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Supporting Information

A Cyano-bridged Cu(I)-based Organic Framework Coupled with the C-C bond Cleavage of Acetonitrile for Selective and Sensitive Sensing of Fe^{3+} ion

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EXPRIMENTAL SECTION

Materials and Measurements

5-[N-acetato(4-pyridyl)]tetrazole potassium salt and (4-pyridyl)tetrazolate ligands (abbreviated as KAPTZ and PTZ, respectively) were prepared according to literature,[S1] while other chemicals with reagent-grade quality were obtained from commercial sources and used without further purification. Elemental analysis was performed with a German Elementary Varil EL III instrument. The infrared spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR spectrometer as KBr pellets in the range of 400-4000 cm^{-1}. The UV-Vis adsorption spectra were recorded on a Thermo Scientific NanoDrop 2000c spectrometer. Metal elemental analysis was carried out on an Ultima-2 ICP Emission Spectrometer. The powder X-ray diffraction (PXRD) pattern was collected on a Bruker D8 Advance powder diffractometer with Cu $K\alpha$ radiation (λ = 1.5406 Å) at a scanning rate of 3°·min^{-1} for 2θ ranging from 3° to 55°. The emission and excitation spectra were performed on Agilent Cary Eclipse. Thermogravimetric analysis was carried out in the temperature range 30-800 ºC on a TA Q50 apparatus.

Synthesis of Compound 1

Compound 1: A mixture of KAPTZ (0.05 mmol, 12 mg) and CuCl (0.2 mmol, 20 mg) in H_2O / CH_3CN (4/2 mL) was sealed in a 25 mL Teflon-lined autoclave at 120 °C for 48 hours, then cooled slowly at 4 °C·h^{-1} to room temperature. Orange-red prismatic crystals of $Cu_3(CN)_3(MPTZ)$ (**1**) were isolated by filtration, washed with H_2O / CH_3CN (4:2), and air dried (4 mg, 12% based upon KAPTZ). No crystal was obtained when PTZ was employed to instead of KAPTZ via the equivalent synthesis procedures. Anal. Calcd. for compound **1** $C_{10}H_7N_8Cu_3$: calcd. C, 27.94; H, 1.64; N, 26.07. found C, 27.85; H, 1.52; N, 26.11. IR (KBr disk, ν cm^{-1}): 3111 (w), 3057 (m), 2125 (s), 2117 (s), 2073 (s), 1637 (s), 1567 (w), 1536 (m), 1465 (s), 1405 (w), 1374 (w), 1316 (w), 1276 (s), 1210 (w), 1187 (m), 1159 (w), 1140 (w), 1031 (w), 971 (w), 958 (w), 857 (s), 848 (s), 816 (w), 805 (w),754 (s), 724 (w), 712 (m), 662 (w), 629 (m), 533 (s), 490 (w).

X-ray Data Collection and Structure Determination

Data collection for compound **1** was performed on Bruker APEXII diffractometer equipped with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) by using the ω-scan mode at 293 K. The structure was solved by direct methods, the metal atoms were located from the E-maps, and other non-hydrogen atoms were derived from the successive difference Fourier peaks. The structures were refined on F^2 by full-matrix least-squares using the *SHELXTL*-2014 program package.[S2] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. Details of the structure solution and final refinement for compound **1** are given in Table S**1**. CCDC-1583360 (**1**) contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/-data_request/cif.

Table S1. Crystal Data and Data Collection and Refinement Parameters for Compound 1

Compound	***1***
formula	$C_{10}H_7N_8Cu_3$
formula weight	429.86
temperature (K)	293 (2)
wavelength (Å)	0.71073
crystal system	Triclinic
space group	$P\ \bar{1}$
a (Å)	7.978(3)
b (Å)	8.800(3)
c (Å)	10.660(4)
α (°)	112.999(3)
β (°)	97.436(4)
γ (°)	106.403(4)
volume (Å^3)	636.0(4)
Z	2
D_c (Mg/m^3)	2.244
μ (mm^{-1})	4.973
data collected	4878
unique data (R_{int})	2814
parameters	191
GOF on F^2	1.044
R_1 [a] $[I > 2\sigma(I)]$	0.0341
$\boldsymbol{wR_2}$ [b]	0.0847

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

(S1) Y. Zhou, G. W. Yang, Q. Y. Li, K. Liu, G. Q. Gu, Y. S. Ma and R. X. Yuan, *Inorg. Chim. Acta*, 2009, **362**, 1723-1729.

(S2) (a) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.,* 2015, **71**, 3−8. (b) G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.,* 2015, **71**, 3−8.

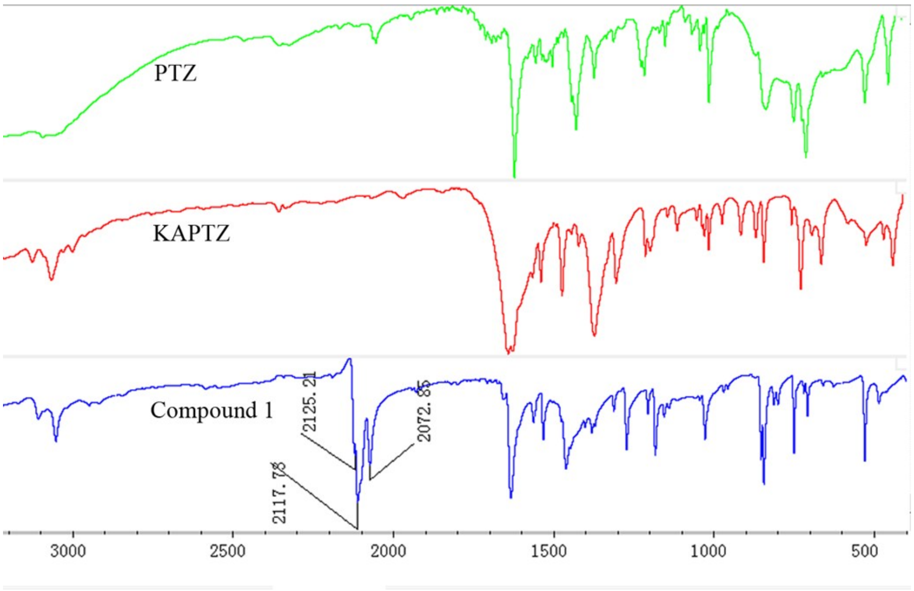

Fig. S1 FT-IR spectra of compound **1**, KAPTZ and PTZ.

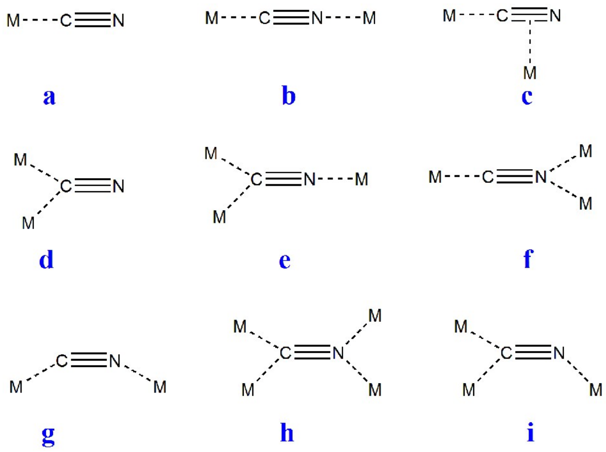

Fig. S2 Coordination modes of cyano anion.

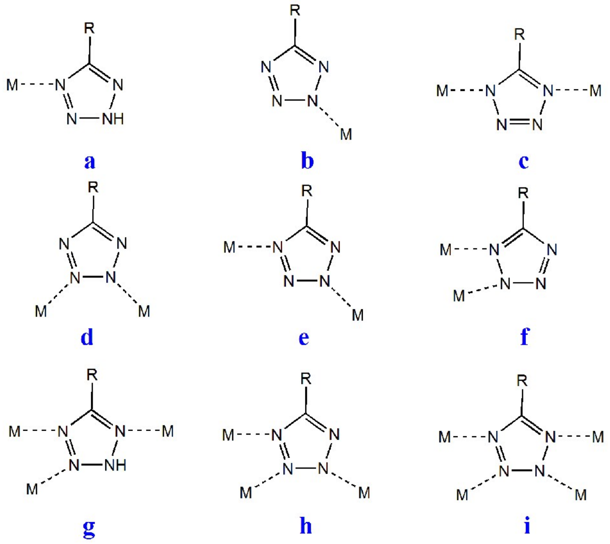

Fig. S3 Nine kinds of coordination modes of tetrazole ligand.

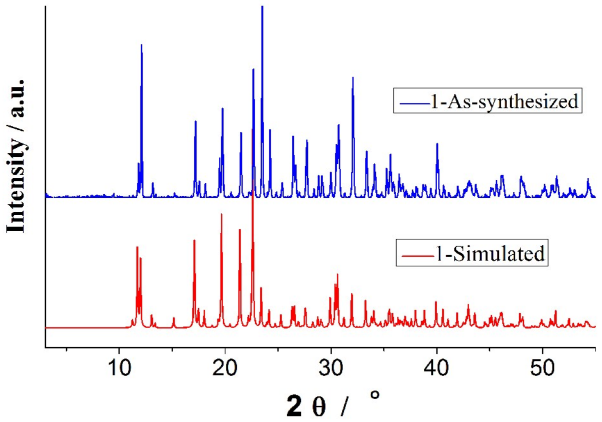

Fig. S4 PXRD of compound **1**.

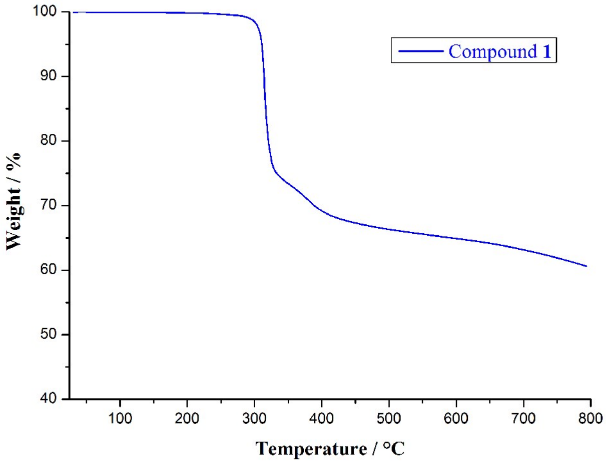

Fig. S5 TGA of compound **1**.

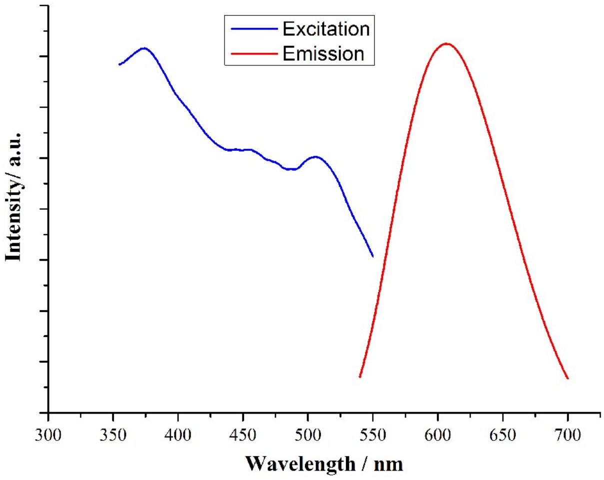

Fig. S6 Excitation and emission spectra of compound **1** in the solid state at room temperature (λ_{ex} = 375 nm).

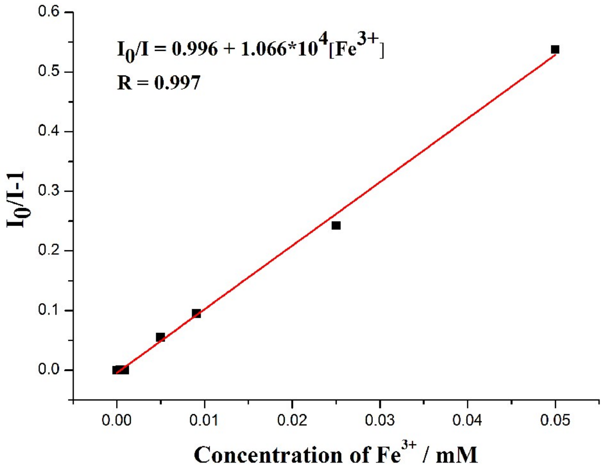

Fig. S7 The Stern−Volmer plot of compound **1** quenched by Fe^{3+} ion in DMF, where I_0 and I are the luminescent intensity before and after Fe^{3+} ion incorporation, respectively. The red line corresponds to a fit to the linear relationship.

Table S2. The K_{SV} of the title compound and some reported metal-organic frameworks acting as luminescent Fe^{3+} probes

Compounds	**Solvents**	K_{SV}	**References**
$[Cd_3(dpa)(DMF)_2(H_2O)_3]\cdot DMF$	DMF	5327.15	*Dalton Trans.*, 2015, 44, 17222.
$[H_2N(CH_3)_2][Cd_4(Hdpa)_2(DMA)_2(H_2O)_3]\cdot 1.5DMA\cdot 2H_2O$	DMF	37751.58	*Dalton Trans.*, 2015, 44, 17222.
$\{[Eu(L)(H_2O)_2]\cdot NMP\cdot H_2O\}_n$	DMF	383395.8	*Inorg. Chem.,* 2016, 55, 10114.
Eu−HODA	H_2O	20900	*Inorg. Chem.*, 2016, 55, 12660.
$\{[Eu(bpda)1.5]\cdot H_2O\}_n$	H_2O	12500	*New J. Chem.*, 2016, 40, 8600.
Eu^{3+}@1	H_2O	5120	*J. Mater. Chem. A.*, 2014, 2, 13691.
$[La(TPT)(DMSO)_2]\cdot H_2O$	EtOH	13600	*Dalton Trans.*, 2015, 44, 13340.
$\{[Tb_4(OH)_4(DSOA)_2(H_2O)_8]\cdot(H_2O)_8\}_n$	H_2O	3543	*J. Mater. Chem. A.*, 2015, 3, 641.
$Cu_3(CN)_3(MPTZ)$	DMF	10660	This work

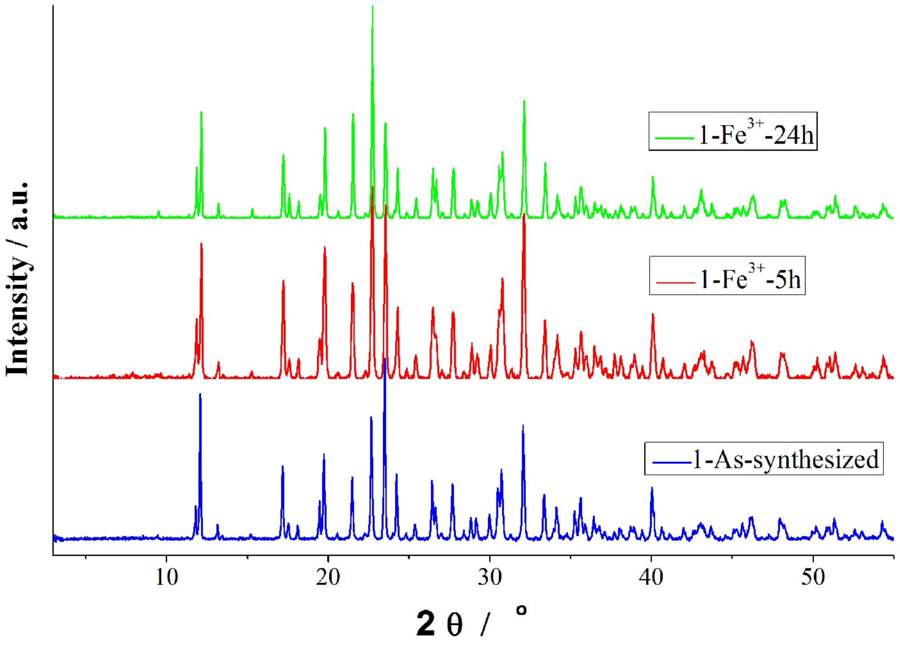

Fig. S8 PXRD patterns of compound **1** and the as-synthesized samples immersed in Fe^{3+} ion for 5 or 24 hours.

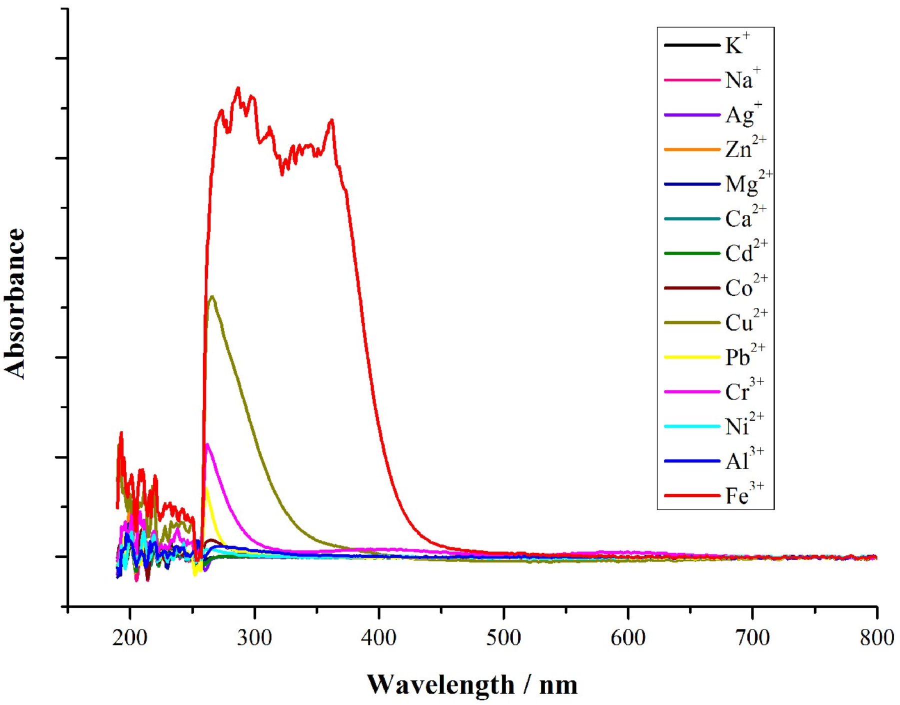

Fig. S9 UV-Vis adsorption spectra of $M(NO_3)x$ in DMF solutions (1.5 mM).