Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information

Intensely luminescent gold(I) phosphinopyridyl clusters: visualization of unsupported aurophilic interactions in solution

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I. Experimental details

Materials and reagents. All of the reagents employed were commercially available and used as received. The solvents were purified and distilled by standard procedures prior to use. 2,6-dichloropyridine and ^{n}BuLi (1.6 M hexane solution) were obtained from J&K Chemicals. Triphenylphosphine and diphenylphosphine were purchased from Shanghai Boka Chem. Tech. Inc. The phosphine ligand 2,6-bis(diphenylphosphino)pyridine (PNP) was prepared according to literature procedures with modification.[1]

Physical Measurements and instrumentation. The C, H, N microanalyses were carried out with a Vario EL III elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} with a Nicolet AVATAR FT-IR360 spectrometer. UV-Vis spectra were recorded on a Varian Cary5000 UV-VIS-NIR Spectrophotometer. Luminescence and quantum yield were measured on a Hitachi F-7000 spectrometer. Lifetime was measured on Horiba Jobin Yvon Fluoromax-4P-Tcspc spectrometer. NMR data were recorded on a Bruker Avance II spectrometer (500MHz). Chemical shifts, δ, are reported relative to the external standard 85% H_3PO_4 for ^{31}P NMR. Mass spectrum was recorded on a ESI-TOF-MS. Luminescence imaging, including xy-scan, lambda-scan, T-scan, and time-lapse imaging, was performed with an Leica TCS SP5 confocal fluorescence microscope and a 100 × oil-immersion objective lens.

X-ray Crystallography. Intensity data of compounds **1** and **2** were collected on an Oxford Gemini S Ultra system (Cu Kα for **1**; Mo Kα for **2**) at 173 K. Absorption corrections were applied by using the program CrysAlis (multi-scan). The structure was solved by direct methods. Non-hydrogen atoms except counter ions BF_4^- were refined anisotropically by least-squares on F^2 using the SHELXTL program. The hydrogen atoms of organic ligands were generated geometrically. SQUEEZE tool of

PLATON was applied to both structures due to the existence of large solvent accessible voids. CCDC-790855(**1**) and CCDC-1021795(**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DFT calculations. Density functional theory (DFT) calculations were performed with the quantum chemistry program Turbomole V6.4. Geometry optimization was done with the functional of BP86. The def2-SV(P) basis sets were used for C, N, P, H, and the def2-TZVP basis sets for Au. The calculations were performed without symmetry constraints, and the resolution of the identity method was used to speed up calculations.[2-4]

Cell culture. The HeLa line was provided by the Institute of Biochemistry and Cell Biology, SIBS, CAS (China), grown in DMEM (Dulbecco's modified Eagle's medium) supplemented with 10% FBS (fetal bovine serum) and kept at 37℃ in a humidified incubator with 5% CO_2.

Luminescence imaging. Cells (5×10^8 /L) were plated on 14 mm glass coverslips and allowed to adhere for 24 h. The cells were washed with PBS and then incubated solely with 10 μM complex **1** or **2** in DMSO/culture medium (1:99, v/v) for 20 min at 37℃. Cell imaging was then carried out after washing the cells with PBS. Cells incubated with complex **1** were excited at 405 nm with a semiconductor laser, and the emission was collected at 500 ± 20 nm. Cells incubated with complex **2** were excited at 488 nm, and the emission was collected at 580 ± 20 nm.

For co-localization experiments of **1**, the cells were first incubated with MitoTracker Red for 10 min, then incubated with **1** for another 20 min before imaging. (Concentration: 10 μM for **1**, 100 nM for MitoTracker Red; λ_{ex} = 405 nm for **1**, 543 nm for MitoTracker Red; λ_{em} = 500 ± 20 nm for **1**, 600 ± 20 nm for MitoTracker Red)

For co-localization experiments of **2**, the cells were first incubated with

MitoTracker Green for 10 min, then incubated with **2** for another 20 min before imaging. (Concentration: 10 μM for **2**, 100 nM for MitoTracker Green; λ_{ex} = 488 nm for **2** and MitoTracker Green; λ_{em} = 580 ± 20 nm for **2**, 510 ± 15 nm for MitoTracker Green)

II. Synthesis

$[Au_2(PNP)_2](BF_4)_2$: To a solution of Me_2SAuCl (147.5 mg, 0.50 mmol) in dichloromethane (10 mL) were added PNP (223.5 mg, 0.50 mmol). The resulting solution was stirred for 30 min, then $AgBF_4$ (98.0 mg, 0.50 mmol) was added and stirred overnight. After filtration, the filtrate was collected, and the solvent was removed under reduced pressure to obtain crude product as a pale yellow solid. X-ray quality crystals were grown from dichloromethane at 4℃. Yield: 325.5 mg (89.1%, based on gold). Anal. Calcd for $C_{58}H_{46}B_2N_2F_8P_4Au_2 \cdot CH_2Cl_2$: C, 45.80; H, 3.13; N, 1.81. Found: C, 46.05; H, 3.22; N, 1.90. IR (KBr, cm^{-1}): υ1058 (br, B-F). ^1H NMR (400.1MHz, CD_3CN, ppm): δ7.94(t, 2H, py), 7.72-7.52(m, 40H, Ph), 7.27(d, 4H, py). ^{31}P NMR(162MHz, CD_3CN, ppm): δ44.90(s).

$[Au_9(PNC)_6](BF_4)_3$ (1): A solution of $[Au_2(PNP)_2](BF_4)_2$ (141.7 mg, 0.10 mmol) in dichloromethane (10mL) was added into a mixed solution of potassium hydroxide (15.0 mg, 0.27 mmol) and sodium tetrafluoborate (110.5 mg, 1.00 mmol) in methanol (50 mL), and the mixture was stirred and refluxed for 24 h. The suspension was then evaporated to dryness under reduced pressure to give a green solid, which was extracted with dichloromethane (30 mL × 3). The extract was collected and filtered. Evaporate the collection to dryness under reduced pressure to afford a yellow-green crude solid. Green block-like crystals were obtained by slow evaporation of a dichloromethane solution of the product after a week. Yield: 51.6 mg (64.4 %, based on gold). Anal. Calcd for $C_{102}H_{78}B_3N_6F_{12}P_6Au_9$: C, 33.97; H, 2.18; N, 2.33. Found: C, 33.84; H, 2.12; N, 2.25. IR (KBr, cm^{-1}): υ1062 (br, B-F). ^1H NMR (400.1 MHz, CD_2Cl_2, ppm): δ7.78-7.47 (m, 60H, Ph), 7.43 (d, 6H, py), 7.08 (t, 6H, py), 6.44 (d, 6H, py). ^{31}P NMR (162 MHz, CD_2Cl_2, ppm): δ36.85(s). Lifetime: $\tau = 21.75 \pm 1.24$ μs in the solid state; $\tau1 = 3.4$ ns (5.3%), $\tau2 = 297$ ns (94.7%) in CH_2Cl_2. Quantum yield in CH_2Cl_2: 21.0%.

$[Au_{11}(PNC)_6(PPh_3)_2](BF_4)_5$ (2): To a solution of **1** (24.0mg, 0.0067mmol) in 5mL dichloromethane and 1 mL methanol was added freshly prepared Ph_3PAuBF_4 (11.0mg, 0.02mmol) and stirred for 5 min. The resulting solution was filtered and layered with 5mL Et_2O. After ca. 2 days, orange-red block-like crystals were obtained. Yield: 29.6mg (94.6 %, based on **1**). Anal. Calcd for $C_{138}H_{108}B_5N_6F_{20}P_8Au_{11}\cdot 1.5CH_2Cl_2$: C, 34.72; H, 2.32; N, 1.74. Found: C, 33.88; H, 2.39; N, 1.85. IR (KBr, cm^{-1}): υ1084 (br, B-F). ^1H NMR (400.1 MHz, CD_2Cl_2, ppm): δ7.73-7.40 (m, 96H, Ph+py), 7.08 (t, 6H, py), 6.38 (d, 6H, py). ^{31}P NMR(162MHz, CD_2Cl_2, ppm): δ36.81(s, 6P, PNC), 37.85(s, 2P, PPh_3). Lifetime: $\tau = 3.37 \pm 0.21$ μs in the solid state; $\tau = 31.73 \pm 1.48$ μs in CH_2Cl_2. Quantum yield in CH_2Cl_2: 48.0%.

III. Characterization

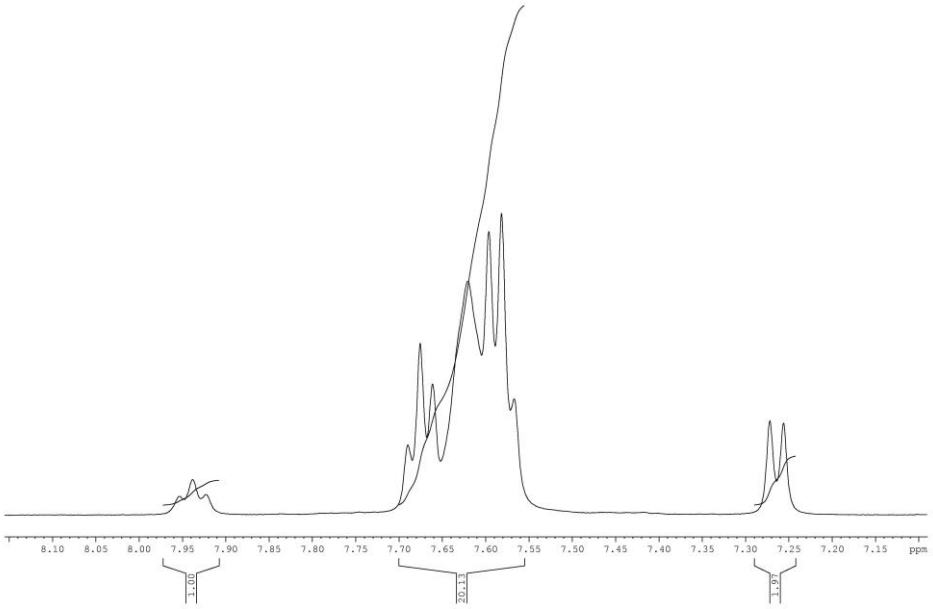

Figure S1. ^{1}H NMR spectrum of $[Au_2(PNP)_2](BF_4)_2$ in CD_3CN

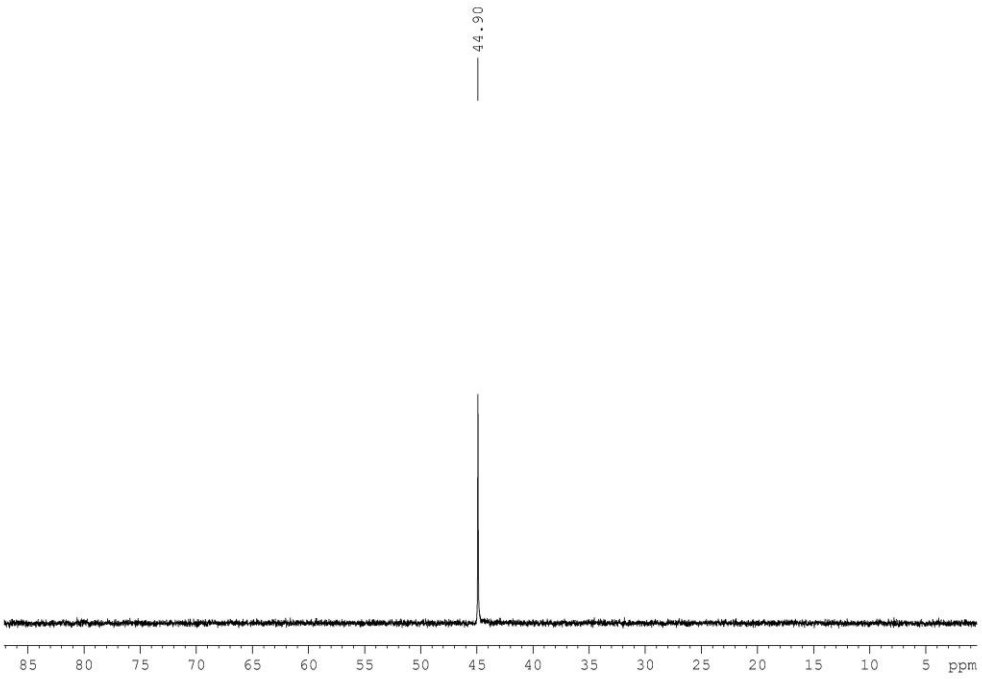

Figure S2. ^{31}P NMR spectrum of $[Au_2(PNP)_2](BF_4)_2$ in CD_3CN

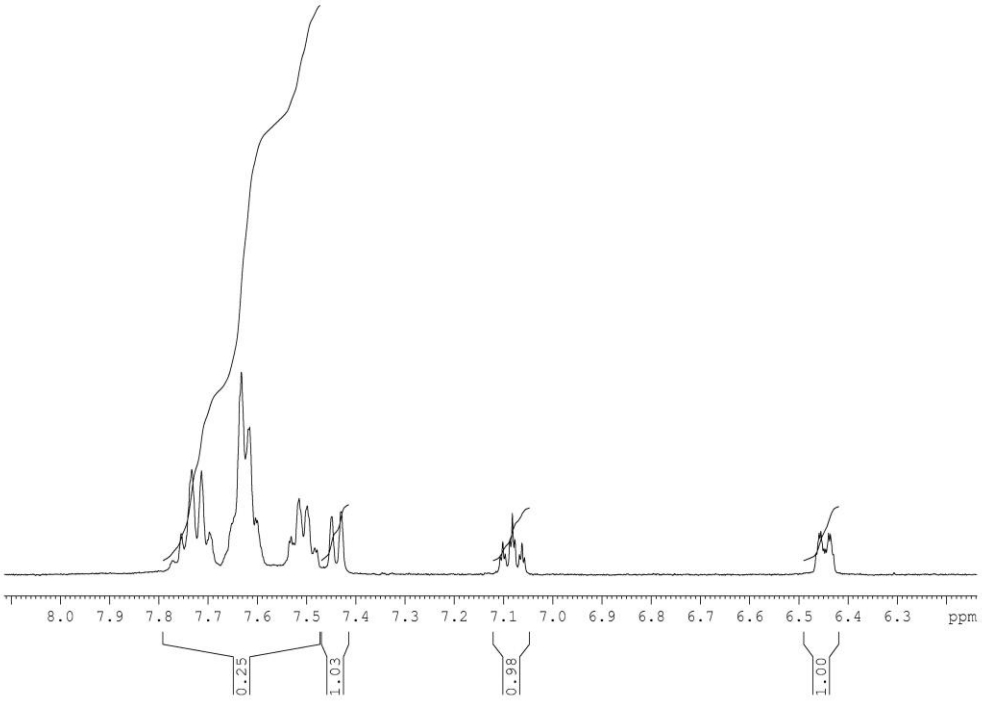

Figure S3. ^{1}H NMR spectrum of **1** in CD_2Cl_2

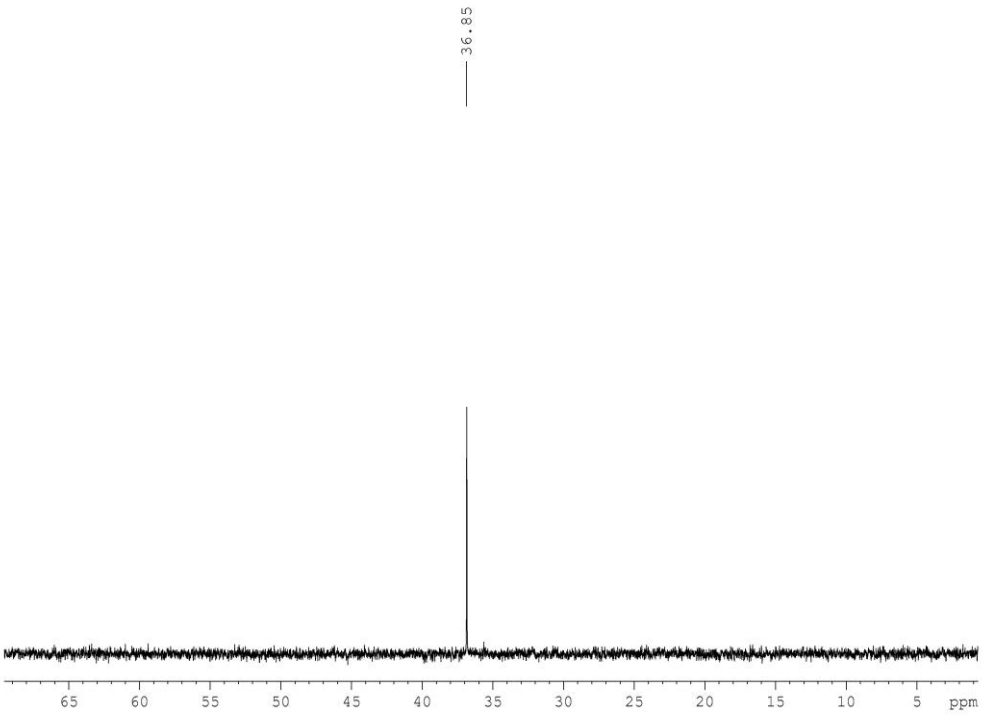

Figure S4. ^{31}P NMR spectrum of **1** in CD_2Cl_2

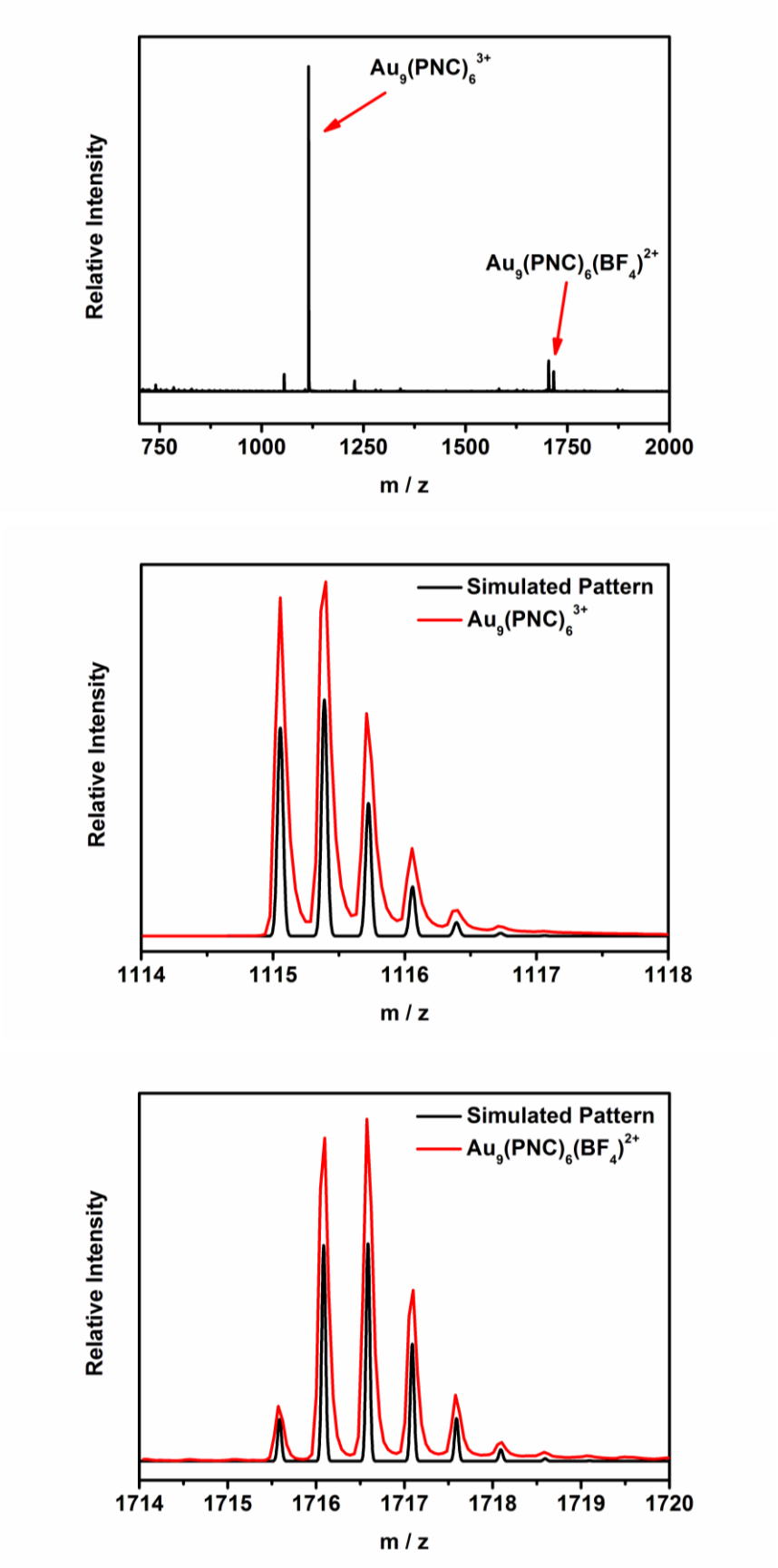

Figure S5. ESI-MS of **1**

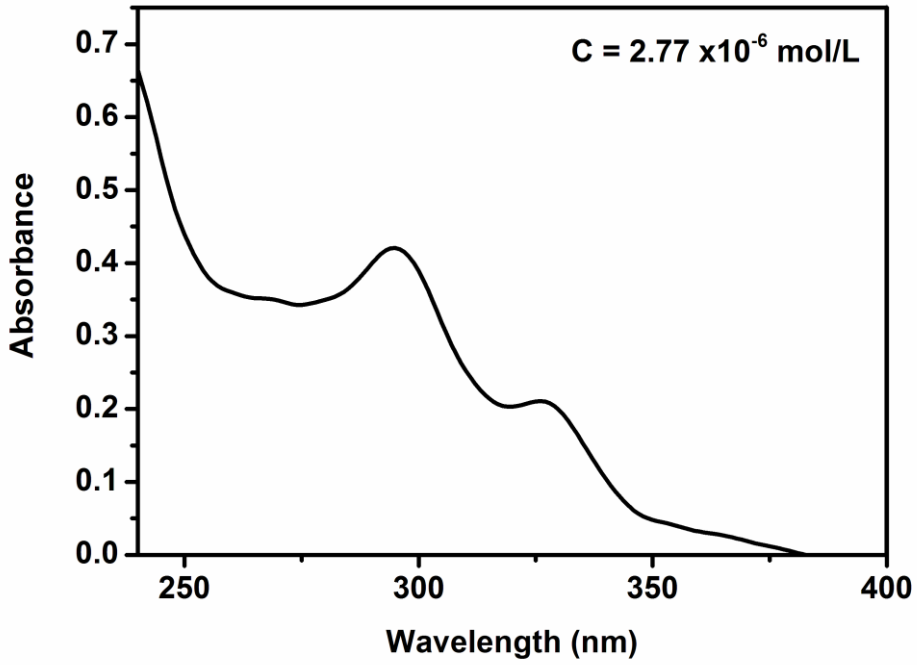

Figure S6. Electronic absorption spectrum of **1** in CH_2Cl_2

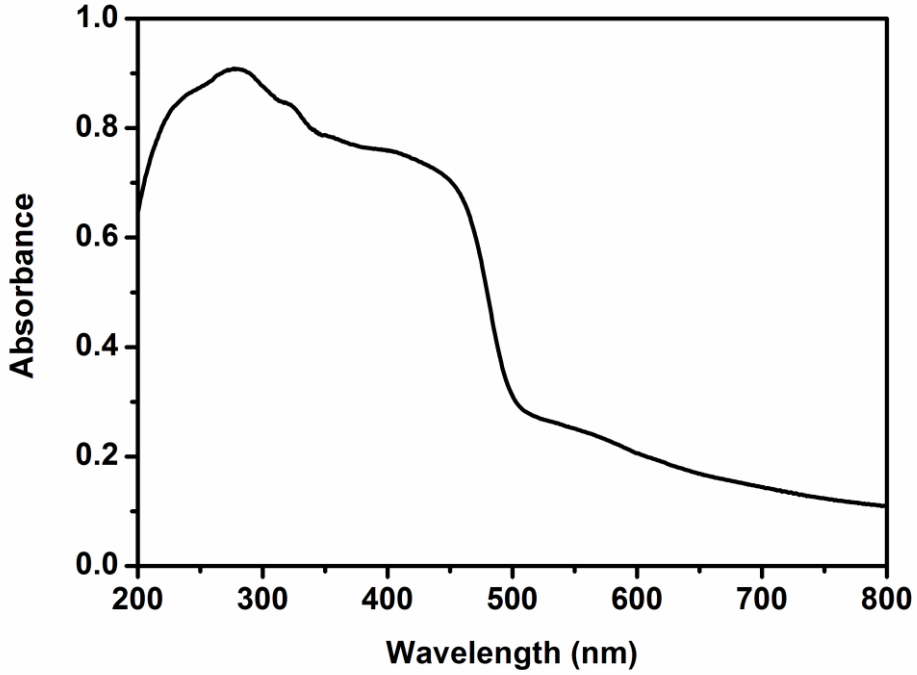

Figure S7. Reflectance UV-Vis spectrum of solid **1**

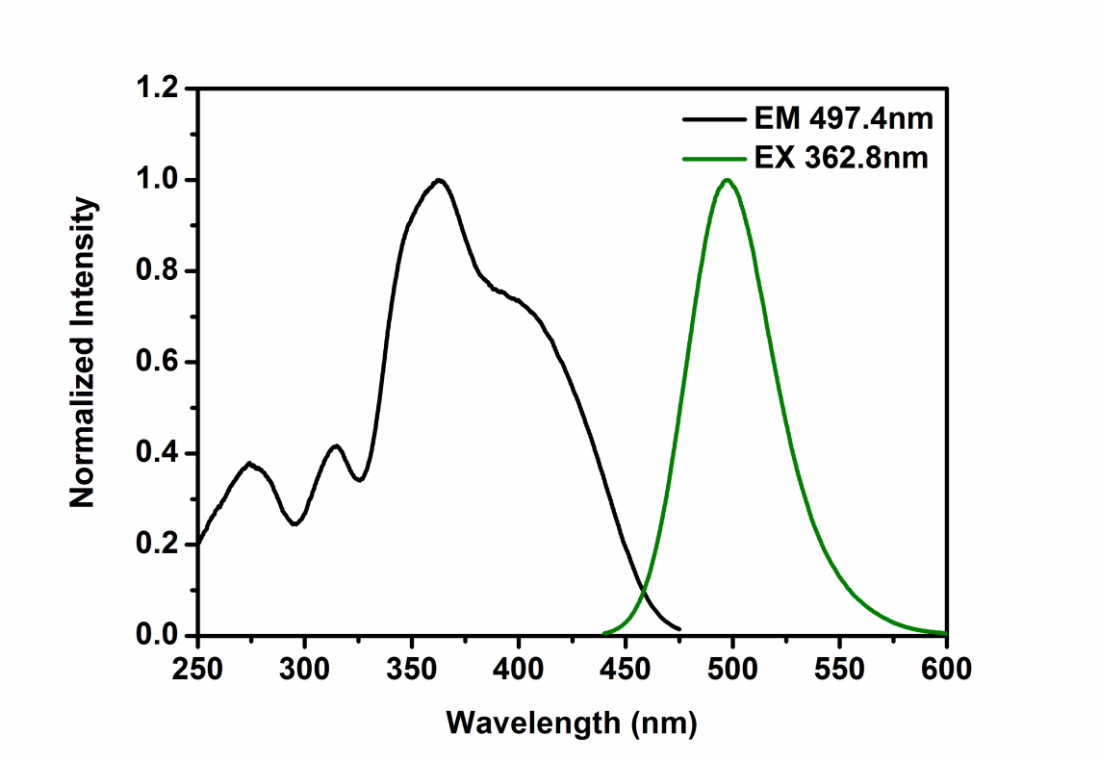

Figure S8. Excitation and emission spectra of **1** in CH_2Cl_2

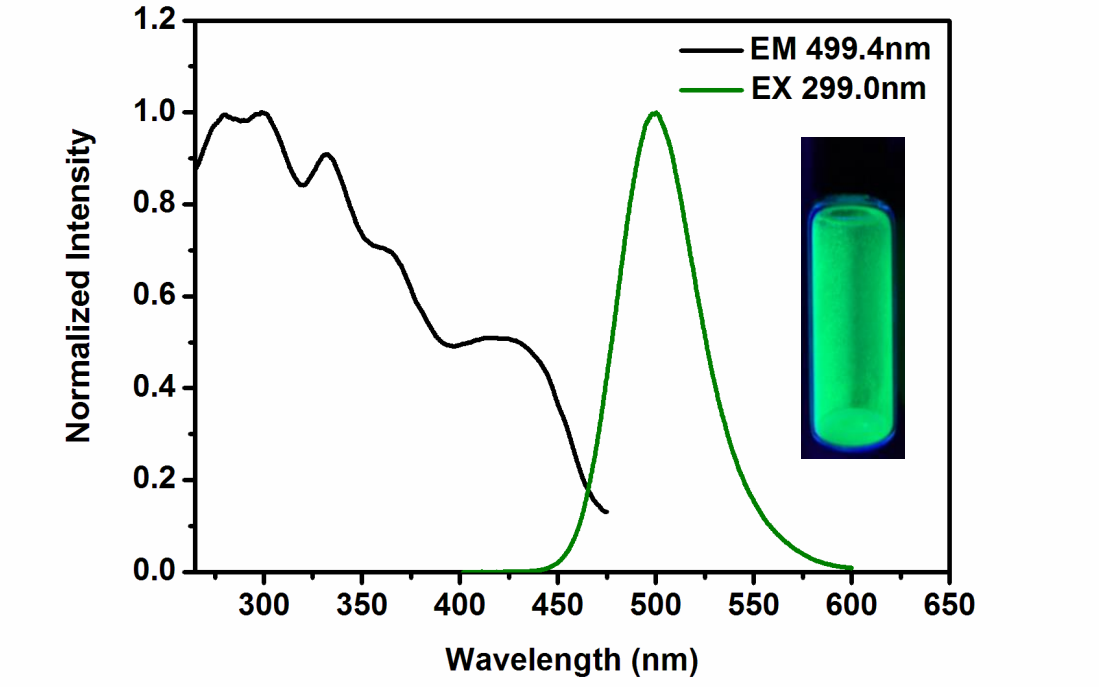

Figure S9. Excitation and emission spectra of **1** in the solid state. Inset: photo of luminescence of **1** in the solid state.

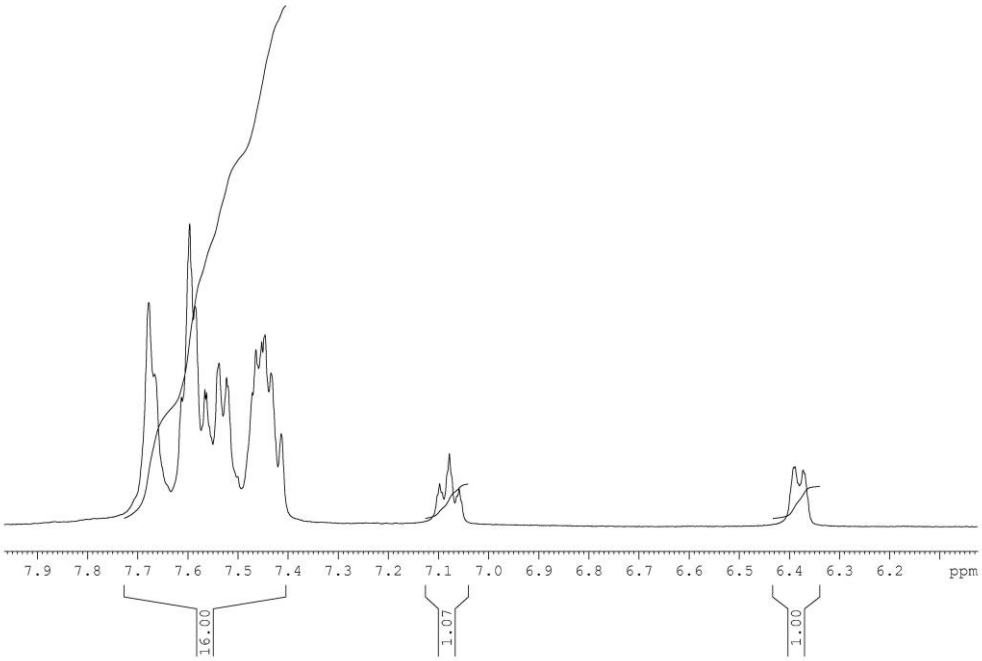

Figure S10. ^{1}H NMR spectrum of **2** in CD_2Cl_2

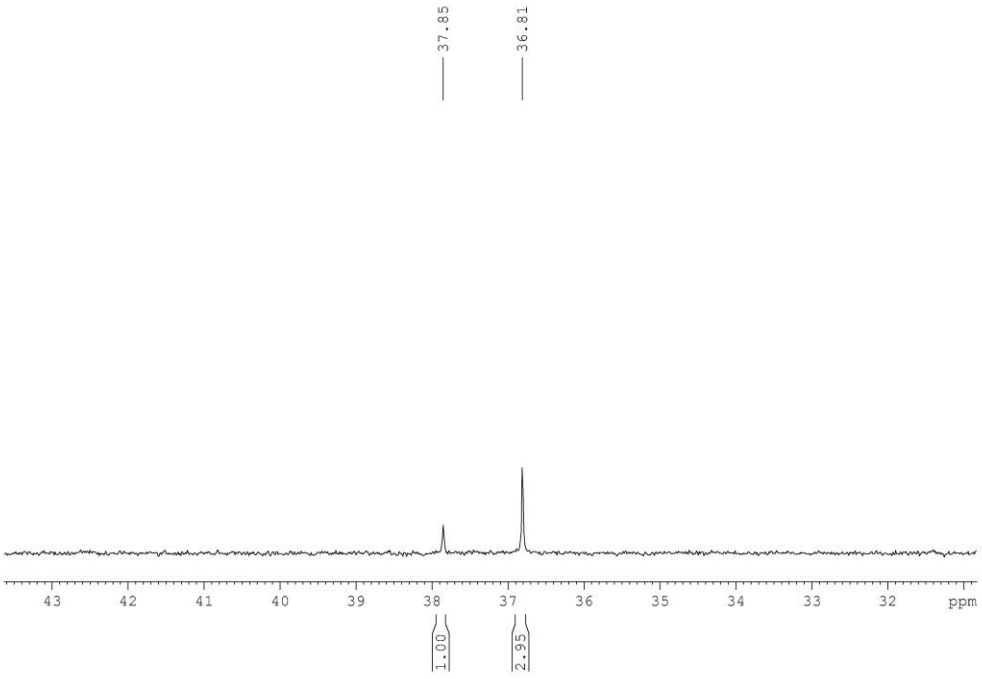

Figure S11. ^{31}P NMR spectrum of **2** in CD_2Cl_2

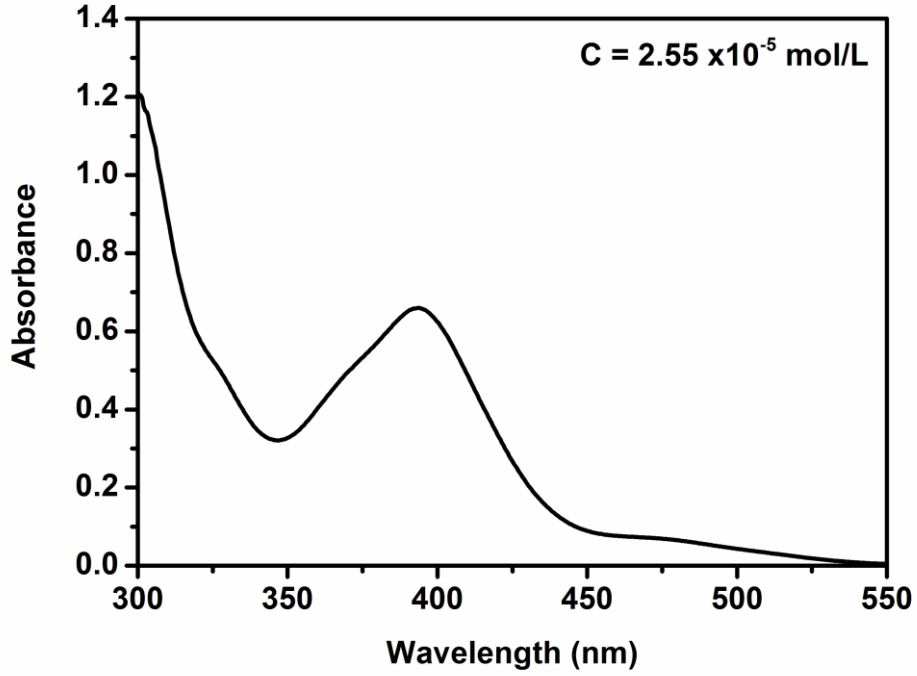

Figure S12. Electronic absorption spectrum of **2** in CH_2Cl_2

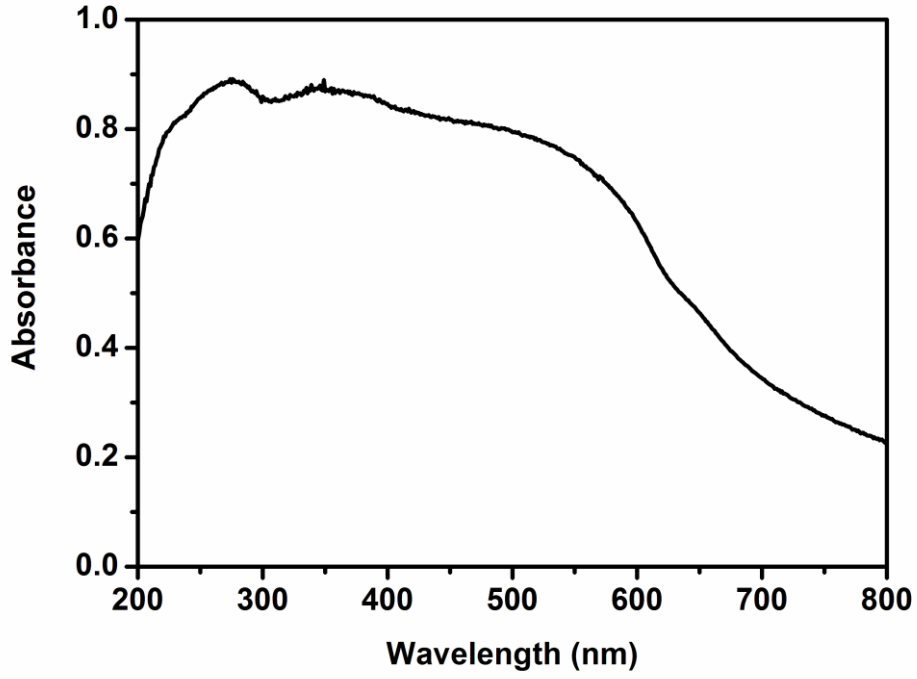

Figure S13. Reflectance UV-Vis spectrum of solid **2**

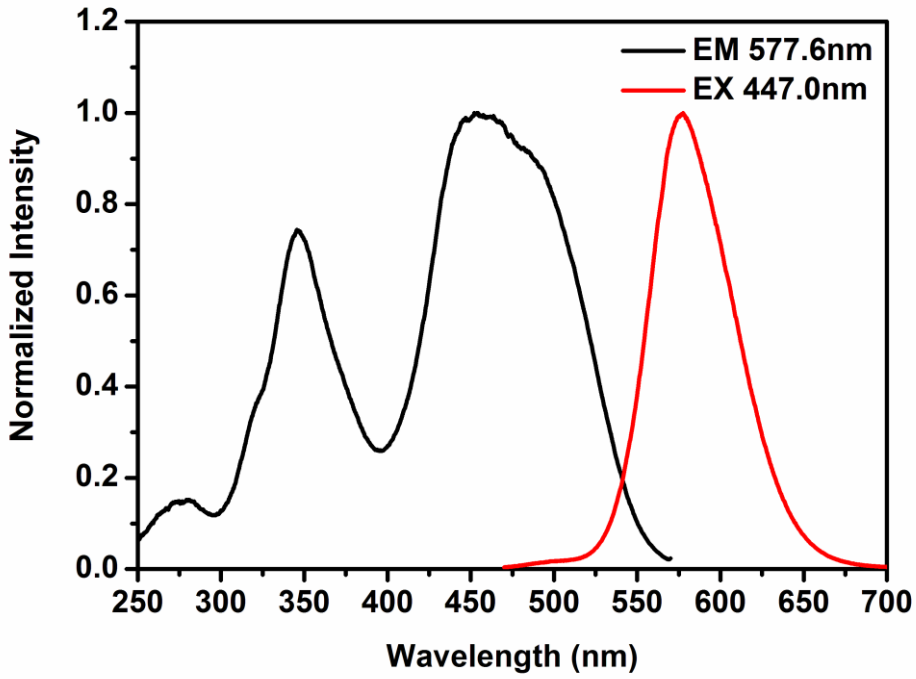

Figure S14. Excitation and emission spectra of **2** in CH_2Cl_2

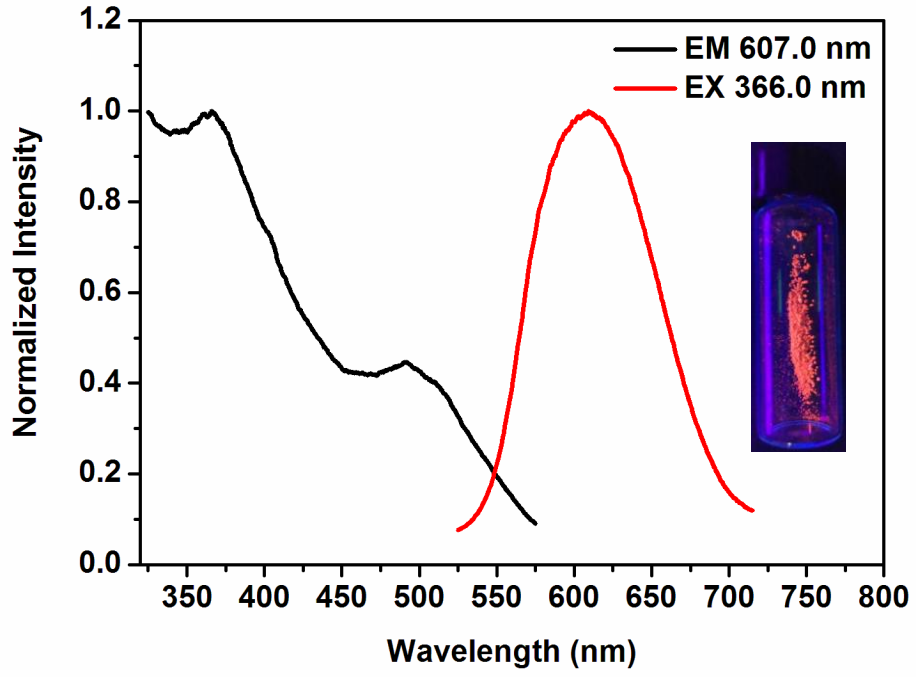

Figure S15. Excitation and emission spectra of **2** in the solid state. Inset: photo of luminescence of **2** in the solid state.

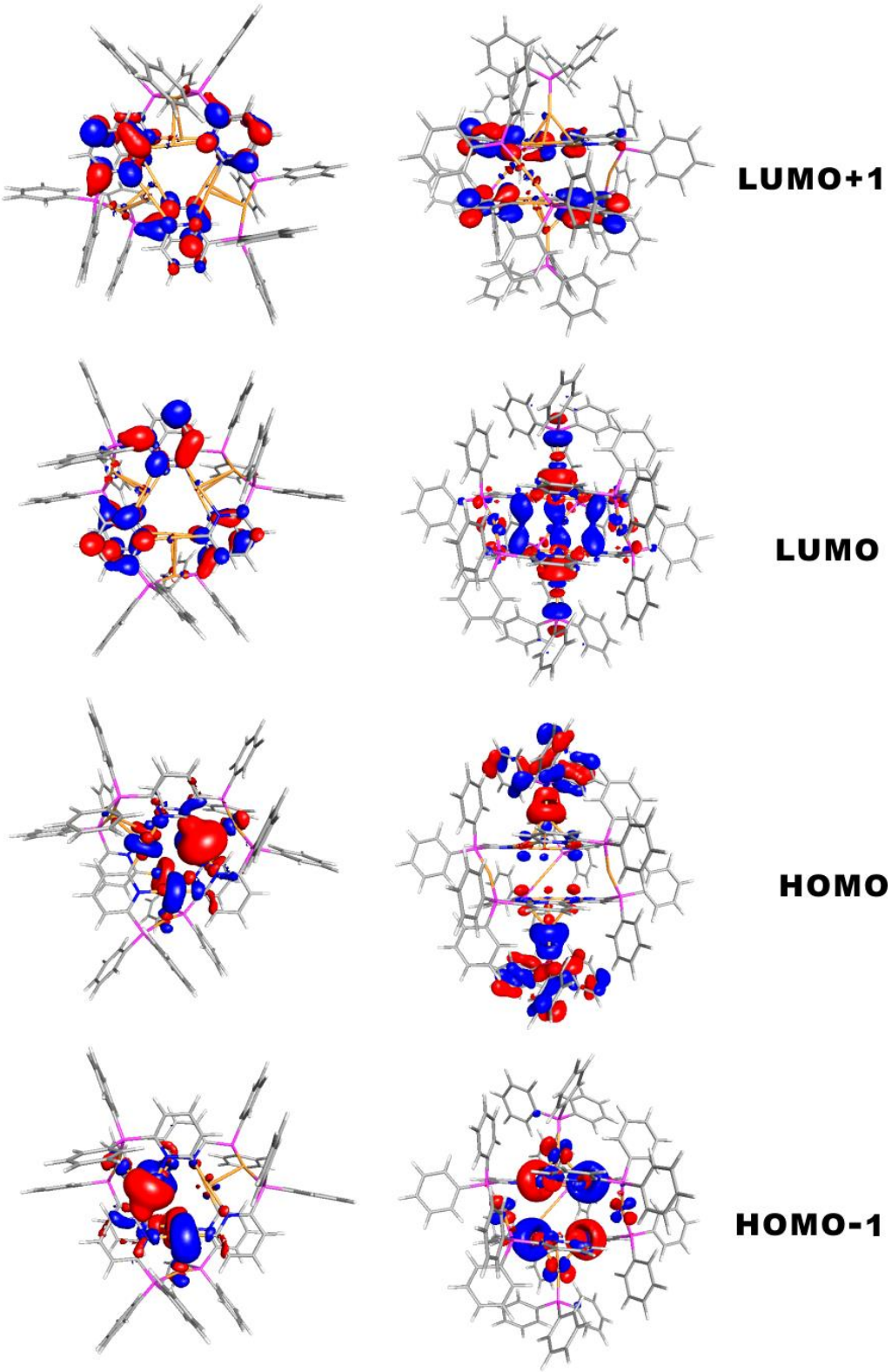

Figure S16. Frontier orbitals of cluster **1** (left) and **2** (right)

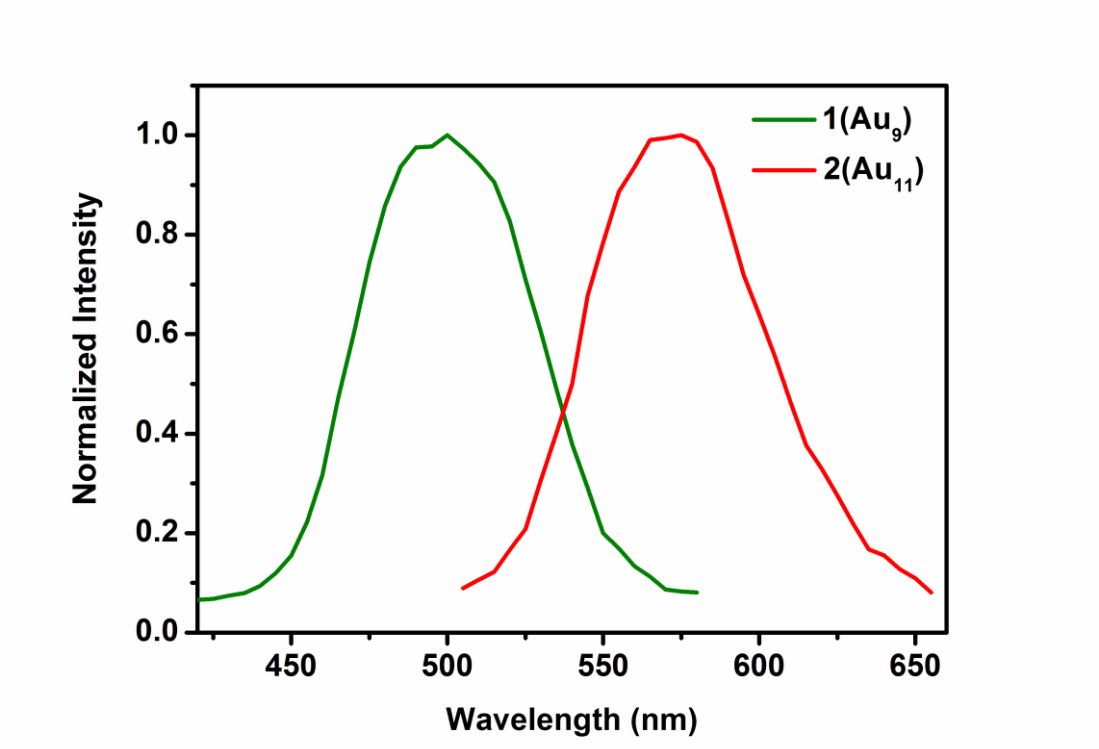

Figure S17. Luminescence spectra of **1** and **2**-incubated live HeLa cells measured by confocal luminescence microscopy (λ_{ex} = 405 nm for **1** and 488 nm for **2**)

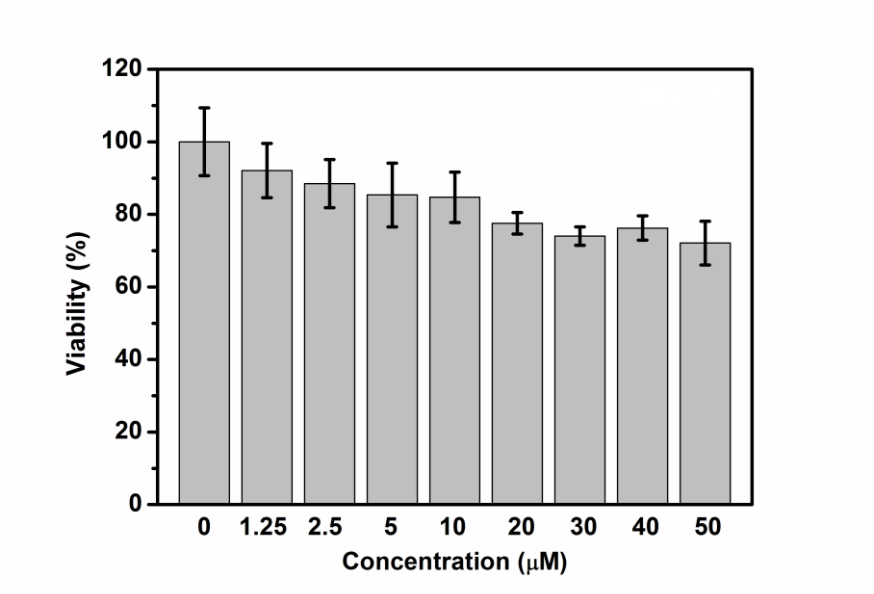

Figure S18. In vitro cytotoxicity of **1** by MTT assay. HeLa cells were cultured in the presence of 0-50 μM of **1** at 37 ℃ for 24h.

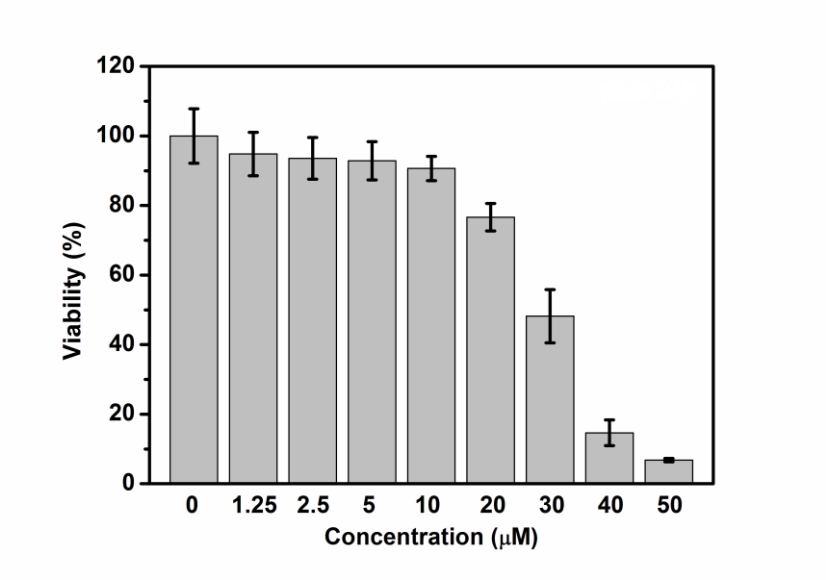

Figure S19. In vitro cytotoxicity of **2** by MTT assay. HeLa cells were cultured in the presence of 0-50 μM of **2** at 37 ℃ for 24h.

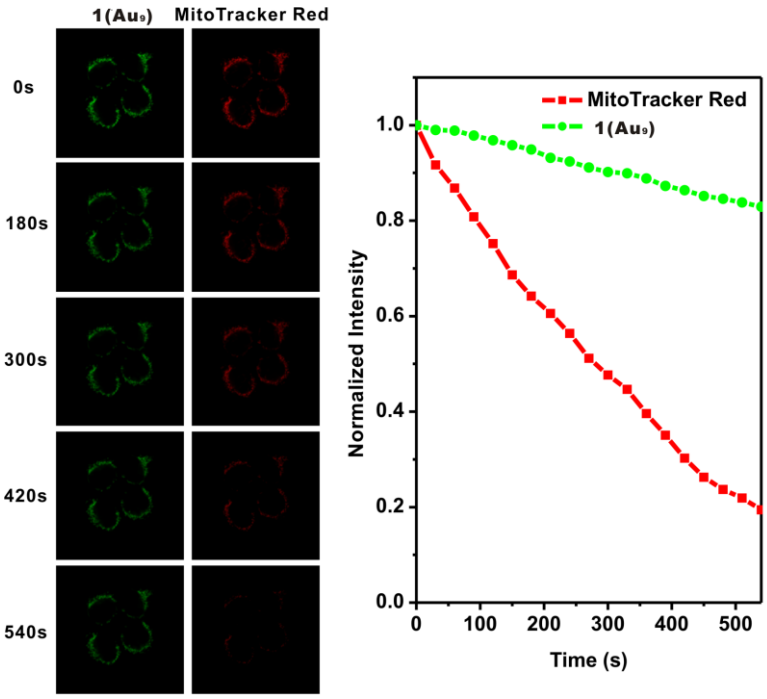

Figure S20. Comparison of **1** and MitoTracker Red for resistance to photobleaching. (a) Confocal luminescence images of HeLa cells stained with **1** and MitoTracker Red under continuous excitation. (b) luminescence decay curves of **1** and MitoTracker Red during the same period. (Concentration: 10 μM for **1**, 100 nM for MitoTracker Red; λ_{ex} = 405 nm for **1**, 543 nm for MitoTracker Red; λ_{em} = 500 ± 20 nm for **1**, 600 ± 20 nm for MitoTracker Red)

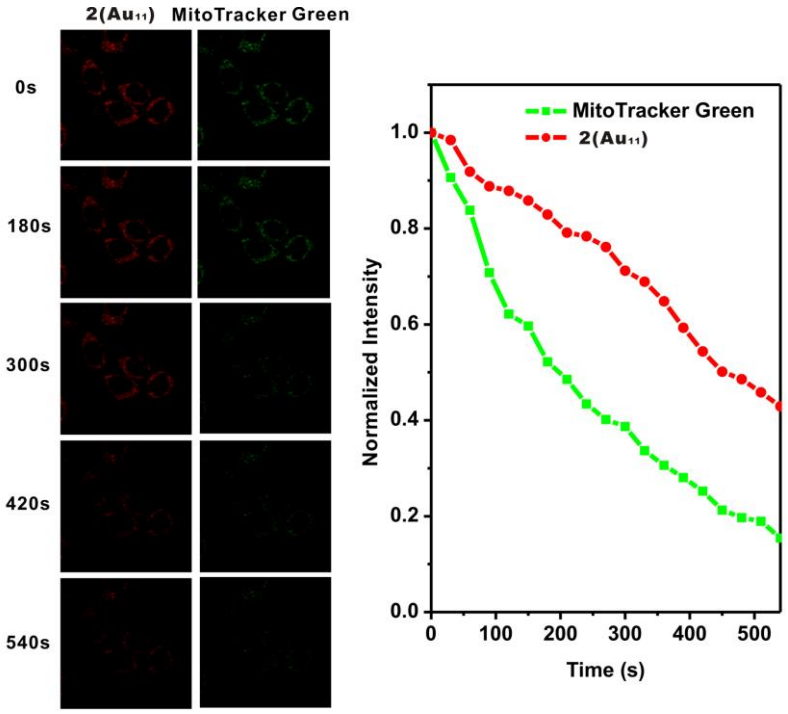

Figure S21. Comparison of **2** and MitoTracker Green for resistance to photobleaching. (a) Confocal luminescence images of HeLa cells stained with **2** and MitoTracker Green under continuous excitation. (b) luminescence decay curves of **2** and MitoTracker Green during the same period. (Concentration: 10 μM for **2**, 100 nM for MitoTracker Green; λ_{ex} = 488 nm for **2** and MitoTracker Green; λ_{em} = 580 ± 20 nm for **2**, 510 ± 15 nm for MitoTracker Green)

IV. Reference

(1) G. R. Newkome and D. C. Hagen, *J. Org. Chem.*, 1978, **43**, 947.

(2) F. Furche and R. Ahlrichs, *J. Chem. Phys.*, 2002, **117**, 7433-7447.

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