Supporting Information

From Luminescence Quenching to High-efficiency Phosphorescence: A Theoretical Study on the Monomer to Dimer of Platinum (II) Complexes with Both 2‑Pyridylimidazol-2-ylidene and Bipyrazolate Chelates

Bo-Hua Zhang,[a] Jun-An Li,[b] Min Wang,[c] Teng-Fei He,[a] Pan-Pan Lin,[a] Yun-Li Zhang,[a] Ai-Min Ren,[a] and Lu-Yi Zou[a*]

[a]Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, P. R. China.

[b]Gastroenterology and center of Digestive Endoscopy, The Second Hospital of Jilin University, 218Ziqiang Street, Changchun 130041, P. R. China.

[c]Department of Prosthodontics, School of Stomatology, Jilin University, Changchun 130021, P. R. China.

*Corresponding author E-mail addresses: zouly@jlu.edu.cn.

Computational details

The displacement (ΔQ) of any molecular structure can be obtained from eqn (I), which is the projection we mentioned, and then by the eqn (II) can get reorganization energy λ.

$$\Delta Q = C^T m^{1/2}(R - R_0)\cdots\cdots\cdots(I)$$

$$\lambda = \sum_i \lambda_i = \sum_i 1/2\omega_i^2 \Delta Q_i^2 \cdots\cdots\cdots(II)$$

Here, the C^T represents the matrix of the normal modes obtained by the optimized single molecule, R_0 represents the Cartesian coordinates of the optimized single molecule, and R represents the Cartesian coordinates of any molecular structure. Therefore, R here is the Cartesian coordinates of the excited state optimized structure, R_0 is the Cartesian coordinates of the ground state optimized structure.

We have carried out a vertical displacement operation on the geometry of the excited state of the dimer, and freezing operation is adopted for the whole molecular skeleton of the geometry structure obtained by each operation. The local geometry optimization is carried out to ensure that the most stable geometric junction is obtained under fixed molecular distance. After that, the single point energy of each geometry is calculated.

The crystal structure is essential to calculate the luminescent properties of aggregates. Among all molecules studied, only complex **4** can grow a single crystal. Therefore, we focus on complex **4** with the experimental crystal structure.
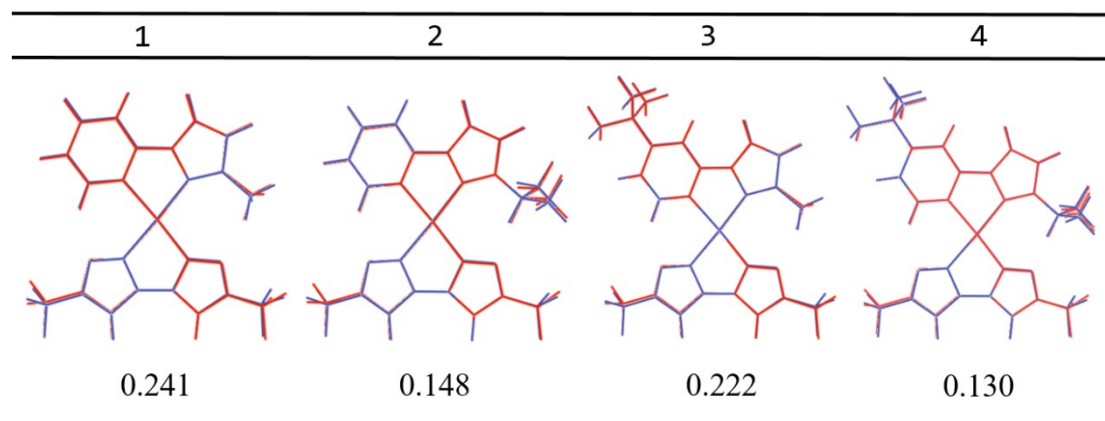

1	2	3	4
0.241	0.148	0.222	0.130

Fig. S1. Geometrically superimposed structures of S_0 (blue) and T_1 (red) states of the studied complexes.
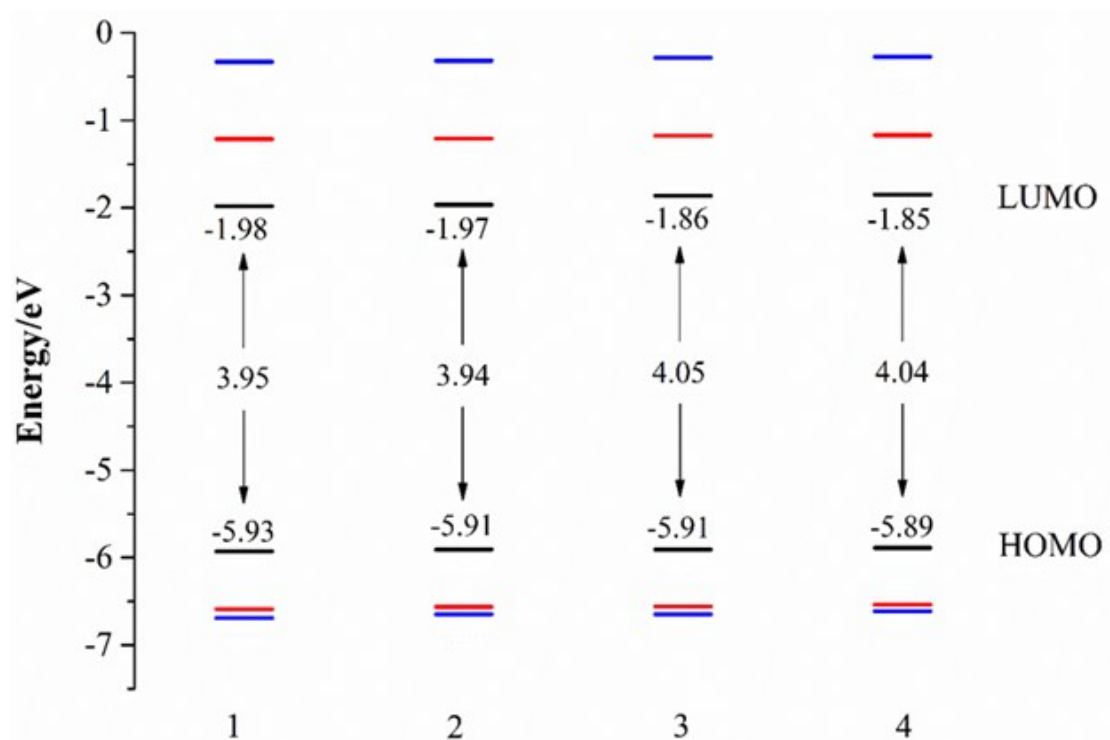

Fig. S2. Frontier molecular orbitals energy levels and the HOMO and LUMO energy gaps of monomers **1-4**.
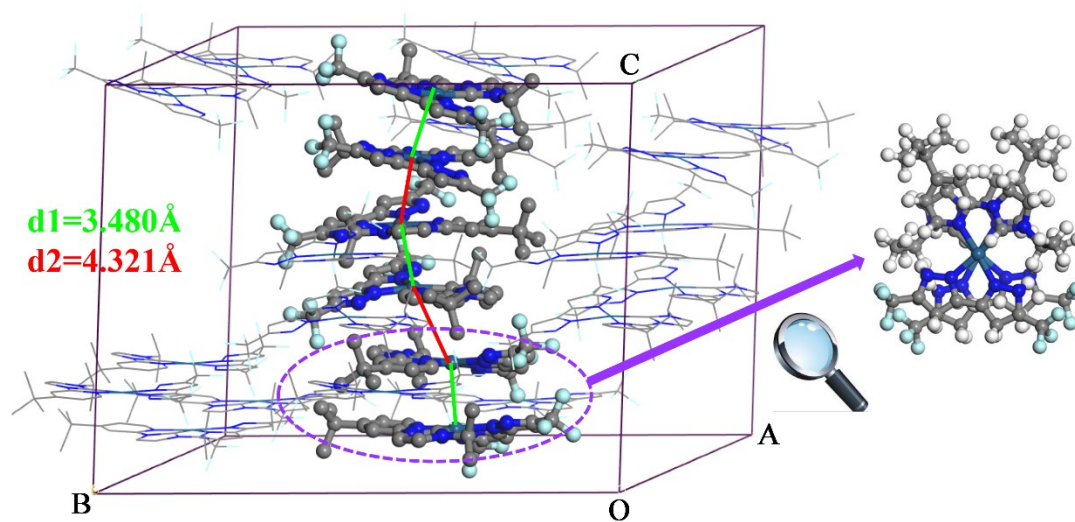

Fig. S3. Molecular stacking diagram with Pt···Pt contacts of 3.480(4) Å and 4.3214(4) Å and Pt···Pt···Pt angle of 154.4° and Top view.

Table S1. Optimized geometric parameters at the S_0 state of monomer **4** by different functionals as well as the experimental bond lengths (Å) and dihedral angles (°)

	B3LYP-D3(BJ)	PBE0-D3(BJ)	M062X-D3(BJ)	CAM-B3LYP-D3(BJ)	ωB97XD	Exp.[a]
$Pt-N_1$	2.0783	2.0531	2.0857	2.0677	2.0741	2.0326
$Pt-C_4$	2.0105	1.9967	2.0025	2.0109	2.0111	1.9870
$Pt-N_5$	2.0390	2.0194	2.0403	2.0281	2.0318	2.0191
$Pt-N_4$	2.0815	2.0591	2.0914	2.0668	2.0740	2.0524
C_3-N_2	1.3988	1.3921	1.4015	1.3980	1.3985	1.3934
C_5-C_6	1.4443	1.4411	1.4514	1.4471	1.4476	1.4528
$C_1-C_{R'}$	1.5286	1.5219	1.5253	1.5253	1.5279	1.5360
$N_3-C_{R''}$	1.4801	1.4700	1.4774	1.4757	1.4748	1.4984
N_1-Pt-C_4	78.6	78.8	78.5	78.6	78.5	78.9
C_4-Pt-N_5	105.5	105.2	105.5	105.3	105.6	105.8
N_4-Pt-N_5	77.3	77.6	77.4	77.5	77.4	77.8
N_1-Pt-N_4	98.7	98.5	98.7	98.7	98.6	98.0
$C_{R'}-C_1-C_2$	119.8	119.9	119.6	119.8	119.8	120.1
$C_{R''}-N_3-C_4$	123.2	122.7	123.3	123.1	123.1	122.2
Relative Error	0.83%	0.55%	0.88%	0.72%	0.76%	--
RMSD	0.520	0.516	0.533	0.521	0.519	--

[a] Experimental values.

Table S2. The emission spectra λ_{em} (nm) obtained by TDDFT method with different functionals for dimer **4** (basis set: 6-31+G*/ma-def2-TZVP).

	B3LYP -D3(BJ)	PBE0 -D3(BJ)	M062X -D3(BJ)	CAM-B3LYP -D3(BJ)	ωB97XD	Exp.[a]
$T_1 \rightarrow S_0$	1200.6	1033.4	546.8	602.2	514.5	501.0

[a] Experimental values.

Table S3. Frontier molecular orbital energies (eV) and compositions (%) of different fragments in the optimized S_0 state geometries for the monomers **1-4** calculated by PBE0-D3(BJ).

	MO	Energy (eV)	Pt contribution (%)	Pyim contribution (%)	Bipz contribution (%)
1	L+1	-1.215	1.6	98.0	0.4
	L	-1.981	7.8(3.8d_{yz})	87.2	5.0
	H	-5.929	6.7	1.2	92.0
	H-1	-6.590	34.6 (21.5d_{xz} +13d_{yz})	19	46.4
	H-2	-6.691	39(13.2d_{xz} +25.4d_{yz})	8.9	52
2	L+1	-1.207	1.7	97.9	0.4
	L	-1.965	7.7(3.9d_y)	87.3	5.0
	H	-5.908	6.7	1.7	91.5
	H-1	-6.564	34.5 (30d_{xz} +4.3d_{yz})	19.5	45.9
	H-2	-6.649	39.1(4d_{xy} +34.5d_{yz})	9.6	51.2
3	L+1	-1.176	1.5	98.1	0.3
	L	-1.861	7.7(2.2d_{xz} +1.5d_{yz})	86.9	5.4
	H	-5.907	7.1(3.8 d_{xz}+3.3d_{yz})	1.3	91.6
	H-1	-6.560	35.1 (1.1d_{xz} +33.9d_{yz})	19.9	45.1
	H-2	-6.649	40.1(37.8d_{xz} +1.8d_{yz})	9.6	50.4
4	L+1	-1.169	1.6	98.0	0.4
	L	-1.849	7.8(3.8d_{yz})	87.0	5.4
	H	-5.888	7.0(4.5 d_{xz}+2.5d_{yz})	1.8	91.2
	H-1	-6.539	34.9 (3.3d_{xz} +31.5d_{yz})	20.4	44.6
	H-2	-6.613	39.8(34.4d_{xz} +4.6d_{yz})	10.3	50.0

Table S4. Frontier molecular orbital energies (eV) and compositions (%) of different fragments in the optimized T_1 state geometries for the monomers of **1-4** calculated by PBE0-D3(BJ).

	MO	Energy (eV)	Pt contribution (%)	Pyim contribution (%)	Bipz contribution (%)
1	L+2	-0.466	$14.3(5.1d_{xy})$	47.2	38.6
	L	-2.223	$8.7(4.6d_{yz})$	86.0	5.4
	H	-5.360	$4.4(4.3d_{xz})$	0.9	94.7
2	L+2	-0.441	$15.6((5.8d_{xy})$	45.8	38.6
	L	-2.194	$8.5(4.6d_{yz})$	86.1	5.3
	H	-5.332	$4.3(3.9d_{xz})$	1.4	94.3
3	L+2	-0.435	$13.3((4.6d_{x^2-y^2})$	98.1	0.3
	L	-2.094	$8.6(2.6d_{xz}+1.7d_{yz})$	86.9	5.4
	H	-5.339	$4.5(2.3d_{xz}+2.2d_{yz})$	1.3	91.6
4	L+2	-0.415	$14.8((5.9d_{x^2-y^2})$	45.3	40.0
	L	-2.065	$8.2(2.1d_{xz}+2.1d_{yz})$	85.5	6.0
	H	-5.314	$4.4(2.8d_{xz}+1.5d_{yz})$	1.5	94.0

Table S5. Transition dipole moments M_{S_m} (a u) for $S_m \rightarrow S_0$ transitions, singlet-triplet splitting energies $\Delta E(S_m-T_1)$ (eV) and SOC matrix elements $\langle T_1^\alpha | H_{SOC} | S_m \rangle$ (cm^{-1}) of monomers **1-4** at their respective T_1-optimized geometries are calculated.

	1	$E(T_1) = 17\ 340$ cm^{-1}		**2**		$E(T_1) = 17\ 423$ cm^{-1}	
S_m	M_{S_m}	$\Delta E(S_m\text{-}T_1)$	$\langle T_1^\alpha \| H_{SOC} \| S_m \rangle$	S_m	M_{S_m}	$\Delta E(S_m\text{-}T_1)$	$\langle T_1^\alpha \| H_{SOC} \| S_m \rangle$
S_1	0.0101	1857	12.358	S_1	0.0101	1899	14.746
S_2	0.0085	10729	203.047	S_2	0.0076	10692	201.262
S_3	0.3069	10943	82.609	S_3	0.2609	10950	85.817
S_4	2.3512	12886	253.867	S_4	1.8094	12853	251.256
S_5	0.1911	13073	818.565	S_5	0.7082	13215	812.344
S_6	0.2357	14797	54.948	S_6	0.3001	14803	59.177
S_7	0.5218	16699	216.982	S_7	0.5088	16935	210.638
S_8	0.4678	18470	99.243	S_8	0.5528	18464	86.089
S_9	0.0899	19818	21.378	S_9	0.0554	20000	15.296
S_{10}	0.7061	20059	39.848	S_{10}	0.7404	20040	37.084
	3	$E(T_1) = 17\ 825$ cm^{-1}		**4**		$E(T_1) = 17\ 931$ cm^{-1}	
S_m	M_{S_m}	$\Delta E(S_m\text{-}T_1)$	$\langle T_1^\alpha \| H_{SOC} \| S_m \rangle$	S_m	M_{S_m}	$\Delta E(S_m\text{-}T_1)$	$\langle T_1^\alpha \| H_{SOC} \| S_m \rangle$
S_1	0.0108	2209	11.289	S_1	0.0115	2172	17.524
S_2	0.0078	10403	51.496	S_2	0.0092	10247	145.615
S_3	0.3163	11244	47.476	S_3	0.2763	11163	143.933
S_4	2.9157	12873	244.393	S_4	2.7632	12831	247.095
S_5	0.1754	13419	378.342	S_5	0.2870	13421	768.871
S_6	0.3550	14596	621.390	S_6	0.4382	14461	151.378
S_7	0.5792	16392	311.106	S_7	0.5916	16529	179.403
S_8	0.4276	18649	16.480	S_8	0.4756	18556	92.451
S_9	0.6631	19605	22.357	S_9	0.7818	19476	19.631
S_{10}	0.0414	20061	38.943	S_{10}	0.0278	20112	32.483

Table S7. The calculated triplet optical properties of the vertical displacement of the dimer **4**

Pt···Pt (Å)	2.42	2.62	2.82	3.02
λ (nm)	1900.0	907.9	637.3	514.5
E-LUMO (eV)	-1.42	-1.26	-1.14	-1.05
E_{gap} (eV）	4.56	4.86	5.10	5.28
E-HOMO (eV)	-5.98	-6.13	-6.24	-6.33
[a]Spe (Hartree)	-3982.381	-3982.472	-3982.522	-3982.539
Excitation energies(eV)	0.65	1.37	1.94	2.41
Pt···Pt (Å)	3.22	3.42	3.62	3.82
λ (nm)	489.6	474.4	468.5	461.1
E-LUMO (eV)	-0.97	-0.92	-0.87	-0.83
E_{gap} (eV）	5.43	5.54	5.63	5.67
E-HOMO (eV)	-6.40	-6.45	-6.50	-6.50
Spe (Hartree)	-3982.538	-3982.527	-3982.521	-3982.502
Excitation energies(eV)	0.65	1.37	1.94	2.41

[a] Single point energy.

Table S8. Frontier molecular orbital energies(eV) and compositions (%) of different fragments in the optimized T_1 geometries calculated by ωB97XD for the monomer and dimer of complex **4**.

	MO	Energy (eV)	Pt contribution (%)	Pyim contribution (%)	Bipz contribution (%)
Monomer	L+4	2.128	$25.1(2.5d_{yz})$	48.2	26.7
	L+2	1.376	$16.3(1.7dx^2\text{-}y^2)$	44.2	38.5
	L+1	0.583	2.4	97.1	0.4
	L	-0.500	$9.4(2.0d_{xz}+1.9d_{yz})$	87.1	4.5
	H	-6.945	$3.1(1.9d_{xz}+1.2d_{yz})$	0.7	96.2
	H-1	-8.387	$37.8(36.9d_{yz})$	30.8	31.4
	H-2	-8.506	$42.7(41.9d_{xz})$	9.9	47.3
	H-3	-9.002	$86.7(69.9d_z{}^2)$	4.1	9.2
	H-4	-9.199	$6.0(2.3d_z{}^2+2.0d_{xz})$	48.9	45.0
Dimer	L+6	0.808	20.2	31.7	40.1
	L+4	0.308	2.3	62.9	27.1
	L+1	-0.552	$3.3(2.6d_{xz})$	92.0	4.1
	L	-1.455	$7.8(3.6d_{xz})$	84.4	6.3
	H	-6.792	$2.2(2.1d_{yz})$	0.8	95.7
	H-1	-6.973	$1.6(0.6d_{xz}+0.9d_{yz})$	2.4	95.0
	H-2	-7.632	$60.6(46.7d_z{}^2+5.7d_{xz})$	1.8	36.1
	H-3	-7.937	$16.8(15.6d_{yz})$	2.3	80.4
	H-4	-8.089	$51.9(28.4\ d_z{}^2+8.6d_{xz}+7.2d_{yz})$	9.4	31.0
	H-5	-8.321	$23.1(13.1d_{yz}+6.0d_z{}^2+3.0d_{xz})$	3.7	66.6
	H-6	-8.493	$23.4(21.1d_{xz})$	11.2	58.8
	H-7	-9.046	$30.8(23.6d_{yz}+5.5d_z{}^2)$	29.8	38.6
	H-8	-9.178	1.5	1.4	94.5

Table S9. The singlet and triplet excited state transition configurations of monomer **4**.

Isolated	m-th	Energy (eV)	Transition configuration (%)
S$_m$	1	3.40	H→L (79.0), H→L+2 (7.3), H-2→L (5.8), H-1→L (4.0)
	2	4.09	H-1→L (55.9), H-2→L (11.0), H-4→L (12.6), H→L (6.8)
	3	4.20	H→L+3 (47.9), H-3→L (25.5), H-1→L+3 (10.4)
	4	4.28	H-4→L (62.2), H→L+3 (22.0)
	5	4.37	H-3→L (51.0), H-2→L (20.2), H-9→L (9.0), H-3→L+3 (5.6)
	6	4.55	H-3→L+3 (66.8), H→L+2 (6.6), H-1→L (5.8), H→L+4 (3.9)
	7	4.74	H →L+2 (42.4), H→L+4 (15.7), H-3→L+3 (13.3) H-3→L+1 (10.0), H→L (6.6)
	8	4.89	H-7→L (12.9), H→L+1 (34.1), H-5→L (7.5), H-2→L (6.3), H→L+2 (6.1), H→L+4 (5.0), H-4→L (5.0)
	9	4.91	H-1→L+3 (41.2), H-2→L+3 (32.6)
	10	4.99	H →L+1 (20.8), H-1→L+3 (15.8), H-2→L+3 (11.9) H→L+3 (11.7)
T$_m$	1	2.73	H→L (38.2), H→L+2 (35.0), H→L+4 (19.8)
	2	3.21	H-2→L (25.0), H-4→L (22.8), H-1→L (16.1)
	3	3.56	H-1→L (47.2), H-2→L (14.1), H-9→L (9.2)

Table S10. The singlet and triplet excited state transition configurations of dimer.

Isolated	m-th	Energy (eV)	Transition configuration (%)
S$_m$	1	2.58	H→L (85.2), H-3→L (5.0)
	2	2.61	H-2→L (72.4), H-4→L (19.1)
	3	2.82	H-1→L (81.8), H→L+1 (4.4), H-5→L (4.3)
	4	3.38	H-3→L(56.5), H→7(20.7), H→L(7.9)
	5	3.43	H-4→L (57.3), H-2→L (14.7), H-11→L (8.0), H→L+2 (4.8)
	6	3.52	H-2→L+1 (68), H-2→L+3 (13.0), H-2→L+3 (4.0)
	7	3.63	H-5→L (30.6), H→L+2 (18.0), H-1→L+1 (10.5), H-1→L+1 (8.5), H-4→L (6.7)
	8	3.82	H-5→L (20.7), H→L+2 (61.4)
	9	3.89	H-6→L (35.4), H-1→L+1 (24.5), H→L+3 (16.3), H-4→L+1 (5.2)
	10	3.90	H-6→L (21.3), H→L+3 (54.6), H-1→L+3 (4.5), H-4→L+1 (3.1)
T$_m$	1	2.41	H-2→L (72.2), H-4→L (17.4)
	2	2.42	H→L (70.8), H-3→L (5.0), H-7→L (3.8), H→L+6 (4.1)
	3	2.60	H-1→L (62.6), H-1→L+6 (4.9), H→L+2 (5.3)