

Recent Advances in Mechano-responsive Fluorescent Organic and Organometallic Compounds: Structural Diversity, Phase Transformation and Applications

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October 24, 2022

Abstract

Developing smart luminescent materials, especially stimulus-responsive fluorescent materials, is a goal of great importance, as well as a challenge. Mechano-responsive fluorescence is a property whereby the fluorescence characteristics (i.e., emission color, quantum yield, or lifetime) of a species change as a result of mechanical stimulation. In general, the said mechanical stimulation causes a phase transition in the material, and it simultaneously induces a fresh interaction of the luminous, resulting in a change in the color of the photoluminescence emission. Therefore, the transition of a material from crystalline-to-amorphous, from amorphous-to-crystalline, or from a crystalline to another, as well as the phase transformation of liquid crystals, can contribute to changes in fluorescence emission triggered by a mechanic stimulus. This article briefly reviews the development of such mechano-responsive fluorescent compounds, which consist of organic or organometallic molecules, and the emerging trends in this research field.

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Keywords: Mechano-responsive Fluorescent Compounds, Single Crystal to Single Crystal, Phase Transition, Mechanochromism

Developing smart luminescent materials, especially stimulus-responsive fluorescent materials, is a goal of great importance, as well as a challenge. Mechano-responsive fluorescence is a property whereby the fluorescence characteristics (i.e., emission color, quantum yield, or lifetime) of a species change as a result of

mechanical stimulation. In general, the said mechanical stimulation causes a phase transition in the material, and it simultaneously induces a fresh interaction of the luminous, resulting in a change in the color of the photoluminescence emission. Therefore, the transition of a material from crystalline-to-amorphous, from amorphous-to-crystalline, or from a crystalline to another, as well as the phase transformation of liquid crystals, can contribute to changes in fluorescence emission triggered by a mechanic stimulus. This article briefly reviews the development of such mechano-responsive fluorescent compounds, which consist of organic or organometallic molecules, and the emerging trends in this research field.

1. Introduction

The development of smart compounds that are able to respond to external perturbations, such as radiations^[1-3] or changes in pressure^[4-8] or temperature^[9-11] has recently attracted extensive research interest due to these compounds' potential applications in fields like optical storage devices, pressure sensors, memory chips, and security inks.^[12-17] Mechano-responsive fluorescent compounds make up one of the most important classes of smart compounds. In fact, mechano-responsive fluorescent compounds exhibit mechanochromic luminescence (MCL),^[18-29] a property whereby changes in luminescence are triggered by anisotropic or isotropic mechanical stresses. In their pioneering work, Zink^[30-31] and Mataka^[32] et al. demonstrated triboluminescence of hexaphenylcarbodiphosphorane and mechanochromic polymorphs of 5,6-di(*p*-chlorobenzoyl)-1,3,4,7-tetraphenylbenzo[*c*]thiophene, respectively. Since the publications of the said studies, a number of organic^[33-39] and inorganic compounds^[40-44] exhibiting MCL behavior have been reported; therefore, the field of mechano-responsive fluorescent compounds has increased in size. Indeed, the number of reports focusing on mechano-responsive fluorescent compounds has increased significantly over the past several years, with more than 300 published reports so far.^[45-56] The results of in-depth studies indicated that MCL is to be attributed to the modulation of the morphologies of mechano-responsive fluorescent compounds, including the transformation from the crystalline to the amorphous state, from the amorphous to the crystalline state, and from the crystalline state to another, as a response to an external stimulus.^[57-61] Although mechano-responsive fluorescent compounds have been referred to in several reviews,^[62-67] focused reviews that summarize the properties of these compounds and the principles on which MCL behavior is based are still lacking. In this contribution, recent developments in the study of the mechanochromism of mechano-responsive fluorescent compounds are reviewed. Specifically, we discuss the structural diversity, characterization, and principles of mechano-responsive fluorescent compounds and illustrate in detail the relationship between compound morphology^[68-73] (Table 1) and MCL behavior.

2. MCL induced by the crystalline-to-amorphous phase transition

Phase conversion from the crystalline to the amorphous states is one of the most common transformations that occur as a result of mechano-responsive fluorescent compounds being subjected to a mechanical stimulus.^[74-77] The said transformation contributed to MCL accompanied by structural variation of solvent exclusion, intermolecular interactions transformation, conformational fluctuations, and so on.

2.1. Solvent exclusion

An early work by Ito *et al.*^[78-79] demonstrated a mechano-induced change in the color of the emission by aryl gold isocyanide complex **1** (see the structure of this compound in Table 1). The crystalline state (**1B**) of complexes **1** was transformed into the amorphous state (**1Y**) upon grinding accompanied by solvent release (Figure 1a). Accordingly, the blue luminescence of **1B** was replaced by an intense yellow luminescence. Moreover, the addition of a solvent induced a reversible phase transition back to the original **1B**, which exhibited a blue luminescence emission again. Notably, the solvent exclusion effect was further enhanced by introducing a biphenyl unit into a gold isocyanide scaffold to produce complex **2** (see the structure of this compound in Table 1).^[78] This complex was treated with various solvents to afford several types of **2**/solvent and crystalline phases with dimeric packing (Figure 1b) characterized by different emission properties. As a result of the strong conformational restrictions^[80], **2**/solvent have been observed to release solvent molecules following simple grinding to display other emission colors, enabling the development of effective mechano-responsive emitting compounds.^[81-83]

2.2. Intermolecular interactions transformation

Araki *et al.* designed the amide-substituted tetraphenylpyrene derivative **3** (see its structure reported in Table 1),^[84] which consisted of both sites for Kitaigorodskii's close packing principle^[85] and Etter's first hydrogen-bond rule.^[86] The quadruple amide hydrogen bonds contributed to the construction of the well-defined columnar assembly in the blue-emitting B-form solid of **3** (Figure 1c). Interestingly, applying pressure to the said B-form solid resulted in a disruption of the columnar structure and the generation of the G-form solid, which was characterized by a poorly ordered molecular packing; as a consequence, the sample's luminescence switched from blue to green. Indeed, this is a typical example of piezochromic luminescence induced by the disruption of weak interactions.^[87]

Recently, Chen *et al.*^[88] synthesized a series of 4, 9-diazopyrene-based amphiphiles (**4a** and **4b**; see structures in Table 1) that consist of a hydrophobic diazapyrene core and hydrophilic tetraethylene glycol. In the solid-state, these compounds exhibited orthogonal responses to mechanical forces and water. Evidence indicated that diazopyrene was a multifunctional fluorescent probe for excimer sensing, and the color of its photoluminescence emission clearly switched from blue to green as a result of different stimuli (Figure 2a,b). The results of physical optical characterization indicated that slight structural changes, allowing larger π - π overlapping, had occurred, which led to significant differences in the optical response properties of **4a** and **4b**. By exploiting the different optical response properties of these diazopyrene derivatives, the continuous and selective activation of the excimer triggered by the action of water vapor and mechanical forces provides a multi-modal and efficient method for data encryption and decryption.

In addition, two E/Z isomers of anthracene and cyano-substituted ethylenes (**5E** and **5Z**; see the structures of these compounds in Table 1) were synthesized.^[89] Upon grinding, both compounds exhibited mechanochromic characteristics. The results of powder X-ray diffractometry (PXRD) investigations indicated that, after grinding treatments, the crystals were almost entirely converted into amorphous solids. This modification resulted in an enhanced degree of π -conjugation and an increase in intermolecular π - π interactions, leading to the observed red-shift of emission. Furthermore, **5Z**, which comprises two cyano groups on the same side of the double bond, induced a more intense packing mode and contributed to better sensing performance than **5E**. This contribution provided information of an isomeric effect on piezochromic properties.

Park *et al.*^[90] reported a molecularly tailored 1:1 donor(**6D**)-acceptor(**6A**) (D-A) charge-transfer cocrystal that exhibited intensely red-shifted charge-transfer (CT)-associated luminescent characteristics. Given the non-centrosymmetric chemical structure of molecule **6A**, a loosely packed structure with obvious free volume was obtained, thus affording an easy superposition control between the mixed D-A CT complex and the isolated single D/A phase (Figure 2c,d). Piezo writing on the blue emissive film gave rise to a red emission with mixed-phase formation. D-A portions (**7**) were combined in one unit to form the organic solid-state emitter.^[91] After a gentle crush, the orange- or yellow-colored emission of the organic solid-state emitter underwent a hypsochromic shift to cyan emissive fragments ($\lambda_{em} = 498\text{--}501\text{ nm}$), while further grinding resulted in a bathochromic shift of the said emission to green emissive powder ($\lambda_{em} = 540\text{--}550\text{ nm}$), acting as an unusual "back and forth" fluorescent response. The interplay between intramolecular CT was responsible for such fluorescence switching.^[92-93]

Anthracene and its derivatives have the ability to form excimers which usually feature distinct emission spectra compared to their monomers. For instance, anthracene derivative **8** was studied the forming evolution of an anthracene excimer in response to external pressure.^[94] When the external pressure is within the range of 3.5-5.6 GPa, the excimer structure and π - π intermolecular contacts were formed and boosted fluorescence intensity. This work revealed the influence of excimer on the luminescence properties of compounds and provided a strong guide for future research on mechano-responsive fluorescent devices. In addition, crystal **9** exhibited pure excimer emission at ambient conditions as a result of monodisperse dimeric stacking of anthracene.^[95] The excimer fluorescence peak first kept constant (0.12-1.70 GPa) and then a continuous redshift (1.70-9.41 GPa) during pressurization. Potential energy curves reveal that excited dimer of **9** kept rapidly relaxing itself to the same excimer equilibrium geometry during the initial stage of pressurization

and could not relax itself back to previous equilibrium geometry when pressure at 1.7-9.41 GP because of the restriction of external pressure. This work further provides a reference for the better understanding of intrinsic nature for excimer formation, geometry, and photophysics.

2.3. Close packing of flat accessory

Triphenylamine, a propeller-shaped optoelectronic molecule, has been extensively used to manufacture organic solar dyes as well as solid-state fluorescent and mechanochromic materials.^[96-101] Anthony *et al.*^[102] prepared a rewritten and self-erasing fluorescent platform using a single organic fluorophore, *n*-phenyl-*n*-(4-(quinoline-2-yl)phenyl) aniline (**10**), by combining halogenated isoquinoline with mechanically chromic triphenylamine. The propeller shape of triphenylamine impeded the close packing of isoquinoline in the crystals of **10**. Therefore, **10** exhibited solid-state fluorescence (quantum yield: 20%). Interestingly, the fluorescence of **10** showed a blue shift (from 518 nm to 454 nm) after intense grinding, and the said shift was reversed by heating. The results of PXRD investigations suggested that intense grinding induced the conversion of **10** from the crystalline to the amorphous phase, which was reversed under heating conditions. In the crystalline state, the molecular packing of **10** was highly organized; this packing was however disrupted by grinding, which triggered the formation of a poorly ordered amorphous phase. This transformation contributed to a complete quenching of the fluorescence associated with flat isoquinoline. Thus, in the amorphous state, the blue fluorescence of **10** was entirely due to the propeller-shaped triphenylamine unit.

2.4. Conformational fluctuations

In 2015, Tang *et al.*^[103] reported the design and synthesis of a group of bis(diarylmethylene)dihydroanthracene derivatives with butterfly-like shapes.^[104] Two types of 9,10-bis(di-4'-methylphenylmethylene)-9,10-dihydroanthracene crystals (**11b** and **11g**, Figure 3a) were obtained by crystallization from their solution in *n*-hexane/CHCl₃ mixture. **11b** emitted at a wavelength of 425 nm with a quantum yield of 27.7%. By contrast, **11g** exhibited a red-shifted emission with respect to **11b** (from 425 nm to 464 nm), which was characterized by higher efficiency (quantum yield: 76.8%). Notably, the difference in emission efficiency between **11b** and **11g** is attributed to poorer electronic communication arising from **11b** exhibiting larger dihedral angles than **11g** (Figure 3a). Moreover, the amorphous powders of **11** (**11-am**) exhibited an emission at 520 nm with a quantum yield of 3.3%. This partial emission quenching was due to the poor packing of the luminogenic molecules, which rendered many free spaces for the rotations and vibration of the phenyl rings and dihydroanthracene blade. Thus, the emission of **11** was reversibly switched between three colors (blue, green, and yellow) by fuming or thermal processes.

Another sample was π -conjugated macrocycles (**12** and **12S**), characterized by an interior cavity with a diameter of approximately 0.7 nm.^[105] After grinding **12S** powder, the maximum emission wavelength of **12S** shifted from 458 nm to 490 nm. When the ground powder was fumed with tetrahydrofuran (THF) vapor for 30 min, the emission wavelength shifted back to 458 nm. Similarly, after being subjected to grinding, sample **12**, the precursor of **12S**, also exhibited a subtle red-shift of the emission wavelength from 500 nm to 510 nm; additionally, the emission wavelength shifted back to 488 after annealing with THF vapor. The results of PXRD experiments indicated that the as-prepared samples **12** were characterized by a highly ordered crystal structure. However, the diffraction signal was attenuated after grinding, implying a decrease in arrangement orders and loose packing in the ground sample, leading to a red-shifted emission at 490 nm. By contrast, the original sample **12** was characterized by an amorphous structure. After grinding, **12** became loosely structured, resulting in a slight red-shift of the fluorescence emission. The geometries of **12** before and after grinding were further investigated carrying out density functional theory (DFT) calculations using functional B3LYP with the 6-31G(d) basis set. The results of these calculations suggested that conformational fluctuations of **12** and **12S** rendered conjugated macrocycles the possibility to adjust their conformations within the rigid topology to exhibit different fluorescence emissions. By contrast, the loosely packed crystal structure of the diaminomaleonitrile-modified tetraphenylethene (TPE) compound **13** was destroyed by the application of mechanical force; therefore, turning on the emission due to the restriction of the TPE units.^[106-108]

2.5 Intramolecular conformational transformation

Another TPE derivative, tetrakis(4-(dimethylamino)phenyl)ethylene (**14**), was characterized by a propeller shape and nearly centrosymmetric structure. After grinding, the twisted conformation of molecule **14** was modified so that better intramolecular coplanarity was achieved, along with a large degree of conjugation.^[109] The results of PXRD experiments indicated that crystals of **14** exhibited intense and sharp peaks. At the same time, the ground sample displayed a small and broad diffraction intensity, indicating that the grinding process had triggered the conversion of a crystalline phase into an amorphous phase. Furthermore, **14** was characterized by a twisted conformation, and, after grinding, coplanarity and conjugation were enhanced; as a result, the optical bandgap decreased in size, ultimately leading to the bathochromic shift of the emission. This work illustrated a sample that mechanochromic luminescent changes induced by the intramolecular conformation rather than $\pi\cdots\pi$ stacking and H- or J-aggregation.

In 2018, Tang *et al.*^[110] proposed a strategy to obtain high-performance on-off mechano-responsive fluorescent compounds by controlling the intersystem crossing (ISC) process. Nitrophenyl groups were incorporated into distorted AIEgens (**15** -**16**) to enhance the efficiency of the ISC processes.^[111] Mechanical stimuli modulated the molecular conformation to afford different solid-state luminescent on-off switches. Experiments demonstrated the high contrast and high sensitivity MCL performance, reversibility, and fast response behavior. These properties enable them (**15** -**16**) to be widely used in fields like optical information storage and tactile sensors. Furthermore, the strategy introduced by Tang and co-workers is expected to represent a big step toward the expansion of the on-off MCL family of compounds.^[112]

In order to achieve a deep understanding of the underlying mechanism of MCL, Tang *et al.*^[113] designed and synthesized a group of pyridinium-functionalized TPE luminogens (**17**) to be used in the systematic investigation of the influence of the push-pull electronic effect and molecular conformation on MCL. The results of the relevant experiments indicated that effective intramolecular charge-transfer^[114] resulted in good MCL characteristics, and planar molecular conformation contributed to red fluorescence.^[115] The evidence thus collected afforded a deeper understanding of the behavior of the molecules subjected to external pressure and provided a guide for developing efficient mechano-responsive fluorescent compounds based on conformational fluctuations.^[116-117]

3. MCL induced by the amorphous-to-crystalline phase transition

Given the entropy reduction associated with transforming an amorphous solid into a crystalline one,^[118] endothermal approaches, such as thermal annealing, heating, or fuming, have been reported to promote the molecular packing transition from amorphous to ordered. Notably, only several MCL molecules have been observed to undergo an amorphous-to-crystalline transition triggered by mechanical stimulation.

3.1. Grinding-facilitated annealing

The fluorenyl-containing TPE analog **18** (see structure reported in Table 1) was initially prepared and investigated in the context of the relationship between molecular conformations and MCL behavior.^[119] Only faint marks were left on the sample when the letters were pressed on the original **18** film. After annealing at 130°C for 1 h, the parts of the sample that were subjected to the pressure became crystalline, and the letter-shaped marks thus left on the sample glowed blue while the rest of the sample remained unchanged, so that a high visual contrast was achieved. A mechanism was proposed for this mechano-facilitated crystallization, which is detailed in Figure 3b. In the pristine amorphous sample, every single molecule adopted the planar conformation inherited from the melting process. Specifically, the dihedral angles between the central ethenyl plane and each aryl substituent were proposed to be 51.84° to 53.99° as close to DFT optimization. The material absorbed some energy upon grinding, and, as a consequence, it was converted into a metastable state characterized by the presence of twisted molecules. In the sample in the said metastable state, some of the corresponding dihedral angles became larger, close in value to those observed in the crystalline phase. This state was thus regarded as an intermediate in the transformation from amorphous-to-crystalline, whose formation promoted the subsequent annealing-triggered crystallization. This contribution meant that the mechanical stimulation essentially increased the crystallization capacity of the original amorphous sample.

3.2 Molecular packing transformation

Tong *et al.*^[120] reported that 2-aminobenzophenone derivatives exhibited MCL behavior with a high "off-on" contrast ratio. Ethanol solutions of compounds **19**, **20**, and **21** (see their structures in Table 1) were smeared on glass substrates; following the evaporation of ethanol, no emissions were observed. However, strong cyan (475 nm), blue (463 nm), and green (492 nm) emissions were observed, respectively, after the ethanol-free smears of **19**, **20**, and **21** were scratched with a pipet tip. The results of PXRD and scanning electron microscopy investigations indicated a transformation of the molecular packing from that typical of an amorphous state to that of a crystalline one, as a result of the scratching process. Restrictions to intramolecular rotations specific of the crystalline state subsequently induced fluorescence.^[121-123] However, the driving force of this transformation was not revealed. The formation of a twisted conformation was proposed after scratching, which promoted the crystallization of the sample, thus inducing fluorescence emission.

4. MCL induced by the crystalline-to-crystalline phase transition

Besides the approaches discussed above that involve the transition between crystalline and amorphous states, research on crystalline-to-crystalline state transformation was also vital in the field of MCL. Generally, when mechanical stimulation is applied, the resulting crystalline-to-amorphous phase transition causes an alteration of the emissive properties of the sample.^[124] This phenomenon is intuitively understandable because the applied mechanical forces are non-coherent, so they alter the integrity of ordered molecular arrangements. For such amorphous ground forms, in many cases, it was difficult to investigate the intermolecular interaction patterns, which are important to comprehend in order to gain insight into the underlying mechanism of MCL. By contrast, detailed structural information on crystalline phases characterized by single crystal XRD could be collected in the cases of mechano-responsive fluorescent compounds exhibiting crystalline-to-crystalline phase transitions.

4.1 Disruption of weak interactions

The boron compound **22** (see its structure in Table 1) consisted of a phenylboronic moiety and a ligand.^[125] After the chelation of the boron center, the ligand assumed a planar conformation, which in turn facilitated the π -stacking of the molecules.^[126] During slow solvent evaporation, **22** forms two types of crystals: large, green-emitting prismlike crystals and cyan-emitting needlelike crystals. Indeed, in the green crystal, two molecules are antiparallel to form a dimeric structure through face-to-face $\pi\cdots\pi$ and dipole-dipole interactions. Another solid-state form of this boron material **22** was readily perturbed by external stresses (i.e., molecular perturbations), resulting in a decrease in the intensity of the fluorescence emission. In the crystalline state, molecular arrangements were destroyed and reorganized as a result of the grinding process. Different molecular arrangements, such as π -stacked dimers, were obtained after grinding, causing the luminescence to be red-shifted. Thus, it provides a model for an organic material combining three forms of MCL.^[127]

4.2 Molecular domino transformations

The phenyl(phenyl isocyanide)gold(I) complex **23** bearings both a gold center and phenyl group was initially investigated for its potential to be the subject of a mechano-responsive transformation.^[128] Two polymorphs of this compound **23b** and **23y** were obtained following crystallization from hexane/ CH_2Cl_2 . Each of the molecules in **23b** formed a herringbone-like structure with a head-to-tail arrangement of the phenyl ligand on the gold atoms, and the isocyanide phenyl moiety twisted with a dihedral angle of 71.6° (Figure 4a). Moreover, no aurophilic interactions were present in this structure, as indicated by the large distances (5.733 Å) between the gold atoms of the paired molecules. In the crystalline states of **23y**, the molecules were nearly flat and coupled via an oblique head-to-tail arrangement. In this case, the Au $\cdots$ Au distance was 3.177 Å, suggesting the presence of significant aurophilic interactions. These two polymorphs of **23** (**23b** and **23y**) exhibited two different photoluminescences (blue and yellow, respectively). Mechanical trigger experiments were performed by applying a small mechanical stimulus. Under atmospheric conditions, only a small pit was formed on the surface of a **23b** crystal. By contrast, the grinding of the **23b** sample with a spatula resulted

in a domain transformation from **23b** to **23y** ; consequently, a yellow emission was gradually observed to increase in intensity to almost the entire crystal of **23b** after 9 h at room temperature. Notably, the described transformation could also be triggered by touching a seed crystal of **23y** with a crystal of Ib. Notably, two methyl substituents were introduced in **23** to produce phenyl(3,5-dimethylphenyl isocyanide)gold(**24**). The additional intermolecular interactions brought about by the presence of the said substituents resulted in a new phase that was thermodynamically more stable than its counterpart characterized by auophilic bonds; therefore, **24** exhibited changes in the profile of the crystal structures and emission energies that were opposite to those observed for complex **23** . The intermolecular auophilic interactions in the crystal structure of the green emissive metastable phase I of complex **24** were destroyed^[129] by picking to afford the weakly blue emissive phase II, which included multiple CH... π interactions.

Subsequently, the behavior of the digold(I) isocyanide complex **25** (see its structure in Table 1) was reported; when the relevant study was published, **25** proved to be the first mechanochromic compound characterized by several interconvertible structures with different emission properties.^[130] When complex **25** in the **25G** state was ground for 10 min, the color of the fluorescence emission of the powder switched from green to yellow, indicating the formation of **25** polymorph **25Y** (Figure 4c). Further grinding promoted the transformation of the **25Y** polymorph of complex **25** to the amorphous polymorph **25O** ; as a result, the color of the emission switched from yellow to orange. Complex **25** is a scarce example of a mechanochromic compound exhibiting interconvertible multi-color emissions in the solid state.

4.3 Mutual orientation transformation

Electron donating groups have quite a different effect on the π -delocalization of a conjugate system when bonded at ortho and para as compared to meta positions in the phenyl ring. Complex 1-phenyl-3-(3,5-dimethoxyphenyl)-propane-1,3-dione (**26**) comprises two methoxy groups in the meta positions of one of its phenyl rings.^[131] This compound was observed to exist as two polymorphs. In the crystals of both polymorphs, the antiparallel molecules are stacked onto each other as a result of face-to-face π ... π interactions.^[132] The difference between the two polymorphs was found to consist in the fact that, in polymorph A, the crystal packing was further stabilized with respect to polymorph B by intermolecular hydrogen bonds. When the solid B characterized by yellow fluorescence emission was thoroughly ground in an agate mortar, a dramatic rearrangement ensued, whereby the more stable crystalline phase A was formed, which is characterized by green fluorescence emission.

N-Salicylidene-4-amino-2-methylbenzotriazole (**27**) is a compound whose photophysical properties were observed to be highly dependent on conformational fixation and the π -overlap of adjacent molecules induced by molecular packing.^[133] Mechanical grinding resulted in the progressive transformation of **27** from sensibly twisted to mostly planar, which in turn determined a switch in luminescence emission from poorly red to light yellow. This finding offers a valuable tool for controlling the luminescent output for stimulus-responsive applications.

4.4 Planarization of benzene rings

Donor-acceptor charge-transfer processes play an essential role in mechano-responsive fluorescent compounds. Changes in intermolecular interactions have been observed to contribute to the luminescence emission shift triggered by mechanical grinding or the application of hydrostatic pressure.^[134-135] Recently, our group^[136] reported the behavior of the fluorescent MIC-Au^I complex **28a** and of two emissive MIC organometallic assemblies **28b** and **28c** , which are based on Ag^I/Au^I and mesoionic carbene-decorated tetraphenylethene (MIC-TPE) ligands. The effects of external pressure on the fluorescence emissions of the solid **28b** and **28c** were investigated. Complex **28a** and the organometallic cages **28b** and **28c** were characterized by bright green emissions in ambient conditions, but these emissions underwent obvious red-shifts during the compression process. This phenomenon could be due to the planarization of benzene rings in the TPE units, which would promote tighter intermolecular packing under external mechanical pressure. As the external pressure gradually decreased, the intensity of the fluorescence emissions of **28a** and **28c** returned to the initial state, and the corresponding emission wavelengths blue-shifted back to the original positions. These observations

further supported the hypothesis detailed above whereby the conformational planarization of benzene rings in TPE and intermolecular tighter packing were the main reasons for the observed shift in fluorescence emission.^[137-139]

4.5 Cooperative effect between aggregation-induced emission and energy-transfer suppression

Due to the formation of low-energy emitting species and nonradiative "dark" states, most piezochromic luminescent compounds showed gradual redshift and quenched emission as pressure increases. However, Yang et al. developed a pressure-induced blueshift and emission enhancement compound, 9-(3-(1,2,2-triphenylvinyl)phenyl)-anthracene (**29**), by integration of TPE with anthracene.^[140] The TPE orientations contributed to anthracene dimer formation with discrete π - π stacking. The isotropic hydrostatic pressure was exerted via a diamond anvil cell on **29** crystal, an abnormal blue-shifted emission appeared and strengthened once pressure increased above 1.23 GPa. This could be explained by the cooperative effect between aggregation-induced emission and energy-transfer suppression. When the applied pressure on **29** exceeds 1.23 GPa, the absorption of the anthracene dimer weakened, while TPE remained almost unchanged; thus, the reducing overlap between TPE emission and anthracene dimer absorption led to the suppressed energy-transfer. Otherwise, TPE units aggregated, thereby triggering the AIE behavior to enhance the high-energy emission band.

Others

5.1 Changes in the molecular aggregation state in powder

9,10-Bis[(E)-2-(pyridin-2-yl)vinyl]anthracene (**30**) was first investigated by Tian *et al.* for its MCL characteristics.^[141-142] In fact, powder form **30** exhibited a strong green emission at $\lambda_{\text{max}} = 528$ nm, which underwent a red-shift to yellow ($\lambda_{\text{max}} = 561$ nm) upon **30** being subjected to grinding. Moreover, the ground powder recovered its initial green emission after being heating above 160°C. Indeed, the piezoceramic effect associated with the luminescence of **30** was investigated in more detail. A gradual red-shift of the fluorescence emission from green to red (652 nm) was observed for **30** in powder form as the external pressure increased from 0 to 8 GPa. The relationship between the sample's molecular aggregation state and its luminescent properties was further investigated by single crystal XRD with three different polymorphs of **30** (C1, C2, and C3). The results thus obtained indicated that an increase in the overlap between the anthracene planes of adjacent molecules caused by the applied external pressure brought about a modification of the $\pi \cdots \pi$ stacking states,^[143] leading to a fluorescence emission of a different color with respect to that of the undisturbed sample (Figure 5a). The results of a study focusing on 9,10-bis[(E)-2-(pyridin-4-yl)vinyl]anthracene (**31**) suggested that this compound's piezochromic luminescence was due to changes in its molecular aggregation state.^[144] As a consequence of the application of external pressure, the prevalent intermolecular interactions between **31** molecules switched from $\text{CH} \cdots \pi$ to $\pi \cdots \pi$ stacking (see Figure 5b)^[145]; therefore, the formation of a completely different crystalline structure was brought about.^[146-148]

5.2 MCL induced by a liquid crystal phase transition

Liquid crystals (LC) are soft materials that combine ordered and dynamic states.^[149-155] This duality of characteristics can be exploited to manufacture mechano-responsive materials. Nanostructured liquid crystals consisting of the pyrene derivative **32** comprising two dendritic groups linked to a central pyrene moiety (see structure reported in Table 1) exhibited yellow photoluminescence in the cubic phase.^[156] The cubic phase of LC **32** was observed to be metastable and undergo a shear-induced phase transformation to a thermodynamically more stable columnar phase characterized by blue-green photoluminescence (Figure 6a,b). The segmented columnar structure was mainly due to the formation of hydrogen bonds between the amide groups of adjacent molecules and the π -stack structure of the pyrene nuclei.^[157-158] The described shear-induced isothermal transition from a metastable to a stable phase illustrates a sample of mechano-responsive luminescent LCs.

5.3. Fluorophores anchored to structurally tunable matrices

Mechanical stimuli generally trigger structural transformations in materials like polymers and inorganic ma-

materials due to the broad range of structures they can possess. Consequently, the molecular configurations and aggregation states of fluorophores incorporated in such materials have been observed to exhibit fluorescence emissions of different colors.^[159-160] For instance, the aggregation-induced-emissive molecule niflumic acid (NFC) was assembled into the interlayer region of Zn–Al layered double hydroxides (LDHs).^[161] As a consequence of the slipping of LDH sheets, the molecular conformation of NFC anions and their intermolecular interactions with LDHs were easily tuned by applying perturbations.^[162] XRD-based investigations conducted on the NFC/LDH system suggested that grinding resulted in an increase in the sample’s interlayer spacing. This modification further influenced the samples’ fluorescent properties.^[163] Moreover, the cyclophane mechanophore featured two identical luminophores resulting from mechano-induced conformational changes (Figure 6c),^[164-166] and, upon bulk deformation, the polyurethane elastomer that contained such cyclophanes displayed a readily detectable change in the color of the fluorescence emission (Figure 6d).

Tetrazine dyes anchored on polydiacetylenes (compounds **33a**, **33b**, and **33c**; see structures in Table 1) were assembled into thin films. These were tested using an atomic force microscope (AFM) coupled with a fluorescence microscope.^[167] The AFM served to apply shear stress while the fluorescence microscope probed the activation of the fluorescence. The presence of tetrazine enhanced the fluorescent activation by shear stress due to the spectral overlap and energy transfer; indeed, tetrazine contributed to achieving a facile and errorless detection.^[168-169]

6. Conclusion

The rapid development of new mechano-responsive fluorescent compounds across the world has led to the synthesis of many organic or organometallic molecules with mechanical response characteristics. As made evident by the examples discussed in this review, in almost all reported systems, mechanically induced changes in photophysical properties were associated with changes in molecular morphology, including transitions from a crystalline to an amorphous phase, from an amorphous to a crystalline phase, and from a crystalline phase to a different crystalline phase; notably, they were also associated to liquid crystals undergoing phase transformations. The presence or absence of photoluminescent and polychromatic variations under mechanical stimulation extends the range of use of mechano-responsive fluorescent compounds. They allow the production of high contrast polychromatic images, which may be helpful for data storage, complex information display, and the production of security inks.

Although significant achievements have been made over the past decade in designing and developing mechano-responsive fluorescent compounds, the exploration of MCL-based smart materials is still in its infancy, and several issues need to be addressed before practical applications are possible. First, mechano-responsive fluorescent compounds used for manufacturing smart materials must be of exceptional large-scale availability. Nowadays, the widely used mechano-responsive fluorescent compounds are very costly due to need to carry out multi-step preparation procedures that rely on expensive starting materials. Therefore, additional efforts are necessary to develop novel efficient preparation strategies relying on practically feasible raw materials. Second, quantitative measurements of MCL are currently limited to the implementation of the diamond anvil cell technique via isotropic compression. Therefore, a quantitative measurement involving an isotropic mechanical force should be developed to characterize MCL behavior in-depth. Furthermore, experiments conducted to monitor *in situ* changes in morphology and crystal packing are predicted to be developed to study the effects of these changes on MCL properties. Third, the majority of the herein-presented materials are still at the proof-of-concept stage. Therefore, in-depth investigations (including experiments and theoretical calculations) focusing on crucial structure–property relationships are still needed to manufacture on-demand mechano-responsive fluorescent compounds. Above all, applications of MCL are still in the early stages of exploration. Thus, we can expect considerable growth in engineering innovations to integrate mechano-responsive fluorescent compounds into commercially available working devices.

Although a long-term effort is necessary to address these challenges, mechano-responsive fluorescent compounds have a promising future in terms of widespread use. This review will be of help to readers and investigators working in the development of not only mechano-responsive fluorescent compounds but also of various sensors and optical materials.

Acknowledgements

This work was supported by the National Natural Science Fund for Distinguished Young Scholars of China (No. 22025107), the National Youth Top-notch Talent Support Program of China, the Key Science and Technology Innovation Team of Shaanxi Province (2019TD-007), Natural Science Foundation of Shaanxi Province (2021JQ-432), Xi'an Key Laboratory of Functional Supramolecular Structure and Materials, and the FM&EM International Joint Laboratory of Northwest University.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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TABLE 1 Molecular structures of the mechano-responsive fluorescent compounds discussed in this minireview

MCL* principle	Complex	Molecular structure	Mechanical force	Reference
Crystalline-to-amorphous phase transition	1		Grinding	78
	2		Grinding or ball milling	78
	3		Grinding	84
	4a		Grinding	88
	4b		Grinding	88
	5E		Grinding	89
	5Z		Grinding	89
	6-D		Piezo writing	90
	6-A		Piezo writing	90
	7		Grinding	91
	8		Pressure	94
	9		Diamond anvil cell technique	95
	10		Strong crush	102
	11		Grinding	103

	12S	Grinding	105
	12	Grinding	105
	13	Grinding	106
	14	Grinding	109
	15-1N	Grinding	110
	15-2N	Grinding	110
	16-1N	Grinding	110
	16-2N	Grinding	110
	16-3N	Grinding	110
	16-4N	Grinding	110
	17-OP	Grinding/hydrostatic pressure	113
	17-H	Grinding/hydrostatic pressure	113
Amorphous-to-crystalline phase transition	18	Grinding	119
	19	Scratching	120
	20	Grinding	120
	21	Grinding	120
Crystalline-to-crystalline phase transition	22	Grinding	125
	23	Pricking	128
	24	Mechanical picking	129
	25	Ball-milling	130
	26	Grinding	131
	27	Grinding	133
	28a	Diamond anvil cell technique	136
	28b	Diamond anvil cell technique	136
	28c	Diamond anvil cell technique	136
	29	Diamond anvil cell technique	140
Others	30	Grinding	140
	31	Grinding	144
	32	Grinding	156
	33a	Mechanical friction	167
	33b	Mechanical friction	165
	33c	Mechanical friction	165

* Mechanochromic luminescence.

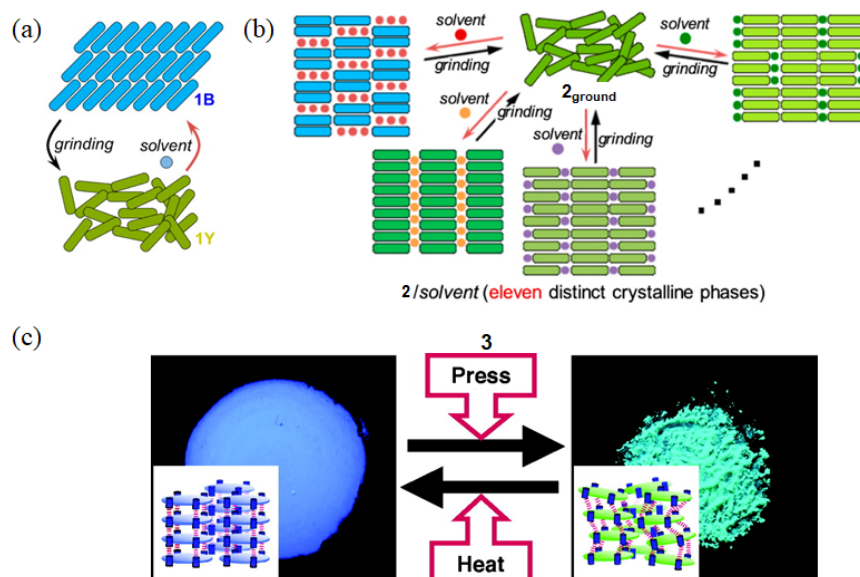


FIGURE 1 (a) Schematic illustration of the phase transitions of **1** induced by various stimuli. Reproduced with permission.^[78] Copyright 2008, American Chemical Society. (b) Schematic illustration of the phase transitions of **2** induced by various stimuli. Reproduced with permission.^[78] Copyright 2016, American Chemical Society. (c) Photographs taken under ultraviolet light irradiation of the B-form (left) and the G-form (right) of compound **3**. Reproduced with permission.^[84] Copyright 2007, American Chemical Society.

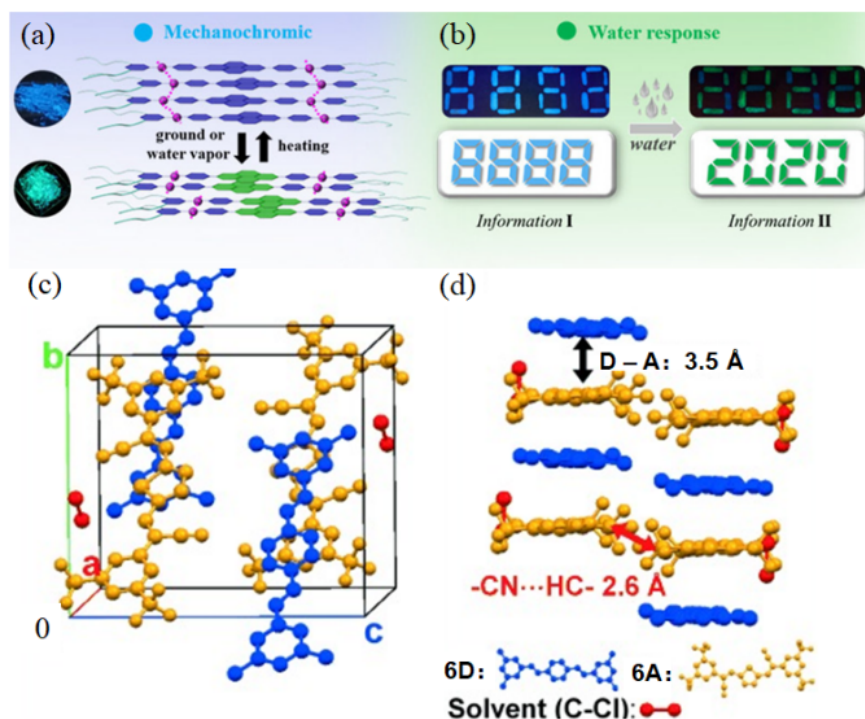


FIGURE 2 (a) Schematic illustration of the proposed stimulus-induced excimer-based densing mechanism

of the fiazapyrene smphiphiles in dolid. (b) Photographs (top; taken under ultraviolet light irradiation) and schematic diagram (bottom) of the paper deposited with **4b** before and after the stimulus of water vapor. Reproduced with permission.^[88] Copyright 2021, American Chemical Society. (c) Molecular arrangement of solvent-including structure. (d) Roll-angle view with information on the **6D–6A** $\pi\cdots\pi$ distance (black arrow) and the A1–A1–CN $\cdots$ HC- distance (red arrow). Reproduced with permission.^[90] Copyright 2016, Wiley-VCH.

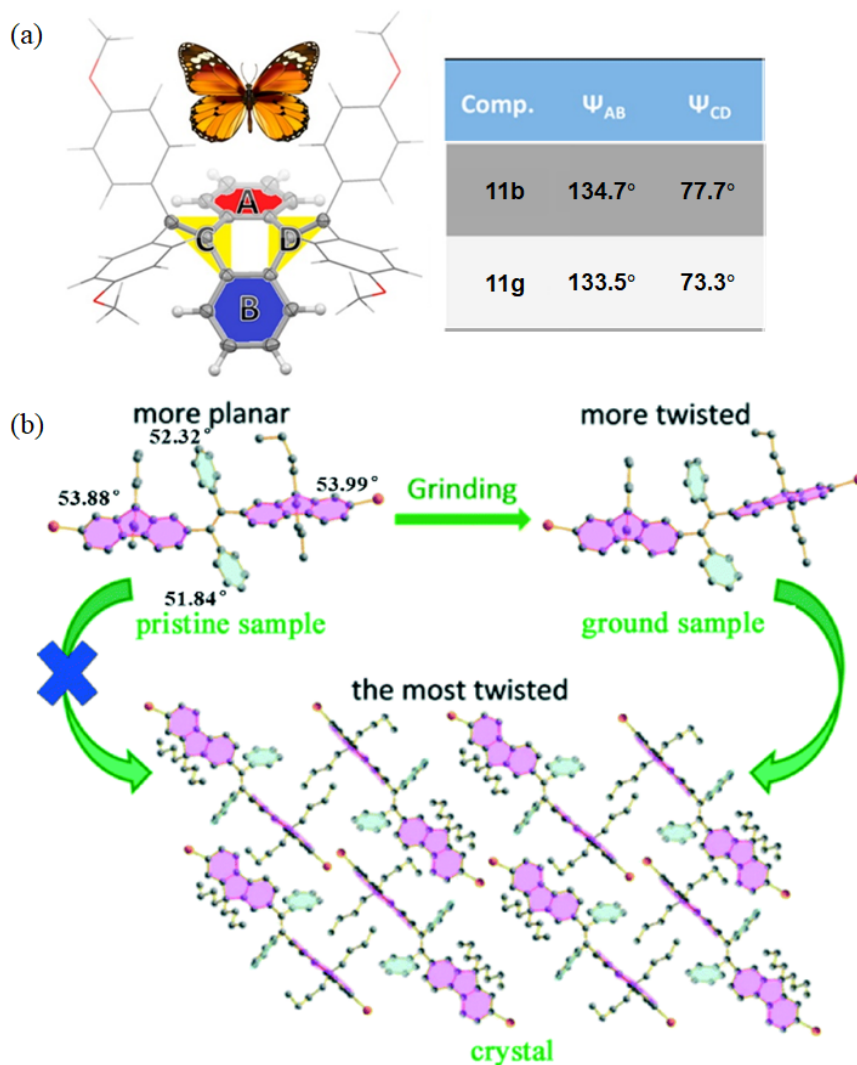


FIGURE 3 (a) Molecular geometry illustration of the crystal structure of **11**, with some of the dihedal angles reported. Reproduced with permission.^[103] Copyright 2015, American Chemical Society. (b) Schematic illustration of the conformation transition of a **18** molecule in different states. Reproduced with permission.^[119] Copyright 2015, Royal Society of Chemistry

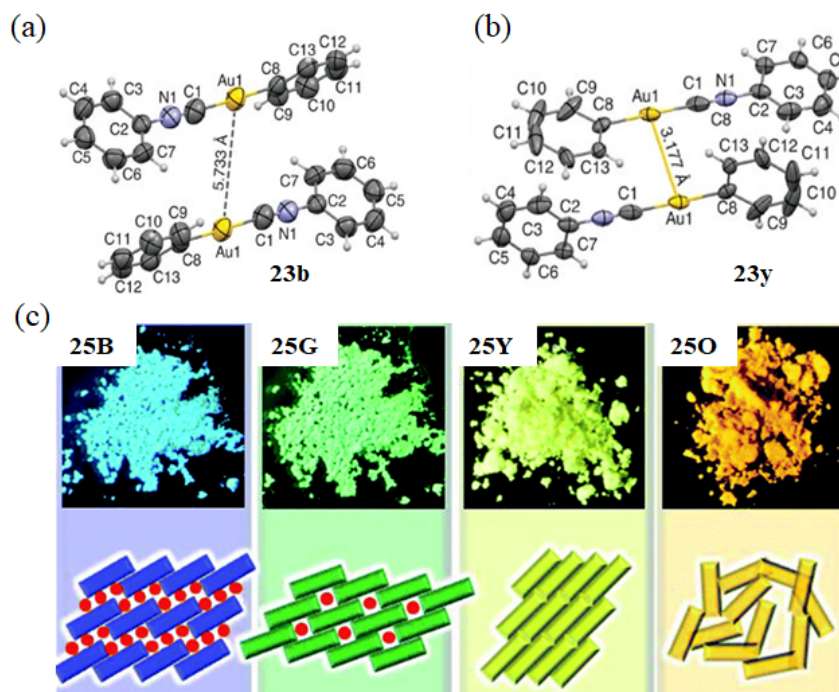


FIGURE 4 (a) ORTEP drawing (50% probability level) of the crystal structure of **23b**. (b) ORTEP drawing (50% probability level) of the crystal structure of **23y**. Reproduced with permission.^[128] Copyright 2013, Nature. (c) Photographs of the powder forms of **25** showing different photoluminescence under UV light at 365 nm (top). Schematic representation (bottom) of the solid state molecular arrangements of **25**, in which a molecule of **25** is denoted as a rectangle, with the colors of the corresponding emission. Solvent molecules are denoted as red circles. Reproduced with permission.^[130] Copyright 2015, Royal Society of Chemistry.

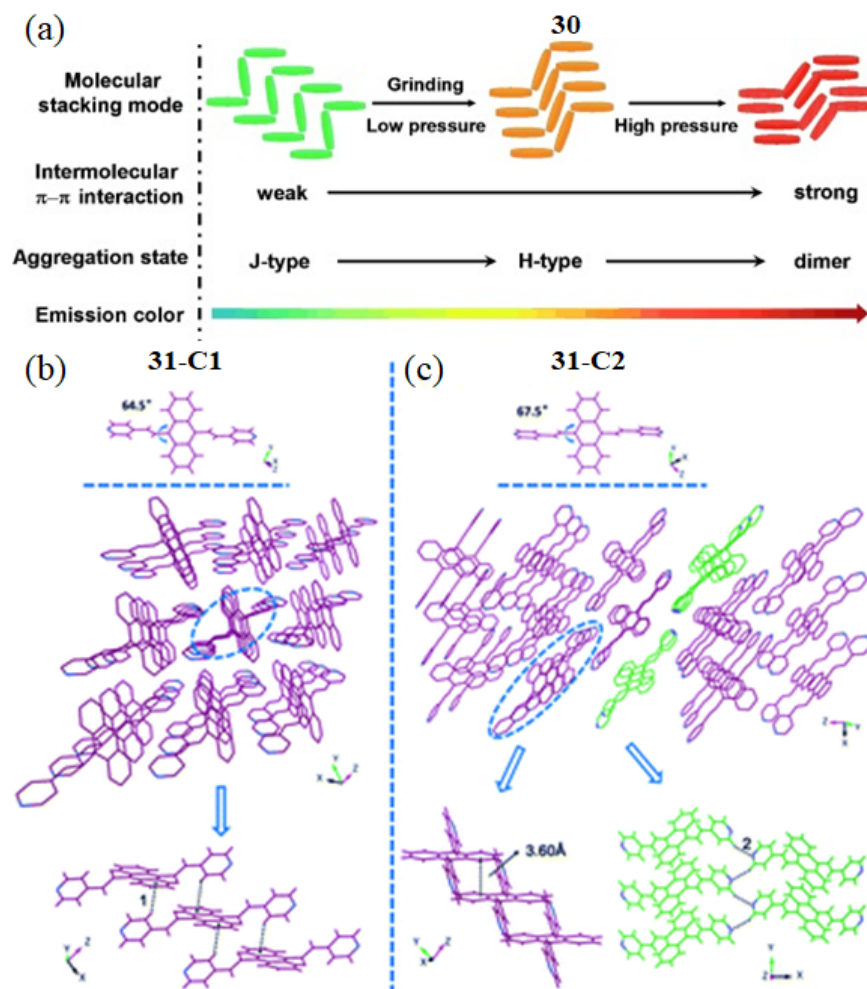


FIGURE 5 (a) Stacking modes and corresponding fluorescence emission colors for the different molecular aggregation states of compound **30** in powder form. Reproduced with permission^[141] Copyright 2012, Wiley-VCH (b) Aggregation state of compound **31-C1**. (c) Aggregation state of compound **31-C2**. Reproduced with permission^[144] Copyright 2013, Royal Society of Chemistry

FIGURE 6 Illustrations of the assembly of **32** in the (a) cubic phase and (b) shear-induced columnar phase. Reproduced with permission.^[156] Copyright 2008, Wiley VCH. Schematic illustrations of (c) the cyclophane-based supramolecular mechanophore and (d) the mechanochromic luminescence of a polymer containing such mechanophores. Reproduced with permission.^[164] Copyright 2021, American Chemical Society.

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Mechano-responsive fluorescent compounds make up one of the most important class of smart materials. They exhibit mechanochromic luminescence, a phenomenon whereby changes in luminescence are triggered by anisotropic or isotropic mechanical stresses applied to the said materials. This review summarizes the recent advances in mechano-responsive fluorescent compounds focusing on their properties and the principles on which they are based.

Mechano-responsive Fluorescent Compounds, Single Crystal to Single Crystal, Phase Transitions, Mechanochromic Luminescence

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Recent Advances in Mechano-responsive Fluorescent Organic and Organometallic Compounds: Structural Diversity, Phase Transformation and Applications

