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COMMUNICATION

A Br substituted phenanthroimidazole derivative with aggregation induced emission from intermolecular halogen-hydrogen interactions

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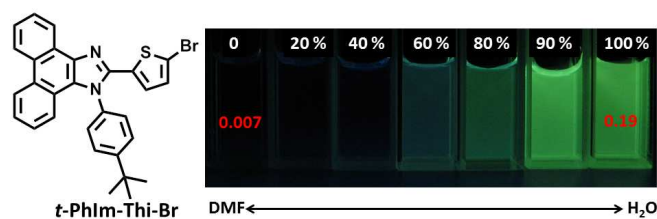
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A unique aggregation induced emission (AIE) active emitter based on Br substituted phenanthroimidazole derivative was reported. The yellowish green emission with high quantum yield and large stokes shift (~150 nm) in the aggregated state is proposed to be from weak interactions especially C-H...Br interactions.

Luminogenic materials with aggregation induced emission (AIE) performance have attracted much attention for their wide application in organic electronics and biosensor.¹ In the past decade, many AIE materials have been reported,²⁻¹⁰ Most of them have been ascribed to an intramolecular restricted rotation (RIR) mechanism proposed by Tang *et al.*,^{2-7b} however, this may not be a full story. Other AIE active complexes from *J* aggregation,⁶ excimer formation,^{7a, c} activated phosphorescence,^{8, 9} aurophilic interactions¹⁰ and so on have also been documented. AIE active molecules are highly luminescent in the solid state, which is a prerequisite for most display applications. In spite of many reports on AIE active materials with various mechanisms, it is still highly significant to find new AIE systems as candidates for developing new functional luminescent materials.

Recently, Kim *et al* reported an interesting AIE emitter.⁹ Unlike most AIE active molecules, Br substituted benzaldehyde shows not only enhanced intensity but also evidently large stokes shift due to the directed heavy atom phosphorescence. The large stokes shift upon aggregation give this material potential significant meaning in bio-imaging or bio-sensing. However, this material can only exhibit phosphorescent emission in bulk crystallization or co-crystal state,

which may hamper its practice application in OLED or bio-sensing.



Scheme 1 Structure of *t*-PhIm-Thi-Br and its photographs in the mixtures of DMF and water (water contents 0 ~ 100%) taken under 365 nm hand-lamp irradiation.

Considering the unique effect of halogen in many interesting luminescent phenomena and the high quantum yield, good stability and diversity available of phenanthroimidazole derivative, herein, we present an AIE active compound based on phenanthroimidazole derivative, 2-(5-bromothiophen-2-yl)-1-(4-(tert-butyl)phenyl)-1H-phenanthro[9,10-*d*]imidazole,¹¹ denoted as *t*-PhIm-Thi-Br (Schemes 1 and S1). The compound exhibits very unique AIE phenomenon with emission intensity significantly enhanced and a new emission band emerged with very large stokes shift in both nano-aggregation state and solid state. In DMF, *t*-PhIm-thi-Br is almost non-emissive with quantum yield of 0.007, whereas it turns on with green-yellow emission of quantum yield up to 0.19 in pure water.

Emission spectra of *t*-PhIm-Thi-Br in DMF/H₂O (water content $f_w = 0\sim 100\%$) solutions show different emission maxima and curve profiles (Fig. 1a) reflecting a process of dynamic aggregations with three different stages in water.

In stage I ($f_w < 50\%$), the blue emissions ($\lambda_{\max} = 410$ nm) of *t*-PhIm-Thi-Br in DMF/H₂O with water content less than 50% are very weak. Since *t*-PhIm-Thi-Br can be well dissolved in DMF, it is reasonable to believe that solute molecules disperse in solutions with such low water portions. The weak emission of *t*-PhIm-Thi-Br might be due to the intramolecular rotation of

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the thiophene and *t*-Bu-benzene rings^{4-7b} or the heavy atom effect of Br. To determine this, a similar molecule *t*-PhIm-Thi-H without Br substitute was synthesized for comparison. In good solvents, *t*-PhIm-Thi-H shows an emission mainly at ~410 nm similar to that of *t*-PhIm-Thi-Br (Fig. S1). The difference is that the emission quantum yield of *t*-PhIm-Thi-H is much higher (0.99 in DMF). Thus heavy atom effect of Br should be the key factor that makes the emission weaker.

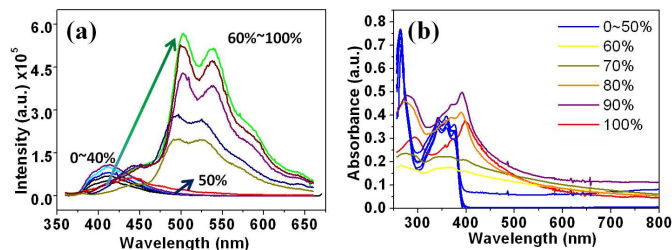


Fig. 1 Emission (a) and UV-Vis absorption (b) spectra of *t*-PhIm-Thi-Br in mixture of DMF and water with water content from 0 to 100% (10 μ M).

When the water content reaches 50% (Fig. 1a, Stage II, $f_w = 50\%$), the emission intensity of *t*-PhIm-Thi-Br decreased slightly and the peak red-shifted from 410 nm to 440 nm. A long tail after 400 nm in UV-Vis absorption curve appears (Fig. 1b). Similar luminescent spectral maxima can also be found both in the solid state and pure water of *t*-PhIm-Thi-H (Fig. S2). We propose that *t*-PhIm-Thi-Br molecules began to aggregate showing an excimer emission in this stage¹².

Increasing the water content to more than 50% (Stage III, $f_w > 50\%$), another new emission band emerged mainly at 500 and 540 nm with two shoulders at 440 nm and 585 nm, with the colour changing from faint deep blue to enhanced yellow-green which can be discerned by naked eyes. Further, the emission lifetime of *t*-PhIm-Thi-Br was determined to be ~4.7 μ s monitored at 450 ~ 585 nm in H₂O (Fig. S3a-e). The lifetime is relatively long for an organic molecule. However, this can not be attributed to phosphorescence by suppression of molecule rotation and vibration reported by others¹³ because of the inexistence of the longer wavelength emission from the spectra of *t*-PhIm-Thi-Br in glassy polymer of PMMA (5 mg / 400 mg). When the concentration increased up to 10 mg / 50 mg, the newly emission around 540 nm emerged, indicating the newly observed emission was caused by intermolecular interaction formation (Fig. S4). We speculate that the gradually enhanced intensity of obvious red-shift emission might be caused by J-aggregate formation, which typically shows distinctly absorption red-shift^{6c,12} (Fig. 1b).

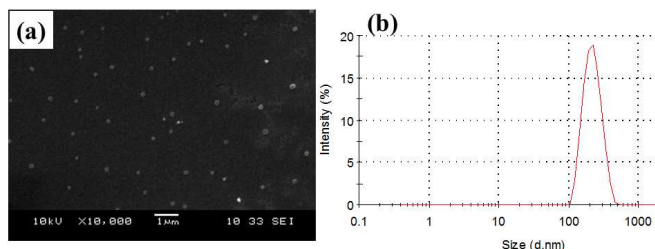


Fig. 2 Morphology (a) and size distribution (b) of *t*-PhIm-Thi-Br in aggregation state in pure water (10 μ M).

To prove the existing form of the aggregation state, SEM and DLS experiments of *t*-PhIm-Thi-Br in pure water at 10 μ M were carried out (Fig. 2). SEM clearly gave an image of uniform nano-particles (~200 nm), which was further proved by the DLS experiment giving size distribution of ~196 nm. Noted that the aggregation nano-particles well dispersed in water and the solution is clear (Fig. S5).

The emission profile of *t*-PhIm-Thi-Br in the solid state (Fig. S2) is similar to those in DMF/H₂O with $f_w > 50\%$ and significant red-shift from those of $f_w \leq 50\%$ (Fig. 1a), peaked at ~440, 500 and 540 nm. A reasonable deduction of the longer wavelength emissions maybe stronger molecular interactions in the solid state¹⁴ and in nano-aggregation state.

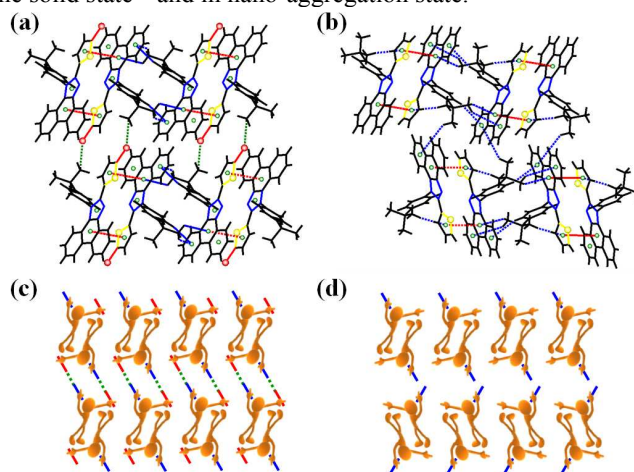


Fig. 3 Crystal packing of *t*-PhIm-Thi-Br (a) and *t*-PhIm-Thi-H (b), color codes for elements: S, yellow ball; Br, red ball. color codes for interactions: π - π , red dot line; C-H... π , blue dot line; C-H...Br, green dot line. Illustration of head-to-tail packing of *t*-PhIm-Thi-Br (c) and *t*-PhIm-Thi-H (d), blue and red bars representing hydrogen-rich *t*-butyl group and -Br, respectively.

Single crystals of *t*-PhIm-Thi-Br and *t*-PhIm-Thi-H were obtained by slow vaporizing dichloromethane solutions of the corresponding compounds. The results showed that both structures (Fig. 3a, b) have a very similar geometry with that thiophene ring is co-planar to phenanthroimidazole conjugate perpendicular to *t*-Bu-benzene with a degree of nearly 90°. In the structure of *t*-PhIm-Thi-Br, two adjacent molecules are dense packing as a dimer by π - π interactions (3.59 Å) between thiophene ring from one molecule and phenanthrene ring from the other in a head-to-tail fashion. The dimers further extend in *b* direction by C-H... π interactions (2.95 Å) forming a packing row (Figs. 3a, S6a, b). A similar packing row is also found in the structure of *t*-PhIm-Thi-H with π - π interactions of 3.62 Å and C-H... π interactions of 2.86 Å (Figs. 3b, S6c, d). One difference in the structures of *t*-PhIm-Thi-Br and *t*-PhIm-Thi-H is their packing between two adjacent rows: *t*-PhIm-Thi-Br in the same direction vs. *t*-PhIm-Thi-H in the opposite (Fig. 3a, b). The other difference is the existing of C-H...Br interactions (3.08 Å) between two adjacent rows in *t*-PhIm-Thi-Br. The PXRD patterns of nano-aggregate of *t*-PhIm-Thi-Br in stage III

matched well with the simulated one from the single crystal structure (Fig S7). The structural differences should response the different emissions of yellow green for *t*-PhIm-Thi-Br and blue for *t*-PhIm-Thi-H.

To find out the origin of the longer wavelength emission of *t*-PhIm-Thi-Br, we further synthesized some other similar molecules (Scheme S1) under the following considerations: 1) replacing Br with benzene (*t*-PhIm-Thi-Ph) to further verify that the Br substituent is crucial; 2) replacing Br with Cl (*t*-PhIm-Thi-Cl) to find the main factor from electron withdrawing effect, heavy atom effect and C-H...X (X= halogen) interaction; 3) replacing thiophene ring with benzene (*t*-PhIm-Ph-Br) to test the role of thiophene; 4) replacing *t*-Bu with H (PhIm-Thi-Br) or COOH (COOH-PhIm-Thi-Br) and 5) opening the rigid phenanthrene (*t*-Blm-Thi-Br) to see if the resulting molecule has any influence on the emission.

Photoluminescence spectra of the above mentioned molecules for comparison in DMF/H₂O ($f_w = 0 \sim 100\%$) solutions are shown in Figs. S8, S9 and S11.

The photoluminescence behaviors of *t*-PhIm-Thi-H and *t*-PhIm-Thi-Ph (Fig. S8) are very different from *t*-PhIm-Thi-Br. They show strong emission in DMF with much higher quantum yield (*t*-PhIm-Thi-H: 0.99, *t*-PhIm-Thi-Ph: 0.75). With water addition more than 70% for *t*-PhIm-Thi-H (60% for *t*-PhIm-Thi-Ph), the emission decreases slightly with a red-shift of about 15 nm (35 nm for *t*-PhIm-Thi-Ph), ascribed to a common ACQ (aggregation caused quenching) phenomenon. This result further implied that C-H...Br in *t*-PhIm-Thi-Br plays a crucial role for the strong yellowish green emission.

t-PhIm-Thi-Cl shows strong blue emission in DMF ($\Phi_f=0.39$, $\lambda_{max} = 412$ nm), suggesting that the heavy atom effect does not exist anymore when Br is replaced by Cl. The replacement of H in *t*-PhIm-Thi-H with Br or Cl only causes a little change in UV-Vis absorption peak (Fig. 1b, Figs. S8c and S9c), indicating electron-withdrawing does not significantly affect the orbital levels (see also HOMO and LUMO orbitals from DFT calculation in Fig. S10).

With increasing water contents, *t*-PhIm-Thi-Cl exhibits a similar emission behavior with *t*-PhIm-Thi-Br (Fig. S9a), peaking at 501 and 538 nm with two shoulders at 459 and 582 nm. However, the intensity ratio of emissions at blue region (~450 nm) and yellowish green region (500-600 nm) is higher than that of *t*-PhIm-Thi-Br, thus the emission color in pure water is cyan than yellowish green. Thus halogen atoms (Br/Cl) responding C-H...X (X=Br, Cl) interactions in the crystal structures should be an important factor to affect the emission energies.

Thiophene ring plays a crucial role which can be proved directly by the emission spectrum of *t*-PhIm-Ph-Br (Fig. S9b). The emission is weak in DMF with maximum wavelength at 391 nm, and its intensity decreases with a small red-shift with increasing water contents. The absorption locates at 362 nm with larger energy band than *t*-PhIm-Thi-Br, due to that thiophene can raise the HOMO energy effectively according to our previous report^{11, 15}. It is very probably that the electronic structure and chemical structure of thiophene ring is important for the unique emission property in this system.

PhIm-Thi-Br (also COOH-PhIm-Thi-Br, *t*-Blm-Thi-Br) shows deep blue emission in DMF and new emission band with large

stokes shift in H₂O (Fig. S11), similar to that of *t*-PhIm-Thi-Br. The difference is that COOH-PhIm-Thi-Br and *t*-Blm-Thi-Br exhibit low luminescent efficiency in pure H₂O (See pictures in the bottom of Fig. S11), likely due to the different aggregation types affected by the different moiety^{6ac, 16}. As shown in Fig. S11e, absorption maximum peaks of COOH-PhIm-Thi-Br is blue-shifted with opposite shift direction towards AIE-active *t*-PhIm-Thi-Br and PhIm-Thi-Br, which can be attributed to be the H-aggregate formation^{6c}.

Thus, N-aromatic moiety, with halogen atom and thiophene ring discussed above, are some main factors that affect the emission behaviour significantly. More concretely, supramolecular interactions of C-H... π , π ... π especially C-H...X (X= halogen) are responsible for the unique emission behaviour of *t*-PhIm-Thi-Br. And the enhanced emission should be caused by the strengthen of C-H...Br interactions for the J aggregate formation¹⁷. The essence of this AIE luminescence is still now under investigation and may be documented in the future.

In conclusion, we report an unique AIE active emitter based on phenanthroimidazole derivative showing high quantum yield and large stokes shift (~150 nm). By careful study on emission property (in good solvents, nano-aggregation state and solid state) and comparison of structures, spectroscopy of a series of designed derivatives, we found that the combination effect of J-aggregate formation and C-H...Br interaction is crucial for the unique emission behaviour, which may provide an opportunity in developing OLED and bio-sensing/imaging materials.

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TOC graphics

