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Aldehyde end-capped terthiophene with aggregation-induced emission characteristics

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ABSTRACT

From the viewpoint of practical application, organic materials that are emissive in aggregate or solid state have been a hot research topic. This work demonstrates that 2,2':5',2"-terthiophene-5-carbaldehyde (TTA) exhibited aggregation-induced emission (AIE) property. The photophysical properties of the aldehyde in THF/H₂O mixtures were studied, and the aggregates formed with different water fractions were studied by scanning electron microscopy. Our results indicated that the presence of an electron deficient aldehyde group as the end-capped group should endow TTA with AIE characteristic. Furthermore, ordered nanoscale aggregates of TTA exhibited distinct AIE behavior when assembled in solutions with appropriate water content.

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1. Introduction

Organic materials possessing highly emissive feature in aggregate or solid state have received increasing attention because of the requirement of these materials in various optoelectronic applications, such as bioimaging, bioprobes, and organic light-emitting diodes (OLED), and so on.^{1–5} While a number of materials are known to be highly fluorescent in dilute solutions, most of them tend to show a decreased or quenched fluorescence in the aggregate or solid state due to the discouraging non-radiative relaxation pathways.^{6,7} Such aggregation-caused quenching (ACQ) has greatly limited the practical applications of organic materials because most of these materials need to be used in the aggregated or solid state. To date, various tactics have been developed to tackle ACQ.^{8–11} However, many of them operate at the expense of other useful properties of the compounds. Development of organic materials to address this problem is still a challenge to researchers.

Aggregation-induced emission (AIE) phenomenon, in which non-luminescent molecules or weak emitters with propeller-like conformations have been shown to exhibit efficient emission because of aggregate formation, has been regarded as a promising

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method to tackle the notorious ACQ.¹² Following the concept of AIE, various aggregated and solid-state emissive organic materials have been prepared through rational coupling of propeller-like AIE building blocks.^{13–18} To satisfy the fundamental and practical demand for optoelectronic active materials, organic materials without propeller-like conformations exhibiting AIE characteristics present a great potential.^{19–22} Therefore, there is still much work to develop classical organic materials with AIE features.

Thiophene and its aldehyde derivatives are highly reactive organic building blocks that provide numerous advantages for synthesizing useful materials such as hole transporters, sensitizers, organic luminophors, and sensors.^{23–26} By comparison, 2':5',2"terthiophene-5-carbaldehyde (TTA, Fig. 1), a long known compound, which can be regarded as an α -aldehyde end-capped oligomer of thiophene with three thiophene units, is commonly used as building block to construct light harvesting dyes, medicals, fluorescence chemosensor, memory device, etc.^{27–32} To the best of



Fig. 1. Molecular structure of TTA and TTOH.

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our knowledge, the fluorescent properties of TTA in aggregate state are rarely studied that undoubtedly limit developing its practical applications much further. Herein, our investigations reveal that the end-capped group of aldehyde should endow TTA with AIE characteristic. Furthermore, its AIE mechanism can be mainly assigned to the ordered nanoscale aggregates formed when assembled in solutions with appropriate water content.

2. Experimental

2.1. Materials and characterization

TTA and (5-(5-(thiophen-2-yl)thiophen-2-yl)thiophen-2-yl) methanol (TTOH, Fig. 1), a reduction compound of TTA, were synthesized using synthetic method described in Scheme 1. Solvents were purified according to the standard procedures. ¹H NMR spectra were recorded at room temperature on Bruker AV 600 MHz. Data are listed in parts per million (ppm) on the delta scale (δ). The

Solvents were removed by rotary evaporation and the residue was purified by silicon gel column chromatography to afford TTA as a yellow solid (0.84 g, yield 86%). ¹H NMR (600 MHz, CDCl₃, ppm): δ =9.83 (s, 1H), 7.64 (d, 1H), 7.25–7.10 (m, 4H), 7.09 (d, 1H), 7.02 (d, 1H). MALDI-TOF: m/z [M]⁺ calcd C₁₃H₈OS₃, 276.3970; found: 276.3968.

2.2.2. 2,2':5',2"-Terthiophene-5-methanol (**TTOH**). To a stirred solution of TTA (0.50 g, 1.80 mmol) in 25 mL of dry THF was added sodium borohydride (0.07 g, 1.80 mmol). After stirring the mixture for 4 h at room temperature, the THF was evaporated, dilute acid (1 M HCI) was added. Yellow precipitate was filtered and washed with water for several times, and then the crude product was recrystallized in hexane/ethyl acetate mixture to afford TTOH as a yellow powder (0.49 g, yield 98%). ¹H NMR (600 MHz, CDCl₃, ppm): δ =7.23 (d, 1H), 7.18 (d, 1H), 7.07–7.05 (q, 2H), 7.04–7.02 (q, 2H), 6.92 (d, 1H), 4.81 (s, 2H). MALDI-TOF: m/z [M]⁺ calcd C₁₃H₁₀OS₃, 278.4129; found: 278.4126.



Scheme 1. Synthesis of TTA and TTOH.

splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet) and br (broad). Mass spectra measured on Microflex MALDI-TOF MS. UV–vis spectra were recorded on a HITIACH U-3900 spectrometer. Photoluminescent (PL) spectra were recorded on a HORIBA FluoroMax-4 spectrometer. The absolute fluorescence quantum yields of solution (10 μ M) and solid powder were measured on HORIBA FluoroMax-4 (excited at 365 nm) by using a calibrated integrating sphere. The quartz cuvettes used were of 1 cm in path length. The scanning electron microscopy (SEM) studies were performed using a JEOL JEM-6700F scanning electron microscope. One drop of the solution was placed on a silicon slice, which was then dried in air. Dynamic light scattering (DLS) measurements were conducted on a Delsa PN A54412AB Nano Submicron Grain Particle Size Analyzer.

Single-crystal X-ray diffraction of TTA was performed on a Bruker SMART APEX II diffractometer with Mo K α radiation (λ =0.71000 Å). The structure was solved with direct method (SHELX-97) and refined with full-matrix least-squares technique. All non-hydrogen atoms were refined anistropically and hydrogen atoms were geometrically placed.

2.2. Synthesis of TTA and TTOH

2.2.1. 2,2':5',2"-Terthiophene-5-carboxaldehyde (**TTA**). A solution of 2,2':5',2"-terthiophene (0.87 g, 3.50 mmol) in CH_2Cl_2 (10 mL) was cooled to 0 °C, then POCl₃ (0.76 g, 5.02 mmol) in dry DMF (0.39 mL, 5.02 mmol) and CH_2Cl_2 (15 mL) were added dropwise. After stirring the resulting mixture overnight at room temperature, the reaction mixture was added with 1 M sodium acetate (30 mL), and then stirred for about 5 h. The resulting solution was extracted with CH_2Cl_2 , and the combined organic layer was washed with water, brine, sequentially, and dried on anhydrous MgSO₄.

3. Results and discussion

3.1. Photophysical properties of TTA

TTA is soluble in common organic solvents such as acetone, dichloromethane, and tetrahydrofuran (THF). The absorption and emission spectra of TTA in dilute THF (10 μ M) at room temperature are shown in Fig. 2. TTA shows relatively strong absorption in the 350–440 nm region, with the absorption maximum located at 397 nm, which corresponds to the π – π * transitions. A weak blue emission of TTA in dilute THF solution (10 μ M) was observed under UV (365 nm) irradiation. The peak emission wavelength of TTA was observed at 479 nm, exhibiting a fluorescence quantum yield ($\Phi_{\rm F}$) of 7.59%.



Fig. 2. UV-vis spectra and PL spectra of TTA in dilute THF (10 μ M).

3.2. AIE phenomenon of TTA

We examined the emission behavior of TTA aggregates formed in THF/water mixtures because TTA is soluble in common organic solvents but insoluble in water, and TTA molecules must aggregate in THF/water mixtures with appropriate water fraction (f_w , the volume percentage of water in THF/H₂O mixtures), which leads to the changes in PL spectra.

The recorded photographs and spectra are displayed in Fig. 3A and B, respectively. When TTA is molecularly dissolved in THF, it emits very faint blue light. As illustrated in Fig. 3A and B, the PL intensity of TTA is evidently intensified with increasing the water fractions in the mixture. The resultant emission is followed by a red-shift of the maximum emission wavelength of TTA by about 60 nm. This shift can be attributed to typical twisted intermolecular charge transfer (TICT) effects arising from increased solvent polarity through an increase in the water fraction. When f_w reaches 70%, the PL intensity is four times higher than that in pure THF. A further increase of the water fraction above 80%, leads to a decrease of the emission intensity. This up-down phenomenon has been observed in some compounds with AIE properties, although the reasons behind this phenomenon are still under debate.^{33,34} To better understand the diverse photoluminescence behavior and mechanism of TTA in solvent mixtures, further testing was carried out. The absolute $\Phi_{\rm F}$ of solutions (10 μ M) was measured to evaluate the emission enhancement quantitatively using a calibrated integrating sphere. As shown in Fig. 3C, increasing the water faction from pure THF to 70% increases the $\Phi_{\rm F}$ value of TTA from 7.59% to 57.96%. These results clearly indicate that TTA possesses typical AIE behavior.

synthesized and studied. TTOH is similar in molecular structure with TTA but differs in an electron rich $-CH_2OH$ replacing the electron deficient aldehyde on the end-capped group. Opposite to the emission behavior of TTA aggregates formed in THF/ water mixtures, the emission behavior of TTOH shows typical ACQ, as illustrated in Fig. 4. The PL intensity of TTOH is evidently weakened with increasing the water fractions in the mixture. When f_w reaches 90%, the PL curve of TTOH is almost flat line parallel to the abscissa, confirming that it is nearly non-emissive. Thus far, we can propose is that the presence of an electron deficient aldehyde group as the end-capped group of terthiophene is a key structural unit respect to the AIE phenomenon.

3.4. AIE mechanism

It has been revealed that the AIE effect in propeller-like conformations is mainly attributed to the restriction of intermolecular rotations (RIR) when forming molecular aggregates.¹² TTA, however, neither shows a propeller-like conformation nor possesses a sterically hindered bulky group in its molecular structure. To gain insight into the AIE mechanism of TTA, the following measurements were carried out.

The recorded UV–vis spectra of TTA (10μ M) in fresh THF/H₂O mixtures are displayed in Fig. 5. When the water fractions are in the range of 0–70%, the mixtures are homogeneous and visually transparent, suggesting that the size of the aggregates is in the nanoscale. The red-shift of absorption maximum from 398 nm to 404 nm can be assigned to the TICT effect. The absorption spectra of the mixtures with f_w above 80% appear to have tails that level-off in



Fig. 3. (A) Photographs of TTA in different water fractions taken under UV illumination (λ_{ex} =365 nm); (B) PL spectra of TTA(10 μ M) in fresh THF/water mixtures with different water fractions (f_w); (C) quantum yield changes of TTA(10 μ M) in THF/water mixtures with different water fractions (f_w).

3.3. Molecular structure-property relationship

To explore the molecular structure–property relationship of TTA, especially the role of aldehyde group in AIE, a referenced terthiophene derivative TTOH (Fig. 1 and Scheme 1) was

the long wavelength region, which can be attributed to the wellknown Mie effect induced light scattering.³³ It is reasonable to speculate that the nanostructures of TTA formed in the mixtures with higher fraction of water should be different from that at lower water content.

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Fig. 4. PL spectra of TTOH (10 μ M) in fresh THF/water mixtures with different water fractions (f_w).



Fig. 5. Absorption spectra of TTA (10 μ M) in fresh THF/water mixtures with different water fractions (f_w).

To get more information about the aggregates of TTA formed in THF/water mixtures, dynamic light scattering (DLS) measurements and scanning electron microscope (SEM) were used for morphological examination. From dynamic light scattering (DLS) measurements, the average diameter of the particles of TTA in water fractions below 80% was less than 3 nm (Fig. 6A and B). However, when f_w reaches 80%, larger particles are formed with an average diameter of approximately 200 nm (Fig. 6C). DLS measurements allow us to make the speculation that in THF/water mixtures, TTA

forms fine suspensions despite their clear appearance. SEM images in Fig. 7 support our hypothesis that aggregates in THF and the aqueous mixtures form differently with variation in the water content. In THF, molecules of TTA cannot form well nanostructured aggregates (Fig. 7A). In the mixtures with 'low' water contents of 60% or 70%, molecules of TTA form ordered nanoscale aggregates akin to the packed nanoribbons (Fig. 7B and C). At a water fraction of 80%, TTA molecules may abruptly form microcrystalline structures, implying that a recrystallization process might take place at water fractions above 80% (Fig. 7D), which causes emission quenching. The test results not only give direct evidence of molecular aggregation during emission enhancement but also reveal that ordered nanoscale aggregates of TTA formed in THF/water mixtures can efficiently prevent non-radiative relaxation pathways, which leads to AIE.

According to the AIE-active molecules reported, distinct emissions probably depend on different conformations and packing modes of the molecules in the aggregates.³⁴⁻³⁶ We thus speculate that: (1) In the pure THF solution, TTA is molecularly isolated without any interaction between adjacent molecules, showing weak fluorescence. (2) The molecules of TTA in the aggregated states associated with the lower water content are arranged in ordered clusters that restrained the non-radiative decay process, leading to an enhancement of the fluorescence. (3) The crystallization of TTA leads to more dense molecular packing that may quench the emission.

To understand how the molecular packing affects the emission behavior of TTA, a single crystal of TTA (CCDC 1006636) was grown by slow evaporation of its hexane solution and the crystallographic data are summarized in Table 1. The crystals exhibit relatively weak fluorescence with a solid-state $\Phi_{\rm F}$ of 5.98%, in accordance with the above hypothesis of the fluorescence decrease during the recrystallization process. In Fig. 8A, we can see that the dihedral angle between T1 plane and the adjacent thienyl T2 plane is 168.4°, whereas the dihedral angle between the T2 and T3 is 169.5°. This indicates that the TTA molecule adopts a certain planar conformations in the crystal. Fig. 8B shows that the two TTA molecules stack together in a face-to-face shape. The intermolecular distance from C6 to C10 in Fig. 8B is 3.443 Å, and the angle between the line C6–C10 and the plane of the molecule, which consists of the line C9-C10-C12 is 87.03°. The vertical distance between the two planes of the whole molecule is 3.438 Å, which is smaller than 3.6 Å. It shows clearly that it has strong $\pi - \pi$ stacking between the two TTA molecules, which promote the decay of the excited species through non-radiative pathways, resulting in the weak fluorescence in TTA crystals.



Fig. 6. Particles size distributions of TTA in THF/water mixtures with different water fractions: (A) TTA in THF/H₂O (40:60, v/v); (B) TTA in THF/H₂O (30:70, v/v); (C) TTA in THF/H₂O (20:80, v/v).

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Fig. 7. SEM images of TTA (10 μM) in THF/water mixtures with different water fractions: (A) TTA in THF/H₂O (100:0, v/v); (B) TTA in THF/H₂O (40:60, v/v); (C) TTA in THF/H₂O (30:70, v/v); (D) TTA in THF/H₂O (20:80, v/v).

Table 1

Crystallographic data for TTA

Compound	TTA
Empirical formula	C ₁₃ H ₈ OS ₃
Formula weight	276.37
Temperature/K	296.21(10)
Crystal system	Triclinic
Space group	P-1
a (Å)	6.4043(5)
b (Å)	13.8631(13)
<i>c</i> (Å)	14.4086(13)
α (°)	77.021(8)
β(°)	79.759(7)
γ (°)	89.528(7)
V (Å ³)	1226.03(19)
Ζ	4
$D_{\text{calcd}} (\text{mg/mm}^3)$	1.497
$\mu ({\rm mm}^{-1})$	0.582
Reflections collected	8863
θ Range (°)	5.9-52.042
Independent reflections	4809
Index ranges	–7≤h≤7, –16≤k≤17, –17≤l≤17
R _{int}	0.0301
wR_2	0.1167
Data/restraints/parameters	4809/0/307
GOF	1.036

4. Conclusions

In summary, the work here demonstrates that 2,2':5',2"-terthiophene-5-carbaldehydeshowed prominent AIE characteristics. Molecular structure—property relationship shows the electron deficient aldehyde group endows TTA with AIE characteristic. SEM analyses revealed that ordered nanoscale aggregates of the aldehyde formed in THF/H₂O mixtures are responsible for the AIE



Fig. 8. (A) ORTEP diagram of TTA. (B) Two molecular packing diagrams of TTA.

behavior. This work expands the study of AIE-active chromophores to aldehyde end-capped oligomer of thiophene.

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