

Electronic Supplementary Information (ESI)

A coumarin-containing Schiff base fluorescent probe with AIE effect for the copper(II) ion

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1 Experimental Section

1.1 Reagents

7-Hydroxy-4-methylcoumarin(98%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Benzophenone(98%) and 4-aminobenzophenone(98%) were purchased from J&K Scientific Co., Ltd. Acetic acid (CH₃COOH) and titanium tetrachloride (TiCl₄) were purchased from Tianjin Fuchen Chemical Reagents Factory. Hexamethylenetetramine(99.5%) was purchased from Shanghai Saan Chemical Technology Co., Ltd. Concentrated hydrochloric acid (HCl), tetrahydrofuran (THF), petroleum ether, ethyl acetate, ethanol (C₂H₅OH), dichloromethane (DCM) and anhydrous sodium sulfate (Na₂SO₄) were all analytically pure grade and supplied by Tianjin Kemiou Chemical Reagent Co., Ltd, China. THF was distilled prior to use. Deionized water was used in the experiment.

1.2 Instruments and Measurements

Fourier transform infrared (FTIR) spectra were recorded on Nicolet iS10 FTIR spectrophotometer (ThermoFisher Scientific, America) using KBr pellets. Nuclear magnetic resonance (NMR) spectroscopy was performed on a Quantum-I 400 MHz digital NMR spectrometer (Q.One Instruments Ltd., China). Chemical shifts were

measured using tetramethylsilane as an internal standard. UV-Visible (UV-vis) spectra were recorded on a Specord 200 plus spectrophotometer (Analytikjena, Germany). Photoluminescent (PL) spectra were recorded on an F-7000 fluorescence spectrophotometer (Hitachi, Japan). High resolution mass spectra (HRMS) were recorded on a Q Exactive UHMR mass spectrometer (ThermoFisher Scientific, America).

2 Synthesis of compounds

2.1 Synthesis of 1-(4'-aminophenyl)-1,2,2-triphenylethene (TPE-NH₂)

TPE-NH₂ was synthesized according to previously published procedures^[1] with slight modification. A dried 250 mL two-necked round bottom flask was charged with 4-aminobenzophenone (2.7 g, 14 mmol), benzophenone (3.0 g, 16 mmol), Zn powder (2.9 g, 44 mmol), and solvent THF (100 mL). The mixture was cooled to -23 °C and then stirred for 20 min. The flask was degassed under vacuum and filled of dry argon gas for three times. Then, the TiCl₄ (2.5 mL, 22 mmol) was added dropwise into the cold mixture in 2 h. After addition, the reaction was stirred for 30 min at -23 °C. Then the mixture was slowly warming up to 78 °C and refluxed overnight. The reaction mixture was quenched by adding 10% K₂CO₃ solution (45 mL). The solvent was then evaporated under vacuum. The residue was purified by column chromatography with petroleum ether/CH₂Cl₂ (1/1, *V/V*) as the eluent to give the product as a yellow solid (2.0 g, 41%). ¹H-NMR(400 MHz, DMSO-*d*₆) (ppm): 7.02-7.16(m, 9H), 6.90-6.99(m, 6H), 6.58(d, *J* = 8.0 Hz, 2H), 6.28(d, *J* = 8.0 Hz, 2H), 5.05(s, 2H). ¹³C-NMR(100 MHz, DMSO-*d*₆) δ(ppm): 147.76, 144.65, 144.43, 144.40, 141.65, 138.32, 132.07, 131.34, 131.26, 131.18, 130.75, 128.23, 128.13, 128.03, 126.71, 126.46, 113.57. HRMS calc. for [M+H]⁺ 348.1747, found 348.1735.

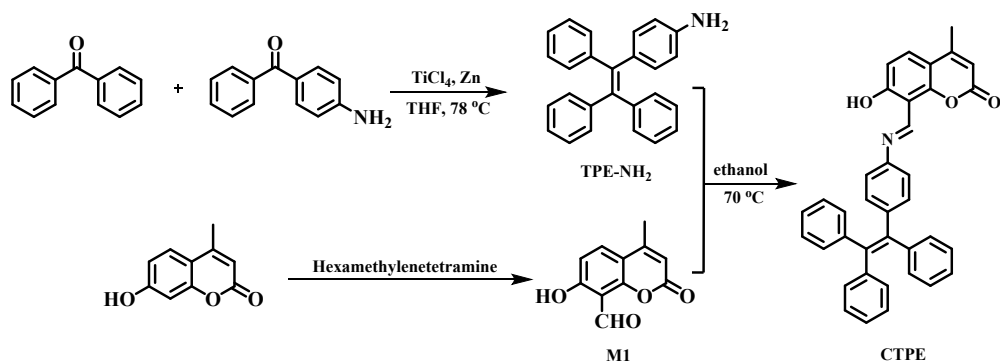
2.2 Synthesis of 8-formyl-7-hydroxy-4-methylcoumarin (M1)

M1 was prepared by the known method^[2] with slight modification. 7-Hydroxy-4-methylcoumarin (5.0 g, 28 mmol) and hexamethylenetetramine (10 g, 71 mmol) in acetic acid (38 mL) were stirred for 5.5 h at 95 °C. Thereafter, hydrochloric acid (75

mL, HCl/H₂O, 84/100, *V/V*) was added and further heated for 30 min. After cooling, the reaction mixture was poured into ice-water (375 mL) and extracted with ethyl acetate three times. The combined organic layer was dried over anhydrous sodium sulfate and filtered. The residue was purified by column chromatography on silica gel using dichloromethane as eluent to provide the product as a light yellow solid (0.95 g, 17%). ¹H-NMR(400 MHz, DMSO-*d*₆) δ (ppm): 11.88(s, 1H), 10.41(s, 1H), 7.90(d, *J* = 8.8 Hz, 1H), 6.94(d, *J* = 8.8 Hz, 1H), 6.28(s, 1H), 2.39(s, 3H). ¹³C-NMR(100 MHz, DMSO-*d*₆) δ (ppm): 191.68, 164.13, 159.16, 155.54, 154.05, 133.75, 114.01, 112.27, 111.55, 109.40, 18.79. HRMS calc. for [M-H]⁻ 203.0339, found 203.0342.

2.3 Synthesis of 7-hydroxy-4-methyl-8-((4-((1,2,2-triphenylvinyl)phenyl)imino)methyl)coumarin (CTPE).

CTPE was prepared in high yield via Maillard reaction of **M1** and **TPE-NH₂** in absolute ethanol^[2]. **TPE-NH₂** (0.25 g, 0.72 mmol) was dissolved in ethanol (20 mL) and **M1** (0.15 g, 0.73 mmol) was added to the solution. The reaction mixture was refluxed for 3 h under argon at 70 °C and then the mixture was cooled to room temperature. The precipitate was filtered off, washed with cold ethanol several times and dried to give the desired product as orange solid (0.34 g, 89%). ¹H-NMR(400 MHz, DMSO-*d*₆) δ (ppm): 14.86(s, 1H), 9.16(s, 1H), 7.78(d, *J* = 8.8 Hz, 1H), 7.29(d, *J* = 8.8 Hz, 2H), 7.11-7.21(m, 9H), 6.97-7.08(m, 8H), 6.91(d, *J* = 9.2 Hz, 1H), 6.24(s, 1H), 2.40(s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 159.28, 154.69, 153.42, 152.28, 142.60, 143.16, 142.44, 142.31, 140.73, 138.90, 131.55, 130.33, 130.27, 128.20, 126.87, 126.77, 126.65, 125.80, 125.64, 125.55, 119.59, 114.11, 109.81, 17.95. HRMS calc. for [M-H]⁻ 532.1907, found 532.1910.



Scheme S1 Synthesis and structures of TPE-NH₂, M1 and CTPE.

3 NMR and MS spectra

3.1 ¹H-NMR, ¹³C-NMR and MS of TPE-NH₂

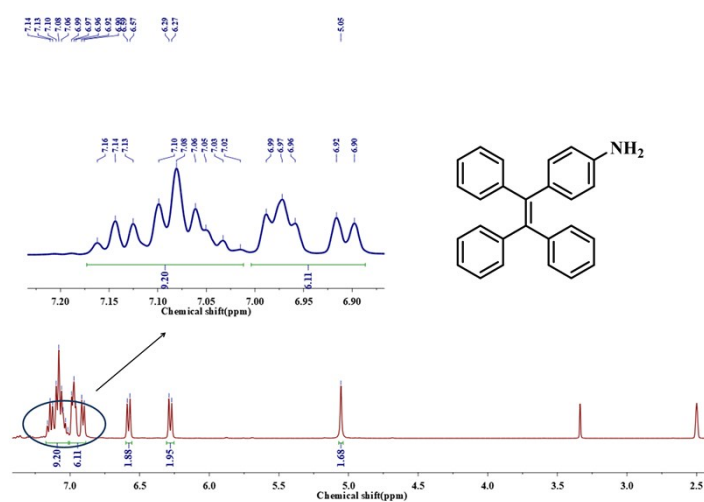


Fig. S1 ¹H-NMR spectrum of TPE-NH₂ in DMSO-*d*₆

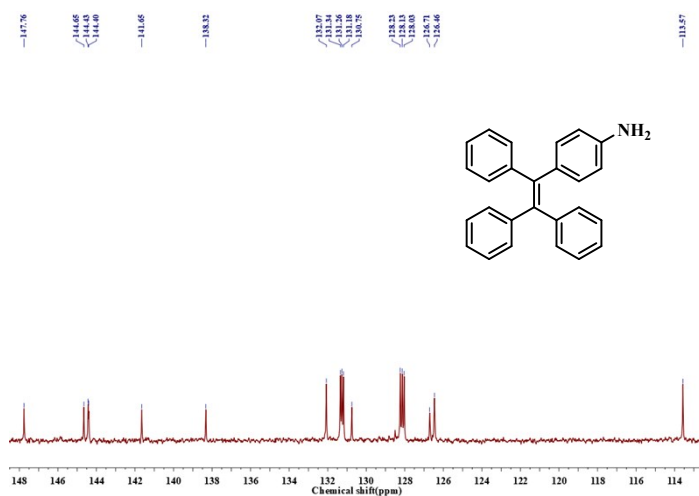


Fig. S2 ¹³C-NMR spectrum of TPE-NH₂ in DMSO-*d*₆

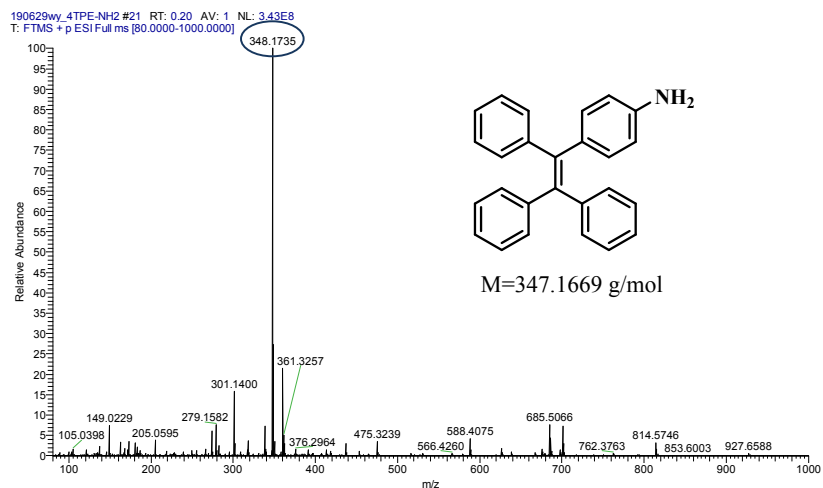


Fig. S3 HRMS spectrum of TPE-NH₂ in CH₃OH

3.2 ¹H-NMR, ¹³C-NMR and MS of M1

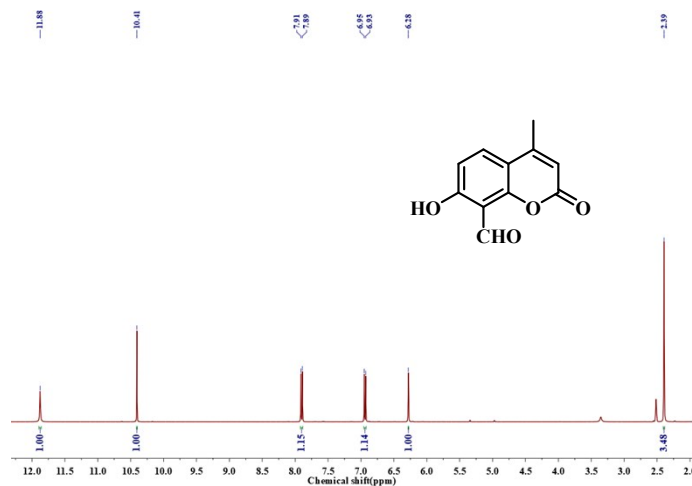


Fig. S4 ¹H-NMR spectrum of M1 in DMSO-*d*₆

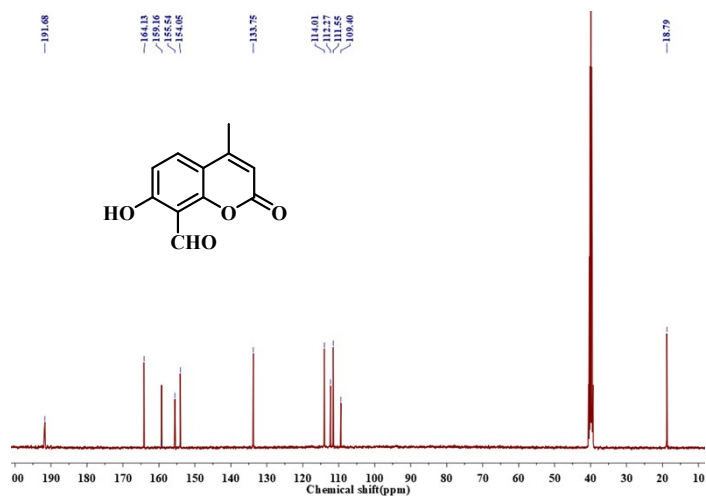


Fig. S5 ¹³C-NMR spectrum of M1 in DMSO-*d*₆

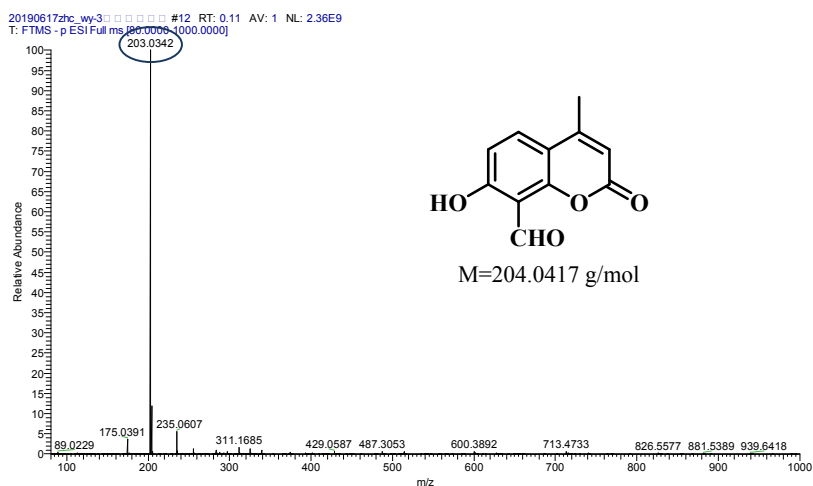


Fig. S6 HRMS spectrum of **M1** in CH₃OH

3.3 ¹H-NMR, ¹³C-NMR and MS of CTPE

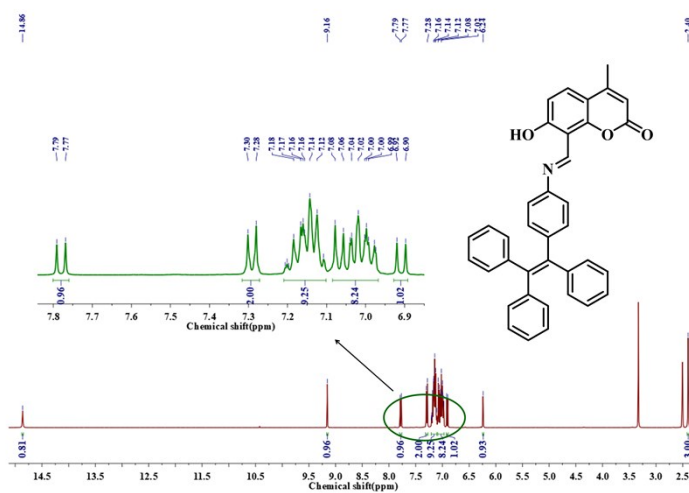


Fig. S7 ¹H-NMR spectrum of **CTPE** in DMSO-*d*₆

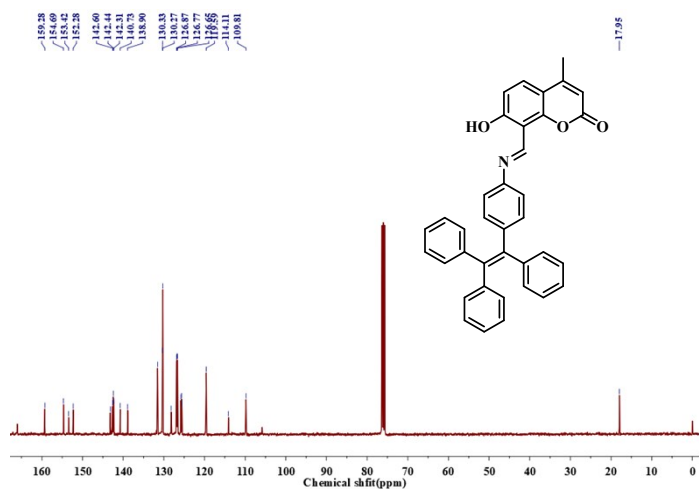


Fig. S8 ¹³C-NMR spectrum of **CTPE** in DMSO-*d*₆

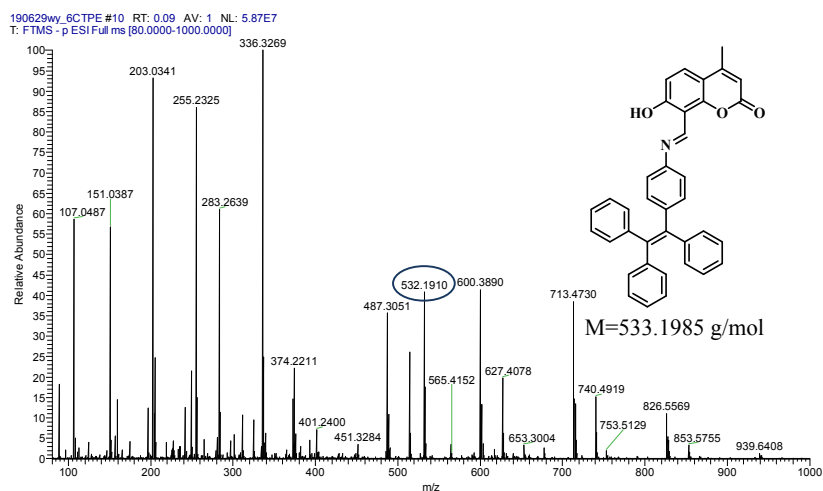


Fig. S9 HRMS spectrum of CTPE in CH₃OH

3.4 FTIR Analysis

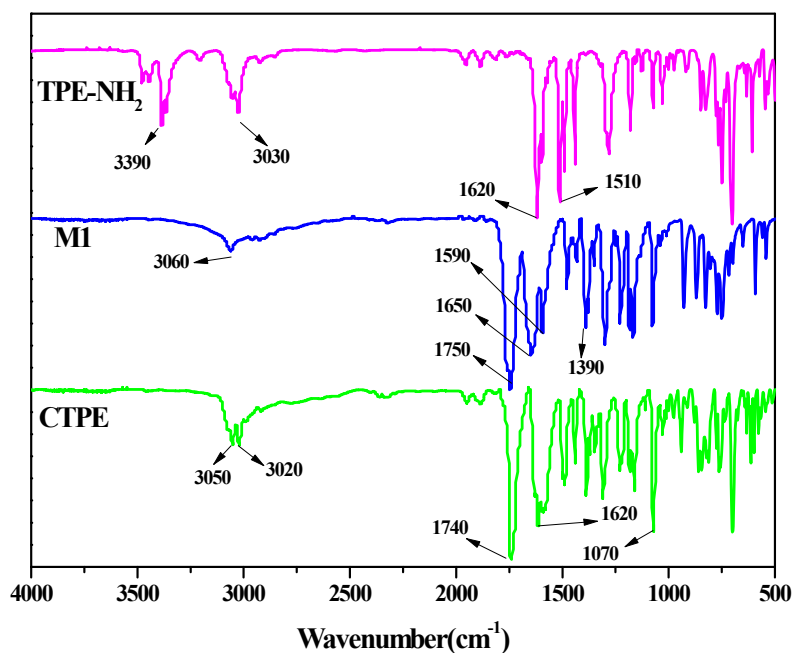


Fig. S10 FTIR spectra of TPE-NH₂, M1 and CTPE

The FTIR spectra of TPE-NH₂, M1 and CTPE were showed in Fig. S10. In the TPE-NH₂ spectrum, 3390 cm⁻¹ was the symmetric and antisymmetric absorption peak of N-H bond; 3030 cm⁻¹ was the tensile vibration absorption peak of C-H bond on the benzene ring; and 1620 cm⁻¹ was the bending vibration absorption peak of N-H bond; 1510 cm⁻¹ was the C=C bond skeleton vibration absorption peak on the benzene ring^[3]. In the M1 spectrum, 3060 cm⁻¹ was the C-H bond stretching vibration absorption peak; 1750 cm⁻¹ was the C=O bond stretching vibration absorption peak;

1650 cm^{-1} was the C=O bond stretching vibration absorption peak on the aldehyde group; and 1590 cm^{-1} was the C=C bond skeleton vibration absorption peak on the benzene ring; 1390 cm^{-1} was the C-H bond stretching vibration absorption peak on the aldehyde group^[4]. In the **CTPE** spectrum, there was an in-plane bending vibration absorption peak of C=N bond at 1620 cm^{-1} , and a C=O bond stretching vibration absorption peak on the aldehyde group at 1740 cm^{-1} , indicating that **CTPE** has been synthesized.

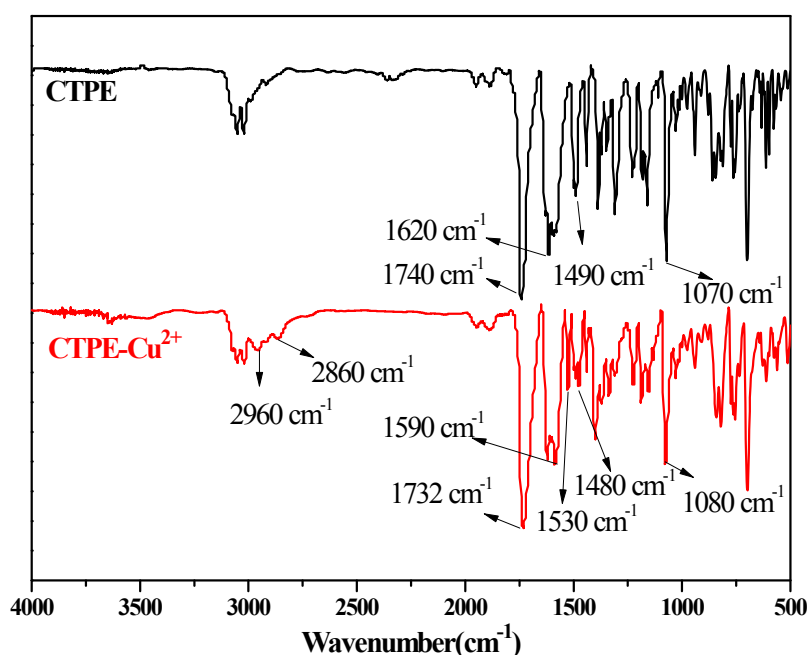


Fig. S11 FTIR spectra of **CTPE** before and after adding Cu^{2+}

Furthermore, the FTIR spectra of **CTPE** before and after adding Cu^{2+} were given in Figure S11. Compared to free **CTPE**, the infrared spectra of **CTPE-Cu²⁺** showed several remarkable changes. When it matched with Cu^{2+} , the characteristic absorption peak of C=O (1740 cm^{-1}) was shifted to 1732 cm^{-1} , which indicated that oxygen in the C=O of **CTPE** participated in coordination^[5]. The absorption peak of the C=N group in the probe at 1620 cm^{-1} showed a shift to 1590 cm^{-1} after coordination with Cu^{2+} , thereby confirming the forming of $\text{Cu}\cdots\text{N}$ coordination bond^[6]. The absorption peak of the C-O group of C-OH in **CTPE** at 1070 cm^{-1} displayed a shift to 1080 cm^{-1} , indicating that oxygen in the hydroxyl group participated in coordination. These results further confirmed the possible complex model.

References

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