Supplementary Information

Solid-State Emission Enhancement in Vaulted *trans*-Bis(salicylaldiminato)platinum(II) Crystals with Halogen Functionality

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Table S1 Photophysical data of **1**–**4** in 2-MeTHF[a]

complex	λ_{abs} (nm)	λ_{em} (nm)[b,c]	Φ[b,c,d]
1b	317, 432	—[e] (530, 561)	<0.01 (0.42)
2b	317, 430	—[e] (529, 563)	<0.01 (0.45)
3a	332, 436	534 (519, 561)	<0.01 (0.61)
3b	317, 430	—[e] (521, 562)	<0.01 (0.57)
3c	336, 457	—[e] (538, 582)	<0.01 (0.53)
3d	338, 447	552 (538, 582)	<0.01 (0.48)
3e	307, 420	—[e] (511, 541)	<0.01 (0.58)
3f	319, 333, 435	—[e] (520, 558)	<0.01 (0.58)
4b	317, 332, 430	—[e] (515, 552)	<0.01 (0.66)

[a]A 2×10^{-4} M solution in 2-MeTHF at 298 K. [b]λ_{ex} = 420 nm. [c]Values in parehtheses are those measured at 77 K. [d]Determined by the absolute method by using an integrating sphere. [e]No emission.

Table S2 Photophysical data of **1g**, **2g**, and **3g** in crystalline state[a]

complex	λ_{abs} (nm)	λ_{em} (nm)	Φ^b	τ(μs)[c]	CIE (x,y)
1g[d]	319, 443, 511	—[e]	<0.01 (0.18)	—[e]	—[e]
2g[d]	324, 441, 522	558, 582	<0.01 (0.60)	—[e]	0.50, 0.50
3g[d]	319, 441, 528	564, 585	0.32 (0.51)	1.7	0.51, 0.48

[a]Data obtained at 298 K under excitation at 420 nm. All crystals were obtained by recrystallization from EtOH. [b]Determined by the absolute method using an integrating sphere. Values in parentheses are those measured at 77 K. [c]λ_{ex}=435 nm. [d]Racemic crystal. [e]No emission.

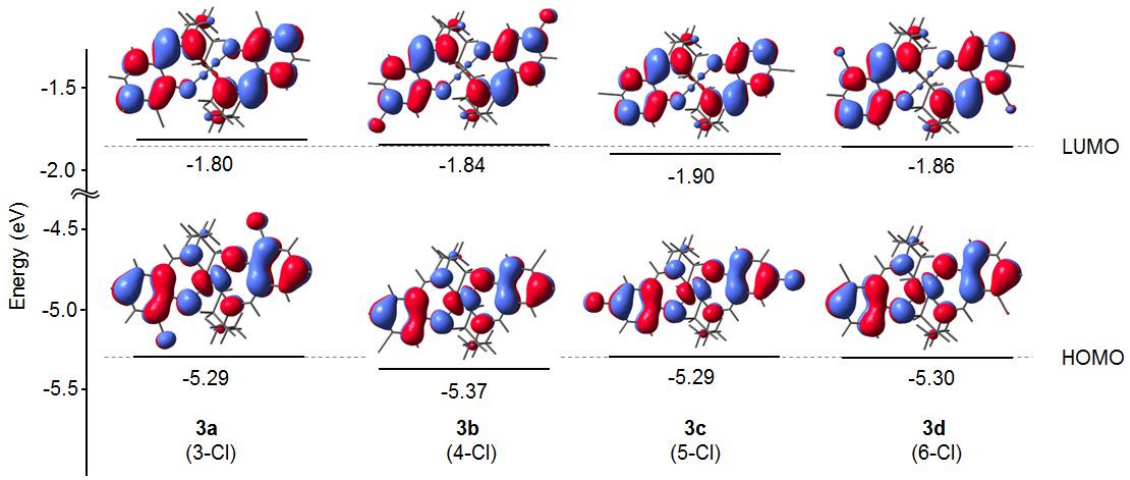

Fig. S1. Frontier orbitals and their eigenvalues (eV) for **3a**–**d** estimated from DFT calculations (B3LYP/6-31G*, LanL2DZ) on the basis of optimized structures.

Table S3 Excitation energy, oscillator strength and major electronic configuration of **3a**–**d**[a]

complex	state	excitation energy / eV	oscillator strength	major configuration[b]	coefficient
3a	Singlet				
	1	2.8307	f = 0.0363	135→136	0.69500
	2	3.0924	0.0006	135→137	0.69573
	3	3.1208	0.0021	135→138	0.67582
	4	3.3460	0.0005	134→136	0.69721
	Triplet				
	1	2.3459		134→137	−0.21880
				135→136	0.64943
	2	2.5175		131→136	−0.10497
				134→136	−0.34839
				135→137	0.59239
	3	2.7422		128→138	0.13985
				130→138	0.23947
				135→138	0.63353
	4	3.0102		131→137	−0.29064
				133→136	0.55896
				134→137	0.15145
3b	Singlet				
	1	2.8686	f = 0.0374	135→136	0.69546
	2	3.1518	0.0007	135→137	0.69537
	3	3.1939	0.0017	130→138	0.16150
				135→138	0.67864
	4	3.3531	0.0010	132→138	0.11633
				134→136	0.69015
	Triplet state				
	1	2.3812		134→137	−0.22414
				135→136	0.64983
	2	2.5516		134→136	−0.34232
				135→137	0.59727
	3	2.7441		130→138	0.26203
				135→138	0.63964
	4	3.0880		131→137	−0.30207
				133→136	0.56927
				135→136	0.11871

[a] Estimated from TD−DFT (B3LYP/6−31G*, LanL2DZ) calculations on the basis of optimized structures.
[b] HOMO is MO135.

Table S3 (continued)

complex	state	excitation energy / eV	oscillator strengt	major configuration[b]	coefficient
3c	Singlet state				
	1	2.7540	f = 0.0344	135→136	0.69558
	2	3.0422	0.0008	135→137	0.69618
	3	3.1587	0.0018	131→138	0.17643
				135→138	0.67514
	4	3.2703	0.0010	134→136	0.69824
	Triplet state				
	1	2.2470		134→137	−0.23738
				135→136	0.65259
	2	2.4093		134→136	−0.36831
				135→137	0.59023
	3	2.7202		131→138	0.28459
				135→138	0.63195
	4	3.0908		130→137	0.27026
				133→136	0.55153
				134→140	0.15619
				135→139	−0.17529
3d	Singlet state				
	1	2.7825	f = 0.0330	135→136	0.69841
	2	3.0699	0.0006	135→137	0.69703
	3	3.2857	0.0010	130→138	0.14535
				135→138	0.67866
	4	3.3994	0.0004	134→136	0.69638
	Triplet state				
	1	2.2972		134→137	−0.21844
				135→136	0.65719
	2	2.4706		134→136	−0.33711
				135→137	0.60476
	3	2.7898		130→138	0.23935
				135→138	0.64288
	4	2.9985		131→137	0.29142
				133→136	0.56404
				134→137	−0.14392

[a] Estimated from TD−DFT (B3LYP/6−31G*, LanL2DZ) calculations on the basis of optimized structures.
[b] HOMO is MO135.

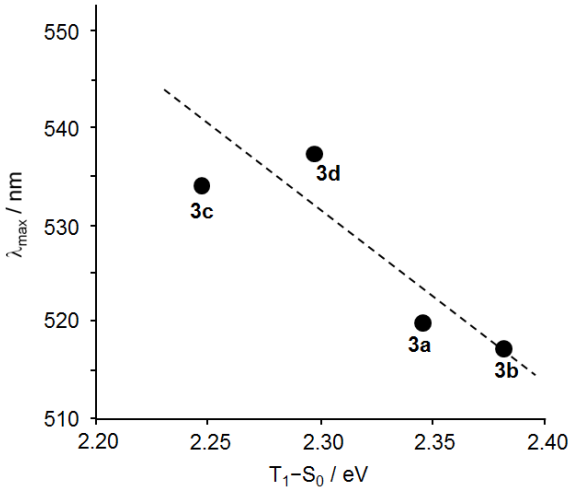

Fig. S2. Relationship between the T_1–S_0 energy gap and emission maxima (λ_{max}) for **3a**–**d** in 2-MeTHF at 77 K. The energy gap was estimated from TD-DFT calculations (B3LYP/6-31G*, LanL2DZ) on the basis of optimized structures.