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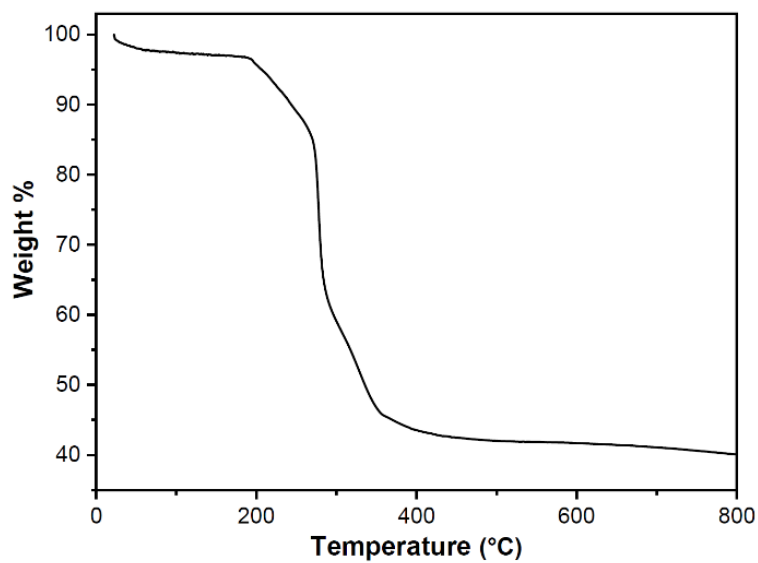


Figure S1. TGA curve of 1-0.5Et₂O-0.5CH₂Cl₂ from room temperature to 800 °C in a N₂ stream.

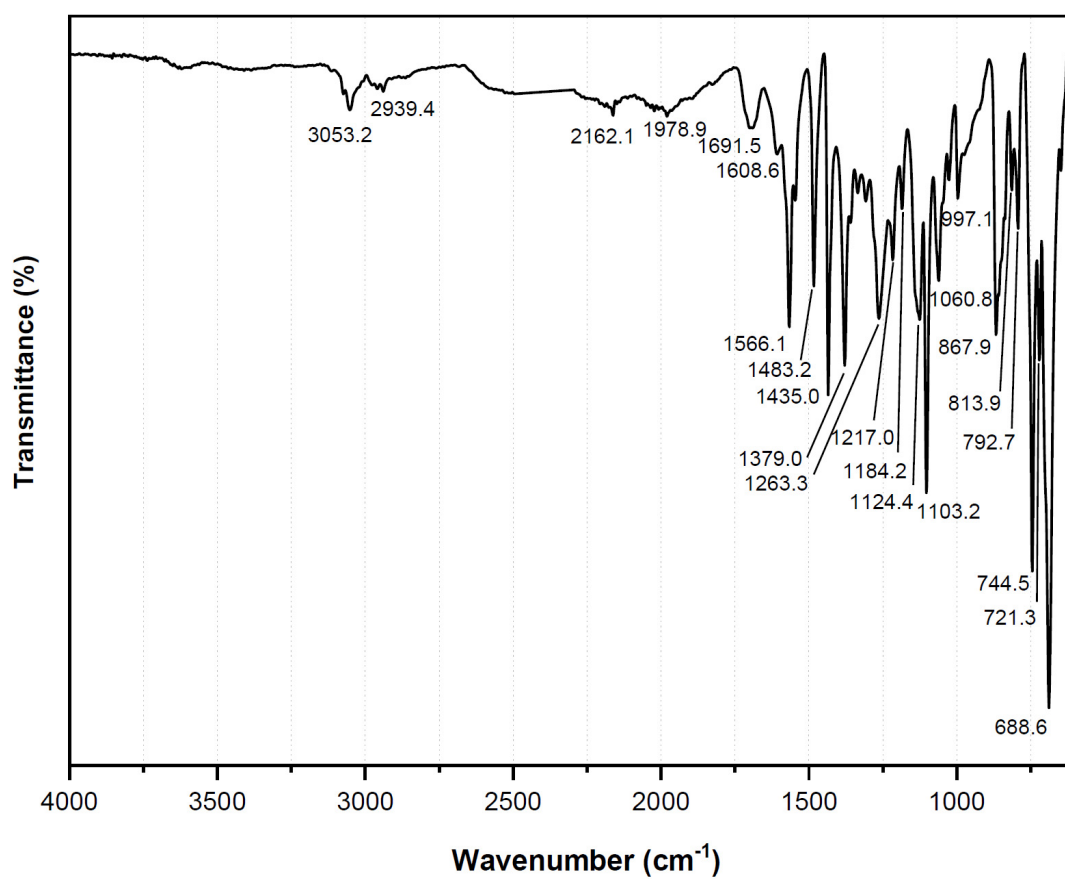


Figure S2. IR spectrum of compound 1.

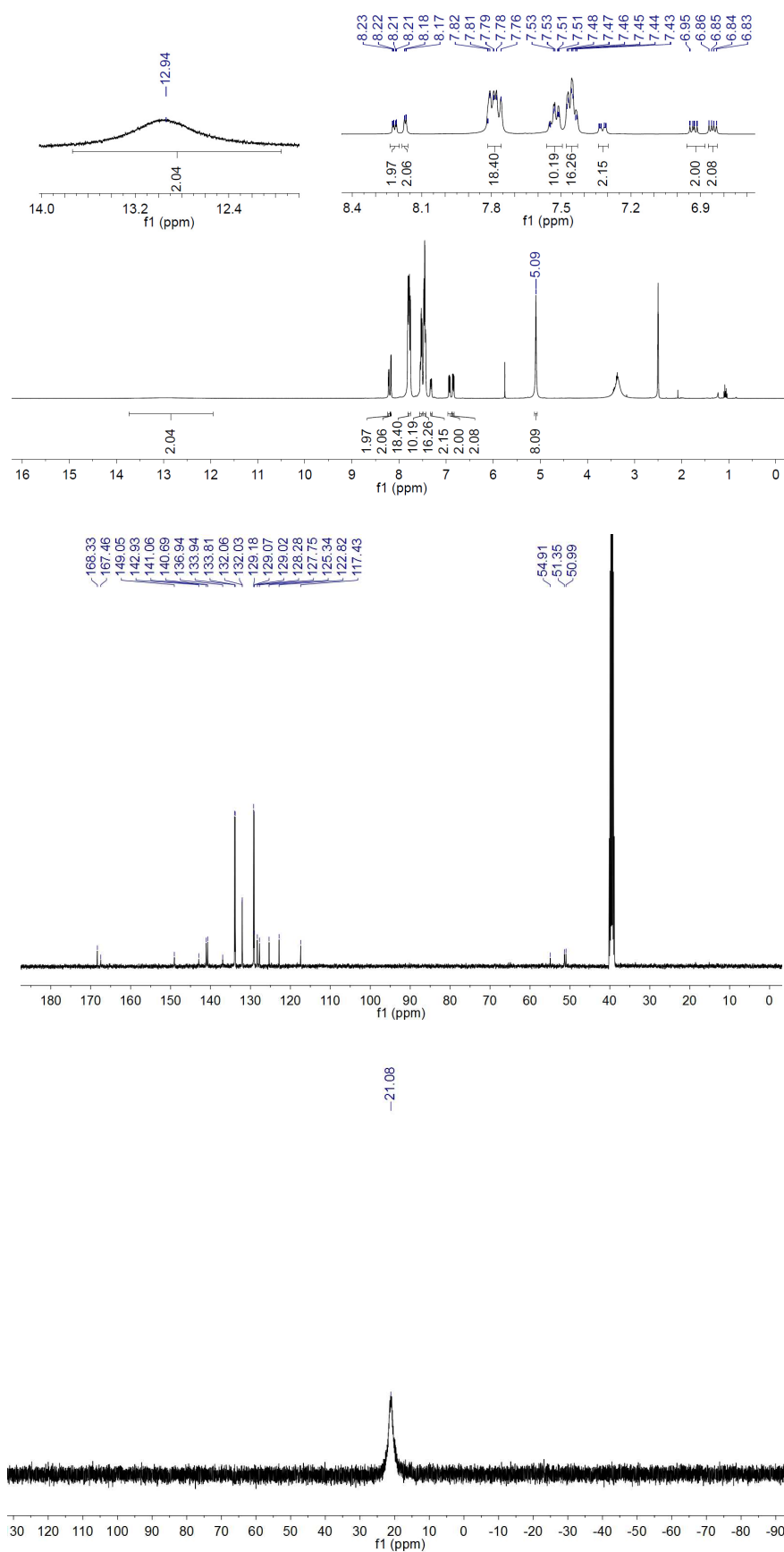


Figure S3. ¹H, ¹³C and ³¹P NMR spectra of **1** in DMSO-*d*₆.

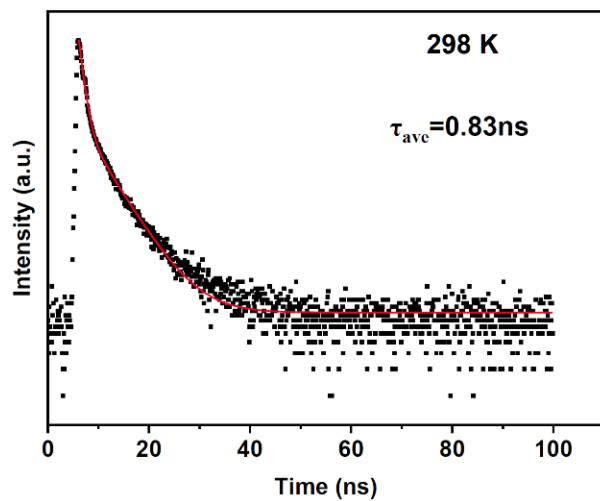


Figure S4. Transient photoluminescence data of **1** at 298 K (excited at 370 nm).

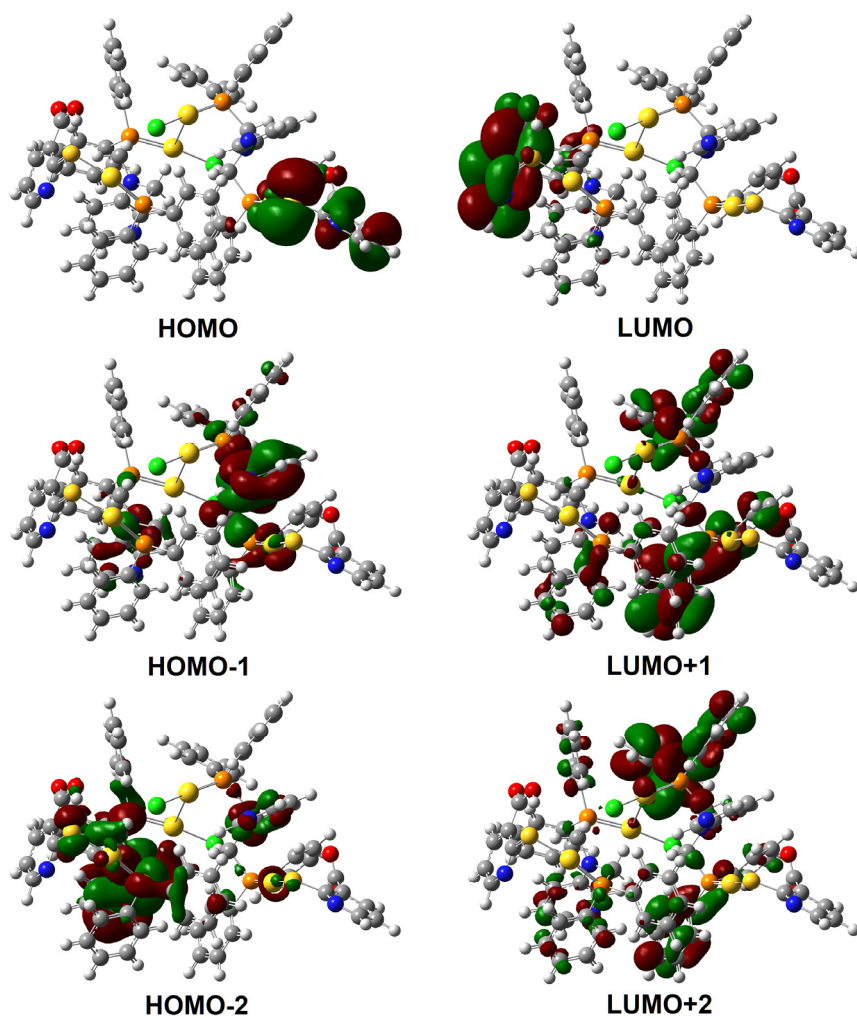


Figure S5. Orbital distributions of HOMOs and LUMOs (isovalue = 0.02) in **1**.

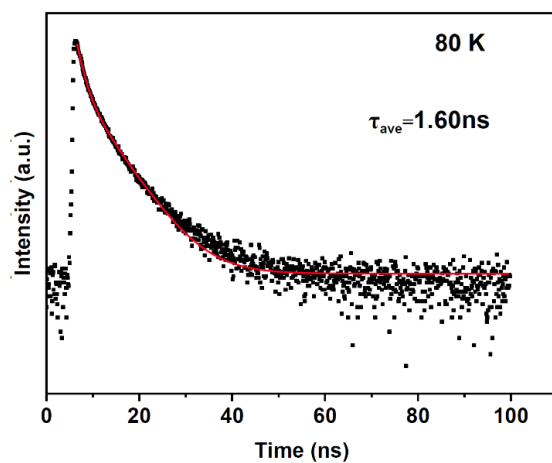


Figure S6. Transient photoluminescence data of **1** at 80 K (excited at 370 nm).

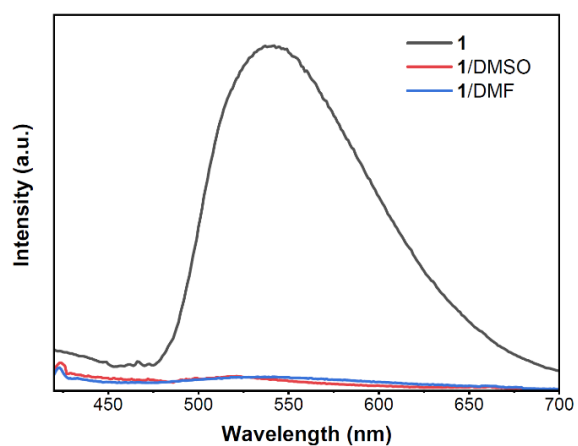


Figure S7. Emission spectra of **1** and the DMSO and DMF solutions of **1** (1 mg/mL, Ex = 377 nm).

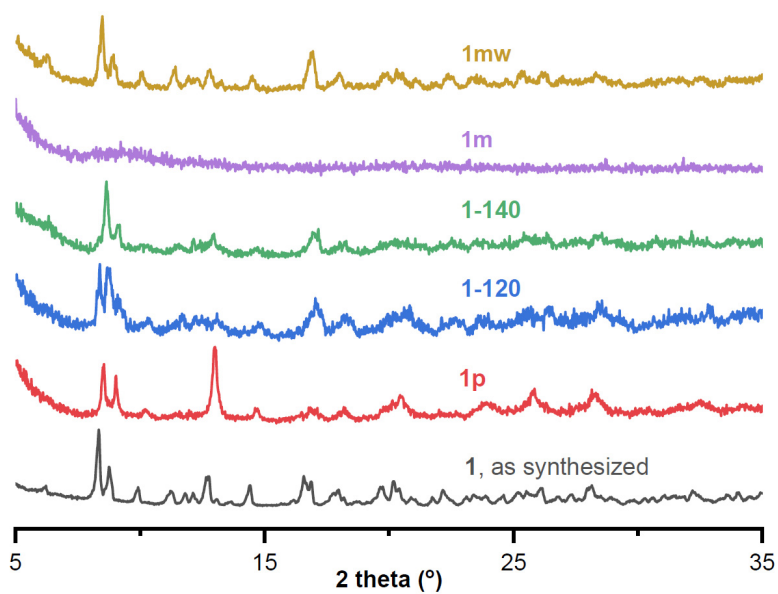


Figure S8. The PXRD patterns of as synthesized **1**, **1p**, **1** heated at 120 °C (**1-120**) and 140 °C (**1-140**), **1m** and **1mw**.

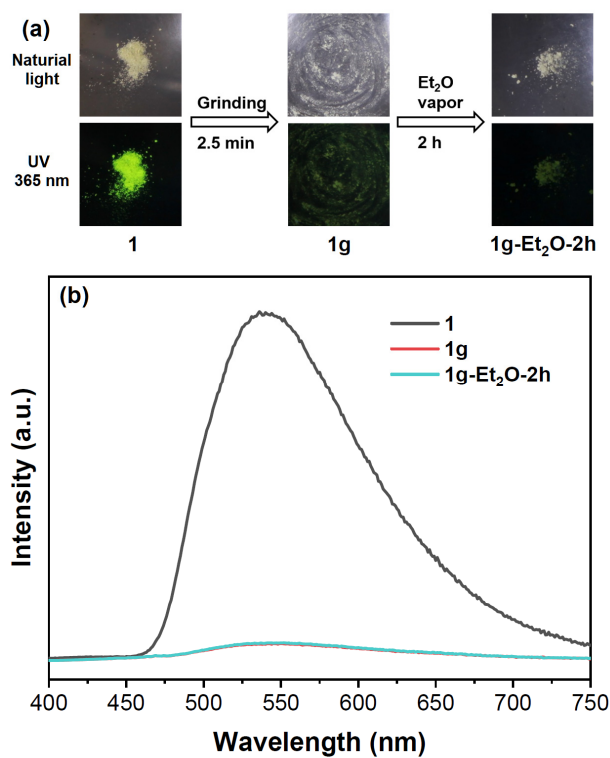


Figure S9. (a) Photographs of **1**, **1g** and **1g** in Et₂O vapor for 2h under natural light (upper) and under 365 nm UV light (lower), and (b) their emission spectra (Ex = 377 nm).

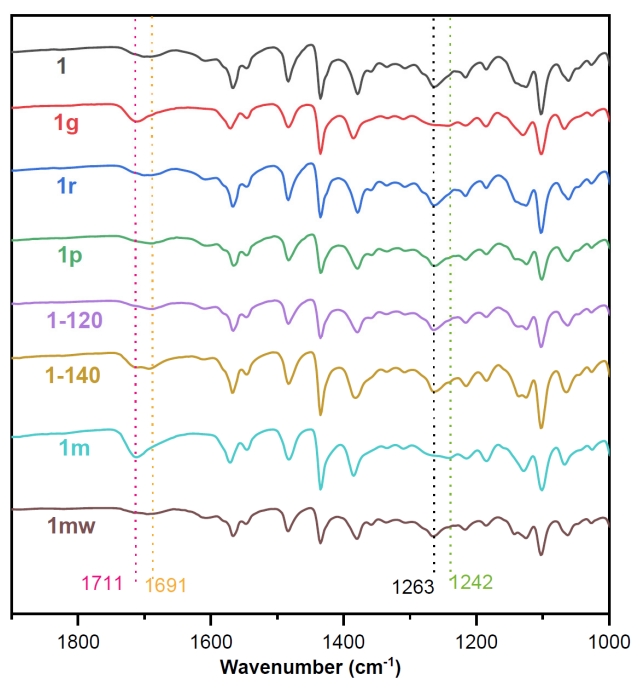


Figure S10. Comparison on the IR spectra in the range of 1000–2000 cm⁻¹ of **1**, **1g**, **1r**, **1p**, **1** heated at 120 °C (**1-120**) and 140 °C (**1-140**), **1m** and **1mw**.

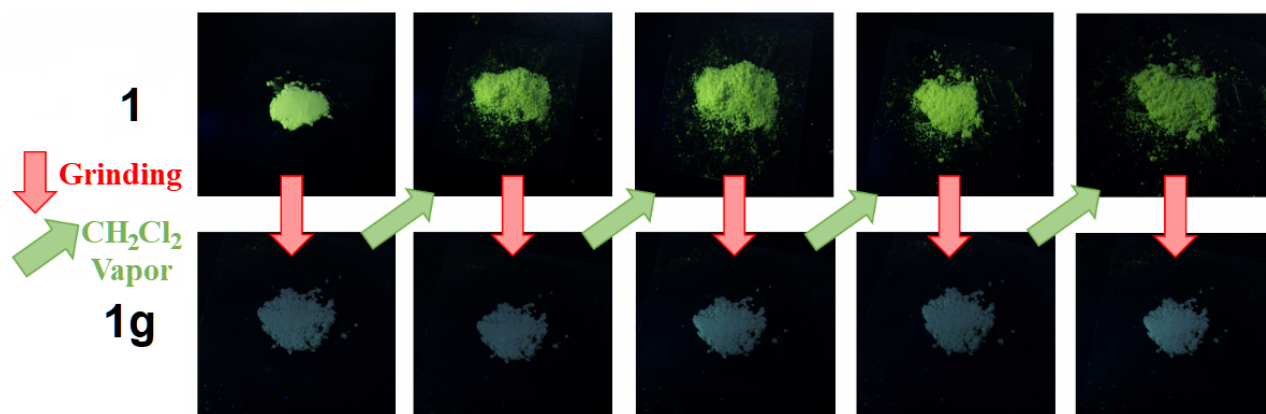


Figure S11. Photographs of **1** (upper) and **1g** (lower) under irradiation at 365 nm over five interconversion cycles. The red and green arrows indicate grinding and exposure to CH₂Cl₂ vapor, respectively.

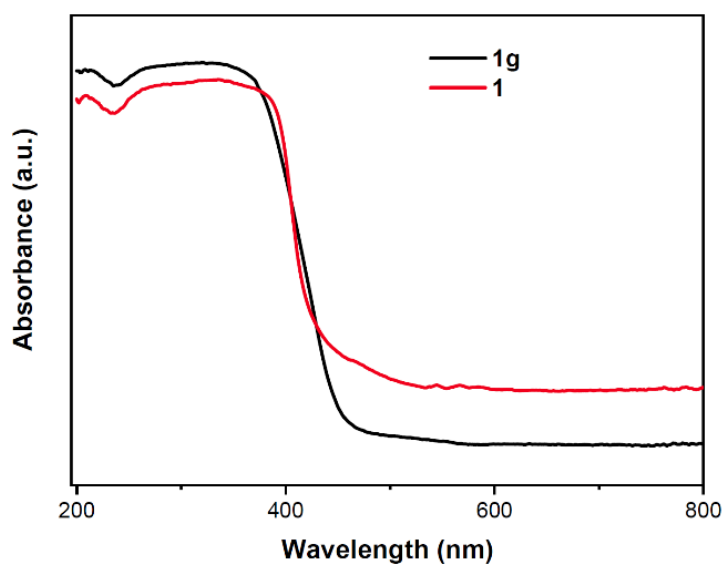


Figure S12. Solid-state UV-Vis spectra of **1** and **1g**.

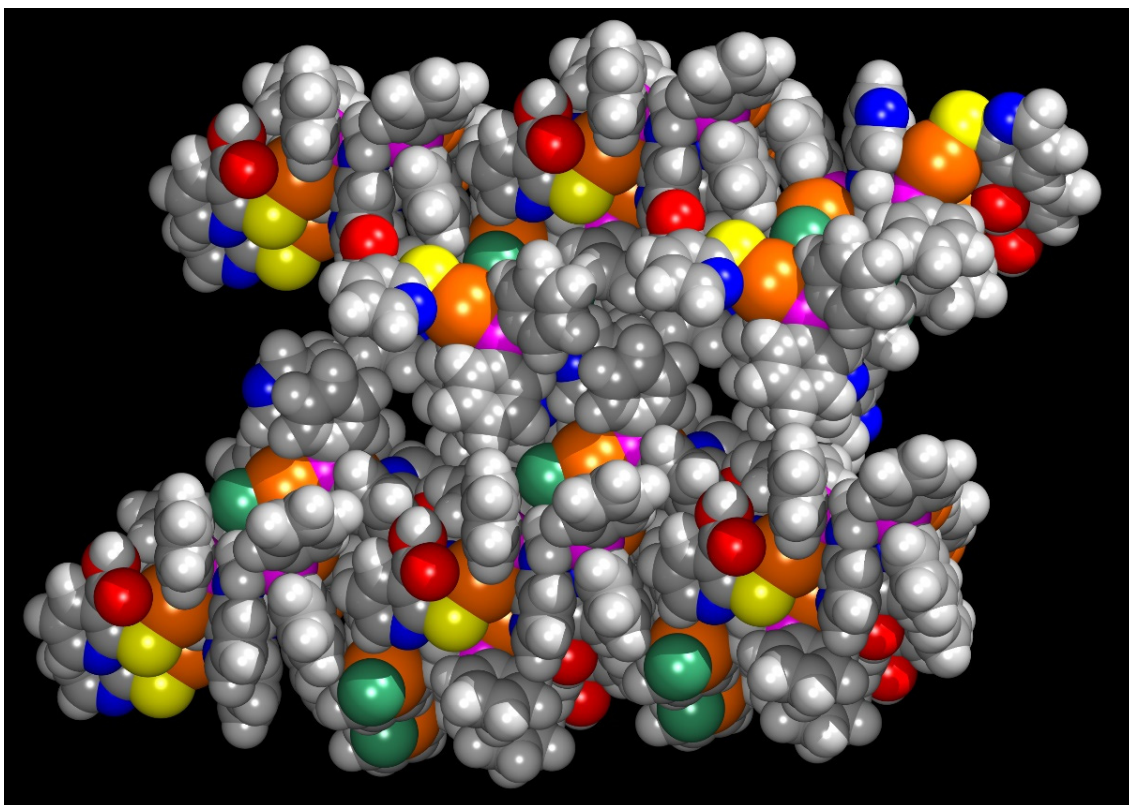


Figure S13. Plot representing the voids in the single crystal of $1 \cdot 0.5\text{Et}_2\text{O} \cdot 0.5\text{CH}_2\text{Cl}_2$ after removing all solvates.

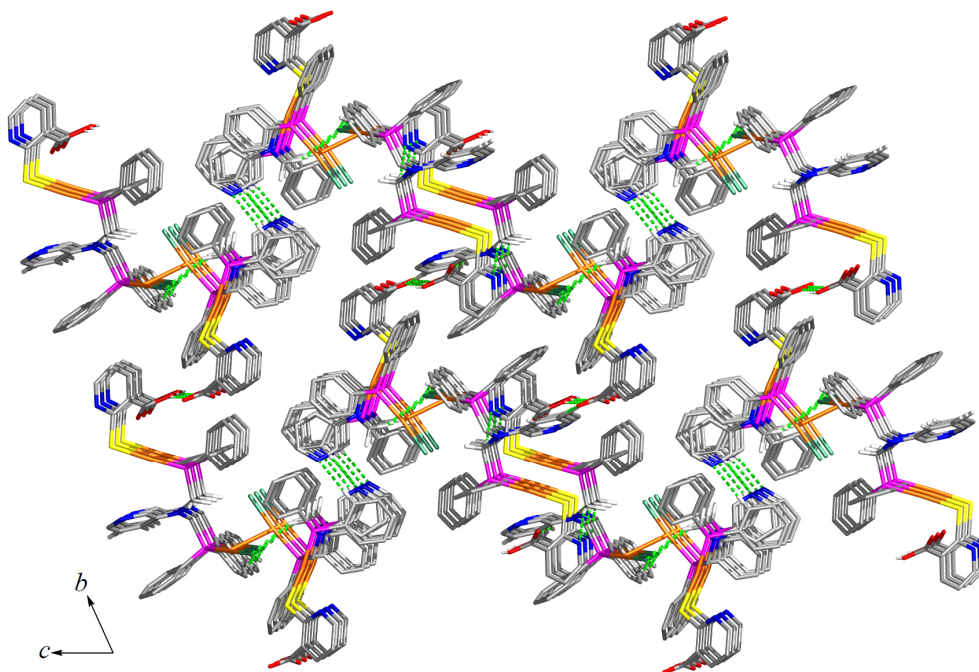


Figure S14. Packing of the main structure of **1** viewed along the a axis in the crystal structure of $1 \cdot 0.5\text{Et}_2\text{O} \cdot 0.5\text{CH}_2\text{Cl}_2$.

Hydrogen bonds were plotted as green dash lines. Atom colours: Au, orange; S, yellow; P, purple; Cl, green; N, blue; O, red; C, dark gray; H, light gray.

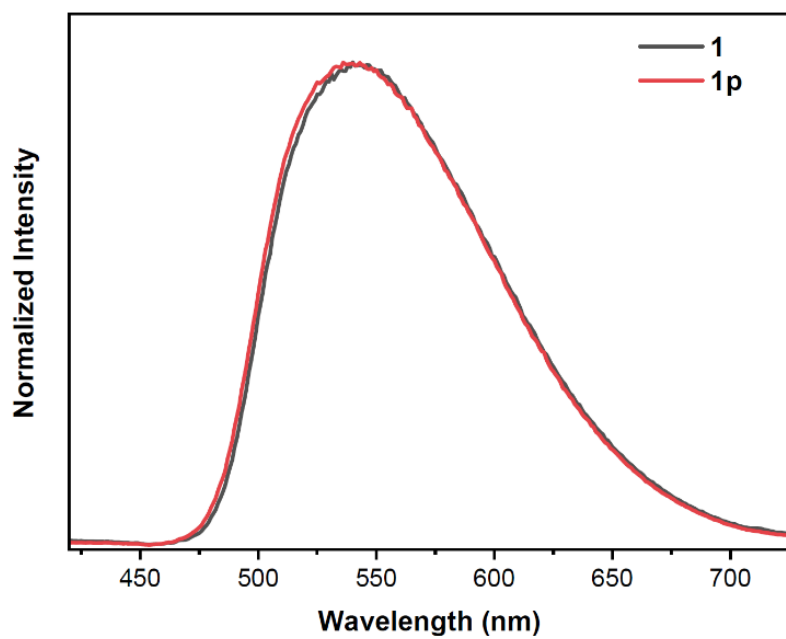


Figure S15. Emission spectra of **1** and **1p** (Ex = 377 nm).

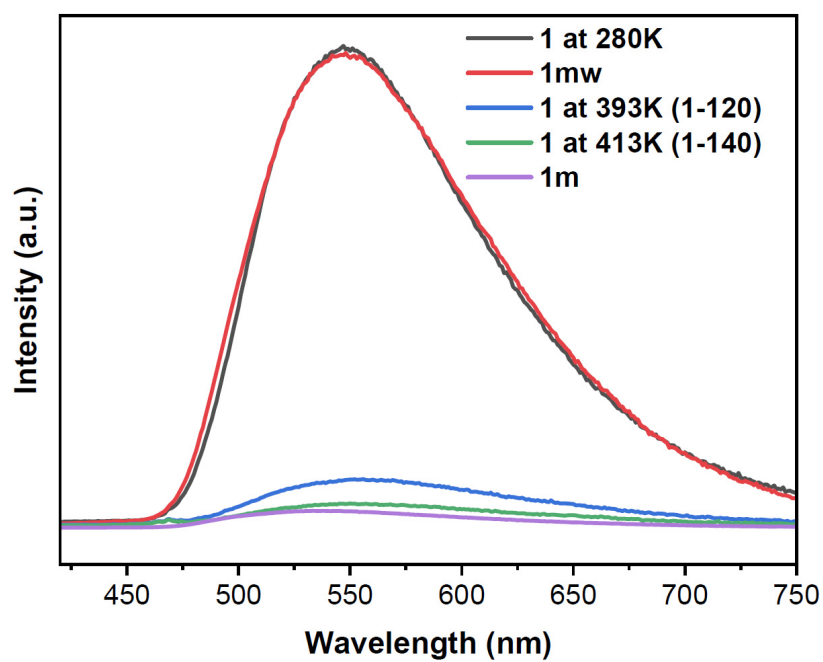


Figure S16. Emission spectra of **1m**, **1mw**, **1** at 280 K, at 393 K (120 °C, **1-120**) and at 413 K (140 °C, **1-140**) (Ex = 377 nm).

Table S1. Emission wavelength (λ_{max}), life time (τ) and quantum yield (QY) of some Au–P complexes in literature.

Formula	λ_{max} (nm)	τ	QY (%)	Ref.
Au(PPh ₃) ₂ Cl	560	19 μ s	N/A	6
Au(PPh ₃) ₂ Br	540	12 μ s	N/A	
(PhCl) ₃ PAuI monoer	472	3.7 ms	4.9	7
(PhCl) ₃ PAuI dimer	543	0.36 ms	70.5	
[Au ₃ (PPh ₂ CH ₂ PPhCH ₂ PPh ₂) ₂](PF ₆) ₃	460	2.4 μ s	64	8
[Au ₁₀ { μ ₃ -Ph ₂ PN(CH ₂ - <i>o</i> -C ₅ H ₄ N)PPh ₂ } ₄ (μ ₃ -S) ₄](PF ₆) ₂	495	μ s regime	26	13
Au ₄ Cu ₂ (decz) ₂ (POP) ₂	565	14.5 μ s	50.2	18
[Au ₂ (nixantphos) ₂](CF ₃ COO) ₂	596	0.3 μ s	N/A	27
Au(XantPhos)Cl	520	19.7 μ s	81	34
[Au(dppb) ₂]Cl	478	3.6 μ s	86	37
[(AuCl)(3-bdppmapy)(AuCl) ₃ (3-bdppmapy)]	530	4.9 ns	1.8	38
{[(3-bdppmapy)(AuCl) ₂]} _n	525	4.1 ns	5	
[(3-bdppmapy) ₂ (AuHmba) ₃ (AuCl)]	522	2.58 ns	4.7	39
[Au ₂ Cu ₂ (3-dppmapz) ₂](PF ₆) ₂ ·4MeOH	560	94.8 μ s	80	42
[Au ₄ (dppmt) ₄ (AgCl) ₂] _n	495	0.78 μ s	22.3	43

Table S2. Selected crystallographic data and refinement parameters for 1·0.5Et₂O·0.5CH₂Cl₂.

Formula	C _{76.5} H ₇₀ Au ₄ Cl ₃ N ₆ O _{4.5} P ₄ S ₂
<i>F</i> _w	2227.60
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> / Å	11.0934(7)
<i>b</i> / Å	16.5890(10)
<i>c</i> / Å	22.8267(16)
α / deg	69.523(3)
β / deg	78.771(3)
γ / deg	74.460(3)
<i>V</i> / Å ³	3767.6(4)
<i>Z</i>	2
ρ_{calc} (g/cm ³)	1.964
μ (mm ⁻¹)	11.646
<i>F</i> (000)	2132
<i>R</i> ₁ ^a	0.0594
<i>wR</i> ^b	0.1417
<i>GOF</i> ^c	1.077

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, ^b $wR_2 = \{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}$. ^c $GOF = \{\sum w((F_o^2 - F_c^2)^2) / (n - p)\}^{1/2}$, where *n* = number of reflection and *p* = total number of parameters refined.

Table S3. Selected bond lengths (Å) and angels (°) in 1·0.5Et₂O·0.5CH₂Cl₂.

Au2–Au3	3.1312(6)
Au1–P1	2.254(2)
Au1–S1	2.305(3)
Au2–P2	2.225(2)
Au2–Cl1	2.286(2)
Au3–P3	2.234(2)
Au3–Cl2	2.300(2)
Au4–P3	2.252(2)
Au4–S2	2.299(2)
P1–Au1–S1	169.89(11)
P2–Au2–Cl1	173.47(9)
P2–Au2–Au3	102.64(6)
Cl1–Au2–Au3	82.25(6)
P3–Au3–Cl2	177.37(8)
P3–Au3–Au2	97.56(6)
Cl2–Au3–Au2	84.66(5)
P4–Au4–S2	175.41(9)