Synthesis of copper nanoclusters stabilized by 2-amino-5-mercapto-1, 3, 4 -thiadiazole and acetate simultaneously and as a sensitive sensor for detecting trace water in organic solvents

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ABSTRACT

We describe the synthesis of a novel copper nanoclusters (AMTD-Ac-CuNCs) stabilized by 2-amino-5-mercapto-1,3,4-thiadiazol (AMTD) and acetate (Ac⁻) simultaneously. The effect of carboxylate on the luminescence of CuNCs was discussed. The as-synthesized CuNCs can be used as a highly sensitive fluorescence sensor to successively detect the trace water in organic solvents. The sensor exhibits high sensitivity with a detection limit as 0.036% for water in EtOH, 0.018 v/v % in THF, 0.024 in ACT and 0.026 in MeCN, respectively. This work broadens the application of CuNCs and provides an extremely sensitive detection method of water.

1. Introduction

The development of efficient sensors for the determination of the water content in organic solvents is highly desirable for a number of chemical industries such as pharmaceutical manufacturing, food processing, biomedical and environmental monitoring [1]. Fluorogenic probes are desirable to quantify low level water due to its high sensitivity and real-time monitoring manner. Some luminescent water sensors based on organic fluorescent molecules, such as anthraceneboronic acid esters, thioxanthone and biindenyl derivatives have been developed [2–7]. Several luminescent MOFs have been tested as humidity sensors for detecting the water content of organic solvents [8–11]. Despite of these preceding advances, it is still very necessary to develop novel materials for water detection.

In recent years, copper nanoclusters (CuNCs) have become an active research area because of their desirable luminescence performance and much lower cost, which enable them attractive candidates of promising nanomaterial suited for sensors to detect various chemicals [12–18]. To the best of our knowledge, most of the CuNCs reported possess aggregation-induced emission (AIE) enhancement property [19–21]. Qian et al. prepared luminescent copper nanoclusters which could be used as a sensitive sensor for the detection of trace amount of water in organic solvents [22].

In this paper, we report a facile synthesis of copper nanoclusters (AMTD-Ac-CuNCs) stabilized by AMTD and acetate with intense blue emission in aqueous solution and nonluminescence in solid state. The

as-prepared CuNCs can be utilized for detection trace water in organic solvents due to the solid state ultrasensitive response to water. The strong hydrogen bonding between water and the protect ligand AMTD and Ac⁻ results in the aggregation of CuNCs and displays fluorescence. The switching of luminescence between on and off accompany with the addition of water and drying. The excellent reversibility enables this sensor to monitor water content in a continuous and recyclable way.

2. Experimental

2.1. Apparatus

Proton nuclear magnetic resonance (^{1}H NMR) experiments were performed on a Bruker AV-300 NMR spectrometer. Fourier transform infrared spectra were taken on a Shimadzu FT-IR-8400S spectrometer with a KBr pellet technique. Ultraviolet-visible (UV–vis) spectra experiments were performed on a Yuanxi UV–vis 8000 A spectrophotometer. Energy Dispersive X-ray Spectroscopy (EDX) was taken with a Hitachi S-4800 scanning electron microscope. The transmitting electron microscopy (TEM) images were recorded on a JEOL-2011 transmission electron microscope. X-ray photoelectron spectra (XPS) experiments were performed on a PHI 5000 VersaProbe multifunctional imaging electron spectrometer (UlVAC-PHI, Japan). Mass spectra were obtained by 6200 LC/MS TOF (Agilent, America). All fluorescence measurements were performed on a FLS920 time-resolved/steady-state lifetime fluorescence spectrophotometer (Edinburgh Instruments). The

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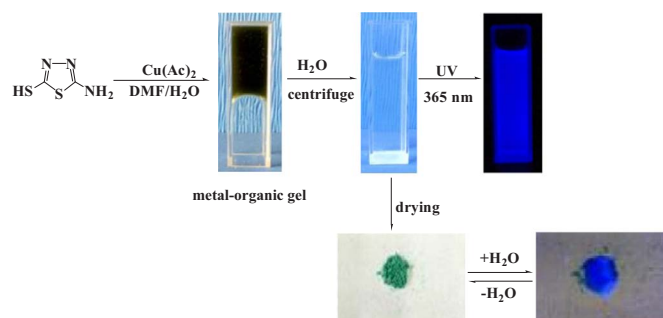
Scheme 1. Photographs of the synthesis of AMTD-Ac-CuNCs and the addition of water under UV (365 nm) lamp.

sample was excited by a 332 nm laser light source. The decay curves were analyzed by FAST 900 software, provided by Edinburgh Instruments along with the fluorophotometer.

2.2. Reagents

All solvents were purified using standard methods. Ethanol was dried over Mg, Acetone was dried over P_2O_5, DMF and THF were dried over finely divided CaH_2, then distilled under argon and degassed before use. 2-Amino-5-mercapto-1, 3, 4-thiadiazole (AMTD) was prepared according to the published procedures [23]. Ethanol (EtOH), N, N-di-methylformamide (DMF), tetrahydrofuran (THF), acetone (ACT), acetonitrile (MeCN) and $CuCl_2$, $Cu(Ac)_2$ were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., China.

2.3. Quantum yield (QY) measurement of AMTD-Ac-CuNCs

The quantum yield (QY) of AMTD-Ac-CuNCs was obtained by comparing the integrated luminescence intensities and the absorbance values of the AMTD-Ac-CuNCs with the standard reference sample. Quinine sulfate in 0.1 mol L^{-1} H_2SO_4 (literature quantum yield 0.54 at 360 nm) was chose as a standard. Absolute values are calculated using the standard reference sample that has a fixed and known fluorescence quantum yield value. Different concentrations of AMTD-Ac-CuNCs and the quinine sulfate were made with the absorbance less than 0.1 at the excitation wavelength of AMTD-Ac-CuNCs. The quantum yield of the AMTD-Ac-CuNCs was determined at the excitation wavelength by the following equation [24]:

$$Q_x = Q_r \frac{I_x}{I_r} \frac{A_r}{A_x} \left(\frac{n_x}{n_r} \right)^2$$

where Q is the quantum yield, I is the measured integrated emission intensity, η is the refractive index of the solvent, and A is the optical density. The subscript "r" refers to standard with known QY and "x" for the sample.

2.4. Prepared AMTD-Ac-CuNCs

AMTD was prepared according to the published procedures [23]. ^{1}H NMR (300 MHz, CDCl$_3$): (d, 1H, 1-SH; d, 1.5, 2H, 2-NH$_2$) (Fig. S1).

10 mL DMF solution of AMTD (0.25 mmol, 0.0332 g) was placed in a beaker. To this, 10 mL aqueous solution of $Cu(Ac)_2$ (0.25 mmol, 0.050 g) was added. This immediately results in a dark blue solution. After little shaking, the mixture was left to stand undisturbed. A dark blue opacity gel appeared after 2 min. After 6 h incubation, 20 mL deionized water added into the gel and stirred continuously for several
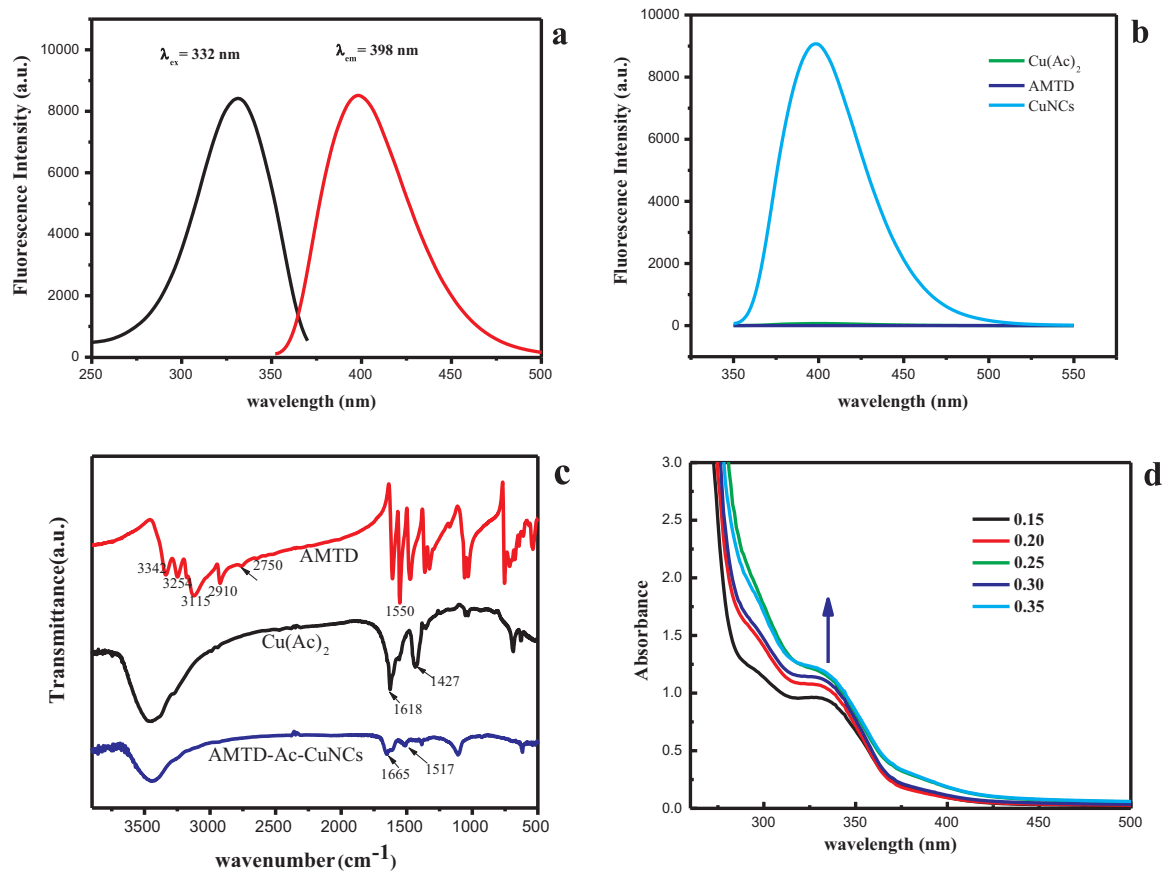
Fig. 1. **(a)** Excitation and emission spectra of AMTD-Ac-CuNCs. **(b)** Fluorescence spectra of AMTD-Ac-CuNCs, AMTD and Cu(Ac)$_2$, respectively. **(c)** FT-IR spectra of AMTD-Ac-CuNCs, Cu(Ac)$_2$ and AMTD. **(d)** The UV–vis absorption spectra of the AMTD-Ac-CuNCs with different concentration (0.15–0.35 mmol L^{-1}).