# **ELECTRONIC SUPPORTING INFORMATION (ESI)**

for

Counteranion-dependent mechanochromism of a photoluminescent platinum(II) complex with mixed terpyridine and thioglucose

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#### **Preparation of complexes.**

**[Pt(H<sub>4</sub>tg-S)(terpy)]ClO<sub>4</sub> ([1]ClO<sub>4</sub>).** To an orange solution containing [PtCl(terpy)]Cl·2H<sub>2</sub>O<sup>-1</sup> (0.20 g, 0.37 mmol) in 40 mL of water was added a solid sample of KH<sub>4</sub>tg·H<sub>2</sub>O<sup>-2</sup> (0.11 g, 0.41 mmol). The mixture was stirred at room temperature for 10 min, which gave a red solution. To the red solution was added a 1.0 M NaClO<sub>4</sub> aqueous solution (5 mL), followed by allowing it to stand at room temperature for 4 days. The resulting orange fiber crystals were collected by filtration. Yield: 0.25 g (87%). Anal. Calcd for [Pt(H<sub>4</sub>tg)(terpy)]ClO<sub>4</sub>·2H<sub>2</sub>O ([1]ClO<sub>4</sub>·2H<sub>2</sub>O = C<sub>21</sub>H<sub>22</sub>N<sub>3</sub>ClO<sub>9</sub>PtS): C, 33.23; H, 3.45; N, 5.54%. Found: C, 33.29; H, 3.37; N, 5.58%. <sup>1</sup>H NMR (D<sub>2</sub>O):  $\delta$  9.11 (2H, d, *J* = 5.6 Hz), 8.31 (1H, t, *J* = 8.2 Hz), 8.26 (2H, td, *J* = 7.8, 1.5 Hz), 8.13 (2H, d, *J* = 8.8 Hz), 8.09 (2H, d, *J* = 7.6 Hz), 7.71-7.68 (2H, m), 4.42 (1H, d, *J* = 8.8 Hz), 3.71 (1H, dd, *J* = 12.1, 1.3 Hz), 3.51 (1H, dd, *J* = 12.2, 5.4 Hz), 3.33-3.26 (4H, m). IR (cm<sup>-1</sup>): 625, 1090 ( $\nu$ (ClO<sub>4</sub><sup>-</sup>)). Orange needle crystals suitable for X-ray analysis were obtained by the recrystallization of the fiber crystals from hot water.

[Pt(H<sub>4</sub>tg-*S*)(terpy)]PF<sub>6</sub> ([1]PF<sub>6</sub>). This complex-salt was obtained as orange fiber crystals by a method similar to that for [1]ClO<sub>4</sub>, using a 1.0 M NH<sub>4</sub>PF<sub>6</sub> aqueous solution instead of a 1.0 M NaClO<sub>4</sub> aqueous solution. Yield: 0.25 g (85%). Anal. Calcd for [Pt(H<sub>4</sub>tg)(terpy)]PF<sub>6</sub>·1.5H<sub>2</sub>O ([1]PF<sub>6</sub>·1.5H<sub>2</sub>O = C<sub>21</sub>H<sub>25</sub>F<sub>6</sub>N<sub>3</sub>O<sub>6.5</sub>PPtS) : C, 31.71; H, 3.17; N, 5.28%. Found: C, 31.57; H, 3.12; N, 5.34%. IR (cm<sup>-1</sup>): 560, 842 ( $\nu$ (PF<sub>6</sub><sup>-</sup>)). Orange needle crystals suitable for X-ray analysis were obtained by allowing the remaining filtrate to stand at room temperature.

## Measurements.

The electronic absorption spectra were recorded with a JASCO V-660 spectrophotometer at room temperature. The IR spectra were recorded on a JASCO FT/IR-4100 infrared spectrometer using KBr disks at room temperature. The luminescent spectra were recorded on a JASCO FP-6600 spectrometer in solid state at room temperature. The light shorter than 370 nm was removed by using a glass filter. The emission spectra in the solid state were recorded by scanning 10 times with a rate

of 500 nm /min. The solid state emission spectrum was accumulated for 10 times scan The internal quantum yields were measured by the absolute method using a spectrofluorometer (Jasco FP-8500) with a fluorescence integrating sphere unit (Jasco ILFC-847) at an excitation wavelength of 340 nm using a Xe lamp as the light source, and the data were corrected using both deuterium and halogen lamps. The elemental analyses (C, H, N) were performed with Yanaco CHN Corder MT-5. The <sup>1</sup>H NMR spectra were recorded with a JEOL GSX400 spectrometer in D<sub>2</sub>O. Sodium 4,4'-dimethyl-4-silapentane-1-sulfonate (DSS) was used as the internal standard. The molar conductivities were measured with a HORIBA DS12 conductivity meter. The powder X-ray diffraction measurement experiments were performed on a Bruker D2 PHASER.

## X-ray crystallography.

Single-crystal X-ray diffraction measurements for [1]ClO<sub>4</sub> were performed on a Rigaku RAXIS RAPID imaging plate and Vari-Max with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71075$  Å) at 200 K. The measurements for [1]PF<sub>6</sub> were performed on a Rigaku R-AXIS VII imaging plate and Vari-Max with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71075$  Å) at 200 K. The intensity data were collected by the  $\omega$ -scan technique and empirically corrected for absorption. The structures of the complexes were solved by direct methods using SHELXS97.<sup>3</sup> The structure refinements were carried out using full matrix least-squares (SHELXL-97).<sup>3</sup> Because of the quite thin needlel-like shape of [1]ClO<sub>4</sub> (0.25 x 0.03 x 0.01 mm<sup>3</sup>) and [1]PF<sub>6</sub> (0.15 x 0.01 x 0.01 mm<sup>3</sup>), the X-ray absorption corrections were not effectively made. Thus, only heavy atoms were refined anisotropically (Pt, S, Cl, and O for [1]ClO<sub>4</sub> and Pt, S, and P for [1]PF<sub>6</sub>), and others were refined by using isotropic models. Hydrogen atoms were placed at calculated positions. All structural parameters are summarized in the Tables S2-S4.

### **Computational details.**

The electronic structures were calculated by using Gaussian09 software.<sup>4</sup> The density functional theory (DFT) and the time-dependent DFT (TD-DFT) calculations were performed by using the B3LYP function with Lanl2dz basis sets on Pt atom, 6-31G\* basis sets on N, S atoms, and 6-31G basis sets on C, H, O atoms.<sup>5</sup> All of the geometries were taken directly from the single-crystal structure coordinates; a single-point calculation was performed on each asymmetric unit.

## **References.**

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**Fig. S1.** <sup>1</sup>H NMR spectra of (a) [1]ClO<sub>4</sub> and (b) [1]PF<sub>6</sub> in D<sub>2</sub>O. (\*) indicates the signal from H<sub>2</sub>O. (c) Drawing of the structure of  $[1]^+$ .



**Fig. S2.** IR spectra of (a) [1]ClO<sub>4</sub> and (b) [1]PF<sub>6</sub>.



Fig. S3. Electronic absorption spectrum of (a)  $[1]ClO_4$  and (b)  $[1]PF_6$  in  $H_2O$ .



**Fig. S4.** Powder X-ray diffraction spectra of [1]ClO<sub>4</sub> (a) simulated based on the single-crystal X-ray analytical data, (b) before grinding and (c) after grinding. Powder X-ray diffraction spectra of [1]PF<sub>6</sub> (d) simulated based on the single-crystal X-ray analytical data, (e) before grinding and (f) after grinding.



**Fig. S5.** (a) Top and (b) side views of the 1D chain structure and (c) the 3D packing structure in [1]ClO<sub>4</sub>·2H<sub>2</sub>O. Orange and blue dotted lines indicate the  $\pi$ - $\pi$  and hydrogen bonding interactions, respectively. H atoms are omitted for clarity. Pt: light green, S: yellow, Cl: pale blue, O: pink N: blue, C: gray.



**Fig. S6.** (a) Top and (b) side views of the 1D chain structure and (c) the 3D packing structure in [1]PF<sub>6</sub>·1.5H<sub>2</sub>O. Orange and blue dotted lines indicate the  $\pi$ - $\pi$  and hydrogen bonding interactions, respectively. H atoms are omitted for clarity. Pt: light green, S: yellow, P: orange, F: olive green, O: pink N: blue, C: gray.



**Fig. S7.** Emission and excitation spectra of (a) [1]ClO<sub>4</sub> and (b) [1]PF<sub>6</sub> in the solid state at room temperature before grinding (black line) and after grinding (red line). Emission and excitation spectra of (c) [1]ClO<sub>4</sub> and (d) [1]PF<sub>6</sub> in H<sub>2</sub>O/EtOH at 77 K. Excitation wavelength is 340 nm.

## [Pt(H<sub>4</sub>tg-S)(terpy)]ClO<sub>4</sub>



Fig. S8. The contour plots of molecular orbitals of the complex cations in  $[1]ClO_4$  and  $[1]PF_6$ . The surfaces are drawn at 0.05 a.u. level.



Fig. S9. Diffuse reflection spectra of  $[1]ClO_4$  (left) and  $[1]PF_6$  (right) in the solid state before grinding (solid line) and after grinding (dashed line).



Fig. S10. Emission spectra of  $[1]ClO_4$  in the solid state before grinding (black line), after grinding (red line), and after recrystallization (blue line). Excitation wavelength is 340 nm.

$\lambda_{ m max}$ / nm ( $arepsilon$ / 10 <sup>3</sup> cm <sup>-1</sup> M <sup>-1</sup> )	
456.6 (0.8802)	
341.8 (11.06)	
328.2 (9.663)	
311.0 (9.267)	
279.0 (18.81)	
242.4 (26.69)	

**Table S1.** Electronic absorption spectral data of [1]ClO<sub>4</sub> in water.

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	$[1]ClO_4 \cdot 2H_2O$	[ <b>1</b> ]PF <sub>6</sub> ·1.5H <sub>2</sub> O
Chemical formula	C <sub>21</sub> H <sub>26</sub> ClN <sub>3</sub> O <sub>11</sub> PtS	C <sub>21</sub> H <sub>25</sub> F <sub>6</sub> N <sub>3</sub> O <sub>6.5</sub> PPtS
Formula weight (M)	759.05	795.56
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub>	<i>P</i> 1
<i>a</i> / Å	4.9262(11)	7.9715(3)
b / Å	38.578(9)	13.0562(4)
<i>c</i> / Å	13.082(4)	14.1600(5)
$\alpha$ /°	90	63.162(5)
$\beta$ /°	94.038(8)	89.461(7)
$\gamma/^{\circ}$	90	77.050(6)
$V / Å^3$	2479.9(10)	1274.4(1)
Ζ	4	2
T / K	200(2)	200(2)
<i>R</i> (int)	0.1765	0.0593
$D_{ m calcd}$ / g cm <sup>-3</sup>	2.033	2.073
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	51.97	57.184
$ heta_{ m Max}$ /°	27.48	27.50
Miller index ranges	$-6 \le h \le 6$	$-10 \le h \le 10$
	$-49 \le k \le 49$	$-16 \le k \le 16$
	$-16 \le l \le 16$	$-17 \le l \le 18$
Reflections collected	22898	14747
Refinement method	Full-matrix least-square on $F^2$	Full-matrix least-square on $F^2$
Data / restraints / Parameters	11010 / 7 / 447	9887 / 3 / 349
Flack	0.0018(16)	0.003(13)
$R_1 (I > 2\sigma(I))^a$	0.1332	0.0748
$WR_2^b$	0.2876	0.1897
Goodness-of-fit on $F^2$	1.123	1.140
Treatment of hydrogen atoms	constr	constr
CCDC number	1005469	1005470

**Table S2.** Crystallographic data of complexes.

<sup>a</sup>  $R_1 = \Sigma |(|Fo| - |Fc|)| / \Sigma (|Fo|).$  <sup>b</sup>  $wR_2 = [\Sigma w (Fo^2 - Fc^2)^2 / \Sigma w (Fo^2)^2]^{1/2}.$ 

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Bond distances (Å)				
	Pt(1)-N(1)	2.11(3)	Pt(2)-N(4)	1.97(2)
	Pt(1)-N(2)	1.89(2)	Pt(2)-N(5)	2.08(3)
	Pt(1)-N(3)	2.08(3)	Pt(2)-N(6)	2.03(3)
	Pt(1)-S(1)	2.326(7)	Pt(2)-S(2)	2.304(9)
Bond angles (°)				
	N(1)-Pt(1)-N(2)	84.2(10)	N(4)-Pt(2)-N(5)	79.6(11)
	N(1)-Pt(1)-N(3)	163.4(10)	N(4)-Pt(2)-N(6)	161.3(11)
	N(2)-Pt(1)-N(3)	79.2(10)	N(5)-Pt(2)-N(6)	81.8(11)
	N(1)-Pt(1)-S(1)	97.5(7)	N(4)-Pt(2)-S(2)	101.5(8)
	N(2)-Pt(1)-S(1)	178.0(7)	N(5)-Pt(2)-S(2)	173.6(7)
	N(3)-Pt(1)-S(1)	99.0(8)	N(6)-Pt(2)-S(2)	97.1(9)
	C(1)-S(1)-Pt(1)	103.1(9)	C(22)-S(2)-Pt(2)	102.3(10)

**Table S3.** Selected bond distances and angles of  $[1]ClO_4 \cdot 2H_2O$ .

Bond distances (Å)				
Pt(1)-N(1)	1.998(14)	Pt(2)-N(4)	2.013(19)	
Pt(1)-N(2)	1.98(3)	Pt(2)-N(5)	1.986(16)	
Pt(1)-N(3)	2.032(14)	Pt(2)-N(6)	2.017(16)	
Pt(1)-S(1)	2.294(7)	Pt(2)-S(2)	2.281(4)	
Bond angles (°)				
N(1)-Pt(1)- N(2)	81.3(7)	N(4)-Pt(2)-N(5)	82.9(7)	
N(1)-Pt(1)- N(3)	163.3(8)	N(4)-Pt(2)-N(6)	161.7(6)	
N(2)-Pt(1)-N(3)	81.9(8)	N(5)-Pt(2)-N(6)	78.9(7)	
N(1)-Pt(1)-S(1)	96.9(6)	N(4)-Pt(2)-S(2)	93.5(4)	
N(2)-Pt(1)-S(1)	176.2(5)	N(5)-Pt(2)-S(2)	176.2(6)	
N(3)-Pt(1)-S(1)	99.8(6)	N(6)-Pt(2)-S(2)	104.6(5)	
C(1)-S(1)-Pt(1)	108.1(7)	C(22)-S(2)-Pt(2)	112.5(5)	

**Table S4.** Selected bond distances and angles of  $[1]PF_6 \cdot 1.5H_2O$ .

Excited state	Energy / eV ( / nm)	Oscillator strength	Major contributions
[ <b>1</b> ]ClO <sub>4</sub>			
1	2.2226 (557.84)	0.0027	HOMO -> LUMO (99%)
2	2.7688 (447.79)	0.0009	HOMO -> LUMO+1 (99%)
3	3.0456 (407.10)	0.0034	HOMO-1 -> LUMO (80%)
			HOMO-2 -> LUMO (13%)
4	3.3131 (374.23)	0.0103	HOMO-2 -> LUMO (55%)
			HOMO-3 -> LUMO (30%)
[ <b>1</b> ]PF <sub>6</sub>			
1	2.3866 (519.51)	0.0547	HOMO -> LUMO (99%)
2	2.8682 (432.28)	0.0251	HOMO -> LUMO+1 (99%)
3	3.0892 (401.35)	0.0033	HOMO-1 -> LUMO (31%)
			HOMO-2 -> LUMO (58%)
4	3.3060 (375.03)	0.0170	HOMO-3 -> LUMO (81%)

Table S5. Energy, oscillator strength and major contribution of calculated transitions for [1]ClO<sub>4</sub> and [1]PF<sub>6</sub>.