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Supporting Information

An AIE-active phosphorescent Ir(III) complex with piezochromic luminescence (PCL) and its application for monitoring volatile organic compounds (VOCs)

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1. Experimental - general information

Materials obtained from commercial suppliers were used without further purification unless otherwise stated. All glassware, syringes, magnetic stirring bars, and needles were thoroughly dried in a convection oven. Reactions were monitored using thin layer chromatography (TLC). Commercial TLC plates were used and the spots were visualised under UV light at 254 and 365 nm. ^{1}H NMR spectra were recorded at 25 ºC on a Varian 500 MHz spectrometer. The chemical shifts (δ) are given in parts per million relative to internal standard TMS. The ^{1}H NMR spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.24 ppm). Powder X-ray diffraction (XRD) patterns of the samples were collected on a Rigaku Dmax 2000. Differential scanning calorimetry (DSC) curves were obtained with a NETZSCH thermal analysis DSC200 F_3 under argon with a heating rate 10 °C min^{-1}. Transmission electron microscopy (TEM) and electron diffraction analyses of the samples were obtained using a TECNAI F20 microscope. The samples were prepared by placing microdrops of the solution on a holey carbon copper grid. UV-vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Photoluminescence spectra were collected on a Shimadzu RF-5301pc spectrophotometer and Maya 2000Pro optical fiber spectrophotometer. PL efficiencies were measured with an integrating sphere (C-701, Labsphere Inc.) with a 365 nm Ocean Optics LLS-LED as the excitation source, and the laser was introduced into the sphere through an optical fiber. The excited-state lifetimes were measured by exciting the samples with 385 nm light pulses with ~3 ns pulse width from a Quanty-Ray DCR-2 pulsed Nd: YAG laser. The X-ray crystal structure data of complex **1** were collected on a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at room temperature.

Warning signal manufacturing method

The warning signal adopted the shape of a ‘triangle’ comprising a central ‘exclamation mark’. A specific mould (filter paper with holes) was made for regulating the shape of as-prepared powder **G**. **G** was carefully spread within the hole and the filter paper removed so that the whole warning signal can be demonstrated.

2. ^{1}H NMR Spectra of 1 at room temperature

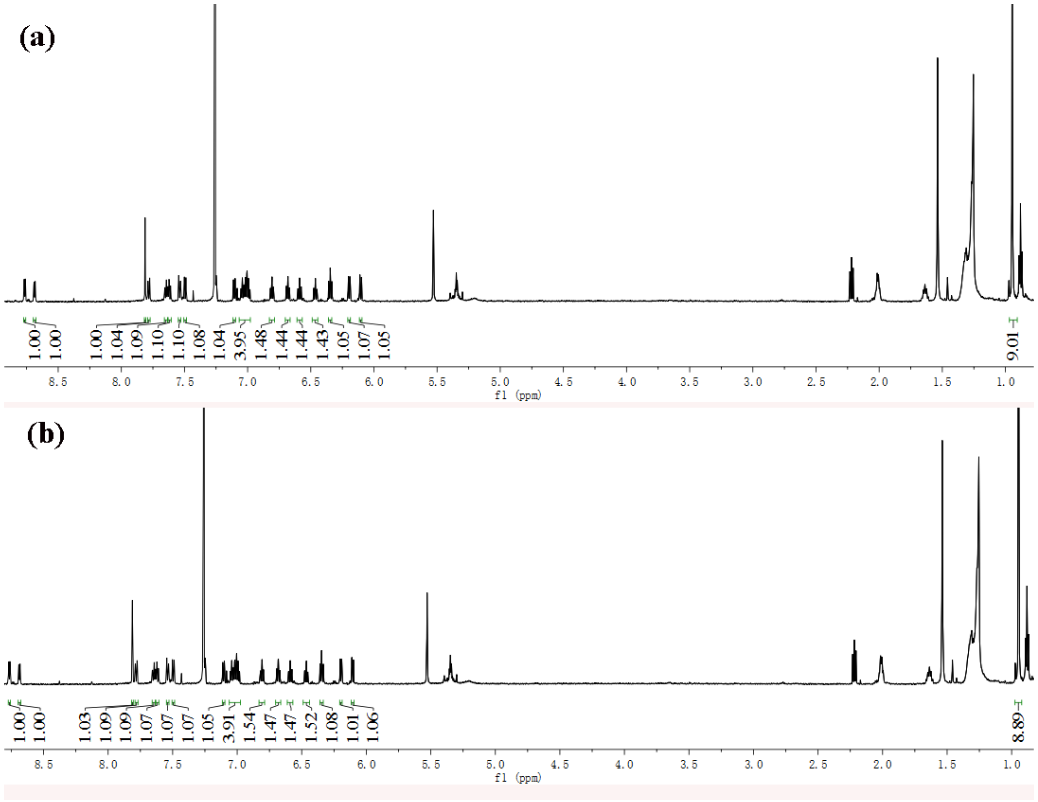

Fig. S1 ^{1}H NMR spectra of **1** in $CDCl_3$ before grinding (a) and after grinding (b).

3. Photophysical properties

Table S1 The phosphorescent emission efficiency (Φ_{em}) and excited-state lifetimes (τ) in various states of **1**.

	As-prepared	Ground	CH_2Cl_2 fumed	Heated
	(P)	**(G)**	**(D)**	**(H)**
Φ_{em}	0.24	0.05	0.26	0.31
τ (μs)	0.67	1.54	0.61	0.64

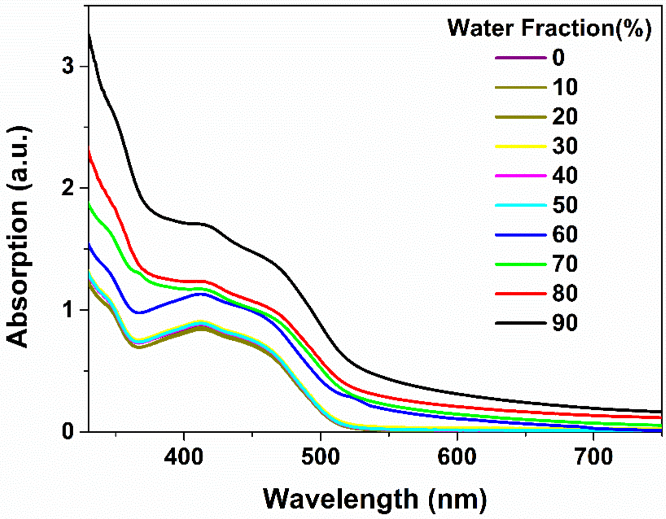

Fig. S2 UV-visible absorption spectra of **1** in THF-water mixtures with different water fractions (0-90%, v/v) at room temperature.

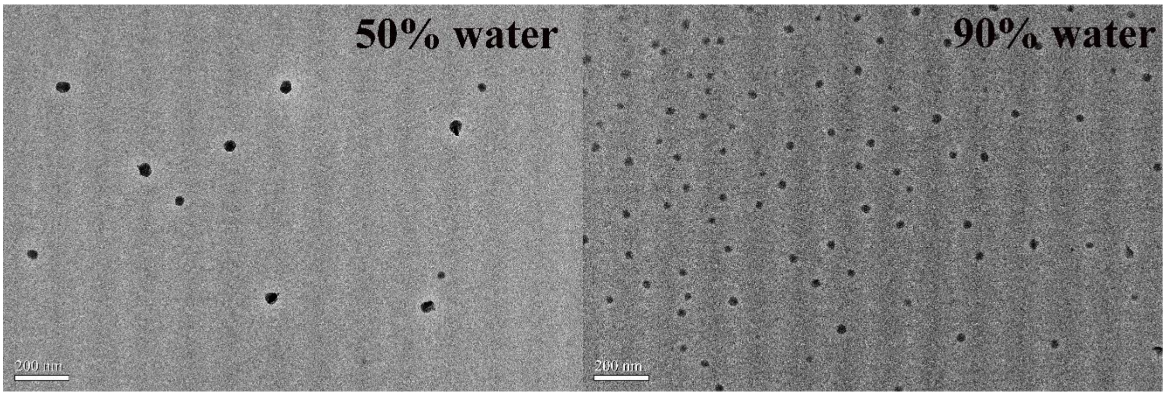

Fig. S3 TEM image of nanoaggregates of **1** formed in THF–H2O mixtures with 50% (left) and 90% (right) water fraction.

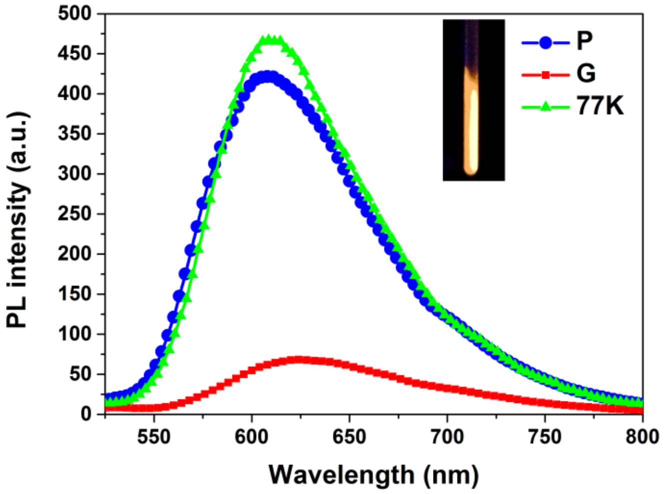

Fig. S4 Emission spectra of **1** in THF solution (10^{-5} mol/L) at 77 K, “as prepared” sample (**P**) and ground sample (**G**), respectively.

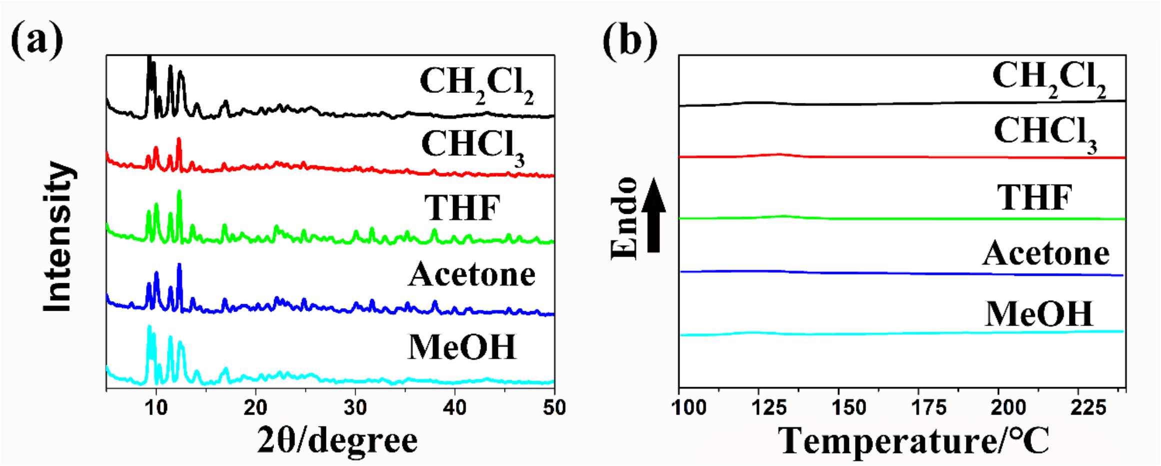

Fig. S5 Powder X-ray diffraction patterns (a) and the DSC traces (b) of **G** after exposure to the corresponding solvent (CH_2Cl_2, $CHCl_3$, THF, Acetone and MeOH).

4. Quantum Chemical Calculations

All calculations were performed with the Gaussian 09 program package.[1] The B3LYP functional was employed for all DFT calculations. The 6-31G* basis set was employed for H, C, N, O atoms, while the iridium atom was described by the Hay-Wadt effective core potential (ECP) and a double-ξ basis set LANL2DZ. Full geometry optimisation with C1 symmetry constraints was carried out in solution for the singlet ground state (S_0) of complex **1**. A solvent effect was taken into account by the polarisable continuum model (PCM) with tetrahydrofuran (THF) as solvent.

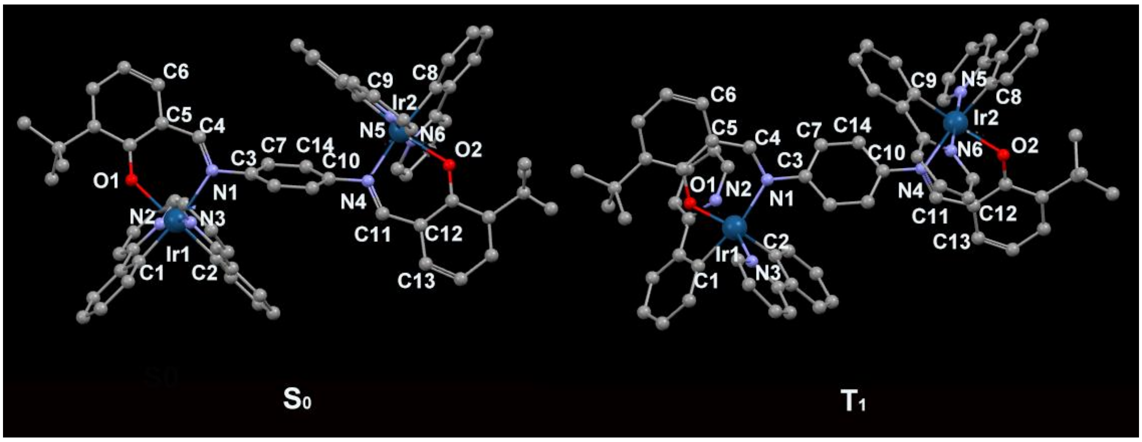

Fig. S6 Optimised geometries of complex **1** at S_0 and T_1 states in solution state.

Table S2 Selected calculated bond lengths (Å), bond angles (°) and dihedral angles (°) at both optimized S_0 and T_1 geometries for complex **1**.

1	T_1	S_0
Ir1-N1	2.232	2.23
Ir1-N2	2.068	2.067
Ir1-N3	2.077	2.078
Ir1-C1	2.019	2.02
Ir1-C2	2.014	2.014
Ir1-O1	2.189	2.192
C1-Ir1-N1	173.62	173.82
C2-Ir1-O1	173.95	174.01
N2-Ir1-N3	176.39	176.17
C2-Ir1-C1	88.49	88.53
C3-N1-C4	115.38	115.51
C5-C4-N1	130.99	130.6
Ir1-N1-C4-O1	0.95	3.4
C6-C5-C4-N1	7.13	9.31
C7-C3-N1-C4	52.18	56.42
Ir2-N4	2.211	2.234
Ir2-N5	2.06	2.065
Ir2-N6	2.095	2.085
Ir2-C8	2.034	2.022
Ir2-C9	2.012	2.013
Ir2-O2	2.17	2.195
C8-Ir2-N2	170.79	172.61
C9-Ir2-O2	173.2	173.88
N5-Ir2-N6	172.12	174.09
C9-Ir2-C8	88.03	88.77
C10-N2-C11	115.17	114.92
C12-C11-N2	129.9	130.8
Ir2-N2-C11-O2	19.67	7.72
C13-C12-C11-N2	2.22	4.95
C14-C10-N2-C11	143	116.77

5. X-ray crystallographic data

The molecular structure of **1** was confirmed by X-ray crystallographic analysis of single crystals. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer using k(Mo-Kα) radiation (k = 0.71069 Å). Cell refinement and data reduction were made by the SAINT program. The structure was determined using the SHELXTL/PC program. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre with CCDC deposition number 1571781. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

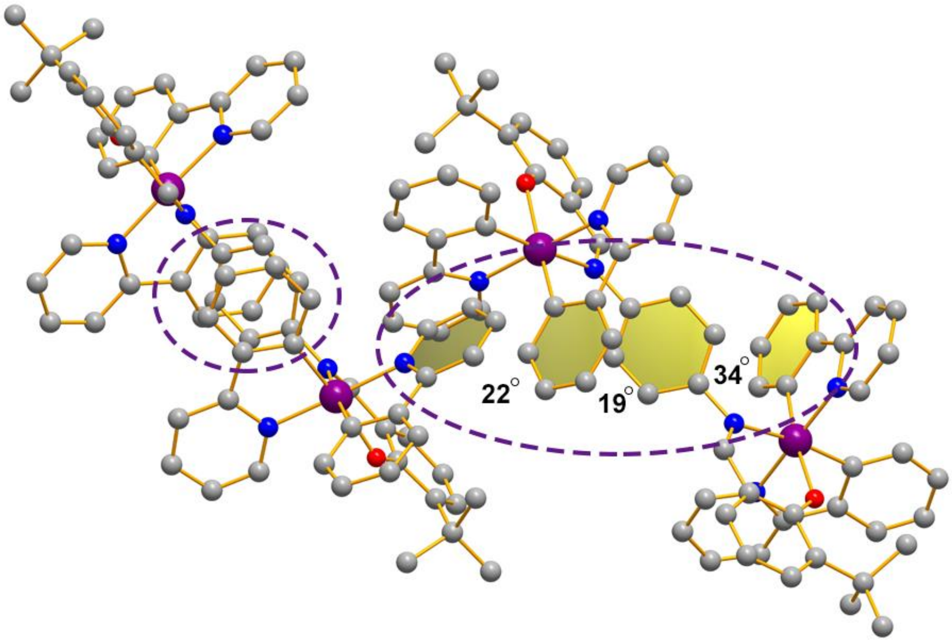

Fig. S7 Molecular packing of **1** in the crystal. Colour code: Ir purple; N blue; O red ; C grey; H atoms are omitted for clarity. The dihedral angles are 22°, 19° and 34°, respectively**.**

Table S3 Crystal data and structure refinement for complex **1**.

	Complex 1
Empirical formula	$C_{72}H_{62}Ir_2N_6O_2$
Formula weight	1428.42
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	P2(1)/c
a/Å	19.8730(14)
b/ Å	12.8050(8)
c/ Å	28.261(2)
α/°	90.00
β/°	103.880(3)
γ/°	90.00
V/ Å^3	6981.7(8)
Z	4
P_{calc}(g/cm^3)	1.404
μ/mm^{-1}	3.858
R_{int}	0.0636
Goodness-of-fit on F^2	1.114
$R_1{}^a$,$wR_2{}^b$[I$>$2σ(I)]	0.0690, 0.1942
R_1,wR_2(all data)	0.1201, 0.2406

$^aR_1=\Sigma||Fo|-|Fc||/\Sigma|Fo|$. $^bwR_2=\{\Sigma[w(Fo^2-Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$

6. References

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