Facile Synthesis of a Terephthalic Acid-Based Organic Fluorophore with Strong and Color-Tunable Emission in Both Solution and Solid States for LED Applications

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ABSTRACT: Dual-state emission (DSE) fluorophores with strong photoluminescence in both solution and solid states have wide applications in fluorescent probes and photoelectric devices. However, most of the existing DSE fluorophores involve complex synthetic strategies or only one or two emission colors in the solid state, which may hinder their practical applications. Herein, we report a facile and effective strategy to fabricate a kind of novel adjustable DSE fluorophore TPAA–Cu based on the small molecule terephthalic acid (TPA) and ascorbic acid (AA) with CuCl₂ as the catalyst. Not only can the TPAA–Cu solution emit blue, blue-green, and yellow colors depending upon the pH of solution, but also it shows reversible pH-tunable fluorescence colors. More importantly, corresponding TPAA–Cu solid fluorophores with blue, blue-green, and yellow colors can also be obtained with the quantum yields of 16.3, 26.7, and 29.6%, respectively.

KEYWORDS: dual-state emission, terephthalic acid, pH tunable, reversible emission, LED

INTRODUCTION

Organic fluorescence materials, especially those with intense and tunable fluorescence, have received much attention owing to their wide range of applications in the fabrication of organic light-emitting diodes (LEDs), fluorescent sensors, and organic luminescent displays. However, traditional organic fluorophores with a planar polycyclic aromatic structure (e.g., perylene, pyrene, and Nile red) usually emit efficiently in dilute solution but are weak or even nonemissive in the solid state owing to inherent strong intermolecular π⋯π stacking interactions that consume the excitation energy. This phenomenon, referred to as aggregation-caused quenching, limits the practical applications of organic fluorophores in the field of photoelectric devices.

To work out this issue, some approaches, such as aggregation-induced emission (AIE) and crystallization-induced emission (CIE), have been developed to enhance luminescence in the aggregation state. AIE- or CIE-active molecules are practically nonemissive in solutions; however, they can emit a bright fluorescence when aggregated or in the solid state because of effectively suppressing the nonradiative relaxation process. However, AIE-active molecules usually have complex structures, which require intricate synthetic processes and various organic solvents. CIE may be one effective strategy to achieve highly emissive organic fluorophores from simple molecules, such as terephthalic acid (TPA), isophthalic acid, and their derivatives. Unfortunately, long-time growth and poor repeatability of the single crystals may restrict their practical uses.

Recently, dual-state-emission (DSE) fluorophores with strong emission in both solution and solid states have received particular attention for their extensive practical applications. For example, Tang and co-workers provided a new strategy about conjugation-induced rigidity in twisting molecules and designed and synthesized efficient fluorogens in both solution and solid states. Ling et al. developed a series of DSE-active diarylmaleic anhydride derivatives with full-color emission. However, the DSE photoluminescence (PL) molecules still focus on complex molecule structures and may show only one- or two-color luminescence in a solid state. Thus, exploration of facile strategies to construct novel DSE fluorophores with strong and adjustable fluorescence in both solution and solid states still remains a big challenge.

In this study, we report a facile and effective strategy to fabricate the strong and adjustable DSE fluorophores TPAA–Cu based on the small molecule terephthalic acid (TPA) and ascorbic acid (AA) with CuCl₂ as the catalyst to catalyze oxidation of AA to dehydroascorbic acid (DAA). Owing to the catalysis of CuCl₂, not only is the reaction time shortened from 12 to 4 h but also the PL intensities of the TPAA–Cu solution and solid are enhanced by ~2.6 and ~3.0 times than those of TPAA in the absence of CuCl₂, respectively. The TPAA–Cu solution can emit blue, blue-green, and yellow colors...
depending upon the pH of solution. Moreover, it shows reversible pH-tunable fluorescence colors. More importantly, the same kind of TPAA−Cu solid material showing blue, blue-green, and yellow colors can also be obtained by freeze-drying their corresponding solutions, with the quantum yields (QYs) of 16.3, 26.7, and 29.6%, respectively. To the best of our knowledge, such a single DSE material with tunable multicolor fluorescence in both solution and especially solid states has seldom been reported until now. The highly emissive TPAA−Cu fluorescence powders have been further used for successful fabrication of LEDs.

■ EXPERIMENTAL SECTION

Chemicals and Materials. Terephthalic acid (TPA, 99.0%), ascorbic acid (AA, 99.0%), cupric chloride dihydrate (CuCl2·2H2O, 99.9%), nickel(II) acetate tetrahydrate (NiC4H6O4·4H2O, 99.9%), manganese acetate tetrahydrate (MnC4H6O4·4H2O, 99.0%), nickel(II) acetate tetrahydrate (NiC4H6O4·4H2O, 99.9%), and cobalt(II) acetate tetrahydrate (CoC4H6CoO4·4H2O, 99.5%) purchased from Aladdin Chemistry Co., Ltd. Zinc nitrate hexahydrate (Zn(NO3)2·6H2O, 99.0%), ferrous sulfate heptahydrate (FeSO4·7H2O, 99.0%), hydrogen chloride (HCl, 36.0–38.0%), sodium hydroxide (NaOH, 96.0%), ammonia solution (NH3·H2O, 25.0–28.0%), potassium hydroxide (KOH, 95.0%), ethanol (EtOH, ≥99.7%), tetrahydrofuran (THF, ≥99.0%), and N,N-dimethylformamide (DMF, ≥99.6%) were purchased from Sinopharm Chemical Reagent Co., Ltd.

Preparation of Terephthalic Acid@Ascorbic Acid@Cu (TPAA−Cu). TPA (0.18 mmol) was dissolved in 56 mL of NaOH solution (0.01 mol/L) in a conical flask and 2 mL (0.48 mmol) of AA and 2 mL (0.088 mmol) of CuCl2·2H2O aqueous solution were successively added to it; then, the solution was stirred at 20 °C for 4 h to produce a TPAA−Cu solution showing a light green color (pH ∼ 5).

For a comparison, terephthalic acid@ascorbic acid (TPAA) was prepared as follows: TPA (0.18 mmol) was dissolved in 58 mL of NaOH solution (0.01 mol/L) in a conical flask; then, 2 mL (0.48 mmol) of AA was added and the solution was stirred at 20 °C for 12 h to produce a transparent solution of TPAA (pH ∼ 5). TPA was prepared as the control using the same procedure as that for TPAA, just without AA.

Powders of TPAA−Cu, TPAA, or TPA. The TPAA−Cu (TPA or TPAA) solution (2.5 mL) was precipitated by the addition of 1 mL of 0.05 M HCl and maintained still at room temperature overnight. Then, the solution was washed and separated by centrifugation 3 times with 3 mL of water. The precipitates were collected and freeze-dried.
Fabrication and Performance Measurement of LEDs. The monochrome blue, blue-green, and yellow LEDs were packaged using the blue, blue-green, or yellow phosphor TPAA−Cu powders on the commercial 365 nm GaN chips. The commercial blue phosphor BaMgAl10O17:Eu or blue phosphor TPAA−Cu, blue-green and yellow phosphor TPAA−Cu powders were used to package the white-light-emitting diode devices on GaN chips. The phosphors were completely mixed with thermal-curable silicone resin OE-6551A and then coated on the surfaces of the InGaN-based LED chips, which were then conducted at 90 °C for 3 h to generate solid-state blue, blue-green, yellow, and white LEDs.

Characterization. A Shimadzu U-4100 UV−vis spectrophotometer was employed to record UV−vis absorption spectra. The fluorescence spectroscopy and luminescence decay curves were obtained with QM40 from Photo Technology International, Inc. (PTI). The absolute quantum yield (QY) of TPAA−Cu was measured on QM40 equipped with an integrating sphere. The morphology of the TPAA−Cu was observed by a scanning electron microscope (SEM Ultra 55, Zeiss, Germany) at an accelerating voltage of 5 kV and a transmission electron microscope (TEM Tecnai G220, FEI Corp.) at an accelerating voltage of 200 kV. Elemental composition was examined by energy dispersive spectroscopy (EDS) conducted on TEM. X-ray photoelectron spectroscopy (XPS) was performed with a VG ESCA-LAB220i-XL spectrometer. Crystallographic information was collected using powder X-ray diffraction (XRD) (Bruker, D8 Advance X-ray diffractometer, Cu Kα radiation (λ = 1.5406 Å)).

RESULTS AND DISCUSSION

Although TPA has strong and effective intermolecular interactions such as hydrogen bonding in the condensed states to facilitate emission, its solution is actually non-luminescent because of its active vibrational and rotational
dissipations.\textsuperscript{24} However, after TPA, AA, and CuCl$_2$ were added
and stirred in NaOH aqueous solution at 20 °C for 4 h (Scheme 1), the obtained TPAA–Cu solution exhibited strong
yellow emission with a maximum at 555 nm ($\lambda_{ex} = 355$ nm) and a large Stokes shift (200 nm; Figure 1a). To gain insight
into the effects of CuCl$_2$ and AA, TPAA and TPA were prepared under the same reaction conditions but without
CuCl$_2$ for the sake of comparison. It is interesting to see that the TPAA solution emits weak yellow fluorescence when AA is
added into the TPA solution for 12 h, and the emission intensity at 555 nm also increases as the AA concentration is
increased from 0 to 8 mM (Figure S1a), indicating that AA has great influence on fluorescence emission. However, the TPAA
solution did not display any emission under the vacuum state even after 1 week. Therefore, we speculated that it is
dehydroascorbic acid (DAA) rather than AA that is playing a critical role in the fluorescence emission of TPAA–Cu because
AA is unstable in aqueous solution and easily oxidized to DAA in air.\textsuperscript{25,26} Because Cu$^{2+}$ is an active catalyst for the oxidation
of AA,\textsuperscript{25} the reaction time for the synthesis of TPAA–Cu is
significantly shortened from 12 to 4 h (Figure S1b,c). More importantly, the TPAA−Cu solution has similar excitation and emission profiles to those of TPAA and the PL intensity of the former is ∼2.6 times higher than that of the latter (Figure 1b). The original solution of TPAA−Cu was dried in air and then measured by X-ray photoelectron spectroscopy (XPS) scanning. The result shows no satellite peak at around 942 eV for Cu 2p3/2 of Cu2+ ions,27,28 and the two intense peaks at 952.7 and 933.0 eV are assigned to Cu 2p1/2 and 2p3/2,29 respectively (Figure S2a), which indicates that the emission of TPAA−Cu is closely related to the interaction between TPA and DAA, whereas Cu2+ ions only catalyze the oxidation of AA and are reduced into Cu nanoclusters (Cu NCs) with the size of 1.5−3 nm (Figure S2b).

The oxidation reactions catalyzed by the other first transition metal ions, e.g., Mn2+, Fe3+, Co2+, Ni2+, and Zn2+, were also investigated. All of the TPAA−metal solutions display the same emission peak, but TPAA−Cu presents the highest PL intensity in the shortest time (Figure S3a,b). Besides NaOH, other alkalies such as NH3·H2O, KOH were also used to prepare TPAA−Cu with yellow emission (Figure S3c). One can see that the emission peak of TPAA−Cu is independent of alkali sources. This result also excludes the influence of Na+, K+, and NH4+ on the emission color of TPAA−Cu, further confirming that the emission is mainly resulted from the interaction between TPA and DAA. TPAA−Cu from NaOH shows the brightest emission owing to the easy conversion of sodium carboxylate groups to protonated

<table>
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<th>QY [%]</th>
<th>τ [ns]</th>
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<td>555</td>
<td>29.6</td>
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*a* The excitation wavelength is 365 nm. *b* The excitation wavelength is 368 nm.

Figure 7. Fluorescence images of the LEDs from TPAA−Cu powders with the emission centered at 425 nm (a), 485 nm (b), and 555 nm (c). (d) Fluorescence image of the white LED fabricated by mixing the commercialized blue phosphor BaMgAl10O17:Eu and blue-green and yellow phosphor TPAA−Cu. (e) CIE chromaticity coordinates of the blue, blue-green, yellow, and white LED. (f−i) The corresponding emission spectra.
carboxyl groups by the acid treatment of AA,\textsuperscript{30} which benefits radiative transition.

More importantly, the solid fluorescence of TPAA—Cu can be easily obtained by an economical and environmentally friendly acid precipitation method due to the low solubility of TPA in water at 20 °C.\textsuperscript{31} The SEM image shows that the TPAA—Cu powder presents well-defined rod-shaped structures with \(\sim 1\) μm width and 10–30 μm length (Figure 2a,b), and TEM elemental mapping indicates C, O, and negligible Cu elements in this powder (Figure 2c). XRD results demonstrate that TPA, TPAA, and TPAA—Cu are of crystalline nature without DAA and Cu phases probably because of the inappricable amount (Figure 2d), in which all of the diffraction peaks are indexed to TPA (JCPDS, No. 31-1916). The inset of Figure 2d displays that TPAA peaks are shifting to a larger angle due to DAA doping, whereas TPAA—Cu peaks are shifting toward a smaller angle with DAA and Cu doping compared to those of TPA powder. Unlike the TPA powder emitting weak blue fluorescence at 400 nm, the TPAA powder emits red-shifted fluorescence from 400 to 485 nm with an increase of emission intensity as the AA concentration increases from 0 to 8 mM (Figure S4). However, the TPAA—Cu powder emits more bright blue-green fluorescence at 485 nm than that of TPAA (Figure 2e), indicating that TPAA—Cu we present here is a kind of good DSE material with high emission in both solution and solid states. When the TPAA—Cu powder is re-dissolved in the same pH aqueous solution, the PL intensity increases (Figure S5). This is probably because there are two competitive effects between Cu NCs and DAA (Figure S6). When Cu NCs are abundant, the complexation of the oxygen atom and Cu NCs plays a predominant role, depressing the interaction between TPA and DAA molecules.\textsuperscript{32}

This fluorescence should be attributed to the strong intermolecular interactions because TPA and DAA have rich −OH and −C═O functional groups.\textsuperscript{33--35} To prove it, we further investigated the fluorescence of TPAA—Cu in various polar solvents through dissolving the powder into THF, DMF, and EtOH. The solvent has little influence on the absorption of TPAA—Cu, whereas the emission is significantly red-shifted from 448 to 517 nm as the solvent polarity increases from THF to EtOH (Figures 3a and S7), which indicates a typical intermolecular charge transfer character of the compounds.\textsuperscript{36--38} When a small amount of water is added into the TPAA—Cu solution in THF, the emission slightly red-shifts and the intensity obviously deceases because of the increasing solvent polarity. With the increase in the amount of water, it exhibits aggregation-enhanced emission characteristics, and this emission intensity reaches the maximum at 50 wt % water (Figure 3b). However, further addition of water continuously attenuates and red-shifts the emission, which is attributed to the increasing solvent polarity. All of these results demonstrate that these are the strong intermolecular interactions that induce the strong yellow emission. Density functional theory (DFT) calculations in water at the B3LYP/6-31G(d,p) level were carried out using the Gaussian 09 program to further investigate the effect of intermolecular interactions on the optical properties of TPAA—Cu. We took single molecule (TPA), dimer (TPA and TPA), and trimer (TPA, TPA, and DAA) as models to evaluate their molecular orbitals and energy levels for excited states (Figure S8). Compared with a single molecule, the highest occupied molecular orbital of a dimer or trimer moves to downshift slightly, whereas lowest unoccupied molecular orbital of a trimer with the strong electron-withdrawing DAA shows a downshift more severely than that of dimer. Therefore, the energy gap of the trimer is smaller than that of the dimer, which can well explain that the emission of TPAA—Cu or TPAA is red-shifted than that of TPA.

Furthermore, we still investigated the effect of pH on the fluorescence of TPAA—Cu aqueous solution. As shown in Figure 4, both the luminescence and the morphology of the prepared TPAA—Cu exhibit efficient pH-sensitive behavior. It is intuitive to see that the TPAA—Cu solution changes from a turbid to a transparent state under daylight and displays vivid blue-green and yellow emission as the pH varies from 2.0–10 but gradually displays blue emission as the pH > 10 under 365 nm UV light (Figure 4a), which corresponds to the emission spectra in Figure 4b. From the TEM images, one can see that the structure of TPAA—Cu changes from rods to sheets and is even hardly observed as the pH increases to 13.5 (Figure 4c–e). At pH ≤ 4, TPAA is almost insoluble in water;\textsuperscript{17} thus, TPAA molecules are agglomerated into rods, in which powerful and effective intermolecular interactions such as hydrogen bonds,\textsuperscript{30} can effectively suppress the molecular motion and boost the emission. However, the intermolecular interactions between TPA and DAA are decreased at the same time, which decrease the electronic delocalization. Accordingly, it emits bright blue-green fluorescence at 485 nm. With the increase of pH, TPA has a better solubility due to its ionization and forms a sheetlike structure. Such a structural feature can not only keep strong intermolecular interactions between TPA and TPA but also improve the intermolecular interactions between TPA and DAA to enhance the electronic delocalization, causing red-shifted emission at 555 nm. This is also the reason why TPAA—Cu emits yellow color in the solution state but blue-green color in the solid state (Figures 1a and 2e). The blue emission at pH 13.5 is mainly attributed to the following two aspects: (i) TPA is well dissolved in high-pH solution; thus, intramolecular motions (rotations and vibrations) and intermolecular collisions become active, which increase the nonradiative dissipations.\textsuperscript{44,41} (ii) The electronic delocalization may be reduced owing to the hydrolysis of DAA at high pH,\textsuperscript{32} which results in blue-shifted emission. This can also explain why there is an emission peak at 435 nm as AA concentration is 2 and 4 mM (Figure S1a), when the AA concentration is low, which is not enough to reduce the pH of the solution, DAA is hydrolyzed at high pH. The UV–vis absorption peak of TPAA—Cu exhibits a blue shift from 420 to 325 nm when the pH changes from 2.0 to 13.5, owing to varying intermolecular interaction against different pHs (Figure S9).

More importantly, the fluorescence emission can be reversibly switched between pH 2 (blue-green color) and 7 (yellow color) (Figure 5a,b), which suggests that the synthesized TPAA—Cu is highly stable at pH ≤ 7. The blue emission does not reversibly switch, which further proves that the structure of DAA has been destroyed at high pH to generate blue fluorescence. The blue-green and yellow phosphor TPAA—Cu powders are probably used as fuming gas probes (ammonia and hydrogen chloride) due to their pH-responsive and reversible fluorescence. For example, the untreated TPAA—Cu powder shows visible blue-green fluorescence under a 365 nm lamp, which is red shifted to yellow fluorescence when the TPAA—Cu powder is fumed by ammonia gas. The yellow fluorescence can be recovered when the fumed sample is treated with the hydrogen chloride gas.
Consequently, the pH-responsive material TPAA–Cu may have a potential application in fuming gas probes. Because quenching of emission does not happen for TPAA–Cu as shown in Figure 2e, the blue, blue-green, and yellow TPAA–Cu powders can also be obtained by freeze-drying their corresponding solutions (pH 13.5, 2, and 7) (Figure 6a). The optical properties of the different fluorescence in solution and solid states are summarized in Table 1. The maximum emission positions of blue-green and yellow-emitting TPAA–Cu are at 485 and 555 nm, respectively, in both solution and powder because the strong intermolecular interactions are firmly locked in rod- or sheet-based structures. For blue-emitting TPAA–Cu, the PL maximum blue shifts by 10 nm from the solution (435 nm) to the powder (425 nm). The PL QYs of blue, blue-green, and yellow emission of TPAA–Cu are estimated to be 6.3, 16.6, and 21.3% in solution but 16.3, 26.7, and 29.6% in the solid state, respectively, which further illustrates that TPAA–Cu is a good DSE material with multicolor fluorescence in both solution and solid states, and more than 5 ns of fluorescent lifetime (Table 1 and Figure S10).

Because the TPAA–Cu powder we present here has strong and tunable emission as demonstrated above, we further used the TPAA–Cu powders as the color conversion materials to fabricate LED devices, by mixing TPAA–Cu powders with thermal-curable silicone resin and then depositing on a commercial UV chip with the emission centered at 365 nm, as shown in Figure 7a–c. Their corresponding emission spectra are shown in Figure 7f–h. The CIE (Commission Internationale de L’Eclairage 1931) color coordinates of the synthesized phosphors blue, blue-green, and yellow are at A (0.23, 0.26), B (0.28, 0.50), and C (0.41, 0.48), respectively, which show high color saturation of blue-green and yellow emission but weak color saturation of blue emission (Figure 7e). The white LED based on the blue, blue-green-, and yellow-emitting TPAA–Cu powders was also fabricated and shows color rendering index (CRI) of 74.2 and color coordinates at (0.33, 0.38), which is very close to the ideal CIE for pure white emission (0.33, 0.33) (Figure S11a). Unfortunately, its luminous efficacy is only 0.35 lm/W, which may be caused by the weak color saturation of blue-emitting TPAA–Cu (Figure S11b). When blue-emitting TPAA–Cu is replaced by commercial blue phosphor BaMgAl\textsubscript{10}O\textsubscript{17}: Eu to mix with our blue-green- and yellow-emitting TPAA–Cu powders, the as-fabricated white LED, shows the CRI of 85.5, the luminous efficacy of 3 lm/W, and color coordinates at (0.33, 0.36) (Figure 7d,e), and its emission spectrum is similar to that of sunlight (Figure 7i). The correlated color temperature (CCT) of the white LED is 5482 K at the coordinate (x, y) = (0.33, 0.36). To examine optical stability of white LED, the CIE, CCT, and CRI were measured at different working currents. As shown in Table S1, with the increase of current from 20 to 180 mA, a minor change of CIE from (0.34, 0.37) to (0.33, 0.35) was observed, which was very close to the ideal CIE (0.33, 0.33). All of these results indicate the great promise of TPAA–Cu we present here as an efficient blue-green and yellow phosphor to construct mild white LED.

**CONCLUSIONS**

In summary, we have successfully designed and synthesized a novel colorful DSE fluorophore TPAA–Cu based on simple small molecules TPA and AA with Cu\textsuperscript{2+} ions as the active catalysts by a facile and green synthetic approach. The obtained TPAA–Cu displays a good pH-sensitive behavior and blue, blue-green, and yellow emission colors by simply adjusting the pH of solution. Correspondingly, the blue, blue-green, and yellow TPAA–Cu florescent powders can be easily obtained with the high PL QYs of 16.3, 26.7, and 29.6%, respectively, and further successfully employed as phosphors to fabricate monochrome and white LEDs. We believe that this simple and efficient strategy of regulating the fluorescence properties of simple molecules in solution and solid states by varying the intermolecular interaction may provide a means to construct a wide variety of colorful DSE materials.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b13352.

Photoluminescence spectra of TPAA and TPAA–Cu solution; XPS and TEM images of the Cu NCs; density functional theory (DFT) calculations; absorption spectra of TPAA–Cu solution; luminescence lifetime of TPAA–Cu solutions and powders; and performance of the white light-emitting diode fabricated by blue (or BaMgAl\textsubscript{10}O\textsubscript{17}:Eu), green, and yellow phosphor TPAA–Cu (PDF)

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**Notes**

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