The abnormal solvatochromism, high-contrast mechanochromism and internal mechanism of two AIEE-active \( \beta \)-diketones

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**ABSTRACT**

Traditional \( \beta \)-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 \( \beta \)-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 \(^1\)H NMR, \(^{13}\)C 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 hypsochromic-shift emission for crystal TPED2T. 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

Traditional \( \beta \)-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 \( \beta \)-diketoneate (BF$_2$bdk) 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 and suppression 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 tri-methoxy providing loose molecular packing and nonplanar molecular...
configuration. Xie et al. [16] obtained a 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...
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 $^1$H NMR spectra without above 10 ppm signal and $^{13}$C NMR spectra with 177, 182, 181 and 183 ppm signals (Figs. S6–9). Secondly, we re-tested fluorescence emission spectra of TPED2F in dry CH$_2$Cl$_2$ 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. 2. Fluorescence emission spectra of (A, E) TPED2F, (C, F) TPED2T in the THF/water mixtures with different fractions of water. Solution concentration: 10 μM. Chart of relationship between FL peak intensity and water fraction for (B) TPED2F, (D) TPED2T. Solution concentration: 10 μM. (Inset: Photographs in THF/water mixtures with different fractions of water under 365 nm UV illumination).
properties. The lack of systematic investigation at the molecular level
ordered molecular arrangement leading to different photophysical
between molecular conformation, packing modes and mechanochromic
materials and the establishment of inherent correlation be
via stimuli-responsive changes of fluorescence emission wavelength/

2.3. Mechanochromic properties

Mechanochromic materials are sensitive to mechanical stimulation
via stimuli-responsive changes of fluorescence emission wavelength/

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-H\( \text{H}_2\text{O} \) 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 \( \pi-\pi \) 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
\( f_w \) from 10\% to 70\%, when \( f_w = 90\% \), only the long emission wavelength
peak remains, and the similar station can be observed for TPED2T due
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 \( f_w = 10–70\% \), 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 \( \text{CH}_2\text{Cl}_2 \)
before/after drying, aqueous THF with \( f_w = 30\% \) (Fig. S2). The un-
treated solvents and aqueous THF have the same absorption maxima
hiding the same ground state, while absorption maxima of drying sol-
vents show apparently perceptible blue-shift, which further verifies that
the variable excited states alter emission spectra of TPED2F in THF of \( f_w 

TPED2F

TPED2T

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

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 \( a = 52.642(16)\,\text{Å}, b = 6.058(2)\,\text{Å}, c = 
36.419(11)\,\text{Å}, \alpha = 90^\circ, \beta = 90^\circ, \gamma = 120^\circ \) and \( D_\text{c} = 1.241\,\text{g/cm}^3 
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 configu-
ration, which is conducive to head-to-head stacking pattern to avoid
steric hindrance of tail. As expected, two adjacent molecules tend to

of the data in Fig. 3, Fig. 4 and Table S2, three interesting phenomena
should be discussed in depth. Firstly, TPED2T shows the bigger wave-
length shifts than TPED2F before/after grinding, whose emission max-
ima 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 ab-
solute fluorescence quantum efficiency (\( \Phi_F \)) of crystal TPED2F (0.22) is
about three times that of TPED2T (0.08) by using integral sphere, while
\( \Phi_F \) 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 \( \text{CH}_2\text{Cl}_2/-\text{hexane} \). 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 inter-
esting, 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,
graing 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 fluo-
rescence emission. The high-contrast mechanochromism and \( \Phi_F \) usually
depend on molecular conformation, intermolecular arrangement and
stacking, following we will discuss them in the section of crystal analysis
and theoretical calculation.
adopt non-parallel head-to-head stacking with two centroid to centroid distances (Cg-Cg) 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 Cg-Cg of 3.572 Å and plane to plane distances (Cp-Cp) 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; α = 90°, β = 101.933(14)°, γ = 90° 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. 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.
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 ($\mu$) 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 Cg-Cg distances of 3.828 Å and Cp-Cp distances of 3.751 Å). In addition to the heavy atom effect of sulfur atom, the crystal analyses including intramolecular π-π stacking are powerless to explain worse crystalline state ΦΦ for TPED2F compared with TPED2T. 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, and the structures and molecule orbitals (MOs) were generated by Multiwfn [20] and VMD.30. 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. Furan/thiophene units were designed and synthesized. The two luminogens show abnormal solvatochromism, water-sensitive fluorescence emission, marked AIEE activity and high-contrast mechanochromism. Furan/thiophene units were designed and synthesized. The two luminogens show abnormal solvatochromism, water-sensitive fluorescence emission, marked AIEE activity and high-contrast mechanochromism.


