



Multiple-color AIE coumarin-based Schiff bases and potential application in yellow OLEDs



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ABSTRACT

Three new coumarin-based derivatives with similar molecular structure were synthesized through a simple Schiff base reaction and their fluorescent properties were investigated in detail. Among of the compounds showed aggregation-induced emission (AIE) characteristics and high quantum efficiency (Φ_F), of which compound **1** powder showed the strongest emission peak 570 nm ($\Phi_F = 25.3\%$), compound **2** solid exhibited 610 nm fluorescence emission peak ($\Phi_F = 3.3\%$), while the maximum emission wavelength of compound **3** powder red-shift to 640 nm ($\Phi_F = 16.8\%$). Meanwhile, compounds **1–3** showed long fluorescence lifetimes with respective 8.86 μ s, 8.97 μ s and 8.51 μ s. The appearance of fluorescence properties can be attributed to efficient the excited state intramolecular proton transfer (ESIPT) and the twisted intramolecular charge transfer (TICT). Furthermore, due to the good luminescent properties, high stabilities and the large Stokes-shifts, the three compounds were ideal candidates for promising applications in organic lightemitting diodes (OLEDs).

1. Introduction

Coumarins, with the structure of benzo- α -pyrones, possess a great many advantages including tunable emission color, considerable fluorescence quantum yield, large Stokes shift, and excellent light stability. Therefore coumarin derivatives have been extensively used in fluorescent dyes, medicine, fragrance, cosmetics and electroluminescence [1–7]. However, coumarin dyes and their derivatives also have an obvious disadvantage called aggregation-caused quenching (ACQ) effect in the aggregated state, which commonly induces to the reduced or quenched fluorescence intensity of a fluorophore by forming excimers or exciplexes between the fluorogen molecules in the excited and ground states [8–10]. Account of such a deleterious effect, their further development been have limited heavily in the real applications of fluorescence sensor and OLEDs. In recent years, materials with AIE or AIEE (aggregation-induced enhanced emission) characteristics have drawn considerable attention to provide a revolutionary approach to solve the problem of ACQ, which reveal strong fluorescence emission in the aggregated state but weak or even not fluorescent intensity in good dissolving solution [11–14].

The AIE-active materials are revolutionary for scientists to construct fluorescent sensors and OLEDs, as they can be directly utilized in the state of aggregation without quenching in the emission intensity. The AIE-active compounds have been used in a wide range of applications, such as OLEDs, liquid crystal displays, optical waveguides,

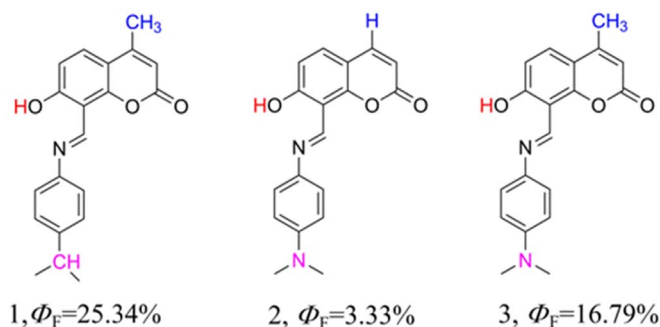
bio-imaging, and fluorescent sensors and so on [15–19]. Among of AIE mechanisms based on RIR (restriction of intramolecular rotation), TICT, *cis-trans* isomerisation and so on [20–23], ESIPT has long been one of the most fundamental issues.

The ESIPT processes always relate to proton of –OH transfer from a pre-existing hydrogen chemical bond, inducing a proton-transfer tautomer between ketone and enol forms in the excited state. Owing to the fast structural transform, the tautomer displays different photophysical properties from that of the original species, providing remarkable versatility in various applications of emitting material, light filter, scintillation radiation source, molecular recognition, etc [24–28]. ESIPT-based fluorophores generally display excellent emission performance in the light of dual emission, large Stokes shift as well as good photostability. The unique photophysical performances of the ESIPT luminophores bring their potential applicability in photoelectricity materials. Nevertheless, poor fluorescence quantum efficiencies and short decay lifetime in the aggregative state are the weaknesses of the existing ESIPT-based solid light-emitting materials [29–32].

In this work, we developed a series of AIE coumarin-based Schiff bases with high quantum yield and long decay lifetime that undergoes ESIPT and TICT mechanisms (Scheme 1). The relationship between the molecular structures and their fluorescence properties were also investigated. In addition, for the first time, an efficient coumarin-based OLEDs was fabricated and realized yellow light with CIE coordinates of (0.51, 0.49).

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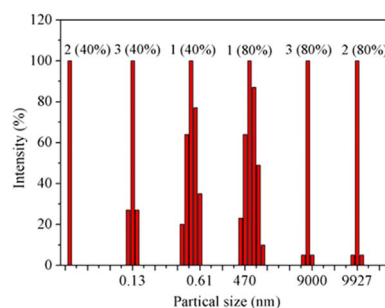
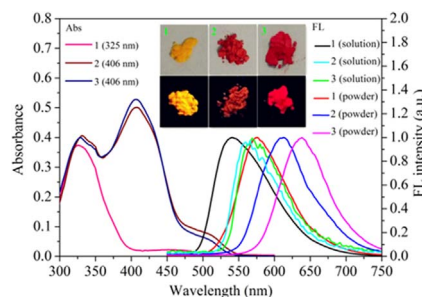


Scheme 1. The molecular structures of compounds 1–3.

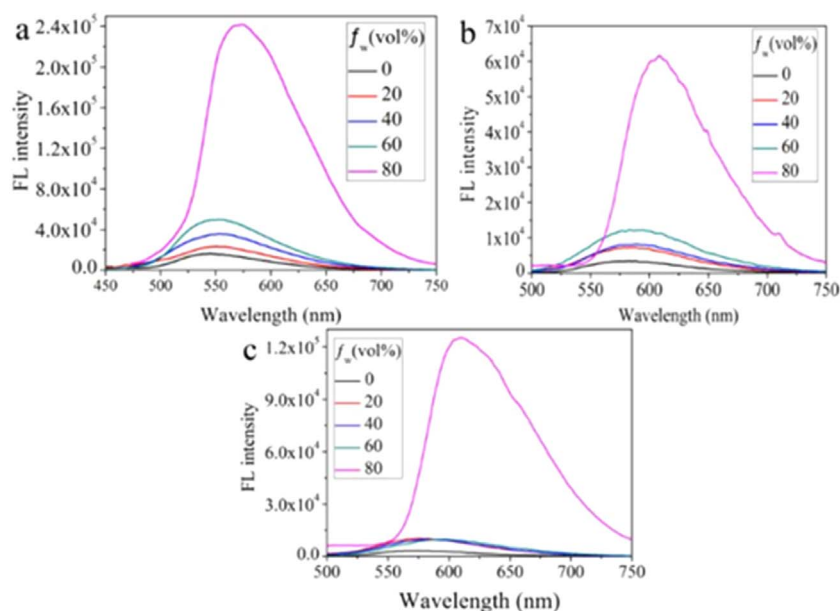
2. Results and discussion

The AIE characteristics of compounds **1–3** as a function of the water fraction (f_w) in a water–CH₃CN mixture were examined because it is well dispersive in common organic solvents but undissolved in water and **1–3** molecules must gather in water/CH₃CN mixtures with a high f_w . As shown in Fig. 1a, the emission intensity of compound **1** was weak in CH₃CN and increased relaxedly until f_w reached 80%. The emission maximum increased by 15-fold from the CH₃CN solution to 80% aqueous mixture. **2** and **3** behaved similarly (Fig. 1b and c): they exhibited weak emission intensity in CH₃CN solution. When f_w were raised to 80%, their fluorescence intensities enhanced dramatically, which increased by 20-fold and 37.5-fold, respectively. The changes of fluorescence spectra in water/CH₃CN mixtures indicated that compounds **1–3** show typical AIE characteristics [33,34]. The aggregation of **1–3** was also monitored by dynamic laser light scattering (DLS) measurements. The particle size distributions of **1–3** (30 μ M) in aqueous solution at different volume ratios f_w are shown in Fig. 2. Obviously, no particle could be observed for **1–3** when f_w is lower 40%. Until f_w up to 40%, particles of nanometer sizes were detected at 0.61 nm (compound **1**), 0.1 nm (compound **2**) and 0.13 nm (compound **3**), respectively. When f_w reached 80%, the aggregate sizes of **1–3** increased to 477 nm, 9875 nm, 8965 nm, respectively.

The absorption and normalized fluorescence (FL) spectra of **1–3** in CH₂Cl₂ solution at a concentration of 1 μ M and solids emission spectra are shown in Fig. 3. The absorption maximum of compounds **1–3** located at 325, 406 and 406 nm, and corresponding emission maximum are 535 nm, 555 nm, 560 nm in solution, and 580 nm, 610 nm, 640 nm

Fig. 2. Dynamic light scattering (DLS) results of **1–3** in aqueous solution of 40% and 80% water/CH₃CN (v:v). Condition: The concentration of **1–3** is 30 μ M.Fig. 3. Absorption and emission spectra of compounds **1–3**. Inset: their photographs under daylight and UV irradiation at 365 nm.

in aggregate state, respectively. Comparing the maxima emission wavelength of these compounds, it's clear that the emission spectra show obvious red-shift from **1** to **3** with the extension of the π -systems and the strong electron donating ability. The different spectral properties can be assigned to the synergistic effect of ESIPT and TICT. Firstly, the essential condition for ESIPT action is the formation of an intramolecular hydrogen bond (H-bond) between the proton donor (–OH) and the proton acceptor (=N–) groups in close enough with each other in one molecule. In good dissolving solution, the molecules of **1–3** undergo continuous movements including C=N isomerization and intramolecular rotation, which seriously limit and prevent ESIPT process. In aggregated states, the fluorescence emission of **1–3** rose dramatically owing to the restricted intramolecular movements and the activated ESIPT. The ESIPT molecules can reveal a large Stokes shift caused by

Fig. 1. Fluorescence emission spectra of **1–3** in water/CH₃CN mixtures with different f_w at excitation wavelength of 406 nm. The concentrations of **1–3** are 30 μ M.

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