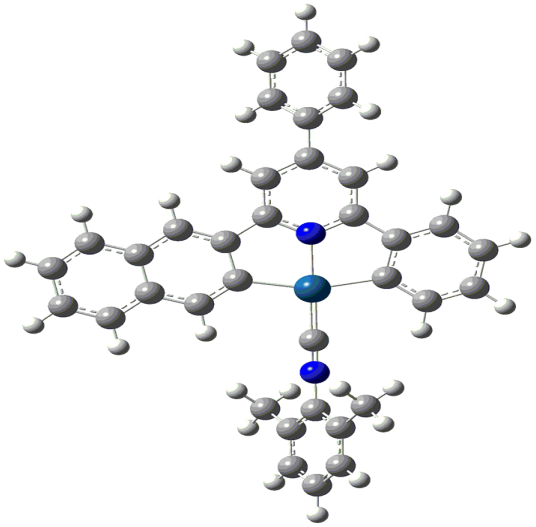
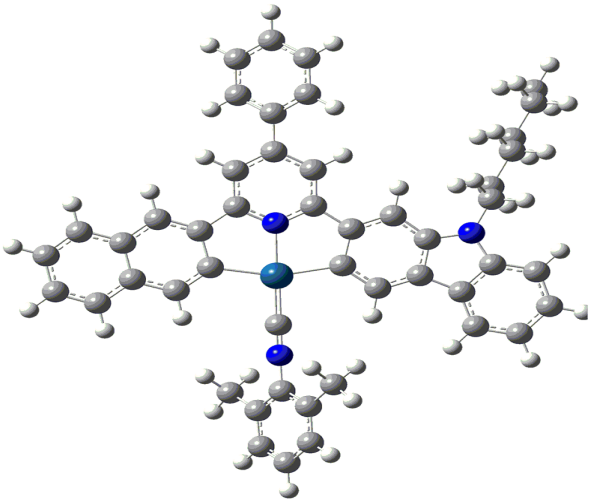
Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information



1a



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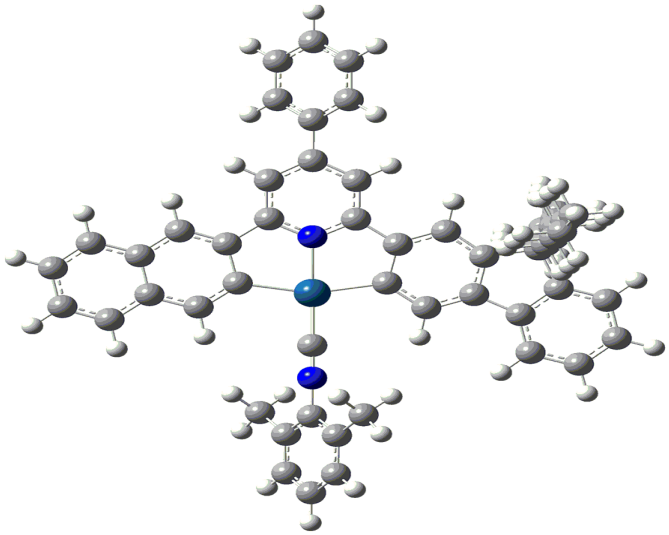


3a

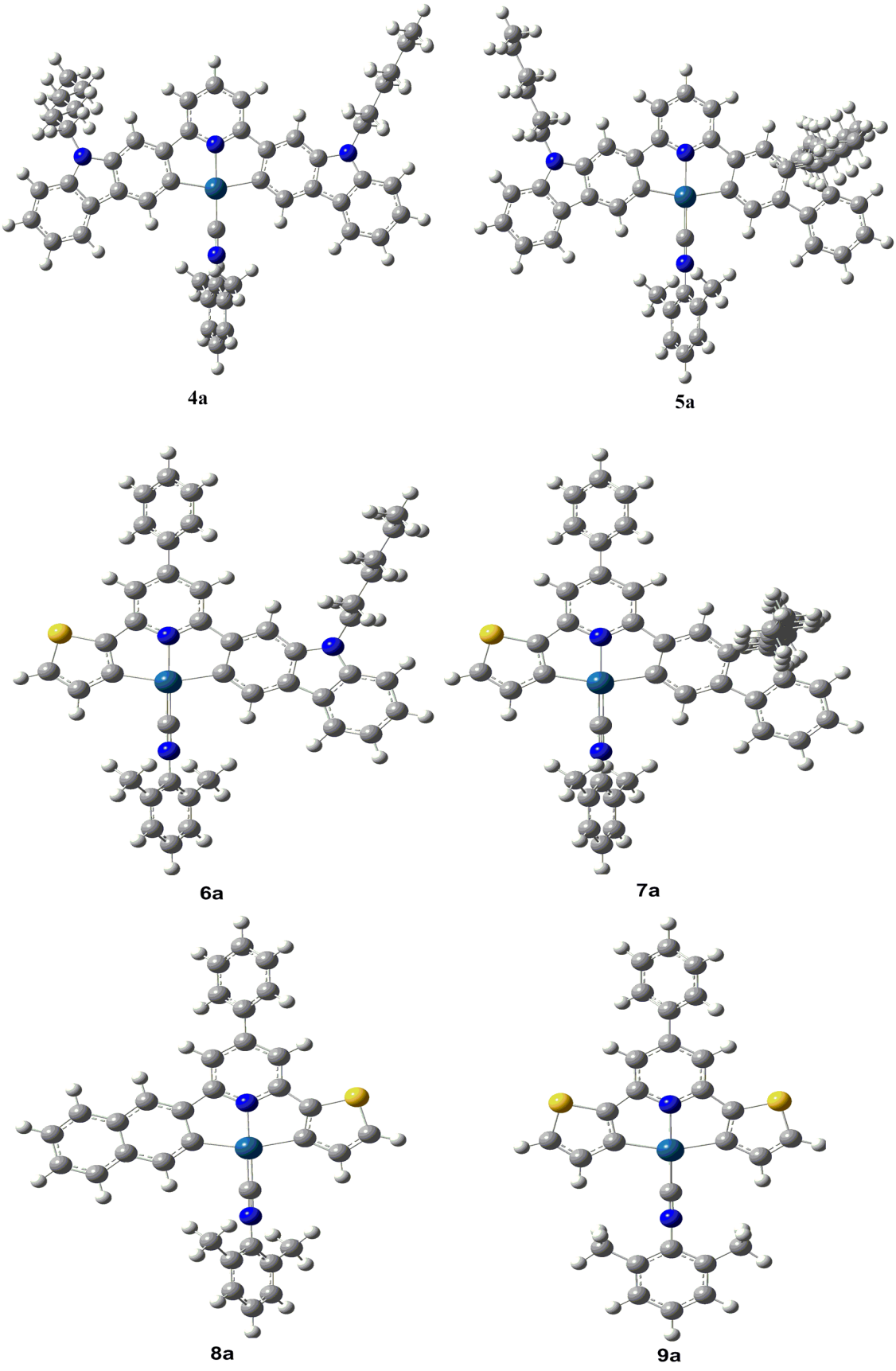


Fig. S1 The optimized ground-state geometric structures for complexes **1a**–**9a** at the B3LYP/6-31G(d)-LANL2DZ level of theory.

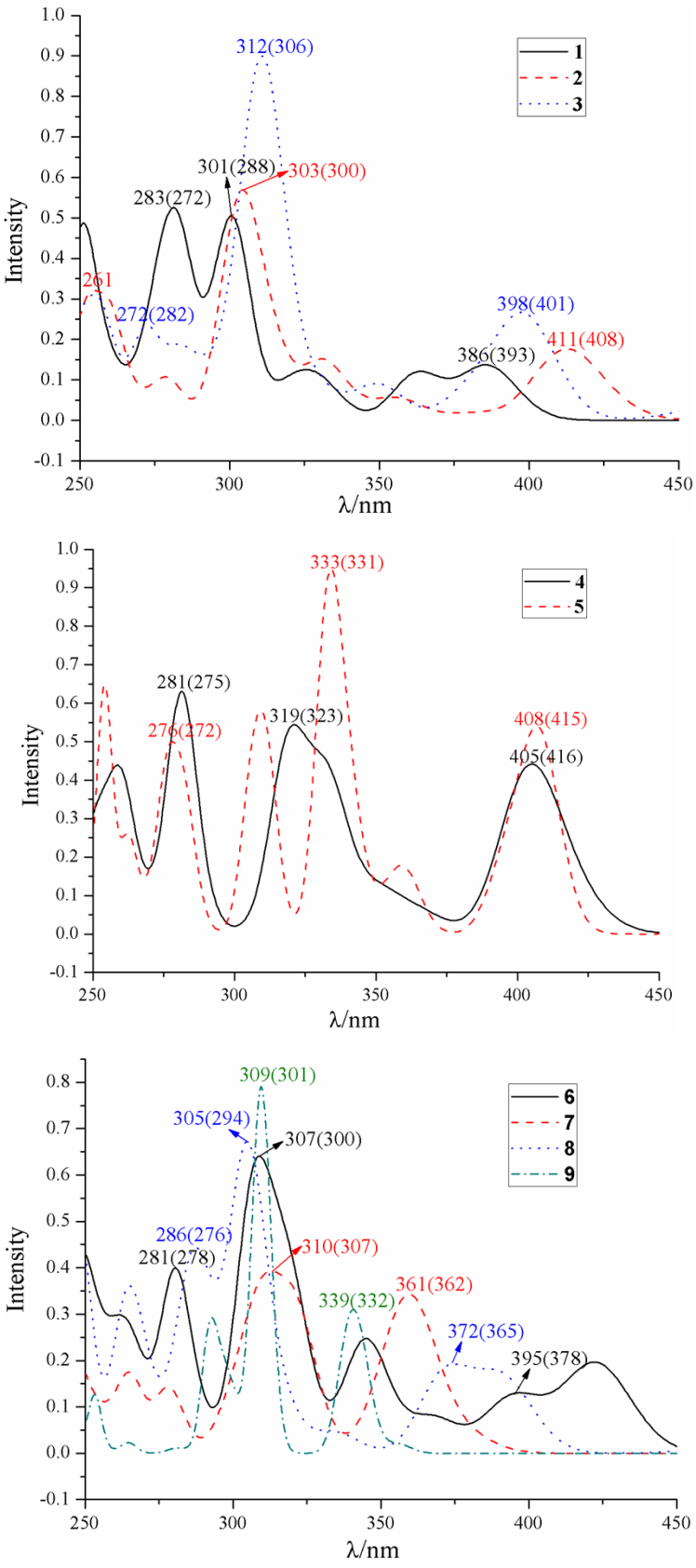


Fig. S2 Simulated absorption spectra of complexes **1**–**9** in dichloromethane solution at the TD-B3LYP/6-31G(d)-LANL2DZ level of theory together with experimental values in parentheses.

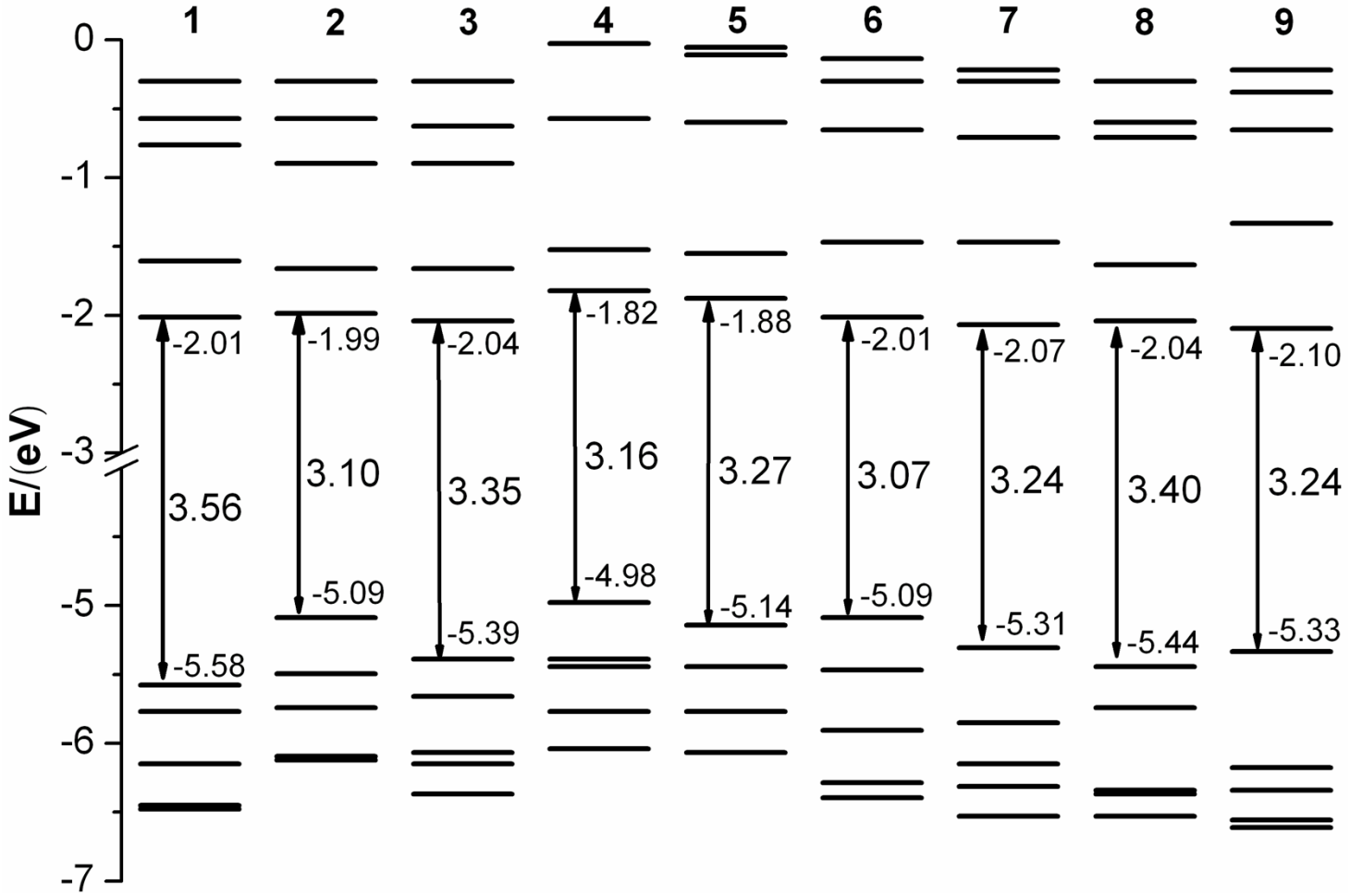
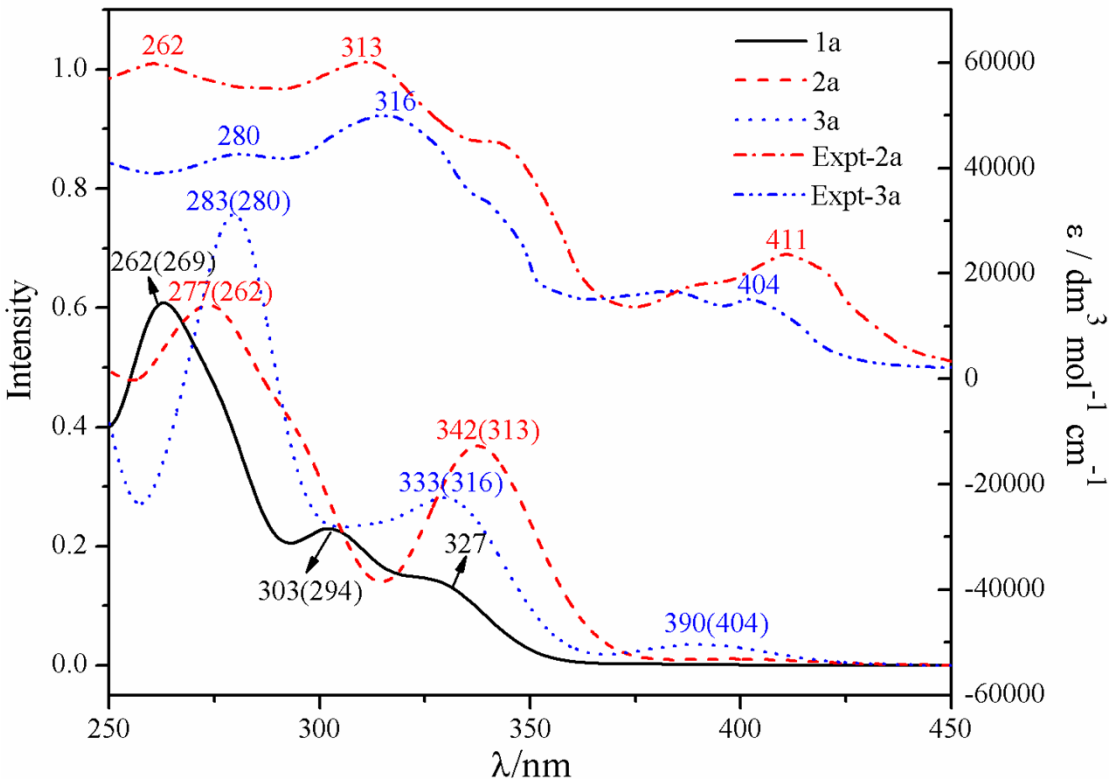
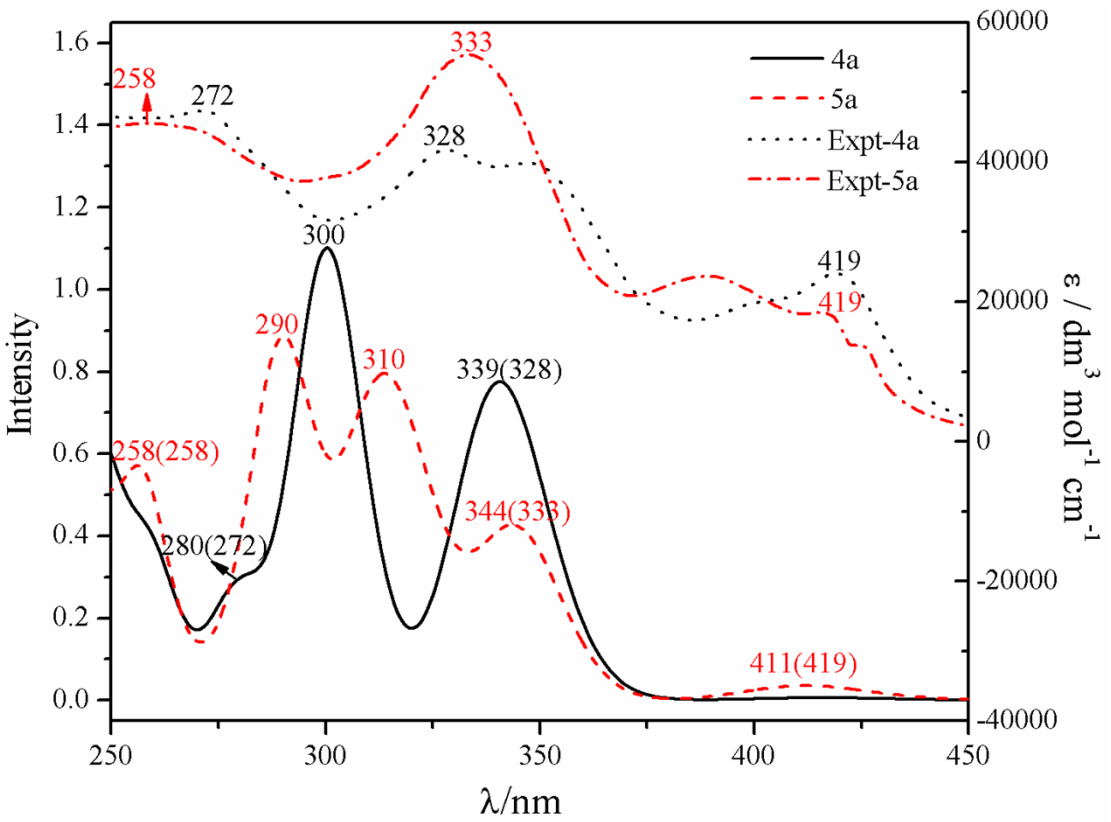


Fig. S3 Pictorial representation of the frontier moleculer orbital energy levels of complexes **1**–**9**.


1a
2a
3a
Expt-2a
Expt-3a
262
313
316
280
283(280)
262(269)
277(262)
411
404
342(313)
333(316)
327
303(294)
390(404)
Intensity
ε / dm3 mol-1 cm-1
λ/nm


4a
5a
Expt-4a
Expt-5a
333
258
272
328
300
419
419
290
310
339(328)
258(258)
344(333)
280(272)
411(419)
Intensity
ε / dm3 mol-1 cm-1
λ/nm

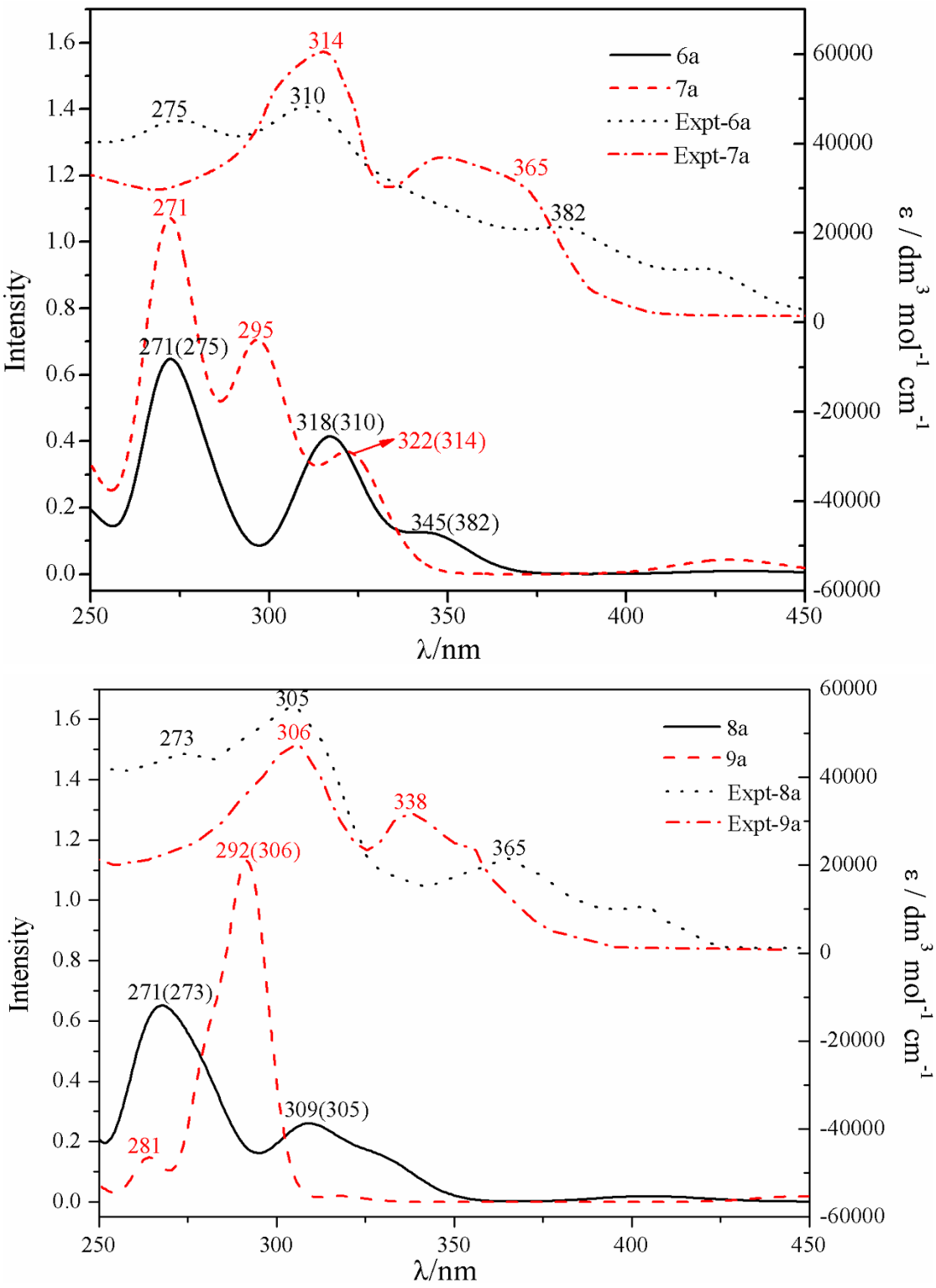
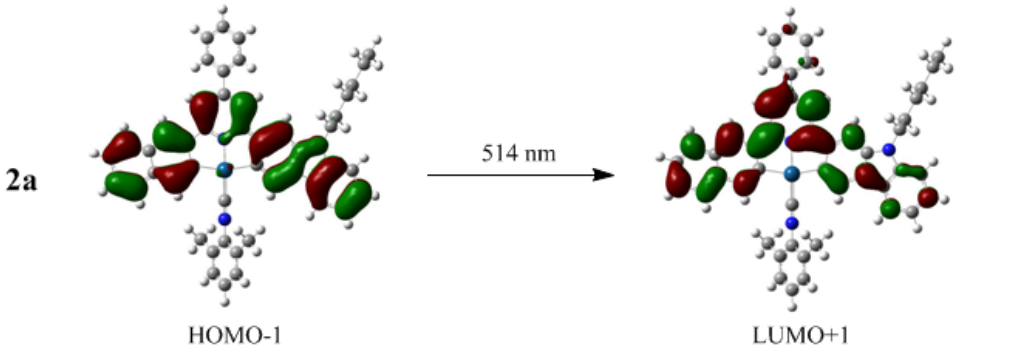
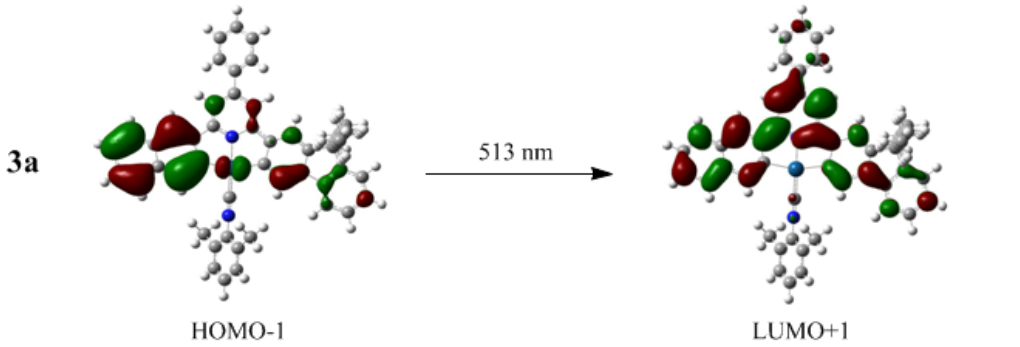
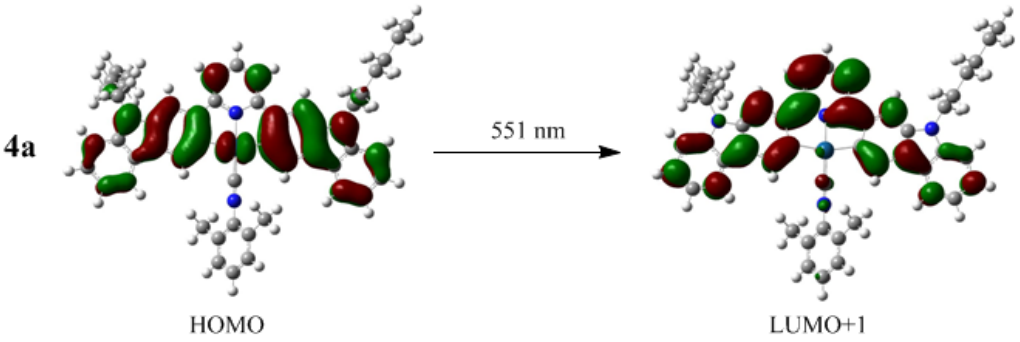
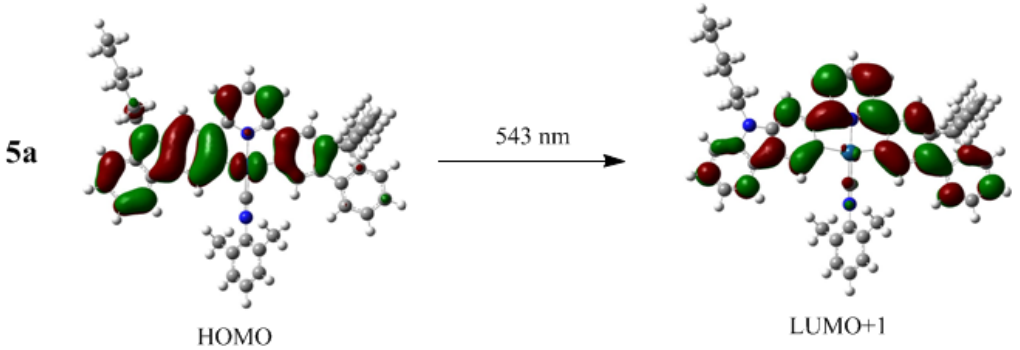


Fig. S4 Simulated and experimental absorption spectra of complexes **1a**–**9a** in dichloromethane solution determined at the TD-CAM-B3LYP/6-31G(d)-LANL2DZ level of theory.


2a
514 nm
HOMO-1
LUMO+1


3a
513 nm
HOMO-1
LUMO+1


4a
551 nm
HOMO
LUMO+1


5a
543 nm
HOMO
LUMO+1

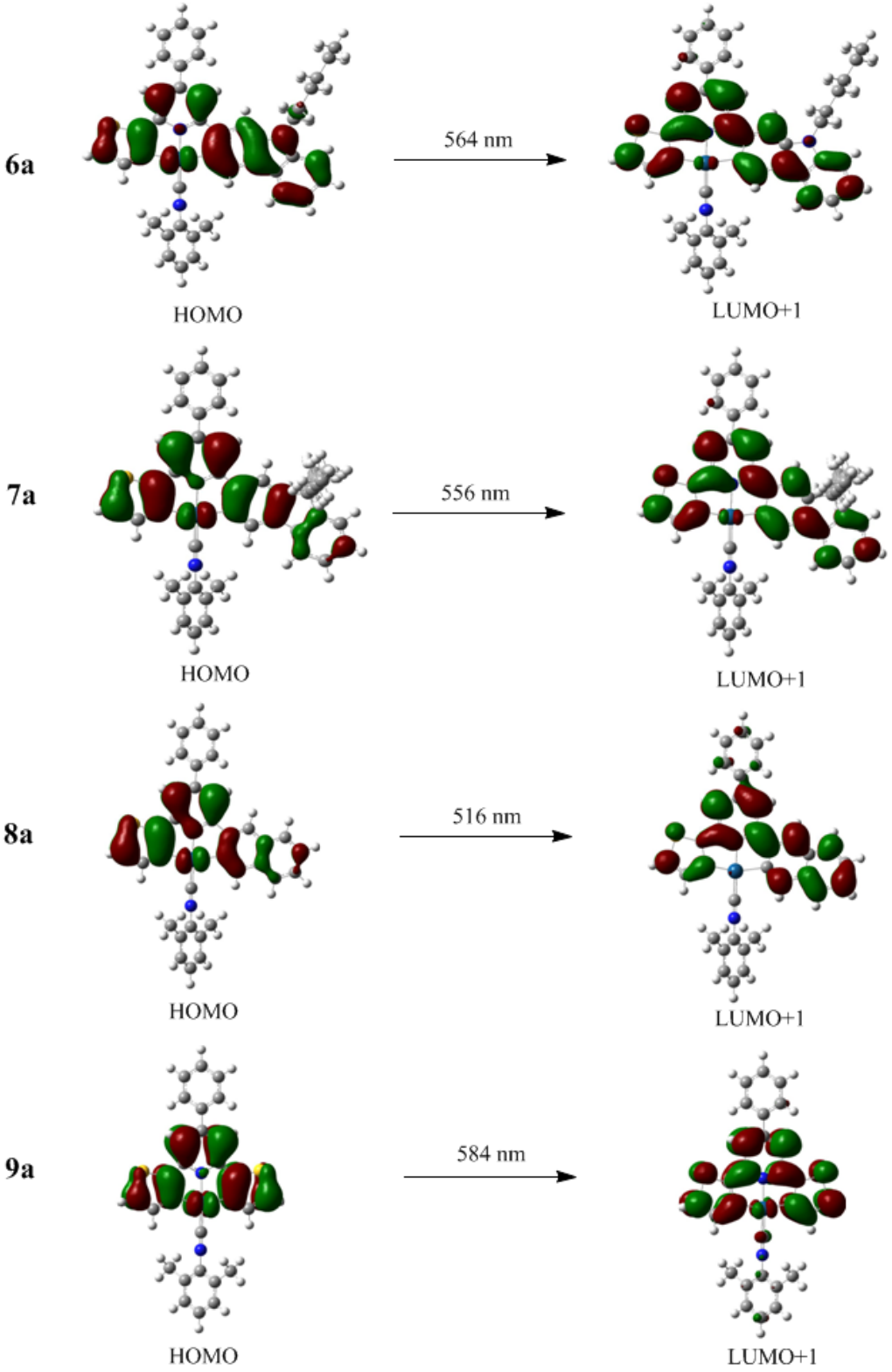
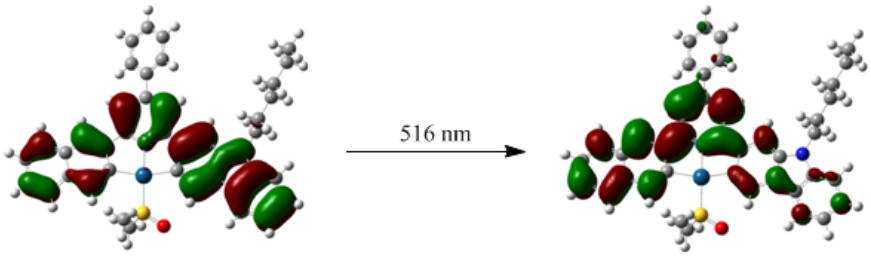


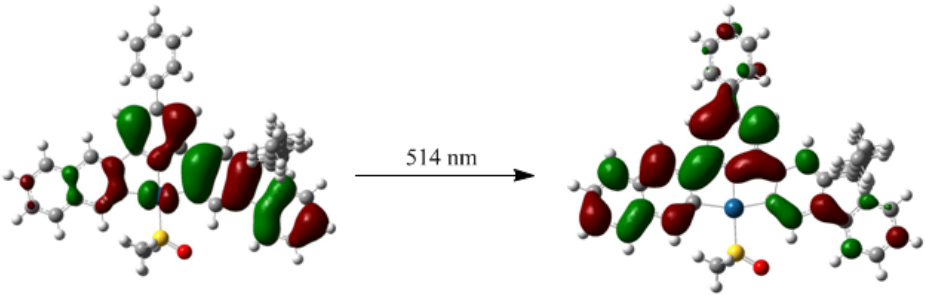
Fig. S5 Single electron transitions for the emissions of T_2 states of complexes **1a**–**9a** determined at the TD-B3LYP/6-31G(d)-LANL2DZ level of theory.

2



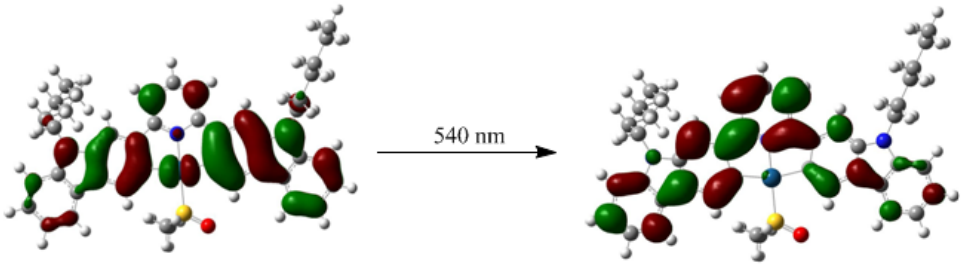
HOMO-1 LUMO+1

3



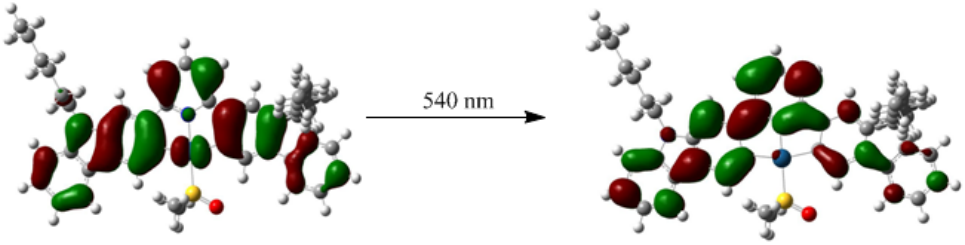
HOMO LUMO+1

4



HOMO LUMO+1

5



HOMO LUMO+1

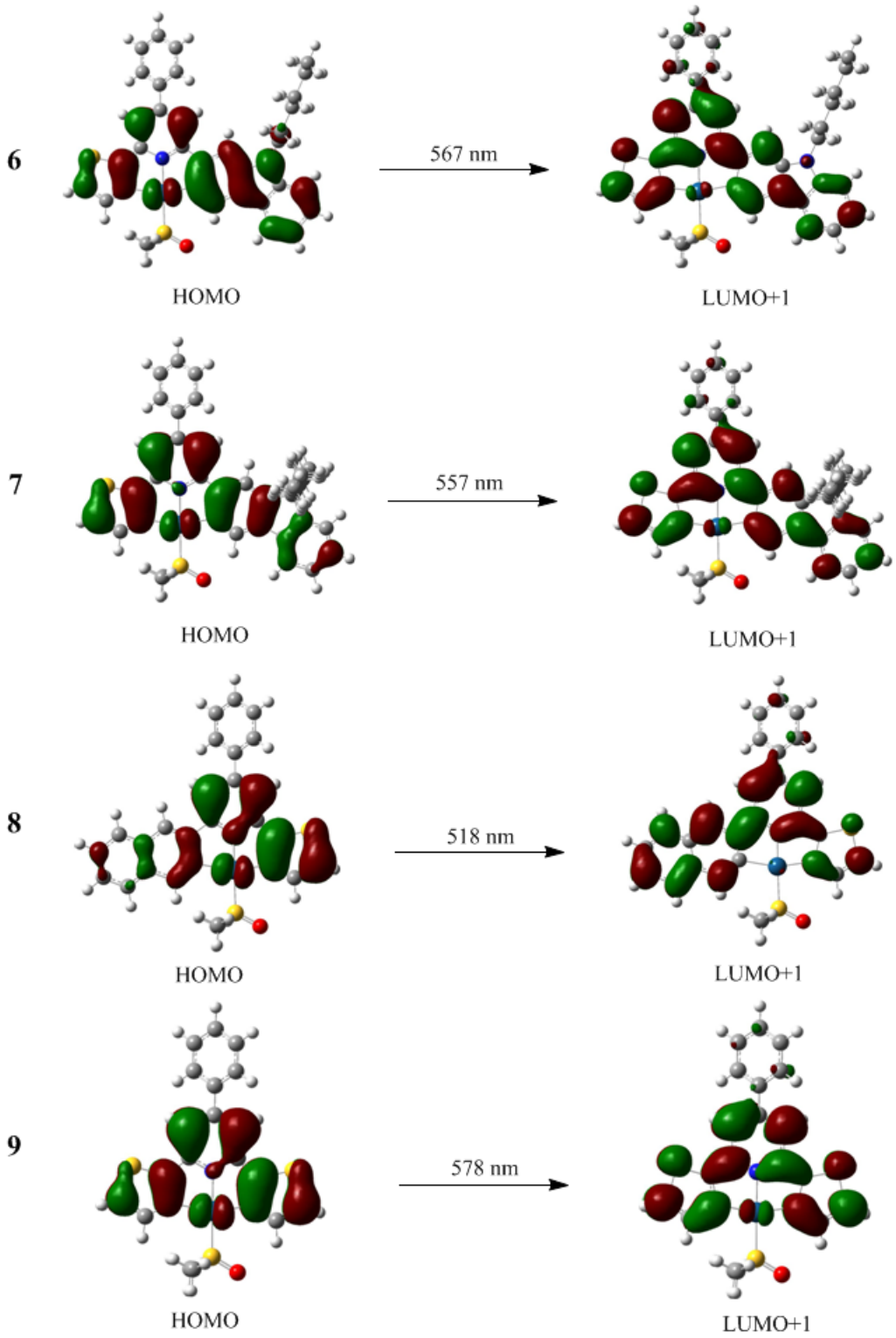


Fig. S6 Single electron transitions for the emissions of T_2 states of complexes **1–9** determined at the TD-B3LYP/6-31G(d)-LANL2DZ level of theory.

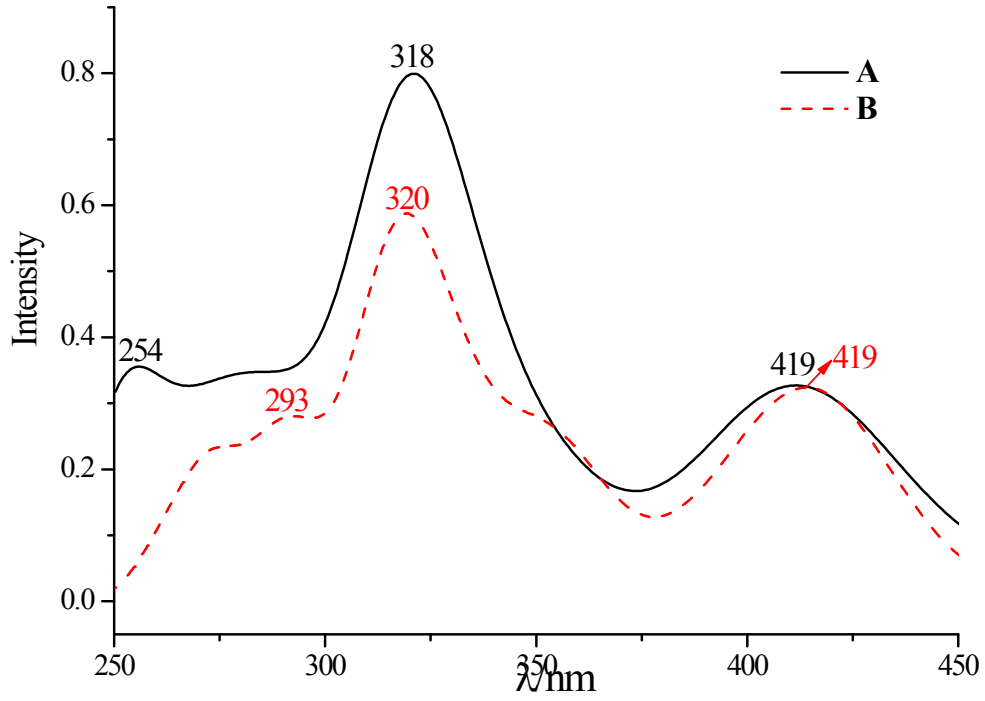


Fig. S7 Simulated absorption spectra of the two designed complexes **A** and **B** in dichloromethane solution at the TD-B3LYP/6-31G(d)-LANL2DZ level of theory.

Table S1 Geometric parameters of the Pt(II) complexes **1**–**9** in the S_0 and T_1 states as determined at the B3LYP/6-31G(d)-LANL2DZ level of theory along with experimental values from X-ray diffraction[a]

	1		**2**		**3**		**4**		**5**	
	S_0	T_1	S_0	T_1	S_0	T_1	S_0	T_1	S_0	T_1
					Bond Length/Å					
Pt–C(1)	2.120	2.129	2.118(2.097)	2.113	2.119	2.115	2.121	2.111	2.122	2.116
Pt–N	2.014	2.003	2.014(2.015)	1.988	2.012	1.990	2.016	1.990	2.016	1.992
Pt–C(2)	2.082	2.081	2.083(2.055)	2.042	2.083	2.053	2.083	2.041	2.082	2.051
Pt–S	2.290	2.295	2.288(2.188)	2.309	2.291	2.302	2.285	2.308	2.289	2.303
					Bond Angle/deg					
C(1)–Pt–C(2)	160.8	160.1	160.9(161.1)	161.7	160.9	161.6	160.8	161.8	160.8	161.6
N–Pt–S	179.2	179.1	179.1(172.2)	179.9	179.1	179.6	179.1	179.7	179.1	179.5
	6		**7**		**8**		**9**			
	S_0	T_1	S_0	T_1	S_0	T_1	S_0	T_1		
					Bond Length/Å					
Pt–C(1)	2.123(2.091)	2.071	2.122	2.073	2.079	2.037	2.108	2.095		
Pt–N	2.020(2.012)	1.996	2.021	1.998	2.022	1.998	2.029	1.999		
Pt–C(2)	2.073(2.068)	2.067	2.072	2.071	2.104	2.102	2.069	2.025		
Pt–S	2.283(2.187)	2.296	2.302	2.300	2.286	2.297	2.282	2.296		
					Bond Angle/deg					
C(1)–Pt–C(2)	160.3(160.4)	161.5	160.2	161.2	160.5	161.6	159.9	161.0		
N–Pt–S	179.5(176.1)	179.7	179.6	179.5	177.4	178.0	178.9	179.2		

[a]from ref.16.

Table S2 Selected absorptions for complexes **1**–**3** in dichloromethane solution determined at the TD-B3LYP/6-31G(d)-LANL2DZ level of theory together with experimental values[a]

Species	State	λ_{cal}(nm)	*f*	Main configuration	Assignment	$\lambda_{Expt.}$(nm)
1	S_1	439	0.0009	HOMO→LUMO(92%)	d(Pt)+π(ph+naph)→π*(py+ph+naph)/ILCT	417
	S_2	386	0.1839	H-1→LUMO(82%)	π(py+ph+naph)→π*(py+ph+naph)/ILCT	393
	S_4	363	0.1600	HOMO→L+1(88%)	d(Pt)+π(ph+naph)→π*(py+ph+naph)/IL/MLCT	359
	S_6	330	0.1140	H-1→L+1(70%)	π(py+ph+naph)→π*(py+ph+naph)/ILCT	325
	S_{10}	301	0.5924	H-6→LUMO(84%)	π(py+ph+naph)→π*(py+ph+naph)/ILCT	288
	S_{15}	283	0.5181	HOMO→L+2(47%)	d(Pt)+π(ph+naph)→π*(py+ph+naph)/IL/MLCT	272
2	S_1	495	0.0135	HOMO→LUMO(94%)	d(Pt)+π(carb)→π*(ph+py)/IL/MLCT	463
	S_3	411	0.3642	H-1→LUMO(74%)	π(py+carb)→π*(ph+py)/ILCT	408
	S_{11}	331	0.3387	HOMO→L+2(87%)	d(Pt)+π(carb)→π*(naph+carb)/IL/MLCT	337
	S_{16}	303	0.6576	HOMO→L+3(56%)	d(Pt)+π(carb)→π*(ph+naph)/IL/MLCT	300
	S_{31}	261	0.3000	HOMO→L+7(37%)	d(Pt)+π(carb)→π*(naph+carb)/IL/MLCT	
3	S_1	460	0.0457	HOMO→LUMO(95%)	d(Pt)+π(py+naph+fluo)→π*(ph+py)/IL/MLCT	458
	S_2	398	0.3856	H-1→LUMO(94%)	π(naph+fluo)→π*(ph+py)/ILCT	401
	S_5	352	0.0796	H-2→LUMO(89%)	π(naph+fluo)→π*(ph+py)/ILCT	376
	S_{11}	312	0.8452	HOMO→L+2(79%)	d(Pt)+π(py+naph+fluo)→π*(naph+fluo)/IL/MLCT	306
	S_{23}	272	0.2718	H-1→L+3(48%)	π(naph+fluo)→π*(ph+naph)/ILCT	282

[a]from ref.16.

Table S3 Selected absorptions for complexes **4**–**5** in dichloromethane solution determined at the TD-B3LYP/6-31G(d)-LANL2DZ level of theory together with experimental values[a]

Species	State	λ_{cal}(nm)	*f*	Main configuration	Assignment	$\lambda_{Expt.}$(nm)
4	S_1	498	0.0032	HOMO→LUMO(95%)	d(Pt)+p(N)+π(carb)→π*(py)/IL/MLCT	476
	S_3	405	0.4294	H-1→LUMO(44%)	p(N)+π(carb)→π*(py)/ILCT	416
	S_8	350	0.1135	H-2→L+1(85%)	π(py+carb)→π*(py+carb)/ILCT	345
	S_{10}	333	0.5060	H-3→L+1(92%)	π(carb)→π*(py+carb)/ILCT	345
	S_{12}	319	0.6672	HOMO→L+2(90%)	d(Pt)+p(N)+π(carb)→π*(py+carb)/IL/MLCT	323
	S_{19}	281	0.4912	HOMO→L+5(45%)	d(Pt)+p(N)+π(carb)→π*(py+carb)/IL/MLCT	275
5	S_1	482	0.0101	HOMO→LUMO(94%)	d(Pt)+p(N)+π(fluo+carb)→π*(py)/IL/MLCT	467
	S_2	408	0.4023	H-1→LUMO(79%)	p(N)+π(py+fluo+carb)→π*(py)/ILCT	415
	S_5	361	0.0947	H-2→LUMO(87%)	p(N)+π(fluo+carb)→π*(py)/ILCT	386
	S_9	333	0.7014	H-2→L+1(95%)	p(N)+π(fluo+carb)→π*(py+fluo+carb)/ILCT	331
	S_{11}	311	0.3310	HOMO→L+2(58%)	d(Pt)+p(N)+π(fluo+carb)→π*(fluo+carb)/IL/MLCT	
	S_{19}	276	0.2900	HOMO→L+3(57%)	d(Pt)+p(N)+π(fluo+carb)→π*(fluo)/IL/MLCT	272

[a]from ref.16.

Table S4 Selected absorptions for complexes **6**–**9** in dichloromethane solution determined at the TD-B3LYP/6-31G(d)-LANL2DZ level of theory together with experimental values[a]

Species	State	λ_{cal}(nm)	*f*	Main configuration	Assignment	$\lambda_{Expt.}$(nm)
6	S_1	516	0.0003	HOMO→LUMO(92%)	d(Pt)+p(N)+π(carb)→π*(ph+py+thio)/IL/MLCT	487
	S_2	423	0.2276	H-1→LUMO(87%)	p(N)+π(py+carb+thio)→π*(ph+py+thio)/ ILCT	421
	S_3	395	0.1443	HOMO→L+1(86%)	d(Pt)+p(N)+π(carb)→π*(py+carb+thio)/IL/MLCT	378
	S_6	345	0.2815	H-1→L+1(94%)	p(N)+π(py+carb+thio)→π*(py+carb+thio)/ ILCT	
	S_{13}	307	0.6184	H-6→LUMO(80%)	d(Pt)+π(ph+py)→π*(ph+py+thio)/IL/MLCT	300
	S_{17}	281	0.1970	H-4→L+1(60%)	d(Pt)+π(carb+thio)→π*(py+carb+thio)/IL/MLCT	278
7	S_1	496	0.0390	HOMO→LUMO(97%)	d(Pt)+π(py+fluo+thio)→π*(py)/IL/MLCT	440/515
	S_3	361	0.4361	HOMO→L+1(82%)	d(Pt)+π(py+fluo+thio)→π*(py+fluo+thio)/IL/MLCT	362
	S_7	322	0.4683	H-1→L+1(84%)	π(fluo+thio)→π*(py+fluo+thio)/ILCT	317
	S_8	310	0.4722	H-5→LUMO(70%)	π(ph+py+fluo+thio)→π*(py)/ILCT	307
	S_{17}	278	0.2206	HOMO→L+4(82%)	d(Pt)+π(py+fluo+thio)→π*(fluo)/IL/MLCT	
	S_{22}	265	0.2527	H-7→L+1(35%)	d(Pt)+π(fluo+thio)→π*(py+fluo+thio)/IL/MLCT	
8	S_1	467	0.0145	HOMO→LUMO(98%)	d(Pt)+π(py+naph+thio)→π*(py+thio)/IL/MLCT	458
	S_2	391	0.1835	H-1→LUMO(89%)	π*(naph)→π*(py+thio)/ILCT	402
	S_3	372	0.2024	HOMO→L+1(84%)	d(Pt)+π(py+naph+thio)→π*(py+naph+thio)/IL/MLCT	365
	S_{10}	305	0.6224	H-6→LUMO(68%)	d(Pt)+π(ph+py+naph)→π*(py+thio)/IL/MLCT	294
	S_{15}	286	0.3754	HOMO→L+3(67%)	d(Pt)+π(py+naph+thio)→π*(ph+thio)/IL/MLCT	276
	S_{20}	265	0.2203	H-1→L+3(43%)	π*(naph)→π*(ph+thio)/ILCT	
9	S_1	510	0.0163	HOMO→LUMO(99%)	d(Pt)+ π(py+thio)→π*(py)/IL/MLCT	505
	S_2	356	0.0181	H-1→LUMO(80%)	p(N)+π(thio)→π*(py)/ILCT	354
	S_5	339	0.1735	H-2→LUMO(93%)	p(S)+d(Pt)+ π(py+thio)→π*(py)/IL/MLCT	332
	S_8	309	0.7272	H-5→LUMO(91%)	π(ph+py)→π*(py)/ILCT	301
	S_{11}	292	0.2484	H-1→L+1(73%)	p(N)+π(thio)→π*(py+thio)/ILCT	

[a]from ref.16.

Table S5 Calculated vertical triplet absorption of complexes **1**–**9** in dichloromethane solution determined at the TD-B3LYP/6-31G(d)-LANL2DZ level of theory together with experimental values[a]

Species	State	λ_{cal}(nm)	*f*	Main configuration	Assignment	$\lambda_{Expt.}$(nm)
1	T_4	419	0.0000	H-1→LUMO(54%)	π(py+ph+naph)→π*(py+ph+naph)/ILCT	417
2	T_2	483	0.0000	HOMO→LUMO(54%)	d(Pt)+π(carb)→π*(ph+py)/IL/MLCT	463
3	T_3	454	0.0000	HOMO→L+1(46%)	d(Pt)+π(py+naph+fluo)→π*(py+naph)/IL/MLCT	458
4	T_3	472	0.0000	H-2→LUMO(30%)	π(py+carb)→π*(py)/ILCT	476
5	T_3	462	0.0000	H-1→LUMO(42%)	p(N)+π(py+fluo+carb)→π*(py)/ILCT	467
6	T_3	474	0.0000	H-1→LUMO(58%)	p(N)+π(py+carb+thio)→π*(ph+py+thio)/ILCT	487
7	T_2	529	0.0000	HOMO→L+1(56%)	d(Pt)+π(py+fluo+thio)→π*(py+fluo+thio)/IL/MLCT	515
8	T_2	506	0.0000	HOMO→L+1(54%)	d(Pt)+π(py+naph+thio)→π*(py+naph+thio)/IL/MLCT	483
9	T_2	536	0.0000	HOMO→L+1(63%)	d(Pt)+ π(py+thio)→π*(py+thio)/IL/MLCT	540

[a]from ref.16.

Table S6 Contour plots of the highest cooupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of complexes **1a**–**9a**

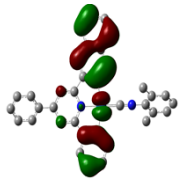
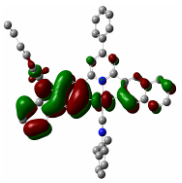
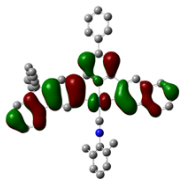
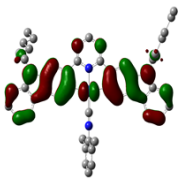
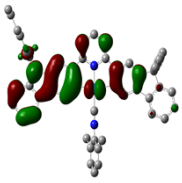
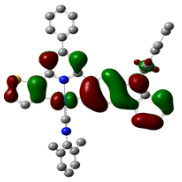
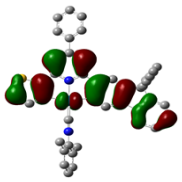
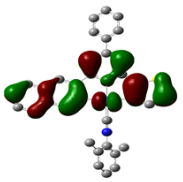
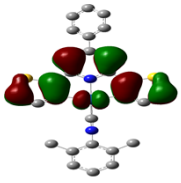
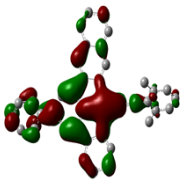
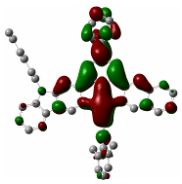
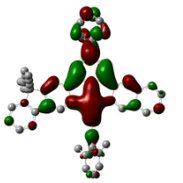
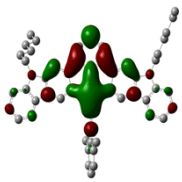
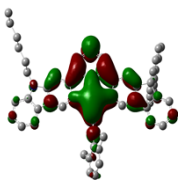
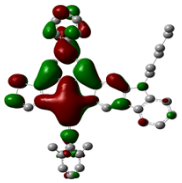
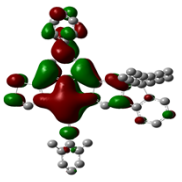
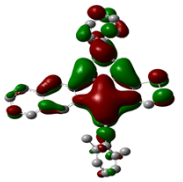
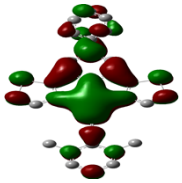
	1a	2a	3a	4a	5a
HOMO					
	6a	**7a**	**8a**	**9a**	
					
	1a	**2a**	**3a**	**4a**	**5a**
LUMO					
	6a	**7a**	**8a**	**9a**	
					

Table S7 Contour plots of the highest cooupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of complexes **1**–**9**

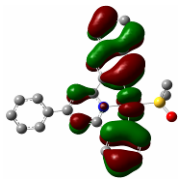
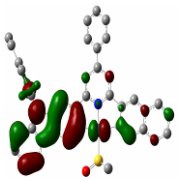
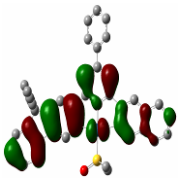
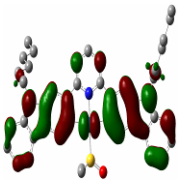
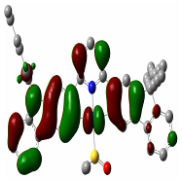
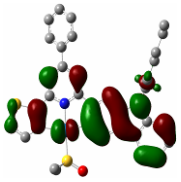
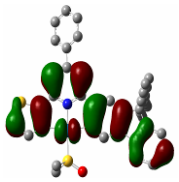
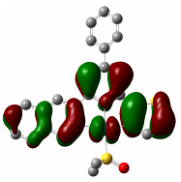
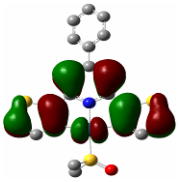
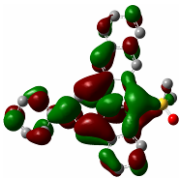
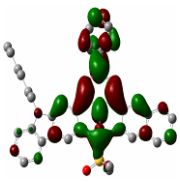
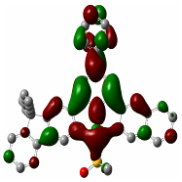
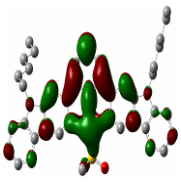
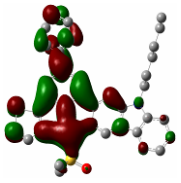
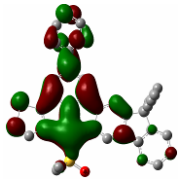
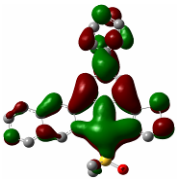
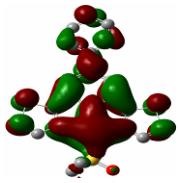
	1	2	3	4	5
HOMO					
	6	**7**	**8**	**9**	
					
	1	**2**	**3**	**4**	**5**
LUMO					
	6	**7**	**8**	**9**	
					

Table S8 Phosphorescent emissions of complexes **2**–**9** in dichloromethane solution determined at the TD-B3LYP/6-31G(d)-LANL2DZ level of theory together with the experimental values[a]

Species	State	λ_{cal}(nm)	Main configuration	Assignment	λ_{Expt}(nm)
2	T_2	516	H-1→L+1(32%)	π(carb+py+naph)→π*(py+carb+naph)/ILCT	590
3	T_1	675	HOMO→LUMO(85%)	d(Pt)+π(py+fluo)→π*(ph+py+fluo)/IL/MLCT	669
	T_2	514	HOMO→L+1(29%)	d(Pt)+π(py+fluo)→π*(py+fluo+naph)/IL/MLCT	568
4	T_2	540	HOMO→L+1(50%)	d(Pt)+p(N+C)+π(carb)→π*(py+carb)/IL/MLCT	600
5	T_2	540	HOMO→L+1(50%)	d(Pt)+p(N)+π(py+carb+fluo)→π*(py+carb)/IL/MLCT	572
6	T_2	567	HOMO→L+1(39%)	d(Pt)+p(N)+π(py+carb+thio)→π*(py+carb+thio)/IL/MLCT	600
7	T_2	557	HOMO→L+1(52%)	d(Pt)+π(py+fluo+thio)→π*(py+fluo+thio)/IL/MLCT	593
8	T_2	518	HOMO→L+1(39%)	d(Pt)+π(py+thio+naph)→π*(py+thio+naph)/IL/MLCT	582
9	T_2	578	HOMO→L+1(52%)	d(Pt)+π(py+thio)→π*(py+thio)/IL/MLCT	611

[a]from ref.16.

Table S9 Calculated metallic character of phosphorescence (M_c, %), $k_r/10^5$ s^{-1}, $T_2 \rightarrow S_0$ vertical transition energy (ΔE, eV) for complexes **2**–**9**, together with the experimental quantum efficiency (Φ_{em}, %)[a]

Species	M_c(%)	$k_r/10^5$ s^{-1}	ΔE(eV)	Φ_{em}(Expt.)
2	3.01	0.69	2.40	0.05
3	8.49	1.84	2.41	0.09
4	8.08	1.76	2.30	0.06
5	8.78	1.90	2.30	0.02
6	9.36	2.00	2.18	0.15
7	9.57	2.04	2.23	0.12
8	9.30	1.99	2.40	0.13
9	10.41	2.19	2.14	0.11

[a]from ref.16

Table S10 Ionization potentials (IP, eV), electron affinities (EA, eV), extraction potentials (HEP and EEP, eV), stabilization energy (SPE, eV), and internal reorganization energies (λ, eV) for complexes **1**–**9** determined at the B3LYP/6-31G(d)-LANL2DZ level of theory

Species	IP_v	IP_a	HEP	SPE(h)	EA_v	EA_a	EEP	SPE(e)	λ_{hole}	$\lambda_{electron}$	Δ_{SPE}	$\Delta\lambda$
1	6.59	6.43	6.05	0.16	0.72	0.87	1.01	0.15	0.54	0.29	0.01	0.25
2	5.94	5.84	5.72	0.10	0.76	0.90	1.04	0.15	0.22	0.29	0.05	0.07
3	6.24	6.16	6.07	0.08	0.84	0.97	1.10	0.13	0.17	0.26	0.05	0.09
4	5.78	5.69	5.59	0.09	0.53	0.64	0.75	0.11	0.19	0.22	0.02	0.03
5	6.02	5.94	5.87	0.07	0.62	0.72	0.82	0.10	0.15	0.20	0.03	0.05
6	5.98	5.87	5.76	0.11	0.70	0.84	0.98	0.14	0.22	0.28	0.03	0.06
7	6.21	6.13	6.05	0.08	0.79	0.92	1.05	0.13	0.17	0.25	0.05	0.08
8	6.48	6.38	6.28	0.10	0.73	0.87	1.01	0.14	0.20	0.28	0.04	0.08
9	6.45	6.34	6.24	0.10	0.69	0.83	0.96	0.14	0.21	0.27	0.04	0.06