

## Supporting Information

# **Visible-light Regulated Luminescent Switch Based on Spiropyran-derived Pt(II) Complex for Advanced Anti-counterfeiting Materials**

*Xin Lei, † Ying Jiang, † Qingguo Zeng, Yuncan Dou, Haokun Zhang, Jiatao Ni, Yinuo Zhuo, Wei Wang, Yeye Ai, \* Yongguang Li\**

## Table of Contents

1. Material and Methods .....	4
1.1 Chemicals.....	4
1.2 Physical Measurements and Instrumentations .....	4
1.3 Calculation of FRET efficiency .....	5
2. Synthetic Methods and Characterization .....	5
Scheme S1. Synthetic route of switch complex <b>Pt-SP-Ph</b> .....	6
2.1 Synthesis of Pt-NH <sub>2</sub> .....	7
2.2 Synthesis of Pt-SP.....	7
2.3 Synthesis of Pt-SP-Ph .....	8
2.4 Preparation of visible light photorewritable patterning .....	8
2.5 Preparation of anticounterfeiting ink .....	9
2.6 Preparation of dynamic photo-controlled patterns.....	9
2.7 Preparation of temperature response anti-counterfeiting icon .....	9
3. Supporting Figures.....	9
Figure S1. Absorption spectra of <b>Pt-SP-Ph</b> and <b>Pt-MC-Ph</b> .....	10
Figure S2. The photochromic performance of <b>Pt-SP-Ph</b> under alternate 450 nm / 580 nm visible light irradiation.....	10
Figure S3. <sup>1</sup> H NMR spectra of <b>Pt-SP-Ph</b> and <b>Pt-MC-Ph</b> in CDCl <sub>3</sub> .....	11
Figure S4. Absorbance of <b>Pt-SP-Ph</b> at 575 nm during repetitive switching cycles consisting of alternate 450 nm / 580 nm visible light irradiation.....	11
Figure S5. Emission spectra of <b>Pt-SP-Ph</b> in deaerated THF solution upon 450 nm visible light irradiation.....	11
Figure S6. Emission spectra of <b>Pt-SP-Ph</b> and <b>Pt-MC-Ph</b> .....	12
Figure S7. Fluorescence color changes of <b>Pt-SP-Ph</b> upon increasing irradiation time at CIE (1931) chromaticity diagrams.....	12
Figure S8. Normalized excitation spectra of <b>Pt-SP-Ph</b> at different emission wavelengths.....	13
Figure S9. The reversible switch of emission intensity of 1.7 w% <b>Pt-SP-Ph/PMMA</b> at 646 nm by alternate 450 nm / 580 nm irradiation.....	13
Figure S10. Emission decay profiles monitored at 530 nm of (A) <b>Pt-SP-Ph/Pt-MC-Ph</b> ( $2.0 \times 10^{-5}$ M) in THF solution and (B) 1.7 w% ( <b>Pt-SP-Ph/PMMA</b> )/( <b>Pt-MC-Ph/PMMA</b> ). Emission decay profiles monitored at 646 nm of (C) <b>Pt-SP-Ph/Pt-MC-Ph</b> ( $2.0 \times 10^{-5}$ M) in THF solution and (D) 1.7 w% ( <b>Pt-SP-Ph/PMMA</b> )/( <b>Pt-MC-Ph/PMMA</b> ).....	14
Figure S11. <sup>1</sup> H NMR spectrum of <b>Pt-SP-Ph</b> .....	15

Figure S12. $^{13}\text{C}$ NMR spectrum of <b>Pt-SP-Ph</b> .....	15
Figure S13. HRMS spectrum of <b>Pt-SP-Ph</b> ( $[\text{M}+\text{H}]^+$ , calculated 1030.3251). ....	16
<b>4. Supporting Tables</b> .....	16
Table S1 Summarized photophysical data.....	16
Table S2 The related SP switches in the literatures. ....	16
5. References.....	20
6. Author Contributions .....	20

## 1. Material and Methods

### 1.1 Chemicals

All chemical and solvents were used without further purification. 2,3,3-Trimethyl-3H-indole (98 %, energy chemical), 2-hydroxy-5-nitrobenzaldehyde (98 %, energy chemical), 3-iodopropanoic acid (>98 %, TCI), methyl 3,5-dibromobenzoate (98 %, Adamas), 2-(tributylstannyl)pyridine (98 %, energy chemical), 4-dimethylaminopyridine (DMAP, 99 %, Alfa Aesar), *N*-Boc-1,2-cyclohexanediamine (98 %, energy chemical), 1-hydroxybenzo-trizole (HOBt, 99 %, energy chemical), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl, 98 %, Aladdin), K<sub>2</sub>PtCl<sub>4</sub> (99 % (metals basis), Pt 46.4 % min, energy chemical), LiCl (99 %, energy chemical), phenylacetylene (>98 %, TCI), sodium hydroxide (98 %, energy chemical) poly(methyl methacrylate) (energy chemical), polyethylene glycol(M=8000, energy chemical).

### 1.2 Physical Measurements and Instrumentations

<sup>1</sup>H NMR spectra and temperature-dependent <sup>1</sup>H NMR spectra were recorded on a Bruker DPX 500 FT–NMR spectrometer 500 MHz. Matrix assisted laser desorption ionization time of flight mass were performed on a Bruker Autoflex speed TOF mass spectrometer. Elemental analyses of the complexes were performed on a Vario EL elemental analyzer.

Electronic absorption spectra were recorded using a Shimadzu UV–2600 spectrophotometer. The photoluminescence spectra were measured on PerkinElmer FL 6500 and Edinburgh Instruments FLS980 fluorescence spectrophotometers. All solutions for photophysical studies were prepared under high vacuum in a 10-cm<sup>3</sup> round-bottomed flask equipped with a sidearm 1-cm fluorescence cuvette and sealed from the atmosphere by a Rotaflo HP6/6 quick-release Teflon stopper. Solutions were rigorously degassed on a high-vacuum line in a two-compartment cell with no less than four successive freeze-pump-thaw cycles.

### 1.3 Calculation of FRET efficiency

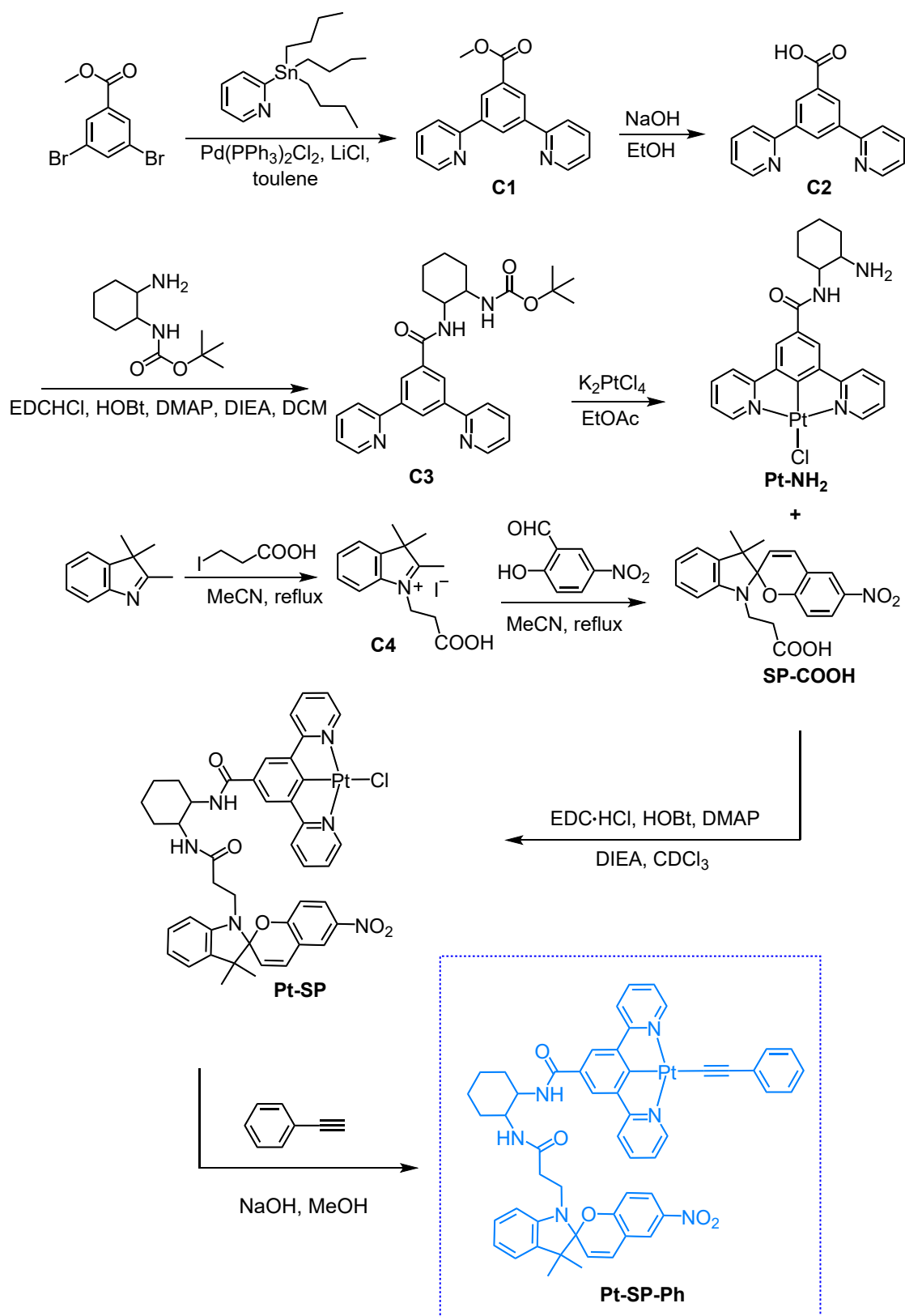
The FRET efficiency of <sup>S/R</sup>**Pt-SP** were calculated using equation (1),

$$E = 1 - \frac{I}{I_0} \quad (1)$$

Where  $E$  is the FRET efficiency and  $I$  and  $I_0$  are the PL intensity of **Pt-SP-Ph** in the presence and absence of **Pt-MC-Ph** after 30 s UV irradiation, respectively.

## 2. Synthetic Methods and Characterization

Compounds **C1-C4**, **Pt-NH<sub>2</sub>**, **SP-COOH**, and **Pt-SP** were synthesized according to the reported literatures.<sup>1-5</sup> The synthetic routes of **Pt-SP-Ph** were shown in Scheme S1.



Scheme S1. Synthetic route of switch complex **Pt-SP-Ph**.

## 2.1 Synthesis of Pt-NH<sub>2</sub>

**C3** (520 mg, 0.98 mmol) and K<sub>2</sub>PtCl<sub>4</sub> (480 mg, 1.17 mmol) were added into glacial acetic acid (20 mL) and the mixtures were refluxed for 3 days under N<sub>2</sub> atmosphere. After cooling to room temperature, Na<sub>2</sub>CO<sub>3</sub> aqueous solution (100 mL) was added and the pure product was afforded as an orange solid. **Pt-NH<sub>2</sub>**: orange solid, 441 mg; yield, 65 %. <sup>1</sup>H NMR (500 MHz, 298 K, DMSO-*d*<sub>6</sub>, relative to Me<sub>4</sub>Si,  $\delta$  / ppm): 9.16 (d, *J* = 6.1 Hz, 2H), 8.43 (d, *J* = 8.8 Hz, 1H), 8.25–8.29 (m, 4H), 8.20 (d, *J* = 7.9 Hz, 1H), 7.91 (s, 0H), 7.64 (td, *J* = 6.2, 5.3, 1.5 Hz, 2H), 7.30 (s, 2H), 3.90–3.97 (m, 1H), 3.02–3.10 (m, 1H), 2.07 (d, *J* = 13.1 Hz, 1H), 1.95 (d, *J* = 12.1 Hz, 1H), 1.70–1.77 (m, 2H), 1.39–1.48 (m, 2H), 1.22–1.32 (m, 2H); <sup>13</sup>C NMR (125 MHz, 298 K, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 166.79, 165.90, 164.72, 151.41, 140.60, 140.08, 129.60, 124.51, 124.39, 120.69, 52.93, 51.20, 31.43, 29.68, 24.25, 23.63; MS (MALDI): *m/z*: 603.15 [*M*+H]<sup>+</sup>.

## 2.2 Synthesis of Pt-SP

To a solution of **Pt-NH<sub>2</sub>** (216 mg, 0.67 mmol) and **SP-COOH** (307 mg, 0.80 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) in a 250 mL flask were added 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC·HCl, 620 mg, 3.20 mmol), 1-hydroxybenzo-trizole (HOBT, 360 g, 2.40 mmol), and 4-(dimethylamino)pyridine (DMAP, 13 mg, 0.11 mmol). The mixture was stirred for overnight at room temperature. Upon completion of the reaction, the solvent was removed under reduced pressure. The remaining solid was redissolved in DMF (15 mL), which was poured into 250 mL water and white precipitate was afforded. **Pt-SP**: green solid, 306 mg; yield, 80 %. <sup>1</sup>H NMR (500 MHz, 298 K, CDCl<sub>3</sub>, relative to Me<sub>4</sub>Si,  $\delta$  / ppm): 9.27 (d, *J* = 6.5 Hz, 2H), 7.65–7.70 (m, 8H), 7.26–7.29 (m, 2H), 7.22 (d, *J* = 6.8 Hz, 1H), 7.11 (t, *J* = 7.1 Hz, 1H), 6.99 (d, *J* = 6.8 Hz, 1H), 6.82 (t, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 10.2 Hz, 1H), 6.51–6.57 (m, 1H), 5.92 (d, *J* = 8.1 Hz, 1H), 5.60 (d, *J* = 10.3 Hz, 1H), 3.80–3.87 (m, 2H), 3.61–3.66 (m, 1H), 3.21–3.28 (m, 1H), 2.50–2.57 (m, 1H), 2.40–2.46 (m, 1H), 2.22–2.28 (m, 1H), 1.76–1.86 (m, 2H), 1.35–1.41 (m, 2H), 1.25–1.32 (m, 2H), 1.16 (s, 3H), 1.02 (s, 3H); <sup>13</sup>C NMR (125 MHz,

298 K, DMSO- $d_6$ ,  $\delta$  / ppm): 172.03, 168.60, 166.48, 165.64, 159.15, 152.03, 146.28, 141.07, 140.63, 139.16, 135.99, 129.77, 128.45, 127.92, 126.02, 123.58, 122.85, 121.95, 121.73, 119.87, 118.54, 115.36, 106.82, 54.97, 54.39, 53.01, 39.99, 36.28, 32.23, 25.87, 24.91, 19.88; MS (MALDI):  $m/z$ : 965.21  $[M+H]^+$ .

### 2.3 Synthesis of Pt-SP-Ph

To a round-bottomed flask, CH<sub>3</sub>OH (50 mL), phenylacetylene (102 mg, 1.0 mmol) and NaOH (80 mg, 2.0 mmol) were added and stirred at room temperature for 20 min. Subsequently, **Pt-SP** (300 mg, 0.31 mmol) was added, and stirred at room temperature overnight. Upon completion of the reaction, the dark-purple product was obtained as precipitate by adding diethyl ether (150 mL) to the above reaction. The product was filtered and washed with diethyl ether for three times (25 mL). **Pt-SP-Ph**: dark-purple solid, 184 mg; yield, 57 %. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 9.50 (d,  $J$  = 4.2 Hz, 2H), 7.70–7.95 (m, 9H), 7.59–7.63 (m, 2H), 7.26–7.31 (m, 4H), 7.17–7.25 (m, 5H), 6.97–7.06 (m, 2H), 6.80 (t,  $J$  = 7.4 Hz, 1H), 6.66 (d,  $J$  = 10.3 Hz, 1H), 6.52–6.58 (m, 2H), 5.58 (d,  $J$  = 10.3 Hz, 2H), 3.76–3.85 (m, 2H), 3.60–3.69 (m, 1H), 3.40–3.49 (m, 2H), 2.48–2.57 (m, 1H), 2.24–2.30 (m, 1H), 1.72–1.84 (m, 2H), 1.21–1.41 (m, 4H), 1.15 (s, 3H), 1.02 (s, 3H); <sup>13</sup>C NMR (125 MHz, 298 K, CDCl<sub>3</sub>,  $\delta$  / ppm): 171.14, 167.61, 167.17, 157.88, 154.38, 145.03, 141.87, 139.92, 137.76, 134.83, 130.75, 128.43, 127.38, 127.04, 124.90, 124.51, 124.50, 122.77, 121.79, 121.74, 120.80, 118.71, 117.33, 114.27, 114.19, 105.57, 105.56, 53.93, 52.45, 51.82, 38.74, 35.00, 34.59, 31.08, 28.68, 24.74, 23.66, 21.67, 18.73, 13.11; MS (MALDI):  $m/z$ : 1031.37  $[M+H]^+$ ; elemental analysis calcd (%) for C<sub>44</sub>H<sub>41</sub>ClN<sub>6</sub>O<sub>5</sub>Pt: C 60.63, H 4.50, N 8.16; found: C 60.59, H 4.65, N 8.21.

### 2.4 Preparation of visible light photorewritable patterning

The obtained complex **Pt-SP-Ph** was dissolved in THF to prepare a solution with a concentration of  $6 \times 10^{-4}$  mol/L. The optically erasable paper was made by immersing in the **Pt-SP-Ph** solution and drying at room temperature.



### 2.5 Preparation of anticounterfeiting ink

The complex **Pt-SP-Ph** (1 mM, 1mL; 0.5mM, 1mL) were dissolved and mixed with PMMA (5.0 w%, 1mL) in THF, respectively, after ultrasonic treatment for 1 min, 1.7 w% **Pt-SP-Ph/PMMA** and 0.85 w% **Pt-SP-Ph/PMMA** were prepared, and the obtained solution was used as anti-counterfeit ink directly.

### 2.6 Preparation of dynamic photo-controlled patterns

The complex Pt-SP-Ph (1 mM, 1mL) and PMMA (5.0 w%, 1mL) were dissolved and mixed in TH, after ultrasonic treatment for 1 min, 1.7 w% **Pt-SP-Ph/PMMA** was prepared. The filter paper was soaked in the 1.7 w% **Pt-SP-Ph/PMMA** mixture. Subsequently, the filter paper was dried at room temperature.

### 2.7 Preparation of temperature response anti-counterfeiting icon

The complex **Pt-SP-Ph** (1 mM, 1mL; 0.5mM, 1mL) were dissolved and mixed with PMMA (5.0 w%, 1mL) and PEG8000 (5.0 w%, 1mL) in THF, respectively. After ultrasonic treatment for 1 min, 1.7 w% **Pt-SP-Ph/PMMA** and 0.85 w% **Pt-SP-Ph/PEG8000** were prepared and then the corresponding anti-counterfeiting patterns were drawn on the quartz sheet.

## 3. Supporting Figures

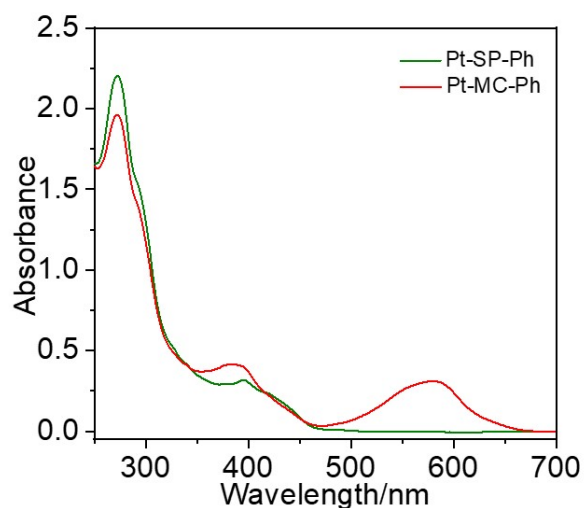


Figure S1. Absorption spectra of **Pt-SP-Ph** and **Pt-MC-Ph** in THF solution ( $8.0 \times 10^{-5}$  M).

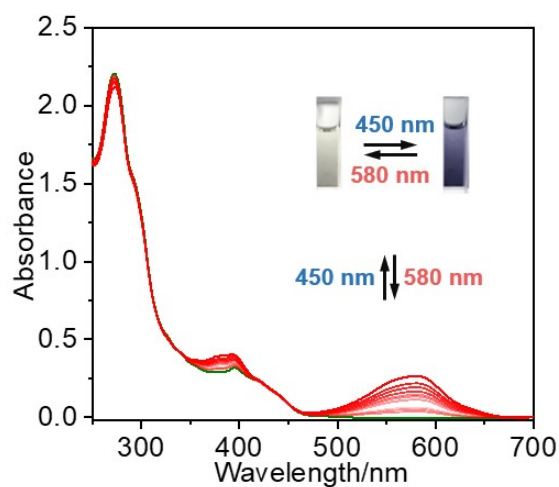


Figure S2. The photochromic performance of **Pt-SP-Ph** ( $8.0 \times 10^{-5}$  M) under alternate 450 nm / 580 nm visible light irradiation. Insets: photographs of color changes of **Pt-SP-Ph** in THF solution before and after irradiation.

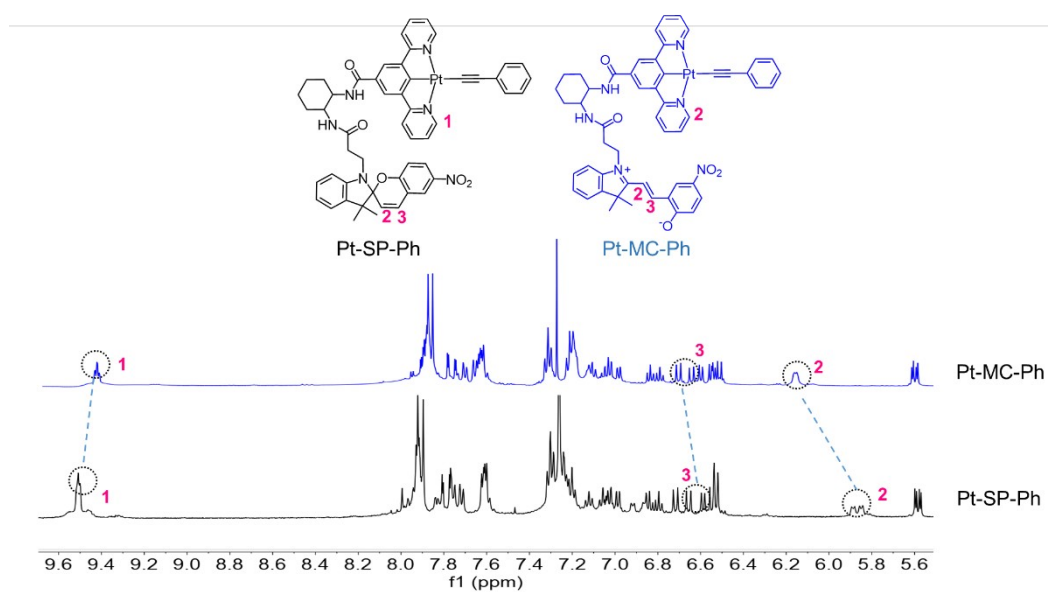


Figure S3.  $^1\text{H}$  NMR spectra of **Pt-SP-Ph** and **Pt-MC-Ph** in  $\text{CDCl}_3$ .

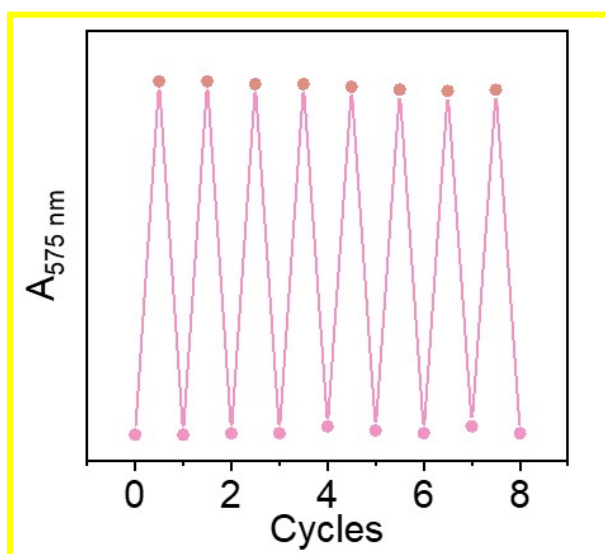


Figure S4. Absorbance of **Pt-SP-Ph** ( $8.0 \times 10^{-5}$  M) at 575 nm in THF during repetitive switching cycles consisting of alternate 450 nm / 580 nm visible light irradiation.

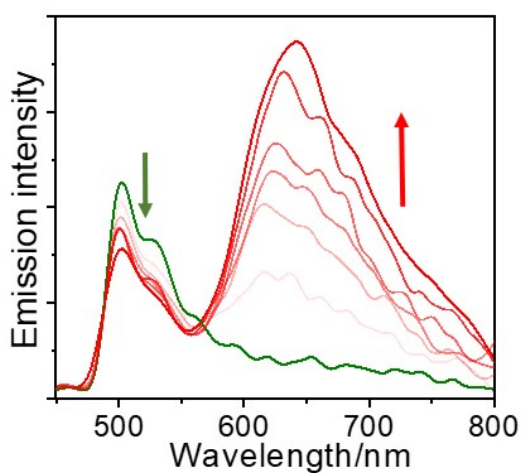


Figure S5. Emission spectra of **Pt-SP-Ph** ( $8.0 \times 10^{-5}$  M) in deaerated THF solution upon 450 nm visible light irradiation.

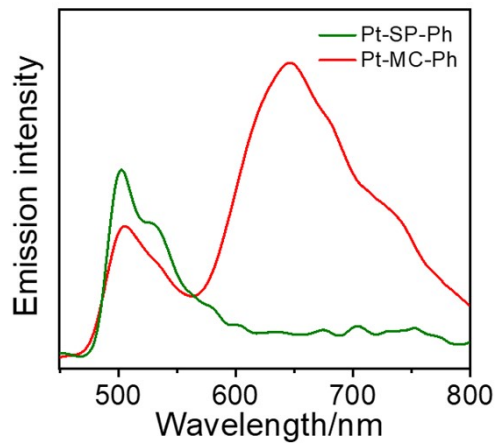


Figure S6. Emission spectra of **Pt-SP-Ph** and **Pt-MC-Ph** in THF solution ( $8.0 \times 10^{-5}$  M).

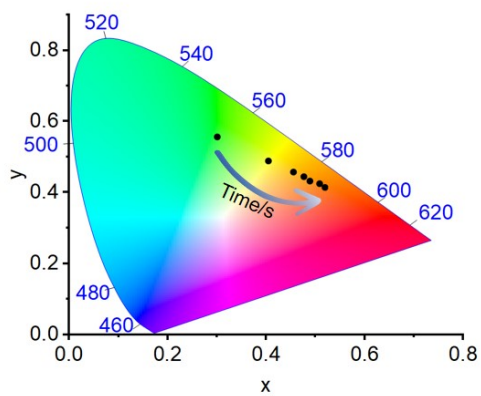


Figure S7. Fluorescence color changes of **Pt-SP-Ph** ( $8.0 \times 10^{-5}$  M) in THF solution upon increasing irradiation time at CIE (1931) chromaticity diagrams.

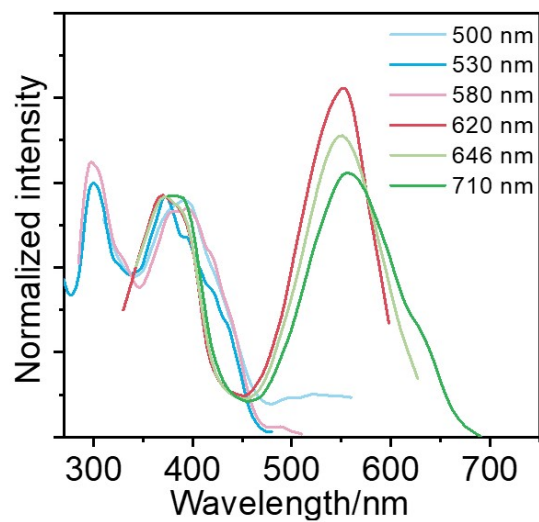


Figure S8. Normalized excitation spectra of **Pt-SP-Ph** ( $8.0 \times 10^{-5}$  M) at different emission wavelengths in THF solution.

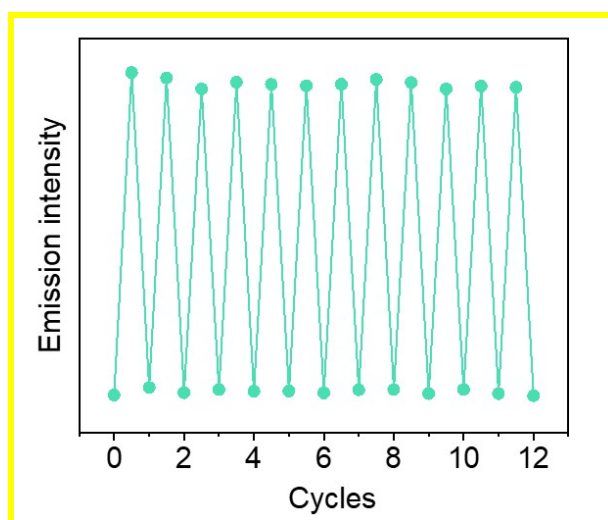


Figure S9. The reversible switch of emission intensity of 1.7 w% **Pt-SP-Ph/PMMA** at 646 nm by alternate 450 nm / 580 nm irradiation.

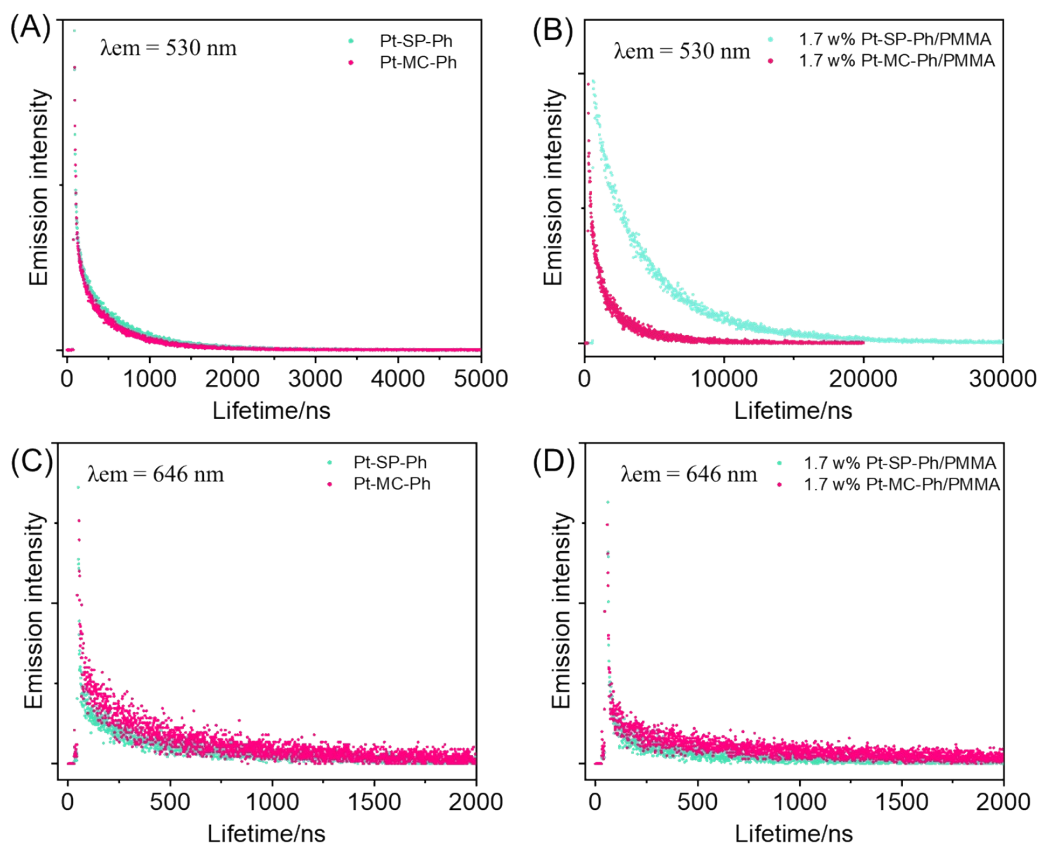


Figure S10. Emission decay profiles monitored at 530 nm of (A) **Pt-SP-Ph/Pt-MC-Ph** ( $2.0 \times 10^{-5}$  M) in THF solution and (B) 1.7 w% (**Pt-SP-Ph/PMMA**)/(**Pt-MC-Ph/PMMA**). Emission decay profiles monitored at 646 nm of (C) **Pt-SP-Ph/Pt-MC-Ph** ( $2.0 \times 10^{-5}$  M) in THF solution and (D) 1.7 w% (**Pt-SP-Ph/PMMA**)/(**Pt-MC-Ph/PMMA**).

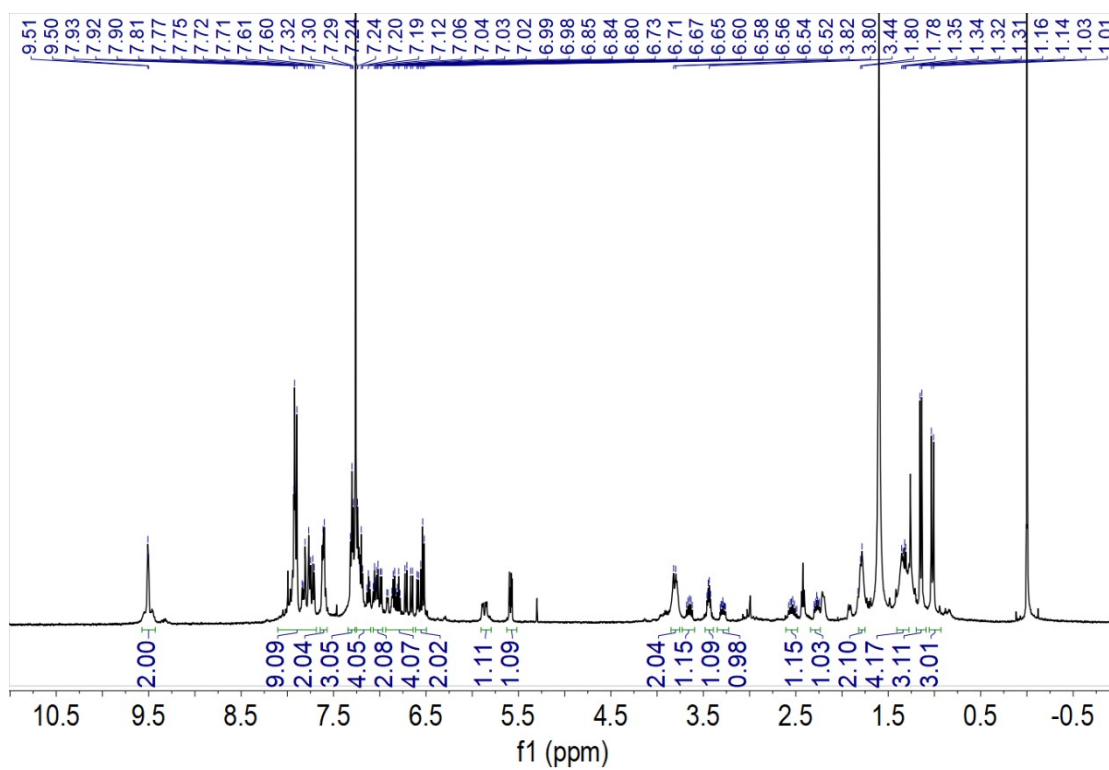


Figure S11.  $^1\text{H}$  NMR spectrum of **Pt-SP-Ph**.

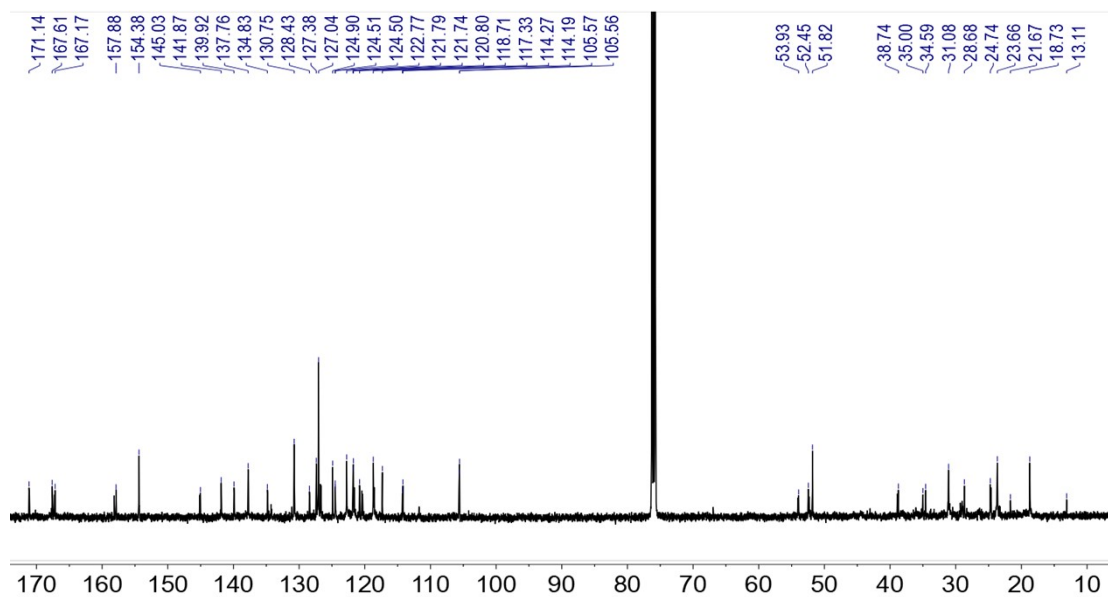


Figure S12.  $^{13}\text{C}$  NMR spectrum of **Pt-SP-Ph**.

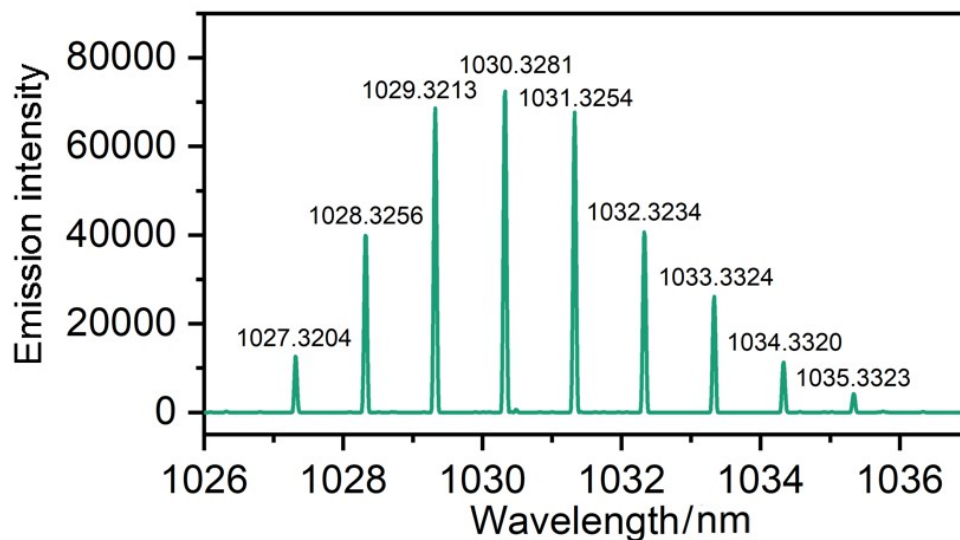


Figure S13. HRMS spectrum of **Pt-SP-Ph** ( $[M+H]^+$ , calculated 1030.3251).

#### 4. Supporting Tables

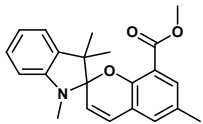
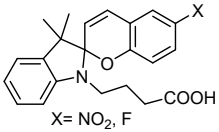
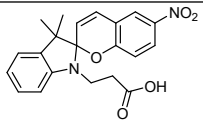
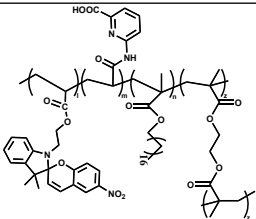
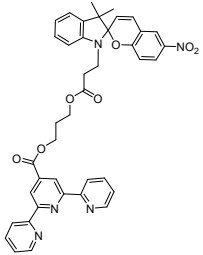
Table S1 Summarized photophysical data.

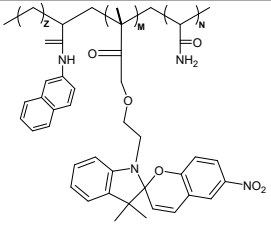
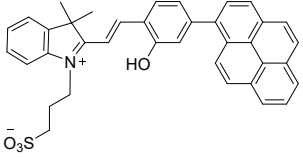
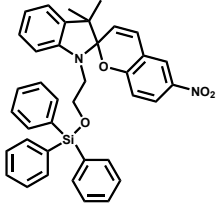
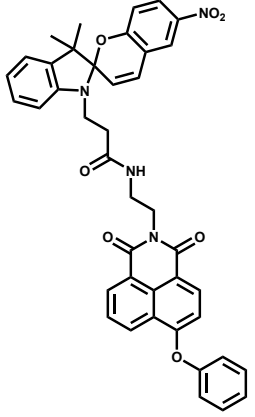
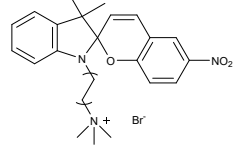
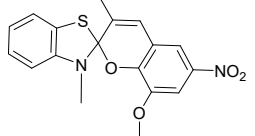
Complexes	PL Quantum yields / %	Lifetimes / $\mu$ s		FRET efficiencies / %	
		530 nm	646 nm	Lifetime method	Emission intensity method
<b>Pt-SP-Ph</b> <sup>[a]</sup>	0.6	0.5	0.4	20 %	20 %
<b>Pt-MC-Ph</b> <sup>[a]</sup>	0.9	0.4	0.5		
<b>1.7 w% Pt-SP-Ph/PMMA</b>	5.2	4.4	0.2	66 %	75 %
<b>1.7 w% Pt-MC-Ph/PMMA</b>	6.2	1.5	0.5		

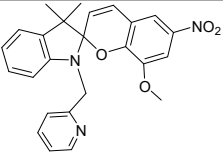
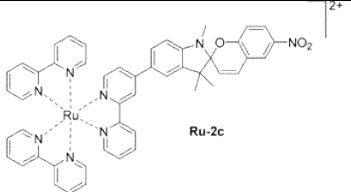
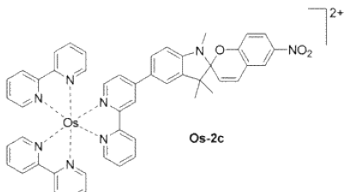
[a] The related photophysical data were measured with the concentration of  $2.0 \times 10^{-5}$  M in THF solution.



Table S2 The related SP switches in the literatures.

Photocontrolled SP switch	$\lambda$ ex/nm	Fluorescence resonance energy transfer (FRET) efficiency	Cycles	Lifetime/ns	Ref.
	Metal ions and 365	/	25	/	1
 X= NO <sub>2</sub> , F	365		10		2
	378	Tb <sup>3+</sup> -MC: 47 %	10		3
	254 and 365				4
	365	Solid: 80 %	<b>10</b>	Donor: SP-2.59 ns MC-2.5ns Acceptor: SP-1.56 ns MC-1.77ns	5

	285	17.85 %	5	MC-0.9 ns	6
	365	95 %	5	PSP: 0.28 ns PMC: 1.71 ns	7
	365	/	3	/	8
	365	/	10	SP: 1.71 ns MC: 1.22 ns	9
	365	72.5 %	10	/	10
	365	/	5	/	11

	365	/	6	/	12
 Ru-2c  Os-2c	334	/	/	34 ns-218 ns	13

1. X. Xiao; W. Zheng; Y. Zhao; C.-H. Li; *Chin. Chem. Lett.* 2023, **34**, 107457.
2. G.M. Sylvia; A.M. Mak; S. Heng; A. Bachhuka; H. Ebendorff-Heidepriem; A.D. Abell; *Chemosensors* 2018, **6**, 17.
3. X. Cong; K. Ou; J. Ma; J. Xu; Y. Liao; Y. Yang; H. Wang; *Chem. Eng. J.* 2024, **481**, 148355.
4. D. Guo; X. Le; H. Shang; F. Shan; D. Li; C. Ouyang; T. Chen; *Chin. Chem. Lett.* 2023, **34**, 108347.
5. L. Hu; Y. Yang; Y. Gao; Y. Wei; J. Zhu; W. Wu; *Chem. Eng. J.* 2024, **488**, 150965.
6. Y. Yang; A. Li; Y. Yang; J. Wang; Y. Chen; K. Yang; B. Z. Tang; Z. Li; *Angew. Chem. Int. Edit.* 2023, **44**, 62.
7. X. Chen; X.-F. Hou; X.-M. Chen; Q. Li; *Nat. Commun.* 2024, **15**, 5401.
8. Z. Wang; Z. Ding; Y. Yang; L. Hu; W. Wu; Y. Gao; Y. Wei; X. Zhang; G. Jiang; *Chem. Eng. J.* 2023, **457**, 141293.
9. H. Wu; W. Wu; L. Hu; J. Zhu; Q. Li; Y. Gao; Y. Wei; G. Jiang; Y. Yang; *Chem. Eng. J.* 2023, **469**, 143781.
10. J. Kim; H. Yun; Y. J. Lee; J. Lee; S.-H. Kim; K. H. Ku; B. J. Kim; *J. Am. Chem. Soc.* 2021, **143**, 13333–13341.
11. R.Q. Zhang, L.P. Hu, Z.X. Xu, Y.X. Song, H.Q. Li, X. Zhang, X.C. Gao, M.X. Wang, C.Y. Xian; *J. Mol. Struct.* 2020, **1204**, 127481.
12. G. Li, Z. Pan, Z. Jia, J. Wang, J. Wang, N. Zhang, M. Pan, J. Yuan; *New. J. Chem.* 2021, **45**, 6386-6396.
13. R. T. F. Jukes; B. Bozic; F. Hartl; P. Belser; L. De Cola; *Inorg. Chem.* 2006, **45**, 8326.

## 5. References

- 1 M. Cocchi; D. Virgili; V. Fattori; D. L. Rochester; J. A. G. Williams, *Adv. Func. Mater.* 2007, **17**, 285–289.
- 2 J. Uchida; M. Yoshio; S. Sato; H. Yokoyama; M. Fujita; T. Kato, *Angew. Chem. Int. Ed.* 2017, **56**, 14085–14089.
- 3 J. Tang; X. Yang; J. Li; D. Zhang; Y. Wang; Y. Ye, *Sens. Actuator B Chem.* 2022, **350**, 130814.
- 4 C. Liu; D. Yang; Q. Jin; L. Zhang; M. Liu, *Adv. Mater.* 2016, **28**, 1644–1649.
- 5 Y. Ai; M. H.-Y. Chan; A. K.-W. Chan; M. Ng; Y. Li; V. W.-W. Yam, *Proc. Natl. Acad. Sci. U. S. A.* 2019, **116**, 13856–13861.

## 6. Author Contributions

Y.A. and Y.L. designed the experiments. X.L., Y.J. synthesized the compounds and carried out the characterizations, collected and analyzed the data. X.L., Y.J., Y.A. and Y.L. wrote the paper. Y.A. and Y.L. conceived the work. X.L., Y.J., Q.Z, Y.D., H.Z., J.N., Y.Z., W.W., Y.A. and Y.L. participated in the discussion and revised the manuscript. The work was supervised by Y.L.