

Supplementary information

Efficient Fluorescence-enhanced Probe for Cyanide Ion Based on Tetraphenylethene Pyridine Coordinated Copper- Iodide Complex

Fenqiang Luo¹, Meng Guo¹, Liyan Zheng^{*3}, Zhixiong Cai^{*2}

1. College of Chemical Engineering; College of Food and Biological Engineering; Collaborative Innovation Center of Fine Chemicals in Fujian Province, Zhangzhou Institute of Technology, Zhangzhou, China, 363000

2. College of Chemistry, Chemical Engineering and Environment; Fujian Provincial Key Laboratory of Modern Analytical Science and Separation Technology, Minnan Normal University, Zhangzhou, China, 363000

3. School of Chemical Science and Technology, Yunnan University, Kunming, China, 650091

Materials and Methods

All employed reagents were of analytical grade and commercially available and were used as received without further purification. TPE-2OH was purchased from Beijing HWRK Chem Co., Ltd., 3-(bromomethyl)pyridine hydrobromide was purchased from Accela ChemBio Co., Ltd., and potassium *tert*-butanolate was purchased from TCI Shanghai.

The NMR spectra were recorded using an AVANCED RX400 NMR spectrometer (Bruker, Germany) operated at 400 MHz. High-resolution mass spectrometry (HRMS) was measured by an Agilent 6540 Q-TOF mass spectrometer (Agilent Technologies, USA). Fluorescence spectra were performed on a Hitachi High-Technologies Corp. (Tokyo, Japan) 5J2-0022 model F-4700 FL spectrofluorometer. UV–vis spectroscopy was performed with a UV-2600 UV–vis spectrophotometer (Shimadzu, Japan). Fourier transform infrared spectroscopy (FT-IR) spectra were recorded in the range 4000–400 cm^{-1} using a Thermo Nicolet spectrometer with KBr pellets (Thermo Nicolet 365). The morphologies and the distribution of elements of the as-prepared catalysts were characterized by scanning electron microscope (SEM, Thermos Scientific Apreo 2C) under an accelerating voltage of 15.0 kV. The fine microstructure and the distribution of elements of the as-prepared catalysts were characterized by transmission electron microscopy (TEM, Talos F200S G2) and the acceleration voltage was 200 kV. Powder X-ray diffraction (PXRD) patterns were taken using a YRIII30 X-ray diffractometer (Rigaku, Japan) with Cu K α radiation at 40 kV and 200 mA, with a scan speed of 20° min^{-1} and a step size of 0.02°. Single-crystal fluorescence pictures were taken by a

* Corresponding author.

E-mail addresses: czx1816@mnnu.edu.cn (Z. Cai); zhengliyan@ynu.edu.cn (L. Zheng)

BX53 fluorescence inverted microscope (Olympus, Japan). Raman spectra were recorded in the range 2000-200 cm^{-1} using high-resolution evolution (Horiba Jobin Yvon, Japan) with 633 nm laser excitation. Thermogravimetric analysis (TGA) was performed by using a NETZSCH STA 449F3 instrument with a heating rate of 10 $^{\circ}\text{C min}^{-1}$ under a N_2 atmosphere. X-ray photoelectron spectroscopy (XPS) spectra was performed using a K-Alpha⁺ X-ray photoelectron spectrometer (Thermo Fisher Scientific, USA). The crystallographic data collection was performed at room temperature on an XtaLAB Synergy R, DW system, HyPix diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$). To obtain the crystal data of CIT-Z with reddish-brown color, the crystal was illuminated continuously by a torch with UV light (the same single crystal in the same position as that used before irradiation). Using *Olex2*, the structures were solved with the *SHELXT* structure solution program using intrinsic phasing and refined with the *SHELXL* refinement package using least-squares minimization. Fluorescence emission lifetimes were determined on a Horiba Jobin Yvon Fluorolog-3 with a light-emitting-diode lamp (340 nm). Light intensity was performed by using a TP100 optical densitometer (Changchun New Industries Optoelectronics Tech. Co., Ltd., China). UV light (3 W, 18.0 mW cm^{-2}) and green light (12 W, 1.0 mW cm^{-2}) were used in irradiation experiments.

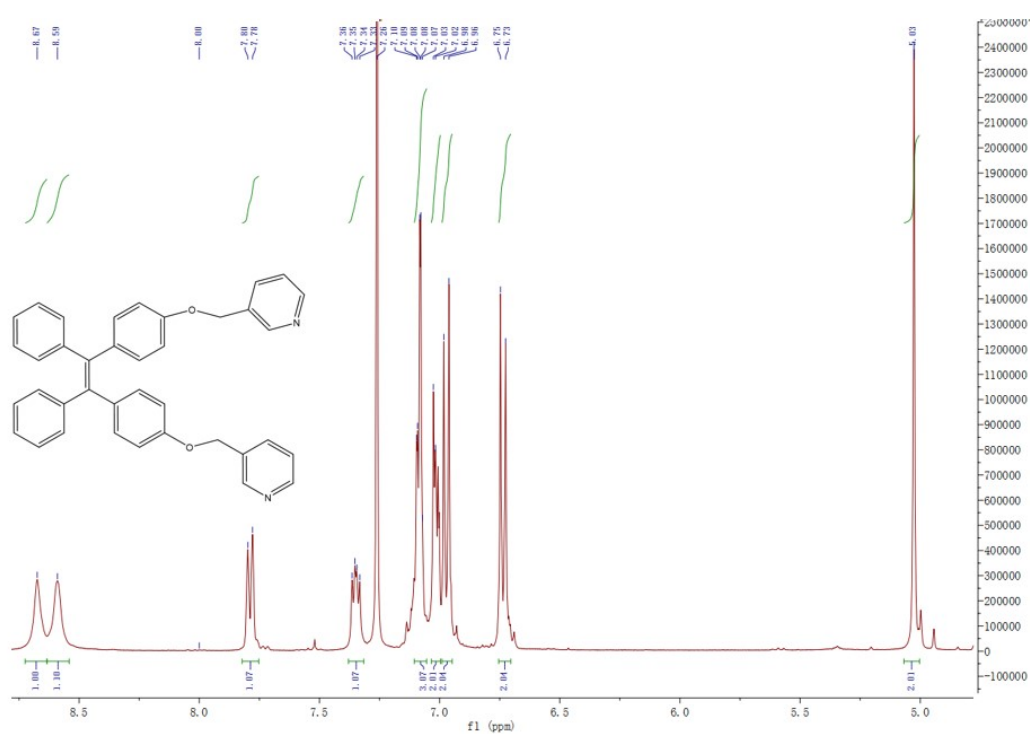


Figure S1. $^1\text{H NMR}$ spectrum of TPE-2by-2-Z in CDCl_3

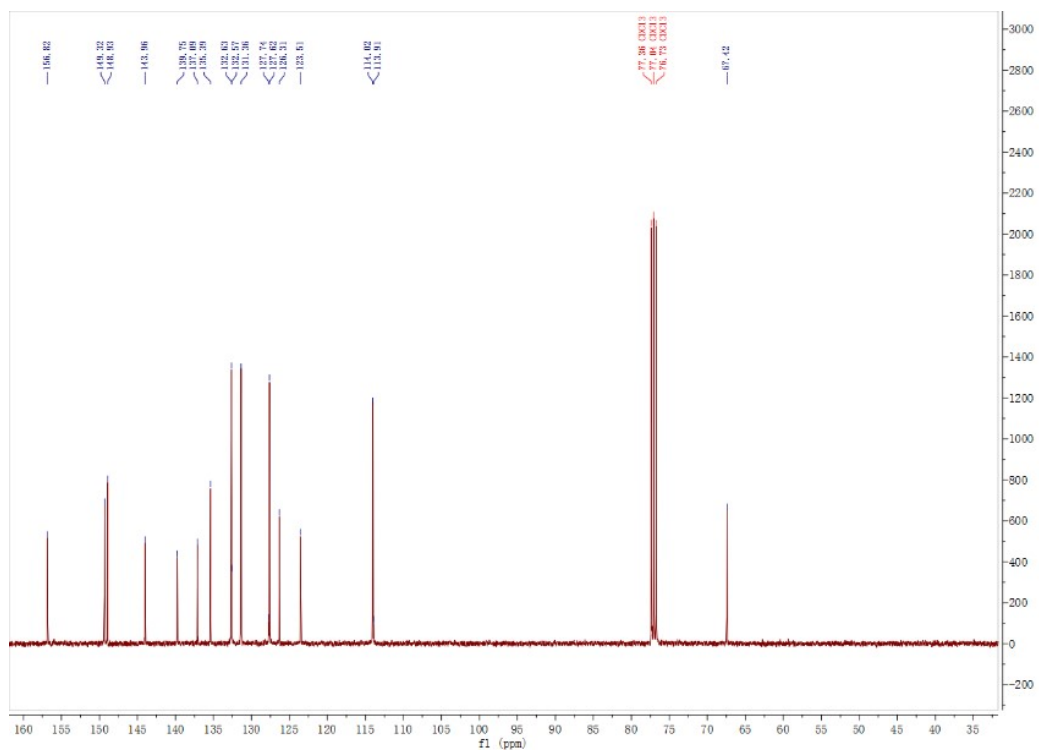


Figure S2. ^{13}C NMR spectrum of TPE-2by-2-Z in CDCl_3

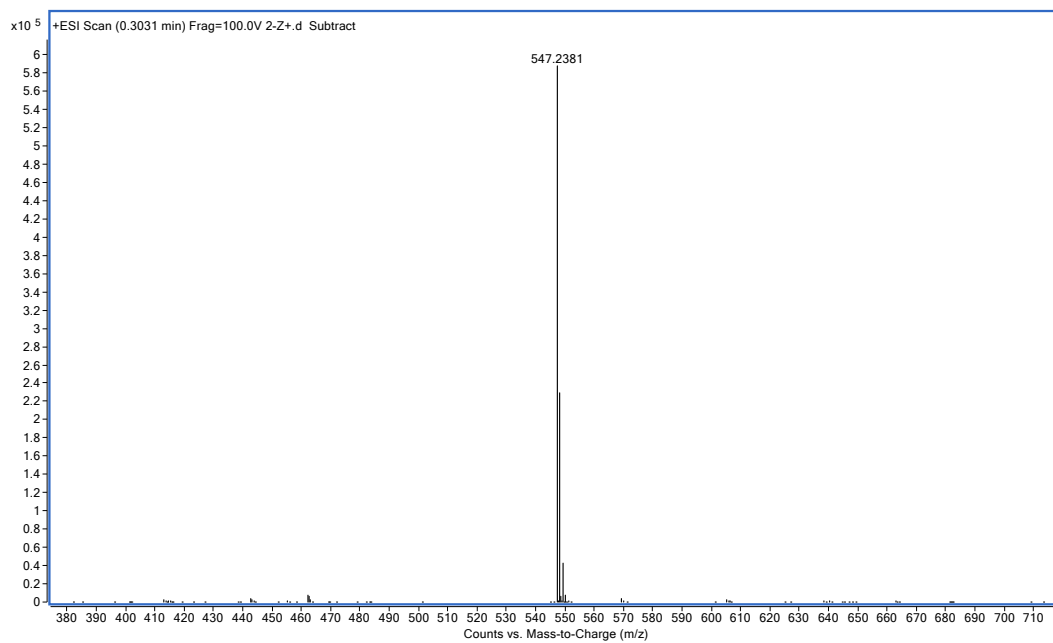


Figure S3. High-resolution mass spectrum of TPE-2by-2-Z

Table S1. Crystal Data and Structure Refinement Summary for CIT-Z.

CIT-Z	
formula	C ₃₈ H ₃₀ CuIN ₂ O ₂
formula weight	737.08
temperature/K	293(2)
crystal system	Monoclinic
space group	P2 ₁ /n
a/Å	19.0059(2)
b/Å	9.07299(9)
c/Å	20.0473(3)
α /°	90
β /°	108.7137(13)
γ /°	90
V/Å ³	3274.21(7)
Z	4
ρ_{calc} /cm ³	1.495
μ /mm ⁻¹	8.620
F (000)	1480.0
$\theta_{\text{min}}-\theta_{\text{max}}$ [deg]	5.578-152.05
R/W _r [$I > 2\sigma(I)$]	0.0265/0.0678

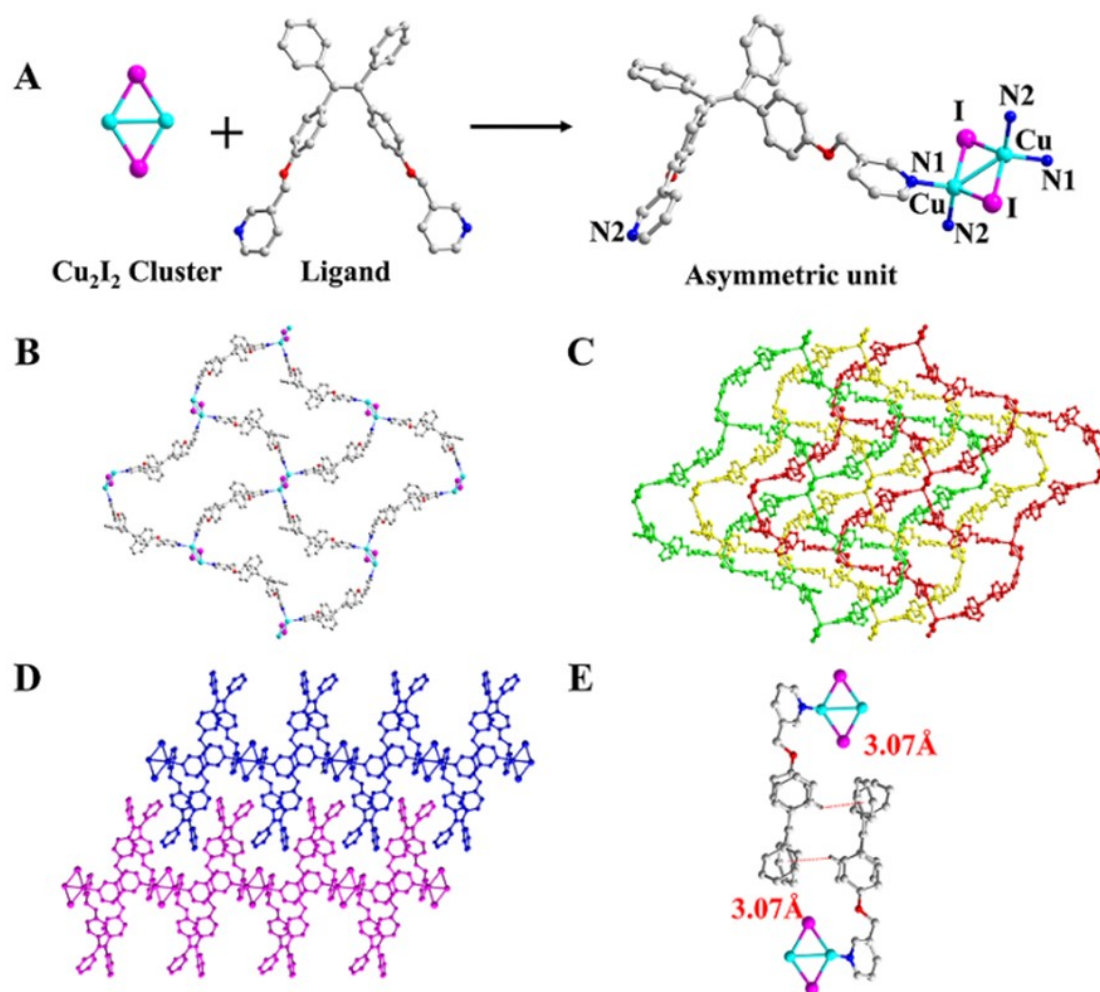


Figure S4. (A) Structures of the Cu_2I_2 cluster and ligand **1Z** and the asymmetric unit of CIT-Z. Views of the (B) single network and (C) 3-fold-interpenetrating network structure of CIT-Z from the a direction. (D) Two layers of CIT-Z network crystals viewed from the b direction. (E) $\text{C}-\text{H}\cdots\pi$ interaction of CIT-Z between two layers. Some of the H atoms were omitted for clarity. Color legend: Cu, blue; N, deep blue; I, purple; O, red; C, gray; H, deep gray.

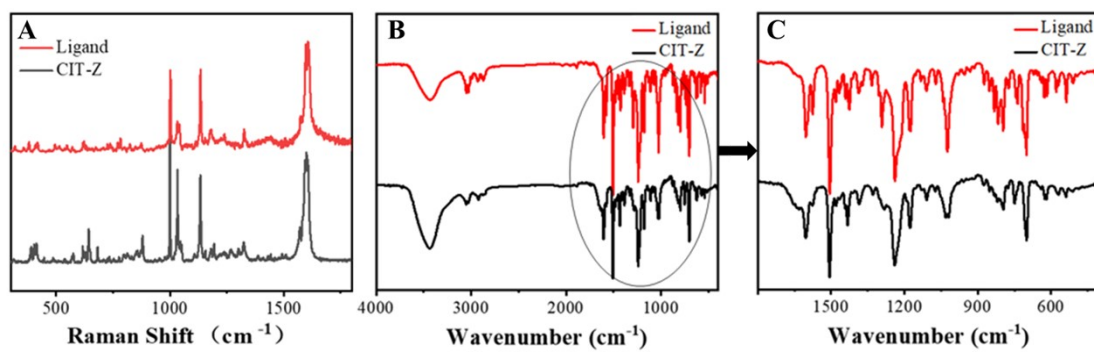


Figure S5. (A) Raman and (B,C) infrared spectra of ligand TPE-2by-2-Z and coordination polymer CIT-Z.

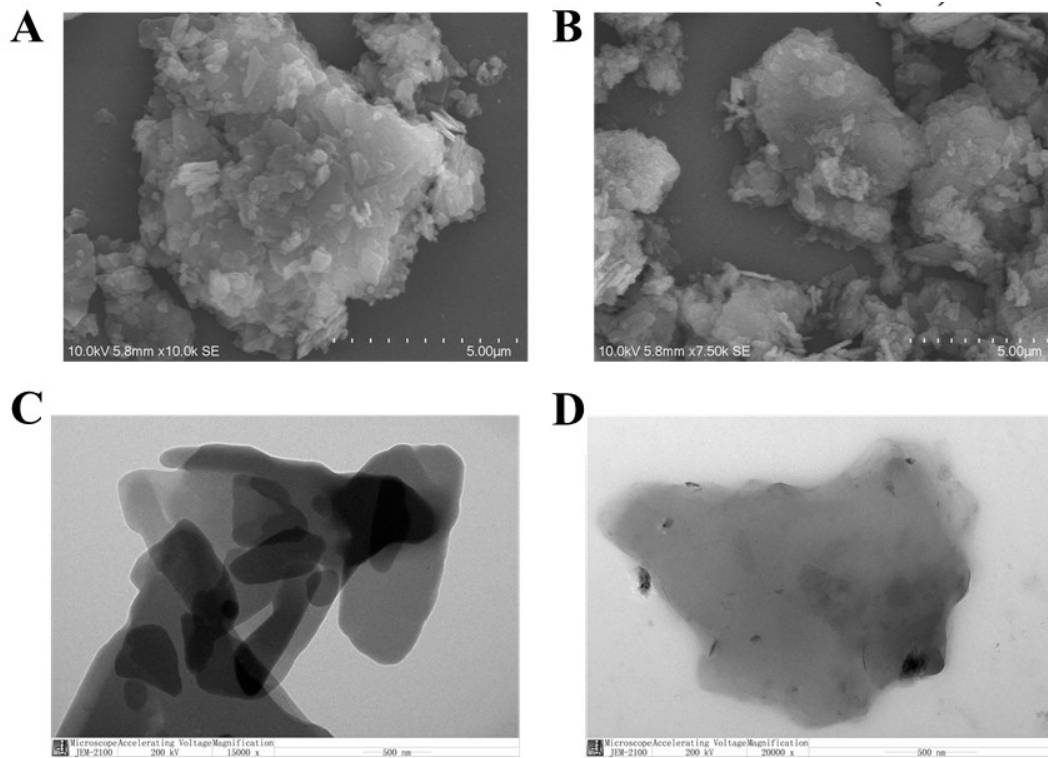


Figure S6 (A), (B) scanning electron microscope images and (C) (D) transmission electron microscope images of CIT-Z before and after cyanogen treatment.

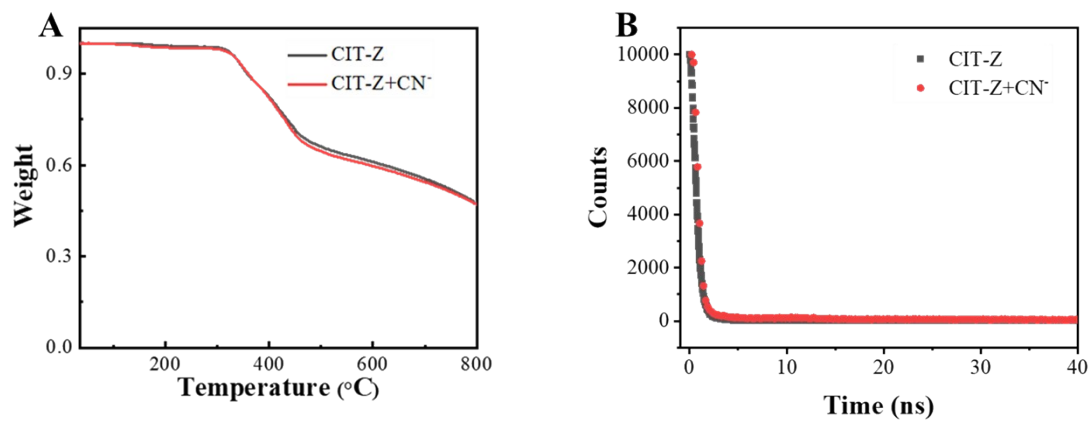


Figure S7 (A) thermogravimetric and (B) fluorescence lifetime of CIT-Z before and after cyanogen treatment.

Table S1. Performances of various fluorescence sensors for CN⁻ detection using sensing functional materials

Sensing functional materials	Linear range (μM)	LOD (μM)	Reference
5-(4-(diphenylamine)phenyl) thiophen-2-formaldehyde	8-38	0.068	1
fluorescein-Zn-naphthalene ensemble	ND	0.509	2
dual-functional Cu ²⁺ -based ensemble	ND	0.471	3
conjugated naphthoquinone-benzothiazole	ND	0.497	4
BBCN	0-20	0.189	5
fluorogenic naphthalene based receptor	ND	0.21	6
CIT-Z	1-500	0.1	This work

ND denotes not determined

References

1. Shi Q, Wu S T, Shen L, *Frontiers in Chemistry*, 2022, **10**, 727.
2. Goswami S, Paul S, Manna A, *Tetrahedron Letters*, 2014, **55**, 3946-3949.
3. Wang J, He J, Zhang J, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2021, **252**, 119526.
4. Kim I J, Ramalingam M, Son Y A, *Sensors and Actuators B: Chemical*, 2017, **246**, 319-326.
5. Munusamy S, Swaminathan S, Jothi D, *RSC advances*, 2021, **11**, 15656-15662.
6. Yilmaz B, Keskinates M, Aydin Z, *Journal of Photochemistry and Photobiology A: Chemistry*, 2022, **424**, 113651.