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## Aggregation-Induced Emission: Mechanistic Study of Clusteroluminescence of Tetrathienylethene

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In this work we have investigated the aggregation-induced emission (AIE) behaviour of 1,1,2,2-tetra(thiophen-2-yl)ethene (tetrathienylethene, TTE). The semi-locked and fully-locked derivatives (sl-TTE and fl-TTE) have been synthesized to better understand the mechanism behind the solid state photoluminescence of TTE. TTE is a typical AIEgen and its luminescence can be explained through the mechanistic understanding of the restriction of intramolecular motions (RIM). The emissive behaviour of TTE in the THF/water aggregates and crystal state have also been studied revealing a remarkable red-shift of 35 nm. A similar red-shift emission of 37 nm from the THF/water aggregates to the crystal state, is also observed for (*E*)-1,2-di(thiophen-2-yl)ethene (*trans*-dithienylethene, DTE). Crystal analysis has revealed that the emission red-shifts are ascribable to the presence of strong sulfur-sulfur (S··S) intra- and intermolecular interactions that are as close as 3.669 Å for TTE and 3.679 Å for DTE, respectively. These heteroatom interactions could help explain the photoluminescence of non-conventional luminophores as well as luminescence of non-conjugated biomacromolecules.

KEYWORDS: clusteroluminogen, aggregation-induced emission, AIE, mechanistic study, tetrathienylethene, TTE.

### Introduction

Luminescence has continued to the light the way in many important research fronts. In the recent years, researchers worldwide have continually developed and improved luminescent materials in the fields of OLED,<sup>1-3</sup> light emitting organic field effect transistors (LEOFETs),<sup>4-6</sup> bioimaging agents,<sup>7, 8</sup> and super resolution microscopy.<sup>9-11</sup> Many of these scaffolds are often designed with rigid, planar structures as this enhances conjugation allowing researchers to tune and produce the desired emission wavelength. However, many of these planar systems undergo a phenomenon known as aggregation-caused quenching (ACQ). Intermolecular interactions quenching luminescence occur when the molecules are in close proximity of each other enhancing non-radiative decay pathways of the molecules resulting in a loss of emission. For systems, whose emission intensity is highly affected by concentration effects, a delicate balance is

required to find the optimal working conditions as both high and low concentration results in weak intensity due to quenching or a lack of dye molecules, respectively. The next generation of luminescent materials will need to overcome this ACQ phenomenon while maintaining desirable properties such as strong emission intensity. One method to aid in the production of the next generation luminogens is to study and understand existing systems that are unaffected by the ACQ phenomenon. Drawing mechanistic understanding from these molecules could allow those principles to be applied in the rational synthesis of new systems.

One such research development in the field of luminescence is the aggregation-induced emission AIE platform.<sup>12</sup> AIE research first started in order to understand the poor solution state but strong solid state emission of the structural derivative of hexaphenylsilole (HPS), an archetypal AIEgen.<sup>13</sup> Mechanistic understanding of the AIE process has currently shown that molecular motions such as vibrations or rotations, (*e.g.* phenyl ring rotations in HPS), deactivate radiative pathways in the solution state rendering the molecule virtually non-emissive. In contrast, the restriction of intramolecular motions (RIM) taking place in the aggregate or solid state due to physical constraints, blocks non-radiative decay restoring emission. Capitalizing on this understanding has led to a boom in the development of a large array of AIEgens showing exceptional performance in many areas such as, OLED,<sup>14-18</sup> bioimaging,<sup>19-23</sup> chemosensing,<sup>24-28</sup> and stimuli responsive materials.<sup>29-34</sup>

In the continual process of understanding luminescence and developing new emissive scaffolds, researchers have increasingly reported new AIE systems that cannot be adequately explained by the current understanding of the photophysics. Displaying strong emission in the aggregated or solid state, many of these systems lack conventional chromophores, *i.e.* conjugated  $\pi$ -systems, in their molecular structures. For instance, particularly hard to explain is the luminescence observed in poly(isobutene succinic anhydride),<sup>35</sup> poly(maleic anhydride) (PMAH),<sup>36</sup> polyurea,<sup>37</sup> and

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even starch.<sup>38</sup> All of these systems lack any sort of conjugated units but produce blue emission in the aggregate or solid state. One common attribute that many of these non-conventional luminescent systems share is electron-rich heteroatoms. It has been observed that these heteroatoms are often in close proximity to each other, especially when the polymers adopt a folded conformation. The clustering of heteroatoms can result in observable emission. Thus, the displayed luminescence can be defined as “clusteroluminescence”.

Could through-space interactions between heteroatoms be key to the observed luminescence? We have proposed the theory of clusteroluminescence<sup>12</sup> to explain the luminescent phenomena of these non-conventional systems: close through-space interactions between the heteroatoms could create a new channel to radiatively dissipate energy, turning on luminescence. The clusteroluminogen hypothesis mirrors the mechanism of AIE molecules. When the molecules are well dissolved, excitation energy is easily dissipated via molecular motions. Upon aggregation, visible emission is observed if two important criteria are met: 1) the molecular motions that dissipated energy become blocked, and more importantly 2) the heteroatoms come into close proximity of each-other such that close through-space interactions can take place. Understanding the cause of this photophysical phenomenon could have far reaching implications. For instance, biomolecules often have a rich array of heteroatoms incorporated into their structure. Grasping the mechanics could allow us to create new luminogens with enhanced properties. This can also help us identify new sources of autofluorescence in bio-systems, which might allow us to overcome this obstacle in the future.

There has been an increasing number of published work regarding weak through-space nonbonding interactions between second and third row heteroatoms.<sup>39-43</sup> These interactions have shown a gain in stabilization of the system. Stabilizing nonbonding through-space interactions have been reported even in the 1960s in dioxane species.<sup>44, 45</sup> Indeed, it has been described that these nonbonding interactions can form a new set of orbitals which could narrow the energy gap between the HOMO and LUMO of the system.<sup>46, 47</sup> These reports corroborate the clusteroluminogen hypothesis. Unfortunately, many of the reported luminescent systems lacking conjugated  $\pi$ -networks, and rich in heteroatoms, are polymeric in nature, rendering a detailed study into the heteroatom interactions near impossible.

If there was a small molecular system that also exhibited strong heteroatom interactions, we could use it as a model with the purpose to explain the clusteroluminescence of non-conventional chromophores. Herein we report a small molecule:

1,1,2,2-tetra(thiophene-2-yl)ethene (tetrathienylethene, TTE, Chart 1 and Scheme 1) whose AIE feature was qualitatively observed before.<sup>48</sup> In this work we have thoroughly investigated its AIE behaviour, rationalizing the mechanism behind, by synthesizing its locked counterpart: tetrathieno[2,3-a:3',2'-c:2'',3''-f:3''',2'''-h]-naphthalene<sup>49</sup> (fully-locked TTE, fl-TTE, Scheme 2). The AIE mechanism of TTE accounts for the restriction of

intramolecular rotations (RIR). Similar to other AIE luminogens (AIEgens), TTE also exhibits morphochromism phenomenon, since there is a change in the emission going from the THF/water aggregate to the crystal. However, its morphochromism is unusual with respect to the other AIEgens, since a red-shift (rather than a blue-shift) of 35 nm occurs from its emission in the THF/water aggregates to its crystal emission. Crystal analysis showed that due to the spatial

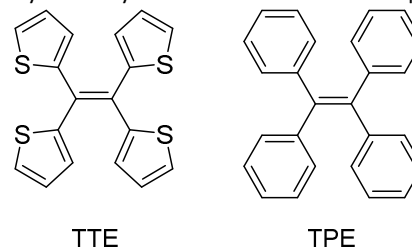


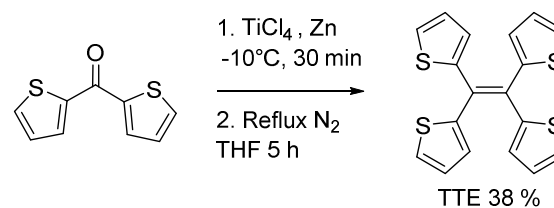
Chart 1. Chemical structure of tetrathienylethene (TTE) and tetraphenylethene (TPE).

arrangement of the thiophene rings in the crystal no  $\pi$ - $\pi$  interactions exist, while strong intra- and intermolecular S...S interactions have been found, with a measured distance as close as 3.669 Å, below the theoretical equilibrium one of 4.0 Å.<sup>50</sup> Investigating the photoluminescence (PL) behaviour of the lower homolog of thiophene-substituted ethene series, (*E*)-1,2-di(thiophene-2-yl)ethene (*trans*-dithienylethene, DTE), we have encountered a similar phenomenon: a 36 nm red-shift emission occurs when comparing its THF/water aggregate emission to its crystal emission. Analysing the crystal structure of DTE, we have found a similar S...S interaction distanced at 3.679 Å. As no  $\pi$ - $\pi$  interactions were found neither in TTE nor in DTE, the red-shifts in emission in both these systems seem to be as a result of the through-space S...S interactions. Detailed studies of the photophysical properties and crystal structure analysis of TTE are presented below. These are compared and contrasted with archetypal AIEgen tetraphenylethene (TPE, Chart 1) and the other synthesized TTE derivatives to better understand the photophysics behind the AIE mechanism and the through-space interactions.

## RESULTS AND DISCUSSION

### Photophysical properties

TTE has been synthesized by McMurry coupling shown in Scheme 1.<sup>51</sup>



Scheme 1. Synthesis of tetrathienylethene (TTE) by McMurry coupling.



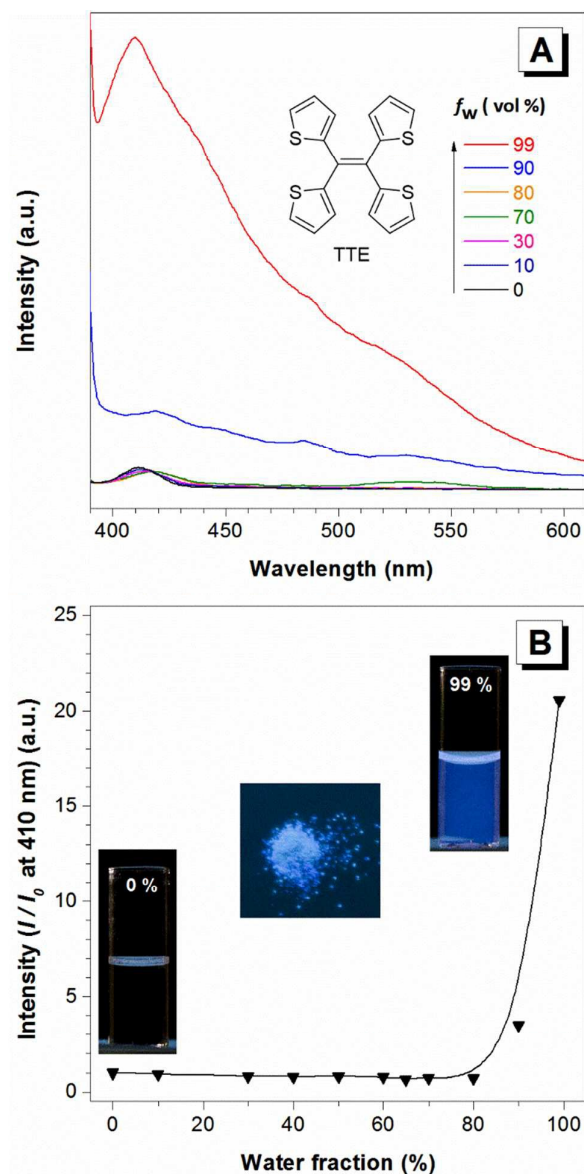


Figure 1. The AIE feature of TTE molecule. (A) The photoluminescence (PL) spectra of TTE in THF and THF/water mixtures with increasing water fractions ( $f_w$ ) to 99%. (B) Change in PL intensity of TTE at 410 nm versus water fraction in THF/water mixtures. Concentration:  $10^{-5}$  M. Excitation at 368 nm. Inset: from left to right fluorescence of TTE in pure THF, powder, and in THF/water mixture at 99%  $f_w$ .

Having a similar structure to the TPE, TTE also has good solubility in common organic solvents such as THF, dichloromethane, and chloroform, and due to its hydrophobic nature, it has poor solubility in water. Therefore, we chose a THF/water mixture system to investigate its luminescent behaviour upon aggregation. The pure THF solution of TTE is virtually non-emissive (Figure 1A and Figure 1B, inset).

When the fraction of poor solvent, water, is increased while keeping a fixed TTE concentration of  $10^{-5}$  M, emission intensity increases with the maximum peak observed at 410 nm. Figure 1B shows the emission intensity enhancement with increasing water fraction. Faint emission is detectable in the pure THF

solution (0% water fraction), but no prominent enhancement is observed until the water fraction reaches 90%. The proposed RIM mechanism<sup>12</sup> is employed to explain the above data. In the solution state, the TTE molecules experience minimal interactions between each other. Surrounded by solvent molecules, this allows each of the thiophene rings of TTE to freely rotate and vibrate. Upon excitation, this freedom causes the molecules to relax back to the ground state *via* non-radiative processes resulting in weak solution emission. With increasing water volume fractions, the hydrophobic molecules aggregate together. The proximity of neighbouring molecules induces steric effects which block the intramolecular motions of TTE thus preventing relaxation via non-radiative channels. With the excited state non-radiative decay processes prohibited upon aggregation, emission becomes strongly enhanced.<sup>52</sup> It's worth noting that TTE molecules only begin to show emission enhancement at the high water fraction of 90%, whereas TPE exhibits emission enhancement when water fraction is above 60%.<sup>53</sup>

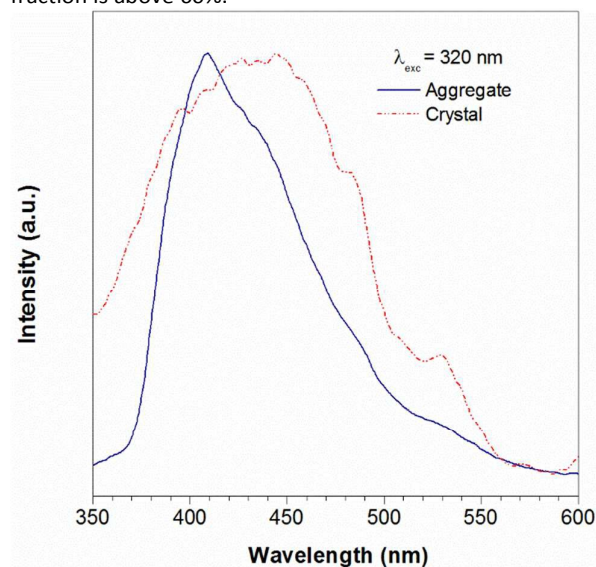


Figure 2. The photoluminescence of TTE THF/water aggregates and crystal. The photoluminescence spectrum of TTE in aggregate (blue line), and crystal (red line) state. Excitation at 320 nm.

According to the reported method as described in the experimental section, we successfully obtained the crystal of TTE. To further study the luminescent properties of solid state TTE, we have conducted the photoluminescence study of TTE in crystal and THF/water aggregation states (Figure 2). These photoluminescence studies were performed using an excitation wavelength of 320 nm. The emission maximum peak for the crystal was measured at 444 nm and at 410 nm for the THF/water aggregate. Further discussion and explanation of the photophysical properties of TTE will be included in the following crystal packing section.

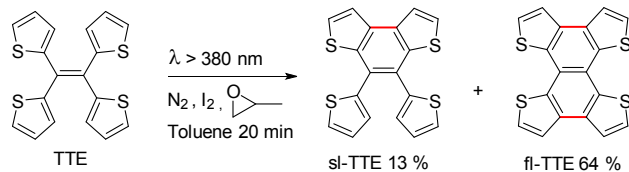
Currently, the restriction of intramolecular motion (RIM) is one of the leading theories for explaining AIE phenomena.<sup>12, 54</sup> To explore the AIE activity in the TTE system, we adopted a feasible synthetic route to obtain the locked structures of TTE





## ARTICLE

(Scheme 2),<sup>49</sup> 4,5-bis(thiophene-2-yl)thieno[3,2-e]benzo[b]thiophene, (semi-locked TTE, sl-TTE) and tetrathieno[2,3-a:3',2'-c:2'',3''-f:3''',2'''-h]-naphthalene (fully-locked TTE, fl-TTE). sl-TTE was also further characterized by single crystal X-ray diffraction (Figure S113-19).



Scheme 2. Synthesis of semi-locked TTE (sl-TTE) and fully-locked TTE (fl-TTE).

The photoluminescence experiments of sl-TTE and fl-TTE were conducted and the data is shown in Figure 3 and 4, respectively. With the same experimental condition used for TTE, sl-TTE was also studied with the THF/water mixture system. Starting from a pure THF solution, which has 0% water fraction, two out of three fluorescent peaks are detected in ultraviolet region while the third one is located at 489 nm (Figure 3A). Increasing of the water fraction, both ultraviolet peaks are enhanced in terms of emission intensity. In contrast, the fluorescence emission at 489 nm is dramatically decreased. Comparing the 0% and 90% water fractions, the fluorescence at 489 nm experiences a 0.25 fold change while the fluorescent peaks below 400 nm increased with a 1.47 fold change as shown in Figure 3B. The broad unstructured band at 489 nm is likely due to the emission from the benzodithiophene core conjugated with the thiophene rings. The rotations of the rings change the conjugation efficiency between the core and the thienyl rings resulting in the broad and unstructured nature of the emission band. As the molecules aggregate the emission intensity of this broad band is reduced, indicating that the original electronic conjugation is disrupted. This electronic disruption could be due to the formation of intermolecular steric interactions which twist the thienyl rings out-of-plane with the benzodithiophene core. These intermolecular steric interactions also rigidify the molecules resulting in the increase of emission intensity for the peaks below 400 nm. The peaks below 400 nm are attributable to the emission of the thiophene rings. Indeed, the two freely rotatable thiophenes, like AIEgens, decrease radiative decay in solution by dissipating energy through vibrational motions. However, in the aggregation state, the thiophene rings become more emissive as a result of the restriction of the intramolecular motions of sl-TTE, specifically the rotational motion of the thiophene rings and vibrational motion of the whole molecule. This causes the emission in ultraviolet region to be stronger in the aggregation state than in solution state. In this way, sl-TTE exhibits both ACQ and AIE characteristics.

The fully locked structure of TTE (fl-TTE) displays photoluminescent properties much more similar to

conventional luminophores. In Figure 4A, the photoluminescence spectrum is recorded with the same methodology as previous compounds. Strong emission is observed in the solution state. When the water fraction of the solution is increased, the emission decreases and the maximum emission peak is red-shifted. Due to the fully locked structure, its discotic shape endows the molecule with the

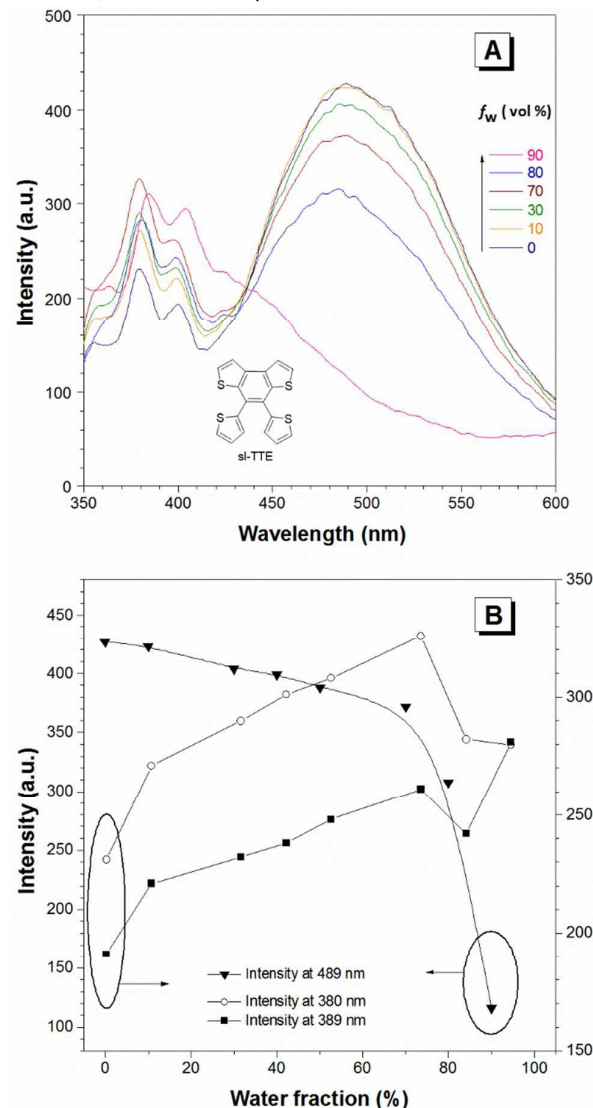


Figure 3. The AIE and ACQ feature of sl-TTE molecule. (A) The photoluminescence (PL) spectra of sl-TTE in THF and THF/water mixtures with increasing water fractions ( $f_w$ ) to 90%. (B) Change in PL intensity of sl-TTE at 489, 389 and 380 nm versus water fraction in THF/water mixtures. Concentration  $10^{-5}$  M. Excitation at 323 nm.

ACQ effect, shown in Figure 4B. Potential intensive  $\pi$ - $\pi$  stacking interactions between molecules can lead to the narrowing of the energy gap of the molecule upon aggregation. As there are no freely rotatable moieties in fl-TTE, no AIE activity is observed from this molecule. Typical of ACQ dyes, fl-TTE is emissive in solution state with two peaks as a result of its rigid nature. When the water fraction reaches 90%, the emission is greatly weakened likely due to the formation of



excimers as evidenced by the red-shifted emission to the visible region of the spectrum.

Shown in Figure 5, the complete series of TTE, sl-TTE and fl-TTE, constructed with the number of locking position. Thanks to the rotatable parts of the four thiophenes on TTE, it has typical AIE characteristics. Gradually, as two thiophenes become

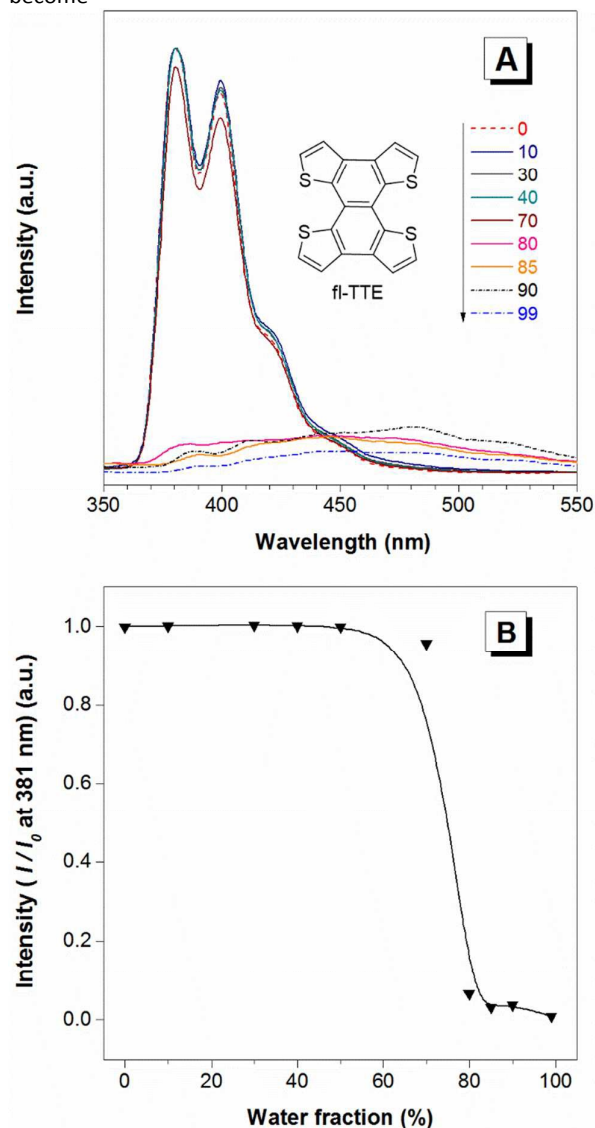


Figure 4. The ACQ feature of fl-TTE molecule. (A) The Photoluminescence (PL) spectra of fl-TTE in THF and THF/water mixtures with increasing water fractions ( $f_w$ ) to 90%. (B) Change in PL intensity of fl-TTE at 381 nm versus water fraction in THF/water mixtures. Concentration  $10^{-5}$  M, excitation at 299 nm.

locked by a covalent bond at the  $\beta$  positions, the molecule sl-TTE shows both AIE and ACQ properties. Eventually, when the four thiophenes are locked into a planar structure, the molecule suffers from the ACQ effect. This reinforces the theory behind the AIE mechanism where rotatable moieties non-radiatively dissipate excited-state energy. Upon aggregation, their motions become hindered and emission is

enhanced. Due to the propeller-shape molecular structure, intermolecular  $\pi - \pi$  stacking interactions are prevented, allowing for strong solid state emission. By locking the rings, the AIE property is lost as a consequence of the formation of a conventional planar luminophore which becomes afflicted with the ACQ phenomenon.

As TPE is an archetypal AIEgen that has been widely studied and due to its structural similarity to TTE, it is useful to compare the two molecules. A set of photophysical data of TPE

Table 1. Summary of Optical Properties of TPE, TTE, sl-TTE and fl-TTE

	$\lambda_{em}$ (nm)		Stokes shift (nm)	$\Phi_{AF}^c$ (%)	$\tau_f^c$ (ns)	$\alpha_{AIE}$	Remark
	Aggregation	Crystal					
TPE	462 <sup>a</sup>	450	153	23	1.29	344	AIE
TTE	409	444	40	2.6	0.47	20	AIE
sl-TTE	380 <sup>a</sup>	389 <sup>a</sup>	60 <sup>d</sup>			1.47	AIE and ACQ
TTE	489 <sup>b</sup>						
fl-TTE	381 <sup>b</sup>		3			0.1	ACQ
DTE	401 <sup>a</sup>	438	59	15	0.85	0.25	ACQ <sup>e</sup>

Table legend:  $\lambda_{em}$  = first photoluminescence (PL) peak;  $\Phi_{AF}$  = absolute fluorescence quantum yield;  $\tau_f$  = fluorescence lifetime;  $\alpha_{AIE}$  = PL Intensity peak aggregation / PL Intensity peak solution.

<sup>a</sup> peak with AIE characteristic; <sup>b</sup> peak with ACQ characteristic; <sup>c</sup> measurement performed in powder state;

<sup>d</sup> calculated considering the first emission peak, it is worthy to note that the emission of this molecule is a dual emission and the first and second emission peaks are ascribable to the emission of the thiophene rings, as explained in the manuscript; <sup>e</sup> DTE is an ACQ molecule as the PL intensity decreases upon occurring of the aggregation condition (see Figure S15 in ESI) but it is also emissive in powder (see quantum yield and lifetime values in table herein) and in crystal state (see Figure S16 in ESI).



Figure 5. Trend of the AIE phenomenon as a function of the molecular structure. The blue arrows indicate the possible rotation of the thiophene rings around the single bond.

has been included in Table 1 for comparison. The absolute quantum yield of powder TTE is 2.6%, which is much lower than the quantum yield of TPE. This is understandable as the thiophene rings in TTE are not generally considered as excellent emitting species as the heavy sulfur atom enhances excited state intersystem crossing. Thus, the  $\alpha_{AIE}$  value of TTE is reasonably less than that of TPE.<sup>55</sup> The  $\alpha_{AIE}$  value is the emission enhancement defined as  $\alpha_{AIE} = I_{agg} / I_{soln}$ , where  $I_{agg}$  is the emission intensity of the aggregated state in the



## ARTICLE

## Journal Name

water/THF fraction mixture and  $I_{\text{soln}}$  is the emission intensity of the solution state in the pure THF solution.

The maximum absorption of TTE is more red-shifted than TPE. This is reasonable because thiophene rings are more electron-rich than the phenyl rings, since the same number of  $\pi$ -electrons are delocalized over 5 atoms instead of 6, respectively. As a consequence, TTE has an energy gap (both optical -see Table S11 in ESI- and electrochemical<sup>48</sup>) that is smaller than TPE.<sup>48</sup> However this behaviour is not mirrored in the photoluminescence, because the emission maxima of TTE in the THF/water aggregates, and crystal state are consistently more blue-shifted than TPE (Table 1, see Figure S11 for aggregate PL comparison). Why do these molecules have such difference in the luminescence properties while sharing structure similarity?

### Crystal analysis

Single crystal analysis of TTE (Figure 6) allow us to study the molecule in further detail. The comparison between the crystal structures of TTE and TPE<sup>56</sup> provides us a precious opportunity to better understand the emission behaviour of TTE and why the emission is regularly more blue-shifted than TPE. The measured dihedral angle between each ring and the central double bond plane for both TPE and TTE are listed in Table 2. Unlike the TPE, TTE does not adopt a propeller-shaped structure. Neither are the dihedral angles similar to TPE. Moreover, the highly symmetrical structure of TTE turns out to have two pairs of identical dihedral angle values of 24.61° and 84.72°, respectively. The smaller angle value of 24.61° suggests that two thiophenes in TTE are better conjugated with the double bond centre than the phenyl rings of TPE, which have dihedral angles between 45° to 56°. The other angle of 84.72° indicates there are two thiophenes which are nearly perpendicular to the double bond plane and thus have minimal electronic communication with the central double bond and the other thiophene rings.

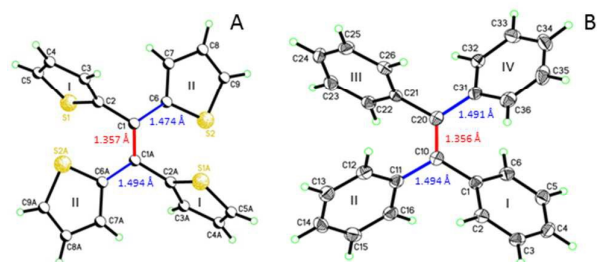


Figure 6. ORTEP figures of (A) TTE and (B) TPE, in which are highlighted the double and single bond lengths.

Table 2. Dihedral Angle<sup>a</sup> of TTE and TPE.

Aromatic Ring <sup>b</sup>	TTE	TPE
I	84.72	45.50
II	24.61	47.33
III	/	44.59
IV	/	56.37

<sup>a</sup> Angle between the plane of each ring and the one of the double bond. (see example in Figure S14 ESI).

<sup>b</sup> Aromatic rings for both molecules are labelled in Figure 6.

As a result, the crystal structure of TTE is quite different to the structure of TPE. The thiophene rings of TTE can be resolved into two mentioned sets: i) the orthogonal set of the thiophenes have the sulfur atom labelled S1 and S1'; and ii) the more conjugated set of thiophene rings with S2 and S2' (Figure 7). When the double bond plane is placed horizontally, the S1 and S1' thiophene rings can be seen adopting positions which are parallel to each other (Figure 7, side view). When the thiophene with the S1 atom is closest to the viewer, the thiophene ring is tilted to the right ("right-handed"); when the S1' ring is closest to the readers, the ring is tilted to the left ("left-handed"). The same phenomenon is also observed for the S2/S2' rings. This contrasts with the TPE molecule where all its aromatic rings have a left-handed orientation (Figure S12). The two sets of thiophene rings play a large role in the conjugation of the entire system and consequently strongly influences its photophysical behaviour. The S1 and S1' thiophene rings, due to their almost orthogonal positioning (Figure 7), can be seen as almost being isolated from the conjugation system. On the other hand, S2 and S2' rings are almost in the same plane as the double bond. This closely mirrors the structure of (*E*)-1,2-di(thiophen-2-yl)ethene (trans-dithienylethene, DTE), where the two thiophene rings lie in the

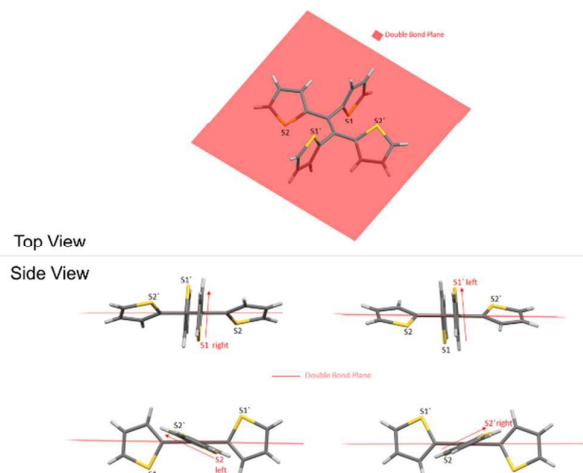


Figure 7. Top and side view of the orientation of the thiophene rings with respect to the double bond.



same plane as the double bond (Figure S17 and S18). The emission of DTE has a maximum peak at 401 nm in the aggregated state (Figure S15). Thus, the emission observed for TTE (Table 1) can be explained by the emission from the backbone of S2 and S2' thiophenes connected by the double bond, which is structurally analogous to DTE, and that the S1 and S1' thiophenes barely contribute to its emission.

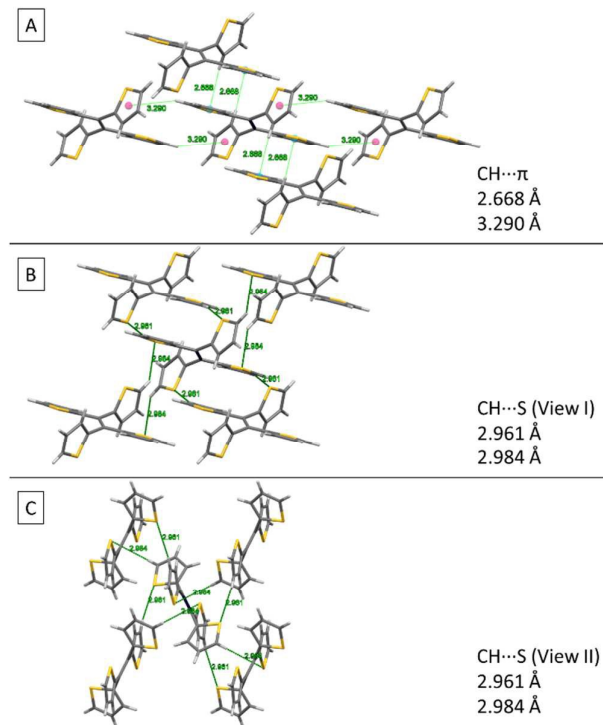


Figure 8. Non-covalent interactions in TTE crystal. (A) CH... $\pi$ , (B) side view and (C) top view of CH...S interactions in TTE crystal.

Figure 8 shows two kinds of non-covalent interactions: CH... $\pi$  (Figure 8A), CH...S (Figure 8B and 8C) in TTE crystal packing, whereas TPE only has CH... $\pi$  interactions (Figure S13). The CH... $\pi$  interactions in TTE have lengths of 2.668 Å and 3.290 Å. The shorter distanced CH... $\pi$  interaction is between one of the perpendicular thiophene hydrogens to the nearest adjacent intermolecular thiophene unit, which lies in the same plane as the double bond. Meanwhile, one of the coplanar thiophene hydrogens points to the  $\pi$ -system of its nearest orthogonal thiophene ring resulting in the CH... $\pi$  interaction with a distance of 3.290 Å (Figure 8A). The CH...S interactions have measured distances of 2.961 Å and 2.984 Å. One of the CH...S interactions exists between the perpendicular thiophene sulfur atom and its nearest intermolecular aromatic hydrogen at the distance of 2.961 Å. In addition, the sulfur of the thiophene ring lying coplanar to the double bond interacts with its adjacent hydrogen at a length of 2.984 Å. Such interactions exist abundantly in the TTE crystal packing and together these interactions rigidify and stabilize the packing preventing the free rotation of each thiophene ring. Thus, non-radiative

relaxation becomes blocked and the fluorescence can be observed in the crystal via the radiative decay.

As it has been reported for hexaphenylsilole (HPS), PL behaviour can show dependency on the aggregation state of the luminogen in a phenomenon called: "morphochromism".<sup>55, 57</sup> Comparing the emission spectrum of TTE for both its THF/water aggregates and crystals (Figure 2), the peak for the crystal emission is *red*-shifted from its aggregation state. However, this type of morphochromism is atypical for AIEgens, where the crystal emission is usually *blue*-shifted from its aggregation state. In typical AIEgens, crystal structures show that due to the packing, the aromatic rings usually adopt a highly twisted conformation. High dihedral angles reduce electronic communication in the  $\pi$  system likely resulting in the more blue-shifted emission. TPE exemplifies this perfectly, whose emission as THF/water aggregates occur at 462 nm while the crystal state emission is *blue*-shifted to 455 nm. In contrast, the THF/water aggregate sample of TTE emits at 409 nm while its crystal state emission is *red*-shifted to 444 nm, as shown in Figure S133, from the powder X-ray diffraction (pXRD) analysis the aggregate formed from THF/water mixture is amorphous in nature, lacking any distinctive crystal peaks. Why does TTE have an opposite morphochromic behaviour although it is a typical AIEgen?

#### S...S interactions

From our previous studies of non-conventional luminescent systems, the clusteroluminogenic effect, as proposed by our group,<sup>12</sup> can be one of the causes which results in the observed luminescence for systems that lack conventional  $\pi$ -conjugated moieties but are rich in heteroatoms. Such effect has been primarily observed in systems with an abundance of oxygen atoms,<sup>36</sup> such as carbonyl and ester functional groups. The well-aligned oxygen atoms and intensive interactions between the oxygens which have been found in the theoretical packing of the polymer chains, are the major factors thought to be responsible for clusteroluminogenic effect. Inspired by our previous clusteroluminogenic studies, we have further investigated the existence of S...S interactions (Figure 9) in TTE. It was exciting to discover the existence of both intermolecular and intramolecular S...S interactions.

Firstly, due to the symmetry of the crystal structure there are two identical intramolecular S...S interactions between the S1 and S2 atoms distanced at 3.669 Å (Figure 9A). Secondly, there are two different kinds of intermolecular S...S interactions: S1...S2 and S2...S2 types with the distance values of 3.840 Å and 4.252 Å, respectively. These interactions are abundantly interlaced throughout the TTE crystal packing. To more clearly illustrate these interactions, Figure 9B shows a layer of this very packing consisting of rows of TTE molecules. S2 to S2 intermolecular interactions are found between TTE molecules with the same coloured backbone; in other words, between red/red or grey/grey carbon skeleton with a distance of 4.252 Å. S1 to S2 intermolecular interactions are found between red carbon skeletons and grey carbon skeletons with distances of 3.840 Å. This crystallization-induced red-shifted emission is





also observed in DTE (Figure SI6). The DTE crystals show a 37 nm emission red-shift with respect to the aggregate state

(Table 1); its crystals have an emission maximum at 438 nm and its

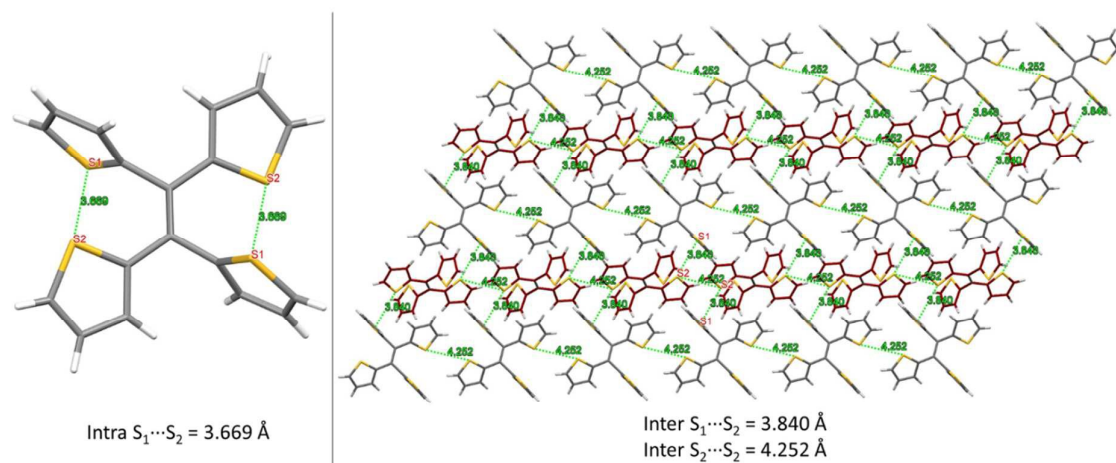


Figure 9. S...S interactions in TTE crystal. Left: intramolecular interactions in the asymmetric unit of TTE crystal; right: intermolecular interactions in TTE crystal network.

aggregates emit at 401 nm. It is remarkable that this red-shift is of the same magnitude as TTE, which has a red-shift of 35 nm. Examining the packing of DTE crystals, similar S...S interactions are also seen (Figure SI12). The intermolecular S...S distances of 3.679 Å are comparable to TTE (3.669 Å). Shorter intramolecular and intermolecular S...S interactions have been also found in both the sl-TTE and fl-TTE crystals. In sl-TTE, intramolecular S...S interactions has distances of 3.602 Å and 3.463 Å, whereas intermolecular interactions have a distance of 3.513 Å (Figure SI19). Further examination of the published fl-TTE crystal<sup>58</sup> revealed that it has intramolecular S...S distances of 3.062 Å and 3.077 Å, and intermolecular S...S interactions of 3.425 Å (Figure SI28). It is also worth noting that although fl-TTE is a classic ACQ dye, it is emissive in the powder state (Figure SI20-21). The reason could lie in the existence of S...S interactions, where the non-bonding through-space interaction might extend electronic communication, and to create a radiative channel for dissipating energy.

To better highlight the significance of these S...S distances, a comparison between van der Waals radii of several atoms has been made (Figure 10).

Sulfur atoms have a van der Waals radius of 1.80 Å. Based on this, the inter-atomic distances between two sulfur centres would measure 3.60 Å (Figure 10); this highlights proximity of the intramolecular and intermolecular distances for both crystal, of TTE (3.669 Å) and DTE (3.679 Å). A similar consideration can be drawn for the PMAh system.<sup>36</sup> The solution of the maleic anhydride monomer shows no visible emission while the solution of PMAh displays sky blue emission. The optimized structure of PMAh exhibited very close oxygen-oxygen distances of 3.1 Å and it was theorized that these interactions were highly significant for the observed emission. The van der Waals radius for oxygen is 1.52 Å (Figure 10). As such, the inter-atomic distances between two oxygen centres would only be 3.04 Å. This is very close to the calculated value in PMAh. The fact that both of these systems

have interactions close to the limit of their van der Waals radii mirrors another commonly known through-space interaction:  $\pi$ - $\pi$  interactions between aromatic carbon systems. Strong  $\pi$ - $\pi$  interactions between carbon atoms have measured distances in the vicinity of 3.4 Å to 3.5 Å, which is the inter-atomic distances of carbon atoms based on its van der Waals radius (Figure 10). Prof Cheng et al. have also found selenium-selenium interactions in the crystal state of naphthodiselenophene<sup>59</sup> and with Se...Se distances nearing the van der Waals radii of selenium atoms. For TTE and other clusteroluminogens, the exact nature of the heteroatom interaction still needs to be identified, *i.e.* how the interactions between the orbitals result in the observed change in photoluminescence, but one thing seems apparent and that is the strength of the interaction and thus the observable change in emission is highly dependent on the inter-atomic distances. Therefore, in the case of TTE and DTE, it is reasonable to believe that the S...S interactions play a crucial factor in the observed red-shift in emission. One possibility could be that the sulfur-sulfur interactions are able to extend electronic communication or perhaps stabilize the excited electronic state. The red-shifted emission in the crystal state of TTE and DTE, in other words its clusteroluminescence, is thus likely due to the emergence of S...S interactions.

The S...S interactions exemplify how intra/intermolecular heteroatom interactions can lead to luminescence offering a model that can be applied to other heteroatom rich systems such as PMAh,<sup>36</sup> and perhaps can help to understand the luminescent behaviour of other clusteroluminescent systems including starch.

In addition, due to the polarity of the sulfur atom, this likely facilitates interactions between TTE and water molecules. As such, it is possible when the molecules are in an aqueous environment that the water molecules insert themselves between sulfur atoms splitting intramolecular S...S interactions. As such in the aggregation state which is induced upon the addition of water, water molecules could be trapped



impeding the formation of intramolecular S...S interactions, preventing the clusteroluminogenic effect. Thus, the aggregation emission is blue-shifted when compared to its crystal emission.

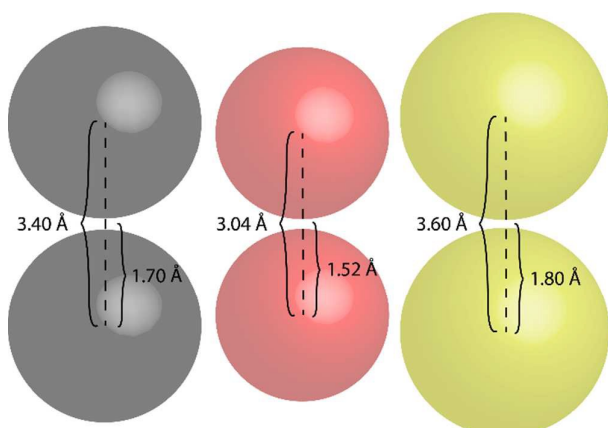


Figure 10. Space-filling models of carbon (grey), oxygen (red) and sulfur (yellow) atoms illustrating their van der Waals radii and centre-to-centre distances.

## CONCLUSION

In this work, tetrathienylethene (TTE) has been shown to be AIE active, non-emissive in solution but emits light in the aggregated, amorphous, and crystalline state. Thanks to the presence of the sulfur heteroatoms, non-covalent S...S interactions emerge in the crystalline state and are likely the cause of the emission red-shift when compared to the amorphous emission. Indeed, similar interactions in DTE also red-shift the emission. These heteroatom interactions help explain the clusteroluminescence observed in systems that lack conventional  $\pi$ -conjugation but rich in heteroatoms such as poly(maleic anhydride). The conversion of AIE to ACQ activity in the fully-locked TTE (fl-TTE) supports that luminescence of TTE is due to the restriction of intramolecular rotation, and that through locking its thiophene rings fl-TTE becomes a classic ACQ luminogen. This is further evidenced in semi-locked TTE, which displays both ACQ and AIE activity. Both sl-TTE and fl-TTE reveal that locking the thiophene rings diminishes AIE activity. In other words, AIE activity can be tuned by selectively locking the thiophene rings. AIE activity is premised upon rotatable/vibratable moieties which first lead to non-radiative decay, and when such motions are restricted the non-radiative channels become blocked resulting in radiative decay. The quantum yield of TTE is not particularly high due to the presence of the sulfur atoms, but its emission in the aggregate or solid state is still fairly strong, and hence TTE could be used in biosensor applications which are already under investigations. With these promising results and thanks to the ease of functionalization of TTE<sup>17</sup> we are currently investigating the development of TTE as a base for the construction of new TTE-based AIEgens for more specialized applications.

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## Notes and references

In the supplemental information are reported: the crystal data of TTE, sl-TTE and DTE, the photophysical data of data of DTE, the optical data and Uv-vis spectra of TTE, sl-TTE and fl-TTE. The crystallographic data for TTE (1509230), DTE (1509231), and sl-TTE (1509232) have been submitted to the Cambridge Crystal Data Centre (CCDC).

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