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The abnormal solvatochromism, high-contrast mechanochromism and internal mechanism of two AIEE-active β -diketones



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ABSTRACT

Tradition β -diketones are rarely used as fluorescent emitters and mechanochromic materials. Here, **TPED2F** and **TPED2T** with tiny structural differences (Furan unit and thiophene unit) and the same asymmetric β -diketone skeleton were designed and synthesized. Both of them show abnormal solvatochromism, water-sensitive fluorescence emission, marked aggregation-induced enhanced emission (AIEE) activity and high-contrast mechanochromism. Furthermore, crystal TPED2T displays inferior quantum efficiency (0.08) and hypsochromic-shift fluorescence emission (493 nm) in contrast with crystal TPED2F presenting 0.20 quantum efficiency and 516 nm emission maxima. However, ground and cured TPED2T exhibit deeper bathochromic-shift (54 nm and 59 nm in turn) than ground (37 nm) and cured (1 nm) TPED2F. In addition, ground TPED2F show reversible mechanochromism by heating, but mechanochromism of ground TPED2T is irreversible whether heating or solvent fuming. Based on ¹H NMR, ¹³C NMR, UV-vis absorption spectra, emission spectra, XRD, DSC, single crystal analysis and theoretical calculation, the abnormal solvatochromism and water-sensitive fluorescence emission are attributed to enol-keto tautomerism and solvent polarity induced conformation changes of excited states, while heavy atom effect and wide band gap respectively lead to inferior quantum efficiency and hypsochromicshift emission for crystal TPED2T compared with TPED2F. Moreover, excellent crystallization ability and close melting point before/after grinding endow TPED2F with thermal reversible mechanochromism. The amorphous state provided grinding and melting may contain distinct local energy traps, resulting in different fluorescence emission. Finally, existence forms of TPED2F and TPED2T depend on intramolecular hydrogen bonds, conjugate structure and small relative energy.

1. Introduction

Tradition β -diketones (bdks) have been widely used as ultraviolet absorbent, metal ligands, catalysis, vapour deposition, extractants and preparation of heterocyclic compounds owing to facile synthesis, efficient cost, and tailorable scaffolds [1–6]. Specially, difluoroboron β -diketonate (BF₂bdk) complexes have showed fascinating optical properties in the field of polarity and viscosity detection, mechanochromism, thermally activated delayed fluorescence (TADF), room temperature phosphorescence (RTP) and so on [7–14]. However, bdks themselves as valuable fluorescent materials are rarely reported until now. The reported literatures together with minimum energy calculation indicated that bdks often undergo enol-keto tautomerism, excited state intramolecular proton transfer (ESIPT) and following conformation change leading to high non-radiation rate in solution [15–17]. In solid state, it is possible for bdks to enhance fluorescence emission due to intramolecular hydrogen bonds and suppressed conformational changes. Therefore, bdks are potential AIE materials.

Recently, Fraser et al. [18] incorporated 3,4,5-trimethoxy-substituted benzene (TMB) into bdks scaffolds endowed with AIE and mechanochromic properties due to steric interactions of crowded trimethoxy providing loose molecular packing and nonplanar molecular

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Scheme 1. Synthetic routes of TPED2F and TPED2T.



Fig. 1. Normalized UV-vis and fluorescence spectra of (A) TPED2F, (B) TPED2T in various solvents. Solution concentration: 10 µM.

configuration. Xie et al. [16] obtained а series of water-vapour-recoverable mechanochromic and AIE materials by introducing hydrophilic pyridine unit and selectively bind to cellulose. Li et al. [19] obtained mechanochromic and self-healing materials by investigating the substitution effect of bdks. To improve solid-state quantum efficiency and extend fluorescence lifetimes, Wu et al. [17] chose respectively phenoxazine and 9,9-dimethyl-9,10-dihydroacridine as electron donor incorporated into bdks core with strong electron-accepting ability via phenyl bridges. The two D-π-A-π-D type bdks exhibited record-high external quantum efficiency in organic light-emitting devices (OLEDs) and remarkable TADF (Thermally activated delayed fluorescence, means that when the triplet excited state and the singlet excited state are close in energy, the triplet excited state can be crossed to the singlet excited state by thermally activated inverse systems, also known as E-type delay fluorescent) features with up to 1.94 µs fluorescence lifetime in film. Obviously, researchers have made efforts to expand the luminescence and application properties of bdks. Even so, the molecular design for bdks with strong solid-state fluorescence emission and stimulus-responsive fluorescence is still in its infancy. In addition, the relationships between molecular structures, intermolecular stacking modes and mechanochromism are still unclear. Developing new fluorescent chromophores will be important to reveal internal mechanism of mechanochromism and obtain efficient sensors, security ink and data storage materials.

In this paper, two asymmetric bdks named as **TPED2F** and **TPED2T** were designed and synthesized by furnishing bdks with propeller-like tetra (phenyl) ethylene (TPE), furan or thiophene unit (Scheme 1). As a highly efficient measure of constructing AIE-active luminogens, TPE unit not only can endow traditional fluorophores with strong fluorescence emission in the solid state, but also mechanochromic property due to inhibited C–C bond rotation and loose molecular stacking. Meanwhile, the relationship between structure and photophysical properties is easy to be highlighted based on the tiny structural difference between

furan and thiophene [20] possibly triggering high contrast intermolecular arrangement and stacking patterns. Here, the relationship between structure and photophysical properties of two bdks were analyzed and discussed in depth based on UV–vis absorption and fluorescence spectra, quantum efficiency, X-ray diffraction (XRD), differential scanning calorimeter (DSC) analysis, X-ray single crystal and theoretical calculation.

2. Results and discussion

2.1. Solvatochromism

The UV-Vis absorption and fluorescence emission spectra of two bdks in various organic solvents are investigated. As shown in Fig. 1 and Table S1, tiny shifts of absorption maxima hint stable ground state with the increasing polarity from hexane to dimethyl sulfoxide, while marked bathochromic-shifts of emission maxima demonstrate the bdks have easily polarized excitation state. More interesting, TPED2F shows different fluorescence emission peaks in four solvents. In tetrahydrofuran (THF), one main peak and one unobvious shoulder peak can be observed, but n-hexane solution with single emission peak. Two emission peaks are located separately at 421 nm and 505 nm in dichloromethane (CH₂Cl₂). Different from CH₂Cl₂, the main peak is located at low energy band of 530 nm, while shoulder peak is located at high energy band of 440 nm in dimethyl sulfoxide (DMSO) solution. Furthermore, TPED2T also exhibits two distinct fluorescence emission peaks at 445 nm and 513 nm in CH₂Cl₂. Moreover, it is worth noting in particular that emission maxima of TPED2F do not conform to normal bathochromic-shifts with the increase of solvent polarity. Why do the variable fluorescence emission peaks and abnormal wavelength shifts come into being? It is well known that enol-keto tautomerism often occur in solutions of bdks, and the enol with large π - π conjugation will become more stable and occupy an increased proportion in



Fig. 2. Fluorescence emission spectra of (A, E) TPED2F, (C, F) TPED2T in the THF/water mixtures with different fractions of water. Solution concentration: 10 μ M. Chart of relationship between FL peak intensity and water fraction for (B) TPED2F, (D) TPED2T. Solution concentration: 10 μ M. (Inset: Photographs in THF/water mixtures with different fractions of water under 365 nm UV illumination).

tautomerism. Whether enol-keto tautomerism contribute to the above fluorescence emission? Firstly, no enol form but keto form exist in **TPED2F** and **TPED2T** based on ¹H NMR spectra without above 10 ppm signal and ¹³C NMR spectra with 177, 182, 181 and 183 ppm signals (Figs. S6–9). Secondly, we re-tested fluorescence emission spectra of **TPED2F** in dry CH₂Cl₂ and THF, whose main peaks and shoulder peaks show significant decline and enhancement respectively, presenting mirror-like emission spectra before/after drying (Fig. 1A). Thus, it can be concluded that fluorescence emission of **TPED2F** and **TPED2T** are very sensitive to water, and enol-keto tautomerism possibly plays an

important role in abnormal emission spectra. In undried solvents, **TPED2F** and **TPED2T** mainly exists in the keto form because intermolecular hydrogen bonding interactions between water molecules and carbonyl inhibit the formation of intramolecular hydrogen bonds, which takes responsible for blue-shift of the main emission peak compared with that of enol form after drying, while n-hexane as a non-protonic and non-polar solvent is advantageous to stability of enol form, leading to red-shift fluorescence emission.



Fig. 3. Photographic images of TPED2F, TPED2T in different solid states under natural light and UV light (365 nm).

2.2. Aggregation induced emission

AIE as a wonderful photophysical phenomenon has received wide attention as soon as it appeared. Fig. 2 shows TPED2F and TPED2T emit faint light in dilute THF solution, when the volume fraction of water (f_w) in THF-H₂O solution increase to 90%, rapidly increasing fluorescence intensities present two definite AIE scenes, which are attributed to the formation of aggregated state due to decreased solubility by the addition of water. As expected, propeller-like TPE unit plays an active role in terms of inhibiting π - π stacking of the aggregated state. Meanwhile, fluorescence emission spectra undergone significant changes in the test of AIE. Compared with THF solution, a new emission peak occurs accompanied by red shifted wavelength for TPED2F with the increase of $f_{\rm W}$ from 10% to 70%, when $f_{\rm W}$ = 90%, only the long emission wavelength peak remains, and the similar station can be observed for TPED2T due to formation of the aggregated state. Wonderfully, the emission spectra of **TPED2F** are similar comparing dry THF with that of $f_w = 10-70\%$. As we know, protonic polar solvents are more conducive to the stability of keto form, but it is obviously inconsistent with the enhanced signals near 500 nm at $f_{\rm W}$ = 10–70%, which may be due to conformation changes of excited states caused by polarity enhancement. To further verification, we compared the absorption spectra of TPED2F in the THF and CH₂Cl₂ before/after drying, aqueous THF with $f_w = 30\%$ (Fig. S2). The untreated solvents and aqueous THF have the same absorption maxima hinting the same ground state, while absorption maxima of drying solvents show apparently perceptible blue-shift, which further verifies that the variable excited states alter emission spectra of **TPED2F** in THF of f_w = 30%.

2.3. Mechanochromic properties

Mechanochromic materials are sensitive to mechanical stimulation via stimuli-responsive changes of fluorescence emission wavelength/ intensity, quantum yields or fluorescence lifetime [21–25]. However, most of literatures are limited to conversion between the ordered molecular arrangement and disordered molecular arrangement or another ordered molecular arrangement leading to different photophysical properties. The lack of systematic investigation at the molecular level affect discovery of high-contrast, reversible and quantifiable mechanochromic materials and the establishment of inherent correlation between molecular conformation, packing modes and mechanochromic properties. To do this, photophysical properties of the two bdks are firstly investigated in solid states. After careful analysis and comparison of the data in Fig. 3, Fig. 4 and Table S2, three interesting phenomena should be discussed in depth. Firstly, TPED2T shows the bigger wavelength shifts than TPED2F before/after grinding, whose emission maxima red shifts up to 54 nm from 493 nm to 547 nm, accompanied obvious color changes from cyan to yellow under ultraviolet radiation, which is also perceptible to the naked eye. Secondly, TPED2F exhibits reversible mechanochromism by heating, while mechanochromism of TPED2T is irreversible whether heated or fumigated. Thirdly, the absolute fluorescence quantum efficiency (Φ_F) of crystal **TPED2F** (0.22) is about three times that of TPED2T (0.08) by using integral sphere, while Φ_F of ground **TPED2F** and **TPED2T** is almost equal. To make clear the above phenomena, X-ray diffraction (XRD, Fig. 4B, D), fluorescence microscope and differential scanning calorimeter (DSC, Fig. 4E, F) analysis were also completed. The XRD spectra indicated two dyes exhibit strong diffraction peaks before grinding, but they become wider and weaker after grinding, therefore, mechanochromism of two dyes can be attributed to the incomplete transition from crystalline state to amorphous state. Under fluorescence microscope (Fig. S1), crystal **TPED2F** display bundle-like long rod morphology, as a sharp contrast, crystal TPED2T forms needle-shaped morphology mixed with opaque films, which illustrate TPED2F have better crystallinity than TPED2T obtained by slow evaporation of CH₂Cl₂/n-hexane. Moreover, ground TPED2F still have stronger diffraction peaks than TPED2T, which means that ground TPED2F contains more microcrystals. Thereby, we infer that the better crystallization ability and more seed crystals lead to reversible mechanochromism for TPED2F after heating. More interesting, XRD spectra of heating and fumigating samples show almost identical diffraction peaks for TPED2F or TPED2T, thereby the discrepancy of emission maxima probably come from tiny differences in morphology by heating and fuming, but not intermolecular arrangement and stacking. Furthermore, two exothermic peaks ascribed to cold-crystallization transition at 88 and 85 °C are respectively observed in DSC curves of ground TPED2F and TPED2T samples, moreover, grinding not only produces the meta-stable amorphous phase, but also causes a distinct change of melting point, especially for TPED2T with a drop of 14 °C, which may also be another reason for irreversible mechanochromism of TPED2T by heating. To obtain the amorphous state of two dbks, two samples are heated and melted, then cooled rapidly with liquid nitrogen. XRD spectra show that both cured samples are amorphous characterized by wide diffraction peak, however, the two cured samples show the opposite wavelength shift compared with the corresponding ground samples. Therefore, the degree and acquisition mode of amorphous state affect the contrast of fluorescence emission before/after phase transition. As far as we know, amorphous state is a disorder stacking and arrangement, furthermore, different amorphous state may contain distinct local energy traps, resulting in diverse fluorescence emission. The high-contrast mechanochromism and Φ_F usually depend on molecular conformation, intermolecular arrangement and stacking, following we will discuss them in the section of crystal analysis and theoretical calculation.

2.4. Crystal structures and theoretical calculation

To make clear the internal mechanism of optical properties and mechanochromism, first, we completed crystal analysis of **TPED2F** (CCDC 1957971) and **TPED2T** (CCDC 1957972) (Fig. 5). The crystal **TPED2F** belong to monoclinic system with two space groups C2/c and C12/c1, the cell parameters are a = 52.642(16) Å, b = 6.055(2) Å, c = 36.419(11) Å, $\alpha = 90^{\circ}$, $\beta = 120.220(7)^{\circ}$, $\gamma = 90^{\circ}$ and Dc = 1.241 g/cm³. **TPED2F** chooses two kinds of enols named as **TPED2F-1** and **TPED2F-5** (Fig. 6) rather than keto form as stable configuration, whose oxygen atoms in furan, ketone and enol are located on the same side of the molecule. Relative to propeller-like TPE unit defined as tail, the head containing plane A, B and C adopts a more planar molecular configuration, which is conducive to head-to-head stacking pattern to avoid steric hindrance of tail. As expected, two adjacent molecules tend to



Fig. 4. FL spectra of complex (A) TPED2F, (C) TPED2T in different solid states (cured: after the crystal is melted, it is placed in liquid nitrogen for quenching), and XRD patterns of (B) TPED2F, (D) TPED2T in various solid states. DSC thermograms of (E) TPED2F, (F) TPED2T crystals in different state.

adopt non-parallel head-to-head stacking with two centroid to centroid distances (C_g - C_g) of 4.434 Å and 5.115 Å and link together by intermolecular C–H···C hydrogen bond (d = 2.893 Å) and C–H··· π weak interaction (d = 3.117 Å). Then, the layer-by-layer stacking in order of **TPED2F-1-TPED2F-5-TPED2F-5-TPED2F-1**(Fig. 5B), which lead to intermolecular π - π stacking in furan moiety with C_g - C_g of 3.572 Å and

plane to plane distances (C_p-C_p) of 3.506 Å. Crystal **TPED2T** is also a monoclinic system with the space groups I2/c and I12/c1 [a = 36.435(5) Å, b = 5.9429(11) Å, and c = 47.086(6) Å; $\alpha = 90^{\circ}$, $\beta = 101.933(14)^{\circ}$, $\gamma = 90^{\circ}$ and Dc = 1.291 g/cm³]. However, only one enol form exists in **TPED2T**, and its sulfur atom and oxygen atoms of ketone and enol are distributed on the same side rather than on both sides like **TPED2F**. It is



Fig. 5. Single crystal structure of (A) TPED2F, (C) TPED2T and molecular stacking mode of (B) TPED2F, (D) TPED2T.



Fig. 6. Molecular configurations, relative energy (Re) and dipole moment (μ) of TPED2F and TPED2T in KJ mol⁻¹ and d respectively.



Fig. 7. Molecular orbital amplitude plots of HOMO and LUMO levels for crystal TPED2F and TPED2T.

worth noting that TPED2F and TPED2T show similar head-to-head stacking, twisted molecular configuration and varied hydrogen bonds and weak interactions (Fig S5-6). Meanwhile, **TPED2T** have weaker π - π stacking in comparison with TPED2F (Intermolecular thiophene moiety with C_g - C_g distances of 3.828 Å and C_p - C_p distances of 3.751 Å). In addition to the heavy atom effect of sulfur atom, the crystal analyses including intermolecular π - π stacking are powerless to explain worse crystalline state Φ_F for **TPED2T** compared with **TPED2F**. To theoretically analyze the stable form and optical properties of two dbks, minimum energy calculation of different configurations were completed and geometries were optimized at the B3LYP [26] level of theory. The def-TZVP [27,28] basis set was employed for all atoms. Frequencies were analytically computed at the same level of theory to confirm whether the structures are minima (no imaginary frequency). Single-point energy calculations were performed at the M06-2X [29] level of theory, and ma-def2-TZVP [28] basis set with the optimized structures. All of the calculations were performed using Gaussian 16 program package, and the structures and molecule orbitals (MOs) were generated by Multiwfn [30] and VMD30. The results showed that TPED2F-1, TPED2F-5, TPED2T-1 and TPED2T-5 are the most stable configurations characterized with enol form and intramolecular hydrogen bond. Compared with TPED2F-5 and TPED2T-5, TPED2F-1 and TPED2T-1 have lower minimum energy ascribed to larger conjugate structure. However, it is difficult to explain that TPED2F-1 coexists with TPED2F-5 in crystal TPED2F according to the same molar equivalent, but only one enol form in crystal TPED2T. In addition, enol forms have larger dipole moments than keto forms. Furthermore, TPED2F-1, TPED2F-5 and TPED2T-1 show intramolecular charge transfer effect. The electron density distribution between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) (Fig. 7) appear obviously shift from TPE unit to furan unit for TPED2F-1 and TPED2F-5, while electron density distribution of TPED2T-1 shift from bdk unit to TPE and furan units. Obviously, not only HOMO but LUMO electron cloud distribution also spread on sulfur, meaning presence of heavy atom effect and intersystem crossing process. TPED2F-1 and TPED2F-5 have almost the same energy level, but energy gap of TPED2T-1 relative to TPED2F-1 and TPED2F-5 decreases markedly leading to wider bandgap, which is confirmed that crystal TPED2T exhibits blue-shift fluorescence emission compared with that of TPED2F.

3. Conclusions

In summary, TPED2F and TPED2T furnished with dbks, TPE and furan/thiophene units were designed and synthesized. The two luminogens show abnormal solvatochromism, water-sensitive fluorescence emission, marked AIEE activity and high-contrast mechanochromism. Furthermore, the abnormal solvatochromism and water-sensitive fluorescence emission are attributed to enol-keto tautomerism and solvent polarity induced conformation changes of excited states by test of ¹H NMR, ¹³C NMR, UV-vis absorption spectra and emission spectra in various solvents. Compared with quantum efficiency (0.20) and emission maxima (516 nm) of crystal TPED2F, crystal TPED2T displays inferior quantum efficiency (0.08) and hypsochromic-shift fluorescence emission (493 nm) probably due to heavy atom effect and wide band gap based on theoretical calculation and crystal analysis. Ground TPED2F and TPED2T relative to the corresponding crystals respectively present bathochromic-shift of 37 nm and 54 nm ascribed to twisted molecular conformation and incomplete phase transition from crystalline to amorphous on the basis of XRD. Moreover, excellent crystallization ability and close melting point before/after grinding endow TPED2F with thermal reversible mechanochromism based on the investigation of fluorescence microscopy and DSC. More interesting, amorphous TPED2T further increases the wavelength shift (nm) before/after curing, while amorphous TPED2F almost has the same emission maxima with its crystal, which is a rare report that the degree and acquisition mode of amorphous state affect the contrast of fluorescence emission. Last but not least, crystal **TPED2F** and **TPED2T** exist in enol form including **TPED2F-1**, **TPED2F-5** and **TPED2T-1** rather than keto form may depend on intramolecular hydrogen bond, long conjugate structure and small relative energy according to theoretical calculations.

Declaration of competing interest

There are no conflicts to declare.

CRediT authorship contribution statement

Wenjing Liu: Writing - review & editing. Yongtao Wang: Writing review & editing. Jinfeng Yang: Writing - review & editing. Xueming Li: Writing - review & editing. Xiaojuan Wang: Writing - review & editing. Lei Ma: Writing - review & editing.

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Appendix A. Supplementary data

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