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Photo-switching in the multi-stimuli responsive low Z'-high Z' co-crystal polymorphs

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Abstract: Emission switching in crystalline materials, though uncommon for multi-component polymorphic crystals, is an intruguing phenomenon with wide range of applications in optics and optoelectronics. We report co-crystal polymorphs by crystallisation of 2-aminobenzene arsenic acid (2-ABAA-2H) and 4,4'-bipyridyl (4,4'-BPY) in different solvent systems. Structural studies establish that the crystal forms exist as low \mathbf{Z} (=1), \mathbf{Z}'' (=3) $[(4,4'-BPY-2H)^{2+}(2-ABAA-H)_2]$ (1) and its high \mathbf{Z}' (=6), \mathbf{Z}'' (=18) $[4,4'-BPY-2H)_6^{2+}(ABAA-H)_{12}$ (2) form, and undergo proton transfer between crystal forms to exist as ionic solids. Form 1 is a green emitter (λ_{max} 512 nm, ϕ 2.6%, τ 2.5 ns), while 2 is non-emissive. Mechano-chromic studies establish retention of green emission in 1G and emission turn on in 2G forms, and the grinded forms respond to basic fumes of ammonia by undergoing emission turing to cyan and intense blue in 1.NH₃ and 2.NH₃, respectively. Thin films of both 1 and 2 exhibit green emissions when prepared in a range of solvents, implying retention of their microcrystalline phases on dissolution. Aggregation induced emission (AIE) studies of the products have been reported and supported through FE-SEM and DLS studies. Structural studies indicate slipped π - π interactions in the lattice of 1 forming J-type aggregates, are responsible for its solid-state emission, where 2 devoid of notable π - π is non-emissive due to loose crystal packing, plausibly leading to vibrational quenching.

Introduction

Luminescence switching in π -conjugated solids mainly arises due to differences in stacking modes and the materials provide immense opportunity for the development of optical and optoelectronic devices with a vast range of applications.^{1, 2} Establishment and study of structure-property correlations in luminescent molecular solids is of significance to understand the undelying mechanisms and arrive at design strategies. Crystal engineering focuses on understanding of the intermolecular interactions and utilisation of the understanding to design materials, and provides an opportunity to corelate structure with properties.³⁻⁵ Polymorphism i.e. crystallization of the same compound in different crystal forms with different properties, is an intriguing phenomenon of immense significance and provides a unique possibility to establish structure-function correlations and understand the molecular interconversions through external stimuli.⁶⁻¹² The difference in physicochemical properties between polymorphs, range from mild to striking visà-vis solubility, mechanical behaviour, stability, conductivity, magnetism, luminescence, etc.¹³

Research efforts for the development of organic functional materials are fuelled by a recent shift involving development of organic alternatives of inorganic functional materials, including luminescent solids.¹⁴ Solid-state luminescence, an important

material property, is however limited by challenges like aggregation-caused quenching (ACQ) and its late exploration in organic solids.¹⁵⁻¹⁹ The materials provide more opportunities and convenience for device processing, development, fabrication and have been exploited for the development of organic light-emitting diodes (OLEDs)^{20, 21}, optoelectronics^{22, 23}, optical waveguides(OWGs)^{24, 25}, organic solid-state lasers (OSSLs)^{26, 27}, organic light emitting transistors (OLETs)^{28, 29}, sensors^{30, 31}, biotags^{32, 33}, stimuli-responsive materials (SRMs)^{34, 35}, bio-imaging,^{36, 37} and up-conversion emission³⁸⁻⁴¹.

Crystal engineering of luminescent organic crystalline materials has been reported through crystallochromism, polymorphism and coformer variation.⁴²⁻⁴⁵ Emission tuning and realisation of multicolour emission through polymorphism in particular is well reported for single component crystals, but is rare in multicomponent systems. ON/OFF emission switching is even more rarely observed in organic crystals. For example, Shimei and coworkers have realised emission switching in a pyrene dimer. The pristine crystal is non-emissive due to the ordered and longrange π stacking and undergoes reversible emission turn-on on grinding/UV irradiation exposure, due to dimerisation.^{46, 4} Similarly, Zhenguo and co-workers designed donor-accepter based photo-switchable thermally activated delayed emission (TADF) luminogen and utilised it for the development of sequential and combinational single-component logic gate systems.48 Our exhaustive survey indicated "on-off" luminescent switching is unreported in co-crystal polymorphs. Polymorphism in molecular crystals can arise due to multiple

factors and has been classified as conformational, packing and synthon polymorphism.⁴⁹ High Z' and low Z' crystal forms of molecules, where Z' represents the number of molecules or formulae units in an asymmetric unit, represent another rare

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Electronic Supplementary Information (ESI) available: NMR, Hydrogen bonding parameters, Hirshfeld surfaces, crystal structure diagrams, solution phase studies, mercury sensing.

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form of polymorphism. Well reported for single component crystals, high Z'-low Z' co-crystal polymorphs are sparse [Table S1,ESI[†]] and has not been investigated for property studies including luminescence.⁵⁰

In this work we report exceptional high Z'-low Z' co-crystal polymorphs **1** and **2**, with unique "ON/OFF" emission switching, arising due to differences in π -stacking interactions. The nonemissive polymorph exhibits striking emission turn-on on grinding, and grounded forms of both crystal forms exhibit vapo-fluorochromic response, on exposure to base fumes. AIE studies of both forms have also been reported.

Results and Discussion

We have observed intriguing properties, including optics, in the materials based on sulfonate-pyridinium supramolecular synthon. Therefore, we have extended the design of materials to the structural analogue of organo-sulfonates i.e. organo-arsenate and tested its reactions with 2,2'-bipyridyl. Co-crystallization of equimolar mixtures of 2-aminobenzene arsenic acid and bipyridyl in acetone led to the formation of $[(4,4]-BPY-2H)^{2+}(2-ABAA-H)_2]$ **1** as pale-yellow solid in a couple of days after slow evaporation at ambient conditions, while keeping the conditions same, change in solvent system to methanol/water (30/70 v/v) led to isolation of intense orange high Z' polymorph $[(4,4'-BPY-2H)_6^{2+}(ABAA-H)_{12}]$ **2**. The color polymorphs also exhibit different crystal morphologies and rare emission on-off switching, as **1** shows intense green emission, while emission of **2** is quenched, (Scheme 1).

Formation of the polymorphs is supported by Fourier transform infrared (FT-IR) spectroscopy: absorption bands at around 3400 cm⁻¹ and 3300 cm⁻¹ correspond to the symmetric and asymmetric stretching of v(N-H) of the amine groups while the peak at around 3100 cm⁻¹ corresponds to the N⁺-H stretching, indicating proton transfer between acid-base precursors. Bands at 915 and 715 cm⁻¹ correspond to symmetric and asymmetric stretching of the As-OH group, (Fig. 1a). Powder X-ray diffraction studies validate the crystalline nature of the

bulk solids and establish phase purity and stability of the bulk solid of the high Z polymorph while the minor discrepancies in the differaction pattern of computed crystal form and bulk solid plausibly arise due to the packing changes on conversion to microcrystalline state, (Fig. 1b-c.) Both ¹H and ¹³C NMR have been carried in which the observed chemical shifts and peak area ratio validate the formation of **1** and **2**, (Fig. S1-4, ESI⁺)



Scheme 1. Chemical composition and synthetic scheme of molecular salts **1** and **2**.

Molecular salts exhibit moderate thermal stability and melt at 145-148°C (1) and 159-162°C (2). Thermogravimetric analysis (TGA) depicts higher thermal stability of 2, as the weight loss starts at 210°C, compared to 1 for which weight loss initiates at 196°C, (Fig. 1d). Differential scanning calorimetry (DSC) analyses further substantiate the thermal behavior as sharp endothermic dips at 147°C and 162°C, corresponding to their melting points, are observed in 1 and 2, respectively, (Fig. 1e). Careful analyses of DSC curves rule out any phase transformation before melting points, particularly for high Z' polymorph, ruling out inter-conversion of the polymorphic forms.

Optical properties

Notable colour and luminescence differences in the two polymorphic forms prompted us to study their optical



Fig. 1. Characterisation data of 1 and 2: (a) FT-IR spectra, (b,c) powder X-ray differaction data compared with their simulated data, (d) DSC plots and (e) TGA plots.

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properties in detail. Solution phase absorption studies of the polymorphic forms indicate absence of any type of intramolecular charge transfer interaction in their aqueous solutions, as no absorption activity is observed beyond 400 cm⁻¹, (Fig. S5-6, ESI[†]). Colour difference in **1** and **2** is corroborated by their diffuse reflectance studies as absorption spectra are significantly red-shifted, implying stronger intermolecular charge transfer interactions in later.

Solvent dependent absorption and emission studies are nearly identical for both 1 and 2, but emission behavior varies with nature of the solvent, (Fig. 2). Aqueous solutions of both forms are non-emissive, while emission is blue shifted in ethanol, compared to methanolic solutions with a shift in the λ_{max} values by 51 nm. This shift of 51nm can be attributed to change in molecular packing, aggregation effects and solute-solvent interactions.(Fig. S7,ESI†) Solutions of both polymorphs in other solvents: dimethylforamide (DMF), tetrahydrofuran (THF), acetonitrile (MeCN) and acetone (Ace) are green emitting with subtle variations in the λ_{max} emission intensity and quantum vield values, (Table S2-3, ESI†). Nearly identical solution phase optical properties of two forms hint towards the possible interconversion of high Z' form to its low Z' form. While as the dissociation of co-crystals/salts on dissolution is ruled out based on comparative studies with starting materials; which is also supported by retention of green emission on dissolution. (Fig. 2, Fig. S8,ESI⁺) Dynamic light scattering (DLS) studies indicate different extent of particle aggregation in different solvents and the emission variation possibly arises due to difference in particle sizes, (Table S4, ESI⁺).

Solvent and particle size dependent luminescence studies of **1** and **2**, prompted us to investigate them further for their aggregation-induced emissions (AIE). AIE of non-emissive aqueous solutions was carried out against ethanol. Aqueous solutions of both **1** and **2** exhibit AIE with ethanol as a bad solvent and the emission of AIEgens of **2** is more intense, and

red shifted by nearly 40 nm compared to **1**, which shows structured emission bands of lower intensity, (Fig. 3a,b). I/I_{or} , where I represents emission intensity of solution in water only and I_o is emission intensity for a solution of definite $f_{H2O/EtOH}$ fractions, also validate better AIE response of **2**, (Fig. 3c,d).

With gradual addition of ethanol, the emission of aqueous solutions of polymorphs **1** and **2**, turns on until maximum intensity is observed at $f_{H2O/EtOH}$ value of 1:9 i.e. 10% of water fraction (f_w), with quantum efficiency values of 53.79 and 67.41%, for **1** and **2**, respectively. DLS studies validate particle size increase with addition of ethanol; hence emission can be attributed to increase in aggregation, (Fig. S9, ESI†). Field emission-scanning electron microscopy (FE-SEM) analysis also validates aggregation and gradual increase in the particle size as the ethanol concentration increases, (Fig. 3e-g and 3h-j). Fe-SEM images of **1** and **2** in pure water and pure ethanol

in the supporting information, (Fig. S10,ESI†).⁵¹



Fig. 2 (a, b) Optical images of solutions of **1** and **2** in different solvents under 365 nm Uv light (c, d) PL spectra of **1** and **2** in different solvents at λ_{ex} 365 nm and concentration of 10⁻³M.



Fig. 3. AIE studies of **1** and **2**. Photoluminescence (PL) spectra in different $f_{H2O/EtOH}$ fractions of **1** (a) and **2** (b)recorded for 10⁻³ M solutions, relative I/I₀ PL intensity plot at different $f_{H2O/EtOH}$ values for **1** (c) and **2** (d), with optical images of vials under 365 nm Uv lamp, and FE-SEM images of AIE fractions at $f_{H2O/EtOH}$ value of 3:7, 7:3 and 9:1, respectively, for **1** (e-g) and **2** (h-j).



Fig. 4 Optical images of 1 and 2 (a) crystals in day light, bulk solid in UV-light, and their grinded forms, vapochromic forms and piezochromic forms captured under 365nm UV-light source, (b,c) DR-UV spectra of different forms of 1 and 2 and (d, e) solid-state PL spectra of different forms of 1 and 2 at λ_{ex} 365nm.

Solid-state PL-spectra of **1** shows an intense emission peak with λ_{max} at 512 nm corresponding to observed green emission, with a quantum efficiency of 2.6%, and CIE chromaticity coordinate values of 0.25, 0.48, while **2** is non-emissive with a flat emission spectrum, (Fig. 4). Fluorescence decay of crystalline solid form of **1** using Time-Resolved Photoluminescence (TRPL) and time correlated single photon counting (TCSPC) method calculated the average lifetimes value of 2.5 ns, (Fig. S11 ESI† and Table S5, ESI†).

Thin films. The practical applications of the luminescent materials are realized through their fabrication into thin films which provide operational convenience. As thin film formation involves slurry coating, it may result in phase changes hence varied optical properties. Therefore, thin film optical studies of polymorphic forms are reported. Interestingly, the thin films of both 1 and 2 prepared in different solvent systems yield only green emitting films, (Fig. S12, ESI†). Diffuse reflectance absorption and emission plots of the thin films are provided as supporting information (Fig. S13-14, ESI†). The studies indicate possible phase changes of 2 on dissolution and as established by the solution phase optical studies its possible conversion to phase 1 on dissolution.⁵²



Fig. 5 Powder X-ray diffraction pattern of **1** and **2** compared with their forms obtained after mechanical grinding **1-G**, and **2-G** and vapochromism **1-NH**₃ and **2-NH**₃.

Multi-stimuli responsive studies. Polymorphic systems are suitable for investigation of stimuli-responsive behavior as they have the tendency to interconvert on application of external energy. The co-crystal polymorphs **1** and **2**, though not interconvertible, respond to mechanical grinding and exposure to base fumes. Mechano-fluorochromic response in **1** is not remarkable, as the shift in λ_{max} is of 6 nm accompanied by a nearly 10% decrease in emission intensity,⁵³ but is striking in **2**, which undergoes emission turn on and the grounded form has brilliant green emission with λ_{max} at 521 nm, (Fig. 4d-e.) Diffuse reflectance studies of grinded forms **1G** and **2G** also indicate a blue shift in the absorption behavior, (Fig. 4b-c). The emission variation and switching may be attributed to phase changes in the molecular solids upon grinding, which are evident in the powder X-ray diffraction pattern, (Fig. 5).



Fig. 6 Depiction of π -interaction **1**(a) and **2**(b).



Fig. 7 a) Molecular structure fragment of 1, (b, c) unit cell of 1 along a-axis represented in capped stick and space fill models and (d), packing fragment of 1.

The piezochromic studies, carried out by applying pressure up to 30 kPa, using hydraulic IR-pellet press for compression of crystalline forms of **1** and **2**, result in red-shifted emission of 9 nm in **1** and emission turn-on in **2** with red-shift of **8** nm from its grinded form **2G**, (Fig. 4 and Fig. S15-16, ESI†). The results are in accordance with tight binding model, which explains compression caused red-shift due to closer approach of π -rings. Both the polymorphs on exposure to ammonia fumes under ambient conditions result in a remarkable fluoro-chromic change. As visualized under UV exposure, the ammoniated solid forms 1.NH₃ and 2.NH₃ shows bright blue emissions, which have been validated by solid-state fluorimetry. Emission spectra of **1.NH₃** (λ_{max} 478 nm) and **2.NH₃** (λ_{max} 525 nm) are significantly blue shifted compared to their grinded forms, (Fig. 4 and Fig. S17-18, ESI†). The FT-IR spectra of **1.NH₃ and 2.NH₃ show new** vibration peaks, which substantiate the incorporation of the $m NH_3$

in the materials. Ammonia-treated solids show asymmetric Vasym(NH₃) and symmetric Vsym(NH₃) stretching modes for **1** at 3321 and 3185 cm⁻¹, while for **2**, these bands are present at 3311 and 3171 cm⁻¹, respectively. Peak broadening in the 3400–2500 cm⁻¹ region may be attributed to hydrogen bonding and the overlap of v(N–H) and v(O–H) absorptions of amine and water, respectively, (Fig. S19, ESI⁺).

Diffuse reflectance spectra also indicate blue shifts in the absorption spectrum of ammoniated samples. Powder X-ray diffraction pattern show prominent change in the phases of ammoniated forms, (Fig. 5), resulting in emission tuning of the ammoniated solid forms.

Structural studies of the polymorphic forms, discussed vide infra, provide essential insights into the structure property relationship. Of the two polymorphs, **2** forms head-to-tail π dimer in its crystal lattice, with slipped π -type stacking



Fig. 8 a,b) Molecular structure fragments of 2, (c,d) depiction of unit cell of 2 along c-axis and a-axis in capped stick and space fill models.

(centroid-centroid distance 3.636 and 3.748 Å, slip angle 76.84° and 86.24°, pitch angle 149.1°), (Fig. S20, ESI†). While there is no significant π - π interactions observed in 1, as the π centroid distances are too long (greater than 4 Å), (Fig. 6a-b). The observations are in agreement with the observed properties, as π - π interactions are primely responsible for aggregation caused quenching of emission, rendering 2 non-emissive in crystalline form, while 1 devoid of π interactions is emissive. The emission turn-on in 2 on grinding or compression is plausibly triggered by displacement of the π -stacked rings, resulting in reduced interactions.

Crystallographic studies

1 crystallizes in monoclinic space group $P_{21/c}$. The asymmetric unit consists of two anions of arsenate and a cation of bispyridinium, validating its non-stoichiometric composition of $[(4,4^{1}-BPY-2H)^{2+}(2-ABAA-H)^{2-}]$. Crystal components are associated by direct ionic arsenate-pyridinium interaction: 03...H4-N4 [D-H...A: 170.23(3)°; D...A: 1.673(2) Å] and 04...H3-N3 [168.88(3)°; 1.733(2) Å], (Fig. 7a.)

The hydroxyl group and oxygen atom of the arsenate group are involved in the formation of cyclic centrosymmetric $R_2^2(8)$ synthon: 06...H5-05 [112.64(3)°; 2.112(2) Å] and 01...H2-02 [120.37(3)°; 1.891(2) Å], about the non-equivalent arsenate acids. The amine groups in two non-equivalent arsenate acids also exhibit the same pattern of intermolecular interactions i.e. one of the two amine hydrogen is involved in an intramolecular interaction with adjacent oxygen atoms: N2-H2B...03 [78.25(3)°; 2.866(2) Å] and N1-H1A...04 [142.94(3)°; 2.221(2) Å], while other hydrogen forms intermolecular bond, N2-H2A...01 [18.70(3)°; 2.016(2) Å] and N1-H1B...06 [169.24(3)°; 2.046(2) Å]. Interestingly, there are no other significant intermolecular interactions in the crystal lattice of 1 and the hydrogen bonding interactions lead to the formation of a supramolecule of two interpenetrated hydrogen-bonded lattices, as shown in (Fig. 7b-d.)

2 crystallize in monoclinic space group $P_{2_1/c}$. The asymmetric unit consists of twelve anions of organo arsenate and six cations of bis-pyridinium, validating the non-stoichiometry composition of $[4,4^{1}-BPY-2H)_{6}^{2+}(ABAA-H)_{12}^{-1}$ and the empirical formula same as **1**. All of the organo-arsenates are mono-deprotonated and pyridyl centers are protonated, and there are direct ionic N⁺-H...O interactions between two types of charged centers, (Fig. 8a, Table S6, ESI[†]). Bipyridyl cations are planar in 1, but of the six non-equivalent bipyridyl cations in 2, five are twisted with a torsion angles ranging from -140° to 180°, (Table S7, ESI[†]). The planar cation with torsion value of 5.18°, is present twice with half occupancy in the asymmetric unit.

Interestingly supramolecular aggregation through non-covalent interaction in all of the organo arsenate anions is similar as the arsenate groups engage in the formation of $R_2^2(8)$ homosynthon, while third oxygen atoms are involved in the formation of direct ionic arsenate-pyridinium (N+-H...O) interactions, in addition to intramolecular interaction with one of the protons of the amine group. While other proton of amine group forms intermolecular hydrogen bonds with one of the arsenate oxygen atoms involved in formation of the homo-synthon. With these interactions, the arsenate anions grow into independent 2dimensional network, (Fig. S21, ESI†), which are linked by bipyridyl cations into three dimensional network, (Fig. 8b) and (Fig. S22, ESI⁺).) Through weak C-H... π and π ... π interactions there is multiple fold interpenetration of the hydrogen bonded networks, resulting in formation of a 3-dimension solid. Structure and packing diagrams of **2** are depicted in (Fig. 8).

Hirshfeld analysis

The Hirshfeld surface analysis (graphical representations) and the two-dimensional Hirshfeld surface fingerprint plots (HSFP) were calculated with the Crystal Explorer.⁵⁴ Hirshfeld surface (d_{norm}) is given in (Fig 9a-b), with transparency using the balland-stick. Hirshfeld surfaces have been generated and analyzed based on color coding; red, blue, and white. Red identifies contacts closer than the sum of their van der Waals radii, whereas blue surfaces depict distances longer than the sum of their van der Waals radii and white surfaces show contacts equal to the sum of the van der Waals radii. Atoms involved in short contacts or H-bonding interactions are displayed by red spots on the surface mostly visualized over electronegative oxygen and arsenic atoms generated over d_{norm} surfaces in case of both **1-2**. Hirshfeld surface analysis fingerprint plots quantify contribution of various intermolecular contacts towards crystal packing and suggest H-H (37.8%) is predominant contact in 1 while in 2 it is O-H (39.9%) is the most predominant contact. C-H contacts representing C-H... π interactions are third and second most important contacts in 1 and 2, respectively. Contribution of various other contacts is depicted in (Fig. 9e).⁵¹ Predominantly higher contribution of O-H contacts, corresponding to hydrogen bonding interactions, in nonemissive form **2**, possibly promotes non-radiative vibration pathways resulting in emission quenching.

 π - π Stacking are not dominant interactions in the polymorphs and are further specified by constructing HS over the shape index while the curvedness provides information about planarity provided in (Fig. S23-24, ESIT). The existence of consecutive red and blue triangular-shaped regions around the phenyl rings on the shape index is an indication of π - π stacking. Quantification of interaction is also useful when structural differences are very subtle and may be misleading as in case of



Fig. 9 Hirshfeld analysis of 1 and 2. (a) d_{norm} surface of 1, (b) dnorm surface of 2, (c) electrostatic potential map of 1, (d) electrostatic potential map of 2 and (e) fingerprint analysis of 1-2, plotted as bar-chart.

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polymorphs. To study the distribution of charge and the nature of potential, electrostatic potential maps were generated which depict varying potential according to their colour differences as shown by blue, The negative electrostatic potential is shown by an intense red region in both **1-2** and is covered by oxygen and arsenic atoms while the positive electrostatic potential is covered by bipyridine and phenyl ring of arsenate, (Fig. 9c-d). The application part is mentioned in^{56, 57} (Fig. S25, ESI† and Table S8, ESI†).

Experimental section

Methods and Materials: O-Arsanilic acid (PAA-2H) (99%, Sigma-Aldrich), 4,4'-bipyridyl (99%, Sigma-Aldrich), were used as received. Distilled methanol and water were used for the cocrystallization. Crystallization was carried out via the slow evaporation method. Melting points were determined on the MP70 melting point system capillary apparatus (Mettler Toledo) in closed-end capillaries. Infrared spectroscopic data for molecular solids and their cocrystals were obtained using Agilent technologies Cary 630 FT-IR (4000-400 cm⁻¹) made in Malaysia. DR-UV-vis studies (both absorbance and reflectance) were carried out on a Shimadzu 2600 spectrometer in a BaSO4 medium. Fluorescence emission spectra were recorded on an Agilent spectrophotometer with different exciting wavelengths in liquid as well as solid phases. Thermal gravimetric analyses and differential thermal analyses of these samples were performed on a simultaneous thermal analyzer-STA (LINSEIS, USA 6807/8835/16) using an alumina crucible at a heating rate of 10 °C. Data Collection and Refinement of Single Crystal Analysis: Single-crystal data were collected on a Rigaku Saturn 724+ CCD diffractometer using a graphite monochromator (Mo $K\alpha$, λ = 0.71075 Å). The selected crystals were mounted on the tip of a glass pin using mineral oil and placed in the cold flow produced of nitrogen gas. Complete hemispheres of data were collected using ω and ϕ scans (0.3°, 16 s per frame). Integrated intensities were obtained with Rigaku Crystal Clear-SM Expert 2.1 software, and they were corrected for absorption correction. Structure solution and refinement were performed with the SHELX package. The structures were solved by direct methods and completed by iterative cycles of ΔF syntheses and fullmatrix least-squares refinement against F. The crystallographic table is shown in (Table S9, ESI[†]).

Hirschfield studies: Hirshfeld analysis was carried out through CrystalExplorer 17.5 software. Color coding mapped on the dnorm surface represents those contacts that indicate short (red color), intermediate (blue color), and long contacts (white color) compared to the sum of van der Waals interactions.

PXRD studies: Powder X-ray diffraction studies were carried out on the X-ray diffractometer Rigaku Japan D/max 2500 using Cu–K α radiation having λ = 1.54178 Å with a 2 θ ranging from 5 to 50° at a scanning rate of 5° per minute in a step size range of 0.05° per second.

Vapochromic studies: The vapochromic test in **1-2** were carried out at room temperature by exposing the two compounds to volatile organic vapours of amine i.e. ammonia, showing emission tuning upon different exposures. Compounds at room temperature were kept in an uncapped glass vial (3 mL) containing 10 mg of the compound which was placed inside a 100 mL glass beaker containing 20 mL of ammonia. The vial was then sealed and allowed to form a saturated solvent vapor. The vapochromic properties in the solid state were evaluated by UV/Vis diffuse reflectance spectroscopy and fluorescence

spectroscopy.

Mechanochromic studies: The mechanochromic studies in **1-2** were carried out by grinding the compounds in mortar and pestle for 20 minutes, the products underwent mechanochrmomic changes between 3-5 minutes, after which no further changes in optical properties were observed. Resultant change in colour as well as emission was evaluated by UV/vis diffuse reflectance and fluorescence spectroscopy.

Piezochromic studies: Piezochromic studies were carried out by using hydraulic IR-pellet press and applying pressure up to 30 kPa, which resulted in change in florescence and was evaluated by fluorescence spectroscopy. applying pressure up to 30 kPa.

Solubility Studies: Solubility in 1-2 was evaluated by measuring the absorbance values using a Shimadzu UV-2600 UV-visible spectrophotometer. To create the calibration standards, volumetric flasks were filled with precisely weighed amounts of the reference samples. The necessary amount of water was added to fill the volume, and the resulting solutions were sonicated to produce homogeneous solutions. A standard calibration curve was built using the stock solutions. These standard calibration curves were used to calculate the molar extinction coefficients (ε). Water was added to the volumetric flask along with the products until the saturation point was reached. For the absorbance measurements, the resulting solution was filtered and transferred to another volumetric flask. The concentrations of the products dissolved were calculated using the Beer-Lambert equation: $A = \epsilon Cl$ (A = absorbance measured using a UV-visible spectrophotometer, ϵ = molar extinction coefficient calculated from standard calibration curves, C = concentration of compounds dissolved, and l = path length).

Quantum yield: The quantum yield of **1-2** in the solution phase was calculated following the standard protocol using quinine sulfate as reference (0.1 M H_2SO_4 , $\eta = 1.33$, $\Phi = 0.54\%$) as reported in the literature. The absorbance and the emission of 1-4 was recorded for quinine sulfate at the same excitation wavelength. The solution of 1-4 was prepared in different solvents and the calculations were done as per the equation given below:

$$\frac{\Phi_{\rm s}}{\Phi_{\rm R}} = \frac{A_{\rm s}}{A_{\rm R}} \times \frac{Ab_{\rm R}}{Ab_{\rm s}} \times \frac{\eta_{\rm s}^2}{\eta_{\rm R}^2}$$

where "S" represent sample **1-2** and "R" represents reference (quinine sulphate, $\phi R = 0.54$) respectively, $\phi S =$ quantum yield of the sample, Ab is the absorbance, A designates area under emission and η represents the refractive index of the solvent.

Solubility studies: All absorbance values were calculated using a Shimadzu UV-2600 UV-visible spectrophotometer. To create the calibration standards, volumetric flasks were filled with precisely weighed amounts of the reference samples. The necessary amount of water was added to fill the volume, and the resulting solutions were sonicated to produce homogeneous solutions. A standard calibration curve was built using the stock solutions. These standard calibration curves were used to calculate the molar extinction coefficients (ϵ). Water was added to the volumetric flask along with the products until the saturation point was reached. For the absorbance measurements, the resulting solution was filtered and transferred to another volumetric flask. The concentrations of

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compounds dissolved, and l = path length). **Florescence Lifetime and Quantum yield studies:** The fluorescence quantum yields of powders were measured using a calibrated integrating sphere from Horiba combined with the Horiba JOBIN YVON Fluoromax-4 spectrometer. The timeresolved photoluminescence lifetimes (TRPL) were investigated using an Edinburgh Life Spec II instrument. Temperaturedependent (100–300 K) photoluminescence (PL) and delayed fluorescence lifetime measurements were carried out using a liquid nitrogen-cooled optical cryostat (Optistat, Oxford Instruments) to an Edinburgh FSP-920 instrument.

Field Emission Scanning Electron Microscopy: SEM analysis was carried out on a Jeol 10.0 kV instrument with a CCD camera. The instrument has a resolution of 0.36 mm (point to point) and can magnify up to 6 lakh times to know the morphology of aggregation-induced emission-generating species at different fractions.

Synthesis of 1: Compound **1** was synthesized by the in-situ reaction of o-arsanalic acid (217mg, 1mmol) and 4,4'-bipyridyl (156 mg, 1mmol) in Acetone solvent resulting in light yellow colour blocks formed after 7 days by the slow evaporation method. Yield: 300 mg; 40.1%; MP: >250°C; pH: 4.25; FT-IR, ν (neat): 3410 (s), 3343 (s), 3000 (s), 2301 (br), 2107 (br), 1660 (s), 1320 (vs), 1140 (vs), 900 (s). UV-visible =334nm. ¹H NMR δ , 500 MHz, DMSO-*d*₆, ppm: 8.7 (dd, *J* = 5Hz, 1H), 7.8 (dd, *J* = 5Hz, 1H), 7.3 (m, 1H), 6.6 (m, 1H), 4.6 (s, 8H). ¹³C NMR δ , 101 MHz, DMSO-*d*₆, ppm: 150.39, 150.20, 143.99, 133.44, 130.83, 120. 96, 115.65, 115.46, and 112.50.

Synthesis of 2: Compound **2** was synthesized by the in-situ reaction of o-arsanalic acid (217mg, 1mmol) and 4,4'-bipyridyl (156 mg, 1mmol) in MeOH/H₂O (**30**/70 v/v) solvent system resulting the formation of dark yellow colour blocks after 10 days by slow evaporation method. Yield: 300 mg; 40.1%; MP: >250°C; pH: 4.25; FT-IR, ν (neat): 3410 (s), 3343 (s), 3000 (s), 2301 (br), 2107 (br), 1660 (s), 1320 (vs), 1140 (vs), 900 (s). UV-visible =382nm. ¹H NMR δ, 500 MHz, DMSO-*d*₆, ppm: 8.7 (dd, *J* = 5Hz, 1H), 7.8 (t, 1H), 7.2 (m, 1H), 6.6 (m, 1H), 6.54 (s, 8H). ¹³C NMR δ, 101 MHz, DMSO-*d*₆, ppm: 150.99, 150.80, 144.65, 134.17, 131.48, 121.60, 116.36, 116.17 and 112.99.

CONCLUSION

Unusual Low Z'-high Z' cocrystal polymorphs with unique optical properties have been reported and studied in detail. High Z' polymorph shows significant thermal stability and no phase changes before its melting point, however undergoes striking emission turnon on grinding. Mechanochromic change in low Z polymorph is mild, while grounded forms of both polymorphs exhibit notable vapochromism on exposure to base fumes. Powder diffraction studies establish multi-stimuli response of polymorphic forms arises due to phase changes. Solvent dependeny, AIE and thin film studies of the polymorphic forms have been reported.Diffraction studies have been carried out to understand structure-property correlations. Single-crystal diffraction analysis indicate on/off emission switching between two polymorphic forms arises due to variation in π -stackings, which are not significant in emissive polymorph **1** and prominent in the non-emissive polymorph 2.

Ishtiyaq Ahmad has carried the experiments, collected and compiled the manuscript. Siriyara Jagannatha has supported with crystal refinement and analysis. Aijaz A. Dar has conceived the problem supervised the work and compiled the manuscript.

Conflicts of interest

There are no conflicts to declare

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Author Contributions

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