

Supporting Information

for

HOMO-LUMO Energy Gap Control in Platinum(II) Biphenyl Complexes Containing 2,2'-Bipyridine Ligand

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1. Method Exploration.

Table S1. Platinum-ligand Bond Lengths (Å) and Ligand Bite Angles (°) optimized for Isolated Complexes in Singlet Ground State (SGS) in Acetonitrile Solvent Using the B3LYP/TZVP-QZV-P/CPCM and PBE0PBE/TZVP-QZV-P/CPCM Methods.

Optimized	Pt(bph)(4,4'-(NH ₂) ₂ bpy)	Pt(bph)(4,4'-Me ₂ bpy)	Pt(bph)(bpy)	Pt(bph)(4,4'-Ph ₂ bpy)	Pt(bph)(4,4'-Br ₂ bpy)	Pt(bph)(4,4'-(COOC ₂ H ₅) ₂ bpy)
			B3LYP			
Pt-C	2.021	2.022	2.022	2.021	2.020	2.021
Pt-N	2.185	2.184	2.182	2.180	2.185	2.175
C-Pt-C	80.4	80.4	80.3	80.4	80.4	80.4
N-Pt-N	75.3	75.4	75.5	75.6	75.4	75.8
			PBE0PBE			
Pt-C	2.001	2.002	2.003	2.001	2.001	2.001
Pt-N	2.142	2.140	2.138	2.137	2.143	2.134
C-Pt-C	80.6	80.6	80.5	80.6	80.6	80.6
N-Pt-N	76.1	76.3	76.4	76.4	76.2	76.4

Figure S1. Calculated ¹MLLCT State Energies vs σ_p for the Pt(bph)(4,4'-X₂bpy) Complexes Using the B3BPE/TZVP-QZV-P/CPCM, B3LYP/TZVP-QZV-P/CPCM and PBE0/TZVP-QZV-P/CPCM Methods. The linear fitting analysis results are listed in Table S2.

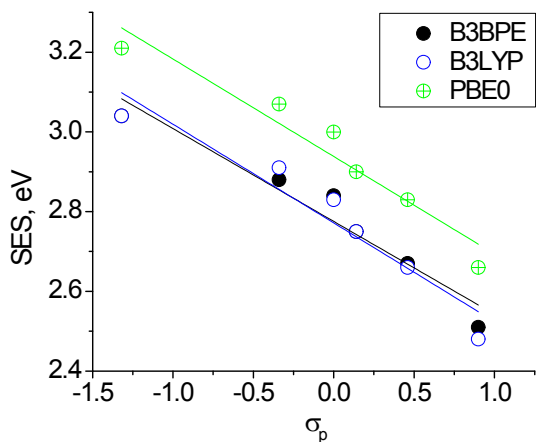


Table S2. Linear fitting analysis results for the correlations shown in Figure S1.

Correlation	Slope	Intercept	R ²
B3BPE	-0.23	2.78	0.93
B3LYP	-0.25	2.77	0.90
PBE0	-0.24	2.94	0.92

2. Results.

Figure S2. Electron Spin Density Distribution Around Pt(bph)(4,4'-(NH₂)₂bpy) Optimized in the T₁ State Constrained to C₂ Symmetry Plotted at Isovalue of 0.003 e/Å³ for the LLTS of Isolated Molecules in Acetonitrile Solvent Computed Using the B3PBE/TZVP-QZV-P/CPCM Method. The α and β spin densities are shown as tan and green meshes, respectively.

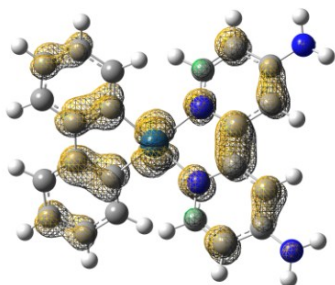
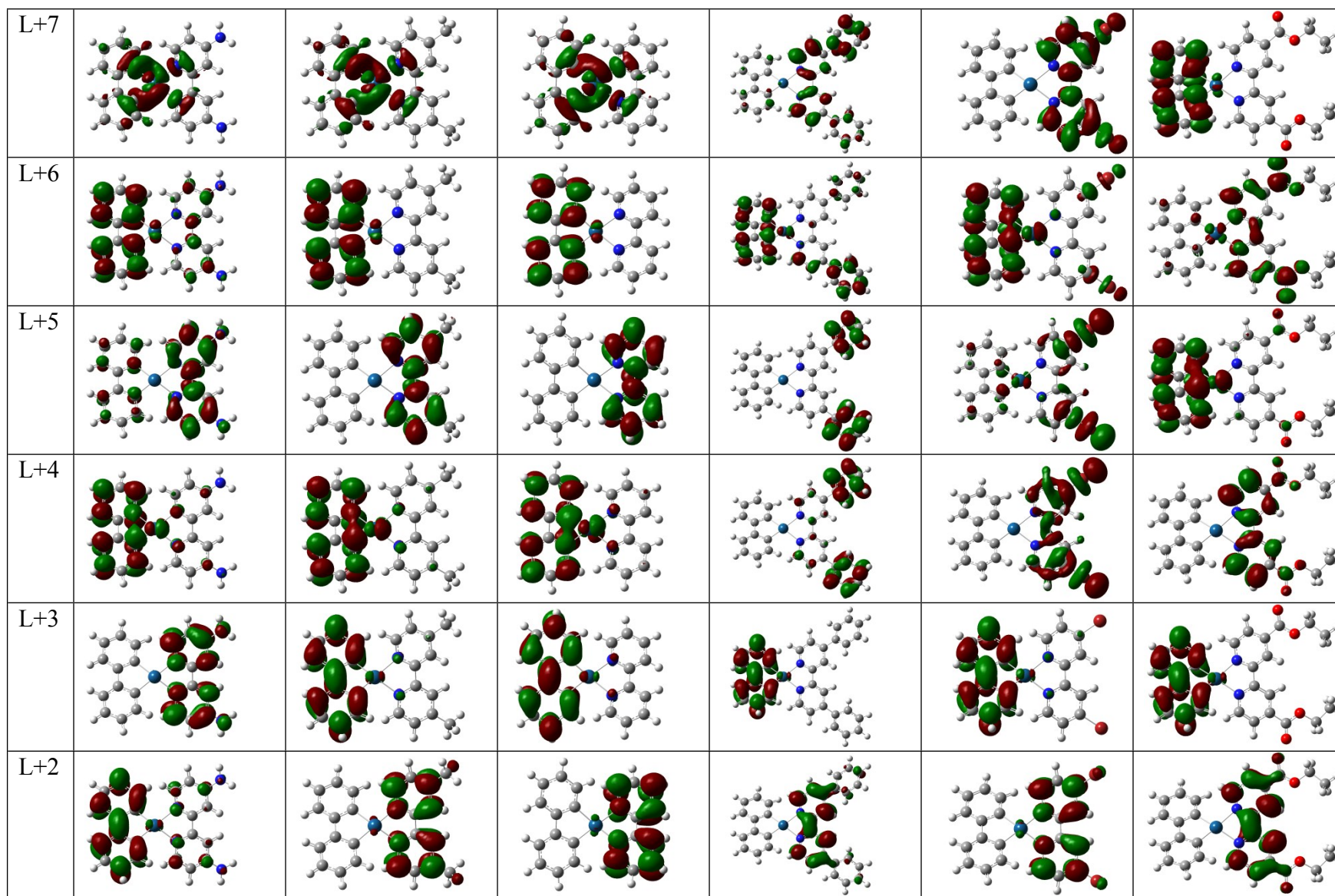
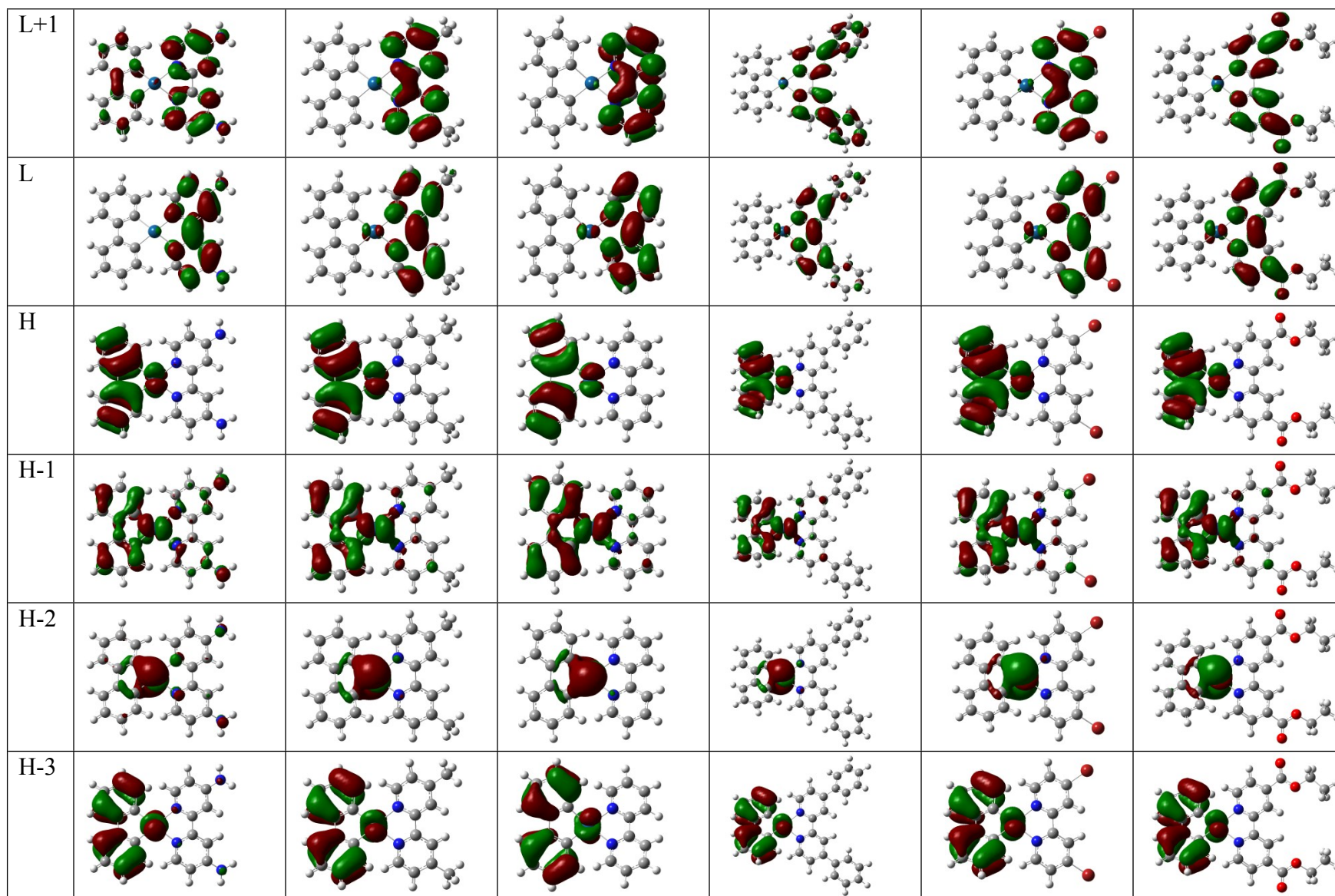


Figure S3. Spatial distributions of the 10 highest occupied (labeled H-9 to H) and 10 lowest unoccupied molecular orbitals (labeled L to L+9) of the complexes in the singlet ground state plotted at isosurface of 0.03 e/Å³ calculated using the B3PBE/TZVP-QZV-P/CPCM method. Red and green isosurface colors denote + and – nodes, respectively.

	Pt(bph)(4,4'-(NH ₂) ₂ bpy)	Pt(bph)(4,4'-Me ₂ bpy)	Pt(bph)(bpy)	Pt(bph)(4,4'-Ph ₂ (bpy)	Pt(bph)(4,4'-Br ₂ bpy)	Pt(bph)(4,4'-(COOC ₂ H ₅) ₂ (bpy)
L+9						
L+8						





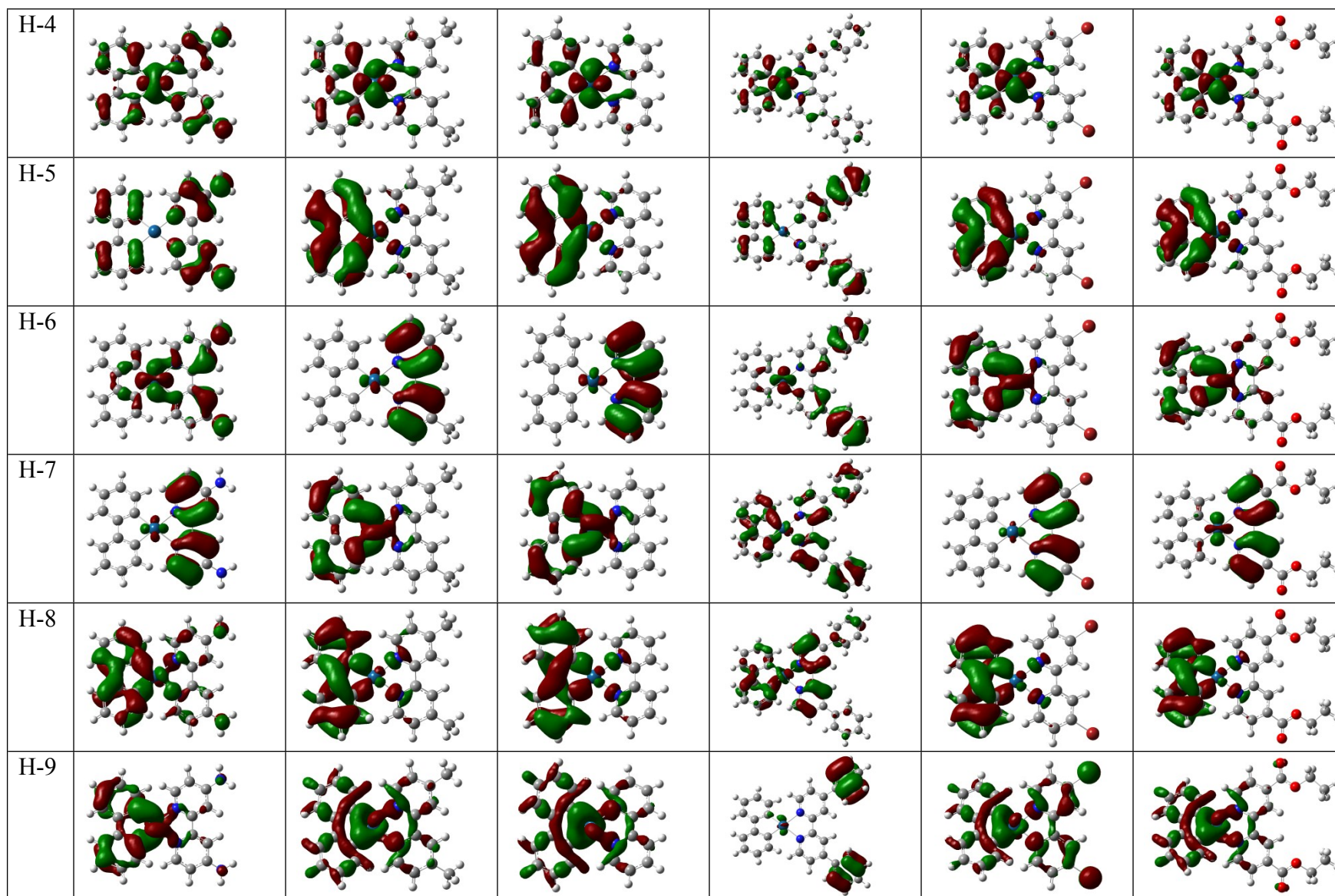
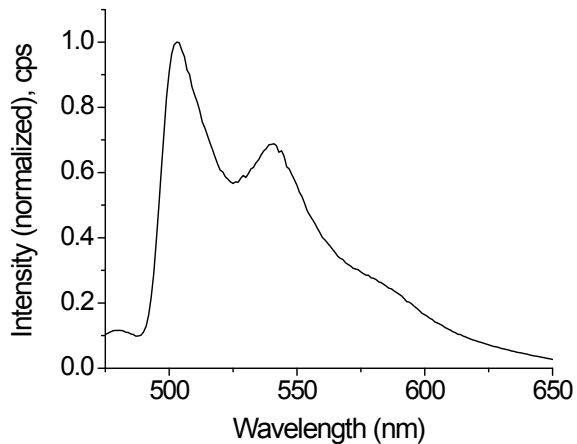


Figure S4. Emission spectrum of Pt(bph)(4,4'-(NH₂)₂bpy) in a butyronitrile glass at 77K with excitation at the low energy absorption maximum. The emission spectrum differs from the others due to the difference of the emitting excited state resulting in a different profile.



3. Discussion.

Figure S5. Electron Affinity (EA) vs σ_p for Pt(bph)(4,4'-X₂bpy) Calculated Using the B3PBE/TZVP-QZV-P/CPCM Method. The linear fitting analysis results are $R^2= 0.99$, slope= -0.43, intercept= -2.77.

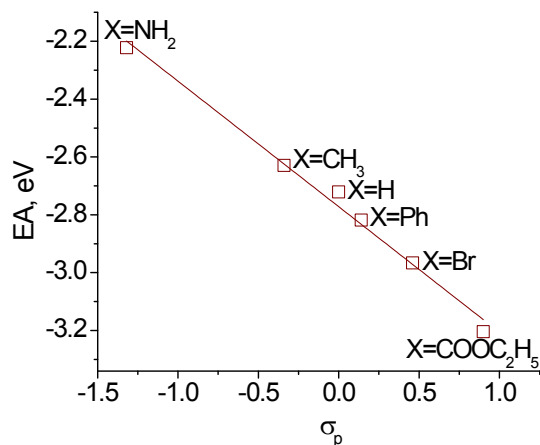


Figure S6. The HOMO-LUMO Gap Calculated as the Lowest-lying SES vs σ_p for Pt(bph)(4,4'-X₂bpy) Using the B3PBE/TZVP-QZV-P/CPCM Method. The linear fitting analysis results are $R^2= 0.98$, slope= -0.34, intercept= 2.22.

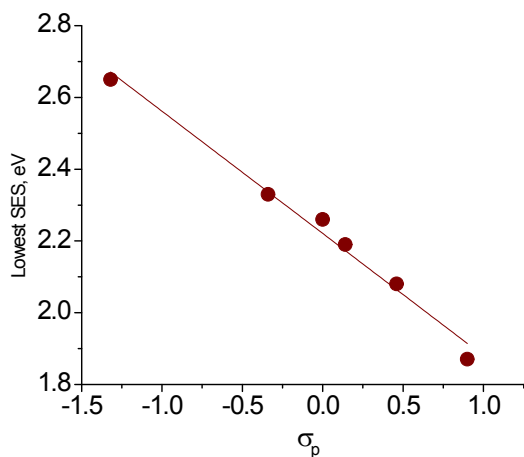


Figure S7. Geometries of the Complexes in the SGS Optimized Using the B3PBE/TZVP-QZV-P/CPCM Method Highlighting the bph-bpy Torsion Angle Characteristic of the X-configuration.

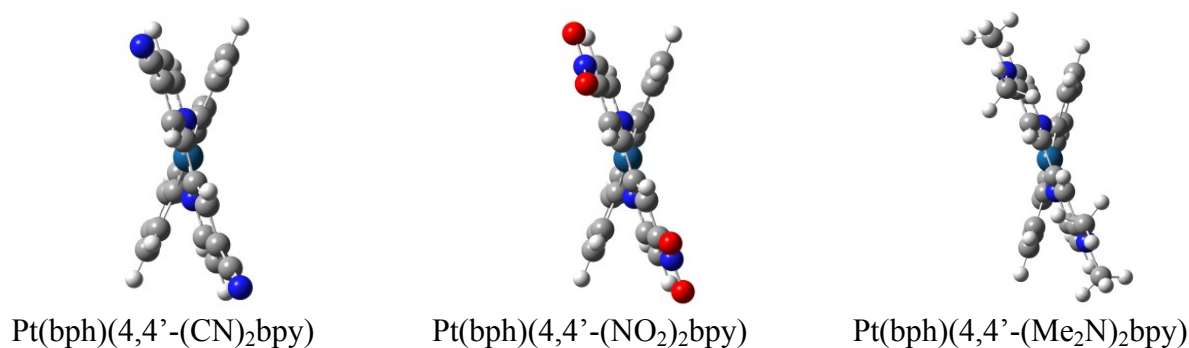


Figure S8. Electron Spin Density Distributions Around the Complexes in the LLTS Plotted at an Isovalue of 0.003 $e/\text{Å}^3$ of Isolated Molecules in Acetonitrile Solvent Computed Using the B3PBE/TZVP-QZV-P/CPCM Method. The α and β spin densities are shown as tan and green meshes, respectively.

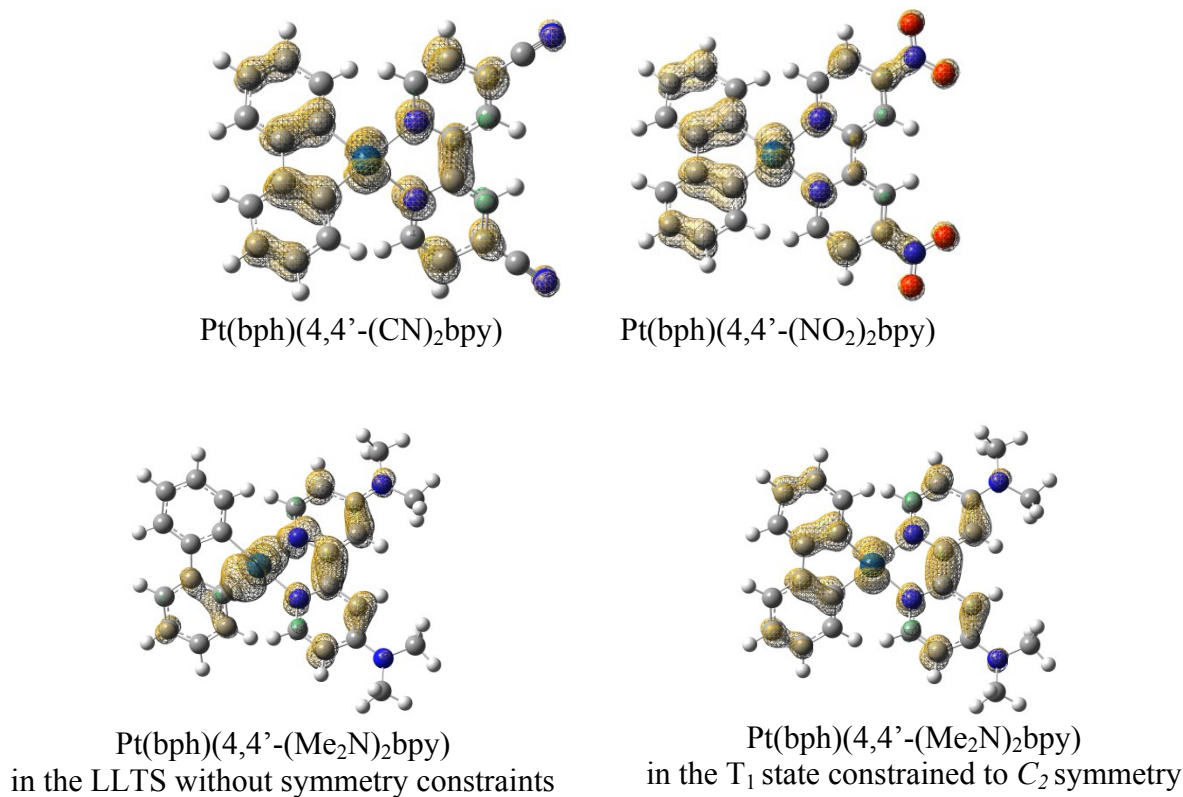


Table S3. Linear fitting analysis results for the correlations shown in Figures 7 and 8.

Correlation	Figure	Slope	Intercept	R ²
Experimental E _{Abs} (MLLCT) vs σ_p	7(a)	-0.27	2.77	0.90
Calculated ¹ MLLCT SES vs σ_p	7(a)	-0.23	2.78	0.93
Experimental E _{Em} vs σ_p	7(b)	-0.27	2.12	1.00
Calculated ³ LLTS vs σ_p	7(b)	-0.24	1.88	0.88
Emission lifetime vs σ_p	7(c)	-0.91	0.86	0.87
Experimental E _{1/2red} vs σ_p	7(d)	0.40	-1.38	0.99
Calculated E _{LUMO} vs σ_p	7(d)	-0.44	-2.61	0.98
Calculated E _{HOMO} - E _{LUMO} vs σ_p	8	-0.34	2.85	0.97

Table S4. Platinum-ligand Bond Lengths (Å), Ligand Bite Angles (°) and bph-bpy Torsion Angle (°) Optimized for Isolated Complexes in Singlet Ground State (SGS) and Lowest-lying Triplet State (LLTS) in Acetonitrile Solvent Using the B3PBE/TZVP-QZV-P/CPCM Method. The Mulliken atomic charges ($|e|$) of the Pt atoms q (Pt) are also listed.

Optimized	Pt(bph)(4,4'-(NO ₂) ₂ (bpy)		Pt(bph)(4,4'-(CN) ₂ bpy)		Pt(bph)(4,4'-(Me ₂ N) ₂ bpy)	
	SGS	LLTS	SGS	LLTS	SGS	LLTS
Pt-C	2.005	1.971	2.006	1.972	2.004	2.019, 2.000
Pt-N	2.137	2.139	2.141	2.119	2.144	2.106, 2.053
C-Pt-C	80.5	80.2	80.5	81.3	80.5	80.8
N-Pt-N	76.4	77.0	76.4	77.5	76.0	78.1
bph-bpy	42.0	35.8	40.5	33.3	36.4	41.9
q (Pt)	0.68	0.87	0.66	0.88	0.56	1.06
q (bpy)	0.27	-0.46	0.29	-0.39	0.47	-0.10
q (bph)	-0.94	-0.41	-0.96	-0.49	-1.03	-0.96

Table S5. Lowest-lying Triplet States (LLTS) (in eV and in parentheses in nm) of Isolated Molecules Fully Optimized in Acetonitrile Solvent Using the TD-DFT/B3PBE/TZVP-QZV-P/CPCM Method. The LLTS type is assigned based on the distribution of the 2 unpaired electrons, labeled as spin densities (ρ_s) among the Pt atom and the bpy and bph ligand moieties. The spin density distributions are presented in Figure S6.

Complex	LLTS	Type	ρ_s (Pt)	ρ_s (bpy)	ρ_s (bph)
Pt(bph)(4,4'-(NO ₂) ₂ bpy)	1.09 (1135)	³ LC _{bpy-bph} / ³ MLCT	0.26	0.96	0.78
Pt(bph)(4,4'-(CN) ₂ bpy)	1.40 (887)	³ LC _{bpy-bph} / ³ MLCT	0.29	0.95	0.76
Pt(bph)(4,4'-(Me ₂ N) ₂ bpy)	2.17 (571)	³ MLCT	0.66	1.14	0.20
T ₁ of Pt(bph)(4,4'-(Me ₂ N) ₂ bpy)	2.30 (540) ^[a]	³ LC _{bpy-bph} / ³ MLCT ^[a]	0.38 ^[a]	1.04 ^[a]	0.58 ^[a]

^[a] Refer to the T₁ state of Pt(bph)(4,4'-(Me₂N)₂bpy).

Table S6. Singlet Excited States (SES) (in eV and in parentheses in nm) with Oscillator Strength (f) Higher Than 0.09 of Isolated Molecules in Acetonitrile Solvent Calculated as Vertical Electronic Transitions Using the TD-DFT/B3PBE/TZVP-QZV-P/CPCM Method. The transition types are assigned based on the major contributing electronic transitions with percentages listed in parentheses. The spatial distributions of the molecular orbitals participating in these transitions are shown in Supporting Information Figure S1. MLCT = metal-to-ligand charge transfer; LC = ligand-centered; MLLCT = metal-and-ligand-1-to-ligand-2 charge transfer (see subscripts for ligand 1 and ligand 2); deloc. = delocalized with distribution throughout the entire molecule. Subscripts denote the major contributing moiety.

Complex	SES	f	Type	Transition
Pt(bph)(4,4'-(NO ₂) ₂ bpy)	2.13 (583)	0.24	ML _{bph} L _{bpy} CT	H-1→L (93%)
	4.04 (307)	0.10	L _{bph} L _{bpy} CT, $\pi \rightarrow \pi^*_{bph}$	H-9→L (70%)
	4.43 (280)	0.11	$\pi \rightarrow \pi^*_{bph}$, ML _{bph} CT	H-3→L+5 (54%)
			$\pi \rightarrow \pi^*_{bph}$, ML _{bph} CT	H-2→L+5 (19%)
	4.85 (255)	0.10	$\pi \rightarrow \pi^*_{bph}$, ML _{bph} CT	H-3→L+5 (36%)
			$\pi \rightarrow \pi^*_{bpy}$	H-8→L+2 (20%)
4.88 (254)	0.53	$\pi \rightarrow \pi^*_{bpy}$	H-8→L+2 (54%)	
		$\pi \rightarrow \pi^*_{bph}$, ML _{bph} CT	H-3→L+5 (16%)	
Pt(bph)(4,4'-(CN) ₂ bpy)	2.53 (491)	0.21	ML _{bph} L _{bpy} CT	H-1→L (36%)
			ML _{bph} L _{bpy} CT	H→L+1 (64%)
	4.11 (302)	0.13	ML _{bph} L _{bpy} CT	H-9→L (54%)
			$\pi \rightarrow \pi^*_{bpy}$	H-8→L (28%)
	4.26 (291)	0.15	π ML _{bph} L _{bpy} CT	H-4→L+2 (78%)
	4.83 (257)	0.39	$\pi \rightarrow \pi^*_{bph}$	H-3→L+3 (62%)
$\pi \rightarrow \pi^*_{bph}$			H→L+8 (18%)	
Pt(bph)(4,4'-(Me ₂ N) ₂ bpy)	3.03 (409)	0.24	Deloc.→ π^*_{bpy}	H-1→L (100%)
	3.73 (332)	0.10	ML _{bph} L _{bpy} CT, $\pi \rightarrow \pi^*_{bph}$	H→L+2 (90%)
	3.79 (327)	0.20	deloc.→ deloc.	H-1→L+1 (100%)
	4.40 (282)	0.14	ML _{bph} →deloc.	H-3→L+1 (75%)
	4.64 (267)	0.18	deloc.→ deloc.	H-4→L+1 (49%)
			$\pi \rightarrow \pi^*_{bpy}$	H-7→L (28%)
	4.66 (266)	0.17	ML _{bph} →deloc.	H-3→L+2 (59%)
			$\pi \rightarrow \pi^*_{bpy}$	H-7→L (11%)
	4.69 (264)	0.10	ML _{bph} L _{bpy} CT	H-9→L (73%)
	4.71 (263)	0.29	$\pi \rightarrow \pi^*_{bpy}$	H-7→L (38%)
			deloc.→ deloc.	H-2→L+2 (23%)
	4.75 (261)	0.10	deloc.→ deloc.	H-2→L+2 (49%)
deloc.→ deloc.			H-4→L+1 (20%)	
4.83 (257)	0.11	ML _{bph} L _{bpy} CT	H-3→L+3 (87%)	
4.86 (255)	0.26	deloc.→ deloc.	H-6→L+1 (82%)	