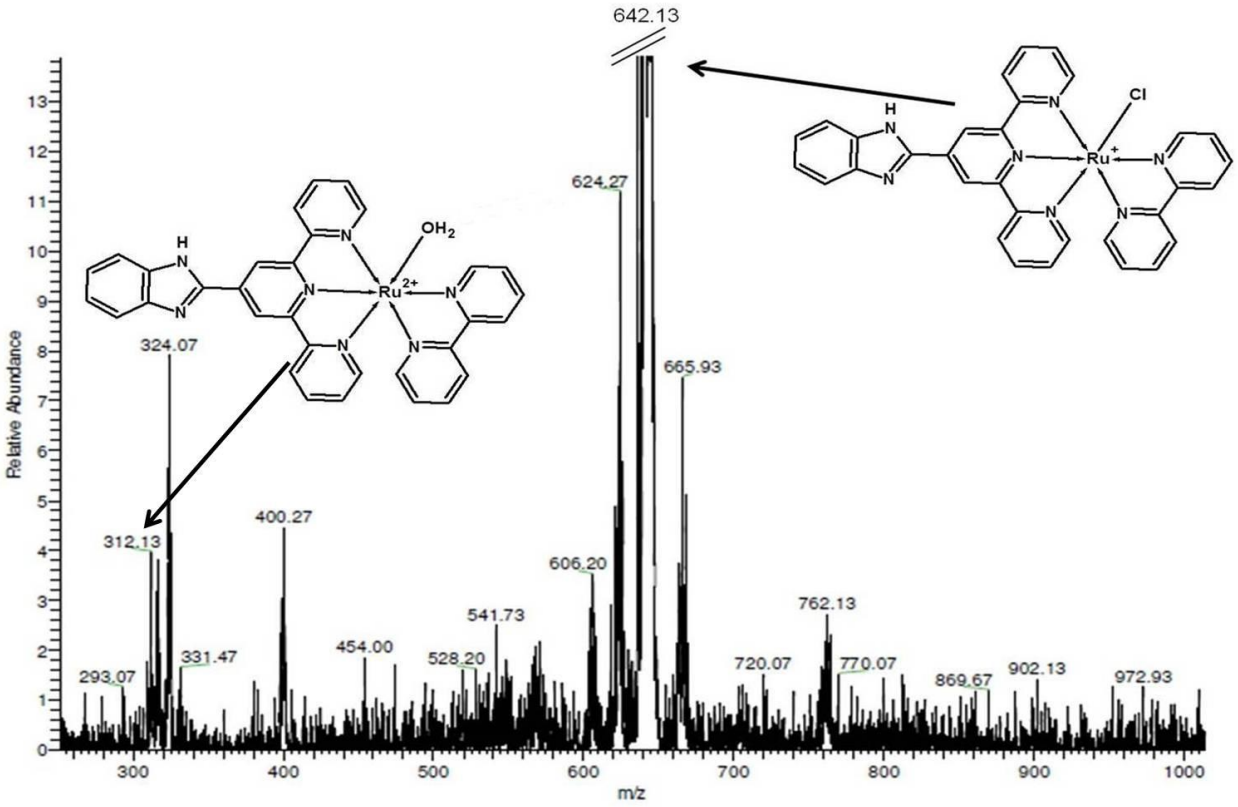

Fig. S9 ESI-MS spectra of acetone-water solution of complex **3** after irradiation at 440 nm for 50 min.

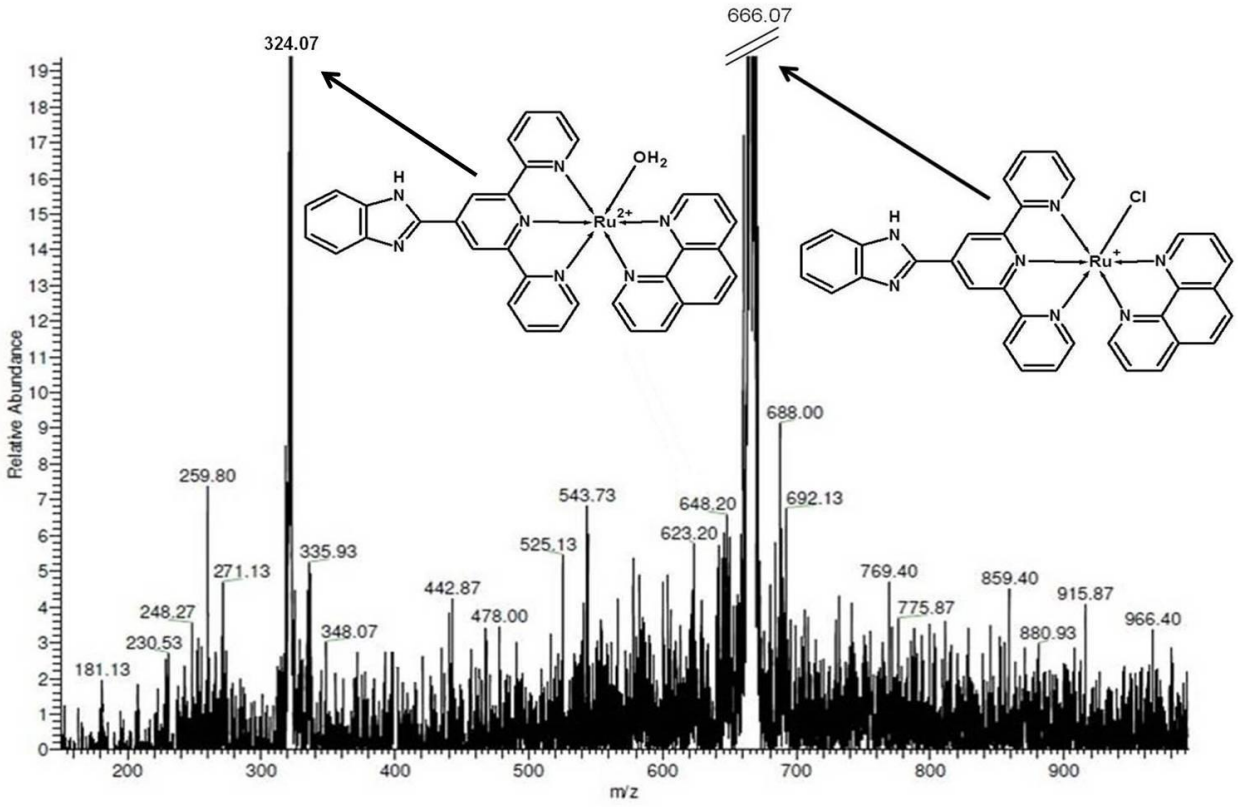

Fig. S10 ESI-MS spectra of acetone-water solution of complex **4** after irradiation at 440 nm for 50 min.

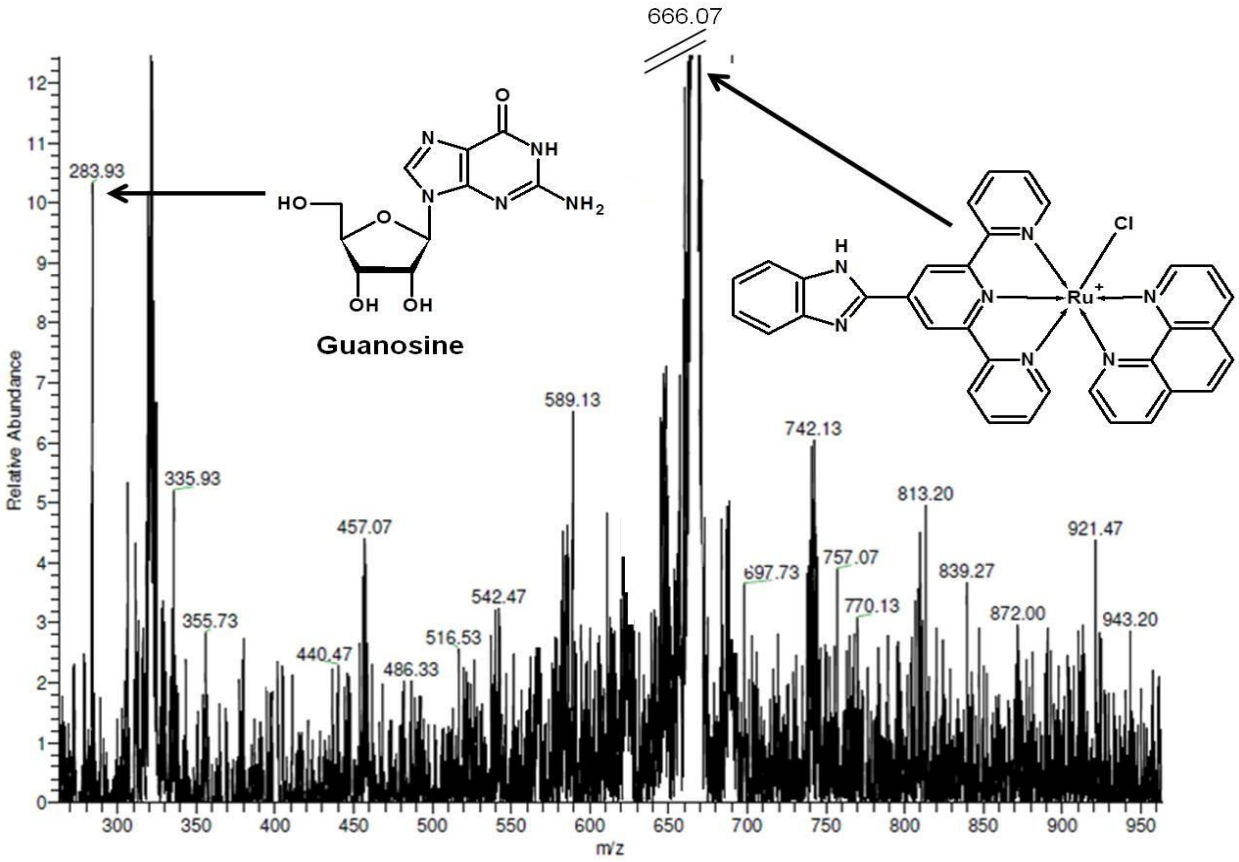

Fig. S11 ESI-MS spectra of acetone-water solution of complex **4** irradiated in the presence of guanosine.

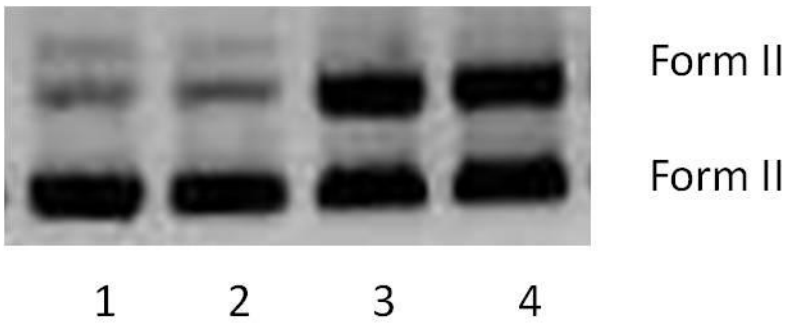

Fig. S12 Cleavage of supercoiled pUC18 by the complex **1**, when incubated for 1 h and followed by irradiation at 440 nm for 30 min. Lane 1- control DNA, lane 2, 3, 4 DNA in the presence of 6, 12, 24 μM complexes **1** respectively.

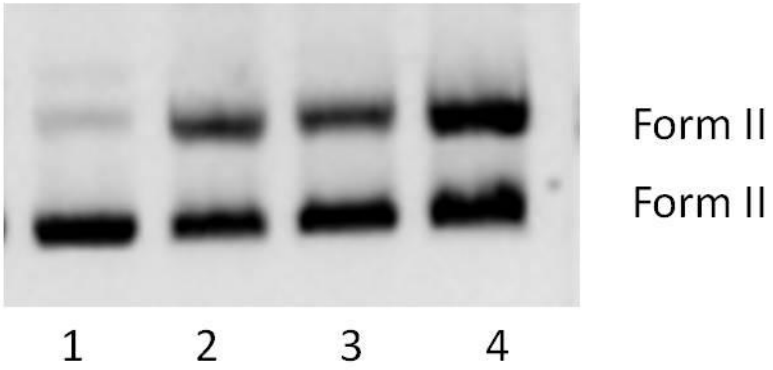

Fig. S13 Cleavage of supercoiled pUC18 by the complex **2**, when incubated for 1 h and followed by irradiation at 440 nm for 30 min. Lane 1- control DNA, lane 2, 3, 4 DNA in the presence of 6, 12, 24 μM complexes **2** respectively.

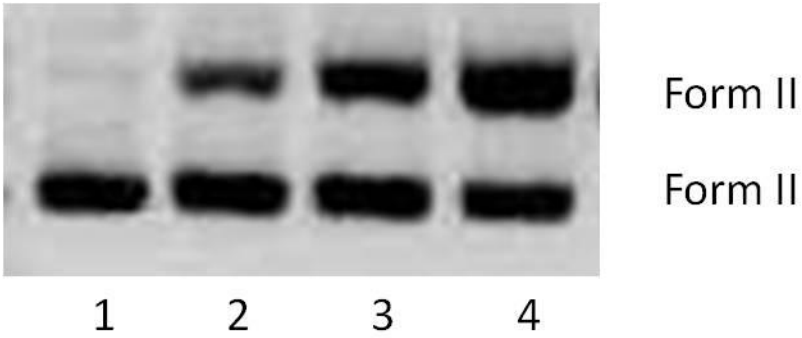

Fig. S14 Cleavage of supercoiled pUC18 by the complex **3**, when incubated for 1 h and followed by irradiation at 440 nm for 30 min. Lane 1- control DNA, lane 2, 3, 4 DNA in the presence of 6, 12, 24 μM complexes **3** respectively.

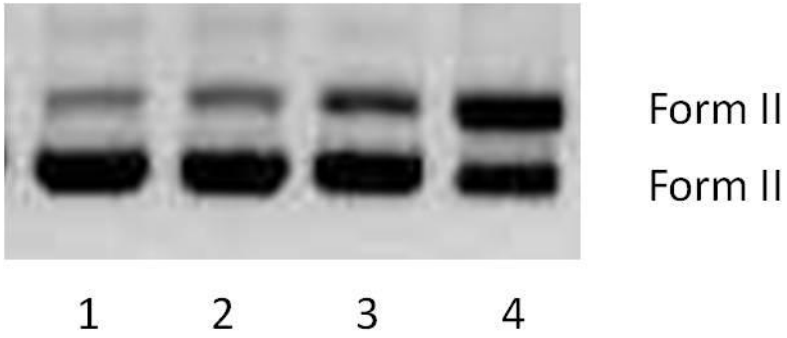

Fig. S15 Cleavage of supercoiled pUC18 by the complex **4**, when incubated for 1 h and followed by irradiation at 440 nm for 30 min. Lane 1- control DNA, lane 2, 3, 4 DNA in the presence of 6, 12, 24 μM complexes **4** respectively.