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Structure-property relationship in multi-stimuli responsive D-A-A' benzothiazole

functionalized isomers.

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TOC



Abstract

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Multichromophoric D-A-A' molecules comprising of benzothiazole (BT) as A', benzothiadiazole (BTD) as A and tetraphenylethylene (TPE) as D were designed and synthesized as positional isomers *p***-BT**, *m***-BT** and *o***-BT** by attaching the BTD-TPE moiety ortho, meta and para to the phenyl BT unit. The positional change exploited in these isomers can influence the acceptor strength and molecular packing. Hence, a comparative study of the photophysical and electronic properties has been carried to study the effect of position. The *p***-BT** and *m***-BT** isomers were synthesized by the Suzuki cross-coupling reaction of BTD-TPE with boronate esters of BT. The Stille cross-coupling reaction was employed for *o*-BT. The structural features of the isomers endowed them with solvatochromism, mechanochromism, acidochromism and aggregation induced emission properties which were studied using emission and absorption spectroscopy. The reversible mechanochromic behaviour was associated with phase transition from crystalline to amorphous and was used to develop rewritable ink free paper. The single crystal X-ray analysis of *p***-BT** and *o***-BT** establishes that mechanochromism synergistically depends on the flexibility and twisting in the donor and acceptor moieties. The isomers can sense trifluoroacetic acid in solution as well as solid state. The opted strategy allows modulation of fluorescence properties making them potential stimuli responsive materials with applications in mechano-sensors, security inks and optoelectronic-devices.

Introduction

The solid state materials which are susceptible to changes by external stimuli (mechanical forces, solvent and acid vapours, heat and light) are beneficial¹; following their utilization in a range of promising applications such as optical information storage, fluorescent switches, memory devices, deformation detectors, optical recording, fluorescent bio-probes, security systems, mechanical sensors and optoelectronic devices.² The category of solid state materials, that manifest change in emission as a response to mechanical force such as grinding or rubbing are known as mechanofluorochromic (MFC) materials.³ A significant emission in the solid state is crucial for mechanofluorochromism and is primarily determined by the nature of molecular packing and intermolecular interactions in the solid state.⁴ The response to mechanical forces is associated with phase transitions or the disturbance in the basic molecular stacking interactions, consequently producing metastable states.⁵ The factors such as effective conjugation, donor-acceptor interaction, and incorporation of alkyl or aryl substituent, electronegative or heavy atoms and their position play a pivotal role in regulating the MFC properties.⁶ The common organic dyes in their aggregated state quench their emission due to the aggregation caused quenching (ACQ) which restricts their usage as MFC materials.⁷ Recently, the concept of aggregation induced emission (AIE) contributed by Tang et al. has successfully resulted in materials with enhanced emission in aggregated state. The non-planar architecture of AIE luminogens diminishes π - π stacking in aggregated state and by the virtue of restriction of intramolecular rotations (RIR) induces extensive emission in aggregated state.⁸ The ACO fluorophores have been successfully converted into solid state emitting materials by attaching to well known AIEgens.⁹ Tetraphenylethylene (TPE) is one of the widely used AIEgen because of its easy synthesis, bulky size and propeller shape. The TPE has been used as a weak electron donor in donor-acceptor systems resulting in highly emissive solid materials with a range of applications in material chemistry and electronics.¹⁰

It is familiar that organic molecules constituting of donor and acceptor fragments allowing fine tuning of the MFC properties. Organic molecules with D-A, D-A-D, D- π -A *etc.* serve as excellent candidates for MFC with applications in optoelectronics.¹¹ Benzothiazole (BT) and benzothiadiazole (BTD) are well established electron acceptors and have been successfully explored for the synthesis of AIE active MFC materials.¹² Both BT and BTD based materials have been successfully employed in organic light emitting diodes (OLEDs) and organic solar cells (OSCs) and can be combined for potential applications in a multichromophoric assembly.¹³

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Our group is interested in design and synthesis of MFC materials. We have reported BT-TPE and BTD-TPE for MFC and successfully tuned their AIE and MFC behaviour and have shown that MFC behaviour can be tuned by controlling the strength of donor or acceptor.^{11(c),} ¹⁴ Herein, we have designed and synthesized series of multichromophoric isomers p-BT, m-BT and o-BT based on BT, BTD and TPE with an aim of achieving high solid state emission and MFC behaviour. In this design strategy, we aim to control the acceptor strength and molecular packing by changing the position of BTD-TPE unit ortho, meta and para to BT unit. The variation of the position with respect to BT unit is expected in modulating the acceptor strength and molecular packing. The BT unit was selected because of moderate electron accepting behaviour and presence of two hetero atoms "S and N", as S-atom is well known for its strong supramolecular interactions. The comparative study of the change in the photophysical, AIE and MFC properties of isomers with position has been carried out using crystal analysis and theoretical calculations. The photophysical, thermal, electrochemical, solvatochromic, mechanochromic, AIE and acidochromic properties of **p-BT**, **m-BT** and **o**-**BT** have been investigated. The isomers exhibit enhanced emission on aggregation with distinct MFC and acid sensing.

Results and discussions

Synthesis

The *p*-BT, *m*-BT and *o*-BT are D-A-A' type molecules and were designed to evaluate the change in the photophysical and electronic properties as a result of altering the position of attachment of the BTD-TPE unit to the Ph-BT moiety. The synthetic route to the isomers *p*-BT and *m*-BT is given in Scheme 1 and for *o*-BT is as outlined in Scheme 2.

The benzothiadiazole-tetraphenylethylene (**BTD-TPE**) moiety was attached at the 4-position, 3-position and 2-position of the phenyl ring of benzothiazole to furnish the para (p-BT), meta (*m*-BT) and ortho firstly (*o*-BT) isomers respectively. То achieve this, the 4.7tetraphenylethylene selectively side of was coupled to one dibromobenzo[c][1,2,5]thiadiazole using the Suzuki cross-coupling reaction to yield intermediate BTD-TPE (Scheme S1).¹⁴ Further, the benzothiazole intermediates BT 4 and BT 5 required for coupling **BTD-TPE** 2-(4with were synthesized. bromophenyl)benzo[d]thiazole (BrBT1), 2-(3-bromophenyl)benzo[d]thiazole (BrBT2) and 2-(2-bromophenyl)benzo[d]thiazole (BrBT3) were obtained by the condensation reaction of 2-aminothiphenol and respective bromo-benzaldehydes using literature procedures.¹⁵ The Miyaura borylation reaction of **BrBT1** and **BrBT2** with bis(pinacolato)diboron using [1,1'bis(diphenylphosphino)ferrocene]palladium(II) dichloride as catalyst generated the boronate esters of benzothiazole at 4 position (BT4) and 3 position (BT5) respectively. ¹⁶ However. the

Miyaura Borylation reaction of **BrBT3** did not proceed successfully to yield the boronate ester; alternatively the Stille intermediate *o*-**TBT-BT6** was synthesized. The in-situ anion formation of **BrBT3** using n-BuLi followed by addition of tributyltin chloride supplied the intermediate *o*-**TBT-BT6** in 71% yield.

The Suzuki cross coupling reaction of **BTD-TPE** with **BT4** and **BT5** using Pd(PPh₃)₄ as catalyst afforded *para* and *meta* isomers *p*-**BT** and *m*-**BT** with a yield of 73% and 69% respectively. The Stille cross-coupling reaction of **BTD-TPE** with *o*-**TBT-BT6** and Pd(PPh₃)₄ as a catalyst resulted in the *ortho* isomer *o*-**BT** with a yield of 51%. All the target compounds (*p*-**BT**, *m*-**BT** and *o*-**BT**) and the newly synthesized intermediate *o*-**TBT-BT6** were characterized with ¹H, ¹³C NMR spectra and HR-ESI mass spectroscopy. The *para* (*p*-**BT**) and *ortho* (*o*-**BT**) isomers produced good crystals for single crystal X-ray analysis. The synthesized isomers are highly soluble in common organic solvents such as dichloromethane (DCM), tetrahydrofuran (THF), chloroform *etc.*, although insoluble in ethanol, methanol, water and acetonitrile.

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Scheme 2 Synthetic route for o-BT

Thermogravimetric analysis

High thermal stability is essential for molecules to be utilized in solid state applications. The thermal properties of *p*-BT, *m*-BT and *o*-BT were evaluated by thermogravimetric analysis (TGA). The TGA curves are shown in Fig. S1 and the decomposition temperature (T_d) are listed in Table 1. The isomer *p*-BT exhibits the highest decomposition temperature of 405 °C corresponding to 5% weight loss. The isomer *m*-BT and *o*-BT show thermal decomposition temperatures of 398 °C and 363 °C respectively for 5% weight loss. The lower twisting in *p*-BT provides an extended conjugation leading to high thermal stability as compared to *m*-BT and *o*-BT.

The optical properties of *p*-BT, *m*-BT and *o*-BT were analysed in THF by UV-vis absorption (Fig. 1 (A)) and fluorescence spectroscopy (Fig. 1 (B)) and the results are compiled in Table 1. The isomers possess two major absorption bands arising from π - π * transitions in lower wavelength region (250–330nm) and intramolecular-charge transfer (ICT) transitions

(A)

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between the donor-acceptor strands in higher wavelength region (390–415nm) with a high extinction coefficient. The emission maxima of the isomers is in the range of 555–575nm with blue shifted emission for *o*-**BT** as a result of the decrease in the conjugation induced by the highly twisted structure.

Fig. 1 (A) UV-vis absorption spectra and (B) normalized emission spectra of *p*-BT, *m*-BT and *o*-BT in THF (2×10^{-5} M).

Table 1 Photophysical and thermal properties of *p*-BT, *m*-BT and *o*-BT.

Compounds	$\lambda_{ab}[nm] (\epsilon [Lmol^{-1}cm^{-1}])^{a}$	$\lambda_{\rm em} ({\rm nm})^{\rm b}$	$T_{\rm d} (^{\rm o}{\rm C})^{\rm c}$
<i>р</i> -ВТ	321(45939), 411(25544)	570	405 °C

<i>m</i> -BT	300(75575), 402(27525)	567	398 °C
<i>o</i> -BT	279(28335) 307(28838), 396(10068)	559	363 °C

^{a,b} Recorded in tetrahydrofuran, ^c Decomposition temperature

Density functional theory calculations:

The density functional theory (DFT) calculations were conducted at the B3LYP-6-31G(d,p) level for further accurate examination of the ground state electronic structures and geometries of the isomers *p*-BT, *m*-BT and *o*-BT.¹⁷ The calculated frontier molecular orbitals are depicted in Fig. 2 and the values are compiled in Table 2. The DFT optimized structures of the *p*-BT and *o*-BT isomers are in well accordance with the crystal structures. The isomers have propeller shaped geometry for TPE moiety and twisted structures with highest twisting in *o*-BT. The highest occupied molecular orbital (HOMO) is localized on the weakly donating TPE moiety whereas the lowest unoccupied molecular orbital (LUMO) resides on the benzothiadiazole moiety which confirms its higher electron accepting nature over benzothiazole. The HOMO-LUMO gap for *p*-BT, *m*-BT and *o*-BT are 2.79 eV, 2.89 eV and 2.99 eV respectively. The HOMO and LUMO are well separated allowing a distinct intramolecular charge transfer (ICT) from the donor to acceptor. In order to achieve correlation with the absorption studies, the time-dependent density functional theory (TD-DFT) calculations were done for the isomers at the CAMB3LYP-6-31G (d,p) level. Fig. S2 contains the calculated orbitals and the related computed vertical transitions, their oscillator

strengths, and configurations are tabulated in Table S1. The absorption spectra are in good agreement with the excited state calculations and affirm an ICT transition.



Fig. 2 Energy level diagram showing the HOMO and LUMO energy levels of *p*-BT, *m*-BT and *o*-BT as determined at the B3LYP/6-31G(d,p) level.

Electrochemical properties

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The energy levels and electrochemical properties were examined by employing cyclic voltammometry using tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte for a solution of the isomers in DCM. Fig. S3 shows the irreversible nature of the cyclic voltammograms and Table 2 lists the corresponding data for the electrochemical study of *p*-BT, *m*-BT and *o*-BT. The HOMO and LUMO values were calculated from the onset value of oxidation or reduction wave (E_{onset}) utilizing the equation HOMO/LUMO = - (E_{onset})

+ 4.4) eV.¹⁸ The values for HOMO levels of *p*-BT, *m*-BT and *o*-BT are -5.54 eV, -5.56 eV and -5.58 eV respectively and the values of LUMO levels are -3.62 eV, -3.62 eV and -3.68 eV respectively. The electrochemical HOMO-LUMO gaps for *p*-BT, *m*-BT and *o*-BT are 1.92 eV, 1.94 eV and 1.90 eV respectively. The CV graphs exhibit one oxidation wave and

	Electrochemical properties		DFT calculations			
~ .	HOMO ^a	LUMO ^a	HOMO-LUMO	HOMO ^b	LUMO ^b	HOMO-LUMO
Compounds	eV	eV	gap eV	eV	eV	gap eV
<i>р</i> -ВТ	-5.54	-3.62	1.92	-5.31	-2.52	2.79
<i>m</i> -BT	-5.56	-3.62	1.94	-5.30	-2.41	2.89
<i>о-</i> ВТ	-5.58	-3.68	1.90	-5.24	-2.25	2.99

two reduction waves corresponding to a donor TPE and acceptors BTD and BT respectively.

Table 2 Electrochemical properties and DFT calculations of *p*-BT, *m*-BT and *o*-BT.

 $^{\rm a}$ Calculated from CV: Reference electrode- Ag/AgCl $^{\rm b}$ Theoretical values at B3LYP/6-31g(d,p) level.

Solvatochromism

The intramolecular charge transfer (ICT) transition is greatly influenced by change in solvent polarity and is a distinct feature in donor-acceptor molecule.¹⁹ The target isomers are comprised of a D-A-A' structural unit owing to which the result of change in the solvent polarity was investigated using electronic absorption spectroscopy (Fig. S4) and fluorescence spectroscopy (Fig. 3) in a range of solvents from non-polar to polar (cyclohexane, toluene, diethyl ether, 1,4-dioxane, THF, chloroform, dichloromethane(DCM), acetone and N,N-

dimethylformamide(DMF)). In comparison to the fluorescence spectra, the absorption spectra exhibited minor changes on changing the polarity of solvent which suggests the presence of more polarized excited states than the ground electronic states. The *p*-**BT** and *m*-**BT** isomers manifest a bright green fluorescence in cyclohexane at 515 nm and 513 nm respectively whereas the *o*-**BT** isomer emits at 504 nm in cyclohexane with a bluish green fluorescence. The isomers *p*-**BT**, *m*-**BT** and *o*-**BT** emit a yellow fluorescence in moderate polar solvents like 1,4-dioxane, THF, CHCl₃. In polar solvent like DMF, a bright orange fluorescence was observed at 626 nm, 625 nm and 616 nm respectively enabling the isomers to achieve a wide range of colours in the visible region. The isomers *p*-**BT**, *m*-**BT** and *o*-**BT** exhibit similar changes in emission on gradually increasing the solvent polarity and a bathochromic shift of 111 nm, 112 nm and 112 nm respectively was observed (Fig. 3). The transfer of electron from donor to acceptor enhances the dipole moment creating a polarized excited state which can be stabilized by the reorganization of polar solvent molecules resulting in reduced energy of the excited state leading to noteworthy bathochromic changes in the emission spectra.

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Fig. 3 Emission spectra of the isomers (A) *p*-BT, (B) *m*-BT and (C) *o*-BT (excitation wavelength or λ_{ex} =370 nm) in solvents of different polarities. (Photographs taken under 365 nm illumination.)

Aggregation induced emission

The isomers were designed with tetraphenylethylene core to accomplish solid state emission induced by aggregation. The formation of nano-aggregates was initiated by progressive addition of non-solvent (water) to the solvent system (DMF) and the AIE character of the isomers was measured using fluorescence (Fig. 4) and absorption spectroscopy (Fig. S5). The isomers **p-BT**, **m-BT** and **o-BT** emit at 626 nm, 627 nm and 618 nm respectively with a pink fluorescence at 0% water fraction or pure DMF solution due to significant ICT transition, unlike other TPE containing molecules that are non-emissive in solution. The relative quantum yields (QY) for *p*-BT, *m*-BT and *o*-BT at 0% water fraction are 0.37, 0.20 and 0.21 respectively. The o-BT isomer shows reduction of intensity upto 40% while m-BT and o-BT isomer exhibit reduction of intensity upto 30% water fraction. This behaviour can be attributed to the stabilized CT states resulting from increase in solvent polarity. The **p-BT**, **m**-**BT** and *o*-**BT** isomers display sharp intensity enhancement and a blue shift in wavelength (bright green emission) above 40-50% water fraction due to formation of nano-aggregates. The relative QY for p-BT, m-BT and o-BT at 90% water fraction are 0.60, 0.34 and 0.26 respectively. It can be concluded that the emission at lower water percentage is governed by ICT; however greatly influenced by aggregate formation at higher water percentage. Above 70% water fraction, a slight drop in emission intensity is observed due to the formation of the large-sized aggregates, which decreases the effective dye concentration in the solution and are less exposed to radiation as compared to smaller aggregates.²⁰ The Mie scattering effect of light can be witnessed in the electronic absorption spectra (Fig. S5) of p-BT, m-BT and o-BT as a consequence of nano-aggregate formation at 40% water fraction for the isomers.²¹ The recorded AIE phenomenon can be visualized from the photographs given in Fig. S6.



Fig. 4 Emission spectra of (A) *p*-BT, (B) *m*-BT and (C) *o*-BT in DMF-water mixtures (0%–90% water), (D) Plot of fluorescence intensity vs. % of water fraction (fw). Luminogen concentration: 10 μ M; intensity calculated at λ max.

Single crystal X-ray analysis



Fig. 5 Crystal structure of *p*-BT 1 and *p*-BT 2; (A) Intermolecular interactions in (C-H $\cdots\pi$ depicted by red centroid, $N \cdots \pi$ and $S \cdots \pi$ depicted by yellow centroid) in the crystal packing diagram of *p*-BT 1 (1-D ladder), (B) Intermolecular interactions (C-H $\cdots\pi$ depicted by red and yellow centroid, N $\cdots\pi$ and S $\cdots\pi$ depicted by blue centroid, C-H \cdots N weak hydrogen bonding

interactions depicted by purple lines) in the crystal packing diagram of p-BT 2 (2-D framework).



Fig. 6 (A) Crystal structure of *o*-**BT**. (B) Crystal packing diagram of *o*-**BT** (anti-parallel arrangement and 3-D framework) (C) Intermolecular interactions (C-H··· π depicted by red centroid and green line, C-H···N weak hydrogen bonding interactions depicted by purple lines) in the crystal packing diagram of *o*-**BT**.

The successful interpretation of the observed properties can be achieved by deducing the structural information achieved from single crystal X-ray analysis. The slow evaporation of dichloromethane (DCM)/hexane and chloroform/hexane solvent mixtures was used to grow

good quality crystals for *p***-BT** (fluorescent green) and *o***-BT** (yellow) respectively. However, the crystallization of *p***-BT** isomer in different batches using the same solvent system by slow evaporation serendipitously resulted in two different crystal forms namely *p*-BT 1 and *p*-BT 2. The *o*-BT isomer belongs to monoclinic crystal system and P21/n space group. The two crystalline forms of *p***-BT** isomer belong to the triclinic crystal system with P-1 space group but differ from each other in orientation of the TPE moiety and degree of twisting resulting in different crystal packing diagrams. The difference in the crystal packing of *p***-BT** 1 and *p***-BT** 2 results in interesting emission properties. The crystal structures of *p*-BT 1, *p*-BT 2 (Fig. 5) and o-BT (Fig. 6 (A)) revealed twisted geometries for the tetraphenylethylene moiety as predicted and extensive twisting was observed in o-BT as compared to p-BT 1 and p-BT 2. The unit cell of *o*-BT crystal (Fig. S7 (C)) consists of four molecules arranged anti-parallel with multiple intermolecular interactions in contrast to the unit cell of *p*-BT 1 and *p*-BT 2 (Fig. S7 (A, B)) having absence of interactions between two anti-parallel arranged molecules. The crystal packing diagram of *p***-BT 1** (Fig. 5 (A)) reveals C(22)–H(22) $\cdots \pi$ (red centroid-C34-C35-C36-C37-C38-C39, 3.302 Å) and lone-pair π i.e. N(2) π (3.859 Å) and S(1) $\cdots \pi$ (3.738 Å) (π depicted by yellow centroid- C40–C41–C42–C43–C44–C45) leading to 1-D ladder type formation. The p-BT 2 (Fig. 5 (B)) contrarily displays extensive intermolecular interactions leading to a densely packed 2-D framework. The interactions observed in *p*-BT 2 are C(20)–H(31)··· π (red centroid-C20–C21–C22–C23–C24–C25, 3.211 Å), C(35)–H(24)··· π (yellow centroid-C34–C35–C36–C37–C38–C39, 3.226 Å), lonepair π i.e. N(1) π (3.842 Å) and S(1) π (3.729 Å) (π depicted by blue centroid- C40– C41–C42–C43–C44–C45) and weak H-bonding with N of the benzothiazole moiety C-H(18)...N(3) 2.748 Å. The crystal packing diagram of **o-BT** (Fig. 6 (C)) confirms C- $H(38)\cdots\pi$ 3.118 Å, C-H(32) $\cdots\pi$ 3.730 Å (π -red centroid) and weak H-bonding with N of the benzothiazole moiety C-H(12)...N(1) 2.686 Å. The presence of abundant intermolecular

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interactions in *o*-**BT** constructs a head to tail driven tightly packed 3-D framework which could possibly make it resistant to changes caused by mechanical stimuli.¹⁹ The top view and side views of the crystal packing diagrams for *p*-**BT 1**, *p*-**BT 2** and *o*-**BT** are given in Fig. S8, Fig. S9 and Fig. S10 respectively.

Mechanochromism

The *p*-BT, *m*-BT and *o*-BT were predicted to exhibit mechano-responsive solid state emission taking in account the non-planar framework and AIE nature of TPE. The para, meta and ortho attachment of BTD-TPE to benzothiazole moiety could vary the mechanochromic nature owing to the amount of twisting and/or acceptor strength in these isomers. The isomers were subjected to mechanical stimuli by grinding with mortar and pestle and the behaviour was explored using solid state emission spectroscopy (Fig. 7) and the data are tabulated in Table 3. The crystals of *p*-BT isomer (*p*-BT 1 and *p*-BT 2) and *o*-BT isomer were considered as pristine samples while the *m***-BT** isomer did not form any crystal owing to which the assynthesized sample was considered as pristine. The *p*-BT 1 and *p*-BT 2 crystals have same structure but differ in their orientation in space resulting in different crystal packing. The pristine crystals *p***-BT 1** and *p***-BT 2** exhibit a bright green emission at same wavelength of 519 nm. Grinding of the *p*-BT 1 and *p*-BT 2 bathochromically shifts the wavelength to 552 nm with a yellow emission. The fumigation of the grinded forms of *p*-BT 1 and *p*-BT 2 using DCM-hexane for 15-20 minutes reverted the emission to 513 nm and 516 nm respectively. The reversibility by fumigation for *p***-BT 1** and *p***-BT 2** was repeated up to 7 times and obtain wavelength of the fumed samples in the range of 513-518 nm (Fig. S11). The pristine solid of *m***-BT** and *o***-BT** exhibit a bright green emission at 518 nm and dark green emission at 519 nm respectively. The grinded forms of *m***-BT** and *o***-BT** display yellow and greenish yellow fluorescence at 542 nm and 537 nm respectively. The fumed (DCM and hexane) solids of *m*-**BT** and *o*-**BT** emit at 519 nm and 518 nm, respectively. The spectral shift generated due to

grinding in *p*-**B**T 1, *p*-**B**T 2, *m*-**B**T and *o*-**B**T is 39 nm, 36 nm, 26 nm and 19 nm respectively and follows the order *p*-**B**T>*m*-**B**T>*o*-**B**T.

The powder X-ray diffraction technique was used for interpretation of the reversible mechanochromic behaviour. The PXRD patterns (Fig. S12) for the pristine solids of the isomers reveal sharp diffraction patterns due to the crystalline nature. The grinded solids exhibit broad diffused PXRD pattern due to its amorphous nature. However, the sharp diffraction patterns reappeared on solvent fumigation indicating reversion to crystalline nature. The reversible mechanochromism can be assigned to morphology change from crystalline to amorphous caused due to modification of molecular arrangement on grinding.

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The different crystalline pristine forms *p*-BT 1 and *p*-BT 2 exhibit similar mechanochromic behaviour but difference in their absolute quantum yields. The absolute quantum yields for the crystalline pristine forms *p***-BT 1** and *p***-BT 2** are 0.33 and 0.51 respectively. The absolute quantum yields of the grinded and fumed form for *p***-BT 1** are 0.53 and 0.65 respectively and for **p-BT 2** are 0.51 and 0.63 respectively. The grinded and fumed forms of **p-BT 1** and **p-BT** 2 exhibit similar quantum yields but a noticeable difference can be seen in the quantum yields of the pristine forms. The *p*-BT 1 pristine crystal has very low quantum yield as compared to the pristine crystal *p*-BT 2 and the grinded and fumed forms of *p*-BT 1 and *p*-BT 2. The difference in the quantum yields of the two pristine crystals could be a consequence of their crystal packing.²² The *p*-BT 2 crystal confirms presence of abundant intermolecular interactions and weak H-bonding forming a tightly packed 2-D framework. On the other hand, the crystal packing of *p***-BT 1** possesses a loosely packed 1-D structure which may result in the loss of excited state energy in terms of vibrational relaxation, lowering the quantum yield substantially. The two crystals exhibit difference in packing due to different orientation of TPE in space resulting in distinct PXRD patterns and absolute quantum yields. The fumed forms *p***-BT 1** and *p***-BT 2** are also crystalline in nature and possess similar PXRD

patterns and quantum yields, however exhibit higher quantum yields as compared to pristine crystals of p-BT 1 and p-BT 2. The fumigation of the sample is done over a short period of time which does not allow the molecule to orient in different ways resulting in similar quantum yields. The fumed forms of p-BT 1 and p-BT 2 exhibit highest quantum yields and blue shifted emission as compared to the two pristine crystalline states which may possibly be an outcome of highest twisting of TPE in these crystalline forms resulting in a densely packed crystal structure. The absolute quantum yield of m-BT in its pristine, grinded and fumed forms is 0.74, 0.65 and 0.76 respectively. The absolute quantum yield of o-BT in its pristine, grinded and fumed forms is 0.34, 0.40 and 0.33 respectively.

The difference in the mechano-responsive nature of the isomers can be inferred from the crystal analysis. The aromatic fragments in the *p*-BT and *o*-BT isomers were depicted as BT (benzothiazole), **BT phenyl** (phenyl attached to benzothiazole), **BTD** (benzothiadiazole) and **TPE** (tetraphenylethylene) as shown in Fig. S13 for the measurement of dihedral angles. The dihedral angle between the **BT** plane and **BT phenyl** plane for *p*-BT 1, *p*-BT 2 and *o*-BT is 8.26°, 8.14° and 37.80° respectively and between **BT phenyl** and **BTD** for *p*-BT 1, *p*-BT 2 and *o*-BT is 35.09°, 34.42° and 62.25° respectively. The higher values of dihedral angle for *o*-BT over *p*-BT 1, *p*-BT 2 suggests an extremely twisted structure for *o*-BT reducing its susceptibility towards higher bathochromic shift on grinding. The highly twisted structure of *o*-BT makes it difficult in achieving planarity or furnishing meta-stable states after grinding thereby leading to poor mechanochromism. The twisting of donor moiety is essential for mechanochromism but higher twisting between the donor-acceptor moieties makes the structure rigid to move towards a planar structure. The dihedral angle between BTD plane and TPE plane in *p*-BT 1, *p*-BT 2 is 44.13°, 46.22° and in *o*-BT is 40.53°. The higher twisting of the donor moiety in *p*-BT can also be one of the reasons for increased

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mechanochromism. The combined effect of the twisting and flexibility of the D-A moieties

varies the degree of mechanochromism in the isomers.

Table 3 Peak emission wavelengths (λ , in nm) of *p*-BT, *m*-BT and *o*-BT as pristine, grinded and fumed solids.

	Emission			
Compounds	λ _{pristine} (nm)	$\lambda_{ m ground}({ m nm})$	λ _{fumed} (nm)	Δλ ^a (nm)
<i>p</i> -BT 1	519	552	513	39
<i>p</i> -BT 2	519	552	516	36
<i>m</i> -BT	516	542	519	26
<i>o</i> -BT	519	537	518	19

^a Grinding-induced spectral shift, $\Delta \lambda = \lambda_{\text{ground}} - \lambda_{\text{fumed/pristine}}$



Fig. 7 Solid state emission spectra of pristine, grinded and fumed solids of (A) *p*-BT 1 and *p*-BT 2, (B) *m*-BT and (C) *o*-BT (D) writing and erasing on a filter paper coated with *p*-BT,

illustrating ink free rewritable system. (Photographs taken under 365 nm UV light) (Inset: Pristine crystals *p*-**BT 1** and *p*-**BT 2**)

Acidochromism

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The spectral behaviour of the isomers towards acid was analysed taking in account the lone pair of N atoms which are susceptible to protonation.²⁰ The solutions of the isomers p-BT, m-**BT** and *o*-**BT** in CHCl₃ (2×10^{-5} M) were titrated against known amounts of trifluoroacetic acid (TFA in CHCl₃ stock solution) and studied using emission spectroscopy (Fig. 8). The emission maxima for the isomers *p***-BT**, *m***-BT** and *o***-BT** at 569 nm, 566 nm and 562 nm respectively display quenching in emission intensity on gradual addition of TFA from 10µL to 100µL. The emission intensity at maximum wavelength quenched upto 91%, 90 % and 51% for *p***-BT**, *m***-BT** and *o***-BT** respectively on excess addition of TFA. The *p***-BT** isomer shows highest red shift of the emission maxima from 569 nm to 613 nm with reduced intensity on addition of 100µL TFA. Similarly, o-BT exhibits a bathochromic shift for the emission maxima from 562 nm to 576 nm on addition of 100µL. However in case of *m***-BT**, the excess addition of acid only resulted in extensive decrease of emission maxima. The peak between 460-465 nm was unaffected and appeared prominently on excess addition of TFA for all the isomers. The reduction in intensity for emission maxima confirms the response of isomers towards acid. The increased acceptor strength due to protonation of N atom by acid could result in a higher donor-acceptor interaction consequently causing a bathochromic shift. The isomers were exposed towards TFA vapours to further explore the changes in its solid state emission. The emission intensity of *p***-BT**, *m***-BT** and *o***-BT** was extensively decreased on fumigation with TFA (Fig. 9) for few minutes. The quenching of intensity can also be visualized by the colour change of the fluorescent green solids to pale yellow. The

absolute quantum yield of *p*-**BT**, *m*-**BT** and *o*-**BT** in its pristine form is 0.33, 0.74 and 0.34 respectively which on fumigation with TFA decreases to 0.01, 0.05 and 0.09 respectively. The isomers are highly reactive towards TFA in solution as well as solid state allowing its use as a fluorescent sensor for TFA.



Fig. 8 Emission spectra of (A) *p*-**BT**, (B) *m*-**BT** and (C) *o*-**BT** in response to known amounts of TFA in CHCl₃.(Concetration- 2×10^{-5} M in CHCl₃)

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Fig. 9 Emission spectra of the pristine and TFA fumed solids of (A) *p*-BT, (B) *m*-BT and (C) *o*-BT.

Conclusion

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In conclusion, we have designed and synthesized multichromophoric D-A-A' isomers incorporating benzothiazole (BT) and benzothiadiazole (BTD) as acceptors and tetraphenylethylene (TPE) as donor. The acceptor strength was varied by changing the

position of BTD-TPE with respect to the ortho, meta and para positions of BT. A comparative study about the structure-property relationship has been established for the isomers. The *p*-BT, *m*-BT and *o*-BT isomers were synthesized by coupling BTD-TPE with BT using the Suzuki and Stille cross-coupling reactions. The isomers exhibit high thermal stability essential for fabrication in solid state devices. The isomers display distinct solvatochromic behaviour in various polarity solvents with emission ranging from blue to orange with high bathochromic shifts. The non-planar framework of the isomers results in enhancement of intensity in the aggregated state. The *p*-BT, *m*-BT and *o*-BT exhibit reversible mechanochromism between green to vellow in the order p-BT > m-BT > o-BT and has been exploited for the development of ink-free rewritable papers. The PXRD studies reveal that a morphological conversion from crystalline to amorphous state is responsible for mechanochromism and leads to formation of metastable states. The single crystal X-ray analysis shows that the *o*-BT isomer has an extensively twisted structure and tightly packed 3-D framework as compared to *p***-BT**, which explains the reason of lower response to mechanical stimuli. The higher twisting and tight packing of *o***-BT** reduces the flexibility of the donor moiety to achieve planarization on grinding. The DFT studies reveal good separation of HOMO and LUMO supporting a distinct ICT transition. The isomers display changes in emission wavelength and intensity in solution and solid state in response to trifluoroacetic acid and can act as potential sensors for its detection. The combination of the three chromophores helps in achieving enhanced emission in solid state suitable for mechanochromic materials. The positional changes allow fine tuning of acceptor strength and molecular packing inducing changes in the mechano-responsive behaviour. The opted strategy provides a new pathway in design of AIE active mechanochromic materials suitable for application as mechano-sensors, security paper, light emitting devices and other optoelectronic applications.

Experimental details

General methods

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Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under nitrogen/argon atmosphere. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Bruker Avance III instrument by using CDCl₃. ¹H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak (CDCl3, 7.26 ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet) and m (multiplet), and the coupling constants, J, are given in hertz. ¹³C NMR chemical shifts are reported relative to the solvent residual peak (CDCl3, 77.0 ppm). Thermogravimetric analyses were performed on the Mettler Toledo thermal analysis system. UV-visible absorption spectra were recorded on a Cary-100 Bio UV-visible spectrophotometer. Emission spectra were taken in a The Fluoromax-4C, S/n.1579D-1417-FM Fluorescence software Ver 3.8.0.60. The relative quantum yields in solution were calculated using Rhodamine 6G in ethanol as standard. The quantum yields in solid state were measured using K-sphere Integrating sphere. The excitation and emission slits were 2/2 nm for the emission measurements and 3/3 for solid quantum yield measurements. All of the measurements were done at 25 °C. HRMS were recorded on a Bruker-Daltonics micrOTOF-Q II mass spectrometer. The voltammograms were recorded on a CHI620D electrochemical analyzer in dichloromethane solvent and 0.1 M $TBAF_6$ as the supporting electrolyte. The electrodes used were glassy carbon as a working electrode, Pt wire as a counter electrode and Ag/AgCl as a reference electrode. Single-crystal X-ray structural studies of 1 and 4 were performed on a CCD equipped SUPERNOVA diffractometer from Agilent Technologies with Oxford Instruments low-temperature attachment under argon/nitrogen using standard Schlenk and vacuum-line techniques. The acidochromism was performed using 0.1 M stock solution of

TFA in CHCl₃. The rewritable-ink free paper was prepared using Whatman filter paper. The compound p-BT was dissolved in DCM, and then the filter paper was coated with p-BT. After drying, an ink-free plastic tip was used to write "IIT" on the p-BT loaded paper.

Synthesis and characterization of *p*-BT and *m*-BT

General procedure for synthesis of *p*-BT and *m*-BT. Pd(PPh₃)₄ (0.04 mmol) was added to a well degassed solution of **BT4** (0.4 mmol), **BTD-TPE** (0.4 mmol), K₂CO₃ (2.0 mmol) in a mixture of toluene (24.0 mL)/ethanol (8.0 mL)/H₂O (4.0 mL). The resulting mixture was stirred at 80 °C for 24 h under an argon atmosphere. After cooling, the mixture was evaporated to dryness and the residue was subjected to column chromatography on silica (Hexane–DCM 30:70 in vol.) to yield the desired product *p*-BT as a green crystals. The same procedure was employed using **BT5** and **BTD-TPE** to obtain the desired product *m*-BT as a yellowish green powder.

p-BT: Yield: 73%; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 8.27 (d, *J* = 8.0 Hz, 2H), 8.11-8.14 (m, 3H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 3H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.05-7.15 (m, 15H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 167.5, 154.3, 154.0, 144.0, 143.7, 143.6, 141.6, 140.4, 139.9, 135.2, 135.1, 133.5, 133.3, 131.9, 131.6, 131.5, 131.4, 131.3, 129.8, 128.4, 128.3, 127.8, 127.6, 126.6, 126.5, 126.4, 125.3, 123.3, 121.6, 0.0 ppm; HRMS (ESI): Calcd. for C₄₅H₂₉N₃S₂ [M + Na]⁺: 698.1695. Found: 698.1690.

m-**BT**: Yield: 69%; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 8.69 (s, 1H), 8.17 (d, J = 8.0 Hz, 1H), 8.12 (t, J = 8.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 3H) 7.68 (t, J = 8.0 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.06-7.14 (m, 15H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 167.8, 154.2, 154.0, 153.9, 144.0, 143.7, 143.6, 141.5, 140.5, 138.3, 135.1, 134.1, 133.4, 132.0, 131.8,

131.6, 131.5, 131.4, 131.3, 129.3, 128.4, 128.2, 127.8, 127.7, 127.6, 127.4, 126.6, 126.5, 126.4, 125.3, 123.3, 121.6, 0.0 ppm; HRMS (ESI): Calcd. for C₄₅H₂₉N₃S₂ [M + Na]+: 698.1695. Found: 698.1687.

Synthesis and characterization of *o***-BT**: The mixture of **BTD-TPE** (0.4 mmol) and *o***-TBT-BT6** (0.4 mmol) in toluene (15 mL) was degassed and Pd(PPh₃)₄ (0.01 mmol) was added to it. The resulting mixture was heated at 80 °C for 72 h. The reaction was monitored using thin-layer chromatography. The mixture was cooled and the solvent was evaporated to dryness. The residue was subjected to column chromatography on silica (Hexane-DCM 20:80 in vol.) to yield the desired product *o*-**BT** as orange-yellow crystals. Yield: 51%; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 8.20-8.22 (m, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.80-7.83 (m, 2H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.60-7.64 (m, 5H), 7.37 (dt, *J* = 8.0 Hz, 1H), 7.26-7.27 (m, 1H), 7.23-7.25 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.09-7.15 (m, 12H), 7.04-706 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 167.1, 165.1, 153.2, 152.8, 144.0, 143.7, 143.6, 141.5, 140.4, 137.0, 136.0, 135.0, 133.5, 132.6, 131.6, 131.5, 131.4, 131.3, 130.6, 130.5, 130.2, 128.8, 128.4, 129.3, 128.4, 127.8, 127.7, 127.6, 126.6, 126.5, 125.9, 124.9, 123.2, 121.2, 0.0 ppm; HRMS (ESI): Calcd. for C₄₅H₂₉N₃S₂ [M + H]⁺: 676.1876. Found: 676.1874.

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Synthesis and characterization of *o*-TBT-BT6: n-BuLi 1.6 M (1.89 mmol) was added dropwise to a stirred solution of **BrBT3** dissolved in THF under argon atmosphere at -78 °C (10.0 ml). The solution was stirred for 1 h at -78 °C. To this solution, tributyltin chloride (1.89 mmol) was added dropwise and the reaction was left overnight. The reaction mixture was neutralized using aqueous NH₄Cl and the aqueous layer was extracted using dichloromethane. The combined extracts were dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the product was isolated by column chromatography on silica (Hexane-DCM 50:50 in volume) to give desired product *o*-TBT-BT6 as colourless oil. Yield: 71%; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 8.01 (d, *J* = 8.0 Hz,

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1H), 7.88-7.92 (m, 2H), 7.75 (d, J = 8.0 Hz, 1H), 7.38-7.53 (m, 4H), 1.45-1.55 (m, 6H), 1.23-1.32 (m, 6H), 1.09 (t, J = 8.0 Hz, 6H), 0.82 (t, J = 8.0 Hz, 9H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 170.2, 153.1, 144.0, 139.1, 137.8, 135.1, 129.9, 129.0, 128.4, 126.1, 125.0, 122.6, 121.6, 29.2, 27.4, 13.6, 12.6, 0.0 ppm; HRMS (ESI): Calcd. for C₂₁H₂₆NSn [M - nBu]⁺: 444.0804. Found: 444.0803.

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