Progress Report

Mechanoresponsive Luminescent Molecular Assemblies: An Emerging Class of Materials

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Abstract: The possibility to change the morphology of organic and organometallic materials through mechanical stimulation is emerging as a general and powerful concept for the design of functional materials. In particular the photophysical properties, such as photoluminescence color, quantum yield and emission lifetime of organic and organometallic fluorophores can significantly depend on the molecular packing, enabling the development of molecular materials with mechanoresponsive luminescence characteristics. Indeed, an increasing number of studies have shown in recent years that mechanical force can be utilized to change the molecular arrangement, and thereby the optical response, of luminescent molecular assemblies of π-conjugated organic or organometallic molecules. This report reviews the development of such mechanoresponsive luminescent (MRL) molecular assemblies consisting of organic or organometallic molecules and summarizes emerging trends in this research field. After a brief introduction of mechanoresponsive luminescence observed in molecular assemblies, the concept of “luminescent molecular domino” is introduced, before molecular materials that show turn-on/off of photoluminescence in response to mechanical stimulation are reviewed. Mechanically stimulated multi-color changes and water-soluble MRL materials are also highlighted and approaches that combine the concept of MRL molecular assemblies with other materials types are presented in the last part of this progress report.

1. Introduction

The construction of ordered assemblies of organic and/or organometallic compounds has attracted much attention in the past decades, because such architectures possess great potential as sophisticated functional materials.[1] Indeed, a broad range of ordered molecular assemblies ranging from crystals with high stiffness[2] to relatively soft self-assembled materials such as liquid crystals[1c, 3] and physical gels consisting of fluids and self-assembled fibers[4] has been intensely studied. In aqueous conditions, spherical micelles, cylindrical micelles, vesicles or membranes have been constructed by a variety of amphiphiles.[5, 6] Organic and organometallic molecules having extended π-electron conjugated moieties are adequate building blocks to prepare such ordered assemblies through noncovalent intermolecular interactions.[4f, 6, 7] In particular their rigid nature supports the formation of ordered assembled structures. Moreover, the extended π-conjugated system leads to various functions such as charge carrier transport,[8] nonlinear optical responses,[9] and luminescence[6, 7, 10]. Therefore, the resulting molecular assemblies are promising candidates for materials used in electronic devices including light emitting diodes,[11] photovoltaic devices[12] and field-effect transistors.[13] In devices where a high charge carrier mobility is essential, the materials are typically designed to form well-ordered structures,[8a-c, 8f, 11-13] and it is desirable that no morphological changes occur during operation to achieve and retain high performance. In other words, such molecular packed structures are desired to be “static”.

By contrast, the possibility to impart changes to ordered molecular assemblies composed of organic and/or organometallic molecules having extended π-conjugated moieties by applying an external stimulus is useful to create “dynamic” functional materials, which change their properties “on command” and without cleavage of covalent bonds. Since the photoluminescent properties of many fluorescent compounds are significantly influenced by their molecular arrangements, rearrangement of the molecular packing of such materials *via* external stimuli can be utilized to alter their photophysical properties.[1g, 14, 15] Such materials would be good candidates for sensors, memories, informational displays and security features. For example, a variety of compounds changing the photoluminescent properties through thermal treatment without melting process have been prepared, because temperature change is well-known way to induce dynamic change in molecular assembled structures.[14, 16] An increasing number of studies has also shown that mechanical simulation can be utilized to control the molecular arrangement, and thereby the optical response, of luminescent molecular assemblies of π-conjugated organic or organometallic molecules. Indeed, during the last decade the possibility to change the morphology of such materials by mechanical stimuli has emerged as a general design tool to create functional materials.[1g, 15, 17] Most of the mechanoresponsive luminescent (MRL) materials developed to date show switching between only two colors, but recently, several organic or organometallic compounds have been found to display MRL behavior with unconventional properties, such as a "luminescent molecular domino effect", turn-on/off behavior, multi-color changes and water-soluble behavior. It has also been shown that it is possible to covalently attach MRL molecular assemblies to other materials and bestow them with mechanoresponsive functionality. In this progress report, we focus on these emerging topics, after first providing a brief introduction of MRL effects and some promising design approaches to create such materials.

2. Brief Introduction on Mechanoresponsive Luminescence

In order to enable the reader to put the more recent developments into context, this section provides a concise overview of the field using representative examples of MRL effects and materials. Since several excellent papers and book-chapters have recently reviewed the field,[1g, 15, 17] the account is held in a succinct manner.

2.1. Definition of Terms

The term “piezochromic luminescence” was introduced in 2007 to describe a mechanically induced change of the luminescent color,[18] while in the meantime the expressions “mechanochromic luminescence”, “mechanofluorochromism”, “piezofluorochromism” and “luminescence mechanochromism” have established themselves and are often used in the literature in an interchangeable manner. In this report, we mainly use two terms “mechanochromic luminescence” and “mechanoresponsive luminescence”. The term “mechanochromic luminescence” is defined as the phenomenon in which a material displays a major and reversible change in photoluminescence color in response to mechanical stimulation. While the initial photoluminescence color must be restorable under this definition, such recovery typically requires subsequent exposure to stimuli other than mechanical force, e.g. temperature treatment or exposure to solvent vapors. A mechanically induced turn-on or turn-off of the photoluminescence is not included in this definition, because only one photoluminescence color is involved and no color change is at play. We thus refer to such changes using the broader definition of “mechanoresponsive luminescence”, which is used to describe a major change of the photophysical properties, including the luminescence color, intensity or lifetime by mechanical stimulation. Mechanochromic luminescent (MCL) materials belong to MRL materials.

2.2. Crystalline Compounds

2.2.1. Organic Crystalline Compounds

To our best knowledge, the first organic compound that exhibits mechanoresponsive luminescence in the solid state was reported by Gawinecki *et al.* in 1993,[19] who showed that the yellow-green luminescence of a solid-state sample of 4-*tert*-butyl-1-(4’-dimethylaminobenzylideneamino)pyridinium perchlorate could be quenched by squeezing the material with a spatula and provided the first example of a turn-off type MRL material.

The number of organic compounds with MCL properties has rapidly increased since the 1,3,6,8-tetraphenylpyrene derivative **1** (**Figure 1**) was reported to exhibit mechanochromic luminescence by Sagara and Araki *et al.* in 2007.[18] Kunzelman and Weder *et al.* showed that cyano-substituted oligo(*p*-phenylene vinylene) derivatives (cyano-OPVs) **2a** and **2b** exhibit mechanochromic luminescence in 2008.[20] A series of heteropolycyclic donor–acceptor π-conjugated fluorescent dyes including **3a**-**c** were found to display mechanochromic luminescence by Ooyama and Harima *et al.*.[21] Since the difluoroboron avobenzone **4** was reported to show mechanochromic luminescence by Fraser's group,[22] the relationship between molecular structures and the mechanoresponsive luminescence of many compounds with similar molecular structures have been intensely investigated.[23] Jia *et al.* described that the pyrene derivative **5** bearing an oligopeptide-based flexible group exhibits mechanochromic luminescence.[24] The same group also reported another pyrene derivative with MCL properties.[25] Zhang and Wang *et al.* reported a benzothiadiazole derivative[26] and anthracene derivatives[27] with MCL properties in 2011. A benzodifuran derivative,[28] a salicylaldehyde azine derivative[29] and 4-[bis(4-methylphenyl)amino]benzaldehyde[30] were found to show MRL properties in 2011. In 2012, Mizoshita *et al.* introduced the perylene bisimide dye **6** that shows MCL behavior.[31] Isothermal recovery of the initial color at room temperature was observed when a small amount of silicon oil was mixed in the thin film of **6**. Tuning the efficiency of fluorescent resonance energy transfer (FRET) by mechanical stimulation also leads to mechanochromic luminescence. In 2012, Baumgartner *et al.* demonstrated that a mixture of two π-extended phospholium salts **7a** and **7b**, which function as energy donor and acceptor respectively, changes its photoluminescence color from blue to orange upon mechanical stimulation.[32] Several carbazole-based dyes have been also shown to exhibit mechanochromic luminescence by Ooyama *et al.* since 2012.[33] In 2013, two groups demonstrated that divinylanthracene derivatives can exhibit mechanochromic luminescence.[34] A cyano-substituted diarylethene derivative[35] and a series of boron difluoride dyes[36] were also found to show MCL behavior in 2013. After these reports, several other organic compounds showing mechanoresponsive luminescence have been introduced.[37]

Recently, aggregation-induced emission (AIE) has become an attractive research object for researchers interested in the photophysical properties of organic and organometallic compounds and their applications.[38] The effect is an inversion of the common phenomenon that chromophore aggregation generally causes quenching of light emission. Thus, in AIE compounds the emission intensity is enhanced upon aggregation. Several AIE-active compounds have been also reported to show mechanochromic luminescence. Park *et al.* prepared cyanostilbene derivatives such as **8** with both AIE and MCL properties.[39] Tang *et al.* developed several AIE-active molecules that show mechanochromic luminescence, including compound **9**.[40] In addition, a variety of AIE-active compounds with MCL properties have been developed by Chi and Xu's group[41] and other groups.[42]

2.2.2. Organometallic Crystalline Compounds

Several gold complexes have been reported to show mechanoresponsive luminescence by Fackler's group,[43] Reber's group,[44] and Eisenberg's group.[45] In 2008, Ito *et al.* reported a typical mechanochromic luminescence effect for gold complex **10**.[46] After this report, several gold(I) complexes with MCL properties have been prepared.[47] In 2005, Mizukami and Kanesato *et al.* described that the helical zinc complex **11** exhibits mechanoresponsive luminescence.[48] In 2010, Tzeng *et al.* reported MRL properties of a zinc(II)-based coordination framework.[49] An AIE-active zinc complex was also found to exhibit mechanochromic luminescence in 2011 by Chi and Xu *et al.*.[50] Platinum (II) complexes also show mechanoresponsive luminescence. In 2009, Shinozaki *et al.* reported that yellow emission of simple platinum (II) complex **12** changes to orange.[51] Chen's group has examined mechanochromic luminescence observed for some square-planar platinum(II) complexes.[52] Other researchers have also reported platinum complexes having MRL behavior.[53] The first MCL copper complex was reported by Perruchas and Boilot *et al.* in

2010.[54] The copper(I) iodide cluster **13** exhibits a change in photoluminescence color from faint green to intense yellow and the initial green emission recovers after thermal treatment. The same group reported another MCL copper complex.[55] Other groups have also developed copper complexes with MRL properties.[56] In 2010, Tsukuda and Tsubomura *et al.* demonstrated a silver(I) complex (**14**) which exhibits mechanochromic luminescence.[57] The luminescence color of the silver complex changes from blue to green and the blue color is restored after annealing at 200 °C for 10 min. Babashkina *et al.* reported one silver complex shows mechanoresponsive luminescence that is accompanied by mechanical stimuli-induced reaction.[58] Mechanochromic luminescence of tris(8-hydroxyquinoline)aluminium (Alq_3) was also reported by Zhang and Wang *et al.* in 2011.[59] Ghedini *et al.* reported that rubbing the surface of a thin film of an ionic iridium complex **15** induces change the photoluminescence color from green to orange.[60] Su *et al.* have reported mechanochromic luminescent iridium complexes[61] as well as AIE-active iridium-containing complexes.[62] Other iridium complexes have been also reported to show mechanoresponsive luminescence.[63] In 2014, Sun and Liu *et al.* reported ionic iridium complexes showing mechanochromic, vapochromic and electrochromic luminescence.[64] In 2013, Zhang *et al.* reported a beryllium complex with MRL properties.[65]

In 2011, Lu and Wei *et al.* reported that layered host–guest materials in which self-assembled organic fluorophores were sandwiched between layered double hydroxides change both absorption and photoluminescence color in response to the pressure applied to the host-guest materials.[66] The color changes were explained with changes in the molecular packing of the dyes between the layered double hydroxides.

2.3. Liquid-Crystalline Compounds

The liquid-crystalline (LC) properties of organic compounds represent another attractive basis for the development of MRL materials, [1g, 15] in particular because such materials can offer states that offer both, a high level of order and significant molecular mobility.[3] Indeed, phase transitions between different LC phases can induce dynamic changes of the molecular assemblies, which in turn may translate into changes of the materials' photophysical characteristics. Kato's group has demonstrated this at the examples of pyrene-,[67] anthracene-[68] and bithiophene-based[69] liquid crystals **16-18** in which dendrons induce LC properties. These LC materials change their photoluminescence color upon mechanically induced phase transition from cubic to columnar phases. A naphthalene moiety was also exploited as an emissive core for this type of LC mechanochromic luminescent material.[70] A smectic LC material comprising 10,10'-bis(phenylethynyl)-9,9'-bianthryl moieties (**19**) has also been reported to exhibit mechanochromic luminescence by Yamane and Kato *et al.*.[71] In this case, ordered assemblies of the 9,9'-bianthryl moieties showing green photoluminescence, can be disturbed by mechanical shearing, causing a transition to afford blue-green photoluminescence.

Liquid crystals having organometallic moieties also exhibit mechanochromic luminescence. For example, Kozhevnikov and Bruce *et al.* showed that a thin film of the LC platinum (II) complex **20** changes its photoluminescence color from yellow to red by rubbing.[72]

2.4. Polymer-based Materials

MRL materials can also be created by introducing suitable dyes into ductile polymer mechanoresponsive matrices.[17l, 17m] In this case, the MRL properties are typically based on the formation of nano-scale aggregates of excimer-forming dyes in the polymeric host, which are irreversibly or reversibly dispersed upon deformation of the material, and thus cause a change of the material's optical properties.[17c-e, 17j, 17l, 17m] In some cases, this can be achieved by creating physical blends of the dye and the host polymer, *e.g.* by conventional melt-processing techniques. First examples of such materials were reported by Weder's group,[73] who showed in 2002 that linear low-density polyethylene films containing small amounts of cyano-OPVs **21** or **22** change their photoluminescence color upon plastic deformation.[73a] In subsequent studies, this effect was extended to other polymers, including polyesters,[73c] polyurethanes,[73d, 73g] and fluorinated polymers,[73g] and it was shown that during tensile deformation, a breakup of nano-scale dye aggregates occurs and promotes a change of the photoluminescence color from excimer-dominant to monomer-dominant emission.[73e] Pucci *et al.* adapted the concept and reported MRL films comprising bis(benzoxazolyl)stilbene **23**[74] or the perylene bisimide derivative **24**.[75]

It is noteworthy that breaking covalent bonds by mechanical force is also a promising way to change the photophysical properties of chromophore-containing polymers.[76] Moore and Sottos *et al.* first demonstrated this when they reported a mechano-active polymer in which spiropyran groups are covalently introduced to polymer chains as a mechanically responsive motif, or “mechanophore”.[77] Upon elongation, the spiropyran mechanophore undergoes a (reversible) force-induced ring opening reaction to the merocyanine form. As a result, an intense reddish color appears; at the same time, an increase of the emission intensity can be observed. Craig’s group and Weng’s group also evaluated mechano-active fluorescence properties of polymers in which the spiropyran group is covalently introduced to polymer chains.[78, 79] Extending the scope of mechanochemical transduction, Sijbesma’s group introduced the bis(adamantyl)-1,2-dioxetane unit covalently introduced into polymer chains and demonstrated the mechanoluminescent behavior, i.e., emission upon mechanical stimulation without the need for excitation light by way of mechanically triggered chemiluminescence.[80] The luminescence color was tuned by changing dyes that work as energy acceptors.

3. Mechanisms for Changes of the Photoluminescence Color of Molecular Assemblies

The requirements to develop molecular materials with MRL properties are as follows. Firstly, the molecules of interest should be luminescent and form at least two different stable molecular assemblies under ambient conditions. In other words, the presence of at least two thermodynamically (meta)stable states is the most significant requirement to achieve MRL behavior. Secondly, the arrangement and/or conformations of the π-conjugated moieties that give rise to the photoluminescence of the materials must be completely different in these different assembly states, which in turn can impact the photophysical properties on account of excimer formation,[81] exciton coupling,[82] conformational changes of individual molecules[14] and other intermolecular interactions such as aurophilic interaction.[83] Thirdly, it must be possible to change the molecular packing by application of mechanical force. Finally, aggregation-induced quenching should not occur for all molecular assembled forms, as otherwise no photoluminescence changes will be observable.

Most of the compounds showing mechanoresponsive luminescence have been found serendipitously or as a consequence of screening of compounds. However, the emerging knowledge regarding the relationship between molecular structures and mechano-responsiveness permits to formulate several strategies to deliberately design materials with MRL characteristics. Some approaches to fulfill the first and most important requirement described above are overviewed in this section using specific examples.

Competitive effects between different sorts of intermolecular interactions represent an effective way to achieve molecular assemblies that are thermodynamically metastable. Various types of intermolecular interactions, such as hydrogen bonding, π-π stacking, ionic interactions and Van der Waals forces, function concurrently in molecular materials ranging from hard crystals to soft materials such as supramolecular polymers and liquid crystals. In conventional supramolecular design approaches, researchers design molecules so that the intermolecular interactions concertedly work to afford the targeted molecular assemblies, which often represent the thermodynamically most stable state. By contrast, thermodynamically metastable states can be accessed by using intermolecular interactions in a competitive manner (**Figure 2a**).

For example, as depicted in Figure 2b, 1,3,6,8-tetraphenylpyrene derivative **1**[18] forms two different states on account of the competitive effect between hydrogen bonding and π-π stacking. In the as-prepared white powder showing blue photoluminescence (B-form), **1** forms columnar structures due to the quadruple hydrogen bonds between amide groups of adjacent molecules. The assembled structure is thermodynamically stable. However, the emissive cores are not closely packed because the length between amide groups forming hydrogen bonds is normally longer than distance between arenes moieties forming π-π stacks. Therefore, the formation of columnar structures is driven by hydrogen bonding-dominated assembly. After mechanical grinding, linear hydrogen bonds are disturbed and the emissive cores form more closely packed structures, leading to blue-green photoluminescence (G-form). The mechanical stimuli-induced G-form is thermodynamically metastable and a closed packing-dominated molecular assembly. In fact, a 1,3,6,8-tetraphenylpyrene derivative without amide group forms a closed packing-dominated molecular assembly not columnar structures similar to B-form.[84]

Weder's group showed in 2008 that in cyano-OPVs such as **2a** and **2b** a subtle balance between π-π stacking of the chromophores' cores (which can be moderated by the presence of electron donating or withdrawing groups on the central core) and Van der Waals interactions among the aliphatic peripheral groups (which can be moderated by their length) leads to the formation of two polymorphs, whose different crystal structures lead to blue and yellow emission, respectively.[20]

Another example in which the competitive effect works well is an MCL fluorenone derivative **25** (Figure 2c) reported by Wang *et al.* in 2014.[85] The compound **25** forms red emissive crystal **25R** or yellow emissive crystal **25Y**, depending on the preparation procedure. Mechanical grinding induces transformation from **25Y** to **25R** and thus the emission color also changes from yellow to red. After subsequent exposure to dichloromethane vapor, the initial yellow photoluminescence recovers. The yellow emissive **25Y** is a thermodynamically metastable state, while **25R** is a thermodynamically stable state. X-ray single crystal structure analyses of **25R** and **25Y** reveal that the competitive effect between hydrogen bonding and π-π stacking also functions effectively in this case. In the crystal structure of **25R**, the π-π stacks dominate the packing, although weak hydrogen bond formation was also observed. Therefore, **25R** is regarded as π-π stacking-directed molecular assembly. By contrast, in **25Y**, the molecules form hydrogen bonds and the resulting 2D sheet-like structures stack on top of each other to form the crystal structures, where no π-π stacking exists. Thus, **25Y** is formed by hydrogen-bond-directed molecular assembly. A competitive effect between intermolecular interactions also works well for an amphiphilic oligo(phenylenevinylene) derivative described below, which shows a tri-colored change in photoluminescence.[86]

Another way to achieve two different stable states is to interfere with the formation of thermodynamically stable assemblies, for example by kinetically trapping molecular assemblies in thermodynamically metastable forms. The kinetically trapped molecular assemblies can be converted to thermodynamically stable states by mechanical stimulation (and typically also other mechanisms, including heating, exposure to solvents, etc.). One typical approach to induce such kinetically-trapped metastable states is the introduction of relatively bulky and flexible substituents. For instance, in the case of an MCL liquid crystal **16**,[67] the dumbbell-shaped molecules firstly form a kinetically-trapped cubic phase on cooling from the isotropic states. In the cubic phase, amide groups of **16** form disordered hydrogen bonds (Figure 2d). Mechanical shearing induces transformation from the metastable cubic phase to a thermodynamically stable columnar phase. The phase transition induces a change in the arrangement of the pyrene moieties, leading to interference with excimer formation. As a result, the photoluminescence color change from yellow to blue-green. Some arenedicarboxamides without such bulky dendrons have been reported to form one-dimensional columnar structures in which the amide groups form linear hydrogen bonds in the crystals.[87] Therefore, the dendrons introduced to the luminescence core play a significant role to induce the metastable cubic phase. Hydrophobic dendrons are introduced to develop several MCL liquid crystals[67-70, 88], one of which exhibits a tri-colored change,[88] while some water-soluble MRL materials have been obtained by using hydrophilic dendrons.[89-91]

AIE-active molecular structures are also useful moieties to induce MRL properties. Most of the known AIE-active molecules have several aromatic rings that are introduced to π-conjugated groups through C-C single bonds. The aromatic rings freely rotate around the C-C single bond, leading to non-radiative deactivation in solution.[38] Therefore, inherently, crystals consist of AIE-active molecules often have void and have potential to be transformed to more closed packed molecular assembled structures by mechanical stimulation.

4. Luminescent Molecular Dominos

To achieve a complete change of the photoluminescence properties over an entire sample or object made from a crystalline or LC MRL material, upon mechanical stimulation such as grinding, pressing, shearing or rubbing, the mechanical stimulus must normally be applied over the entire materials, as a locally applied change remains confined and the resulting optical change does not spread to the other parts of the material. Recently, however, Ito *et al.* succeeded in changing the photoluminescence properties of molecular materials by remote mechanical stimulation using a simple gold complex.[92] Gold complex **26** (**Figure 3a**) has a more simplified molecular structure than the gold complex **10** reported by the same group in 2008.[46] One crystalline form (I_b) of **26** was obtained through rapid crystallization from a mixture of hexane and dichloromethane, while the other crystalline polymorph (II_y) was prepared by slow crystallization from the same solvent mixture. Polymorphs I_b and II_y exhibit blue and yellow photoluminescence under UV irradiation, respectively. The difference in photoluminescence color between the two crystalline states is ascribed to aurophilic interactions[83] that occur when one gold atom is located in the proximity (distance < 3.5 Å) to another gold atom. Aurophilic interactions cause a red shift of the emission band. In the crystal structure of I_b, only longer distances (> 4.65 Å) between gold atoms were observed (Figure 3b). By contrast, in II_y, the distance between adjacent gold atoms is much shorter (3.177 Å) and indeed short enough to support aurophilic interactions, leading to yellow photoluminescence (Figure 3c). Mechanical grinding of crystals I_b was found to change the photoluminescence color from blue to yellow. The photoluminescence spectrum and X-ray diffraction pattern of the ground sample are identical to those obtained from crystal II_y, indicating that the transition from crystal I_b to crystal II_y was achieved by mechanical stimulation. After confirming that the gold complex **26** shows “conventional” MRL behavior, the authors examined the mechanoresponsiveness of the complex by applying a much smaller mechanical force in a localized manner (Figure 3d). When a small pit was made on the surface of single crystal of I_b using a thin needle, a tiny spot showing yellow photoluminescence appeared on the surface of the crystal, indicating that mechanically induced transformation from I_b to II_y occurred at the position of mechanical stimulation. However, the yellow-emitting area was observed to gradually spread over the entire single crystal within several hours. This effect was shown to be caused by a single-crystal to single-crystal (SCSC) transformation that was accompanied by change of the photoluminescence color. The transition from I_b to II_y was confirmed by examining the photophysical properties and XRD results obtained from the yellow-emitting, converted crystal. The author also found that the same SCSC transformation is achieved by contacting a seed crystal II_y to other crystals in I_b polymorph (Figure 3e).

The same group also reported another gold complex **27** that shows both picking- and seeding-induced SCSC transformations.[93] Compound **27** has a molecular structure similar to **26** (Figure 3f). However, this compound exhibits a mechanically induced blue shift of the photoluminescence spectrum, though compound **26** shows a red-shift responding to mechanical stimuli. In the initial metastable crystals (Figure 3g), aurophilic interactions occur between gold atoms to afford green photoluminescence. The SCSC transformation gradually occurs from a cracked part as shown in Figure 3f, which is associated with a change of the photophysical properties. A single-crystal X-ray analysis for the resulting crystal showing faint blue photoluminescence reveals that compound **27** forms multiple CH-π interactions between the introduced methyl groups and the aromatic rings of adjacent molecules and no aurophilic interactions exist after the SCSC transformation (Figure 3h). The authors concluded that the introduction of the methyl groups stabilized structures which display no aurophilic interactions and, consequently, the emission band shows a blue shift upon transformation from the green emissive, metastable crystals. In the case of **26**, crystal II_y exhibiting aurophilic interactions is thermodynamically more stable than crystal I_b in which aurophilic interactions are absent.

5. Mechanically Induced On-Off Switching

Several organic or organometallic compounds have been found to show on-off switching of the photoluminescence upon mechanical stimulation, although most reported MRL materials show changes in luminescent colors. The first example of organic MRL materials exhibiting on-off switching of emission was reported in 1993 by Gavinecki *et al.*.[19] 4-*Tert*-butyl-1-(4'-dimethylaminobenzylideneamino) pyridinium perchlorate shows yellow-green fluorescence and the fluorescence is quenched upon mechanical shearing. However, the detailed mechanism of the observed switching was not described in the original report. As for metal complexes, Fackler Jr. *et al.* reported a gold (I) complex that exhibits luminescent on-off switching upon mechanical stimulation.[43] A single crystal of $[(TPA)_2Au][Au(CN)_2]$ shows no luminescence, while the ground powder exhibits strong green emission at room temperature. The authors suggested that the mechanism for increased luminescent intensity after grinding involves a change of the molecular packed structures in the surface defects of the crystals. However, there were no examples whose relationships between on-off switching behavior and alteration in molecular assembled structures upon mechanical stimulation were unambiguously clarified until the early 2000's.

In 2005, Mutai and Araki *et al.* reported a clear change in the molecular architecture accompanied by switching of photoluminescence intensity by thermal treatment, although it was not an MRL material.[14] The authors found that 2,2':6',2''-terpyridine (TPY) forms two polymorphs depending on the cooling conditions to which hexane solutions were subjected. Fast cooling resulted in the formation of non-luminescent needle crystals, whereas slow cooling afforded blue emissive plate crystals. The emission quantum yield of the needle crystals was found to be smaller than 0.01, whereas that of the blue emissive plate crystals was 0.2. Heating treatment of the needle crystals at 89.5 °C for 10 min caused the transition to the plate crystals, while no melting was involved. The X-ray crystallography reveals that the crystal structures of the two forms are completely different from each other. The authors suggested that the difference in dihedral angles between the pyridine rings in the crystals affects the luminescent properties of TPY. This study indicates that controlling molecular architecture by an external stimulus can be a promising way to achieve on-off switching in photoluminescence. After this report, several thermoresponsive luminescent materials have been prepared and the relationship between the assembled structures and the luminescent properties was investigated.[16]

5.1. On-Off Switching Single Component Materials

In 2009, Park *et al.* reported that the mechanoresponsive cyano-substituted stilbene derivatives **28** and **29** show luminescence turn-on by smearing or photo irradiation (**Figure 4a**).[94] Both molecules form antiparallel π-dimer stacks that show no photoluminescence in the crystalline states. Directly applied mechanical force (external mechanical stimuli) causes the displacement of molecules that form the π-dimer stacked structures, resulting in a blue photoluminescence. Upon UV irradiation, topochemical [2 + 2] cycloaddition reaction occurs between the central double bonds of two adjacent molecules forming the π-dimer stacks. The resultant σ-dimers, which are bulkier than the initial π-dimers, induce stress and pressure in the crystals. Consequently, the internal mechanical forces lead to the displacement of molecules of the surrounding π-dimers. Upon prolonged UV irradiation, most of π-dimers are converted to σ-dimers and a small amount of the remaining monomers exhibits the blue photoluminescence because monomers are not surrounded by π-dimers that function as energy transfer acceptors. The blue emission is turned off by heating to its melting point of 240 °C.

In 2012, Park *et al.* demonstrated on-off luminescent switching using the donor-acceptor-donor triad **30**.[95] The cyano-stilbene derivative **30** has two carbazole moieties that are connected to the cyano-stilbene core via alkyl spacers (Figure 4b). The pristine powder of **30**, obtained by adding methanol to a dichloromethane solution, is an ordered crystalline material that shows no photoluminescence. A red emissive amorphous phase is induced by applying a mechanical force to the pristine powder. The luminescence intensity increases about 10^3 times upon mechanical stimulation. The conversion from the metastable amorphous phase back to the stable crystalline phase can be induced by heating to 120 °C and, concomitantly, the red luminescence is turned off. In addition to thermal erasing, exposure to THF vapor also erases the red photoluminescence. In the pristine powder, **30** forms an intramolecularly stacked assembly, where the luminescent core is sandwiched between two carbazole moieties. Because of this molecular arrangement, the emissive cyano-stilbene core forms a charge transfer complex with the adjacent carbazole groups after excitation of the core. The instant formation of the charge transfer complex significantly reduces the number of locally excited emissive species, leading to effective quenching. The intramolecularly stacked conformation is supported by the fact that compound **31** having a shorter linker than **30** shows no effective quenching due to conformational limitations to form the intramolecularly stacked structure. In ground samples of **30**, the ordered structures formed in the crystalline phases are disturbed by mechanical stimuli and the rate of electron transfer becomes small, resulting in the relatively strong red luminescence.

Recently, the same group has reported a mechano- and acid-chromic luminescent molecule **32** (Figure 4c).[96] The donor-acceptor-donor triad **32** has a molecular structure that is similar to the one of **30**. The carbazole groups of **30** are replaced with harmane moieties, which were selected because of their responsiveness to acids. Compound **32** exhibits no emission in the pristine solid state, while exposure to a dilute aqueous HCl solution or mechanical stimulation results in red emission. The acid treatment-induced red emission was turned off by subsequent neutralization. Protonation of the harmane groups stabilizes the HOMO of the harmane moieties and the HOMO becomes lower in energy than that of the emission core of **32**, leading to blocking the photo-induced electron transfer that causes the effective quenching. The authors also demonstrated that thin films of a mixture of **32** and a photo acid generator can serve as a force- and light-sensing luminescent material. After the report on **32**, another research group achieved photoluminescence on-off switching using cyano-substituted stilbene derivatives. Chang *et al.* have developed C_3-symmetric molecules having *p*-bromophenyl moieties.[97] The authors found that compound **33** having cyano substituents at the α-position to the central phenyl moiety exhibits on-off switching in photoluminescence upon mechanical stimuli (Figure 4d). By contrast, compound **34**, a constitutional isomer, shows normal mechanochromic luminescence. The exposure to organic vapor recovers the initial emission from each shear-induced state.

On-off switching of the photoluminescence can also be achieved using AIE-active compounds. Tang *et al.* reported on-off switching in photoluminescence exhibited by diphenyldibenzofulvene derivatives **35** and **36** (Figure 4e), although very weak photoluminescence was observed in the “off” states.[98] Compound **35** shows no photoluminescence in good solvents, while intense emission was observed upon increasing the water fraction in the solvent, which is the typical behavior of AIE-active molecules. The amorphous solid of **35** prepared by rapid cooling from the melt also shows very week orange emission (Φ < 0.01). On the other hand, **35** in the crystalline phases shows green or yellow emission depending on the sample preparation condition. The green emissive crystals change into non-luminescent amorphous upon mechanical shearing. The decrease in emission intensity is ascribed to disturbing the ordered structures and formation of excimers. Thermal annealing at 120 °C recovers the green photoluminescence again. DSC studies revealed that the amorphous phase is thermodynamically metastable and phase transition from the amorphous phase to the green emissive crystalline phase occurs without melting, which is consistent with the thermal treatment for the ground sample. It is noteworthy that the emission of **35** recovers spontaneously even at room temperature after mechanical grinding. Compound **36** also shows the mechanoresponsive on-off switching in photoluminescence. The stability of the amorphous phase induced by mechanical shearing is higher than that of **35**.

Several other MRL materials showing on-off switching of photoluminescence have been reported. Zhang *et al.* investigated arylamine derivatives showing the turn-on behavior in response to mechanical stimuli.[99] These compounds are little luminescent in the initial crystalline powder. The mechanical treatment induces a change of the molecular packing and/or the conformation of individual molecules, leading to appearance of strong emission. Zhang *et al.* reported four organoboron compounds exhibiting on-off switching of the photoluminescence in the near-infrared region.[100] Yin and Liu *et al.* prepared gold complexes showing turn-on behavior upon mechanical grinding.[101] Chujo *et al.* reported that an *o*-carbolane-based material exhibits reversible thermo-, vapo-, and mechanoresponsive photoluminescent properties including on-off switching.[102] Furthermore, a metal-organic-framework with a Borromean topology has been reported to show an increased photoluminescence intensity in response to mechanical stimulation.[103] While single crystals of the material show no luminescence, a purplish blue emission is induced upon mechanical grinding. After the ground powder is recrystallized from hot water, the material returns to the initial non-emissive state.

5.2. On-Off Switching Multi Component Materials

Song and Pei *et al.* reported that an MRL mixture consisting of a luminophore and a luminescent quencher shows a high on-off contrast ratio in 2011.[104] They used 2,5-di(*E*)-distyrylfuran **37** as the luminophore and maleimide **38** as the quencher (**Figure 5**). When an equimolar mixture of **37** and **38** was prepared, **37** and **38** form metastable complexes, where the electron transfer from **37** to **38** occurs. As a result, the emission of **37** is quenched in the initial state. After applying mechanical force, **37** and **38** form separate aggregates. This is supported by the fact that the XRD pattern obtained from the as-prepared mixture shows no diffraction peaks attributed to pure **37**, while they appear after applying a mechanical stimulus. The mechanically induced state is thermodynamically more favorable than the co-assembled state because of relatively strong tendency for **37** to form aggregates. Due to the phase separation, the electron transfer from **37** to **38** is disturbed and the greenish-blue luminescence of **37** appears after mechanical grinding. Moreover, the recovered luminescence of **37** can be erased again by exposure to solvent vapor and thus new images can be written again. One of the most important points for the observed on-off switching for the mixture is controlling the stability of the metastable complexes consisting of **37** and **38**. When compound **39** having no alkyl chain is used instead of **38**, the luminescent of **37** is not quenched in as-prepared mixture and no mechano-responsive luminescent property was observed. In this case, compounds **37** and **39** do not form co-assembled complexes in the mixture due to the strong packing nature of **39**. Therefore, the efficient electron transfer does not occur.

6. Multi-Color Photoluminescence Change in Response to Mechanical Stimulation

6.1. Multi-Color Change with a Single Luminophore

One attractive feature of the approach to harness mechanically induced changes of molecular assemblies is the huge potential to create stimuli-responsive materials that exhibit multi-colored photoluminescence. As the photophysical properties of molecular materials depend on the molecular assemblies, the induction of the third molecular arrangement would result in development of MRL materials that exhibit three distinct photoluminescence colors, which are converted to each other by combination of mechanical and other external stimuli. However, most of MRL materials form only two molecular assemblies and, consequently, show only two different luminescence colors. Recently, several research groups have succeeded in preparing MRL materials that exhibit multi luminescence colors based on the concept described above.

The combination of hydrostatic pressure and normal mechanical grinding also leads to the multi-color change in photoluminescence. Gradual changes in photoluminescence color are achieved by applying relatively large pressure to molecular materials. Because the initial photophysical properties recover after releasing the applied pressure (of the order of several GPa), the mechano-sensing phenomenon using hydrostatic pressure is completely different from that observed for typical MCL materials, whose emission colors changed by mechanical stimuli usually remain after mechanical stimulation. However, in this section, MCL materials that show such a temporal color change induced by hydrostatic pressure are also introduced as an emerging subset of MCL materials.

6.1.1. Organic Molecules

The first MCL liquid crystal that shows a multi-color change was reported by Sagara and Kato,[88] who demonstrated that an equimolar mixture of dumbbell-shaped molecule **40** and molecule **41** (**Figure 6a**) exhibits three different photoluminescence colors under ambient conditions, although the LC mixture contains only one fluorophore, 9,10-bis(phenylethynyl)anthracene. The phase transition and color change behavior are depicted in Figure 6a. The LC mixture exhibits a thermotropic micellar cubic phase showing reddish-orange photoluminescence. Mechanical shearing the mixture in the cubic phase at 90 °C induces a phase transition to a columnar phase, which is accompanied by a photoluminescence color change from reddish-orange to green. The green photoluminescence is retained upon cooling to room temperature. On the other hand, the mixture in the cubic or the columnar phase shows a phase transition to an unidentified mesomorphic phase that exhibits yellow photoluminescence when mechanical shearing is applied to the mixture at room temperature. The cubic phase recovers after heating the mixture in the columnar or mesomorphic phase to the isotropic phase and subsequent cooling. The authors concluded that large changes in molecular assembled structures upon mechanically induced phase transitions caused the change in the emission color (Figure 6a). The reddish-orange and yellow photoluminescence are attributed to excimers and partial-overlap excimers of the emission cores, respectively.

Tang *et al.* reported that tetraphenylethylene derivatives **42-44** (Figure 6b) also show multi-color changes upon mechanical treatment or heating.[105] Here, **43** is highlighted as a typical case to explain the mechano-sensing behavior of these compounds. The AIE-active **43** forms deep-blue emissive crystals (**43CA**) after slow evaporation of the solvent. Upon heating, **43CA** shows a phase transition to another crystalline state (**43CB**) showing sky-blue photoluminescence. When mechanical grinding is applied to **43CA** or **43CB**, the photoluminescence colors of both **43CA** and **43CB** turn to green (Figure 6b), which is ascribed to the amorphous state of **43**. The deep-blue (**43CA**) or sky-blue (**43CB**) photoluminescence can be recovered through annealing the ground powder at 90 °C or 115 °C, respectively. The three emission colors of **43** are attributed to the difference in conformation of individual molecule in each state.

Yagai *et al.* prepared the amphiphilic oligo(*p*-phenylenevinylene) derivative **45** (Figure 6c) that also shows a multi-color change by way of controlling the nature of the molecular assemblies *via* external stimuli.[86] The MRL properties were induced by competing effects of intermolecular interactions, the dipole repulsion force and the strong tendency to form phase segregated morphologies. After drop casting, **45** forms tilted, bilayer assembled structures (Figure 6c) where the luminescent cores stack face to face because of phase segregation of the incompatible hydrophobic groups and hydrophilic groups (**45Y**). The imperfect H-type aggregation allows the materials to show a radiative decay from the lower exciton state, leading to yellow photoluminescence. After pressing, the yellow-emitting **45Y** is converted into an LC state that exhibits orange emission (**45O**). In the LC phase, repulsion force between the dipole moments is considerably dissolved. No strong exciton coupling occurs in the LC phase and the molecules adopt twisted structures in the π-conjugated groups. The observed orange emission arises from the intramolecular charge transfer states due to the twisted nature. When **45O** is rubbed, a crystalline state appears (**45G$^{\#}$**) and the photoluminescence color turns to green. Subsequent thermal annealing at 50 °C generates a more crystalline form exhibiting bluish-green photoluminescence (**45G**) (Figure 6c). A seeding-triggered phase transition from **45O** to **45G$^{\#}$** was also demonstrated. Moreover, the authors showed one application as invisible inkjet printing utilizing both the seeding-triggered phase transition and phase stabilization by addition of lithium salt.

3,4-Bisthienylmaleimide **46** shows distinct responses to mechanical grinding and crushing.[106] Crystals showing orange photoluminescence (**46OC**) were obtained by recrystallization from the THF/ethanol solution. Upon being crushed with compressive stress in one direction, **46OC** is converted to a yellow emissive solid (**46YC**) (Figure 6d). Moreover, **46OC** and **46YC** are transformed into an amorphous state exhibiting weak red-shifted emission through continuous mechanical grinding process. Single-crystal X-ray diffraction studies reveal that **46YC** and **46OC** have the same crystal structure. The authors concluded that the different photophysical properties of **46OC** and **46YC** can be ascribed to the difference in particle sizes and the damaged surface structures induced by crushing.

The MCL anthracene derivative **47** (Figure 6e) was reported to show a gradual change in photoluminescence color upon applying hydrostatic pressure.[107] The anthracene derivative exhibits a strong green photoluminescence in the as-prepared powder state. After simple grinding, the photoluminescence color of the powder turns to yellow. The initial green photoluminescence recovers after heating the ground sample above 160 °C. The influence of applied hydrostatic pressure on the photoluminescence was also investigated. As the applied pressure increases, the photoluminescence color of the powder gradually changes from green (at 0 GPa) to red (at 7.92 GPa). The authors attributed the observed change in photoluminescence to transformation of the molecular assembled structures from J-type aggregation (no π-π interaction, green) to H-type aggregation (weak π-π interaction, orange) and then to aggregated dimers (strong π-π interaction, red) (Figure 6e).

Hydrostatic pressure-induced changes of the photoluminescence color were also observed for an intramolecular charge-transfer (ICT) fluorophore **48** (Figure 6f).[108] The crystals of **48** obtained through recrystallization from chloroform/ethanol solution show green photoluminescence (G-form). Upon grinding with a spatula the photoluminescence color changes from green (G-form) to red (R-form). In the hydrostatic pressure experiment, the photoluminescence color also shows a significant red sift from green to red as the pressure increases and subsequent releasing pressure recovers the initial green photoluminescence (Figure 6f). It has been suggested that the twist conformation of the cyanostilbene moiety and the T-type packing prevent tight packing in the G-form, resulting in green photoluminescence from the locally excited state, while the red photoluminescence observed for R-form is ascribed to the charge transfer state. A cruciform conjugated fluorophore with ICT character has been also reported to show luminescence color changes from yellowish green to orange upon simple grinding or applying relatively low hydrostatic pressure (10 MPa).[109]

Saito and Yamaguchi *et al.* have demonstrated an influence of the way to apply mechanical force to molecular materials on resulting changes in photoluminescence colors.[110] A tetrathiazolylthiophene derivative **49** (Figure 6g) shows distinct responses to mechanical grinding and hydrostatic pressure. Compound **49** exhibits a yellow emission in the crystalline state, and the photoluminescence color changes to green after mechanical grinding (Figure 6g). The results obtained from X-ray diffraction analysis, as well as solid-state ^{1}H-NMR and infrared spectroscopic measurements indicate that mechanical grinding induces a transformation from the crystalline state where compound forms face-to-face dimeric structures to a disordered state, leading to the interference with the excimer formation. By contrast, the photoluminescence color gradually changes from yellow to orange upon applying hydrostatic pressure up to 3.2 GPa (Figure 6g). The initial yellow photoluminescence is restored when the pressure is reduced to ambient pressure. The high-pressure single-crystal XRD analysis revealed that the distance between adjacent molecules in the face-to-face dimer becomes shorter under high pressure, resulting in the red-shifted photoluminescence.

6.1.2. Organometallic Compounds

Several organometallic compounds have been also found to display multi-color photoluminescence changes in response to mechanical stimulation. In 2011, Shinozaki *et al.* reported a platinum(II) complex **50** (**Figure 7a**) shows mechanochromic luminescence involving several distinct photoluminescence colors.[111] The Pt(II) complex **50** shows polymorphism and three different crystalline forms (Form Y, Form R and Form G) are prepared selectively. Form Y, Form R and Form G emit photoluminescence in yellow, red and near-infrared regions, respectively. X-ray crystallography revealed that no Pt-Pt bonds exist in Form Y. By contrast, Pt-Pt bonds form between adjacent two molecules in Form R and linear Pt chains were observed in Form G. Such difference in molecular architecture of **50** significantly influences the photophysical properties. Upon being ground, all polymorphs show phase transitions to an amorphous phase that shows dark red photoluminescence. Form R is restored when the ground sample is heated. Because heating process induces irreversible crystal-crystal phase transitions from Form G through Form R to Form Y, the Form R-Form Y-amorphous phase transition cycle is achieved by a combination of heating and grinding (Figure 7a).

The pincer platinum(II) complex **51** (Figure 7b) with amide groups also shows a multi-color change induced by mechanical stimulation.[112] Green emissive crystals are obtained by recrystallization from DMF (**51**·DMF). Upon grinding in a ceramic mortar, the compound shows a conversion to an amorphous morphology, which is accompanied by a change of the photoluminescence color from green to orange (**51**·Powder). Furthermore, subsequent exposure to methanol vapors leads to the formation of a crystalline state that shows yellow emission (**51**·MeOH). The orange photoluminescence of **51**·Powder can be restored by mechanically grinding **51**·MeOH. Single-crystal X-ray diffraction studies indicate that the hydrogen-bonding networks that the amide groups form in **51**·DMF and **51**·MeOH are different from each other, leading to an evident difference in the Pt-Pt distance. The Pt-Pt distance observed in **51**·MeOH is 3.385 Å, which is much shorter than that in **51**·DMF (4.854 Å), resulting in the excimer photoluminescence observed for **51**·MeOH due to the metal-metal interactions. The authors also attributed the orange photoluminescence of **51**·Powder to metal-metal interactions. Interestingly, **51**·DMF or **51**·MeOH is also converted to **51**·Powder by heating. Thermogravimetric analysis for **51**·DMF reveals that release of DMF molecules from the crystals upon heating causes the same color changes as grinding.

Recently, Seki and Ito *et al.* have reported that a gold(I) isocyanide complex **52** (Figure 7c) forms four individual solid states with different photoluminescence colors, which are interconvertible by treatment with acetone and mechanical shearing (Figure 7c).[113] The relatively high polarity of **52** may help the formation of weak interactions with acetone and enable solvent inclusion/release processes. The as-prepared crystalline powder (**52Y**) shows yellow photoluminescence due to aurophilic interactions. After being soaked in acetone, **52Y** turns into a blue emissive powder (**52B**). The single crystal X-ray diffraction analysis of **52B** reveals that the gold(I) complex forms layer-like structures with acetone sublayers, where the Au-Au distance of 3.545 Å is longer than necessary to form aurophilic interactions, resulting in blue photoluminescence. After the subsequent drying process, **52B** transforms to a polymorph that exhibits green photoluminescence (**52G**). As for **52G**, no aurophilic interactions occur and a much lower amount of acetone molecules resides in the crystalline structure compared to **52B**. Increased intermolecular interactions and/or rather flat conformations of the chromophores are attributed to the green photoluminescence. Gentle mechanical grinding applied to **52G** induces release of acetone molecules to afford **52Y** and subsequent hard grinding leads to further transformation to **52O** that exhibits orange photoluminescence. The aurophilic interactions with shorter Au-Au separation are present in **52O**, although the amorphous nature of **52O** does not provide unambiguous information about the nature of the molecular assembly.

6.2. Multi-Color Changes with Two Luminophores

Especially in the context of multi-color changes, MRL systems containing two luminophores represent an interesting alternative to one-component materials, as the larger number of different electronic states from which emission may occur also increases the changes to tune the emission wavelength to the related (meta)stable states. Based on this general concept, several precisely designed MRL materials having two luminophores have recently been developed.

Jia *et al.* reported that a mixture of two dipeptide derivatives **53** and **54** (**Figure 8a**) exhibits a multi-color change in 2012.[114] Compounds **53** and **54** feature a pyrene group and a rhodamine B moiety, respectively. In the crystalline form, compound **53** exhibits blue emission due to partial-overlap excimers of the pyrene groups. By contrast, green luminescence was observed for a mechanically induced amorphous phase. The formation of normal excimers of the pyrene upon mechanical shearing results in the emission color change from blue to green. Compound **54** displays red emission derived from the rhodamine B moieties attached to the dipeptide. The luminescent intensity of **54** is relatively low in a powder state and its red luminescence is intensified by mechanical stimuli, because most of the lactam forms of rhodamine B are converted to more conjugate ring-opening isomers by mechanical stimuli. The initial lactam form recovers through thermal treatment. Blue photoluminescence was observed from the as-prepared mixture obtained by evaporating the cyclohexane suspension of **53** and **54** at 100 °C. After applying mechanical stimuli, the blue photoluminescence changes into green and further shearing induces the change in photoluminescence color from green to red (Figure 8a). The authors concluded that the emission change from blue to green was driven by the morphological change of **53** and the change in photoluminescence from green to red are ascribed to the ring-opening of the lactam forms which enhances the red emission of **54** itself. The initial state showing blue emission recovers by heating both the green and red emissive states induced by mechanical shearing.

The mixture of **53** and **54** shows a multi-color change due to individual MRL properties of the two components. In 2013, Jia *et al.* reported that molecule **55** featuring both pyrene and rhodamine B moieties (Figure 8b) exhibits a multi-color change in photoluminescence.[115] As a powder prepared by evaporation of the dichloromethane solution, **55** shows a blue emission. Slight grinding induces a green emission and further grinding results in a red emission with a new emission peak at 583 nm in the emission spectrum. Emission lifetime measurements reveal that the blue and green emissions are due to partial-overlap excimers and normal excimers of the pyrene moieties, respectively. The appearance of red photoluminescence is based on the ring-opening reaction of the rhodamine B moiety of **55** as observed for dipeptide derivative **54** described above. The blue emission also recovers by heating the red emissive powder at 120 °C for several minutes followed by exposure to dichloromethane vapor.

Although the molecular materials reported by Jia's group show multi-color changes in luminescence exploiting two luminophores, the blue or green emissions still remain present in the heavily ground samples showing red photoluminescence, suggesting that FRET processes between energy donating and accepting groups are absent or inefficient. As a result, the contrast is not very high. Adequate changes of the arrangement of a FRET pair lead to significant changes of the emission spectrum based on changes in the efficiency of the FRET process.[32] Very recently, Park *et al.* reported a high-contrast, red-green-blue (RGB) tricolored change of photoluminescence using a mixture composed of two molecules (Figure 8c).[116] The first component is the cyano-substituted oligo(*p*-phenylenevinylene) derivative **8**[39a] as shown in Figure 1. Compound **8** shows blue luminescence after thermal annealing and green emission after mechanical shearing or solvent vapor annealing with dichloromethane. The second component is compound **30**,[95] introduced in Section 5.1. As described above, the red emission of **30** appears upon mechanical shearing. A spin-coated **8/30** mixture (10:3 w/w) shows blue photoluminescence after thermal annealing at 140 °C for 3 min (λ_{em}= 458 nm) and green emission after solvent vapor annealing (λ_{em}= 527 nm). Both blue and green emissive states change into a red emissive state (λ_{em}= 594 nm) after mechanical shearing and the red luminescence returns to the blue and green emissions upon thermal or solvent vapor annealing, respectively. The FRET from **8** to **30** plays a significant role for the observed phenomena (Figure 8c, top). When energy donor **8** forms assembled structures with dimensions that are larger than the distance at which the FRET occurs efficiently, the photoluminescence from **8** is observed, because the FRET process is suppressed. Consequently, as energy acceptor **30** is in the non-luminescent state before grinding, the as-prepared, phase segregated mixture shows blue or green emission. However, upon grinding the two compounds appear to be molecularly mixed and FRET occurs from **8** to **30**. Therefore, the blue or green emission of **8** is effectively quenched. Because the mechanical stimulation simultaneously turns on the red emission of **30** (see Section 5.1), only red emission was observed for the ground samples. When the mixture shows the blue and green emissions, the efficiencies of FRET (η) estimated from the emission lifetime are 0.06 and 0.03, respectively. On the other hand, mechanical grinding induces the effective FRET from **8** to **30** ($\eta = 0.75$), resulting in almost complete quenching of the emission from **8**. The authors showed that it is possible to create high-contrast RGB patterns using this system, as shown in Figure 8c. The center of the thermally annealed sample was exposed to dichloromethane vapor to access blue and green emissive states, respectively. Subsequent mechanical shearing of the sample induced red photoluminescence at the scratched parts, resulting in the vivid RGB photoluminescent patterning.

7. Water-soluble MRL Materials

While the organic or organometallic molecules that form MRL molecular assemblies discussed so far are insoluble in water, because of their hydrophobic character, water-soluble MRL materials would potentially be useful for biocompatible mechano- and humidity-sensing materials. Araki *et al.* examined the photophysical properties of 1,3,6,8-tetra(4′-carboxyphenyl)pyrene in aqueous conditions and the MCL properties in the solid state in 2012.[117] The four carboxylic acid groups enable the pyrene derivative to dissolve in certain aqueous media, such as water at high pH, a mixture of DMF and water (1:1), as well as methanol and ethanol. Yellow emission, which is characteristic of the dimer form, was observed for the solid state. Upon mechanical stimulation of the compound in the solid state, the emission color turns green, indicative of monomer emission. The authors also reported that exposure of the ground sample to methanol, ethanol, acetone, ethyl acetate, tetrahydrofuran, and dioxane vapor leads to recovery of the initial yellow emission.

It is well known that amphiphilic compounds having a rigid hydrophobic aromatic moiety and flexible hydrophilic chains form a variety of molecular assemblies such as spherical micelles, cylindrical micelles, vesicles and membranes in water.[5-6] The molecular assemblies consisting of amphiphiles were also exploited to develop MCL materials. In 2013, Sagara and Nagano *et al.* demonstrated that pyrene-based amphiphile **56** forms micellar assemblies in water and exhibits mechano- and humidity-sensing characters in the solid state (**Figure 9a**).[89] The dumbbell-shaped amphiphile **56** features two hydrophilic dendrons that are attached to the 1,6-bis(phenylethynyl)pyrene core *via* amide groups. Many micellar structures composed of **56** with diameter between 5 and 10 nm appear in the transmission electron microscope (TEM) images (Figure 9a). The average hydrodynamic diameter of the micelles obtained from dynamic light scattering measurements is approximately 7 nm, which is consistent with diameters of the micellar structures observed in the TEM images. Blue photoluminescence was observed for **56** in methanol under excitation at 365 nm, while **56** exhibits yellow photoluminescence in water, indicative of excimer formation. These results indicate that the emissive cores of **56** form stacked structures in the micelles (Figure 9a). The authors also examined the MCL properties of **56** in the solid state. When **56** was prepared in the form of a cottony solid by simple lyophilization of the aqueous solution, yellow excimer emission was observed. Mechanical stimulation induces a change of the luminescence color from yellow to green (Figure 9a, bottom left). This reflects that the originally assembled excimer-forming structures are changed by mechanical stimulation and the emissive cores are placed in a different arrangement that does not support the formation of excimers. The authors also found that exposure of the ground sample to water vapor leads to recovery of the initial yellow emission. Therefore, amphiphile **56** functions as mechanosensor and humidity sensor. One practical application for water-soluble MCL materials was shown by the same group.[89] Compound **56** was used as a mechano-sensing indicator on friction wear test for grease due to its immiscibility with grease. By contrast, compound **16**, which is one of hydrophobic liquid crystals showing mechanochromic luminescence,[67] is not suitable for such a friction test, because the LC compound easily mixes with grease due to its hydrophobic nature.

While several molecular assemblies consisting of amphiphiles have been reported to change their supramolecular assembly in response to the addition of guest molecules or ions[118] or changes of temperature,[119] redox state,[120] or pH value[121] in water, only a few studies documented alteration of molecular assembled structures with changes in photoluminescence color in water.[90, 91, 122] If an amphiphile having a fluorophore forms supramolecular assemblies in water and this supramolecular architecture is altered in response to mechanical stimulation in water, the photoluminescence properties of the system can be also expected to be responsive to mechanical force. According to this assumption, Sagara and Nagano *et al.* developed the amphiphilic anthracene derivative **57**, which forms supramolecular assemblies in water, which exhibit a photoluminescence color change from yellow to green upon mechanical or thermal stimulation in water.[90] Although amphiphile **56** shows both mechano- and humidity-sensing properties in the solid state,[89] the micelles formed by the self-assembly of **56** did not show any photoluminescence color changes in response to mechanical stimulation or temperature change in water. It appears that the two large hydrophilic dendrons of **56** stabilize the yellow-emissive micellar structures and forbid compound **56** to form two different molecular assembled states in water. Therefore, smaller dendrons were introduced to the emissive core of compound **57**. In water, anthracene derivative **57** forms micellar structures and cylindrical molecular assemblies, which are one-dimensional aggregates of the micelles (Figure 9b, bottom center). In the micellar structures, the anthracene moieties form stacks and thus the hydrophobic parts appear on the surface of the micelles in the direction of the stacks. The formation of one-dimensional cylindrical micelles is ascribed to the weak hydrophobic interaction between the anisotropic micelles. These molecular assemblies exhibit yellow photoluminescence derived from excimers and are shown to readily adsorb on glass substrates bearing amine groups. When the anisotropic micelles were rubbed from the glass substrate, a green emissive solution was obtained (Figure 9b, top center). After mechanical stimulation, amphiphile **57** forms green-emitting micelles where the arrangement of the emissive core is different from that in the initial micellar structures, which leads to a decrease of the hydrophobic surface. Consequently, no cylindrical molecular assemblies appear in the TEM images, because the green-emissive micelles are not able to form one-dimensional aggregates. Thermal stimulation also induces the photoluminescence color change. After annealing the yellow-emissive water solution at 60 °C for 5 min, the emission color becomes green. The green photoluminescence remains after cooling down to room temperature (Figure 9b, top right). After heating, the cylindrical micelles were not observed in the TEM images (Figure 9b, bottom right).

8. Covalent Attachment to Other Materials

Most of the studies on mechanoresponsive luminescence have focused on the relationship between photophysical properties and molecular assembled structures and have examined the influence of mechanical force or other external stimuli on them. The outcomes of these investigations have led to a rather comprehensive understanding of useful mechanisms to design MRL molecular assemblies. Meanwhile, from the viewpoint of practical applications, it is also important to establish possibilities to integrate MRL molecular assemblies with other materials, such as glasses, polymers, metals and biomaterials, to detect mechanical force applied to the materials of interest.

In 2014, Sagara and Nagano *et al.* demonstrated the covalent attachment of MRL micelles to glass and polymer beads. [91] Amphiphilic compound **58** (**Figure 10a**) forms micelles in water and exhibits yellow photoluminescence under UV irradiation (365 nm). The yellow-emitting micelles (Y-micelles) have many amino groups at the peripheral positions. Therefore, using water-soluble linker **59**, Y-micelles can be covalently introduced to other materials with amino groups on the surface as illustrated in Figure 10b. When sufficient mechanical stress is applied to the surface of the materials bearing Y-micelles, Y-micelles transform into green-emitting micelles (G-micelles) in water. The authors described a series of vortex experiments to evaluate the mechanoresponsive properties of the resulting glass beads and polylactic acid (PLA) beads with Y-micelles on the surface. The change in photoluminescence color was observed for the glass beads (Φ = 150–212 μm) bearing the micelles upon vortexing at 2000 rpm for 15 min at room temperature in a glass vial containing the glass beads and water (Figure 10c). These results indicate that transformation from Y-micelles to G-micelles occurs in response to mechanical stimuli derived from collision between the glass beads. Confocal fluorescence microscopic images reveal that G-micelles were not detached from the surfaces of the glass beads due to covalent linkers. Because of the uniform size of Y-micelles (~ 6 nm), there is a threshold of mechanical force to induce transformation from Y-micelles to G-micelles. When the same vortex experiment was conducted for smaller glass beads (Φ < 106 μm) bearing Y-micelles, it required longer time (1 h) to achieve complete color change. Moreover, PLA beads (Φ = 70–150 μm) with Y-micelles on the surface never show any changes in photoluminescence color after vortexing for 1 h under the same condition as the glass beads (Figure 10d). The glass beads are heavier than the PLA beads and the stiffness of the glass beads is much higher than that of PLA beads. Therefore, upon vortexing, mechanical force applied to Y-micelles attached to glass beads is much stronger than that applied to Y-micelles introduced to the PLA beads. It is noteworthy that the PLA beads show the photoluminescence color change when the PLA beads are vortexed with large glass beads (Φ = 425–600 μm) (Figure 10d).

9. Summary and Outlook

The rapidly growing international efforts to develop MRL materials have yielded a large number of organic or organometallic molecules that exhibit mechanoresponsive properties. As is evident from the examples discussed in this contribution, in virtually all materials systems shown here, the mechanically induced changes of the photophysical properties are related to variations of the molecular assembly. Most of the materials developed just switch the photoluminescence color between only two states. However, several compounds show unconventional phenomena such as luminescent molecular dominos, which exhibit an intriguing amplification effect. The appearance or disappearance of photoluminescence and multi-color changes in response to mechanical stimuli expand the usage of MRL materials and permit the production of high-contrast multicolor images, which may be useful for data storage, sophisticated informational displays, and security inks. Water-soluble MRL materials open the door for possible applications in the biomedical domain. Finally, the first example has shown that it is possibly to integrate MRL molecular assemblies with other materials of interest. Some research topics described in this report are at very early stages and one can expect considerable growth of the palette of MRL molecules and effects in the near future. As mentioned in the introduction, mechanically induced "dynamic" property changes driven by changes of the molecular assembly of functional molecules comprising π-conjugated moieties can possibly lead to the control of properties other than their photophysical characteristics. Thus, it appears that the concepts for the design of MRL materials discussed here, may serve as a starting point for other types of mechanoresponsive materials, in which charge carrier transport properties, magnetic properties, and other functions can be changed on command.

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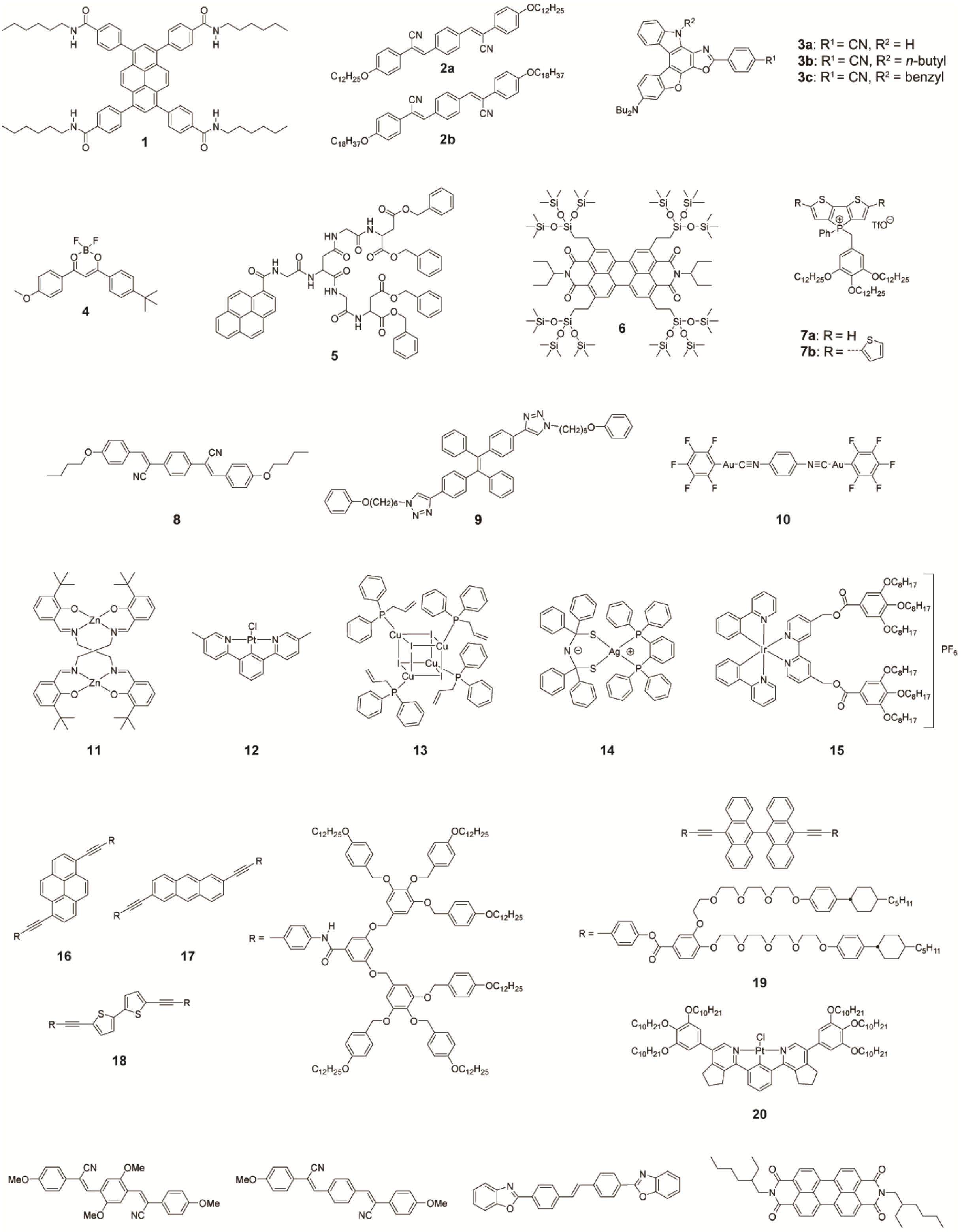

1

2a

2b

3a: R^1 = CN, R^2 = H
3b: R^1 = CN, R^2 = *n*-butyl
3c: R^1 = CN, R^2 = benzyl

4

5

6

7a: R = H
7b: R =

8

9

10

11

12

13

14

15

16

17

18

19

20

21 (in polymer)

22 (in polymer)

23 (in polymer)

24 (in polymer)

Figure 1. Representative molecular structures of MRL compounds.

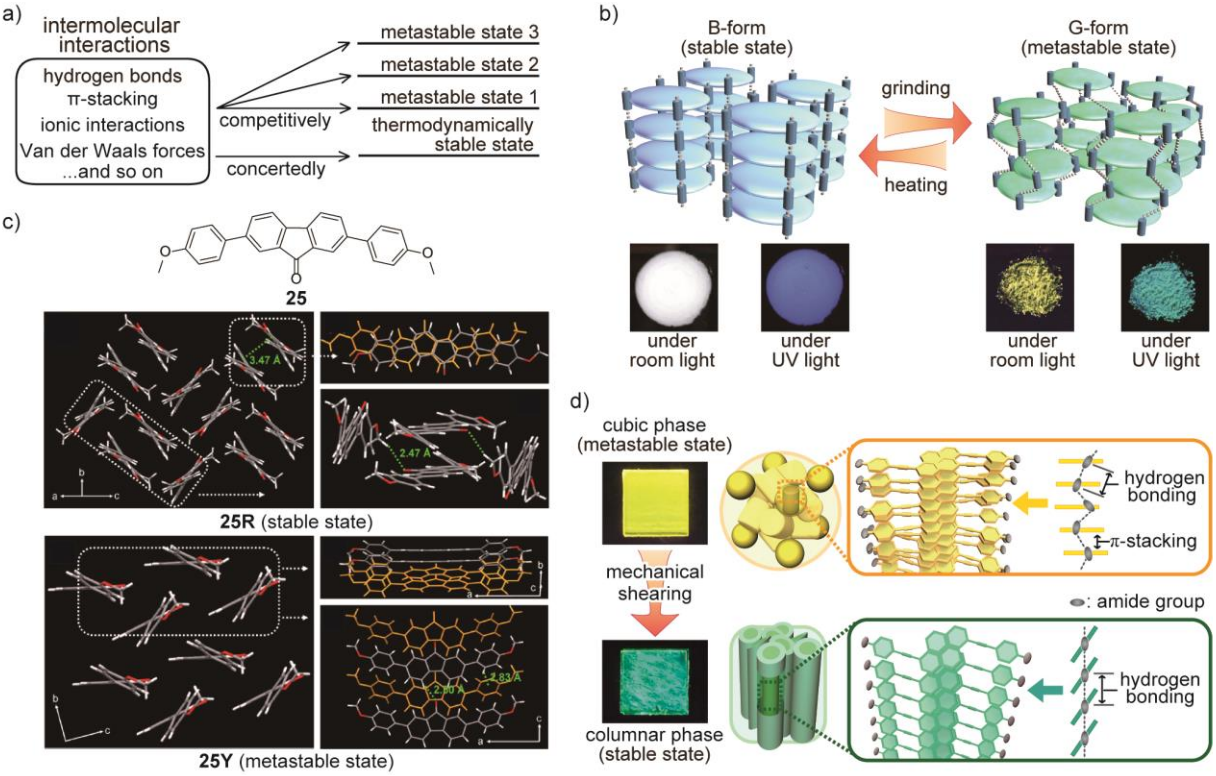


Figure 2. Design approaches for MRL materials. a) Schematic illustration of design approaches to induce metastable states. b) Change in molecular assembled structures and photoluminescence color of compound **1** before and after grinding. c) Molecular structure of compound **25** and X-ray crystallographic packing of **25R** and **25Y**. d) Photoluminescence color change and schematic illustration of molecular assemblies of **16**. Part b is adapted with permission.[1g] Copyright 2009, Nature Publishing Group. Part c is adapted with permission.[85] Copyright 2014, American Chemical Society. Part d is adapted with permission.[67] Copyright 2008, Wiley-VCH.

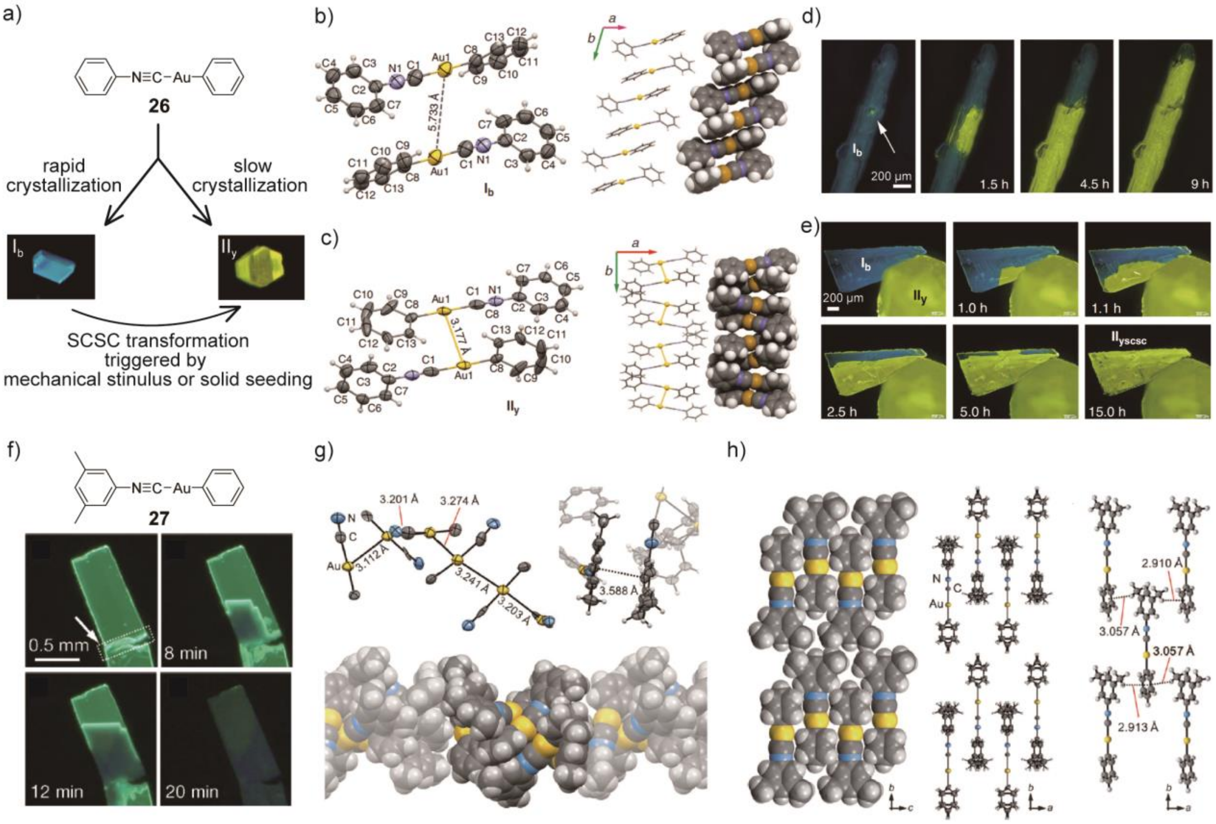


Figure 3. Luminescent molecular dominos. a) Procedure to obtain two different crystals of **26** and scheme of the single-crystal to single-crystal (SCSC) transformation. b,c) Crystal structures of I_b and II_y. d,e) Tiny picking-induced and seeding-triggered SCSC transformations of **26**. f) Molecular structure of **27** and the cracking-induced SCSC transformation of **27**. g,h) Crystal structures of the green emissive crystal and faint blue emissive crystal of **27**. Parts a,b,c,d and e are adapted with permission.[92] Copyright 2013, Nature Publishing Group. Parts f, g and h are adapted with permission.[93] Copyright 2013, Wiley-VCH.

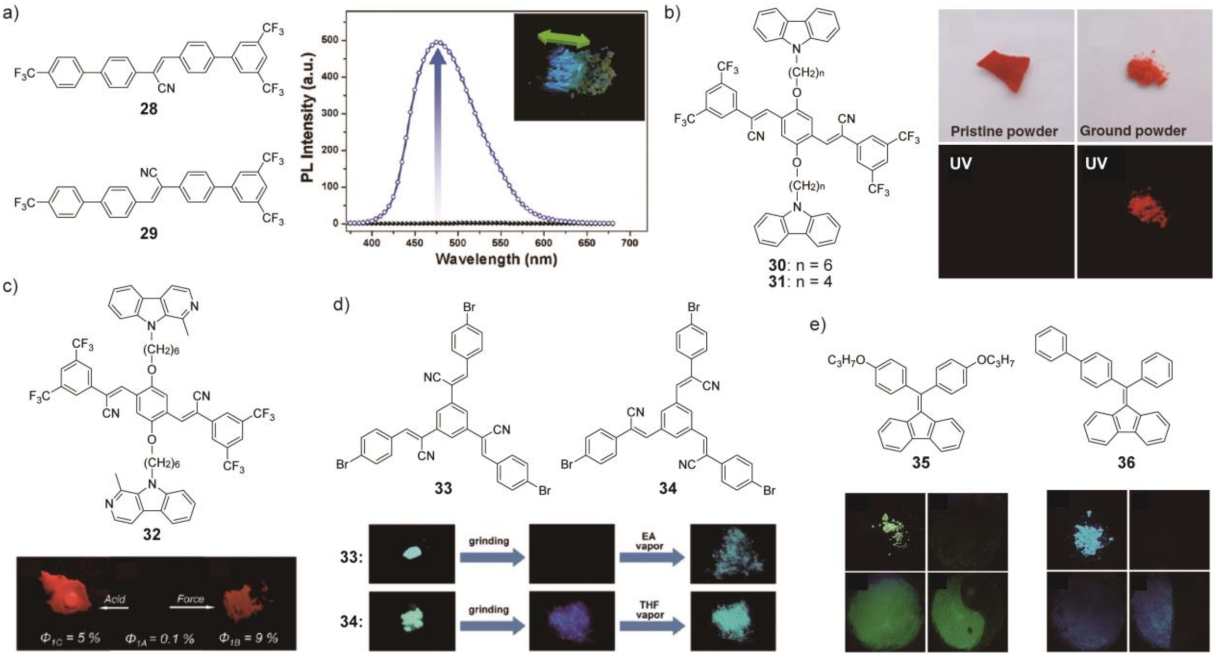


Figure 4. Single-component MRL materials that display mechanically induced on-off switching. a) Molecular structures of compounds **28** and **29** and emission spectra of **28** before and after mechanical grinding. b) Molecular structures of **30** and **31** and photographs of the pristine and ground powders of **30**. c) Molecular structure of **32** and pictures showing mechano- and acid-sensing behavior. d) Molecular structures **33** and **34** and pictures illustrating the mechanoresponsive properties. e) Molecular structures of **35** and **36** and images illustrating their photoluminescence color changes in response to external stimuli. Part a is adapted with permission.[94] Copyright 2009, American Chemical Society. Part b is adapted with permission.[95] Copyright 2012, Wiley-VCH. Part c is adapted with permission.[96] Copyright 2014, The Royal Society of Chemistry. Part d is adapted with permission.[97] Copyright 2014, The Royal Society of Chemistry. Part e is adapted with permission.[98] Copyright 2011, Wiley-VCH.

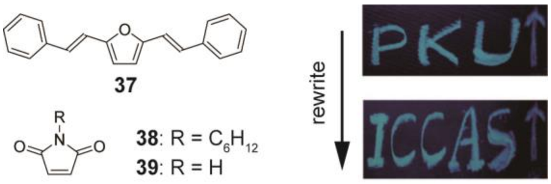


Figure 5. Molecular structures of **37**, **38** and **39** and photographs demonstrating the reversible MRL behavior of the mixture under UV irradiation. Adapted with permission.[104] Copyright 2011, Wiley-VCH.

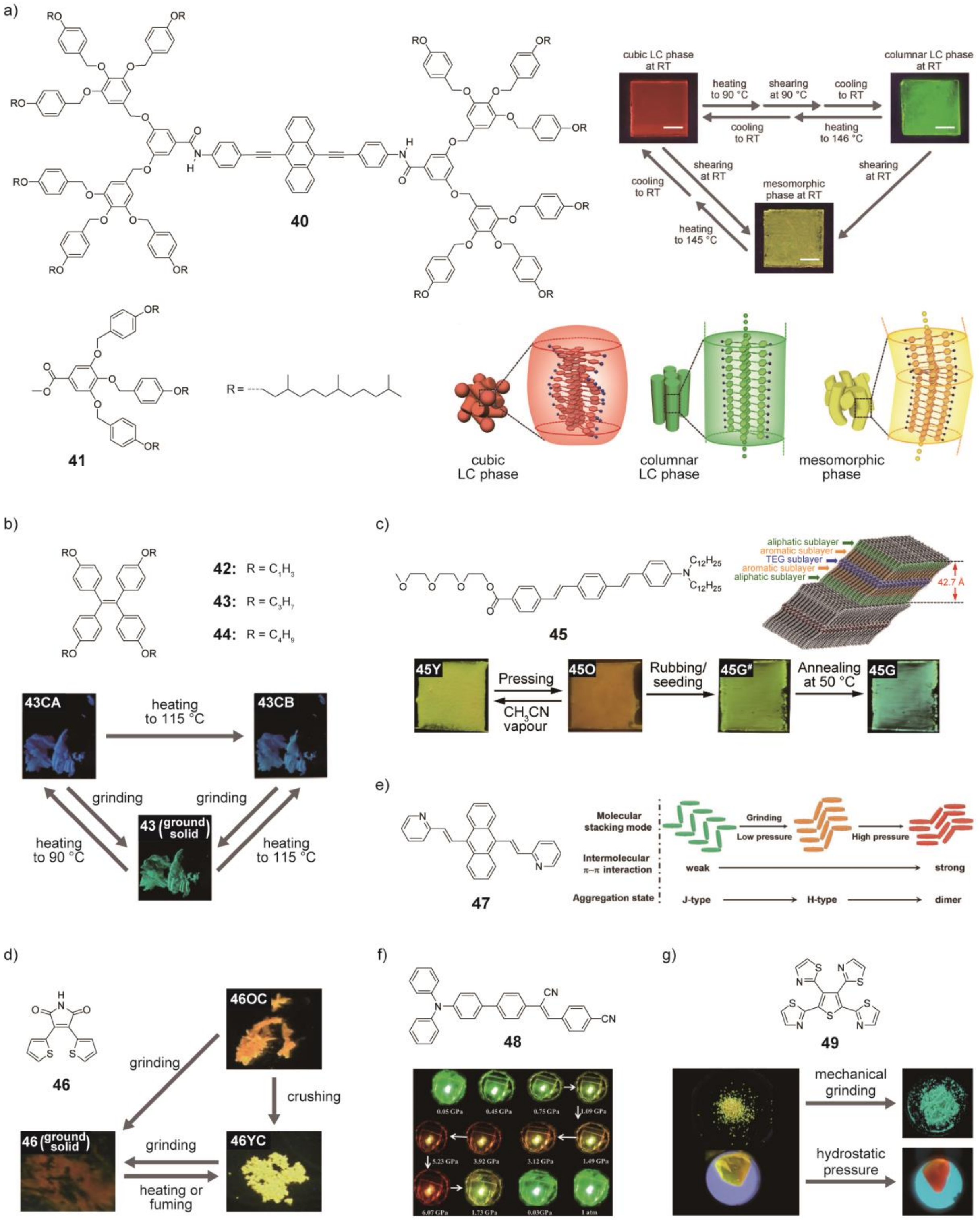


Figure 6. Multi-color MRL materials based on a single component. a) Molecular structures of compounds **40** and **41**, procedures to obtain three different luminescent colors, and schematic illustration of the assembled structures of the LC mixture that from the cubic, columnar and mesomorphic phases. b) Molecular structures of AIE-active compounds **42–44** and pictures illustrating the photoluminescence color changes of **43**. c) Molecular structure of compound **45**, schematic representation of the multilamellar structure of **45Y** and pictures revealing the

photoluminescence color changes induced by external stimuli. d) Molecular structure of compound **46** and pictures showing the photoluminescence color changes. e) Molecular structure of compound **47** and schematic reflecting the relationships between the stacking modes and emission colors. f) Molecular structure of compound **48** and picture illustrating the photoluminescence color changes in response to hydrostatic pressure. g) Molecular structure of compound **49** and pictures documenting the photoluminescence color changes in response to mechanical grinding and hydrostatic pressure. Part a is adapted with permission.[88] Copyright 2011, Wiley-VCH. Part b is adapted with permission.[105a] Copyright, 2012 American Chemical Society. Part c is reproduced with permission.[86] Copyright 2014, Nature Publishing Group. Part d is adapted with permission.[106] Copyright 2014, The Royal Society of Chemistry. Part e is reproduced with permission.[107] Copyright 2012, Wiley-VCH. Part f is reproduced with permission.[108] Copyright 2015, Wiley-VCH. Part g is adapted with permission.[110] Copyright 2013, American Chemical Society.

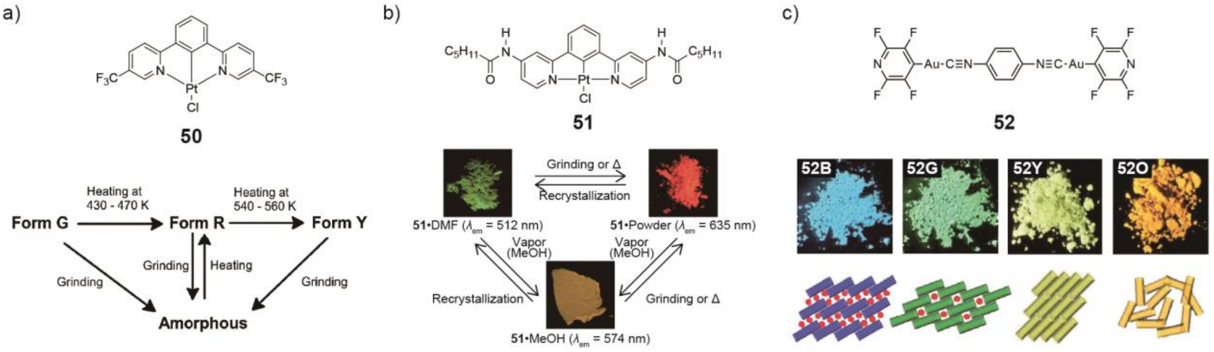


Figure 7. Organometallic multi-color MRL materials. a) Molecular structure of compound **50** and the phase transition diagram for **50**. b) Molecular structure of compound **51** and pictures documenting the photoluminescence color changes in response to external stimuli. c) Molecular structure of compound **52**, photographs of the powder forms of **52** showing different photoluminescence colors and schematic representation of the molecular arrangements of each emitting state. Part a is adapted with permission.[111] Copyright 2011, Wiley-VCH. Part b is adapted with permission.[112] Copyright 2012, The Chemical Society of Japan. Part c is adapted with permission.[113] Copyright 2015, The Royal Society of Chemistry.

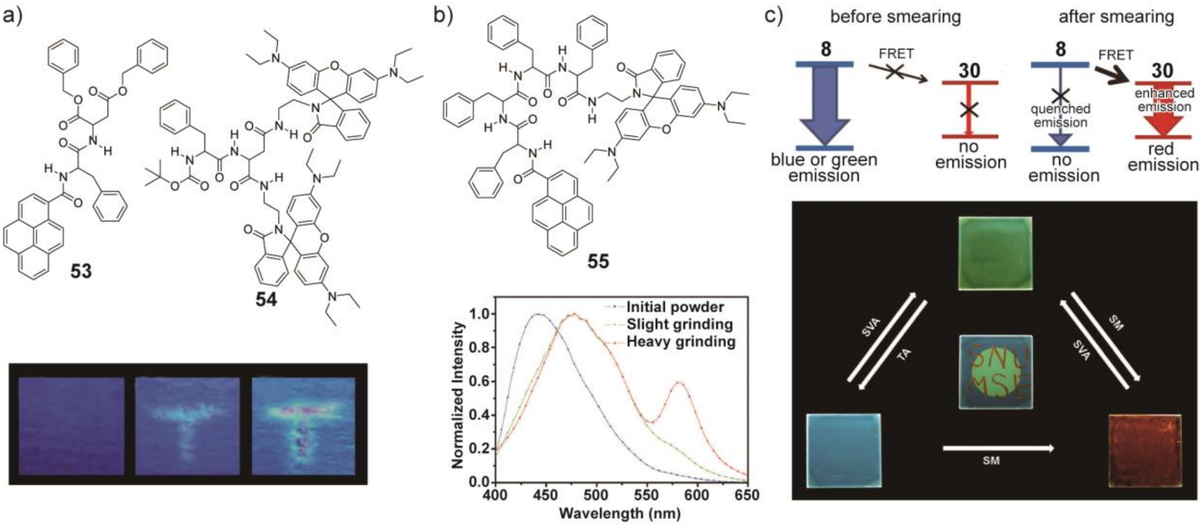


Figure 8. Multi-color MRL materials based on two luminophores. a) Molecular structures of **53** and **54** and pictures showing the mechano-responsive behavior of the mixture. b) Molecular structure of **55** and emission spectra that document changes of the material's

photoluminescence spectra upon grinding. c) Concept of combining FRET with other MRL mechanisms and picture documenting the RGB luminescence capability of a **8/30** mixture on glass substrates. Part a is adapted with permission.[114] Copyright 2012, Wiley-VCH. Part b is adapted with permission.[115] Copyright 2013, Wiley-VCH. Part c is adapted with permission.[116] Copyright 2015, Wiley-VCH.

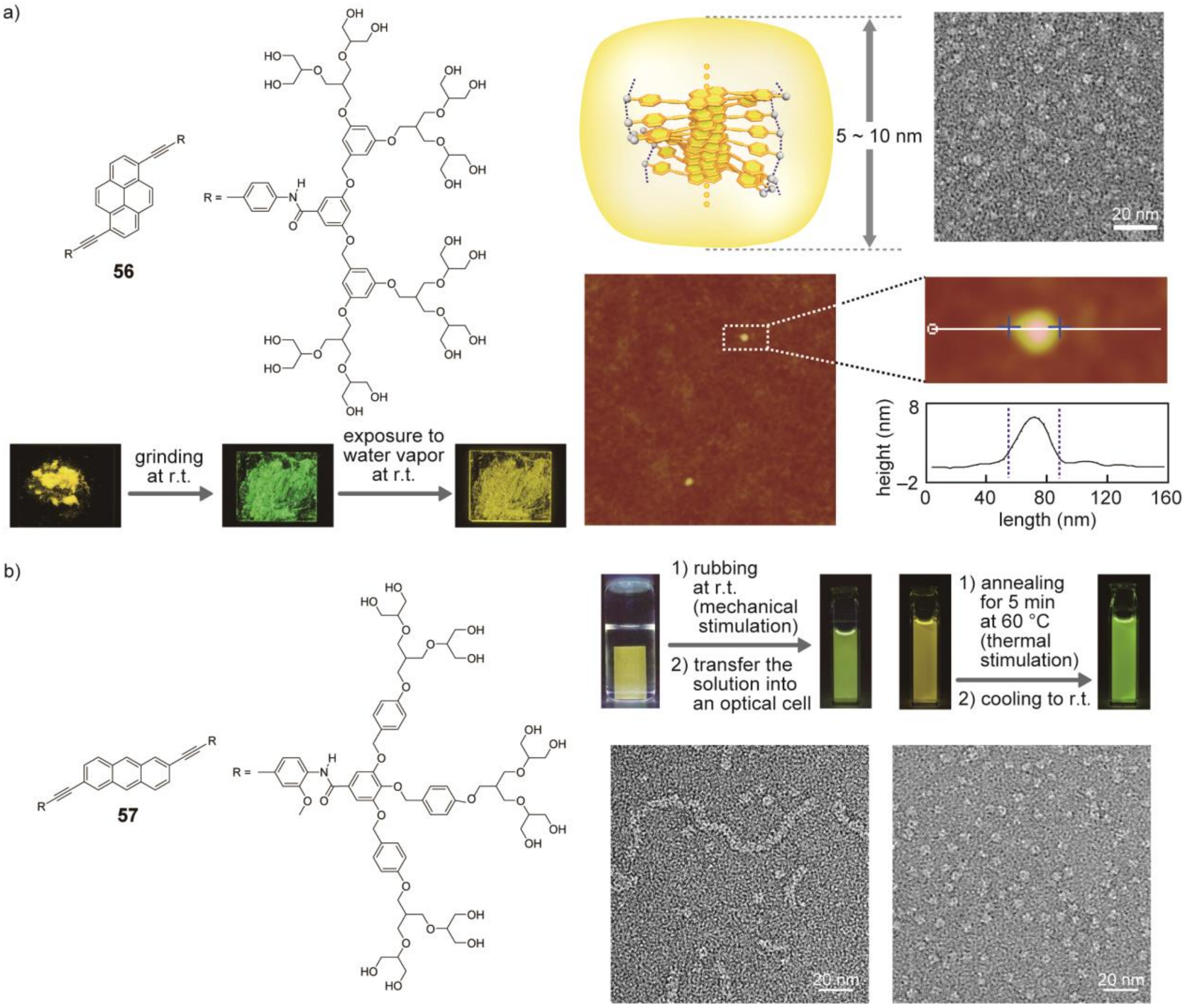


Figure 9. Water-soluble MRL molecular assemblies. a) Mechano- and humidity-sensing behavior of **56** and molecular assembled structures consisting of **56**. b) Mechanical and thermal stimuli-induced changes in photoluminescence color of micelles consisting of **57** and TEM images of the molecular assemblies. Part a is adapted with permission.[89] Copyright 2013, Wiley-VCH. Part b is adapted with permission.[90] Copyright 2014, Wiley-VCH.

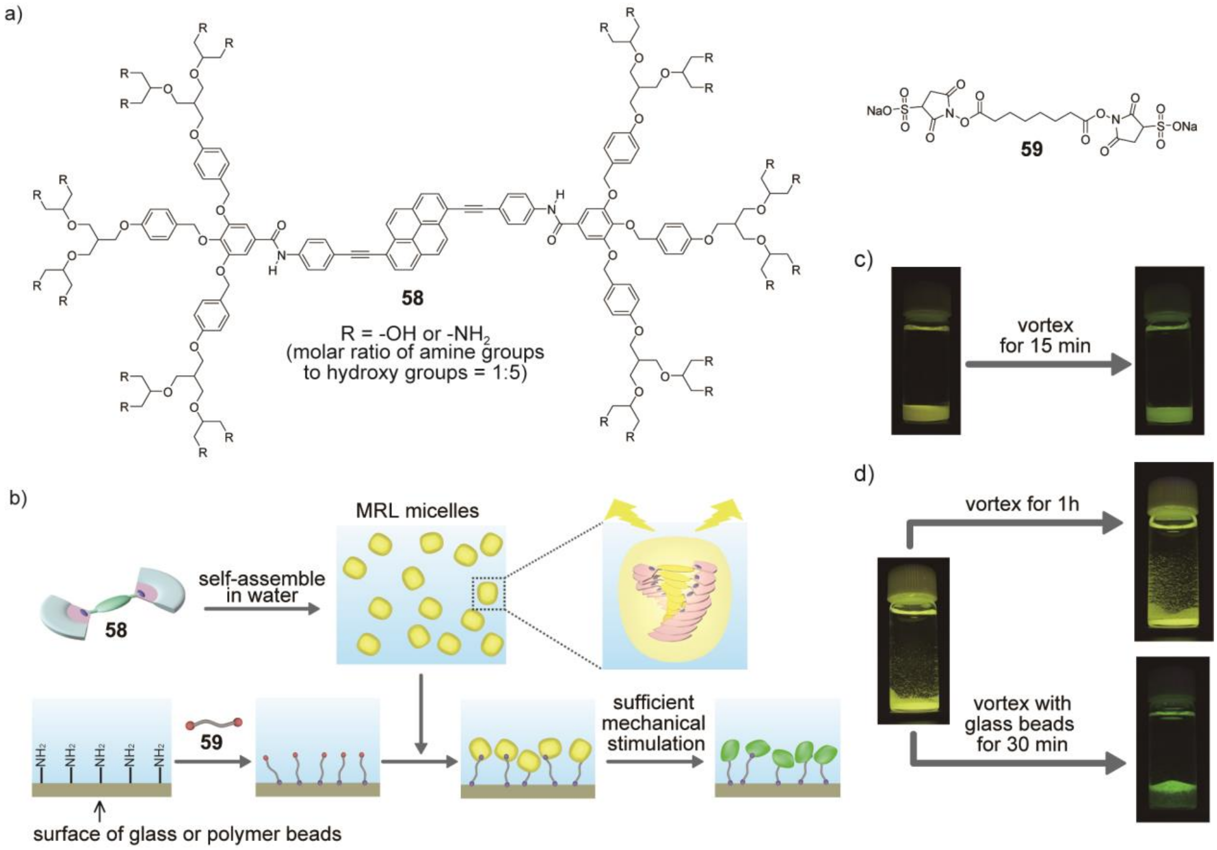
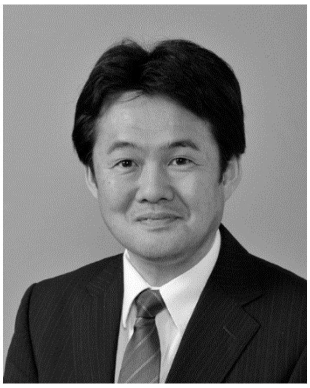


Figure 10. Covalent attachment of MRL materials to other materials of interest. a) Molecular structures of amphiphilic pyrene derivative **58** and water-soluble linker **59**. b) Schematic illustration of the attachment of MRL micelles onto glass or polymer beads. c,d) Pictures documenting the change of the photoluminescence color of the glass or polymer beads. The MRL micelles were covalently attached to the surface of the beads. Adapted with permission.[91] Copyright 2014, American Chemical Society.

Author Biographies and Photographs

Yoshimitsu Sagara received his Ph.D with Prof. Takashi Kato from the University of Tokyo in 2009. After working as a JSPS postdoctoral fellow in Kato's group for one year, he joined Prof. Tetsuo Nagano's group as a JSPS postdoctoral fellow in the University of Tokyo. Then, he joined Prof. Christoph Weder's group as a JSPS Postdoctoral Fellow for Research Abroad. His research interests include various stimuli-responsive photofunctional materials based on liquid crystals, micelles, gels and polymers and their practical appications.

Christoph Weder is professor for Polymer Chemistry and Materials at the Adolphe Merkle Institute of the University of Fribourg (Switzerland). He also serves as the Director of this center for fundamental and applied research on soft nanomaterials and is the Director of the Swiss National Competence Center in Research Bio-Inspired Materials. Weder was educated at ETH Zürich and MIT, held a lecturer appointment at ETH, and served as Professor in the Department for Polymer Science and Engineering at Case Western Reserve University (USA). His main research interests are the design, synthesis, investigation of structure-property relationships, and exploitation of novel functional polymer systems, in particular stimuli-responsive polymers, biomimetic materials, and polymer nanocomposites.



Takashi Kato received his Ph.D from the University of Tokyo in 1988. After doing postdoctoral research at Cornell University under the guidance of Prof. Jean M. J. Fréchet, he joined the University of Tokyo where he is currently a professor. He is also appointed as the Research Supervisor of PRESTO (Sakigake) research "Molecular Technology" of Japan Science and Technology Agency (JST). His research highlights the development of self-assembled materials, including supramolecular materials, liquid crystals, gels, ion-, electro-, and photo-functional materials, functional polymers, and bioinspired organic/inorganic hybrids. He serves as Editor-in-Chief of *Polymer Journal*. He is also on advisory boards of Wiley-VCH journals: *Advanced Materials*, *Small*, *ChemPlusChem* and *The Chemical Record*, and on executive board of *Advanced Science*.

TOC entry

Mechanoresponsive luminescence exhibited by molecular materials is an emerging topic in materials science. This progress report describes the background of this research field, then the concept of “luminescent molecular domino”, turn-on/off behavior, multi-color changes and water-soluble mechanoresponsive luminescent materials are reviewed. Approaches to covalently attach such materials to other materials are also introduced.

Keyword: Mechanoresponsive Luminescence

Yoshimitsu Sagara,* Shogo Yamane, Masato Mitani, Christoph Weder and Takashi Kato*

Mechanoresponsive Luminescent Molecular Assemblies: An Emerging Class of Materials