Supporting Information: Tetradentate Pt(II) Phosphors – a Computational Analysis of Nonradiative Decay Rates and Luminescent Efficiency

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Contents

List of Tables **S-2**

Bibliography **S-19**

List of Tables

S1 Chemical structures (*no.* **1**–**9**) S-5

S2 Chemical structures (*no.* **10**–**17**) S-6

S3 Comparison of calculated adiabatic energy gap $\Delta E_{if}^{\text{Calc.}}$ and energy corresponding to the measured peak of the emission at 77 K [1-6] S-7

S4 Calibration of k_{ph} calculated in optimized ground state geometry. Statistical metrics (R^2, RMSE and MAE) for rates are calculated in logarithmic scale. . S-8

S5 Comparison of predicted and experimental values of k_{ph}. Calculated values are calibrated with optimal value of α_r: $k_{\text{ph}} = \alpha_r k_{\text{ph}}^{\text{Calc.}}$, see Table S4. Statistical metrics (R^2, RMSE and MAE) for rates are calculated in logarithmic scale. . S-9

S6 Calculated values of the spin–orbit coupling between ground and triplet states of the complexes[a] S-10

S7 Broadening parameter of the weak coupling approximation (*wcl*) and corresponding metrics for k_{isc}. Statistical metrics (R^2, RMSE and MAE) for rates are calculated in logarithmic scale. S-11

S8 Broadening parameter of the weak coupling approximation (with separate treatment of slow/fast normal modes, *wcl2*) and corresponding metrics for k_{isc}. Statistical metrics (R^2, RMSE and MAE) for rates are calculated in logarithmic scale. S-12

S9 Broadening parameter of the strong coupling approximation (*scl*) and corresponding metrics for k_{isc}. Statistical metrics (R^2, RMSE and MAE) for rates are calculated in logarithmic scale. S-13

S10 Lifetime of dephasing and corresponding metrics for k_{isc} calculated using the VCF approach. Statistical metrics (R^2, RMSE and MAE) for rates are calculated in logarithmic scale. S-14

S11 Broadening parameter of the weak coupling approximation (*wcl*) and corresponding metrics for Φ_{PL} S-15

S12 Broadening parameter of the weak coupling approximation (with separate treatment of slow/fast normal modes, *wcl2*) and corresponding metrics for Φ_{PL} S-16

S13 Broadening parameter of the strong coupling approximation (*scl*) and corresponding metrics for Φ_{PL} S-17

S14 Dephasing function lifetime parameter τ_{L} and corresponding metrics for Φ_{PL} calculated using the VCF approach. S-18

Chemical Structures of the Complexes

Table S1: Chemical structures (*no.* **1**–**9**)

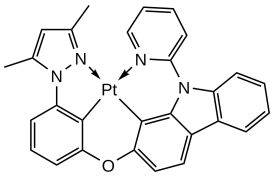
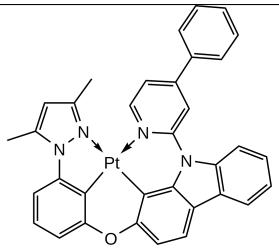
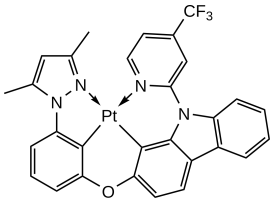
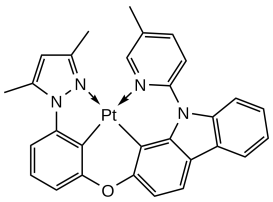
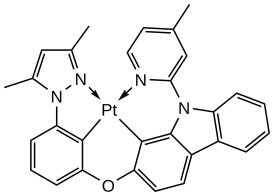
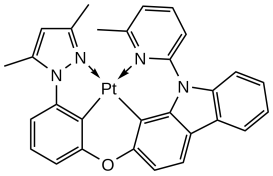
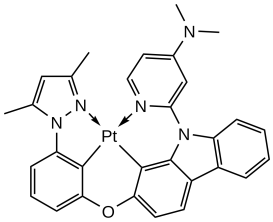
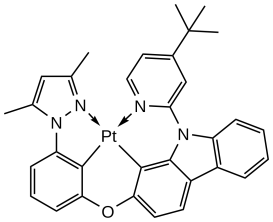
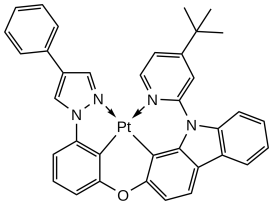
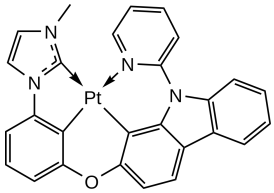
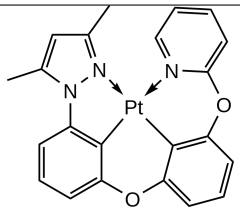
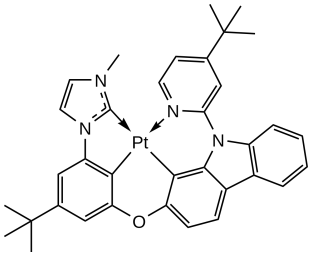
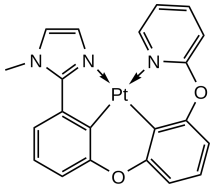
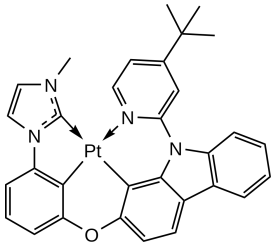
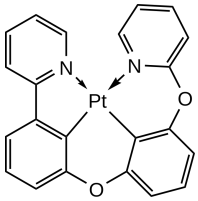
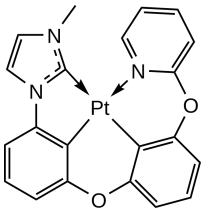
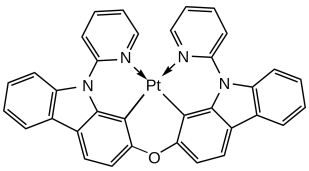
no.	Structure	*Ref.*	*no.*	Structure	*Ref.*
1	 **PtON1**	S1	**5**	 **PtON1-Ph**	S1
2	 **PtON1-CF$_3$**	S1	**6**	 **PtON1-*m*Me**	S1
3	 **PtON1-Me**	S1	**7**	 **PtON1-*o*Me**	S1
4	 **PtON1-NMe$_2$**	S1	**8**	 **PtON1-tBu**	S1
			9	 **PtON6-tBu**	S5

Table S2: Chemical structures (*no.* **10**–**17**)

no.	Structure	*Ref.*	*no.*	Structure	*Ref.*
10	 **PtON7**	S2	**13**	 **PtOO1**	S6
11	 **PtON7-dtb**	S5	**14**	 **PtOO2**	S6
12	 **PtON7-tBu**	S3	**15**	 **PtOO3**	S6
			16	 **PtOO7**	S2
			17	 **PtNON**	S4

Adiabatic energy gap ΔE_{if}

Table S3: Comparison of calculated adiabatic energy gap $\Delta E_{if}^{\text{Calc.}}$ and energy corresponding to the measured peak of the emission at 77 K [1-6]

no.	Complex	$\lambda_0^{77\text{K}}$ $/eV$	$\Delta E_{if}^{\text{Calc.}}$ $/eV$
1	**PtON1**	2.82	2.78
2	**PtON1-CF$_3$**	2.51	2.37
3	**PtON1-Me**	2.83	2.85
4	**PtON1-NMe$_2$**	2.84	3.00
5	**PtON1-Ph**	2.64	2.43
6	**PtON1-*m*Me**	2.82	2.80
7	**PtON1-*o*Me**	2.82	2.81
8	**PtON1-tBu**	2.83	2.85
9	**PtON6-tBu**	2.83	2.85
10	**PtON7**	2.81	2.77
11	**PtON7-dtb**	2.82	2.82
12	**PtON7-tBu**	2.82	2.84
13	**PtOO1**	2.95	2.90
14	**PtOO2**	2.68	2.71
15	**PtOO3**	2.55	2.47
16	**PtOO7**	2.87	2.87
17	**PtNON**	2.82	2.71
		MAE/eV	0.06
		RMSE/eV	0.08

Calibration and results of $k_{\mathbf{ph}}$ prediction.

Table S4: Calibration of k_{ph} calculated in optimized ground state geometry. Statistical metrics (R^2, RMSE and MAE) for rates are calculated in logarithmic scale.

α_r	R^2	MAE/$10^4\,s^{-1}$	RMSE/$10^4\,s^{-1}$
0.67	0.64	0.39	0.47
0.65	0.64	0.38	0.46
0.63	0.64	0.37	0.44
0.61	0.64	0.35	0.43
0.59	0.64	0.34	0.42
0.58	0.64	0.33	0.41
0.56	0.64	0.32	0.40
0.54	0.64	0.31	0.40
0.53	0.64	0.30	0.40
0.51	0.64	0.29	0.40
0.50	**0.64**	**0.28**	**0.40**
0.48	0.64	0.29	0.40
0.47	0.64	0.29	0.41
0.45	0.64	0.30	0.42
0.44	0.64	0.31	0.43

Table S5: Comparison of predicted and experimental values of k_{ph}. Calculated values are calibrated with optimal value of α_r: $k_{\mathrm{ph}} = \alpha_r k_{\mathrm{ph}}^{\mathrm{Calc.}}$. Statistical metrics ($R^2$, RMSE and MAE) for rates are calculated in logarithmic scale.

no.	Complex	$k_{\mathrm{ph}}^{\mathrm{Expt.}}/10^4 s^{-1}$	$k_{\mathrm{ph}}^{\mathrm{Calc.}}/10^4 s^{-1}$
1	**PtON1**	21.52	13.42
2	**PtON1-CF3**	1.83	2.24
3	**PtON1-Me**	8.90	11.77
4	**PtON1-NMe2**	5.93	5.95
5	**PtON1-Ph**	23.75	23.76
6	**PtON1-mMe**	23.43	13.42
7	**PtON1-oMe**	14.52	12.90
8	**PtON1-tBu**	10.67	7.17
9	**PtON6-tBu**	10.95	10.70
10	**PtON7**	18.57	13.83
11	**PtON7-dtb**	15.74	16.18
12	**PtON7-tBu**	12.58	14.74
13	**PtOO1**	13.00	31.63
14	**PtOO2**	7.11	9.85
15	**PtOO3**	31.50	12.45
16	**PtOO7**	23.20	25.47
17	**PtNON**	11.92	12.57
		MAE	0.28
		RMSE	0.40

Spin–orbit couplings

Table S6: Calculated values of the spin–orbit coupling between ground and triplet states of the complexes[a]

no.	Complex	$\lvert H^{SO} \rvert$ $/cm^{-1}$
1	**PtON1**	65.42
2	**PtON1-CF$_3$**	140.51
3	**PtON1-Me**	62.25
4	**PtON1-NMe$_2$**	28.46
5	**PtON1-Ph**	73.68
6	**PtON1-*m*Me**	65.58
7	**PtON1-*o*Me**	58.60
8	**PtON1-tBu**	7.62
9	**PtON6-tBu**	42.72
10	**PtON7**	75.50
11	**PtON7-dtb**	65.67
12	**PtON7-tBu**	52.23
13	**PtOO1**	38.87
14	**PtOO2**	3.64
15	**PtOO3**	34.73
16	**PtOO7**	47.51
17	**PtNON**	91.40

[a] *in optimized ground state geometry*

Analysis of broadening/dephasing parameter in $k_{\mathbf{isc}}$

Table S7: Broadening parameter of the weak coupling approximation (wcl) and corresponding metrics for k_{isc}. Statistical metrics (R^2, RMSE and MAE) for rates are calculated in logarithmic scale.

ω_0^{wcl} $/cm^{-1}$	R^2	MAE/10^4 s^{-1}	RMSE/10^4 s^{-1}
900	0.71	5.92	6.25
950	0.72	5.55	5.89
1000	0.72	5.19	5.53
1050	0.72	4.85	5.20
1100	0.73	4.54	4.88
1150	0.73	4.25	4.57
1200	0.73	3.97	4.28
1250	0.73	3.71	4.00
1300	0.73	3.45	3.73
1350	0.73	3.20	3.48
1400	0.74	2.96	3.24
1450	0.74	2.73	3.01
1500	0.74	2.51	2.79
1550	0.74	2.29	2.58
1600	0.74	2.10	2.39
1650	0.74	1.94	2.21
1700	0.74	1.79	2.04
1750	0.74	1.65	1.88
1800	0.74	1.51	1.74
1850	0.74	1.37	1.62
1900	0.74	1.26	1.52
1950	0.74	1.15	1.43
2000	0.74	1.10	1.37
2050	0.74	1.05	1.32
2100	**0.74**	**1.03**	**1.30**
2150	0.73	1.02	1.30
2200	0.73	1.05	1.32
2250	0.73	1.09	1.36
2300	0.73	1.13	1.41
2350	0.73	1.19	1.47

Table S8: Broadening parameter of the weak coupling approximation (with separate treatment of slow/fast normal modes, *wcl2*) and corresponding metrics for k_{isc}. Statistical metrics (R^2, RMSE and MAE) for rates are calculated in logarithmic scale.

$\omega_0^{wcl}\,/cm^{-1}$	R^2	MAE/$10^4\,s^{-1}$	RMSE/$10^4\,s^{-1}$
900	0.81	3.99	4.29
950	0.82	3.64	3.94
1000	0.82	3.32	3.61
1050	0.82	3.02	3.30
1100	0.82	2.75	3.00
1150	0.82	2.48	2.73
1200	0.82	2.23	2.48
1250	0.83	1.99	2.25
1300	0.83	1.75	2.04
1350	0.83	1.56	1.87
1400	0.83	1.43	1.72
1450	0.83	1.31	1.60
1500	0.83	1.19	1.53
1550	0.83	1.09	1.48
1600	**0.83**	**1.05**	**1.48**
1650	0.83	1.10	1.51
1700	0.82	1.20	1.57
1750	0.82	1.31	1.65
1800	0.82	1.41	1.74
1850	0.82	1.51	1.86

Table S9: Broadening parameter of the strong coupling approximation (scl) and corresponding metrics for k_{isc}. Statistical metrics (R^2, RMSE and MAE) for rates are calculated in logarithmic scale.

$\omega_0^{scl}\,/cm^{-1}$	R^2	MAE/$10^4\,s^{-1}$	RMSE/$10^4\,s^{-1}$
2700	0.91	7.17	7.79
2750	0.91	6.67	7.27
2800	0.91	6.23	6.77
2850	0.91	5.81	6.30
2900	0.91	5.41	5.84
2950	0.91	5.03	5.40
3000	0.91	4.65	4.99
3050	0.91	4.29	4.59
3100	0.91	3.95	4.21
3150	0.91	3.61	3.85
3200	0.91	3.29	3.51
3250	0.91	2.98	3.19
3300	0.91	2.68	2.90
3350	0.90	2.39	2.63
3400	0.90	2.11	2.39
3450	0.90	1.84	2.18
3500	**0.90**	1.61	2.00
3550	0.89	1.43	1.86
3600	0.89	1.29	1.77
3650	0.89	1.25	1.73
3700	0.88	**1.25**	**1.72**
3750	0.88	1.29	1.76
3800	0.88	1.41	1.84
3850	0.87	1.52	1.94
3900	0.87	1.67	2.06
3950	0.86	1.83	2.19
4000	0.86	2.00	2.34
4050	0.86	2.16	2.49
4100	0.85	2.31	2.65
4150	0.85	2.49	2.81

Table S10: Lifetime of dephasing and corresponding metrics for k_{isc} calculated using the VCF approach. Statistical metrics (R^2, RMSE and MAE) for rates are calculated in logarithmic scale.

$\tau_{\mathrm{L}}\,/ps$	R^2	MAE/$10^4\,s^{-1}$	RMSE/$10^4\,s^{-1}$
2.5	0.33	2.33	2.57
5.0	0.34	1.81	2.07
10.0	**0.35**	1.42	1.71
12.5	0.34	1.35	1.64
15.0	0.34	1.32	1.59
20.0	0.33	**1.28**	**1.56**
25.0	0.33	1.27	1.57
30.0	0.32	1.26	1.60
35.0	0.32	1.25	1.63
45.0	0.31	1.26	1.71
50.0	0.31	1.29	1.75
55.0	0.31	1.31	1.79

Analysis of broadening parameter in $k_{\mathbf{isc}}$ for $\Phi_{\mathbf{PL}}$ prediction

Table S11: Broadening parameter of the weak coupling approximation (wcl) and corresponding metrics for Φ_{PL}

$\omega_0^{wcl}\,/cm^{-1}$	R^2	MAE	RMSE
1450	0.60	0.26	0.31
1500	0.62	0.25	0.30
1550	0.63	0.24	0.30
1600	0.64	0.24	0.29
1650	0.65	0.23	0.28
1700	0.66	0.21	0.27
1750	0.67	0.20	0.26
1800	0.67	0.19	0.25
1850	0.67	0.18	0.24
1900	0.67	0.17	0.23
1950	0.67	0.17	0.22
2000	**0.67**	0.16	0.21
2050	0.66	0.15	0.20
2100	0.65	0.14	0.20
2150	0.64	**0.14**	**0.19**
2200	0.62	0.14	0.19

Table S12: Broadening parameter of the weak coupling approximation (with separate treatment of slow/fast normal modes, *wcl2*) and corresponding metrics for Φ_{PL}

$\omega_0^{wcl2}\,/cm^{-1}$	R^2	MAE	RMSE
900	0.58	0.28	0.33
950	0.60	0.27	0.32
1000	0.62	0.26	0.31
1050	0.65	0.25	0.30
1100	0.67	0.24	0.29
1150	0.69	0.23	0.28
1200	0.72	0.22	0.27
1250	0.74	0.21	0.26
1300	0.76	0.20	0.24
1350	0.77	0.19	0.23
1400	0.79	0.17	0.21
1450	0.79	0.15	0.20
1500	0.80	0.14	0.18
1550	0.80	0.13	0.17
1600	**0.80**	0.12	0.16
1650	0.79	**0.11**	**0.15**
1700	0.78	0.11	0.15
1750	0.76	0.12	0.15
1800	0.74	0.13	0.16

Table S13: Broadening parameter of the strong coupling approximation (scl) and corresponding metrics for Φ_{PL}

$\omega_0^{scl}\,/cm^{-1}$	R^2	MAE	RMSE
2700	0.56	0.27	0.33
2750	0.56	0.27	0.33
2800	0.56	0.27	0.33
2850	0.57	0.27	0.33
2900	0.57	0.27	0.33
2950	0.58	0.27	0.32
3000	0.59	0.26	0.32
3050	0.61	0.26	0.31
3100	0.63	0.25	0.30
3150	0.65	0.25	0.29
3200	0.67	0.24	0.28
3250	0.69	0.22	0.27
3300	0.71	0.21	0.25
3350	0.72	0.19	0.24
3400	0.72	0.18	0.22
3450	**0.73**	0.17	0.21
3500	0.72	0.15	0.20
3550	0.71	0.14	0.19
3600	0.70	**0.14**	**0.18**
3650	0.67	0.15	0.18
3700	0.65	0.16	0.19
3750	0.61	0.17	0.21
3800	0.57	0.18	0.24
3850	0.53	0.21	0.27
3900	0.48	0.25	0.30
3950	0.43	0.28	0.34
4000	0.38	0.32	0.37
4050	0.34	0.35	0.40
4100	0.30	0.37	0.43

Table S14: Dephasing function lifetime parameter τ_{L} and corresponding metrics for Φ_{PL} calculated using the VCF approach.

$\tau_{\mathrm{L}}\,/ps$	R^2	MAE	RMSE
2.5	0.12	0.42	0.49
5.0	0.18	0.36	0.42
10.0	0.25	0.27	0.33
12.5	0.28	0.25	0.31
15.0	0.30	0.24	0.29
20.0	0.32	0.22	0.26
25.0	0.33	0.21	0.24
30.0	0.34	0.20	0.23
35.0	0.34	0.19	0.23
45.0	**0.34**	**0.18**	**0.24**
50.0	0.33	0.19	0.24
55.0	0.33	0.19	0.24

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