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Positional isomers of cyanostilbene: two-component molecular assembly and multiple-stimuli responsive luminescence

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An understanding of the aggregates and properties of positional isomers can not only uncover how a slight difference in molecular structure alter crystal packing and bulk solid-state properties, but also plays an important role in developing new types of molecule-based functional materials. Herein, we report a study of the molecular packing and static/dynamic luminescence properties of three cyanostilbene (CS)-based isomers (CS1, CS2, CS3) within their single- and two-component molecular solids. Changing the positions of the cyano substituents in the CS isomers has a marked influence on their packing modes and luminescent properties. Moreover, two-component CS-based materials have been constructed, which exhibit tunable conformations and packing fashions, as well as fluorescence properties, which differ from the pristine CS solids. The CS-based two-component molecular materials show solvent-responsive luminescence due to the dynamic disassembly of the samples. Moreover, it was found that the system based on CS2 and octafluoronaphthalene shows reversible photochromic fluorescence upon alternating light illumination and grinding. Such co-assembly procedures provide a facile way to fabricate patterned luminescent film materials. Therefore, this work not only affords new insight into the relationship between isomers and luminescence from molecular and supramolecular perspectives, but provides an effective strategy to develop multiple-stimuli-responsive luminescent materials.

I somers, the same molecular formula but a different arrangement of atoms in space, have played a crucial role in the development of both chemistry and materials science[1,2]. Since the first discovery of molecular isomers in 1827, continuous study of isomers at the molecular level has led to significant improvements in our understanding of the structure–property relationships of molecules and related materials[3,4]. For instance, stereoisomers (such as pharmaceutical compounds) usually show different medical properties and biological activities[5,6], while positional isomers with the same functional groups at different substituent positions often display similar functionalities[7]. However, up to now, a detailed understanding on the aggregation behavior of a set of molecular isomers and the properties of the resulting materials has rarely been reported. Such an understanding is important however, since for molecule-based functional materials, it is well known that the bulk properties are not just governed by the properties of a single molecule but also by its packing modes[8]. Taking luminescent materials as an example, differences in the molecular stacking of chromophoric solids may lead to different fluorescence properties[9]. Moreover, differences in the substituent positions of the isomers within molecular solids may also result in different intermolecular interaction modes, giving rise to tunable photophysical properties[10].

Materials responding to different external stimuli have great potential applications in information storage devices and smart sensors/switches[11]. In this sense, luminescent materials have attracted great attention during the last few years, due to their highly sensitive signal response and easy recognition and visualization[12,13]. Recently, molecule-based photoactive materials sensitive to a single external stimulus (such as photochromic[14], thermochromic[15], mechanochromic[16], and gas-induced[17] chromic luminescent systems) have been developed. Mechanisms for controlling the luminescence mainly involve chemical reactions[18] or alteration of the molecular packing[19]. Due to the relatively low conversion efficiency of typical solid-state chemical reactions, the latter has become recognized as the more promising way to switch the luminescence properties[20]. However, how to rationally design and tailor the chemical environment of the photoactive molecules within molecular solids in order to obtain the desired stimuli-responsive photophysical properties remains a challenge[21,22]. Moreover, the development of multiple-stimuli responsive luminescence remains in its early stages[23]. In this regard, multi-

component solid-state materials (such as co-crystals)[24,25], in which the molecular organization assembled from photoactive molecules and co-assembled units based on molecular recognition, can serve as ideal systems for the tailoring of supramolecular interactions (such as halogen/hydrogen bonds and π–π interactions)[26,27] by external per-turbations. The dynamic assembly and disassembly of multi-com-ponent molecular materials induced by environmental stimuli potentially offers the combined advantages of both supramolecular chemical reaction and changes in molecular arrangement, which can result in controllable and switchable luminescence[28]; however exam-ples of such multi-component molecular materials with stimuli-responsive properties remain rather rare[29].

Cyanostilbene (CS) compounds have recently attracted consid-erable attention due to their excellent optical and electronic prop-erties, giving rise to their potential applications in the fields of lasers[30,31], sensors[32,33,34] and optoelectronic devices[35,36]. In order to probe the relationship between the solid-state luminescence and multi-component aggregations/assemblies of positional isomers, in this work, three cyanostilbene-based isomers (CS1, CS2 and CS3 as shown in Figure 1A)—which have the same core stilbene dimer unit but cyano substituents in different positions—were chosen as model systems. We describe how a slight difference in substitutent positions can significantly influence the packing fashion and bulk luminescent properties of the solid-state isomers. Moreover, several new types of CS-based two-component molecular materials, which present solv-ent-responsive emission and reversible fluorescence switching prop-erties upon alternative light/grinding stimuli, have been fabricated. Since the pristine solid-state CS-based isomers show no solvochro-mic or photochromic fluorescence (SCF and PCF) behavior at all, the transformation of the SCF-free and PCF-free fluorophore isomers into SCF and PCF materials by the formation of the two-component materials is a distinctive feature of this work. Therefore, this work supplies an understanding on the relationship between the aggrega-tion states and luminescence properties of the CS-based single-/ two-component isomers, which also present stimuli-responsive photofunctionalities based on supramolecular design.

Results and Discussion

The structure and luminescence of the pristine CS-based isomers. Under UV light (365 nm), solutions of three CS-based positional isomers (Figure 1a) have a very similar blue fluorescence emission (inset in Figure 1b) with the maximum emission wavelength (λ_{max}^{em}) at *ca.* 433, 436, and 436 nm respectively for CS1, CS2, CS3 (Figure 1b), while both their powdered and crystalline forms display different fluorescence colors (green, greenish blue, and yellow emission, respectively) with the λ_{max}^{em} values located at 488, 451 and 536 nm respectively (Figure 1c), and their high fluorescence can be easily visible under UV light (inset in Figure 1c). These results show that although the monomer states of the three isomers undergo nearly the same photoexcitation/ emission process in solutions, molecular aggregations of CS1, CS2 and CS3 in the solid-state markedly alters the fluorescence. Fluorescence decay curves (Figure 1d) show that solid CS1 and CS3 have similar excited state properties with fluorescence lifetimes of 18.4 and 20.7 ns, respectively, but the corresponding value for solid CS2 is much lower (1.1 ns). Single crystal X-ray diffraction (Table S1 in the Supplementary Information) can be employed to probe the structure–luminescence relationships. The structures of CS1 (CCDC (Cambridge Crystallographic Data Centre) numbers: 979756) and CS2 (CCDC numbers: 979751) were determined and compared with the previously reported[37] structure of CS3. CS1 and CS3 exhibit layered and ladder structures respectively, with the molecules parallel to one another in the aggregated states; the distances between adjacent molecules are 0.39 and 0.37 Å, respectively (Figure 2). Such stacking results in a strong π–π interaction, which facilitates the formation of an excimer

with long-wavelength emission and long fluorescence lifetime as observed above; in the crystal structure of CS2 however, the CS2 molecules are isolated from one another, and neighboring CS2 molecules in adjacent layers are nearly perpendicular to one another, resulting in weak molecular aggregation. The molecules are therefore essentially isolated in the solid state, which explains why the emission properties of the solid are similar to those of the solution (see above). In addition, it was noted that CS1 and CS3 molecules have torsion angles between two conjugated stilbene groups of more than 175° within the crystals, whereas the 2-cyanostyryl groups in CS2 molecules has a twisted configuration relative to the stilbene units (with torsion angles of 155.4° and 165.0°). This molecular configuration of CS2 results in a decrease in the degree of π-conjugation, consistent with the observed low-wavelength emission. Additionally, periodic density functional theoretical (PDFT) calculations were performed on the crystal structures of CS1, CS2, and CS3 to understand their intermolecular electronic coupling and electronic structures. The calculated solid-state free energies of each CS1, CS2 and CS3 isomer in their crystal unit cells are −1031.574, −2213.223, and −2061.225 hartree, respectively. The calculated energy gaps between valence band (VB) and conduction band (CB) are 1.89, 2.11, and 1.70 eV for the CS1, CS2, and CS3 isomers, respectively. This trend is consistent with that of the fluorescent emission. Moreover, the differences of the theoretical values between CS1 and CS3, and between CS2 and CS3 are 0.19 and 0.41 eV, which is close to those determined from the experimental luminescence results to be 0.23 and 0.42 eV.

Two-component molecular materials containing CS isomers: structure and luminescence. The single-component isomers have exhibited different crystal structures and tunable luminescence as shown above. Considering that the solid-state assembly of a chromophore with a second component may also result in different molecular stacking modes and emission behavior from the pristine chromophore[28], and thus some two-component molecular materials based on the CS-based isomers were fabricated. Three typical fluorine-containing compounds (A–C, Table 1, 4-bromotetrafluorobenzene carboxylic acid (A), 1,4-diiodotetrafluorobenzene (B), and octafluoronaphthalene (C)) without visible fluorescence were chosen as the co-assembled units (co-formers) of CS1, CS2, and CS3. The selection of A–C was based on the expectation that these building blocks can potentially afford different halogen or hydrogen bonding interactions with the cyano groups in CS1, CS2, and CS3 as well as the possibility of π–π interactions between the units. The precursors were co-assembled through supramolecular co-crystallization reactions by the grinding[38] and/or ultrasound-assisted methods[39]. By comparison of the powder X-ray diffraction (PXRD) patterns of the products and their co-assembled precursors, new compositions (Table 1, such as A.CS1, A.CS2, A.CS3, B.CS2, B.CS3, C.CS2 and C.CS3) with different diffraction peaks from those of the precursors were formed (Figure S1 in the Supplementary Information). By a solution crystallization process, the single crystals of A.CS1, A.CS2, A.CS3, B.CS2, B.CS3, C.CS2, and C.CS3 were obtained, and their basic assembly modes based on single crystal X-ray diffractions studies (Table 2, CCDC numbers: A.CS1: 979757; A.CS2: 979753; B.CS2: 979752; C.CS2: 979754; C.CS3: 979755; A.CS3[26]; B.CS3[26]) are shown in Figure 3. In their two-component systems with the co-former A, the three CS-based isomers present totally different molecular interactions with A due to the difference in the positions of the cyano substituents in the stilbene units. For A.CS1 and A.CS2, A and each CS isomer formed 2:1 co-crystals within the molecular solids, in which CS molecules and the carboxylic acid dimers of A are organized by C≡N···Br halogen bonds (distance: 3.55/3.83 and 2.95/3.30 Å). A.CS1 and A.CS2
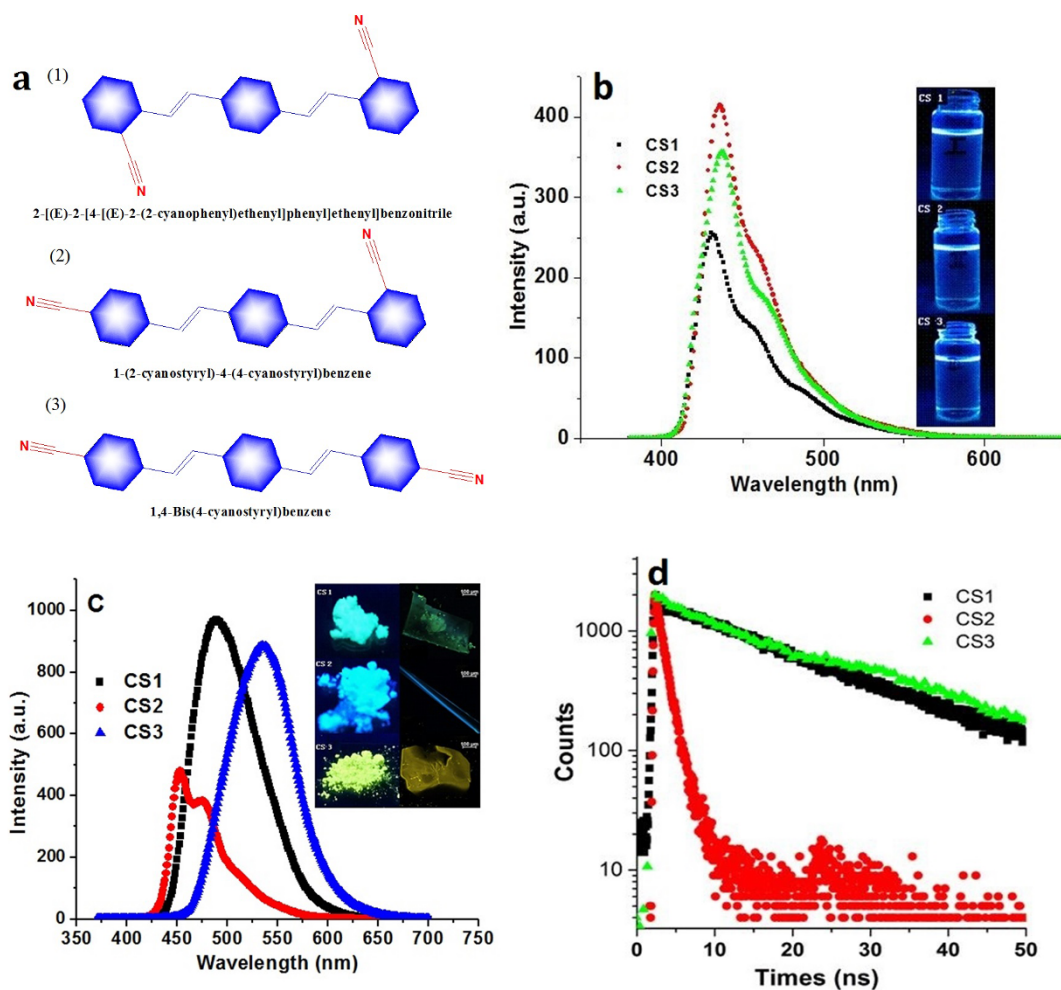
Figure 1 | (a) Molecular structures of three **CS**-based isomers: 2-[(*E*)-2-[4-[(*E*)-2-(2-cyanophenyl)ethenyl]phenyl]ethenyl]benzonitrile (**CS1**), 1-(2-cyanostyryl)-4-(4-cyanostyryl)benzene (**CS2**), and 1,4-bis(4-cyanostyryl)benzene (**CS3**); fluorescence spectra of three **CS**-based isomers in CH$_2$Cl$_2$ solution (10^{-5} mol/L, b) and solid-state (c) forms; the inset in (b) shows the fluorescence photographs of three isomers in solution under UV light (365 nm), and the inset in (c) shows the fluorescence photographs of solid-state isomers in both powdered and crystalline forms under UV light (365 nm); (d) fluorescence decay curves for solid-state **CS**-based isomers.

(Figure 3a and 3b) present one-dimensional and ring-like supramolecular motifs respectively, due to the difference in the positions of their cyano groups, which results in different directions of halogen bonding between **A** and the two isomers. In contrast, in **A.CS3** (Figure 3c) the two co-assembled units with a 1:1 ratio formed a one-dimensional zig-zag structure based on both C≡N···H–O hydrogen bonds and C≡N···Br halogen bonds. The difference between the ratios of **A** to **CS1** and **CS2** and **A** to **CS3** can be attributed to both energy and geometric factors. For example, the length of the co-former **A** monomer is not sufficient to give a 1 : 1 ratio of **A.CS1**, and this may also be the reason why the **B.CS1** two-component system cannot be formed under the same preparation conditions. For **B.CS2** and **B.CS3**, the two-component materials can form 1 : 1 molecular assemblies, as shown in Figures 3d and 3e, which present a ring-like pattern and a one-dimensional supramolecular polymer structure, respectively, based on C≡N···I halogen bonds. **C.CS2** and **C.CS3** also form 1 : 1 molecular assemblies (Figures 3f and 3g), but the co-former **C** isolates the **CS2** or **CS3** molecules from one another within the single crystals, by means of π–π interactions. Moreover, it was observed that in each of the molecular aggregates of **CS1** and **CS3** the torsion angles between the benzene and ethylene groups became more distorted than in the pristine **CS1** and **CS3**, whilst in the case of **CS2** the torsion angles showed that **CS2** was closer to coplanarity than in the pristine **CS2** crystals (Table S2 in the

Supplementary Information), showing how co-crystallization can tailor the degree of conjugation of the chromophore molecules within the solid state.

Since the introduction of different co-formers can alter both the intramolecular conformation and intermolecular aggregation of the **CS** isomers, this should be reflected in their luminescence properties. For example, compared with the pristine solid **CS1** and **CS3**, the two-component molecular materials **A.CS1**, **A.CS3**, **B.CS3** and **C.CS3** show strong blue-shifts with monomer emission behavior (Figures 4a and 4c). Such observations are consistent with the deaggregation of the chromophores induced by the co-formers demonstrated by single crystal X-ray crystallography. For **CS2**-based molecular solids, the fluorescence spectra of **A.CS2** and **B.CS2** are slightly red-shifted (from 451 to 456 and 462 nm), but otherwise similar to the spectrum of the pristine **CS2**; in contrast, **C.CS2** exhibits an obvious red-shift emission ($\lambda_{max}^{em} = 490$ nm), which can be attributed to the π–π stacking of co-planar **CS2** moieties within **C.CS2** (Figure 3f and Table S2 in the Supplementary Information). The above observations confirm that the photophysical properties of the chromophores can be modified by co-assembly with suitable co-formers. To better understand the two-component systems from an electronic structure perspective, PDFT calculation was further performed. Taking the **A.CS3** with obvious emissive change relative to pure **CS3** as the example, the calculated total and partial electronic
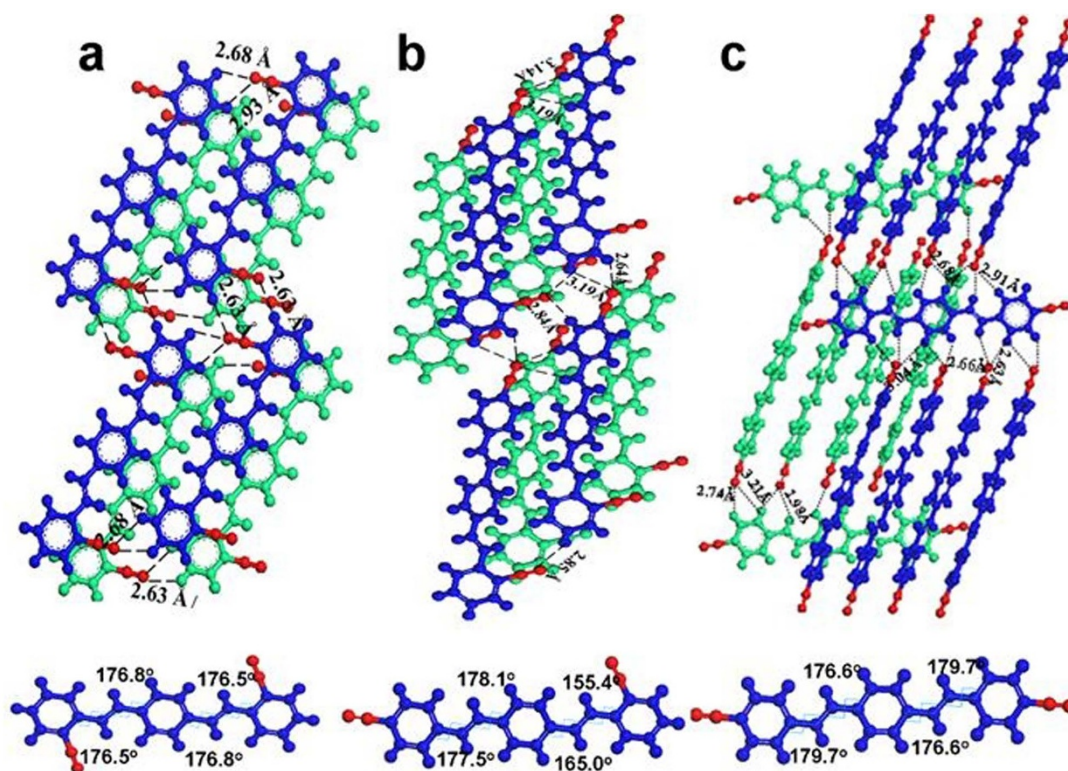
Figure 2 | Stacking fashions of (a) CS1, (b) CS2, and (c) CS3 isomers within the crystal structures; the bottom line shows the torsion angles between the benzene and ethylene groups in the isomers.

densities of states (TDOS and PDOS) of **A.CS3** are shown in Figure S2a and Figure S3 in Supplementary Information. The calculated energy gap between VB and CB is *ca.* 1.93 eV based on the band structure result (Figure S2b in Supplementary Information). The difference of the theoretical value between **A.CS3** and **CS3** are 0.23 eV, and this is consistent with the blue-shift emission of the **A.CS3** relative to the **CS3**. Additionally, based on the PDOS analysis and frontier orbital profiles of **A.CS3** (Figure S4 in Supplementary Information), the HOMO-1, HOMO and LUMO are totally distributed in **CS3**, while the LUMO+1 are mainly populated on the co-formers **A**. Therefore, the co-former **A** may influence the distribution of the frontier orbitals and the electronic structures in the two-component **A.CS3** system.

Solvent-dependent luminescence of two-component systems. Considering external stimuli may affect the weak intermolecular interactions and related photophysical properties within two-

component materials[40], the luminescent response of the **CS**-based co-crystal materials to a variety of different solvents was then investigated. For the pristine isomers **CS1**, **CS2** and **CS3** (Figure S5 in the Supplementary Information), changes in fluorescence intensity but no obvious changes in wavelength can be observed after treatment with a range of typical solvents (acetonitrile, ethanol, tetrahydrofuran (THF), toluene, *N,N*-dimethylformamide (DMF), acetone, pyridine, triethylamine (TETN), and chloroform). In marked contrast however, the emission spectra of the two-component assembled systems (**A.CS1**, **A.CS3**, **B.CS3**, **C.CS2**, and **C.CS3**) exhibit luminescent bathochromic shifts and/or peak broadening in the presence of different solvent stimuli (Figure 5 and Figure S6 in the Supplementary Information). Taking **A.CS1** as an example (Figure 5a), upon treatment with the various solvents (with the exception of toluene and chloroform) the emission wavelength underwent a shift from 448 nm to about 490 nm, accompanied by a change in the emission color from blue to bluish green, which can be observed clearly by the naked eye (inset of Figure 5a). The emission of the final product is very close to that of **CS1**, suggesting that the solvents may induce the disassembly of **A.CS1** into its pristine building blocks **A** and **CS1**. This is confirmed by the PXRD patterns (Figure S7 in the Supplementary Information) which show the characteristic diffraction peaks of **CS1**. Similar obvious solvent-dependent luminescence was also observed for other two-component assembled systems of **A.CS3**, **B.CS3**, **C.CS2**, and **C.CS3** as shown in Figures 5c, 5d, and 5e and Figure S6B in the Supplementary Information. In contrast, in the case of **A.CS2** and **B.CS2** (Figure 5b and Figure S6A in the Supplementary Information) no significant changes in luminescence spectra and color were observed, which may reflect the fact that the emission spectra of **A.CS2** and **B.CS2** are close to that of the pristine **CS2**.

The luminescence-based selective recognition of different solvents can be related to the fact that the high polarity of the solvents disturbs the supramolecular interactions (such as hydrogen/halogen bonds and π–π interactions) between the assembled units, which can result
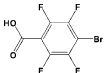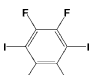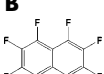
Table 1 | Observed two-component assemblies of CS-based isomers

Assembled units	CS1	CS2	CS3
A	✓(2 : 1)	✓(2 : 1)	✓(1 : 1)
B	✗	✓(1 : 1)	✓(1 : 1)
C	✗	✓(1 : 1)	✓(1 : 1)

Table 2 | Single crystal parameters for CS-based two-component solids

Samples	A.CS1 (CCDC: 979757)	A.CS2 (CCDC: 979753)	B.CS2 (CCDC: 979752)	C.CS2 (CCDC: 979754)	C.CS3 (CCDC: 979755)
Molecular formula	$C_{38}H_{18}Br_2F_8N_2O_4$	$C_{38}H_{18}B_2F_8N_2O_4$	$C_{30}H_{16}F_4I_2N_2$	$C_{34}H_{16}N_2F_8$	$C_{34}H_{16}F_8N_2$
Molecular weight	878.36	878.36	734.25	604.49	604.49
Space group	$P2_1/c$ (No. 14)	$P1/n$ (No. 2)	$P1/n$ (No. 2)	$P1/n$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	14.8196(9)	6.0821(8)	8.0126(4)	6.2454(10)	12.1806(7)
b (Å)	13.4178(7)	7.6708(7)	13.0643(6)	10.8465(18)	28.1415(14)
c (Å)	16.5035(7)	35.136(3)	14.4673(7)	20.174(4)	7.5125(7)
α (deg)	90.00	86.211(7)	108.037(4)	92.310(14)	90.00
β (deg)	97.252(5)	87.821(9)	100.222(4)	90.293(14)	91.151(8)
γ (deg)	90.00	84.373(9)	107.509(4)	93.679(13)	90.00
V (Å³)	3255.4(3)	1627.0(3)	1310.70(11)	1362.6(4)	2574.6(3)
Z	4	2	2	2	4
GooF	1.208	1.149	1.095	1.036	1.016
R_1 ($I > 2$sigma(I))	0.0693	0.0707	0.0199	0.0428	0.0555
wR_2	0.1559	0.1199	0.0432	0.1165	0.1039

in the decomposition of the chromophore-based co-crystals. For example, **B.CS3** can be converted into **CS3** and **B** after treatment with THF or pyridine, as shown by the yellow emission of the product (Figure S6B in the Supplementary Information). This is consistent with the fact that single crystals of the two-component **B.CS3** cannot be obtained by evaporation of THF or pyridine solutions of **B.CS3** powders. Based on the different extents of variation in the luminescence, the series of two-component **CS**-based isomer systems can potentially serve as a new type of luminescent sensor array for solvents.

Photochromic fluorescence of two-component systems. To further develop potential **CS**-based photo-sensitive materials[41,42], the responses of the single-/two-component molecular solids to photostimulation was studied. When crystalline powdered samples of either pristine **CS1**, **CS2**, and **CS3** or the **CS1**-, and **CS3**-based two-component materials were exposed to white-light irradiation, the only observed change was a decrease in fluorescence intensity (Figures S8 and S9 in the Supplementary Information). In contrast, the **CS2**-based two-component systems displayed changes in emission position upon photostimulation (Figure S10 in the Supplementary Information), with **C.CS2** showing the most marked luminescence shift (Figure 6a). After exposure under a xenon lamp (100 mW/cm²) for 5 minutes, **C.CS2** exhibited a significant luminescent blue shift of λ_{em}^{max} from *ca.* 490 nm to *ca.* 450 nm, with a concomitant decrease in emission intensity. The value of λ_{em}^{max}, together with the shoulder band observed at 476 nm is very similar to the typical emission of the pristine **CS2** solid; furthermore, characteristic diffraction peaks of **CS2** also appear in the PXRD pattern of the product after irradiation (Figure S11 in Supplementary Information). These observations indicate that **C.CS2** has undergone photoinduced deformation due

to the weak interactions between the components, since it was reported that several co-crystals can be deformed upon external stimuli (such as temperature)[34]. Additionally, the emission of the photochromic fluorescence (PCF) product can easily be recovered by grinding the powder: after grinding for only 10 seconds, the observed luminescence peak at 489 nm can essentially move back to that of the original **C.CS2** (Figure 6a). This reversible luminescence change can be readily repeated at least eight times (inset in Figure 6a), illustrating that the dynamic assembly-disassembly of the **C.CS2** is completely reversed by cycling the irradiation–grinding treatment, and the PCF mechanism can be deduced as shown in Figure 6c.

Since the powdered forms of the two-component molecular materials are not suitable for practical device and imaging applications, thin films of **C.CS2** on a glass substrate were prepared by a drop-casting method[43]. Upon selective-zone irradiation of the resulting film using a shadow mask for 5 minutes, luminescent patterned films can be easily obtained, in which the irradiated zone exhibits the blue emission of pristine **CS2**, while the irradiation-free zone maintains the green fluorescence of **C.CS2**. This strategy offers a facile way to develop new types of luminescent pattern and/or array films with any desired shape as shown in Figure 6b. Similar luminescent patterns with tunable selective-zone emission and high contrast can also be obtained with other systems, such as **A.CS2** and **B.CS2** (inset in Figure S10 in the Supplementary Information).

Conclusion

In summary, to illustrate a coherent concept on the relationship between the molecular conformation/crystal stacking and luminescent properties of the isomer-based molecular materials, three cyanostilbene-based positional isomers have been employed as model systems to study the structure–luminescence relationships
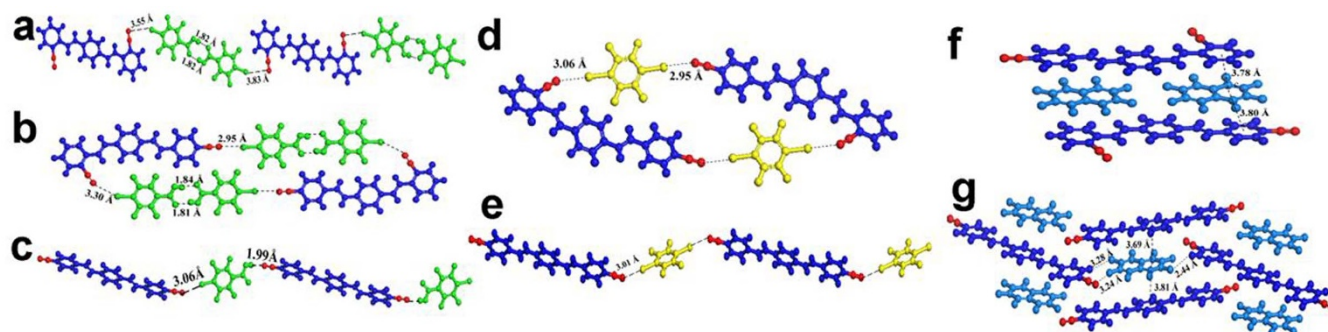

Figure 3 | Assembly modes of (a) A.CS1, (b) A.CS2, (c) A.CS3, (d) B.CS2, (e) B.CS3, (f) C.CS2, and (g) C.CS3.
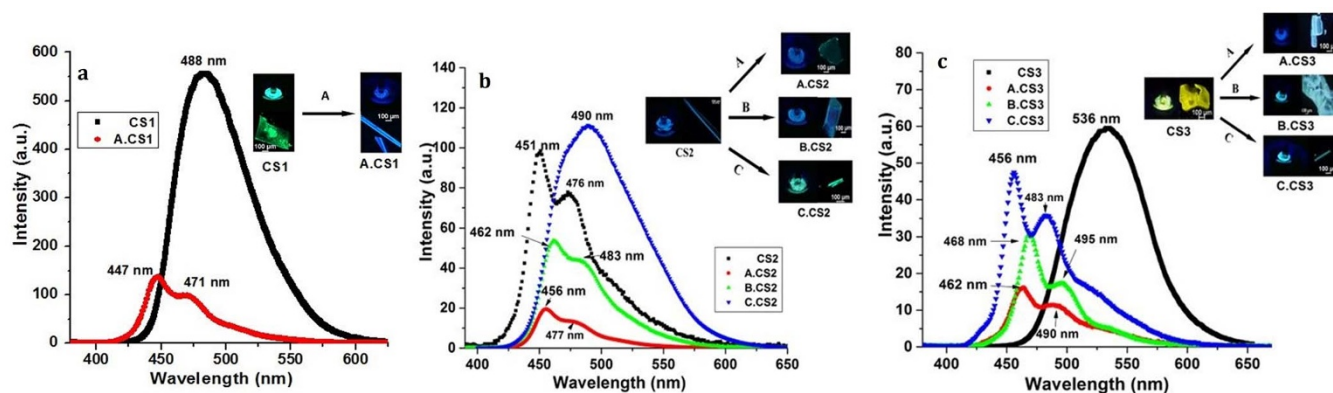
Figure 4 | Fluorescence spectra of (a) CS1, A.CS1; (b) CS2, A.CS2, B.CS2, C.CS2; (c) CS3, A.CS3, B.CS3, C.CS3. Insets show the powdered and crystalline forms of two-component assemblies and their corresponding isomers under UV light (365 nm).

upon formation of aggregates of the isomers within single-/two-component crystalline materials. It was observed that changes in the position of the cyano groups can significantly alter the molecular configurations and crystal structures within the solid states of the isomers, which results in tunable blue, green, and yellow fluorescence, with obvious differences from their spectra in solution. Moreover, two-component molecular aggregates containing the isomers were fabricated based on supramolecular co-crystallization. The as-prepared cyanostilbene isomer-based two-component systems exhibit different luminescence properties from those of the pristine chromophores resulting from the chromophores having different conformations and molecular packing modes within the two-component systems. The two-component isomer-based molecular materials exhibit both selective solvent-sensitive and photo-sensitive

fluorescence since external stimuli can modify the weak intermolecular interactions between the assembled units. The obviously reversible and fast photochromic emission of the **C.CS2** system presents opportunities for applications in optical switching and luminescent patterned films. Previous reports of materials showing fluorescence which is sensitive to external stimuli have involved changes in the molecular structure and/or chemical reaction, which generally have relative high activation energies and low extents of conversion. The advantage of the two-component materials developed here is that the luminescent response to multiple stimuli relies on both the tailoring of weaker intermolecular interactions in aggregates and occurrence of supramolecular reactions, and thus this strategy may provide an effective means to construct new types of molecule-based stimuli-responsive materials. It is
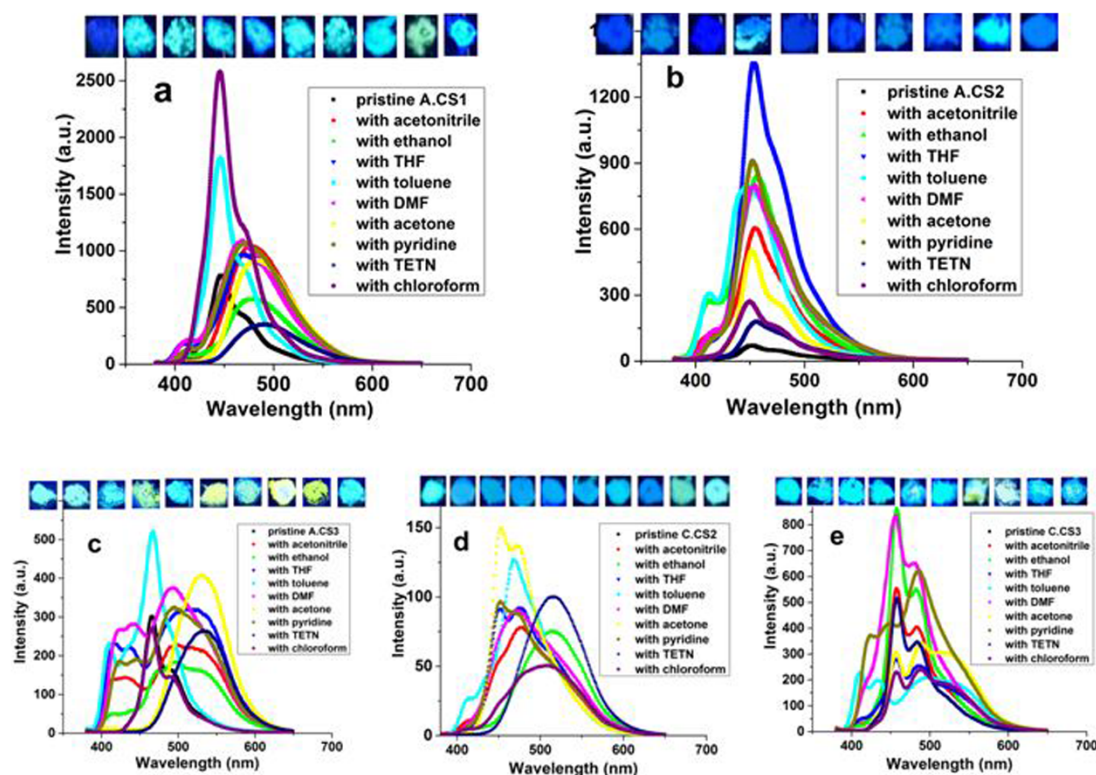

Figure 5 | Fluorescence spectra and images (insets) of (a) A.CS1, (b) A.CS2, (c) A.CS3, (d) C.CS2, and (e) C.CS3 before and after treatment with different solvents (insets from left to right show the fluorescence of the pristine co-crystals treated with acetonitrile, ethanol, THF, toluene, DMF, acetone, pyridine, TETN, and chloroform).
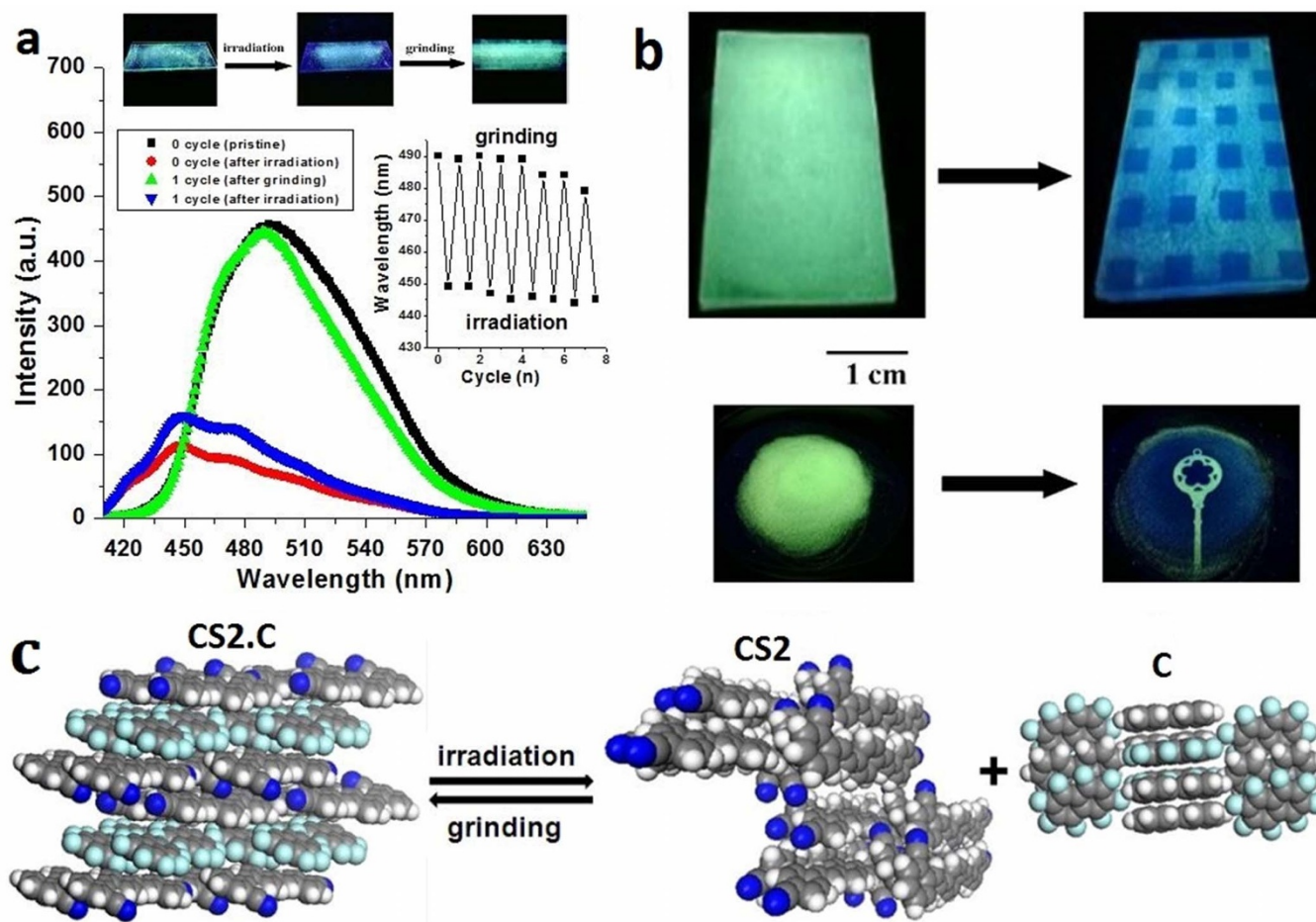
Figure 6 | (a) Fluorescence spectra of **C.CS2** with alternate irradiation and grinding. The inset plots show the reversible change in emission wavelength of the sample over eight consecutive cycles. (b) Fluorescent images of drop-cast **C.CS2** films with different masks upon a xenon lamp irradiation (100 mW/cm²) for 5 minutes. (c) A scheme for the mechanism of deformation and formation of the **C.CS2** co-crystal by irradiation and grinding.

anticipated that such dynamic assembly-disassembly of two-component supramolecular materials can be extended to other systems allowing many new types of stimuli-responsive luminescent materials to be fabricated.

Experimental section

Reagents. 2-[(E)-2-[4-[(E)-2-(2-cyanophenyl)ethenyl]phenyl]ethenyl] benzonitrile (**CS1**), 1-(2-cyanostyryl)-4-(4-cyanostyryl)benzene (**CS2**), 1,4-bis(4-cyanostyryl)benzene (**CS3**), 4-bromotetrafluorobenzene carboxylic acid (**A**), 1,4-diiodobenzene (**B**) and octafluoronaphthalene (**C**) were purchased from Sigma Chemical Co. Ltd., and used without further purification.

Preparation of the two-component systems. The powder forms of CS-based two-component systems can be obtained though a grinding process of the mixture of the assembled units. Typically, 200 mg of a solid reactant mixture with the initial ratio of the two compositions of 2 : 1 (**A:CS1, A: CS2**) or 1 : 1 (**B:CS2, C:CS2, A:CS3, B:CS3, C:CS2**), respectively. The mixture was ground for 10 min in a Retsch MM200 mill operating at a frequency of 20 Hz. In a standard experiment, two stainless steel balls of 7 mm diameter (1.4 g) were used for grinding. **A.CS1** and **A.CS2** can also be synthesized by an ultrasound-assisted method. The pristine powders of the precursors were separately dissolved in chloroform (0.1 g/L). Then the solutions were injected into pure water simultaneously under ultrasonication for 1 minute in a cleaning bath. These experiments gave rise to the new co-crystal powders, and the single crystals were obtained within

one week by slow evaporation of solutions of the co-crystal powders in 50 mL of chloroform solutions (0.1 g/L).

Calculation methods. All calculations were performed with the periodic density functional theory (DFT) method using the DMol³ module[44] in the Materials Studio software package (Version 2.2, Accelrys Inc.: San, Diego, CA, 2003). The initial configurations of CS-based isomer and co-crystal were fully optimized by the Perdew–Wang (PW91)[45] generalized gradient approximation (GGA) method with double numerical basis sets plus polarization function (DNP). The core electrons for metals were treated by effective core potentials (ECP). The SCF convergence criterion was within 1.0×10^{-5} hartree/atom and the convergence criterion of the structure optimization was 1.0×10^{-3} hartree/bohr. The Brillouin zone was sampled by $1 \times 1 \times 1$ k-points, and test calculations revealed that an increase in k-points did not affect the results.

Instrumentation. Characterization of solid materials using powder X-ray diffraction was conducted on a Rigaku XRD-6000 diffractometer, using CuK$_\alpha$ radiation ($\lambda = 0.15418$ nm) at 40 kV and 40 mA with a scanning rate of 10°/min, and a 2θ angle ranging from 3 to 50°. Single crystal X-ray diffraction data were collected for crystals **CS1**, **CS2**, **A.CS1**, **A.CS2**, **B.CS2**, **C.CS2**, and **C.CS3** on a Nonius Kappa CCD diffractometer equipped with a graphite monochromator and an Oxford cryostream, using MoK$_\alpha$ radiation. The solid-state fluorescence spectra were recorded on a RF-5301PC fluorospectrophotometer with 360 nm excitation light. The width of both the excitation and emission slits was 3 nm. The fluorescence decays were measured

using a LifeSpec-ps spectrometer with 372 nm laser excitation, and the lifetimes were calculated with the F900 Edinburgh instruments software. Fluorescence imaging of the single crystals was performed on an Olympus U-RFLT50 fluorescence microscope.

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Author contributions

D.Y. has conceived and designed the experiments; D.Y. and G.F. have performed the synthesis and characterizations, interpreted the data and co-wrote the paper.

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