Multi-responsive red solid emitter: Detection of trace water and sense of relative humidity

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ABSTRACT A multi-responsive D-A type compound (CYQ) based on pyrone and triphenylamine was designed and successfully synthesized. The target compound exhibited distinct aggregation-enhanced emission (AEE) effect. Solvatochromic experiment and density functional theory (DFT) indicated CYQ possessed excellent intramolecular charge transfer (ICT) ability. Besides, its mechano-fluorochromic property (MFC) was found with a 37 nm red-shift. Powder wide-angle X-ray diffraction (PXRD) and differential scanning calorimetry (DSC) measurements were performed to demonstrate the transformation from the crystalline to amorphous states upon grinding. Surprisingly, CYQ displayed a hypersensitive response to trace water in organic solvents with an excellent detection limit as low as 0.0096% in tetrahydrofuran (THF). Furthermore, it was found that the fluorescent intensity of CYQ declined progressively upon humidity rise, and its color change can be witnessed by naked eyes. Therefore, the relative humidity (RH) sensing strategy guarantees the AIEgen to become a colorimetric sensor under various conditions.

Keywords: aggregation-enhanced emission, mechano-fluorochromic, trace water, humidity

INTRODUCTION

With their wide applications in bio-sensors [1], OLED devices [2], pH indicators [3] and pressure sensors [4], designing and synthesizing organic fluorescent probes in response to unique external stimulation has been a hot spot. However, most of these fluorophores suffer from an “aggregation caused quenching” (ACQ) effect, which severely inhibits their applications in practical situations. Excitingly in 2001, aggregation induced emission (AIE) phenomenon was discovered as a remedy to overcome the above question [5]. Then, numerous templates based

on AIE enrich the family of smart materials [6–8]. Among them, red-emitting fluorophores are highly desirable for their distinctive applications in chem- and bio-sensors [9].

Water plays an important role in many water/oxygen free industrial processes. For example, it is detrimental to synthesizing Grignard reagent in the presence of water, only because trace amount of water can reduce the yield and even quench the reaction. Conventional Karl Fischer method used for water detection usually exhibits some drawbacks, such as time-consuming procedure, costly instrumentation and instability [10]. At this point, AIE compounds were reported as alternatives in water-sensing programs [11]. However, trace water detecting strategies among AIEgens are extremely limited by their poor sensitivity. Therefore, developing an AIE probe with high sensitivity to trace water is urgently desired.

As we know, fluorophores based on D-A skeleton are characterized by their explicit intramolecular charge transfer (ICT) characteristic and strong response to different polarity. Under this circumstance, water affects fluorescent behaviors owing to its high polarity. Herein, our red-emitting compound bearing intensive D-A architecture was conceived as a promising candidate for water detection. This multi-responsive compound displayed aggregation-enhanced emission (AEE) effect accompanied with excellent solvatochromic and mechano-fluorochromic (MFC) properties. Moreover, trace water detecting experiment was implemented in three water-miscible organic solvents with an excellent detection limit as low as 0.0096% in tetrahydrofuran (THF). Besides, relative humidity (RH) sensing strategy ensures that the AIEgen can be a colorimetric sensor under various conditions.

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EXPERIMENTAL SECTION

Materials and characterization

^1H NMR and ^{13}C NMR were performed by Bruker Avance 600 MHz spectrometer. High resolution mass spectrum was recorded on a Bruker Paltonicsmicro TOF-Q II instrument. Infrared radiation (IR) data were collected on a Nicolet 380FT-IR spectrometer. UV-vis spectra were implemented on Evolution 300 UV-vis spectrophotometer. Liquid and solid photoluminescence (PL) spectra were operated on Hitachi F-2500 spectrophotometer and Horiba Jobin Yvon Fluorolog-3 spectrophotometer, respectively. Emission quantum yields (Φ_{p}) were determined by a FluoroMax-4 (Horiba Jobin Yvon) fluorometer equipped with an integrated sphere. Powder wide angle X-ray diffraction (PXRD) was obtained on a Miniflex 600 Powder X-ray Diffractometer of Rigaku. Differential scanning calorimetry (DSC) experiments were implemented using a Perkin-Elmer at a heating rate of $10^\circ\text{C min}^{-1}$. Thermal gravimetric analysis (TGA) was measured on an STA 409PC with a heating rate of $10^\circ\text{C min}^{-1}$ from room temperature to 800°C in a stream of N_2 (40 mL min^{-1}). All the above experiments were performed at room temperature.

General synthetic procedures

2-(2,6-dimethyl-4H-pyran-4-ylidene)-1H-indene-1,3(2H)-dione (intermediate 1)

To a round bottle flask containing 2,6-dimethyl-4-pyrone (0.31 g, 2.50 mmol) and 1H-indene-1,3(2H)-dione (0.44 g, 3.00 mmol), acetic anhydride 10 mL was added accordingly. After the mixture was heated under reflux for 6 h, pH was adjusted to 7. The mixture was extracted with ethyl acetate ($3\times 30\text{ mL}$) and the organic phase was washed with brine ($5\times 50\text{ mL}$), and then concentrated to obtain the crude product. Column chromatography (ethyl acetate/petroleum ether, 1/10, v/v) was performed to give the yellow intermediate 1.

2-(2,6-bis((E)-4-(diphenylamino)styryl)-4H-pyran-4-ylidene)-1H-indene-1,3(2H) dione (CYQ)

A mixture of intermediate 1 (0.63 g, 2.50 mmol) and 4-(diphenylamino)benzaldehyde (4.1 g, 15 mmol) was added to CH_3CN (15 mL). Piperidine (3.8 mL) was added subsequently. The mixture was heated under reflux in N_2 for 24 h. After cooling to room temperature, the crude product was purified by column chromatography (dichloromethane, DCM) to yield the target compound, red solid (1.18 g), 62% yield. m.p. $281\text{--}283^\circ\text{C}$. ^1H NMR

(CDCl_3 , 600 MHz) δ (ppm): 8.43 (s, 2H), 7.77–7.75 (m, 2H), 7.61–7.59 (m, 2H), 7.47 (s, 1H), 7.44–7.43 (d, $J=8.4\text{ Hz}$, 5H), 7.33 (s, 2H), 7.31 (s, 4H), 7.30 (s, 2H), 7.16–7.15 (d, $J=7.8\text{ Hz}$, 8H), 7.12 (s, 1H), 7.11 (s, 2H), 7.09 (s, 1H), 7.06–7.05 (d, $J=9\text{ Hz}$, 4H), 6.77 (s, 1H), 6.76 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 192.78, 160.61, 149.61, 148.48, 146.90, 140.79, 136.01, 133.07, 129.53, 128.87, 128.22, 125.43, 124.08, 121.87, 121.25, 117.57, 108.44. HRMS (ESI): calcd. for $\text{C}_{54}\text{H}_{38}\text{N}_2\text{O}_3$: 763.2882 ($\text{M} + \text{H}^+$), found 763.2954. IR (KBr, cm^{-1}): 3,433, 1,691, 1,645, 1,589, 1,494, 1,401, 1,322, 1,278, 1,237, 1,167, 949, 749, 698.

RESULTS AND DISCUSSION

The target compound CYQ was easily obtained from the condensation of pyrone with intermediate 1 [12]. General synthetic route and the structural characterization of CYQ were summarized in the supporting information (Scheme S1, Figs S1–S4). The absorption spectrum of CYQ in DCM is shown in Fig. 1b. It presents two independent peaks. The peak centered at 360 nm can be attributed to the $\pi\text{--}\pi^*$ transition. Meanwhile, the one located at 525 nm was ascribed to the ICT transition due to the strong push-pull effect [13].

The AEE process was confirmed in DCM-hexane system. As we can see in Fig. 1c, in the molecularly dissolved solution (DCM), CYQ emitted weak red fluorescence. In this regard, the molecules exhibit a random torsion pattern, which leads to non-radiative pathway and weak fluorescence [14,15]. However, more distinctive red fluorescence was recorded upon addition of poor solvent (hexane) until reaching the maximum PL intensity at 50% *n*-hexane fraction (Φ_{p} , 33.93%). In this sense, the restriction of intramolecular rotation (RIR) plays a leading role. When hexane was added, the free rotation pathway was limited to some extent. In this case, the non-radiative decay was blocked, giving rise to higher PL intensity [16]. Conversely, the fluorescent intensity began to decline along with the increase of *n*-hexane fraction (Fig. 1d) which may be attributed to the formation of amorphous aggregates [17]. Interestingly, the whole PL profile displayed a hypochromatic tendency. This phenomenon may be ascribed to the repressed ICT process induced by reduced polarity. Moreover, the distorted molecular skeleton aroused by aggregation may also contribute to the blue-shifted spectrum.

Moreover, ICT process was confirmed by solvatochromic experiment. As shown in Fig. 2a, the fluorescent peak of CYQ appears at 566 nm in cyclohexane and displays a bathochromic tendency along with the in-

Figure 1 (a) Chemical structure of **CYQ**; (b) UV-vis absorption spectra of **CYQ**; (c) PL spectra in DCM-hexane mixtures. The inset depicts the emission image under 365 nm UV illumination; (d) changes in PL intensity. Error bars were calculated using Origin 8.

creasing of solvent polarity, with up to 100 nm shift in DMF. According to Guan *et al.* [18], molecules based on D-A type favor charge separation which can be stabilized by solvation, and trigger the reduction of energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Because of the above driving force, a red-shifted PL spectrum was observed, accompanied with the enhanced polarity. This superb linear color change characteristic (Fig. 2b) makes it possible for **CYQ** to serve as a promising candidate to distinguish different solvents [19]. In addition, the spatial distributions of HOMO and LUMO were calculated with density functional theory (DFT). As depicted in Fig. 2c, the HOMO of **CYQ** is exclusively located in the triphenylamine unit while the LUMO orbits are shifted to the pyrone core. This prominent charge separation provides compelling evidence to the above solvatochromic studies. Collectively, an unambiguous ICT transmission through the entire system is anticipated.

The mechanochromic property of **CYQ** (Φ_f , 7.85%) was

examined in Fig. 3a. A conspicuous red-shifted MFC feature can be witnessed, which displays an alternative fluorescence from red to purplish red. The 37 nm shift may be attributed to the planar structure upon grinding. Besides, the excellent ICT process may promote the MFC behavior [20].

TGA was carried out to verify the high thermal stability of **CYQ**, losing 5% of its weight at 410°C (Fig. S5). To obtain a further understanding of the MFC nature, PXRD and DSC measurements were performed. As shown in Fig. 3b, the sharp scattering peaks indicate a regular crystalline structure. However, for the pattern of the ground solid, most diffraction peaks remarkably weakened or disappeared, indicating an amorphous state [21]. The thermal property of **CYQ** was analyzed by DSC. As demonstrated in Fig. 3c, no additional peaks can be detected for the original sample except for the sharp melting peak centered at 281°C, while for the ground solid, the exothermic transition shoulder at 168°C could be ascribed to the cold-crystallization process upon annealing [22].

Figure 2 (a) PL spectrum in cyclohexane, toluene, THF, DCM and *N,N*-dimethylformamide (DMF); (b) plots of maximum wavelength vs. solvent polarity parameter (Δf); (c) B3LYP/6-31G(d) calculated molecular orbital amplitude plots and their calculated HOMO-LUMO energy gap (eV).

Figure 3 (a) Normalized PL emission spectra of CYQ upon grinding. The insets depict the fluorescence images (original and ground state) taken under 365 nm UV lamp. (b) PXRD patterns and (c) DSC curves of original and ground states.

On account of the specific D- π -A skeleton and superb ICT characteristic, it is possible for the target compound to present hypersensitive behavior in response to different polarity. Under this circumstance, three water-miscible

organic solvents were chosen as representatives. As shown in Fig. 4a, the fluorescence intensity in THF (Φ_f , 27.13%) exhibited a descending tendency along with increasing water fraction. A drastic declination to 47% was

Figure 4 PL spectra of CYQ in (a) THF, (b) acetonitrile, and (c) acetone/water mixtures; (d) emission images in 0%–10% water fraction under 365 nm UV illumination.

displayed when the water fraction was reduced to 1.8% (v/v), whereas this downtrend became moderate when the water content exceeded 3.0% (v/v). Meanwhile, the fluorescent intensity of the target compound revealed a linear relationship and issued an excellent detection limit of 0.0096% (Fig. 5a). Unsurprisingly, trace water detection experiment displayed a similar trend in acetonitrile/acetone-water system and yielded a detection limit as low as 0.0191% and 0.0123%, respectively (Fig. 5c, e). Moreover, the fluorescent intensity was performed to show the similar downtrend (Fig. 5b, d, f). In order to demonstrate the effect of trace water, fluorescent images were taken for further discussion. As illustrated in Fig. 4d, a gradual bathochromic emission accompanied with a plunging PL intensity was clearly observed when the water fraction increased from 0% to 10% (v/v). All of the above characteristics pave the way for constructing a highly sensitive sensor for trace water in water-miscible organic solvents.

In addition, the RH sensing strategy was performed at 10%, 24%, 43%, 63% and 96% RH content. As we can see in Fig. 6, the fluorescent intensity declined progressively with humidity rise. As humidity increases, water mole-

cules are gradually absorbed by the target compound. At this point, ICT process was triggered by the higher ambient polarity, which resulted in lower emission intensity. Interestingly, these calibration lines exert linear relationship corresponding to the relevant RH, indicating a great possibility in serving as a colorimetric sensor under various conditions.

CONCLUSION

In this work, we outlined a multi-response red-emitting pyrone derivative characterized by AEE property. Moreover, solvatochromic experiment was implemented to examine the ICT process which was manifested by DFT calculation. Besides, our AIEgen exhibited substantial quenching along with fluorescent color change from red to purplish red upon grinding. The mechanism of this 37 nm MFC feature was demonstrated by XRD and DSC experiments. Moreover, owing to the explicit ICT effect, CYQ was chosen as a trace water sensor in commonly used water-miscible organic solvents. In particular, the detection limit as low as 0.0096% in THF indicates the practical application in daily lives. Furthermore, the solid state CYQ can also serve as a linear colorimetric sensor

Figure 5 Detection limits in (a) THF, (c) acetone and (e) CH₃CN. PL spectrum of CYQ in (b) THF/water, (d) acetone/water and (f) CH₃CN/water. Error bars were calculated using Origin 8.

Figure 6 (a) PL emission spectra under different RH conditions; (b) plots of relative humidity *versus* maximum emission. Error bars were calculated using Origin 8.

under different RH conditions.

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Author contributions Cao Y carried out the experiments with assistance of Chen L. All authors discussed the results and commented on the manuscript and Cao Y wrote the manuscript.

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Supplementary information Supporting data are available in the online version of the paper.

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刺激响应红色发光体: 痕量水及相对湿度的检测

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摘要 本文设计并开发了一种以吡喃酮和三苯胺为母体的多刺激响应D-A型化合物(CYQ)。目标产物表现出优异的聚集诱导发光增强性能(AEE)。溶剂变色实验及密度泛函理论表明CYQ具有极强的分子内电荷转移(ICT)性质。粉末广角X射线衍射(PXRD)及差式扫描量热法(DSC)证明了在外力作用下,分子由晶态向无定形态的转变。研究发现, CYQ对有机溶液中的痕量水非常敏感,在四氢呋喃(THF)中可达到极低的检出限0.0096%。除此之外,随着湿度的增加, CYQ的荧光强度呈现逐渐下降趋势。这一相对湿度检测法为该AIE材料成为不同环境下的比色探针提供了可能。