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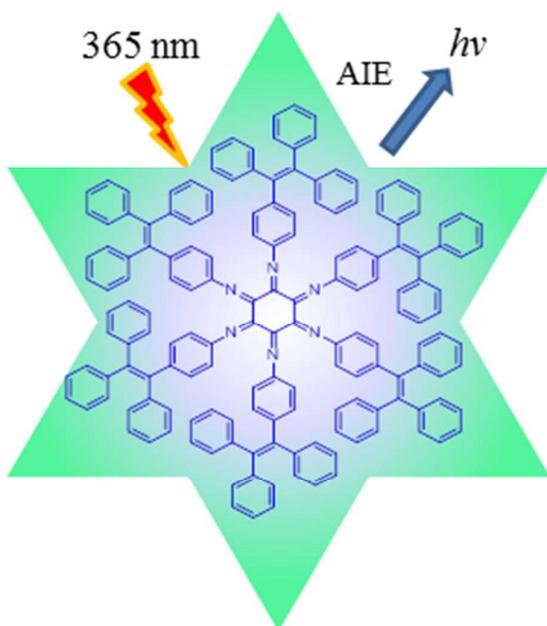
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Graphical Abstract



A rigid star-shaped luminogen (HTCA) exhibits aggregation-induced emission (AIE) characteristics.

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Aggregation-induced emission of star-shape luminogen based on cyclohexanehexone substituted with AIE active tetraphenylethene functionality†Received 00th January 2012,
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We describe a rigid star-shaped luminogen (HTCA) of cyclohexanehexone bearing six tetraphenylethene moieties, which exhibited strong aggregation-induced emission (AIE) characteristics. The twisting amplitude and steric hindrance of the TPE units were found to play a crucial role in their aggregated nano- to micro-structures. Interestingly, HTCA exhibits the reversible piezofluorochromic behaviour through grounding and reversed by treatment with solvents resulting in a cycle that can be repeated several times.

Designing small organic molecules with high efficiency luminescence in solid states has attracted the attention of many researchers for use in many areas such as organic light-emitting diodes, sensing, and imaging applications.¹ However, conventional fluorescent materials show good fluorescence in solution but suffer an aggregation caused quenching (ACQ) effect in the condensed phase and also in solid film.² In 2001, Tang group developed a new phenomenon of aggregation-induced emission (AIE), typical small organic molecules whose emissions are very weak when dissolved in good solvents, such as toluene, THF, and chloroform, but become highly luminescent in the aggregates and solid film state.³ Among the developed AIE-active luminophores, tetraphenylethenes (TPE) have attracted much attention due to their applicability in various fields such as OLEDs,⁴ bio/chemosensors,⁵ bioimaging,⁶ and so on. The AIE effect of TPE is rationalized to be caused by the restriction to its intramolecular rotations through non-radiative channel of phenyl rings and hence making TPE highly emissive.⁷

To determine whether a TPE-luminogen exhibits AIE activity when attach in conjugated form, as in the AIE effect of luminogen conformational planarity and structural rigidity play key roles. Little effort has been placed on studying how the twisting amplitude of the rotors affects the emissive behaviours of nonplanar AIE luminogens. Recently, star-burst materials utilising three or four TPE moieties as peripheries to the core of the propeller-shaped triphenylamine

derivatives exhibited strong AIE characteristics and high performance in OLEDs.⁸ In another example, Tang group used non-planar propeller-shaped hexaphenylbenzene (HPB) and attached end groups to traditional luminophores have exhibited AIE effect.⁹ Very recently, Chang *et al.*¹⁰ synthesised two rigid molecules based on the nonplanar structure of propeller shaped hexaphenylbenzene (HPB) or benzene as core groups and TPE as end groups i.e. BPT and BT, respectively, using Suzuki coupling reactions. The more extended structure BPT showed a much stronger AIE effect and higher quantum yield in the solid state in comparison with that of BT. Nevertheless, BT shows reversible piezofluorochromic behaviour when ground and treated with solvent, however, BPT showed no such effect.

However, conjugated small molecules constructed by more than four TPE units as peripheries present their own challenge in efficiently synthesising multiple branched and rigid molecules. Keeping this in mind, we have designed and synthesised a rigid star-shape conjugated HTCA luminogenic molecule bearing six TPE moieties to the core of cyclohexanehexone (CHHO) building blocks (Fig. 1).

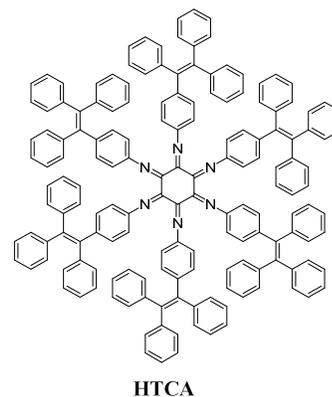


Fig. 1 Chemical structures of HTCA used for this study.

Star-shaped luminophore HTCA was prepared by the condensation of six equivalent of 4-(1,2,2-triphenylvinyl)aniline **1** (TPVA)¹¹ with cyclohexane-1,2,3,4,5,6-hexaone octahydrate in

acetic acid at 135 °C for 16 h. This yielded 35% of HTCA as a white powder. Synthesis and characterisation of intermediate TPVA and also a detailed procedure for HTCA outlined detailed in the Electronic Supplementary Information (ESI).† It is also important to note that HTCA is very stable in acidic as well as basic conditions.

Firstly, the thermal properties of HTCA were investigated by using thermogravimetric analysis (TGA). HTCA showed a high thermal stability, the onset temperature with 5% weight loss is about 485 °C under nitrogen atmosphere. The high residual yield up to 20% was retained when HTCA heated at 800 °C under nitrogen (Fig. 2a). The UV-vis absorption spectra of HTCA in dilute THF solution and solid thin films (obtained by spin-coating) as shown in Fig. 2b. Typically, HTCA exhibited π - π^* transition at 331 nm and in solid film absorption peak is red shifted by 7 nm i.e. at 338 nm. The red-shifted absorption spectra of HTCA in solution as well as in solid film clearly indicate a weak electronic coupling between TPE branch *via* conjugation and the steric repulsion of TPE.¹² It is important to note that the earlier review of the literature showed that absorption of AIE luminogens are not normally affected by aggregate formation.¹⁰

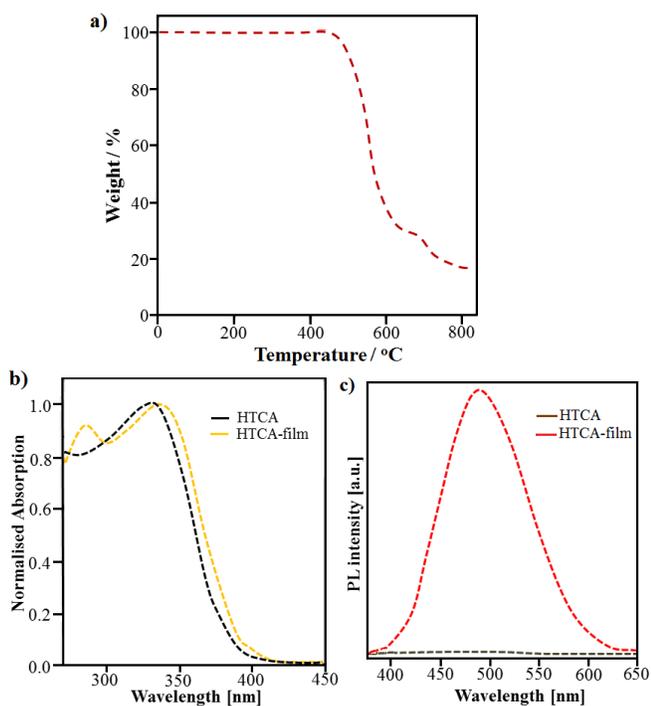


Fig. 2 (a) Thermogravimetric analysis (TGA) of HTCA and with a heating rate of 10 °C min⁻¹, recorded under nitrogen atmosphere. (b) The UV-vis absorption spectra of star-shaped luminophores HTCA in THF solutions (10⁻⁵ M) and in thin films. (c) Photoluminescence (PL) spectra of HTCA in THF and solid thin film.

The fluorescence emission spectra of HTCA showed no detectable signals in dilute tetrahydrofuran (THF) solution (Fig. 2c). The fluorescence quantum yield (Φ_F) of HTCA in THF solution are approximately 0.08%, was measured using Rhodamine B as a standard ($\Phi_F = 70\%$ in ethanol). Which clearly shows that due to the

active intramolecular rotation (IMR) process of phenyl rotors the excited energy state is consumed. The emission of HTCA in thin films exhibited strong luminescence and the maximum emission peaks are located at 485 nm (Fig. 2c). The associated $\Phi_{F,f}$ values of HTCA in thin films measured by integrating sphere reach 54%, which are higher than that of unsubstituted TPE.¹³ The relatively high Φ_F value of HTCA is presumably due to the more rigid structure and the limited amount of free rotation of TPE moieties and such emission enhancement in the solid state clearly indicated that HTCA displayed AIE activity.¹⁴ The AIE effect was determined by using following equation: $\alpha_{AIE} = \Phi_{F,f}/\Phi_{F,s}$ i.e. the emission contrast ratio between the solid state and solution state, respectively. The α_{AIE} data of HTCA is about 161, which is higher than of unsubstituted TPE.¹⁴ The higher α_{AIE} in the case of HTCA is due to rigid and extended π -conjugated structure, results also clearly shows that steric repulsion and conformation had no significant influence on the AIE effect.

To gain in depth knowledge about the AIE effect, we measured the emission of HTCA in THF and THF/water mixtures to study visual observation of the AIE by emission changes (Fig. 3). Typically, HTCA in THF is non-emissive and weak signals remain at water fraction (f_w) up to 30% because the compounds are soluble in those mixtures. However, by addition of more water, the intensity of emission dramatically increased, which was an indication that HTCA had begun to aggregate (Fig. 3a). Some luminogens become emissive in the presence of $f_w = 50\%$ and PL spectra are dominated by the slightly red-shifted and enhanced emission from the solution in THF to aggregated ($f_w = 90\%$) is by 218-fold (Fig. 3b). These results clearly verify their AIE characteristics and show that HTCA aggregates more easily and gives larger emission changes, owing to decreased solubility in THF/water mixtures and its extended π -conjugation. It has been shown in literature that aggregated states restrict the intramolecular rotation which promotes radiative decay of the excited state and allows molecules to have high fluorescence.^{9,10} We presume that the restriction of intramolecular rotation and the molecular conjugation facilitates synergetic effects between the neighbouring segments in the case of HTCA.

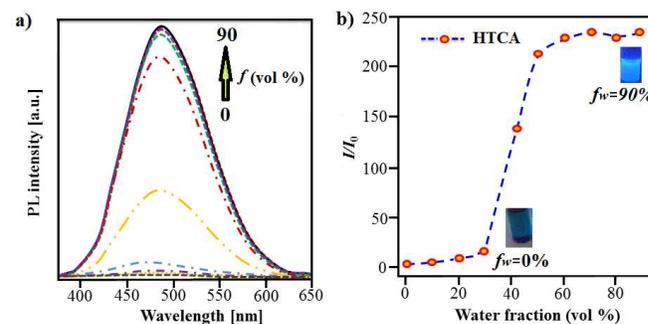


Fig. 3 (a) Photoluminescence (PL) spectra HTCA in THF/water mixtures with different water fractions ($f_w = 0$ –90%). (b) Plots of I/I_0 values versus the compositions of aqueous mixtures of HTCA. Solution concentration: 10 mM; excitation wavelength: 339 (HTCA). The photographs of HTCA in THF/water mixtures with different water fractions (f_w) percentage water is marked in each image, taken under UV illumination ($\lambda_{ex} = 365$ nm).

Scanning Electron Microscopy (SEM) was performed to identify the size and shape of aggregated microstructures. Typically, SEM images of HTCA in the mixture of water/THF ($f_w = 50\%$) assembled into cross-like uniform rod-shapes with a diameter of 5–10 μm with the width of rod being about 100–300 nm (Fig. 4a, b). By changing the concentration of the water fraction up to 70%, HTCA showed extended submicron crossed-fibril aggregates (Fig. 4c). However, in higher fractions of water in THF ($f_w = 90\%$), HTCA assembled into intertwined helical-microstructures with length of tens of micrometres with a width about 0.5–2.0 micrometres (Fig. 4d). Interestingly, upon mixing HTCA (10^{-3} M) in water/THF ($f_w = 80\%$) it assembled into a nanobelt-like assemblies submicron in length with a width of about 150–500 nm (Fig. 6a, b). These results clearly indicated that the assembly with the extended conformation symmetrical directional showed better self-assembly behaviour of star-shaped HTCA which must be related to the diameter and steric effect of the molecules.

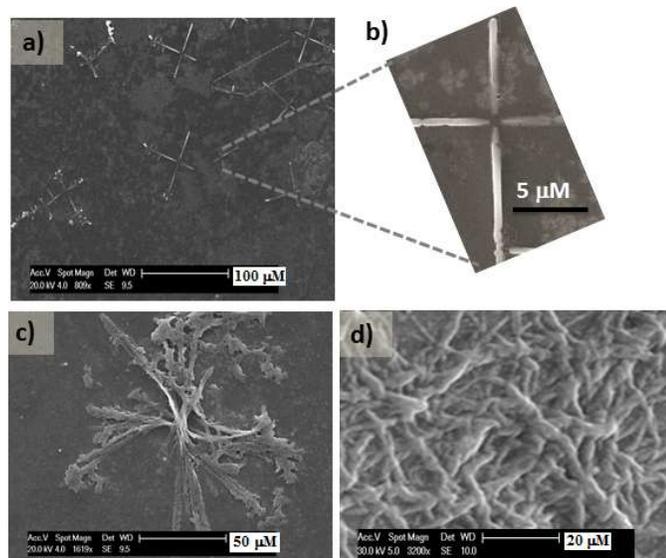


Fig. 4 Scanning electron micrographs of HTCA (10^{-5} M) from water/THF mixes with different water fractions of $f_w = 50\%$ (a & b), $f_w = 70\%$ (c) and $f_w = 90\%$ (d), respectively.

Furthermore, the pivotal role of conjugated TPE bridges, the piezofluorochromic effect of HTCA was investigated. Interestingly, the emission spectrum of the ground powder gives a large red-shift of 31 nm from 469 to 500 nm. These results confirmed HTCA's piezofluorochromic behaviour. This phenomenon can be reversed when pastel treated with acetone or $\text{CHCl}_3/\text{MeOH}$ (1:1, v/v) mixture or by heating (Fig. 5a). Importantly, were reversed many times through an alternation operation with grinding and solvent treatment (Fig. 5b). Fig. 5c shows the sky blue fluorescence of pristine HTCA crystals ($\lambda_{\text{exc}} = 365$ nm), however upon grinding with a pestle it showed a blue-green fluorescence. This is a clear indication that piezofluorochromic mechanism of HTCA is associated with morphology change from the more twist and loose crystalline state to the more compact in amorphous state. The phenomenon is similar to known piezofluorochromic molecules in the literature.^{9,10} We also demonstrated that when the ground paste was used to write "RMIT"

with a glass rod green fluorescence was only observed when irradiated at 365nm (Fig. 5d), which demonstrates the use of HTCA for labeling applications.

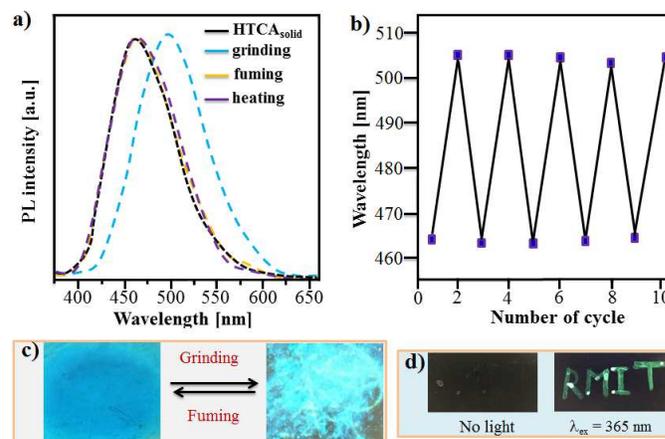


Fig. 5 (a) PL emission spectra of HTCA (1×10^{-5} M) in powder form, upon grinding, fuming (solvent treated) and heating. (b) Cycling behavior of the emission showing the reversibility of the process for number of times. (c) Changes in colour upon grinding and fuming, images taken under UV excitation at 365 nm. (d) Grinded past used to write "RMIT" by glass rod under UV excitation at 365 nm, text shows green fluorescent, however without excitation does not show the written text.

SEM images of HTCA (10^{-3} M) clearly shows amorphous nature upon grinding (Fig. 6c, d) and reversing assembly to belt-like nanostructures upon heating (Fig. 6e, f) Further, to examine the mode of self-organization from crystalline state to the more compact in amorphous state upon grinding is determined X-ray diffraction (XRD) measurements (Fig. 6g, h).

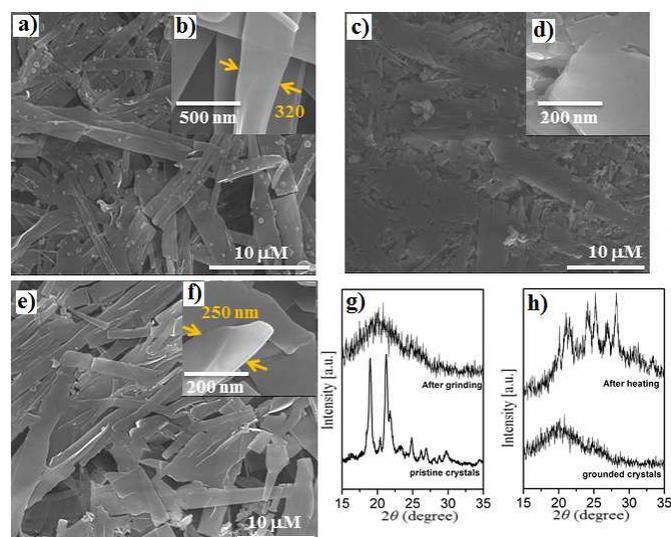


Fig. 6 Scanning electron micrographs of HTCA (10^{-4} M) from in (a & b) water/THF ($f_w = 80\%$) (c & d) upon grinding and dissolving sample in water/THF ($f_w = 80\%$) (e & f) and reversing assembly upon

heating sample ($f_w = 80\%$), respectively. (g, h) X-ray diffraction of HTCA in crystalline state (top), upon grinding (middle) and after heating 90 °C for 20 min.

Low angle XRD measurements displayed that the pristine crystals have sharp diffraction peaks, which indicate the powder is in the crystalline state (Fig. 6g bottom). The diffraction of the powders after grinding, however, have broadened peaks revealing the amorphous state of the HTCA (Fig. 6g bottom). This crystalline-to-amorphous transition is supported by the change of the fluorescence ($\lambda_{ex} = 365$ nm) from blue to green during the grinding process (Fig. 5c). Interestingly, the sharp diffraction peaks of the powder appear again after heating the amorphous HTCA at temperature of 100 °C for 1 hour (Fig. 6h top), which are evidence for transition from amorphous to crystalline state and confirms piezofluorochromic behaviour of HTCA.

In summary, a rigid, star-shaped blue luminogen (HTCA) was synthesized in a reasonable yield by simple condensation of cyclohexanehexone with six AIE-active tetraphenylethene (TPE) luminophores. HTCA is non-emissive in dilute solution, however, it became a strong emitter when aggregated and as a solid film, which demonstrates an aggregation-induced emission phenomenon. The crystalline aggregates of HTCA showed a stronger and bluer light than their amorphous aggregates and unique piezofluorochromic behaviour. Interestingly, a solid-state emission can be reversibly switched between bluish green and blue color by grinding and fuming or heating processes due to the morphological change from the thermodynamically stable crystalline phase to the metastable amorphous state. The fluorescence, visual changes and XRD confirms the piezofluorochromic behaviour of HTCA. We are currently exploring these and other simple synthetic designs for their application in optoelectronic devices. These results will provide the easiest way to the rational and controlled designs of microstructures deriving AIE molecule and may allow construction of highly efficient luminescent solid materials.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Details of UV-vis fluorescence and microscopic data of aggregates in all the solvents. See DOI: 10.1039/c000000x/

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