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An aggregation-induced emissive NIR luminescent based on ESIPT and TICT mechanisms and its application to the detection of Cys

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ABSTRACT

A series of red to near-infrared (NIR) emissive organic compound **1**–**3** based on the 2′-hydroxyacetophenone derivatives were synthesized through a mild condensation reaction, which exhibit typical AIE properties and long fluorescence lifetime in an aggregated state. Compound **2** displays the highest quantum yield (Φ_f) of 0.49 among the reported organic compound with an emission maximum (λ_{em}) 700 nm. Comparison between the bright emissive compound **2** and the weak fluorescence compounds **1** and **3** clearly gives evidence that a subtle structure modification can arouse great property changes, which is instructive in designing new high-efficiency organic luminescent materials. In demonstration of the potential application of these new fluorescence dyes, Probe **4** that is capable of unique detecting Cys in water media is also reported.

1. Introduction

The NIR emitting materials are highly potential demanding in the fields of light-emitting diodes, optical communication devices, biological imaging, and fluorescent Probes [1–8]. Up to now, much effort has been made to develop NIR materials using osmium, iridium, zinc, or platinum metal–organic complexes [9–11]. However, high costs, limited resources and environmental pollution of heavy metal materials remain challenges for their application in long-term mass production. Therefore, it is really significant to design metal-free organic NIR–fluorescent dyes. NIR fluorophores are commonly constructed by adopting large conjugated systems or strong electron donor (D) and acceptor (A) skeleton. Most of these organic molecules, however, suffer from the serious aggregation caused fluorescence quenching (ACQ) effect due to either attractive dipole–dipole interactions or effective intermolecular π-π stacking [12–17]. Therefore, most of the reported efficient NIR fluorophores emit strong fluorescence in dilute solutions but exhibit no or weak fluorescence in the aggregate state. These negative influences of ACQ effect greatly obstruct their practical applications of luminescent materials in optoelectronics and fluorescent sensors, which require organic materials to be films or high concentration [18,19].

To solve effectively the thorny ACQ problem of many widely used luminescence materials, an aggregation-induced emission (AIE) phenomenon was reported by Tang's group in 2001 year [20]. It was found that pentaphenylsilole derives were hardly emissive in solutions, but their aggregates or solid states were strongly luminescent because of the restriction of intramolecular rotations process. AIE fluorogens have been successfully put into application in the construction of photoelectric devices, bioimaging systems, and chemical sensors [21–24]. In recent years, AIE mechanisms involving restriction of intramolecular rotation (RIR), twisted intramolecular charge transfer (TICT), *cis-trans*isomerisation, excited-state intramolecular proton transfer (ESIPT) have been reported [25]. Many different kinds of AIE molecules including from blue to orange fluorescent organic compounds have been developed. Nevertheless, research work about deep-red emission fluorophores, especially about NIR-luminescent AIE-active organic molecules is reported rarely [26–28].

ESIPT-active luminophors generally display large Stokes shifts, which is important to construct long-wavelength organic fluorescent molecules [29–33]. On the other hand, introducing D or A groups into a conjugated fluorogen to controlling the separation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which can result in a progressive red shift of emission by driving up the HOMO energy level and pull down LUMO energy level [34–37]. Following these considerations, we constructed red and NIR-emitting compounds **1**–**3** based on ESIPT mechanism and twisted intramolecular-charge-transfer (TICT) systems containing spatially separated donor

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(tertiary amino groups) and acceptor moieties (2'-hydroxyacetophenone). The relationship between emission properties and structures has been carefully investigated. Notably, compound **2** displays the strongest fluorescence ability and thus its potential as candidate in Cys fluorescent Probe has been systematically exploited.

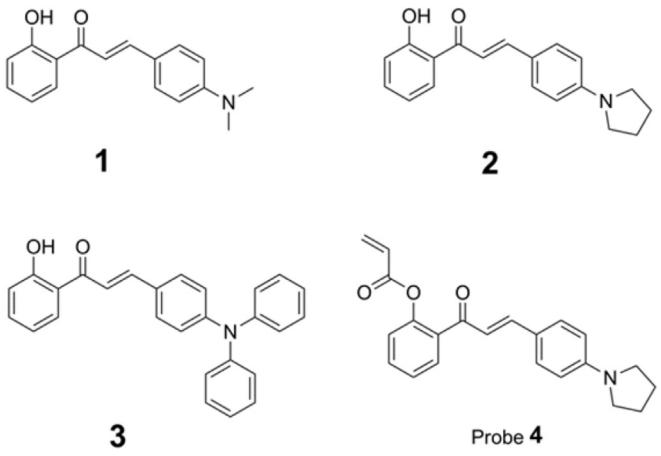
2. Fluorogen preparation

The pre-requisite for ESIPT is the presence of an intramolecular hydrogen bond (H−bond) between the proton donor (−OH) and the proton acceptor (−C═O) groups in close proximity to each other in a molecule, therefore, ESIPT-active 2′−Hydroxyacetophenone moiety was employed to construct NIR-emitting compounds **1**–**3**. One the other hand, *N*, *N*-dialkyl moiety is commonly used as donor to construct red-emitting fluorogens as is well-known. However, one key problem is fluorescence quenching phenomenon, which is caused by the TICT acts. In the TICT state, a dialkylamino donor twists out the fluorophore scaffold by approximately 90° upon photoexcitation, forming a non-emissive and highly reactive chemical species [38,39]. In order to avoid TICT formation, Lavis et al. changed *N*, *N*−dialkylamino substituents to four-membered azetidine rings in several chemical families of fluorophores, such as rhodamines, rhodols, and coumarins [40]. They demonstrated that the azetidine ring simultaneously improves dye brightness and photostability. In this paper, we chose five-membered azetidine ring and diphenyl moieties replace dialkylamino substituents to investigate the effect of azacyclic substituents on minimizing TICT and disclose the effect of strong D−A structure on the emission. Consequently, the aziridine ring leads to improved brightness in a range of fluorophores, in conjunction with enlarged Stokes shifts. Compounds **1**–**3** (Scheme 1) are synthesized in a facile synthetic route according to the literature [41]. In brief, the target molecules were synthesized by a simple one-step condensation reaction of the 2′-Hydroxyacetophenone moiety with 4−(Dimethyamino)benzaldehyle, 4−(1−Pyrrolidinyl)benzaldehyde and 4−Diphenylaminobenzaldehyde moieties, respectively. The experiment details and structure characterization data are described in the Supporting Information (Scheme S1).

3. Result and discussion

3.1. AIE behavior

The fluorescence characteristics of compounds **1**–**3** (30.0 μM) as a function of the water-fraction (f_w) in an EtOH−water mixture were recorded with EtOH being the good solvent and water acting as a nonsolvent at an excitation wavelength (λ_{ex}) of 470 nm. As shown in Fig. 1, the fluorescence emission of compound **2** was weak in EtOH and increased slowly until $f_w$reached 60%. The fluorescence was weaken because that ESIPT was damaged for intramolecular movements freely including phenyl rotation, C═N isomerization and TICT. Afterwards, the fluorescence emission rose swiftly because of the restriction of intramolecular movements in aggregate state, which increased by 5.5-fold from the EtOH solution to 90% aqueous mixture. Meanwhile, the emission peak red shifted 75 nm from 575 nm to 645 nm. Compounds **1** and **3** behaved similarly (Fig. S12 and S13): they exhibited weak fluorescence emission in EtOH solution and in EtOH/water mixtures with f_w lower than 60%. When f_w were beyond 60%, their fluorescence emissions enhanced remarkably, which increased by 2.2− and 3.2−fold from the EtOH solution to 90% aqueous mixture, respectively. Additionally, the emission peak of compound **1** moved to 650 nm from 575 nm, while compound **3** exhibited different emissions action: it shows little blue shift in the aggregated state. The changes of fluorescence spectra in EtOH/water mixtures indicated that compounds **1**–**3** show typical AIE characteristics.



Scheme 1. The molecule structures of compounds **1**–**3** and Probe **4**.

In order to further investigate the aggregation process of f_w–dependent optical properties, the absorption of **1**–**3** was measured (Fig. 2). In ethanol, **1**–**3** showed absorption peaks at 445, 433, and 435 nm, respectively. However, in a poor solvent of 90% water/EtOH, the fine structures of absorption spectra disappeared and level-off tails in the visible region could be clearly observed, which is believed to be due to the light scattering of aggregate suspensions. Besides absorption spectra, more direct evidence for the aggregation of **1**–**3** in poor solvents was obtained from dynamic light scattering (DLS) and transmission electron microscope (TEM) measurements. As shown in Fig. 3, no particle could be observed for **1**–**3** in ethanol, while the particle sizes of **1**–**3**were found to be 200, 500, 8000 nm, respectively in 80% water/EtOH. Interestingly, microstructures of compounds **1**–**3** that formed from H_2O/C_2H_5OH (f_w = 70%) mixture evaporation were also clearly observed by TEM at scale bar 1 μm. As shown in Fig. 4, crystal plated of compound **1** several micrometer in length were observed for the cases of 70% water fraction mixtures (Fig. 4a), while the microstructures of compound **2** were more regular in shape (Fig. 4b). However, for compound **3**, there is only irregular shape of aggregates (Fig. 4c).

We also studied the emission behavior of **1**–**3** in the solid state. As shown in Fig. 5a, the emission peaks of compounds **1**–**3** is at

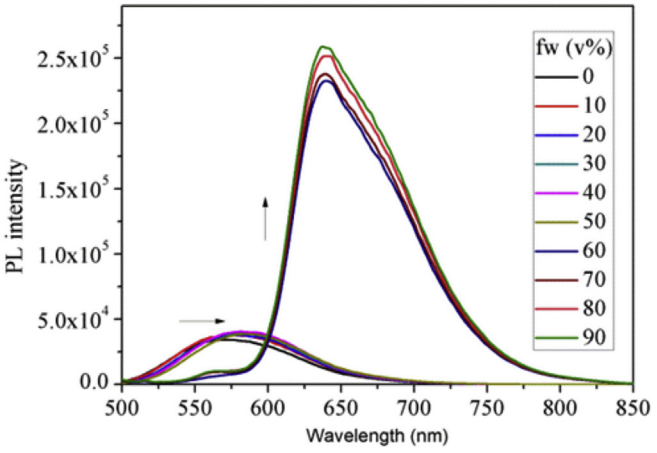


Fig. 1. Fluorescence emission spectra of 2 in EtOH/water mixtures with different fw. Conditions: the concentrations of 2 are 30.0 μM. The excitation wavelength is 450 nm.