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Supplementary Material

Theoretical Studies on Phosphorescent Materials: the Conjugation-Extended Pt^{II} Complexes

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Table S1. MO and d orbital contributions of **A** complex. Only those with *c*(d)> 0.01 are given in the table unless otherwise specified. The following the same.

MO	$c(d_{xy})$	$c(d_{xz})$	$c(d_{yz})$	$c(d_{x^2-y^2})$	$c(d_{z^2})$
129				0.01	
130		0.02			
131	0.01	0.41	0.05		
132		0.01			
133	0.18			0.15	0.10
134	0.21			0.06	0.01
135		0.07	0.44	0.01	0.02
136		0.07			
137			0.03	0.01	0.61
138					
139		0.02	0.01		
140		0.02	0.02		
141					
142			0.11		
143(H)		0.17	0.02		
144(L)			0.01		

Table S2. MO and d orbital contributions of **B** complex.

MO	$c(d_{xy})$	$c(d_{xz})$	$c(d_{yz})$	$c(d_{x^2-y^2})$	$c(d_{z^2})$
129	0.06		0.01	0.10	0.02
130		0.03	0.38	0.02	0.02
131				0.03	0.01
132	0.01	0.35	0.03		
133	0.00	0.12		0.01	0.01
134	0.26			0.19	0.05
135	0.08			0.01	0.02
136		0.07	0.07		
137			0.04	0.01	0.62
138		0.02	0.09		0.01
139					
140		0.01			
141		0.02	0.01		
142					
143			0.14		0.01
144(H)		0.16			
145(L)			0.01		

Table S3. MO and d orbital contributions of **C** complex.

MO	$c(d_{xy})$	$c(d_{xz})$	$c(d_{yz})$	$c(d_{x^2-y^2})$	$c(d_{z^2})$
147		0.37	0.07	0.01	
148	0.08			0.34	0.05
149	0.04			0.04	0.03
150					
151			0.03	0.01	0.62
152		0.03	0.07		
153		0.07	0.03		
154					
153		0.01			
154		0.02	0.01		
155					
156			0.12		
157(H)		0.12	0.01		
158(L)			0.02		
159			0.02		
160		0.01			

Table S4. MO and d orbital contributions of **D** complex.

MO	$c(d_{xy})$	$c(d_{xz})$	$c(d_{yz})$	$c(d_{x^2-y^2})$	$c(d_{z^2})$
169	0.01				0.01
170	0.03	0.16	0.05	0.23	0.02
171	0.02	0.19	0.03	0.13	0.03
172		0.07	0.02		
173		0.01		0.10	0.02
174	0.01			0.01	0.64
175		0.03	0.04		0.01
176		0.02	0.01		
177					
178					
179					
180		0.01	0.01		
181					
182			0.15		
183(H)		0.11	0.01		
184(L)			0.01		

Table S5. SOC matrix elements $<\mathrm{T}_m{}^{\alpha}|H_{\mathrm{SOC}}|\mathrm{S}_n>$ (cm^{-1}),[A] the energy ratios χ_n, the oscillator strengths f_n, as well as the radiative decay rate constant ($k_\mathrm{r}/\mathrm{s}^{-1}$) of **A** complex calculated at the first excited state of optimized geometry with solvent CH_2Cl_2 is given.[B]

$E(\mathrm{T}_1) = 18828\ \mathrm{cm}^{-1}$(2.26eV)								
S_n	χ_n[C]	f_n	$<\mathrm{T}_1{}^{z}\|H_{\mathrm{SOC}}\|\mathrm{S}_n>$	$<\mathrm{T}_1{}^{x}\|H_{\mathrm{SOC}}\|\mathrm{S}_n>$	$<\mathrm{T}_1{}^{y}\|H_{\mathrm{SOC}}\|\mathrm{S}_n>$	$k_n{}^{z}$	$k_n{}^{x}$	$k_n{}^{y}$
S_1	1.36	0.2618	3.8726			4.66		
S_2	1.65	0.0568	47.33	-0.35	-0.03	13.52	-0.10	-0.01
S_3	1.68	0.3462	10.73			7.20		
S_4	1.76	0.0265	-60.32	0.46	0.08	-9.70	0.07	0.01
S_5	1.77	0.0635	129.80	-1.46	-0.14	31.91	-0.36	-0.03
S_6	1.88	0.0916	0.75			0.19		
S_7	1.90	0.0543	12.47	-0.27	-0.03	2.36		-0.05
S_8	1.93	0.0146	0.05			0.01		
S_{10}	2.02	0.3922	17.72	-15.29	-0.50	7.67	-6.62	-0.22
sum						57.81	-7.06	-0.25
$k_\mathrm{r}{}^{\alpha}$						6380.26	0.12	95.02
k_r							6380.97	

[A]the superscript $^{\alpha}$ denotes the spin sub-level (x, y, or z) of the T_m excited state.

[B]$k_n^{\alpha} = \frac{\langle \mathrm{T}_m^{\alpha}|H_{SOC}|\mathrm{S}_n\rangle}{\chi_n{}^{1/2}(\chi_n-1)} \cdot (f_n)^{1/2}$, $k_r^{\alpha} = \frac{\eta^3}{1.5}\left[\sum_n \frac{\langle \mathrm{T}_m^{\alpha}|H_{SOC}|\mathrm{S}_n\rangle}{\chi_n{}^{1/2}(\chi_n-1)} \cdot (f_n)^{1/2}\right]^2$, $k_r = \sqrt{(k_r^z)^2+(k_r^x)^2+(k_r^y)^2}$

[C]$\chi_n = \frac{E(\mathrm{S}_n)}{E(\mathrm{T}_m)}$ $(\chi_n > 1)$

Table S6. SOC matrix elements $<T_m^{\alpha}|H_{SOC}|S_n>$ (cm^{-1}), the energy ratios χ_n, the oscillator strengths f_n , as well as the radiative decay rate constant (k_r/s^{-1} and $k_r=k_r(1)+k_r(2)$)of **B** complex.

$E(T_1)$ = 20405 cm^{-1} (2.53eV)								
S_n	χ_n	f_n	$<T_1^z\|H_{SOC}\|S_n>$	$<T_1^x\|H_{SOC}\|S_n>$	$<T_1^y\|H_{SOC}\|S_n>$	k_n^z	k_n^x	k_n^y
S1	1.36	0.1916	1.5008			1.57		
S2	1.59	0.0607	5.21			1.73		
S3	1.62	0.3252	20.09			14.41		
S4	1.69	0.0747	31.95			9.69		
S5	1.79	0.0447	30.73			6.19		
S6	1.80	0.0387	134.70	-1.12		24.54	-0.20	
S7	1.81	0.0397	56.57	-0.52		10.38	-0.10	
S8	1.83	0.1001	0.44			0.12		
S9	1.84	0.1131	0.23			0.07		
S10	1.91	0.2894	5.33			2.30		
sum						71.00	-0.30	
k_r^{α}						9623.35	0.17	--
$k_r(1)$							9623.35	
$E(T_2)$ =25084 cm^{-1} (3.11eV)								
S_n	χ_n	f_n	$<T_2^z\|H_{SOC}\|S_n>$	$<T_2^x\|H_{SOC}\|S_n>$	$<T_2^y\|H_{SOC}\|S_n>$	k_n^z	k_n^x	k_n^y
S1	1.11	0.1916	0.63			12.73		
S3	1.32	0.3252	0.65			3.10		
S4	1.38	0.0747	-1.00			-8.22		
S5	1.45	0.0447	-1.13			-9.80		
S6	1.47	0.0387	0.31			2.74		
S7	1.47	0.0397	-0.54			-4.73		
S8	1.49	0.1001	-0.29			-1.53		
S9	1.50	0.1131	0.31			1.49		
S10	1.55	0.2894	-2.64			-7.14		
sum						-11.36		
k_r^{α}						246.54	--	--
$k_r(2)$							246.54	
k_r							9869.89	

Table S7. SOC matrix elements $\langle T_m^{\alpha}|H_{SOC}|S_n\rangle$ (cm^{-1}), the energy ratios χ_n, the oscillator strengths f_n , as well as the radiative decay rate constant (k_r/s^{-1} and $k_r=k_r(1)+k_r(2)$) of **C** complex.

$E(T_1)$ =20567 cm^{-1} (2.55eV)								
S_n	χ_n	f_n	$\langle T_1^z\|H_{SOC}\|S_n\rangle$	$\langle T_1^x\|H_{SOC}\|S_n\rangle$	$\langle T_1^y\|H_{SOC}\|S_n\rangle$	k_n^z	k_n^x	k_n^y
S2	1.58	0.0831	2.53			1.00		
S3	1.61	0.3916	7.48			6.05		
S4	1.68	0.1834	7.22			3.51		
S5	1.74	0.0422	-1.47			-0.31		
S6	1.76	0.0349	107.80	-0.92	0.08	19.97	-0.17	0.01
S7	1.79	0.0141	-0.70			-0.08		
S8	1.80	0.0485	1.18			0.24		
S9	1.82	0.0218	-0.02			0.00		
S10	1.85	0.5519	-0.14			-0.09		
sum						30.30	-0.17	0.01
k_r^{α}						1752.16	0.06	--
$k_r(1)$							1752.16	
$E(T_2)$ = 25164 cm^{-1}(3.12eV)								
S_n	χ_n	f_n	$\langle T_2^z\|H_{SOC}\|S_n\rangle$	$\langle T_2^x\|H_{SOC}\|S_n\rangle$	$\langle T_2^y\|H_{SOC}\|S_n\rangle$	k_n^z	k_n^x	k_n^y
S1	1.09	0.2061	0.50			2.46		
S3	1.31	0.3916	1.01			1.75		
S4	1.37	0.1834	1.81			1.77		
S5	1.42	0.0422	-1.54			-0.63		
S6	1.44	0.0349	-9.99		-0.09	-3.55		-0.03
S7	1.46	0.0141	-0.21			-0.05		
S8	1.47	0.0485	3.50			1.35		
S10	1.52	0.5519	1.40			1.62		
sum						4.72		-0.03
k_r^{α}						42.52	--	--
$k_r(2)$							42.52	
k_r							1794.68	

Table S8. SOC matrix elements $\langle T_m^{\alpha}|H_{SOC}|S_n\rangle$ (cm^{-1}), the energy ratios χ_n, the oscillator strengths f_n , as well as the radiative decay rate constant (k_r/s^{-1} and $k_r = k_r(1)+k_r(2)+k_r(3)$)of **D** complex.

$E(T_1)$ = 20118cm^{-1} (2.49eV)								
S_n	χ_n	f_n	$\langle T_1^z\|H_{SOC}\|S_n\rangle$	$\langle T_1^x\|H_{SOC}\|S_n\rangle$	$\langle T_1^y\|H_{SOC}\|S_n\rangle$	k_n^z	k_n^x	k_n^y
S1	1.33	0.2624	-1.17			-1.58		
S2	1.58	0.1295	10.68			5.24		
S3	1.61	0.2879	-5.92			-4.11		
S4	1.63	0.4249	1.21			0.97		
S5	1.67	0.0218	2.11			0.36		
S6	1.74	0.0988	0.47			0.15		
S7	1.79	0.028	118.18	-1.53		18.73	-0.24	
S8	1.80	0.0882	0.39			0.11		
S9	1.83	0.014	-0.63			-0.07		
S10	1.84	0.0334	-0.30			-0.05		
sum						19.76	-0.24	
k_r^{α}						745.16	0.11	--
$k_r(1)$							745.16	
$E(T_2)$ = 25084 cm^{-1} (3.11eV)								
S_n	χ_n	f_n	$\langle T_2^z\|H_{SOC}\|S_n\rangle$	$\langle T_2^x\|H_{SOC}\|S_n\rangle$	$\langle T_2^y\|H_{SOC}\|S_n\rangle$	k_n^z	k_n^x	k_n^y
S1	1.07	0.2624	-1.89			-14.20		
S2	1.27	0.1295	0.37			0.44		
S3	1.29	0.2879	0.07			0.11		
S4	1.31	0.4249	-1.11			-2.03		
S6	1.40	0.0988	-0.37			-0.25		
S7	1.43	0.028	1.31	0.042		0.42	0.01	
S9	1.47	0.0140	-0.33			-0.07		
S10	1.47	0.0334	-0.03			-0.01	0.01	
sum						-15.6	0.02	
k_r^{α}						464.36	--	--
$k_r(2)$							464.36	
$E(T_3)$ = 25406 cm^{-1} (3.15eV)								
S_n	χ_n	f_n	$\langle T_3^z\|H_{SOC}\|S_n\rangle$	$\langle T_3^x\|H_{SOC}\|S_n\rangle$	$\langle T_3^y\|H_{SOC}\|S_n\rangle$	k_n^z	k_n^x	k_n^y
S1	1.05	0.2624	7.12			65.70		
S2	1.26	0.1295	-2.75			-3.45		
S3	1.28	0.2879	1.53			2.63		
S4	1.30	0.4249	1.46			2.83		
S5	1.32	0.0218	0.46			0.18		

S6	1.38	0.0988	-1.14			-0.80		
S7	1.42	0.028	69.00	-0.62		23.16	-0.21	
S8	1.43	0.0882	-23.43			-13.62		
S9	1.45	0.014	-4.32			-0.94		
S10	1.46	0.0334	3.12			1.04		
sum						76.73	-0.21	
k_r^{α}						11237.21	0.17	0.08
$k_r(3)$							11237.21	
k_r							12446.73	