Supplementary Information

Synthesis and properties of new mononuclear Ru(II)-based photocatalysts containing 4,4′-diphenyl-2,2′-bipyridyl ligands

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1. Crystallographic Studies

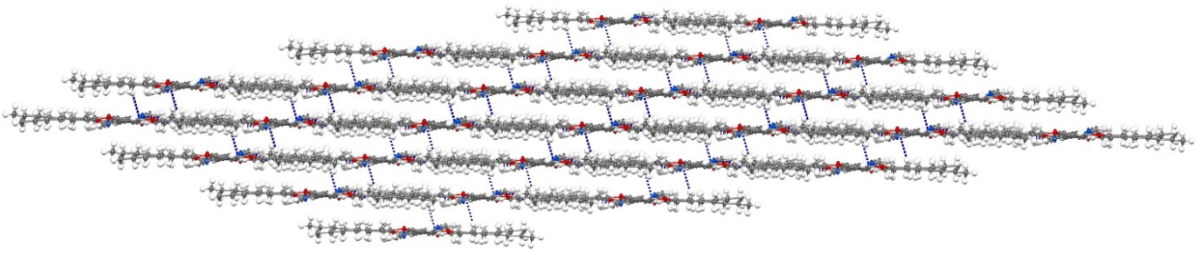

Fig. S1 Crystal packing diagram of the compound 4,4′-bis(3,5-diheptyloxyphenyl)-2,2′-bipyridyl (**L8**) showing N···H (2.610 Å), C···H (2.877 Å) and H···H (2.3909 Å) interactions.

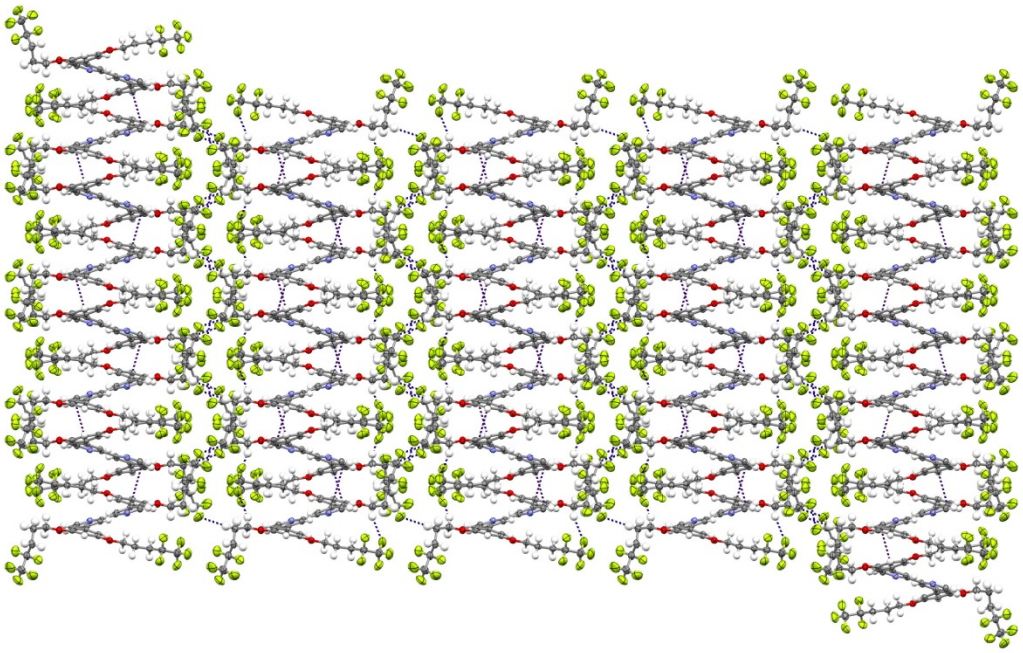

Fig. S2 Crystal packing diagram of the compound 4,4′-bis(3,5-di(4,4,5,5,5-pentafluoropentyloxy)phenyl)-2,2′-bipyridyl (**L12**) showing F···F (2.868(4) Å), F···H (2.624, 2.626(3) Å) and C···C (3.288(2) Å) interactions.

2. Spectroscopic Studies

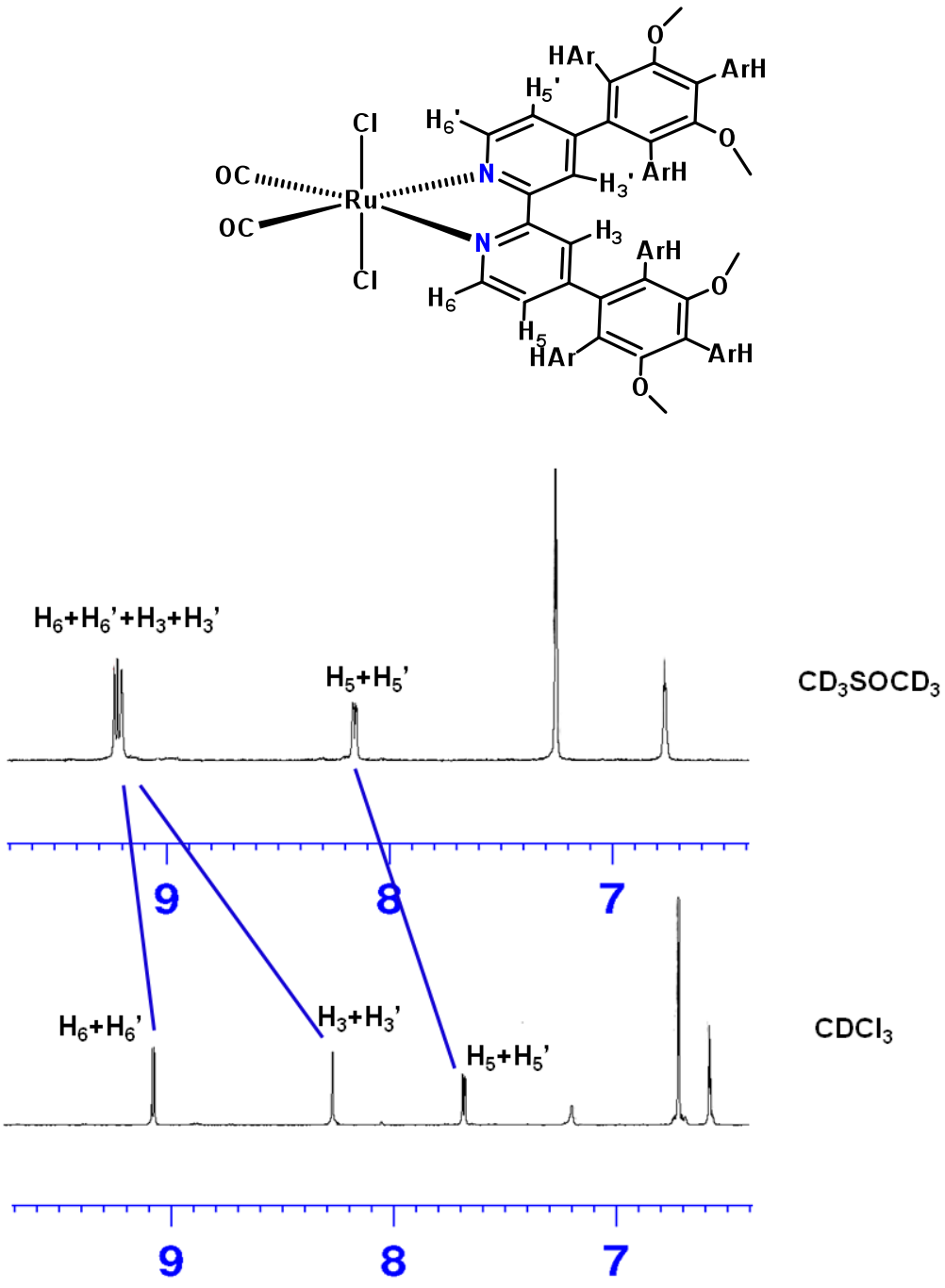

Fig. S3 Aromatic regions of the ^{1}H NMR spectra of complex **4** in CD_3SOCD_3 and $CDCl_3$.

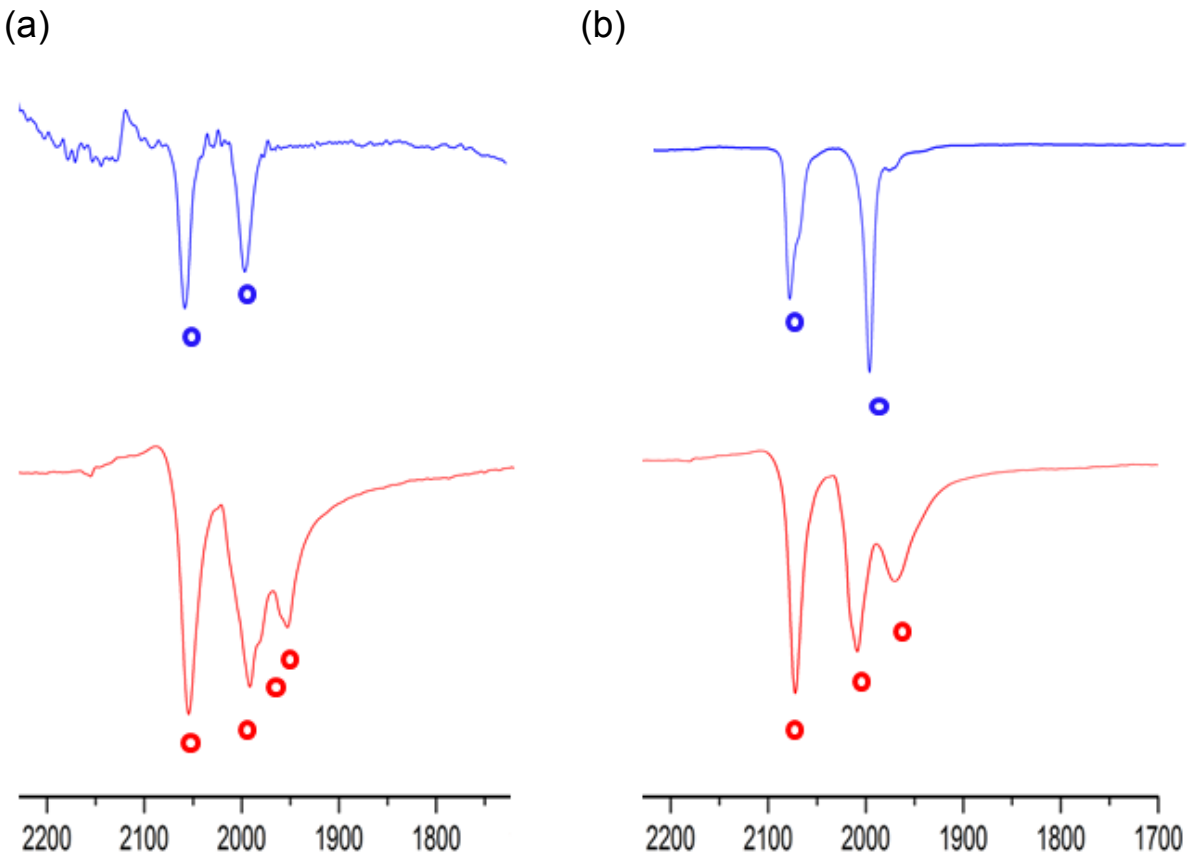

Fig. S4 IR spectra in the ν(C≡O) region of complexes **4** (a) and **10** (b) in the solid state (red) or solution (blue) [DMSO (a); dichloromethane (b)].

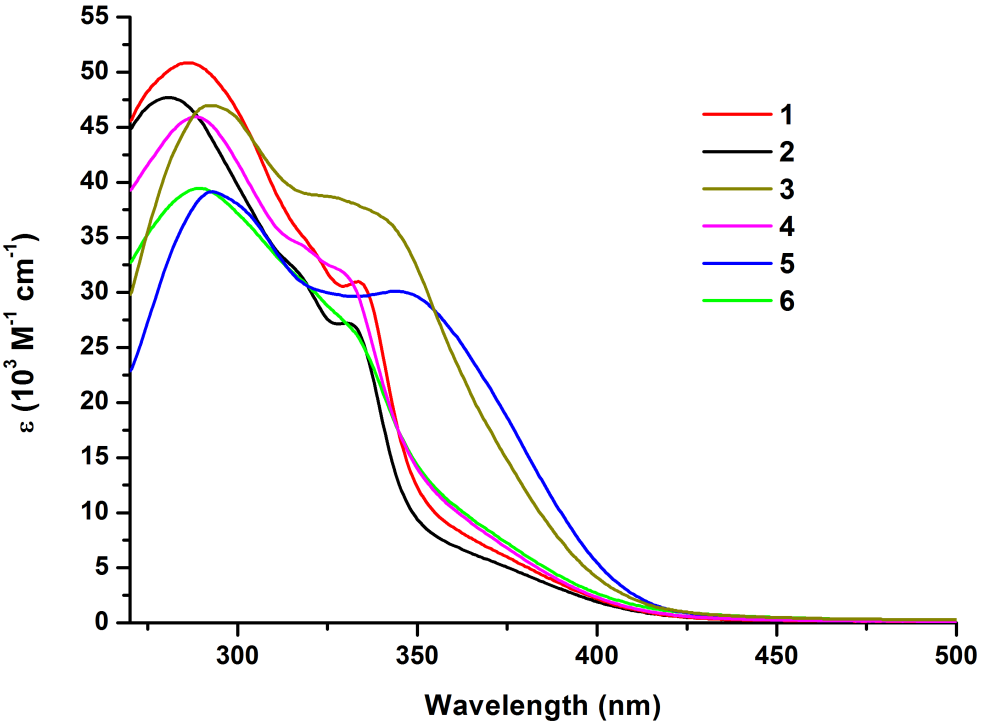

Fig. S5 UV–vis absorption spectra of complexes **1**–**6** in DMSO at 293 K.

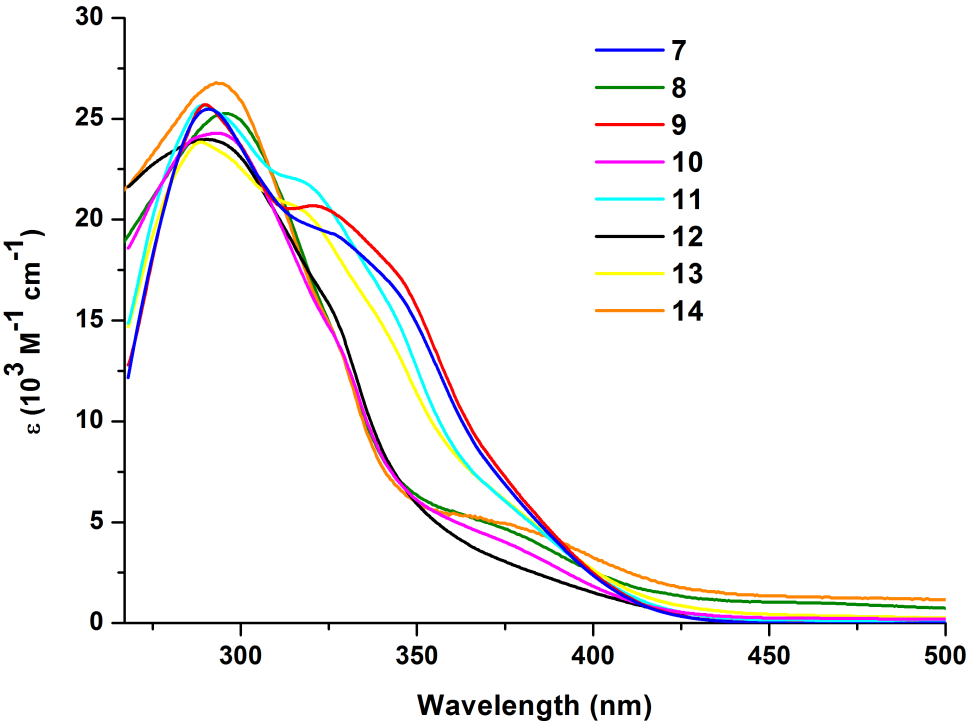

Fig. S6 UV–vis absorption spectra complexes **7**–**14** in dichloromethane at 293 K.

3. Electrochemical Studies

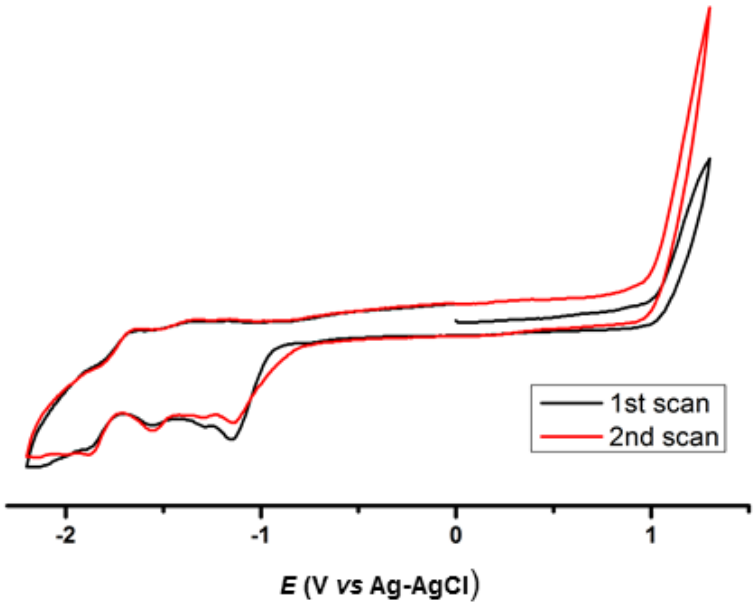

Fig. S7 Cyclic voltammograms of complex **3** in DMSO recorded at 100 mV s^{-1} (0.1 M in $[N^nBu_4]PF_6$) with a Pt disc working electrode.

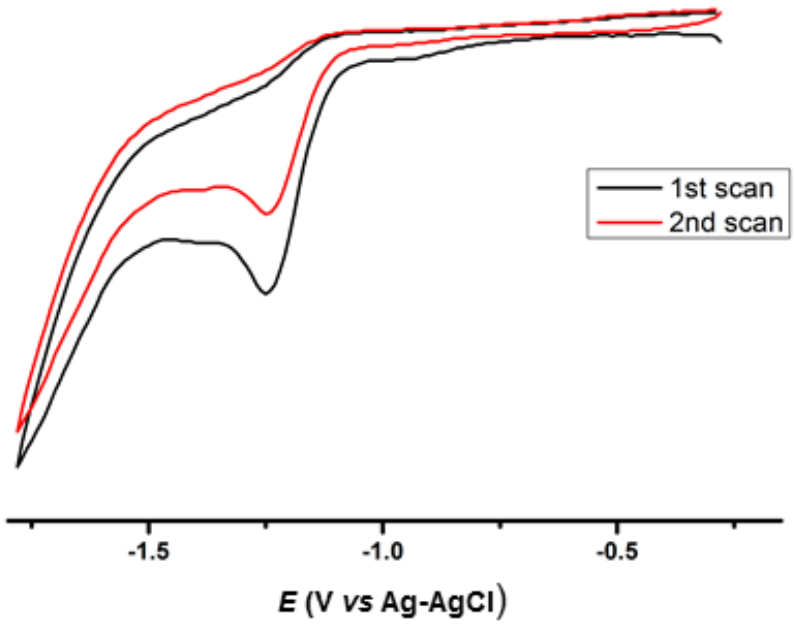

Fig. S8 Cyclic voltammograms of complex **11** in dichloromethane recorded at 100 mV s^{-1} (0.1 M in $[N^nBu_4]PF_6$) with a Pt disc working electrode.

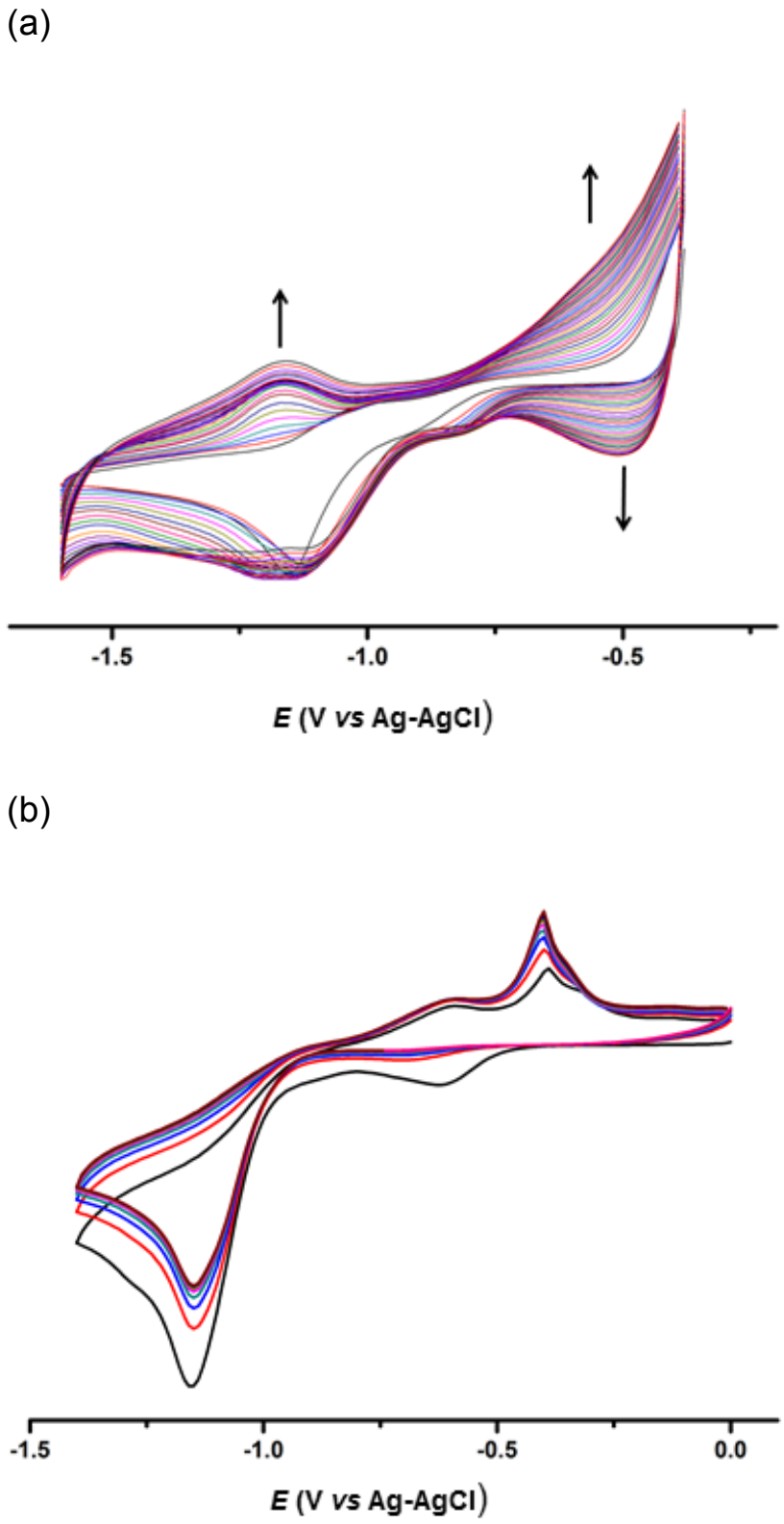

Fig. S9 Multiscan cyclic voltammograms of *trans*-$Ru^{II}Cl_2(bpy)(CO)_2$ in acetonitrile (a) and DMSO (b) recorded at 100 mV s^{-1} (0.1 M in $[N^nBu_4]PF_6$) with a Pt disc working electrode.

4. Theoretical Studies

Table S1 DFT-optimised coordinates for the complexes **3**, **4**, **8** and **11**–**13**

		3	
C	-5.55219	-3.85102	0.07227
C	-4.58326	-4.59493	-0.61435
C	-3.25598	-4.16836	-0.61171
H	-2.52352	-4.74268	-1.17094
C	-2.85943	-3.00174	0.0576
C	-3.84961	-2.2674	0.74012
H	-3.57201	-1.37773	1.29753
C	-5.17145	-2.68257	0.75284
C	0.22474	-0.792	0.02166
C	-1.10983	-1.19839	0.02985
H	-1.8997	-0.45953	-0.00479
C	-1.44994	-2.5586	0.04631
C	-0.38418	-3.47157	0.04873
H	-0.56293	-4.53988	0.08766
C	0.92126	-3.004	0.03873
H	1.75436	-3.69575	0.04894
C	-2.60902	6.30594	-0.15859
C	-2.91578	5.14586	0.56514
C	-2.01236	4.08396	0.58076
H	-2.253	3.20556	1.17239
C	-0.79209	4.14555	-0.10707
C	-0.50117	5.32304	-0.82476
H	0.42244	5.39443	-1.39105
C	-1.39201	6.38359	-0.85596
C	0.63597	0.6308	-0.00886
C	-0.27613	1.68595	-0.0389
H	-1.33844	1.48117	-0.0616
C	0.16167	3.01754	-0.0785
C	1.55007	3.22085	-0.09247
H	1.96887	4.22047	-0.09721
C	2.40492	2.12942	-0.06396
H	3.4785	2.27096	-0.06671
N	1.97096	0.8611	-0.02071
N	1.23081	-1.6991	0.0287
Ru	3.2274	-0.88784	0.03661
C	4.88876	0.03131	0.0429
C	4.1418	-2.55114	0.08833
O	5.87297	0.62619	0.0453
O	4.65555	-3.57967	0.119
Cl	3.07159	-0.79626	2.4941
Cl	3.15318	-0.90839	-2.42612
O	-6.87051	-4.17076	0.14071
O	-3.41076	7.39873	-0.24708
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H	-3.84024	5.06409	1.12379
H	-5.93171	-2.12696	1.29153
H	-4.84992	-5.49378	-1.15678
C	-4.65763	7.38318	0.43548

H	-4.52221	7.2756	1.51882
H	-5.12577	8.34551	0.2255
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C	-7.31911	-5.34873	-0.51738
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H	-7.14789	-5.29543	-1.59964
H	-6.82906	-6.2448	-0.11703

4

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H	5.88164	4.92075	0.33059
C	5.65087	2.88248	0.98596
C	4.87927	1.71447	0.90702
H	5.13963	0.83454	1.48071
C	3.72413	1.70597	0.11206
C	3.34223	2.84907	-0.6057
H	2.4709	2.81167	-1.24658
C	4.131	4.00516	-0.5259
C	0.74082	-0.63688	-0.05886
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C	2.90174	0.4751	0.03094
C	3.4845	-0.79873	-0.02411
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H	7.44806	1.02842	1.84416
H	6.4787	1.58451	3.24133
C	2.72644	5.21183	-2.03909
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O	3.86459	5.16255	-1.19313
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C	-2.67138	-1.92305	-0.09663
H	-3.10289	-2.91473	-0.14977
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H	-7.44746	1.02422	1.84926
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H	-1.80154	5.04683	-1.47988

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H	-2.71954	6.21229	-2.46951
H	-8.13039	2.2026	3.00025

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C	1.34777	-0.61736	2.90166
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H	2.65169	-1.11914	4.56047
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H	4.5265	-1.80326	3.1045
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N	3.53286	-1.43642	1.33267
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C	6.37433	-2.49699	1.34452
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O	7.10521	-2.76948	2.18972
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H	-4.53258	-0.51654	5.37769
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H	-13.10206	-0.85801	-3.70136

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C	3.9703	-1.50281	-1.02268
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C	1.49398	2.01096	-0.15589
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C	2.88483	2.06243	-0.32675
C	3.45687	3.33988	-0.42745
H	4.52082	3.46528	-0.59153

C	2.64895	4.46382	-0.34597
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C	-3.96978	-1.50339	1.02179
C	-3.20292	-0.35034	0.96794
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C	-2.64888	4.46353	0.34669
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C	1.32996	7.43296	-0.194
O	-2.16678	8.21256	0.31577
O	2.16622	8.21283	-0.3164
Cl	0.35452	5.96949	2.43512
Cl	-0.35467	5.96844	-2.43494
O	-5.93785	-2.69378	0.58472
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H	-3.59145	-2.41031	1.48137
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C	-7.27213	-2.77436	0.08731
H	-7.29006	-2.53241	-0.98517
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H	7.91251	-2.047	-0.60842
H	7.28992	-2.53222	0.98468
C	7.7594	-4.19633	-0.32836
H	7.09933	-4.89484	0.1947
H	7.69107	-4.42342	-1.3964
C	9.20305	-4.38366	0.15251
H	9.88666	-3.71985	-0.38697
H	9.2971	-4.15299	1.21889
C	9.68801	-5.80661	-0.05056
C	11.14336	-6.04681	0.3986
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F	8.90786	-6.68248	0.64896
F	9.61791	-6.15423	-1.36932
F	11.50539	-7.31675	0.1945
F	11.27246	-5.76599	1.70823
F	11.97565	-5.24432	-0.2898
C	-7.75919	-4.1966	0.32789
H	-7.09943	-4.89515	-0.1955
H	-7.6905	-4.42381	1.39587
C	-9.20304	-4.38364	-0.15248
H	-9.88635	-3.71973	0.38725

H	-9.29742	-4.15292	-1.21882
C	-9.68821	-5.80651	0.05072
C	-11.14372	-6.04644	-0.39808
F	-11.9757	-5.24384	0.29057
F	-11.50591	-7.31633	-0.19395
F	-9.61784	-6.15414	1.36946
F	-8.9084	-6.68252	-0.64901
F	-11.27311	-5.76553	-1.70766

12

C	3.94252	3.98733	-0.18764
H	4.03038	4.99572	0.19888
C	5.05504	3.1428	-0.18271
C	4.95313	1.83461	-0.67585
H	5.80117	1.1626	-0.6556
C	3.71911	1.37721	-1.16007
C	2.59727	2.21838	-1.16461
H	1.66401	1.85939	-1.57845
C	2.72024	3.5289	-0.68179
C	2.40862	-2.12086	-1.84126
C	2.48636	-0.80542	-1.38045
H	1.70177	-0.40189	-0.7532
C	3.60386	-0.01056	-1.66836
C	4.61613	-0.59648	-2.44072
H	5.4989	-0.03354	-2.72099
C	4.47686	-1.90746	-2.87211
H	5.24849	-2.37653	-3.46967
C	7.3459	2.86243	0.49549
H	7.72854	2.54336	-0.48404
H	7.08258	1.96201	1.06744
C	8.40816	3.68447	1.22171
H	8.43797	4.68071	0.76952
H	9.38145	3.21977	1.02899
C	8.26198	3.80497	2.74775
H	8.2826	2.81811	3.22117
H	9.11847	4.36394	3.13767
C	7.00491	4.50636	3.23533
C	7.05671	4.88291	4.73149
C	0.43333	4.04986	-1.1771
H	0.04555	3.17701	-0.63076
H	0.53084	3.76743	-2.2359
C	-0.50723	5.23657	-1.02032
H	-0.07868	6.10665	-1.52622
H	-0.59748	5.48842	0.04061
C	-1.88863	4.9191	-1.6032
H	-1.82483	4.73109	-2.6801
H	-2.31221	4.02232	-1.13851
C	-2.88003	6.04655	-1.38971
C	-4.26877	5.77308	-2.0026
O	6.1972	3.68717	0.3143
O	1.69993	4.43297	-0.65531
F	7.26878	3.7819	5.47641
F	8.06345	5.74635	4.96022
F	5.91106	5.45019	5.12233
F	6.7887	5.66507	2.54999
F	5.90513	3.71032	3.08181

F	-5.1136	6.77653	-1.76202
F	-4.15523	5.60601	-3.33146
F	-4.78341	4.64087	-1.476
F	-3.06802	6.27389	-0.057
F	-2.42099	7.20486	-1.9464
C	-4.29026	-2.44539	1.81886
H	-5.16793	-2.17192	2.39235
C	-3.50488	-3.52598	2.22496
C	-2.37461	-3.89581	1.48269
H	-1.75029	-4.72623	1.78693
C	-2.02748	-3.15214	0.34638
C	-2.80314	-2.05794	-0.06264
H	-2.53256	-1.51582	-0.96043
C	-3.94945	-1.72287	0.67374
C	1.28628	-3.0291	-1.50903
C	0.15636	-2.62262	-0.79533
H	0.04355	-1.59007	-0.4893
C	-0.82818	-3.54982	-0.43272
C	-0.62614	-4.88068	-0.82145
H	-1.35475	-5.64578	-0.57897
C	0.49916	-5.21271	-1.56221
H	0.66128	-6.22952	-1.89741
C	-3.11368	-5.18761	3.91808
H	-3.06215	-6.04846	3.2369
H	-2.09163	-4.8144	4.07186
C	-3.74804	-5.61493	5.23913
H	-4.82352	-5.73905	5.07872
H	-3.34988	-6.60271	5.49647
C	-3.50157	-4.70093	6.45107
H	-2.43032	-4.59724	6.65152
H	-3.94788	-5.16742	7.33488
C	-4.07341	-3.29622	6.34683
C	-4.10195	-2.54883	7.69734
C	-4.67604	-0.05388	-0.90602
H	-3.7465	0.53432	-0.94345
H	-4.63643	-0.79722	-1.71502
C	-5.89925	0.84257	-1.05399
H	-6.79639	0.22402	-0.95818
H	-5.91745	1.56628	-0.2337
C	-5.92312	1.57906	-2.39855
H	-5.87366	0.87436	-3.23528
H	-5.07662	2.26563	-2.49117
C	-7.19333	2.39409	-2.56179
C	-7.29907	3.14716	-3.90303
N	1.43305	-4.31549	-1.90759
O	-3.93015	-4.17017	3.34417
O	-4.79998	-0.70708	0.35412
F	-2.86009	-2.48046	8.21253
F	-4.8861	-3.20202	8.5749
F	-4.57243	-1.30653	7.54755
F	-5.35739	-3.31814	5.88858
F	-3.33298	-2.52165	5.49974
F	-8.44445	3.83149	-3.97799
F	-7.25005	2.27355	-4.92565
F	-6.27304	4.00783	-4.03519
F	-7.29601	3.32796	-1.57171
F	-8.29226	1.58561	-2.48098

N	3.40581	-2.66032	-2.58301
Ru	3.14723	-4.72135	-3.15071
C	2.73302	-6.53878	-3.51766
C	4.70134	-4.8539	-4.23388
O	2.4469	-7.63529	-3.71184
O	5.6511	-4.89047	-4.88092
Cl	1.79016	-3.93259	-5.04947
Cl	4.40019	-5.33095	-1.11993

13

C	-5.238	1.17591	0.66004
C	-3.92768	1.19919	1.16482
C	-3.16824	2.35513	1.08048
H	-2.16833	2.35903	1.50387
C	-3.68627	3.5287	0.49771
C	-4.99849	3.48932	0.00497
H	-5.41919	4.36742	-0.47559
C	-5.77298	2.33218	0.07725
C	-0.73252	5.87842	0.10961
C	-1.48808	4.70913	0.19982
H	-1.00806	3.74668	0.07976
C	-2.87435	4.75982	0.40425
C	-3.44607	6.03703	0.50859
H	-4.50619	6.16207	0.69628
C	-2.64149	7.16145	0.40204
H	-3.06835	8.15325	0.48434
C	5.23802	1.17592	-0.66014
C	3.92771	1.19921	-1.16492
C	3.16826	2.35515	-1.08055
H	2.16835	2.35906	-1.50394
C	3.6863	3.52871	-0.49775
C	4.99851	3.48932	-0.00502
H	5.41922	4.36741	0.47556
C	5.773	2.33218	-0.07733
C	0.73254	5.87843	-0.1096
C	1.4881	4.70914	-0.19983
H	1.00809	3.74669	-0.0798
C	2.87437	4.75983	-0.40427
C	3.44609	6.03704	-0.50858
H	4.50622	6.16209	-0.69627
C	2.64151	7.16146	-0.402
H	3.06837	8.15326	-0.48428
N	1.31612	7.09698	-0.207
N	-1.3161	7.09698	0.20704
Ru	0.00001	8.79004	0.00004
C	1.32664	10.13105	-0.21729
C	-1.32661	10.13105	0.21742
O	2.16081	10.91077	-0.35403
O	-2.16078	10.91076	0.35418
Cl	-0.39915	8.6675	-2.4281
Cl	0.39918	8.66743	2.42818
O	5.89686	-0.0069	-0.78451
H	6.77718	2.34106	0.32864
H	3.53489	0.29968	-1.62683
H	-6.77716	2.34107	-0.32872
H	-3.53486	0.29965	1.62671

C	7.23778	-0.1074	-0.30934
H	7.27561	0.12085	0.76561
H	7.87786	0.61829	-0.83174
C	-7.23775	-0.10741	0.30919
H	-7.87784	0.61826	0.8316
H	-7.27558	0.12086	-0.76576
C	-7.70123	-1.53307	0.57615
H	-7.03655	-2.22791	0.05373
H	-7.61412	-1.74377	1.64591
C	-9.14812	-1.75045	0.116
H	-9.83718	-1.09764	0.66254
H	-9.26175	-1.52864	-0.94915
C	-9.59762	-3.18519	0.33931
C	-11.08255	-3.42824	-0.03997
O	-5.89684	-0.00692	0.78438
F	-8.83403	-4.043	-0.40269
F	-9.44717	-3.52595	1.6515
F	-11.30146	-2.8988	-1.27138
F	-11.85405	-2.7632	0.85951
C	7.70126	-1.53304	-0.57634
H	7.0366	-2.2279	-0.05393
H	7.61415	-1.74372	-1.6461
C	9.14815	-1.75044	-0.1162
H	9.83721	-1.0976	-0.66273
H	9.26179	-1.52864	0.94896
C	9.59766	-3.18516	-0.33955
C	11.08259	-3.42821	0.03973
F	11.8541	-2.76333	-0.85986
F	9.44722	-3.52588	-1.65175
F	8.83409	-4.043	0.40243
F	11.30153	-2.89858	1.27106
C	-11.52301	-4.92148	-0.08105
C	-13.07026	-5.11156	-0.0549
C	-13.53039	-6.52031	-0.52619
C	-14.99467	-6.86768	-0.14662
C	11.52301	-4.92146	0.08104
C	13.07027	-5.11156	0.05511
C	13.5303	-6.52034	0.5264
C	14.99454	-6.86782	0.14677
F	11.0064	-5.57229	-0.98451
F	11.03671	-5.47199	1.21803
F	13.50016	-4.91583	-1.21324
F	13.64671	-4.19248	0.8642
F	12.72965	-7.4618	-0.02542
F	13.42881	-6.57917	1.87153
F	15.35745	-7.98199	0.79267
F	15.10318	-7.07761	-1.16863
F	15.81683	-5.87174	0.504
F	-11.00627	-5.57218	0.98452
F	-11.03688	-5.47216	-1.21803
F	-13.49997	-4.91585	1.21352
F	-13.6468	-4.19243	-0.86388
F	-12.72984	-7.46184	0.02566
F	-13.42885	-6.57915	-1.87131
F	-15.10336	-7.07759	1.16875
F	-15.35767	-7.98175	-0.79265
F	-15.81684	-5.87148	-0.50378

Table S2 Selected distances (Å) and angles (º) in the DFT-optimised structures of the complexes **3**, **4**, **8** and **11**–**13**

	3	**4**	**8**	**11**	**12**	**13**
Ru–N	2.155	2.155	2.154	2.154	2.153	2.154
Ru–N	2.154	2.155	2.154	2.154	2.156	2.154
Ru–Cl	2.464	2.463	2.463	2.464	2.463	2.464
Ru–Cl	2.464	2.464	2.465	2.464	2.463	2.464
Ru–C	1.899	1.899	1.899	1.899	1.900	1.899
Ru–C	1.899	1.899	1.899	1.899	1.899	1.899
N–Ru–N	76.42	76.45	76.45	76.38	76.31	76.40
Cl–Ru–Cl	174.40	174.13	174.37	174.29	174.29	174.30
C–Ru–C	90.15	90.09	90.15	90.13	90.07	90.14

Table S3 Contributions (%) in terms of metal and ligands to the frontier MOs computed by B3LYP/6-31g(d)/LANL2DZ for complexes **3**, **4**, **8** and **11–13**

	3				**4**				**8**				**11**				**12**				**13**			
	Ru	CO	Cl	N^N	Ru	CO	Cl	N^N	Ru	CO	Cl	N^N	Ru	CO	Cl	N^N	Ru	CO	Cl	N^N	Ru	CO	Cl	N^N
LUMO+10	6	11	0	82	0	3	0	97	2	4	0	95	7	14	0	79	0	2	0	98	7	14	0	79
LUMO+9	21	74	2	3	0	1	0	99	0	3	0	97	22	74	2	2	0	2	0	98	22	74	2	2
LUMO+8	19	62	1	19	17	53	1	29	5	8	0	88	18	59	1	22	21	73	2	4	18	59	1	23
LUMO+7	0	2	0	98	14	41	1	44	21	73	2	4	0	2	0	98	11	26	0	63	0	2	0	98
LUMO+6	20	33	1	47	15	52	1	32	19	63	1	17	25	40	1	34	14	47	1	38	25	41	1	33
LUMO+5	3	4	0	92	0	2	0	98	0	2	0	98	1	0	0	99	0	2	0	98	1	0	0	99
LUMO+4	12	16	0	72	35	51	1	13	34	52	1	13	10	12	0	78	35	51	1	13	9	12	0	79
LUMO+3	56	7	31	5	57	7	31	4	57	7	31	4	56	7	31	5	57	7	31	5	56	7	31	6
LUMO+2	1	0	0	99	1	0	0	99	1	0	0	99	1	0	0	99	0	1	0	99	1	0	0	99
LUMO+1	0	1	0	99	0	1	0	99	0	1	0	99	0	1	0	99	0	1	0	99	0	1	0	99
LUMO	1	2	1	96	1	2	1	96	1	2	1	96	1	2	1	96	1	2	1	96	1	2	1	96
HOMO	32	3	64	1	32	3	65	1	32	3	65	1	32	3	64	1	32	3	65	1	32	3	64	1
HOMO–1	29	3	67	1	28	3	68	1	28	3	68	1	29	3	67	1	28	3	68	1	29	3	68	1
HOMO–2	1	0	5	94	0	0	1	99	0	0	0	100	1	0	8	91	0	0	0	100	1	0	8	91
HOMO–3	1	0	3	96	0	0	1	99	0	0	0	100	4	1	87	8	0	0	1	99	4	1	92	4
HOMO–4	4	1	93	2	1	0	4	95	4	1	93	2	1	0	8	91	0	0	3	97	1	0	3	96
HOMO–5	4	0	93	3	0	0	1	98	4	0	93	3	4	0	93	3	0	0	2	98	4	0	93	3
HOMO–6	10	1	79	10	4	1	93	3	1	0	6	93	10	1	78	11	4	1	93	3	10	1	78	11
HOMO–7	1	0	2	97	4	0	92	4	0	0	1	98	1	0	2	97	4	0	91	4	1	0	2	97
HOMO–8	1	0	0	99	10	0	79	11	10	0	76	13	3	1	2	95	10	0	79	10	3	1	2	95
HOMO–9	1	0	1	98	2	0	2	95	1	0	2	96	1	0	1	98	2	1	2	95	1	0	1	98
HOMO–10	76	21	1	3	35	6	22	37	33	5	21	41	76	21	0	3	36	6	22	36	75	21	0	3

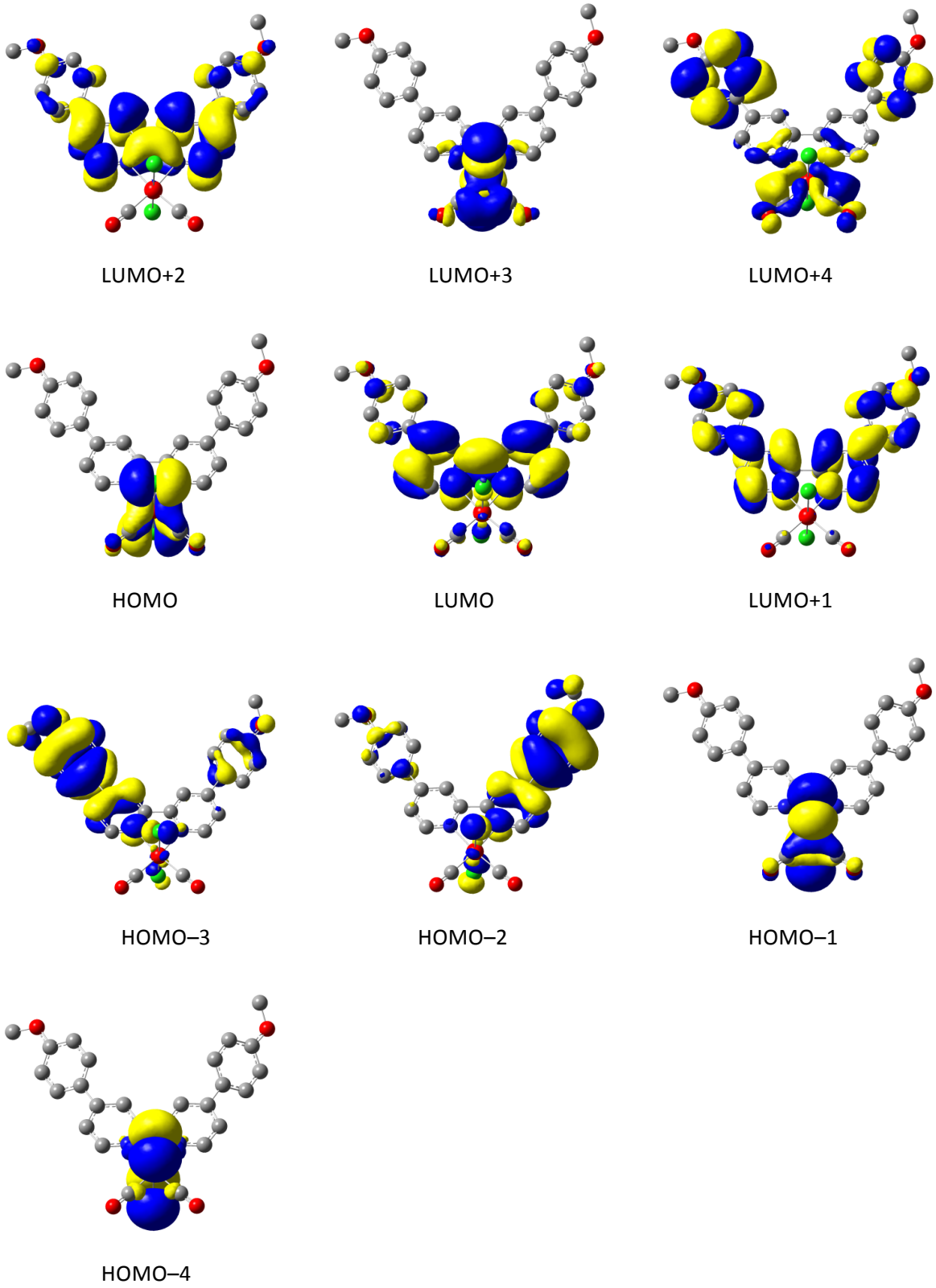

Fig. S10 B3LYP/6-31g(d)/LANL2DZ-derived contour surface diagrams of selected MOs for complex **3** (isosurface value 0.03 au).

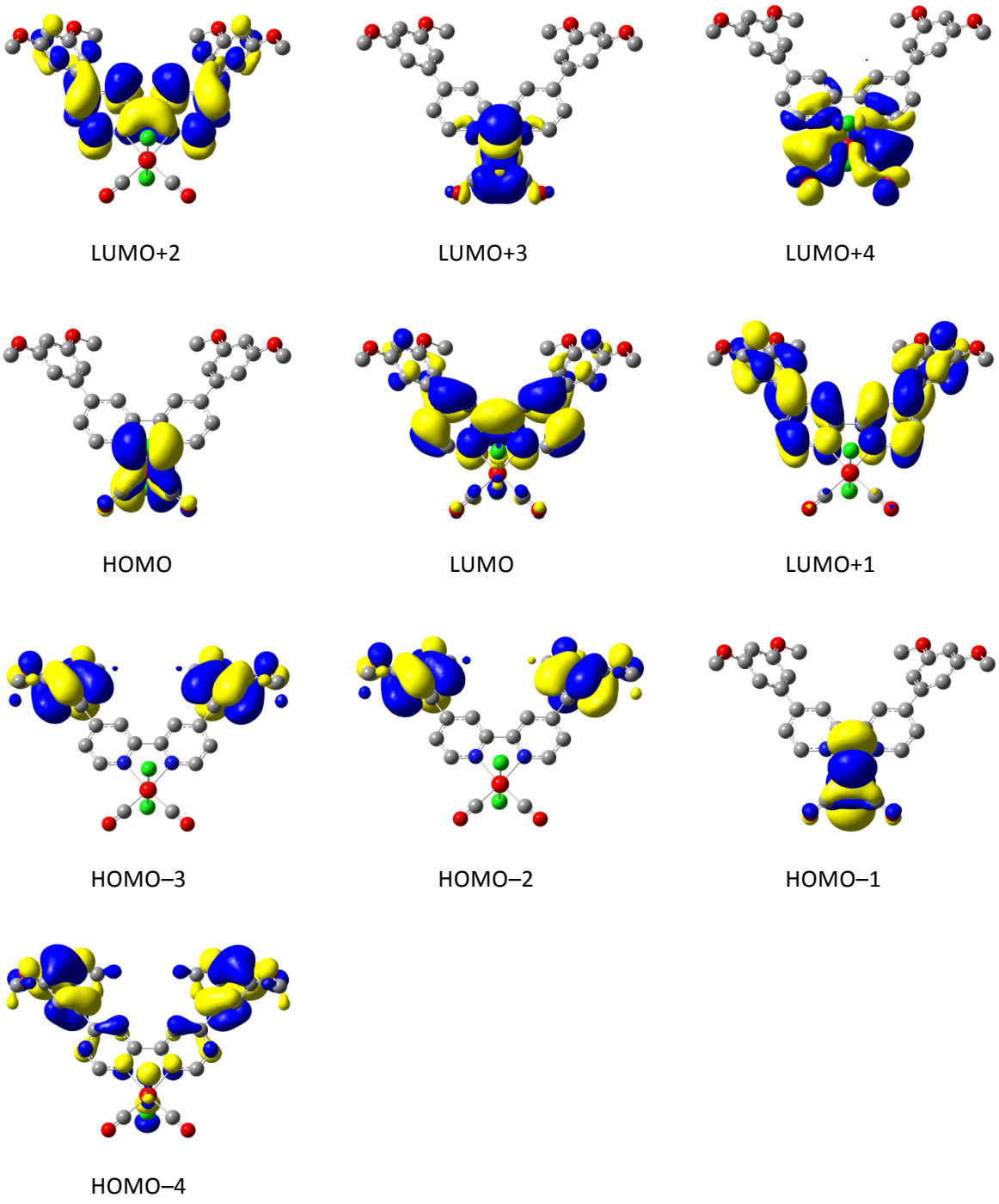

Fig. S11 B3LYP/6-31g(d)/LANL2DZ-derived contour surface diagrams of selected MOs for complex **4** (isosurface value 0.03 au).

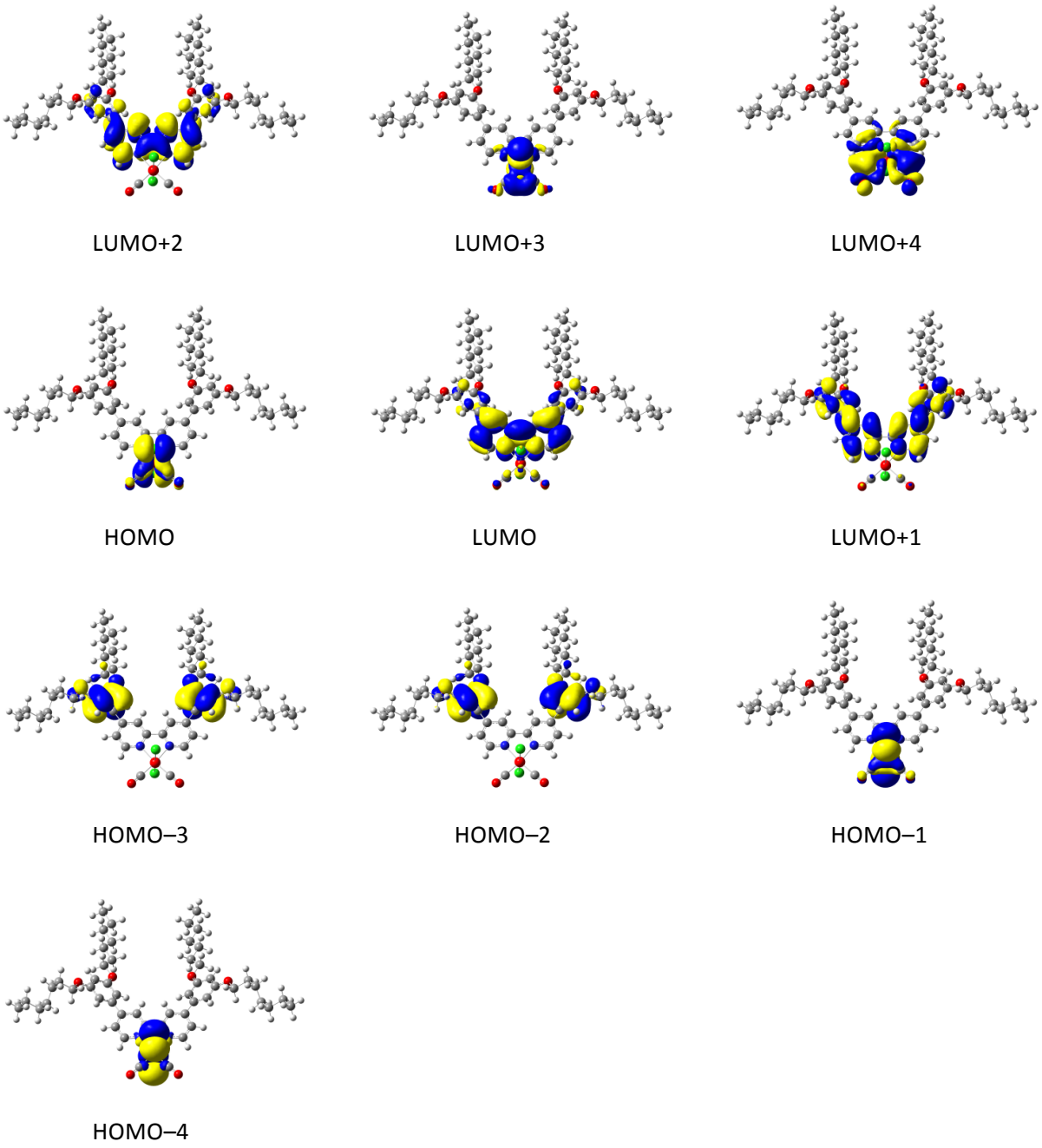

Fig. S12 B3LYP/6-31g(d)/LANL2DZ-derived contour surface diagrams of selected MOs for complex **8** (isosurface value 0.03 au).

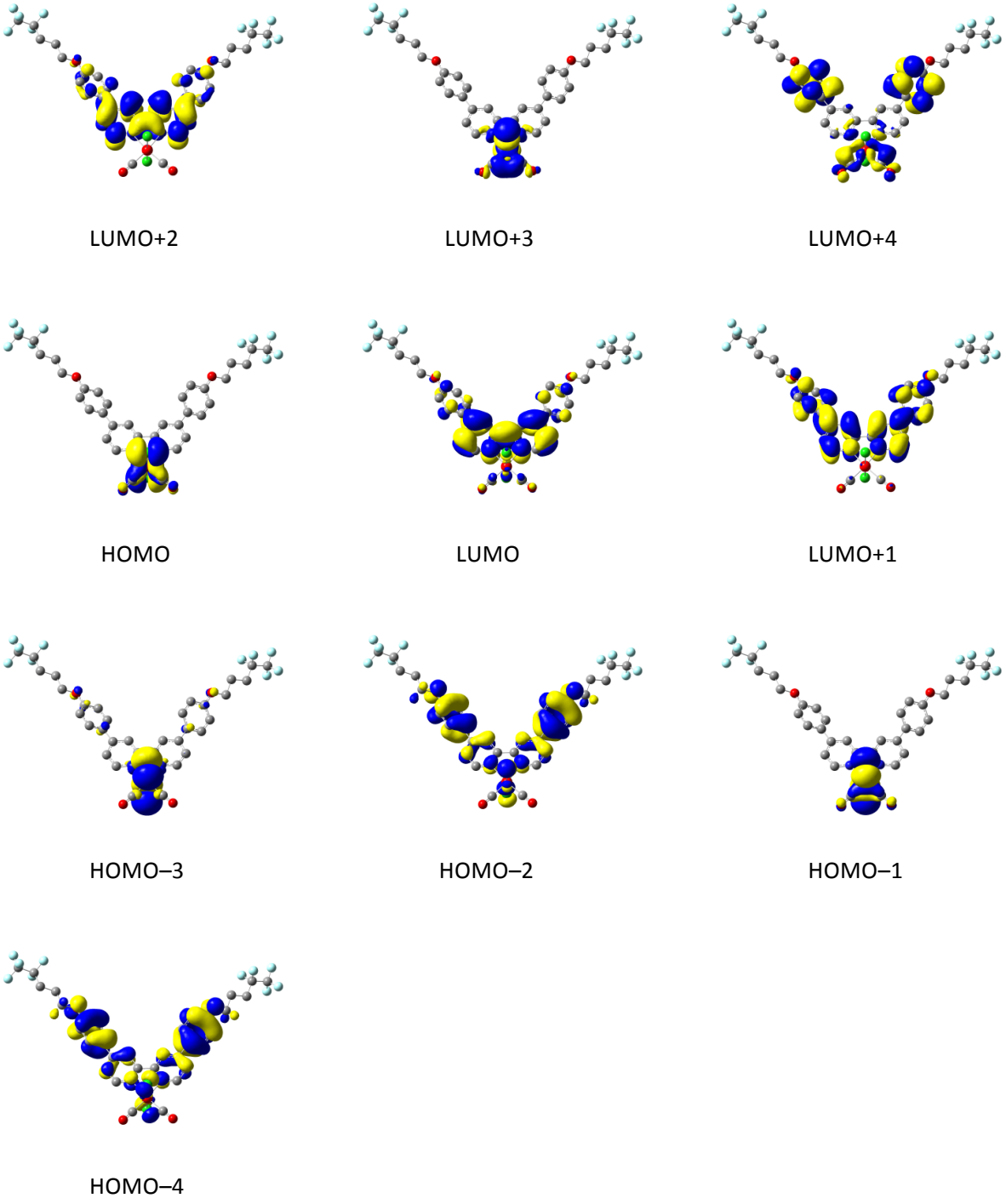

Fig. S13 B3LYP/6-31g(d)/LANL2DZ-derived contour surface diagrams of selected MOs for complex **11** (isosurface value 0.03 au).

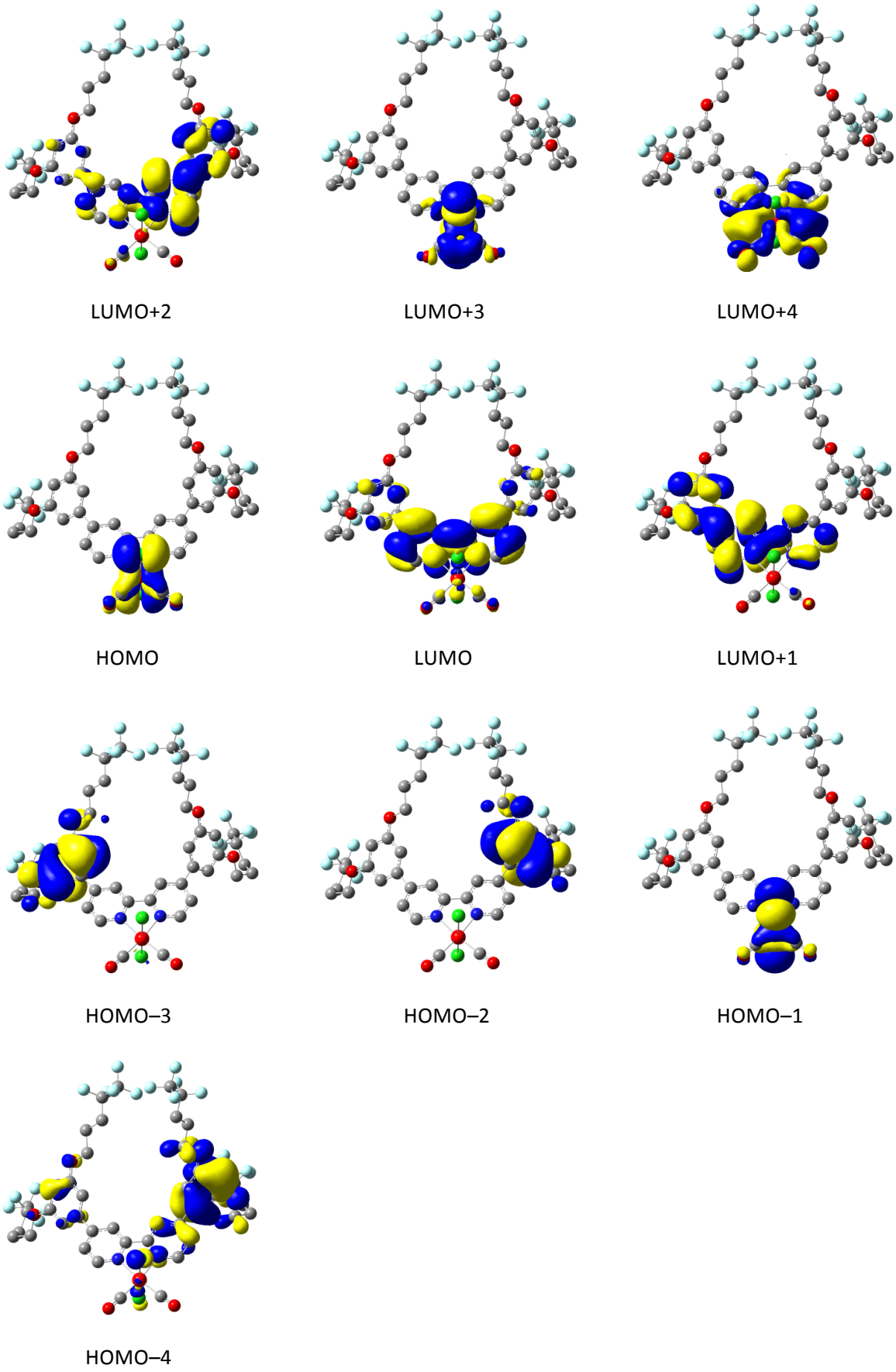

Fig. S14 B3LYP/6-31g(d)/LANL2DZ-derived contour surface diagrams of selected MOs for complex **12** (isosurface value 0.03 au).

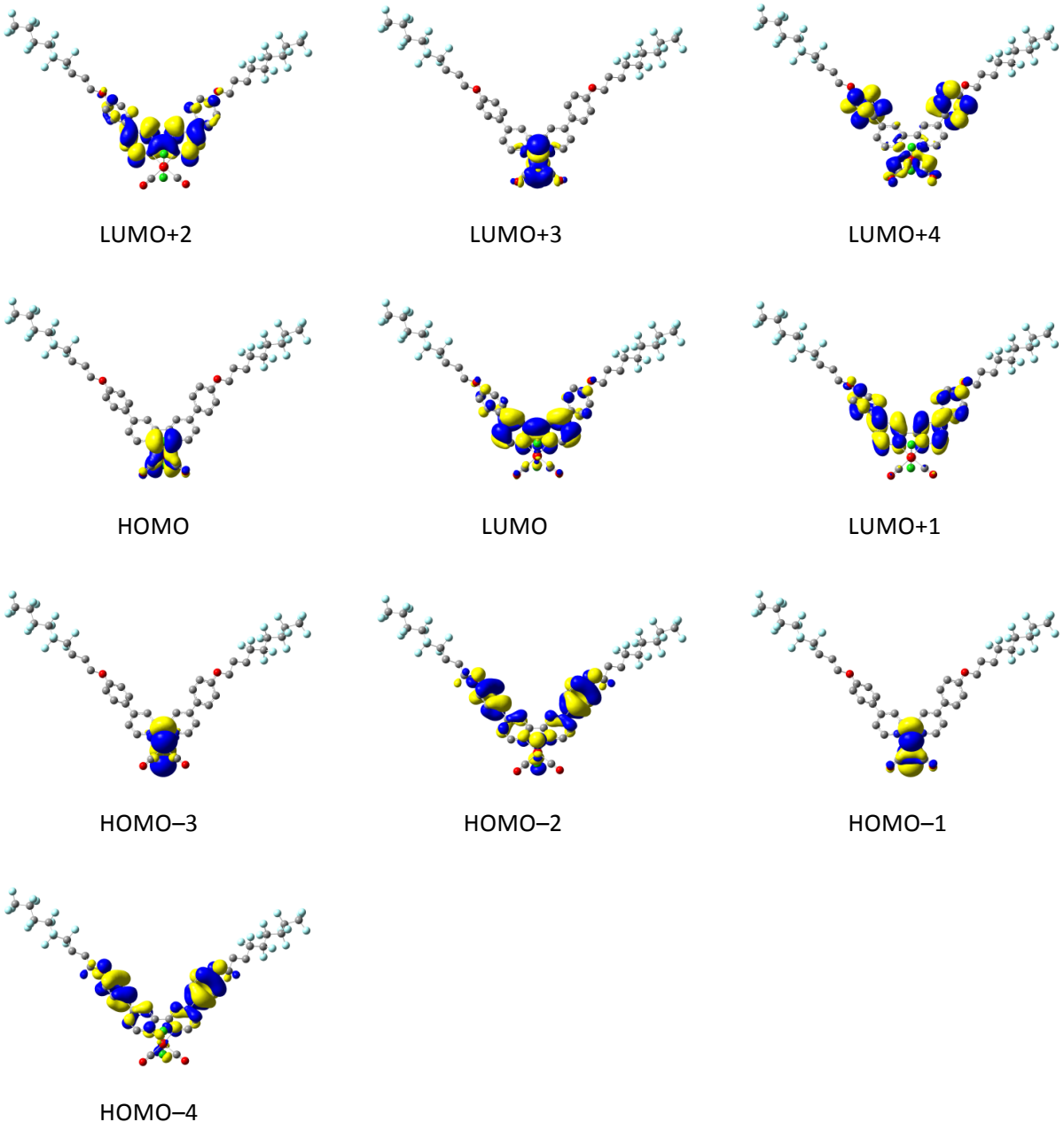

Fig. S15 B3LYP/6-31g(d)/LANL2DZ-derived contour surface diagrams of selected MOs for complex **13** (isosurface value 0.03 au).

Table S4 Selected transitions calculated by TD-DFT for complexes **3**, **4**, **8**, and **11**–**13**

complex	ΔE (eV)	λ (nm)	f_{os}	major contributions
3	3.22	385	0.164	H → L (90%)
	3.28	378	0.289	H–1 → L (92%)
	3.38	367	0.038	H–2 → L (91%)
	4.04	307	0.291	H–1 → L+2 (19%), H → L+2 (24%), H → L+3 (46%)
	4.08	304	0.028	H–2 → L+4 (72%), H → L+4 (10%)
	4.09	303	0.385	H–1 → L+2 (20%), H–1 → L+3 (53%), H → L+2 (10%)
	4.15	299	0.349	H–6 → L (12%), H–4 → L (22%), H–1 → L+2 (34%), H–1 → L+3 (16%)
	4.19	296	0.100	H–3 → L+4 (25%), H → L+2 (35%), H → L+3 (13%)
	4.19	296	0.054	H–3 → L+4 (51%), H–1 → L+4 (10%), H → L+2 (16%)
	4.22	294	0.018	H–6 → L (17%), H–4 → L (60%)
	4.22	294	0.015	H–5 → L (86%)
	4.25	292	0.132	H–6 → L (54%), H–1 → L+2 (11%)
	4.35	285	0.032	H–2 → L+2 (36%), H–2 → L+3 (53%)
	4.37	284	0.001	H–8 → L (97%)
	4.37	284	0.011	H–2 → L+2 (56%), H–2 → L+3 (37%)
	4.44	279	0.011	H–3 → L+2 (57%), H–3 → L+3 (32%)
	4.77	260	0.045	H–9 → L (80%)
	5.06	245	0.037	H–12 → L (24%), H–9 → L (13%), H–6 → L+2 (20%), H–4 → L+2 (20%)
	5.17	240	0.022	H–12 → L+1 (16%), H–9 → L+1 (38%), H–2 → L+10 (21%)
4	3.15	393	0.003	H → L (99%)
	3.26	380	0.024	H–4 → L (64%), H–2 → L (35%)
	3.33	372	0.137	H–5 → L (44%), H–3 → L (56%)
	3.39	366	0.093	H–4 → L (35%), H–2 → L (64%)
	3.44	360	0.044	H–5 → L (56%), H–3 → L (43%)
	3.94	315	0.015	H–1 → L+2 (47%), H → L+3 (51%)
	3.94	315	0.018	H–1 → L+3 (49%), H → L+2 (49%)
	4.19	296	0.243	H–3 → L+3 (44%), H–2 → L+2 (43%)
	4.19	296	0.555	H–6 → L (38%), H–3 → L+2 (43%), H–2 → L+3 (10%)
	4.19	296	0.030	H–5 → L+4 (78%)
	4.26	291	0.044	H–6 → L (16%), H–5 → L+2 (23%), H–4 → L+3 (19%), H–3 → L+2 (23%), H–2 → L+3 (18%)
	4.32	287	0.016	H–4 → L+3 (67%), H–2 → L+3 (15%)
	4.32	287	0.031	H–5 → L+3 (17%), H–4 → L+2 (46%), H–2 → L+2 (32%)
	4.38	283	0.015	H–5 → L+2 (65%), H–3 → L+2 (17%), H–2 → L+3 (10%)
	4.63	268	0.114	H–9 → L (77%), H–6 → L+2 (10%)
	4.64	267	0.015	H → L+4 (97%)

	5.00	248	0.035	H–12 → L (42%), H–6 → L+2 (44%)
	5.04	246	0.010	H–14 → L+1 (14%), H–9 → L+1 (31%), H–4 → L+8 (34%)
	5.12	242	0.221	H–12 → L (51%), H–6 → L+2 (26%)
8	3.06	405	0.018	H–1 → L (99%)
	3.28	378	0.058	H–5 → L (50%), H–3 → L (49%)
	3.51	353	0.138	H–4 → L (71%), H–2 → L (27%)
	3.54	350	0.131	H–5 → L (49%), H–3 → L (50%)
	3.84	323	0.033	H–1 → L+3 (51%), H → L+2 (47%)
	4.12	301	0.021	H–6 → L (31%), H–2 → L+3 (55%)
	4.16	298	0.067	H–4 → L+2 (21%), H–2 → L+2 (76%)
	4.22	294	0.012	H–6 → L (12%), H–5 → L+2 (29%), H–3 → L+2 (35%), H–2 → L+3 (10%)
	4.23	293	0.032	H–5 → L+3 (32%), H–3 → L+3 (64%)
	4.23	293	0.570	H–6 → L (46%), H–3 → L+2 (31%), H–2 → L+3 (14%)
	4.34	286	0.083	H–5 → L+2 (24%), H–4 → L+1 (18%), H–4 → L+3 (39%)
	4.34	286	0.027	H–4 → L+1 (46%), H–4 → L+3 (15%), H–2 → L+1 (25%)
	4.34	286	0.011	H–5 → L+1 (37%), H–3 → L+1 (58%)
	4.35	285	0.145	H–5 → L+3 (44%), H–4 → L+2 (30%), H–3 → L+3 (14%)
	4.44	279	0.031	H–5 → L+3 (20%), H–4 → L+2 (45%), H–3 → L+3 (16%), H–2 → L+2 (16%)
	4.59	270	0.145	H–9 → L (76%)
	4.71	263	0.012	H–10 → L (84%)
11	3.20	387	0.073	H–2 → L (45%), H → L (54%)
	3.28	378	0.211	H–3 → L (34%), H–1 → L (65%)
	3.34	371	0.164	H–2 → L (54%), H → L (44%)
	3.42	363	0.088	H–3 → L (65%), H–1 → L (34%)
	4.04	307	0.039	H–2 → L+4 (59%), H → L+3 (12%), H → L+4 (12%)
	4.07	305	0.223	H–2 → L+4 (13%), H–1 → L+2 (17%), H → L+3 (58%)
	4.11	302	0.013	H–3 → L+1 (14%), H–1 → L+1 (81%)
	4.12	301	0.412	H–1 → L+3 (63%), H → L+2 (25%)
	4.15	299	0.455	H–4 → L (27%), H–2 → L+3 (13%), H–1 → L+2 (51%)
	4.16	298	0.028	H–3 → L+4 (68%), H–1 → L+4 (14%)
	4.17	297	0.031	H–2 → L+2 (25%), H–1 → L+3 (26%), H → L+2 (38%)
	4.23	293	0.149	H–4 → L (51%), H–3 → L+2 (20%), H–1 → L+2 (10%), H → L+3 (12%)
	4.28	290	0.050	H–7 → L (10%), H–6 → L (61%), H–2 → L+3 (18%)
	4.29	289	0.130	H–3 → L+3 (18%), H–2 → L+2 (53%), H → L+2 (19%)
	4.32	287	0.005	H–3 → L+3 (72%), H–2 → L+2 (10%), H → L+2 (10%)

	4.37	284	0.013	H–3 → L+2 (65%), H–1 → L+2 (12%)
	4.70	264	0.046	H–9 → L (86%)
	4.86	255	0.012	H–6 → L+3 (22%), H–5 → L+2 (31%), H–1 → L+7 (14%), H → L+8 (17%)
	5.02	247	0.011	H–12 → L (34%), H–4 → L+2 (47%)
	5.14	241	0.011	H–12 → L+1 (10%), H–9 → L+1 (13%), H–5 → L+1 (54%)
	5.19	239	0.014	H–12 → L+1 (15%), H–9 → L+1 (24%), H–5 → L+1 (32%)
	5.19	239	0.152	H–11 → L+4 (13%), H–10 → L (10%), H–4 → L+3 (43%)
	5.19	239	0.090	H–11 → L+4 (16%), H–4 → L+3 (23%), H–3 → L+9 (12%), H–3 → L+11 (14%)
12	3.19	389	0.010	H–4 → L (48%), H–2 → L (23%), H → L (25%)
	3.27	379	0.070	H–5 → L (69%), H–3 → L (30%)
	3.41	364	0.088	H–4 → L (30%), H–2 → L (64%)
	3.44	360	0.097	H–5 → L (30%), H–3 → L (65%)
	3.97	312	0.016	H–1 → L+2 (96%)
	3.99	311	0.015	H → L+3 (94%)
	4.12	301	0.014	H–6 → L (18%), H–4 → L+2 (22%), H–2 → L+2 (34%)
	4.17	297	0.081	H–7 → L (51%)
	4.17	297	0.063	H–7 → L (38%), H–4 → L+3 (20%), H–2 → L+3 (22%)
	4.19	296	0.036	H–8 → L (86%)
	4.20	295	0.058	H–5 → L+2 (17%), H–4 → L+2 (24%), H–3 → L+2 (42%)
	4.22	294	0.341	H–6 → L (17%), H–3 → L+3 (39%)
	4.23	293	0.036	H–1 → L+3 (92%)
	4.23	293	0.127	H–6 → L (29%), H–5 → L+3 (19%), H–4 → L+3 (17%), H–3 → L+3 (12%)
	4.25	292	0.008	H–4 → L+1 (18%), H–2 → L+1 (68%)
	4.26	291	0.017	H–5 → L+1 (11%), H–3 → L+1 (71%)
	4.28	290	0.053	H–5 → L+2 (44%), H–4 → L+2 (24%), H–2 → L+2 (12%)
	4.29	289	0.025	H–5 → L+3 (47%), H–4 → L+3 (23%), H–2 → L+3 (11%)
	4.37	284	0.025	H–5 → L+2 (15%), H–4 → L+2 (11%), H–3 → L+2 (29%), H–2 → L+2 (29%)
	4.41	281	0.012	H–5 → L+3 (22%), H–4 → L+3 (12%), H–3 → L+3 (28%), H–2 → L+3 (31%)
	4.59	270	0.117	H–9 → L (80%)
	5.10	243	0.057	H–7 → L+2 (50%), H–6 → L+2 (12%)
13	3.20	387	0.073	H–2 → L (45%), H → L (54%)
	3.28	378	0.213	H–3 → L (35%), H–1 → L (64%)
	3.34	371	0.166	H–2 → L (54%), H → L (44%)
	3.43	362	0.090	H–3 → L (65%), H–1 → L (34%)
	4.04	307	0.032	H–2 → L+4 (61%), H → L+3 (10%), H → L+4 (12%)
	4.07	305	0.229	H–2 → L+4 (10%), H–1 → L+2 (17%),

			H → L+3 (60%)
4.11	302	0.011	H–3 → L+1 (14%), H–1 → L+1 (81%)
4.12	301	0.420	H–1 → L+3 (64%), H → L+2 (25%)
4.16	298	0.466	H–4 → L (28%), H–2 → L+3 (14%), H–1 → L+2 (50%)
4.16	298	0.027	H–3 → L+4 (69%), H–1 → L+4 (14%)
4.17	297	0.034	H–2 → L+2 (25%), H–1 → L+3 (26%), H → L+2 (39%)
4.23	293	0.148	H–4 → L (50%), H–3 → L+2 (21%), H–1 → L+2 (11%), H → L+3 (12%)
4.28	290	0.049	H–7 → L (10%), H–6 → L (63%), H–2 → L+3 (18%)
4.29	289	0.130	H–3 → L+3 (20%), H–2 → L+2 (52%), H → L+2 (19%)
4.37	284	0.012	H–3 → L+2 (65%), H–1 → L+2 (12%)
4.70	264	0.046	H–9 → L (86%)
4.88	254	0.012	H–6 → L+3 (22%), H–5 → L+2 (31%), H–1 → L+7 (14%), H → L+8 (17%)
5.02	247	0.011	H–12 → L (34%), H–4 → L+2 (47%)
5.14	241	0.011	H–12 → L+1 (10%), H–9 → L+1 (13%), H–5 → L+1 (53%)
5.19	239	0.015	H–12 → L+1 (15%), H–9 → L+1 (23%), H–5 → L+1 (32%)
5.19	239	0.147	H–11 → L+4 (13%), H–10 → L (10%), H–4 → L+3 (41%)
5.19	239	0.098	H–11 → L+4 (16%), H–4 → L+3 (25%), H–3 → L+9 (11%), H–3 → L+11 (13%)

[a] Geometry optimisations and TD-DFT calculations used the B3LYP functional with the 6-31g(d)/LANL2DZ mixed basis set, and a CPCM DMSO or dichloromethane solvent model was included for TD-DFT. H = HOMO, L = LUMO.

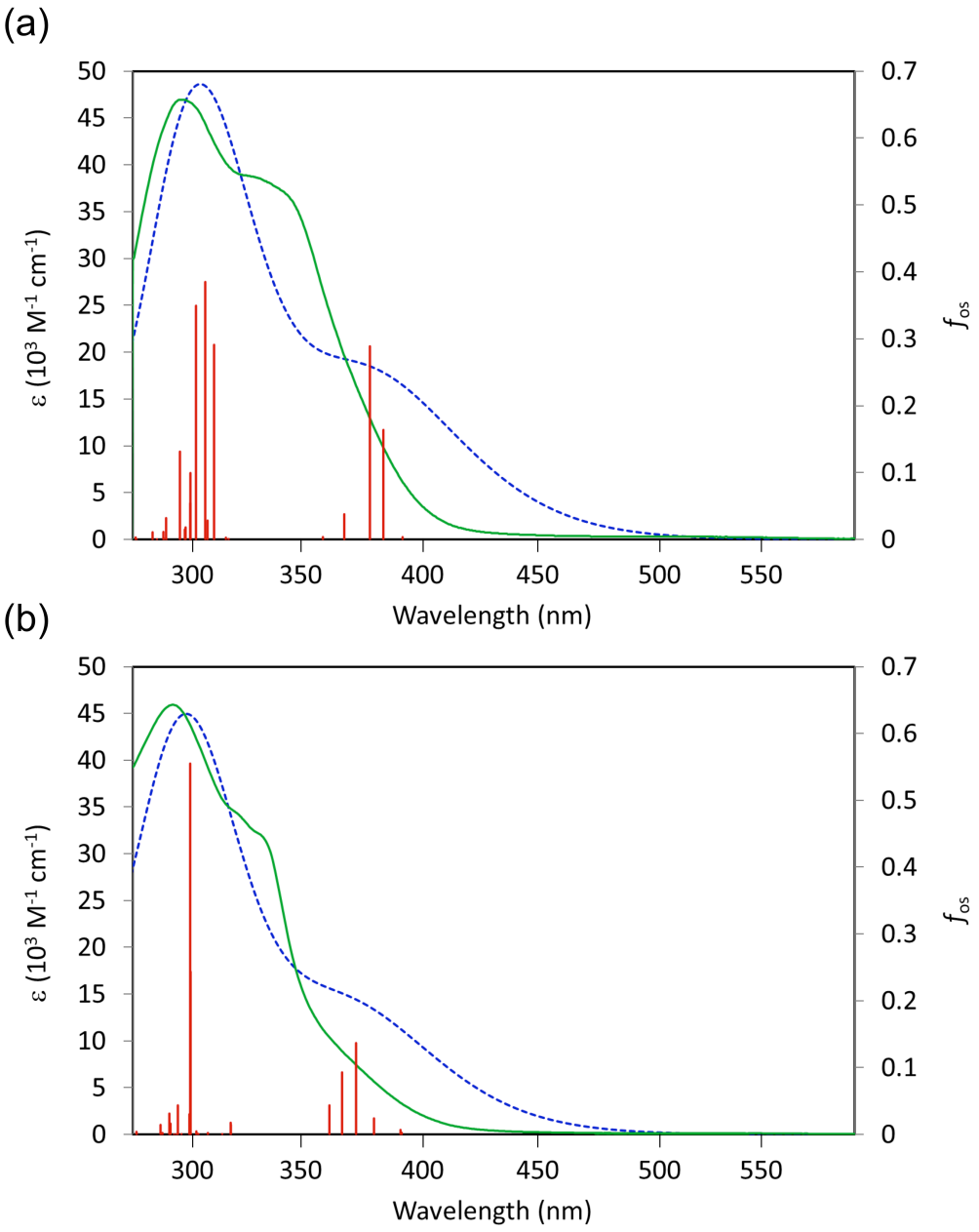

Fig. S16 TD–DFT calculated UV–vis spectra (blue dashed lines) at the B3LYP/6–31g(d)/LANL2DZ level for complexes **3** (a) and **4** (b), together with the experimental spectra (green), all in DMSO. The ε–axes refer to the experimental data only and the vertical axes of the calculated data are scaled to match the main experimental absorptions. The f_{os}-axes refer to the individual calculated transitions (red).