Supporting Information

Luminescence Tribochromism and Bright Emission in Gold(I) Thiouracilate Complexes

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Experimental

Characterization of Compounds and Instrumentation. Infrared spectra in the 4000-400 cm⁻¹ region were obtained from KBr pellets on a Mattson 6020 FT-IR spectrometer. ¹H, ¹⁹F, and ³¹P NMR spectra were recorded on a Bruker Avance-400 NMR spectrometer operating at 400.13 MHz (¹H), 376.44 MHz (¹⁹F) and 161.97 MHz (³¹P) in pulse mode with Fourier transform. Chemical shifts are reported relative to SiMe₄ (¹H), CF₃C₆H₅ (¹⁹F), and 75% H₃PO₄ (³¹P) used as either internal or external standards for the respective nuclei. Mass spectra were measured using a Hewlett Packard 1100 series MSD operated with an electrospray source and the detection of positive and negative ions. The samples were dissolved in CH₂Cl₂/CH₃OH (v/v = 1/1) and pumped into the spray chamber using 100 % CH₃OH. Steady-state emission measurements were performed on FluoroMax-3 spectrofluorometer equipped with an ozone-free Xenon lamp and photomultiplier tube detector (range 200-852 nm). Low temperature emission spectra were recorded in 4 mm diameter quartz EPR tubes placed in a liquid nitrogen dewar equipped with quartz windows. Emission was collected at 90° from the excitation source.

Crystallographic Structure Determinations. Crystals were mounted in inert Paratone-8277 on a glass fiber and immediately placed in a cold nitrogen stream at 193(2) K on the X-ray diffractometer. Data were collected on a standard Siemens SMART CCD Area Detector System equipped with graphite-monochromated Mo K α ($\lambda = 0.71073$ Å). The structures were solved using SHELXS 97 followed by successive difference Fourier synthesis. The nonhydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. All calculations were carried out on a personal computer with use of SHELXS 97 and SHELXL 97. Crystal parameters and procedural information corresponding to data collection and structure refinement are given in CIF format.

Materials. Potassium tetrachloroaurate(III), silver trifluoroacetate,

bis(diphenylphosphino)methane (dppm), sodium carbonate, 2-thiouracil (TU), and 6methyl-2-thiouracil (Me-TU) were purchased from Aldrich and , respectively, and were used without further purification. (μ -dppm)Au₂Cl₂ was prepared according to the literature procedure.

Synthesis and Characterization of 1 and 2

[Au₂(μ-TU)(μ-dppm)](CF₃CO₂) (<u>1a</u>): To a solution of (μ-dppm)Au₂Cl₂ (0.1698 g, 0.20 mmol) in dichloromethane (20 mL) was added CF₃CO₂Ag (0.0884 g, 0.40 mmol) and then was stirred for 30 min. The solution was filtered through celite to remove the AgCl precipitate into a suspension of 2-thiouracil (0.0256 g, 0.20 mmol) in dichloromethane (20 mL). The reaction mixture was stirred for 5h at room temperature. The resulting solution was evaporated to dryness to obtain a crude solid. Slow evaporation of a dichloromethane/MeOH (v/v =1/1) solution of the crude product gave colorless crystals suitable for X-ray crystallography. Yield: 83%. Mp 181 °C. ESMS (m/z): [M-(CF₃CO₂)]⁺ 905, [M-H]⁻ 1017. ¹H NMR (CD₂Cl₂, ppm): 4.43 (t, 2H, PCH₂, ³*J*_{P-H} = 12.5 Hz), 6.09 (d, 1H, *J* = 7.3 Hz), 7.27 (d, 1H, *J* = 7.3 Hz), 7.29 – 7.38 (m, 8H, Ph), 7.42 – 7.48 (m, 4H, Ph), 7.60 – 7.73 (m, 8H, Ph). ¹⁹F NMR (CD₂Cl₂, ppm): -13.0. ³¹P NMR (CD₂Cl₂, ppm): 27.9, 29.9. IR (KBr, cm⁻¹): 1683, 1656, 1436, 1197, 1104. 691, 527. Anal. Calcd for C₃₁H₂₅Au₂N₂O₃P₂S₁F₃·H₂O: C, 35.92; H, 2.63; N, 2.70; S, 3.09. Found: C, 35.84; H, 2.50; N, 2.73; S, 3.08.

[Au₂(μ -Me-TU)(μ -dppm)](CF₃CO₂) (<u>1b</u>): This compound was prepared by the same procedure used for compound <u>1a</u> with 6-methyl-2-thiouracil instead of 2-thiouracil. Slow evaporation of a dichloromethane/MeOH (v/v =1/1) solution of the crude product gave colorless crystals suitable for X-ray crystallography. Yield: 85%. Mp 191 °C. ESMS (m/z): [M-(CF₃CO₂)]⁺ 919, [M-H]⁻ 1031. ¹H NMR (CD₂Cl₂, ppm): 2.03 (s, 3H), 4.61 (t, 2H, PCH₂, ³*J*_{P-H} = 12.5 Hz), 5.77 (s, 1H), 7.23 – 7.31 (m, 8H, Ph), 7.37 – 7.45 (m, 4H, Ph), 7.45 – 7.75 (br, 8H, Ph), 14.61 (br, 1H). ¹⁹F NMR (CD₂Cl₂, ppm): -13.0. ³¹P NMR

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(CD₂Cl₂, ppm): 28.1, 29.1. IR (KBr, cm⁻¹): 1657, 1437, 1263, 1199, 1103, 741, 691, 528. Anal. Calcd for C₁₂₆H₁₀₇Au₈N₈O₁₀P₈S₄F₉: C, 37.68; H, 2.69; N, 2.79; S,3.19. Found: S, 3.66. (C, H, N analysis was not done for **1b**.)

[Au₂(µ-TU)(µ-dppm)] (2a): Method 1. To the reaction solution of 1a was added solid Na_2CO_3 (0.106 g, 1.0 mmol) to neutralize CF₃CO₂H, which is a side-product of the above reaction. After the solid residue was removed by filtration, the filtrate was evaporated to dryness to yield a crude solid. Slow evaporation of a dichloromethane/MeOH (v/v = 1/1) solution of the crude product gave pale yellow-green crystals suitable for X-ray crystallography. Yield: 79%. Method 2. To a solution of $(\mu$ -dppm)Au₂Cl₂ (0.1698 g, 0.20 mmol) in dichloromethane (20 mL) was added AgCF₃CO₂ (0.0884 g, 0.40 mmol). The solution was then stirred for 30 min and filtered into a suspension of 2-thiouracil (0.0284 g, 0.20 mmol) and NaOH (0.0284 g, 0.40 mmol) in dichloromethane (20 mL). The reaction mixture was stirred for 5 h at room temperature. After NaCF₃CO₂ was filtered off, the filtrate was evaporated to dryness to yield a crude product. Slow evaporation of a dichloromethane/MeOH (v/v = 1/1) solution of the crude product gave the same pale yellow-green crystals. Yield: 71%. Mp 242 °C (decomp.). ESMS (m/z): $[M+H]^+$ 905, $[M-H]^{-}$ 903. ¹H NMR (CD₂Cl₂, ppm): 3.72 (t, 2H, PCH₂, ³J_{P-H} = 11.9 Hz), 6.10 (d, 1H, J = 6.3 Hz), 7.25 – 7.33 (m, 8H, Ph), 7.33 – 7.42 (m, 4H, Ph), 7.48 – 7.66 (m, 9H). ³¹P NMR (CD₂Cl₂, ppm): 28.2, 31.0. IR (KBr, cm⁻¹): 1434.3(m), 1173.6(m), 1014.1(s), 818.4(s), 776.2(s), 650.5(s). Anal. Calcd for C₅₈H₄₈Au₄N₄O₂P₄S₂: C, 38.51; H, 2.67; N, 3.10; S, 3.55. Found: C, 38.43; H, 2.67; N, 3.08; S, 3.45.

[Au₂(μ -Me-TU)(μ -dppm)] (<u>2b</u>): This compound was prepared by the same procedure used for compound <u>2a</u> with 6-methyl-2-thiouracil instead of 2-thiouracil. Slow evaporation of a dichloromethane/MeOH (v/v =1/1) solution of the crude product gave pale yellowgreen crystals suitable for X-ray crystallography. Yield: 81% (by method 1). Yield: 71% (by method 2). Mp >250 °C. [M+H]⁺ 919, [M-H]⁻ 917. ¹H NMR (CD₂Cl₂, ppm): 2.16 (s, 3H), 3.70 (t, 2H, PCH₂, ³J_{P-H} = 12.0 Hz), 5.99 (s, 1H), 7.28 – 7.37 (m, 8H, Ph), 7.37 – 7.43

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(m, 4H, Ph), 7.57 - 7.70 (br, 8H, Ph). ³¹P NMR (CD₂Cl₂, ppm): 28.3, 31.0. IR (KBr, cm⁻¹): 1434.3(m), 1173.6(m), 1014.1(s), 818.4(s), 776.2(s), 650.5(s). Anal. Calcd for C₆₀H₅₂Au₄N₄O₂P₄S₂·H₂O: C, 38.84; H, 2.93; N, 3.02; S, 3.46. Found: C, 38.36; H, 2.94; N, 2.96; S, 3.34.

| Identification code | sad/ eisyl38 |
|---------------------------------|--|
| Empirical formula | C32 H24 Au2 F3 N2 O7 P2 S |
| Formula weight | 1093.46 |
| Temperature | 193(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Tetragonal, I4(1)/a |
| Unit cell dimensions | $a = 33.3063(15)$ Å $\alpha = 90$ deg. |
| | $b = 33.3063(15)$ Å $\beta = 90$ deg. |
| | $c = 13.8485(9)$ Å $\gamma = 90$ deg. |
| Volume | $15362.3(14) \text{ Å}^3$ |
| Z, Calculated density | 16, 1.891 Mg/m^3 |
| Absorption coefficient | 7.828 mm ⁻¹ |
| F(000) | 8272 |
| Crystal size | 0.48 x 0.24 x 0.22 mm |
| Theta range for data collection | 1.73 to 28.24 deg. |
| Limiting indices | -36<=h<=44, -42<=k<=44, -16<=l<=18 |
| Reflections collected / unique | 44781 / 9162 [R(int) = 0.0398] |
| Completeness to theta $= 28.24$ | 96.4 % |
| Absorption correction | Empirical; SADABS |
| Max. and min. transmission | 0.801 and 0.169 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 9162 / 4 / 442 |
| Goodness-of-fit on F^2 | 1.073 |
| Final R indices [I>2sigma(I)] | R1 = 0.0516, $wR2 = 0.1441$ |
| R indices (all data) | R1 = 0.0631, $wR2 = 0.1508$ |
| Largest diff. peak and hole | 3.966 and -1.011 e. Å ⁻³ |

Table S1. Crystallographic, Data Collection and Structure Refinement Parameters for 1a

Intensity data collected using 60 s frames.

| Identification code | sad / eisyl40 |
|---------------------------------|---|
| Empirical formula | C132 H104 Au8 F9 N8 O22 P8 S4 |
| Formula weight | 4276.96 |
| Temperature | 193(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Triclinic, P1(bar) |
| Unit cell dimensions | $a = 13.8976(12)$ Å $\alpha = 84.383(2)$ deg. |
| | $b = 21.5548(19)$ Å $\beta = 77.259(2)$ deg. |
| | $c = 26.928(2)$ Å $\gamma = 83.480(2)$ deg. |
| Volume | 7794.9(12) Å ³ |
| Z, Calculated density | 2, 1.822 Mg/m^3 |
| Absorption coefficient | 7.706 mm ⁻¹ |
| F(000) | 4050 |
| Crystal size | 0.26 x 0.12 x 0.10 mm |
| Theta range for data collection | 1.71 to 28.32 deg. |
| Limiting indices | -18<=h<=15, -26<=k<=27, -35<=l<=35 |
| Reflections collected / unique | 44514 / 31312 [R(int) = 0.0301] |
| Completeness to theta $= 28.32$ | 80.6 % |
| Absorption correction | Empirical; SADABS |
| Max. and min. transmission | 0.928 and 0.521 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 31312 / 7 / 1720 |
| Goodness-of-fit on F^2 | 1.073 |
| Final R indices [I>2sigma(I)] | R1 = 0.0556, $wR2 = 0.1472$ |
| R indices (all data) | R1 = 0.0780, wR2 = 0.1545 |
| Largest diff. peak and hole | 3.016 and -1.913 e.A ⁻³ |

Table S2. Crystallographic, Data Collection and Structure Refinement Parameters for 1b

Intensity data collected using 60 s frames.

| T 1 1 M 1 M | 1/1 1/0 |
|----------------------------------|--|
| Identification code | sad/eisy118 |
| Empirical formula | C63 H54 Au4 N4 O5 P4 S2 |
| Formula weight | 1922.97 |
| Temperature | 193(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | <i>P</i> 2(1)/c |
| Unit cell dimensions | $a = 12.3737(6)$ Å $\alpha = 90$ deg. |
| | $b = 29.1208(14)$ Å $\beta = 93.6570(10)$ deg. |
| | $c = 17.4858(8) \text{ Å} \qquad \gamma = 90 \text{ deg.}$ |
| Volume, Z | $6287.9(5) \text{ Å}^3, 4$ |
| Density (calculated) | 2.031 Mg/m^3 |
| Absorption coefficient | 9.523 mm ⁻¹ |
| <i>F</i> (000) | 3632 |
| Crystal size | 0.10 x 0.10 x 0.18 mm |
| Theta range for data collection | 1.36 to 28.27 deg. |
| Limiting indices | -16<=h<=15, -38<=k<=32, -22<=l<=22 |
| Reflections collected | 38825 |
| Independent reflections | 14818 [R(int) = 0.0319] |
| Reflections >2Sig(I) | 11698 |
| Absorption correction | Empirical; SADABS |
| Max. and min. transmission | 0.928 and 0.663 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 14818 / 0 / 729 |
| Goodness-of-fit on F^2 | 0.966 |
| Final R indices [I>2sigma(I)] | R1 = 0.0424, WR2 = 0.0795 |
| R indices (all data) | R1 = 0.0662, wR2 = 0.0862 |
| Largest diff. peak and hole | 1.183 and -0.858 e. Å ⁻³ |

Intensity data collected using 30 s frames. Three methanols of crystallization; two refined anisotropically (hydrogens not included).

| Au(1)-Au(2) | 2.8797(4) | | Au(1)-Au(2)#1 | | 3.3321(5) | |
|----------------------|---------------|-------------|--------------------|----------------|-----------|-------------|
| Au(2)-Au(1)#2 | 3.3321(5) | | Au(1)-N(| Au(1)-N(1) 2.0 | | 78(7) |
| Au(1)-P(2) | 2.235(2) | | Au(2)-P(| 1) | 2.27 | 79(2) |
| Au(2)-S(1) | 2.319(2) | | O(1)-C(4 |) | 1.252(12) | |
| S(1)-C(1) | 1.73 | 30(8) | N(1)-C(1 |) | 1.34 | 48(11) |
| P(2)-C(5) | 1.836(8) | | P(1)-C(5) |) | 1.811(8) | |
| N(1)-C(4) | 1.392(10) | | N(2)-C(1 |) | 1.354(11) | |
| N(2)-C(2) | (2) 1.373(12) | | C(2)-C(3 |) | 1.323(15) | |
| C(3)-C(4) | 1.441(14) | | | | | |
| | | | | | | |
| Au(1)-Au(2)-Au(1)# | ŧ2 | 110.737(13) | Au(2)-Au | u(1)-Au(2)# | ŧ1 | 114.290(14) |
| N(1)-Au(1)-P(2) | | 171.52(19) | N(1)-Au(1)-Au(2) | | | 87.01(18) |
| P(2)-Au(1)-Au(2) 93. | | 93.46(5) | N(1)-Au(1)-Au(2)#1 | | | 80.49(17) |
| P(2)-Au(1)-Au(2)#1 | | 106.92(6) | P(1)-Au(2 | 2)-S(1) | | 174.09(8) |
| P(1)-Au(2)-Au(1) | | 91.34(5) | S(1)-Au(2 | 2)-Au(1) | | 88.59(5) |
| P(1)-Au(2)-Au(1)#2 | | 106.45(6) | S(1)-Au(2 | 2)-Au(1)#2 | | 79.06(5) |
| C(1)-S(1)-Au(2) | | 109.1(3) | C(12)-P(| 1)-C(5) | | 105.3(4) |
| C(5)-P(1)-Au(2) | | 110.5(3) | C(6)-P(1) |)-Au(2) | | 110.7(3) |
| C(5)-P(2)-Au(1) | | 111.7(3) | C(1)-N(1) |)-C(4) | | 120.2(7) |
| C(1)-N(1)-Au(1) | | 127.9(5) | C(4)-N(1) |)-Au(1) | | 111.8(6) |
| C(1)-N(2)-C(2) | | 120.5(8) | N(1)-C(1) |)-N(2) | | 120.5(7) |
| N(1)-C(1)-S(1) | | 125.9(6) | N(2)-C(1) |)-S(1) | | 113.5(6) |
| C(3)-C(2)-N(2) | | 121.8(9) | C(2)-C(3) |)-C(4) | | 118.5(8) |
| O(1)-C(4)-N(1) | | 117.4(8) | O(1)-C(4) |)-C(3) | | 124.2(8) |
| N(1)-C(4)-C(3) | | 118.3(8) | P(1)-C(5) |)-P(2) | | 115.0(5) |

Table S4. Selected Bond Distances (Å) and Angles (deg) for 1a.

Symmetry transformations used to generate equivalent atoms: $\#1 -y+7/4, x+1/4, z+1/4 \quad \#2 \ y-1/4, -x+7/4, z-1/4$

| Au(1)- $Au(2)$ | 2.8671(6) | Au(2)- $Au(3)$ | 3.2497(7) |
|-------------------|-------------|-------------------|-------------|
| Au(3)- $Au(4)$ | 2.8861(6) | Au(4)- $Au(5)$ | 3.2363(6) |
| Au(5)-Au(6) | 2.8864(6) | Au(6)-Au(7) | 3.3538(7) |
| Au(7)-Au(8) | 2.8617(7) | | |
| Au(1)-N(1) | 2.093(8) | Au(1)-P(1) | 2.241(3) |
| Au(2)-P(2) | 2.279(3) | Au(2)-S(1) | 2.321(3) |
| Au(3)-N(3) | 2.078(9) | Au(3)-P(3) | 2.235(3) |
| Au(4)-P(4) | 2.273(3) | Au(4)-S(2) | 2.327(3) |
| Au(5)-N(5) | 2.106(8) | Au(5)-P(5) | 2.252(3) |
| Au(6)-P(6) | 2.276(3) | Au(6)-S(3) | 2.323(3) |
| Au(7)-P(7) | 2.287(3) | Au(7)-S(4) | 2.337(3) |
| Au(8)-N(7) | 2.093(9) | Au(8)-P(8) | 2.236(3) |
| O(1)-C(2) | 1.216(13) | O(2)-C(34) | 1.230(14) |
| O(3)-C(64) | 1.225(12) | O(4)-C(94) | 1.238(13) |
| | | | |
| Au(1)-Au(2)-Au(3) | 107.340(19) | Au(2)-Au(3)-Au(4) | 118.969(18) |
| Au(3)-Au(4)-Au(5) | 106.317(17) | Au(4)-Au(5)-Au(6) | 133.209(19) |
| Au(5)-Au(6)-Au(7) | 93.695(17) | Au(6)-Au(7)-Au(8) | 131.66(2) |
| N(1)-Au(1)-P(1) | 173.1(2) | P(2)-Au(2)-S(1) | 172.67(11) |
| N(3)-Au(3)-P(3) | 168.4(2) | P(4)-Au(4)-S(2) | 176.00(10) |
| N(5)-Au(5)-P(5) | 178.3(2) | P(6)-Au(6)-S(3) | 173.05(11) |
| P(7)-Au(7)-S(4) | 173.06(11) | N(7)-Au(8)-P(8) | 172.9(3) |
| N(1)-Au(1)-Au(2) | 86.2(2) | N(3)-Au(3)-Au(4) | 87.2(2) |
| N(5)-Au(5)-Au(6) | 86.0(2) | N(7)-Au(8)-Au(7) | 84.9(3) |
| S(1)-Au(2)-Au(1) | 89.30(7) | S(2)-Au(4)-Au(3) | 87.67(7) |
| S(3)-Au(6)-Au(7) | 70.55(8) | S(4)-Au(7)-Au(8) | 89.38(7) |
| N(1)-C(1)-S(1) | 125.6(8) | N(3)-C(31)-S(2) | 126.0(8) |
| N(5)-C(61)-S(3) | 125.4(8) | N(7)-C(91)-S(4) | 122.9(9) |
| | | | |

Table S5. Selected Bond Distances (Å) and Angles (deg) for $\mathbf{1b}$.

| Au(1)-Au(2) | 2.8638(4) | Au(2)- $Au(3)$ | 2.9235(4) |
|-------------------|-------------|-------------------|-------------|
| Au(3)-Au(4) | 2.8634(4) | | |
| O(1)-C(4) | 1.246(8) | O(2)-C(34) | 1.232(9) |
| Au(1)-N(1) | 2.087(5) | Au(1)-P(1) | 2.2452(17) |
| Au(2)-P(2) | 2.2820(17) | Au(2)-S(1) | 2.3196(18) |
| Au(3)-P(4) | 2.2867(17) | Au(3)-S(2) | 2.3259(19) |
| Au(4)-N(3) | 2.078(6) | Au(4)-P(3) | 2.2251(18) |
| S(1)-C(1) | 1.759(7) | N(1)-C(1) | 1.354(8) |
| S(2)-C(31) | 1.761(7) | N(3)-C(31) | 1.349(9) |
| Au(1)-Au(2)-Au(3) | 148.344(12) | Au(2)-Au(3)-Au(4) | 145.484(13) |
| N(1)-Au(1)-P(1) | 178.53(15) | P(2)-Au(2)-S(1) | 174.84(7) |
| P(4)-Au(3)-S(2) | 175.75(7) | N(3)-Au(4)-P(3) | 173.18(16) |
| N(1)-Au(1)-Au(2) | 89.57(15) | S(1)-Au(2)-Au(1) | 85.97(4) |
| S(2)-Au(3)-Au(4) | 86.19(5) | N(3)-Au(4)-Au(3) | 89.05(15) |
| N(1)-C(1)-S(1) | 122.3(5) | N(3)-C(31)-S(2) | 122.8(5) |
| O(1)-C(4)-N(1) | 118.2(6) | O(2)-C(34)-N(3) | 118.0(7) |
| | | | |

Table S6. Selected Bond Distances (Å) and Angles (deg) for $\mathbf{2b}$.





Figure S1. Perspective view of 1b (top) and the phenyl rings on the phosphorus atoms are omitted for clarity. Diagram of discontinuous aurophilic helix of 1b (bottom). For clarity, only Au atoms oriented along the c-axis are shown.





Figure S2. IR spectra of $[Au_2(\mu-Me-TU)(\mu-dppm)]Y$ (Y = CF₃CO₂ (a), NO₃ (b), ClO₄ (c), and Au(CN)₂ (d)).



Figure S3. Emission and excitation spectra of **1b** (colorless crystals) in solid state at room temperature.



Figure S4. Emission and excitation spectra of **1b** (crushed colorless crystals) in solid state at room temperature.



Figure S5. Emission and excitation spectra of **2b** (pale yellow crystals) in KBr solid state mixture at room temperature.



Figure S6. Emission and excitation spectra of **1b** in CH₂Cl₂ solution at room temperature (emission spectra at $\lambda_{ex} = 375$ nm and excitation spectra at $\lambda_{em} = 485$ nm).



Figure S7. Emission spectra of **1b** with variation of pH in CH₂Cl₂ solution at room temperature (emission spectra at $\lambda_{ex} = 375$ nm and excitation spectra at $\lambda_{em} = 485$ nm).



Figure S8. Emission and excitation spectra of **1b** in CH₂Cl₂/toluene frozen glass with different concentration at 77 K (emission spectra at $\lambda_{ex} = 375$ nm and excitation spectra at $\lambda_{em} = 485$ nm).



Figure S9. Emission and excitation spectra of **2b** in CH₂Cl₂/toluene frozen glass with different concentration at 77 K (emission spectra at $\lambda_{ex} = 375$ nm and excitation spectra at $\lambda_{em} = 485$ nm).



Figure S10. X-ray powder diffraction patterns of crystalline and crushed 1a and 1b.