



Cite this: *Chem. Soc. Rev.*, 2021, 50, 4100

Received 28th November 2020

DOI: 10.1039/d0cs00940g

rsc.li/chem-soc-rev

Mechanochemical tools for polymer materials

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Mechanochemistry provides a unique approach to investigate macroscopic deformation, failure and healing of polymer materials. The development of mechanophores – molecular units that respond to mechanical force – has been instrumental in the success of this endeavor. This review aims to provide a critical evaluation of the large variety of mechanophores reported in literature, and to assess the molecular and macroscopic factors that determine their activation. Applications in materials science are highlighted, and challenges in polymer mechanochemistry are discussed.

1. Introduction

Energy supplied by mechanical force may be used to drive a chemical reaction across an activation barrier – similar to how light, electricity and, most commonly, heat are used for this purpose.^{1–3} Many mechanochemical reactions are known in both organic^{4,5} and inorganic chemistry,^{6,7} and sometimes, these reactions proceed at room temperature *via* pathways that are

improbable or inaccessible for conventional thermal reactions. The discovery of these reactions has enabled new efficient synthetic transformations, improved insight into the properties of materials under stress, and inspired the creation of stress-responsive materials that are programmable on the molecular level. The force required for such a mechanochemical reaction to proceed can be provided by macroscopic deformation of a material through grinding, ball-milling, compression, extension, or shearing.⁸ Alternatively, forces can be transduced to chemical bonds by sonication,⁹ atomic force microscopy (AFM),^{10–12} optical tweezers, or by the introduction of ring-strain.^{13,14}

Specifically within polymer materials, the use of mechanochemistry has evolved rapidly as a multi-purpose tool for characterization across length scales, and for creating materials

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with a novel response to force.^{15,16} The need to investigate the complex relationship between the molecular structure of a polymer and its mechanical properties as a material has stimulated the development of mechanophores:¹⁷ molecular units that can quantify and locate force on the molecular scale, making them unique tools for understanding and predicting macroscopic behavior.^{18–20} Meanwhile, smart materials can use mechanochemical reactions as triggers to change their own structure (force-responsive materials) or to produce a chemical function useful for catalysis, drug delivery, or soft robotics.^{21–23} Besides the use that mechanochemistry can have in functional polymer materials, polymers themselves are an excellent environment for studying mechanochemical reactions.²⁴ Strong and flexible linear chains are commonly used to transfer force to a mechanophore, and do so both efficiently and controllably. Thus, the use of polymers as a matrix for mechanochemistry helps to advance the physical chemistry behind this useful group of reactions.

As the toolbox of mechanochemistry is expected to be opened more frequently by researchers in other disciplines,

accessibility to all polymer scientists is critical for its successful application. Despite a wealth of application-oriented reviews,^{25–30} the selection of the correct tool is often challenging, indicating a need for guidelines to choose a suitable force-responsive group and a suitable method to incorporate the mechanophore inside a material to implement its function. This review aims to provide a 'field guide' for the implementation of mechanochemistry in synthetic polymers by summarizing the molecules, materials, and methods that have been investigated and applied. It is limited to the use of molecular mechanoresponsive units in polymer materials. Mechanical characterization of biomolecules, inorganic materials, and responsive materials based on microphase separation have been reviewed elsewhere.

Section 2 of this review provides an overview of mechanophores, categorizing them by output and clarifying their activation parameters. In Section 3, the synthesis and activation of mechanophores in polymer materials is discussed, starting with the different ways mechanophores can be implemented in a material, and continuing with their activation in different materials. In Section 4, applications of mechanochemistry in polymers are summarized, paying special attention to the polymer architectures and mechanophores used for each application. Together, these three sections should serve to simplify the daunting task of choosing the right mechanophore implemented in the right manner in the right material, as well as provide a comprehensive overview of the available tools for those looking to expand the available set of mechanophores. The final section concludes the review by summarizing remaining challenges and future applications.

2. Mechanophores and their responses

Mechanophores are molecular units that produce a physical or chemical response when an applied mechanical force brings about a structural rearrangement (such as a conformational change or bond scission). The rearrangement results in a



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between fracture of soft materials in the bulk and at interfaces. More recently he has been one of the pioneers in the quantitative use of mechanochemistry to locate bond scission during macroscopic fracture.

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in dynamic polymer systems, with topics that include self-assembled membranes, biomimetic hydrogels, and dynamic covalent polymers. He shares a fascination for polymer mechanochemistry with the other authors of this review.

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response that varies from a physical signal (such as a change in absorbance or emission of light) to a chemical signal (such as enhanced catalytic activity, formation of a reactive radical or the release of a small molecule).

For any application, a suitable mechanophore must meet several criteria. For each type of response, desired parameters should be identified; such as the excitation and emission wavelength of a mechanofluorescent response. A key parameter for any mechanophore is the threshold force at which it is activated. The threshold force is defined here as the offset force at which a mechanical response is observed in a single mechanophore molecule. Experimentally, this can be measured using a Single-Molecule Force Spectroscopy (SMFS) experiment in which a mechanophore is subjected to a tensile test using an AFM probe or with an optical tweezer setup. With both methods, the mechanophore must be covalently attached to two different surfaces which are then pulled apart until a mechanochemical event occurs at a given force. This way of measuring typically requires extensive synthesis to allow robust (notably, force-insensitive) surface functionalization as well as specialized and labor-intensive measurement procedures. For mechanophores of which the threshold force has not been experimentally characterized, computationally-determined force thresholds are provided instead. Most often, threshold forces have been calculated using the Constrained Geometry simulating External Force (CoGEF) method.³¹ In a CoGEF calculation, the mechanophore is first modelled in its unstrained state, typically using Density Functional Theory (DFT) methods. Then, two anchoring points on opposite sides of the mechanophore are selected and the distance between these points is increased in small steps, selecting for each step the geometry that minimizes the energy. The force profile is extracted from the distance increment and the computed minimal energy, and the activation force is taken as the maximum computed force before a mechanochemical event is found in the simulations. This simulation models events that occur during an SMFS measurement^{32,33} and generally agrees very well with experimental SMFS data across a wide range of mechanophores. Other types of force-dependent calculations – while generally less accessible – do provide additional insight into details of the potential energy surface and the transition state.^{15,34}

For the purpose of this review, we use a hybrid classification of mechanophores based on whether activation results in a physical spectral response (mechanochromic, mechanofluorescent, mechanoluminescent) or elicits chemical reactivity (mechano-catalytic, mechanoradical, or release and rearrangement). These different classes of mechanophores are discussed with specific emphasis on a comparison of their force sensitivity. The force of activation for a large set of mechanophores has recently been evaluated with COGEF calculations.³³

2.1 Mechanochromic moieties

Mechanochromic moieties change their UV-vis absorption spectrum upon mechanical activation. Generally, the change in absorption is caused by expansion of conjugation in the molecular structure, which leads to a bathochromic shift of the absorption maximum. A visible color change provides an easily

observed signal for stress, strain or damage in polymeric materials. A wide range of mechanochromic moieties has been used as mechanophores in polymeric materials. For each of these mechanophores, chemical stability, synthetic accessibility, mechanical activation parameters, and changes in absorption spectrum define their suitability as a reporter of force in various polymer materials.

2.1.1 Spiropyran (SP) derivatives. Spiropyran (SP) consists of indoline and benzopyran moieties connected in a spirocyclic manner. The weak C–O bond of the pyran ring can be broken by force in a formal 6π electrocyclic ring-opening reaction, which converts the SP to a merocyanine (MC) unit. Spiropyran will only be activated by mechanical force if the combination of attachment points puts enough load on the weak C–O bond. Thus, attachment of polymer chains on the opposite side of indole and benzopyran junctions leads to functional mechanophores. However, if the two attachment points are both on the indoline (positions 1–4) or both on the benzopyran (positions 5–10), the molecule will not be activated by mechanical force.³⁵ (Fig. 1a) The critical energy and force for activation have been calculated by simulation and measured by SMFS.³⁶ Due to the perpendicular orientation of indoline and benzopyran fragments, the lowest activation force was found when the attachment points were located at the 2 and 10 positions of the SP. An even lower activation force was observed for an SP derivative with attachment of one of the polymer chains on the indole nitrogen atom and the second polymer chain attached to the 10 position (Fig. 1b).³⁷ SMFS and theoretical values obtained with the CoGEF method³⁸ give critical forces for the two types of attachment of 260 pN and 240 pN, respectively (Fig. 1c). Substituents on the spirocyclic fragment also affect the critical activation force, with electron withdrawing substituents decreasing the value.³⁹ As an example, spiropyran derivatives with H, Br and NO₂ substituents on the benzopyran part show a critical force decreasing from H (410 pN) > Br (360 pN) > NO₂ (240 pN) at a strain rate of 300 nm s^{−1} (Fig. 1b). However, when the attachment points are on nitrogen and the 8, 9 or 10 position,⁴⁰ the materials have nearly identical critical force of activation.

The first use of spiropyran as a mechanochromic mechanophore was reported by Moore's group in 2009.³⁵ Colorless spiropyran was incorporated in the centre of a poly(methyl acrylate) (PMA) polymer backbone. Under uniaxial extension, spiropyran units were converted into highly colored merocyanine, resulting in a color change of the PMA material from yellow to purple. After failure, material turned red. While spiropyran is generally colorless or yellow, the color of merocyanines in a polymer is influenced by the chemical environment,³⁷ and can be blue, purple and red depending on the polarity of the polymer and its water content.⁴² Moreover, merocyanine containing polymers often show different colors in loading and unloading due to isomerization around the bonds connecting the cyclic subunits (Fig. 1d).⁴⁴ The striking optical response of spiropyran containing polymers is very easily observed by eye; and as a consequence, this mechanophore has been incorporated in a variety of polymer materials. These studies will be discussed in detail in Sections 3 and 4.



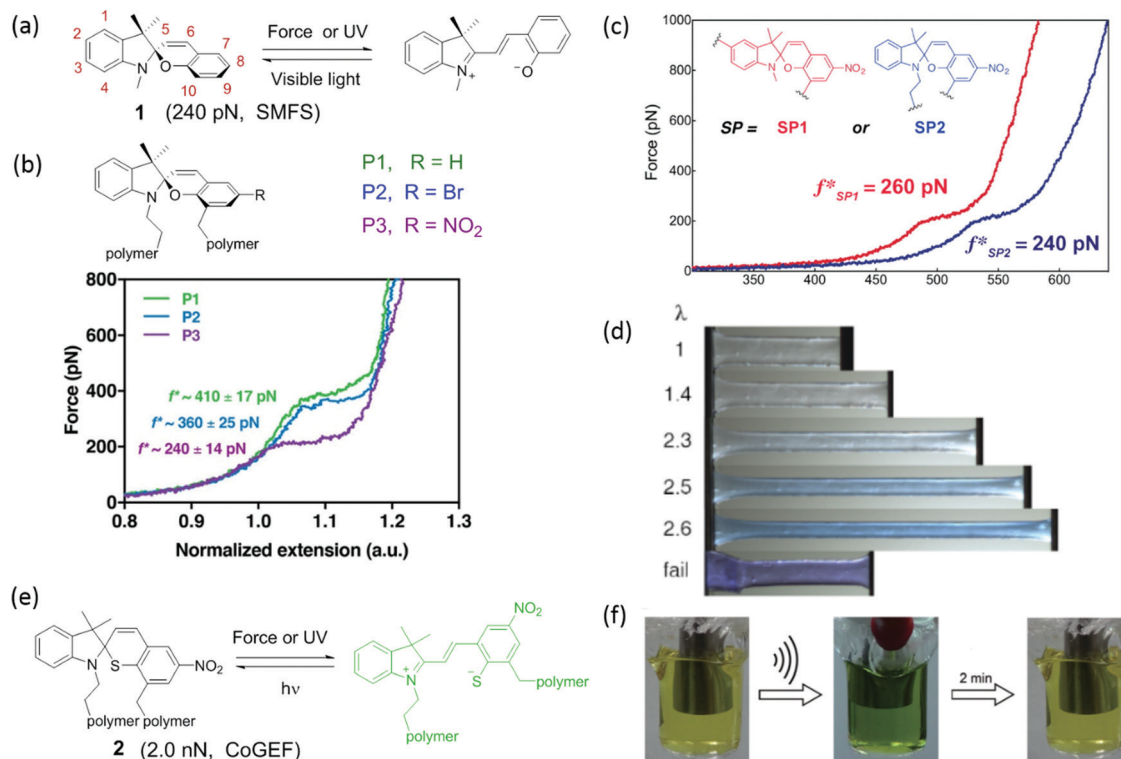


Fig. 1 (a) Activation of spiropyran by mechanical force or UV light; the reverse reaction is accelerated by visible light. (b) Three of spiropyran derivatives and their single-molecular force spectrum.⁴¹ (c) Single-molecular force spectrum of two spiropyran derivatives with varying attachment points.³⁶ (d) Color change of spiropyran in a multiple-network elastomer during uniaxial extension.⁴² (e) Activation of spirothiopyran by mechanical force or UV light and the reverse reaction by visible light. (f) Activation of spirothiopyran in the backbone of a polyester by sonication in solution.⁴³ (b) is reprinted with permission from ref. 41, Copyright 2018 American Chemical Society. (c) is reprinted with permission from ref. 36, Copyright 2015 American Chemical Society. (d) is reprinted with permission from ref. 42, (published under a Creative Commons license, CC BY-NC), Copyright 2020 AAAS. (f) is reprinted with permission from ref. 43, Copyright 2016 Wiley-VCH.

Various pyran analogs such as spirothiopyran (STP),⁴³ naphthopyran (NP),⁴⁵ and bis-naphthopyran (BNP),⁴⁶ have been designed with the aim of tuning reactivity, color and critical activation force. Spirothiopyran is a versatile mechanophore, as it features both mechanochromism and force-activated addition reactions of the sulfur atom (Fig. 1e). Ring opening of the thiopyran ring of STP *via* a 6 π electrocyclic ring-opening reaction to thiomercyanine (TMC) is accompanied by a color change from yellow to green. The nucleophilic thiolate formed after activation is a reactive partner in the thiol-ene click addition reaction with C=C double bonds. Weng's group reported the first example of STP-containing mechanochromic polymer materials, where STP was embedded into the backbones of a polyester and a polyurethane. A yellow solution of the polyester turned green after sonication as shown in Fig. 1f, indicating the formation of the thiomercyanine form of the dye. In the presence of *N*-ethyl maleimide, the green color quickly disappeared due to reaction with the thiomercyanine. When 1,6-bismaleimido-hexane crosslinker was present, sonication of a thiospiropyran-containing polymer led to crosslinking of the linear polymers into insoluble networks.⁴³ Calculations with CoGEF³³ show that the threshold force to activate STP is 2.0 nN – distinctly lower than for SP mechanophores, which have a calculated F_{\max} of 2.6 nN.^{33,47}

Naphthopyran (NP) is also mechanochromic, with a color change from colorless to yellow when the ring opens (Fig. 2a). The calculated threshold force to activate NP ($F_{\max} = 3.7\text{--}4.4$ nN, CoGEF) is higher than for SP. The threshold force depends on the attachment points as well as on the nature of the substituents. Fig. 2b shows three types of attachment of polymer chains; only NP5 was activated in tensile tests when covalently crosslinked into PDMS, while NP8 and NP9 were inactive (Fig. 2c).⁴⁸ Varying the substituents at positions 1 and 3 (Fig. 2a and e) not only gave different colors of the activated merocyanine form, but the critical forces of activation were also different. For instance, in compound 3 the critical force was 4.1–4.4 nN to give a yellow merocyanine; while it was 3.7–3.9 nN for compound 4a–c, with a color change to purple. Each of the six NP's in PDMS studied by Robb *et al.* gave different mechanochromic behavior. All polymers showed color change; but differences in color intensity due to different concentrations of merocyanine illustrate the variation in threshold forces among these mechanophores (Fig. 2e).⁴⁹ The compounds also show differences in fading time in the relaxed state because the merocyanines have different stabilities.

Bisnaphthopyran (BNP) combines two pyran rings and is unique among SP derivatives because it isomerizes *via* two 6 π electrocyclic ring-opening reactions. The two pyran rings can be activated consecutively by UV light, while mechanical force



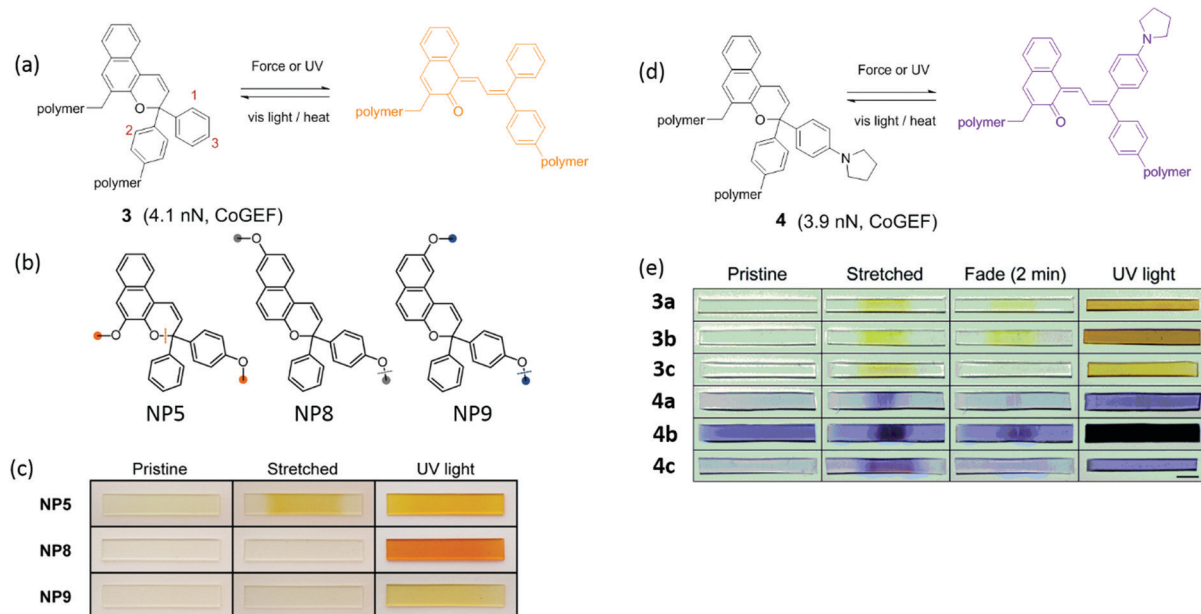


Fig. 2 (a) Activation of naphthopyran (NP) by force and UV light; the reverse reaction is accelerated by heat or visible light. (b) Naphthopyran derivatives with varying polymer attachment points. (c) Images of polymer materials in (b) showed different mechanochromic responsiveness before and after elongation and UV irradiation.⁴⁸ (d) Naphthopyran mechanophore with pyrrolidine substituent (e) naphthopyran derivatives and their color changes in naphthopyran-containing PDMS after extension or UV irradiation.⁴⁹ (b) is adapted with permission from ref. 48, Copyright 2016 American Chemical Society. (c) is adapted with permission from ref. 48, Copyright 2016 American Chemical Society. (e) is adapted with permission from ref. 49, Published by The Royal Society of Chemistry (<https://creativecommons.org/licenses/by/3.0/>).

directly activates both pyran rings in a single step, as has been demonstrated by Robb *et al.* in ultrasonication experiments.⁴⁶ When one of the pyran rings is activated by UV light, the second ring can be activated by mechanical force as shown in Fig. 3. Each of the states of BNP exhibits a different color. State 1 – with one opened pyran ring – is yellow, while open–open state 2 is purple. In CoGEF simulations, the threshold force to open the first ring is 4.1 nN, while opening the second ring requires a force of at least 4.6 nN.³³ This difference is not enough to selectively create a high amount of state 1 in the ultrasonication experiments. In the mechanostationary state, it was assumed

that most, if not all, of the open–closed form was the product of electrocyclic ring closure of the open–open state.⁴⁶

2.1.2 Rhodamine derivatives. Rhodamine is a well-known fluorescent dye used extensively in biochemistry due to its high quantum efficiency, that provides high sensitivity and spatial resolution. Like in spiropyran, a spiro structure can ring-open to a planarized zwitterion under UV irradiation, and the reverse reaction takes place by heating. The isomerization induces a reversible change in both absorption and fluorescence spectra. Although these features are promising for mechanical activation of the ring opening reaction, rhodamine and its derivatives have

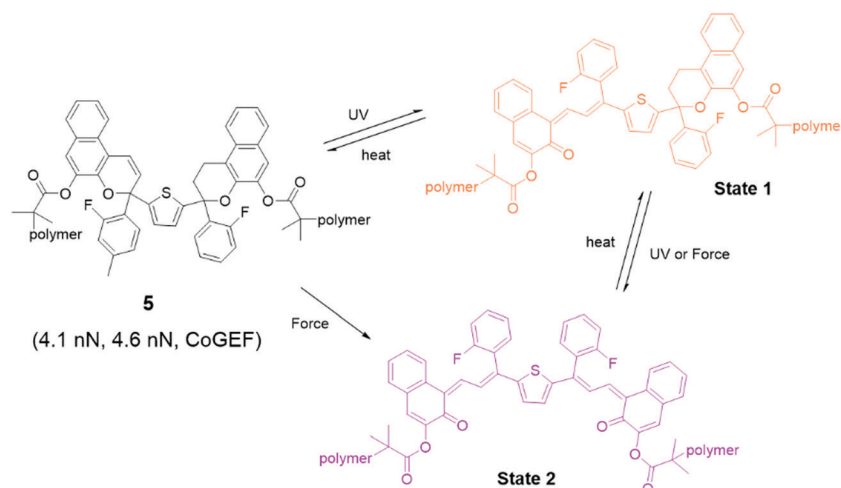


Fig. 3 Activation of bisnaphthopyran **5**. UV light leads to stepwise ring opening *via* state 1, while mechanical force directly converts **5** to state 2.



not been used as mechanophore until 2015, when spirorhodamine **6** was incorporated in a polyurethane,^{50,51} and was found to exhibit mechanochromism (Fig. 4a and b). After activation in a triple network, the rhodamine displayed different fluorescent colors in loading and unloading (red and yellow, respectively)⁵² due to mechanically driven conformational changes (Fig. 4c). This unique behavior indicates the potential of spirorhodamine as a sensor that provides detailed information on local stress and strain.

To effectively activate spirorhodamine, the mechanical force transmitted along the polymer chain should induce the scission of the C–N bond in the spirolactam. Activation is influenced by the position of the attachment points and by the electronic properties of the substituents on spirorhodamine. For example, a spirorhodamine-diol was attached to polyurethane at positions 1 and 3 in Fig. 4a.⁵² The resulting polymer materials show reversible mechanochromism with fluorescent emission in compression (between colorless and reddish). However, when the attachment points were changed from 1+3 to 2+3, mechanical force was not transferred across the C–N bond in spirolactam, and the spirorhodamine was not activated by force. Furthermore, spirorhodamines with varying substituents on the xanthene part of the molecule show different photochromic responses. Rhodamine with two amino groups⁵² shows a strong absorption in the blue-green range of the visible spectrum, and UV light induces the transformation of the open form to the spiro form – in contrast to the spirorhodamine with a single amino group on the chromophore (Fig. 4d).⁵⁰ Trifunctional spirorhodamine (Fig. 4e) was incorporated into the filler network of poly(ethyl acrylate) multiple-network elastomers. The elastomers display a UV-sensitivity that is opposite to that of the polyurethane labelled by spirorhodamine-diols. Furthermore, the elastomers have a red-shifted fluorescence, and the fluorescent color changes from red to yellow when unloading. Interestingly, the

fluorescent color can be tailored by incorporating pyrene in the polymer material.⁵³ Upon stretching, the combination of green fluorescence from the pyrene excimer, blue fluorescence from monomeric pyrene and red fluorescence from mechanochemically-activated rhodamine gives rise to white emission.

2.2 Photoluminescent mechanophores

While the mechanochromic mechanophores discussed in the previous section show some fluorescence in addition to a color change, mechanophores that are exclusively used for their emissive properties deserve separate treatment. Photoluminescent mechanophores display a change in fluorescent or phosphorescent behavior when subjected to a mechanical force. In most cases, a ‘turn-on response’ is generated, meaning that the mechanically active groups display no photoluminescent response at the measured wavelength before a dye is unveiled by a mechanical stimulus. Compared to the colorimetric response of a mechanochromic system, a photoluminescent response is far stronger if a fluorophore with a sufficiently high quantum yield is released. This allows for strong and accurate detection at mechanophore concentrations of the order of 10^{-6} M, and even allows for detection of single bond-breaking events.⁵⁴ In addition to the parameters outlined in Section 2.1, quantum yield is therefore an important parameter for determining the suitability of a photoluminescent mechanophore.

2.2.1 Covalent photoluminescent mechanophores. Most photoluminescent mechanophores rely on a force-induced cyclo-elimination reaction and exhibit a fluorescent response. Diels–Alder adducts of anthracene are among the most applied mechanofluorescent moieties, in part due to their high fluorescent quantum yield. Three of these mechanofluorophores that have been successfully activated in polymers include bis(anthracene) dimer,⁵⁵ anthracene–maleimide adduct,^{56–62} and π -extended

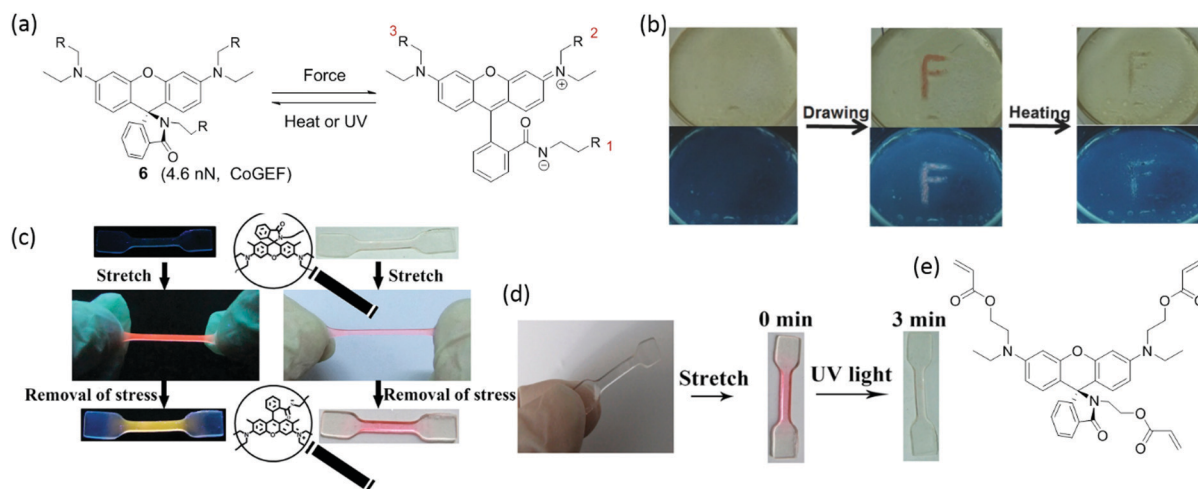


Fig. 4 (a) Activation of rhodamine and the reverse reaction by stimulation with force and heat or UV, respectively. (b) Rhodamine was embedded into polyurethane film. The film was drawn and showed a color change that fades upon heating.⁵⁰ (c) Rhodamine integrated into the filler network of a multiple-network elastomer changes color in extension; different fluorescent colors are observed in loading and unloading.⁵² (d) Bleaching of color in activated elastomer by UV light.⁵² (e) Three-arm rhodamine modified with double bonds. (b) is reprinted with permission from ref. 50, Copyright 2015 Wiley-VCH. (c) is reprinted with permission from ref. 52, Copyright 2017 American Chemical Society. (d) is adapted with permission from ref. 52, Copyright 2017 American Chemical Society.



anthracene–maleimide adduct,⁶³ as shown in Fig. 5a–c. When anthracene adducts are incorporated into a polymer backbone, a mechanical stimulus enables the retro-Diels–Alder reaction of anthracene adducts and releases fluorescent anthracene derivatives. Activation of these mechanophores results in scission of the polymer chains. More sensitive measurements can be achieved by using π -extended anthracene adducts, which have a higher luminescent quantum yield in their dissociated state than regular anthracene, and allow for a more quantitative determination of the polymer fraction that has been cleaved. Anthracene adducts have been especially successful as damage sensors in polymer materials. A compelling example is provided by Moore and coworkers,^{59,64} who linked poly(methyl acrylate) chains to the surface of silica nanoparticles with an anthracene–maleimide adduct. This anthracene derivative was released in ultrasonication, which demonstrated the mechanically-selective activation or scission of mechanophores on a heterogeneous interface.

Other categories of covalent fluorescent mechanophores reported by pioneers include the coumarin dimer (compound **16**),^{67,68} dithiomaleimide moiety (compound **17**),⁶⁹ methanone-tethered cinnamate dimer (compound **18**),⁷⁰ and 2-(2'-hydroxyphenyl)-benzoxazole (compound **19**).⁷¹ Like anthracene adducts, these mechanophores lead to scission of the polymer chain, concomitant with fluorescence. Coumarin dimers have been investigated by Craig *et al.*, who integrated coumarin dimers in the middle of poly(methyl acrylate) chains and characterized the relationship between the activation efficiency of mechanophore and molecular weight of the polymer.⁶⁷ Dithiomaleimide **17** is notable for

being fluorescent before cleavage, thereby being the only example of a mechanophore that loses fluorescence after mechanical activation.⁶⁹ CoGEF calculations provided a force threshold of 4.3 nN and a cleavage mechanism that started with homogeneous bond scission of the C–S bond,³³ although the final reaction products (structure) are not validated in experiment after activation. With the exception of anthracene adducts, many of these fluorescent mechanophores have not yet been taken full advantage of in mechanochemistry for damage research in polymer materials.

2.2.2 Supramolecular photoluminescent mechanophores.

While most photoluminescent mechanophore rely upon breaking a covalent bond, mechanophores in which the weak bond is a supramolecular interaction offer the potential benefit of lower activation force and reversibility. Indeed, weak non-covalent bonds allow for extremely sensitive detection of low stresses and strains in polymer materials when combined with the inherent sensitivity of photoluminescence measurements. Unfortunately, critical activation forces have rarely been reported for supramolecular mechanophores.⁵⁴

Taking this advantage to an extreme, a conjugated polymer of a fluorescent donor doped with an acceptor was shown to be highly sensitive to chain extension.⁵⁴ Poly(dioctylfluorene-*alt*-benzothiaziazole) (F8BT) was copolymerized with a small amount of dithienyl benzothiadiazole (DTBT). Förster resonant energy transfer (FRET) between the excited donor and initially ground-state acceptor occurs in all cases; but the extent of transfer depends on the distance between donor and acceptor, which in turn is influenced by stretching the polymer materials. A threshold

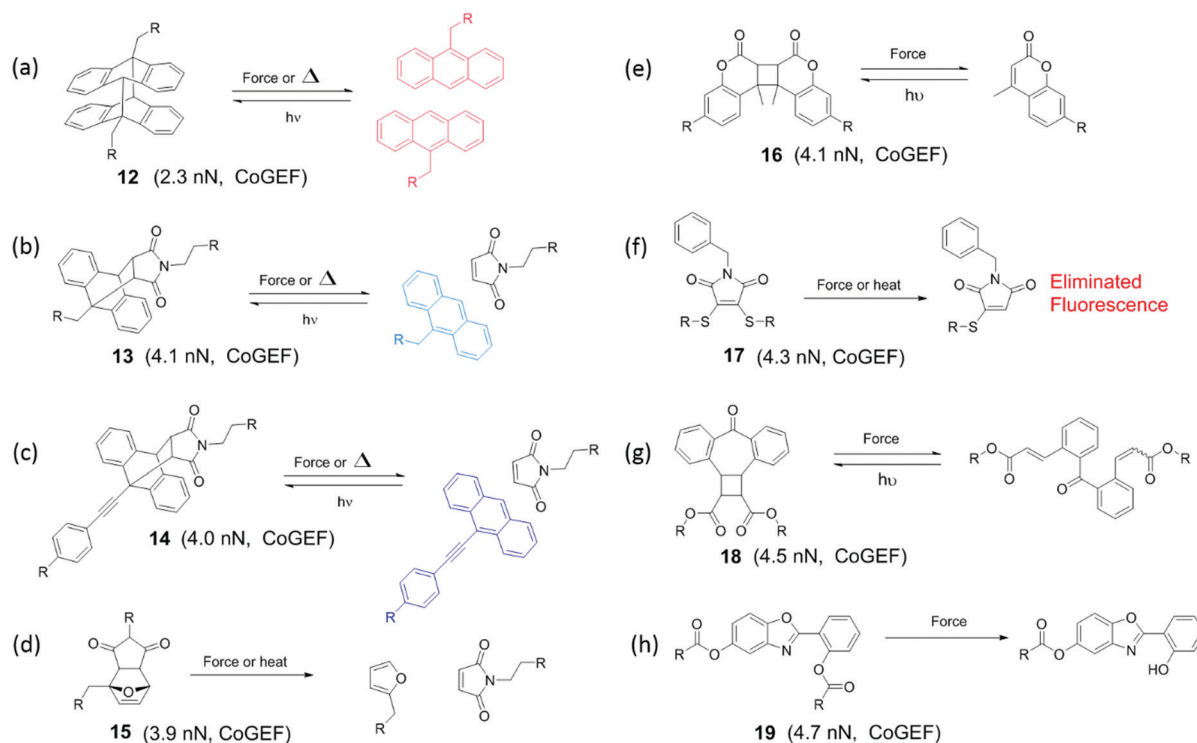


Fig. 5 Structure of various fluorescent mechanophores that are activated by force and display covalent bond scission. (a) Anthracene dimer; (b) Anthracene–maleimide adduct; (c) π -Extended anthracene–maleimide adduct; (d) Furan–maleimide adduct;^{65,66} (e) Coumarin dimer; (f) Dithiomaleimide; (g) Methanone-tethered cinnamate dimer. (h) 2-(2'-Hydroxyphenyl)benzoxazole.



force of approximately 300 fN was determined experimentally – roughly four orders of magnitude lower than a typical covalent mechanofluorophore. No bonds are broken upon activation, as not a chemical bond but the conformational entropy of the coiled polymer chain is destabilized by the applied force.

Moving towards slightly higher interaction energies, we find supramolecular complexes held together by electrostatic interaction,⁷³ π - π stacking,⁷² or hydrophobic interactions.⁷⁴ This category of mechanophores includes dyes of conjugated oligo(*p*-phenylenevinylene) derivatives (OPV) aggregated by π - π stacking interactions (Fig. 6). The aggregated excimers dissociated in response to tensile deformation and resulted in a luminescent color change from either yellow to green, or from green to blue, depending on the OPV derivatives that were used. Recently, another supramolecular mechanophore was accessed by incorporating a fluorophore-quencher pair into a mechanically interlocked rotaxane (Fig. 7a). Sagara's and Weder's groups^{74–76} embedded the rotaxane mechanophore into polyurethane elastomers and the elastomers displayed rapid and reversible fluorescence switching upon extension as shown in Fig. 7b. The fluorescent response correlated with the macroscopic deformation and the optical properties could be tailored by varying the chromophores in rotaxane.

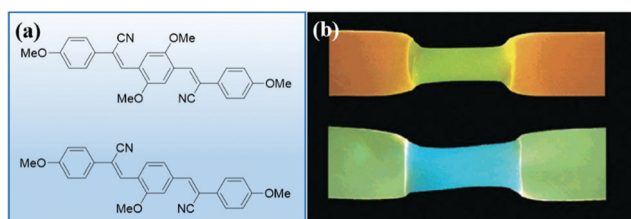


Fig. 6 Conjugated oligo(*p*-phenylenevinylene) derivatives display different fluorescent colors in aggregated or dissociated states. (a) Two conjugated oligo(*p*-phenylenevinylene) derivatives. (b) The two dyes in (a) were physically blended into polymer matrix and the materials revealed fluorescent color change in extension.⁷² (b) is reprinted with permission from ref. 72, Copyright 2020 Springer Nature.

Mechanically active charge-transfer complexes have also been introduced in polymer materials without the stabilization of rotaxane formation. A fluorescent pyrene group was connected to two naphthalene diimide (NDI) groups using a short covalent linker and incorporated in the backbone of a polycaprolactone chain.⁷⁷ Pyrene forms a charge-transfer complex with the neighboring NDI, locally folding the chain and quenching the fluorescence of pyrene. When the polycaprolactone films were stretched, the interaction between pyrene and NDI was broken and a fluorescent response was observed. Sufficiently soft materials allowed enough mobility for the pyrene and NDI to recombine, quenching the fluorescence and displaying reversible behavior. In amorphous polycaprolactone however, an increasing response was observed even after stretching, presumably due to strain-induced ordering and crystallization of the polymer matrix. A different fluorescent mechanophore based on π - π interactions of a pyrene derivative is the sulfonated derivative (hydroxyethyl)-pyrene trisulfonate (HEPTS).⁷⁸ HEPTS forms aggregates in apolar solvents and in polyurethane materials, thereby shifting to a yellow-emitting fluorescence from the blue emission of non-aggregated HEPTS. Stretching materials made from HEPTS-telechelic polyurethane chains mixed in a non-functionalized material showed a shift in the emission spectrum due to dissociation of the aggregates.

A fluorescent mechanophore stabilized by electrostatic interactions was reported by Jen *et al.*⁷³ This thermodynamically unstable mechanophore is formed by a Michael addition reaction and is electrostatically-stabilized by a protonated amine (Fig. 8). Mechanical force initiated the reversible elimination, leading to the release of a conjugated dye. When the mechanophores were covalently crosslinked in an epoxy network, a color change was observed at a low onset of deformation of 0.14 accompanied with a fluorescent color change.

Mechanophores that display photoluminescence due to reduced molecular mobility are a recent addition to the mechanochemical toolbox. Films made from hyperbranched poly(amido amine)s were reported to displayed an increased fluorescent intensity at near-zero

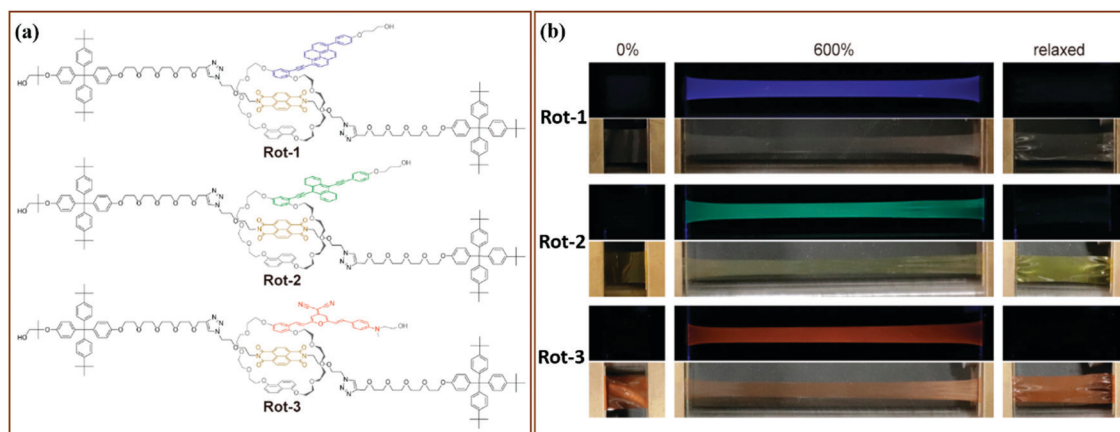


Fig. 7 Supramolecular mechanophores prepared by locking fluorophore and quencher in a rotaxane. (a) Three rotaxane mechanophores with different fluorophores. (b) Fluorescent responses of the three rotaxane mechanophores in tensile tests.⁷⁵ (a) and (b) are adapted with permission from ref. 75, Copyright 2019 American Chemical Society.



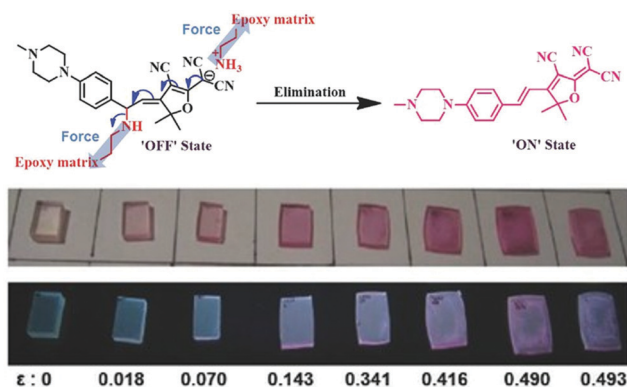


Fig. 8 Breaking an electrostatic interaction by force resulted in a molecular rearrangement. This rearrangement leads to the release of 3-cyano-4,5,5-trimethyl-5H-furan-2-ylidene malononitrile dye; and materials showed a color change, including fluorescent color switching with varying degrees of compressive strain.⁷³ Adapted with permission from ref. 73, Copyright 2016 Wiley-VCH.

strain (Fig. 9).⁷⁹ These materials contain tertiary amines in close proximity to amide groups. The fluorescent properties of these materials, classified as unconventional macromolecular chromophores,⁸⁰ are believed to derive from intramolecular electron overlap of closely clustered amines and amides. Stretching this material resulted in a linear increase of fluorescence intensity at the same wavelength, which could be activated and deactivated reversibly. The applicability of this class of mechanophores to different systems may be limited by the close proximity, and therefore high concentration, of these groups that is required for fluorescence. Additionally, a fluorescent background is present prior to activation and no significant shift in excitation wavelength is observed; so the fluorescent signal is only meaningful when it can be compared to the initial state of the material. Nevertheless, this unique approach may lead to the development of more generally applicable, highly sensitive mechanofluorophores as well as a better understanding of this unusual photophysical response.

Filonenko and co-workers have described a chemically different, yet mechanistically similar approach for force detection in polymers with a Cu(I)-pyridinophane complex (Fig. 9).^{81,82} This complex contains a tetradentate ligand that binds to the metal in a tridentate fashion, leaving one tertiary amine available that can exchange

rapidly with an identical copper-bound ligand. The complex displays a phosphorescent photoluminescent response; however, the dynamic ligand exchange provides a pathway for non-radiative decay, resulting in a low phosphorescence intensity. When the exchangeable ligands are mechanically activated by tensile strain in polyurethane materials, the reduced dynamicity of the system leads to a higher probability of phosphorescent emission occurring before non-radiative decay, thereby enhancing the phosphorescent signal. This normally does not produce a shift in emission wavelength, limiting its use in materials to intensity-based detection. A derivative with a more sterically-hindered co-ligand was reported that did show a hypochromic emission shift upon mechanical activation in a comparable material.⁸³ The origin of this shift was explained by the interaction between the Cu⁺ center and the non-coordinating PF₆[−] or BF₄[−] counterions. This shift also occurred due to different stimuli that affect the ion-pair distance, such as solvent polarity or temperature changes. The reason for a change in ion-pair distance was thought to be related to the change in free volume of the polymer material. Because of the shift in emission wavelength, a ratiometric response could be measured, in contrast to other mobility-based mechanophores. However, the color change is highly dependent on the environment, and it is difficult to predict its behavior in other materials.

2.3 Mechanoluminescent mechanophores

Mechanoluminescence is the emission of light due to a mechanical stimulus. Use of bis(adamantyl)-1,2-dioxetane, shown in Fig. 10a as a mechanophore was introduced by Chen *et al.*⁸⁴ Luminescence of this dioxetane is activated by force which cleaves the mechanophore in two adamantanone units, one of which is in an excited state. Relaxation of the excited adamantanone to its ground state is accompanied by bright-blue luminescence. Adamantyl substituents increase the thermal stability compared to other 1,2-dioxetane derivatives.⁸⁵ For this reason bis(adamantyl)-1,2-dioxetane derivatives have been applied as heat or acid activated chemiluminescence probes for bio-labeling.

When the dioxetane mechanophore was integrated into the center of a PMA polymer backbone or used as a crosslinker in an acrylate polymer network, emission of blue light with a maximum at 420 nm^{85,87} was observed during extension or sonication in polymer solution (Fig. 10b). The sensitivity and

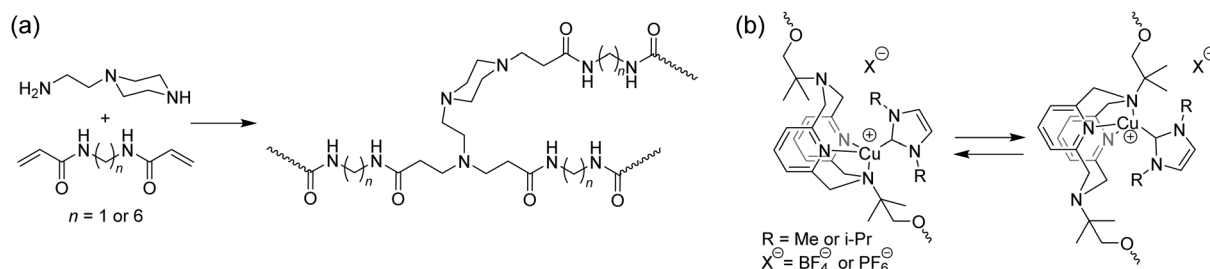


Fig. 9 Structures of mobility-based photoluminescent mechanophores. (a) A hyperbranched network containing amide groups and tertiary amines in close proximity show enhanced fluorescence emission upon increasing strain.⁷⁹ (b) Phosphorescent copper(I)-pyridinophanes ligated to an N-heterocyclic carbenes undergo a rapid ligand exchange, which is hindered by mechanical tension, thereby increasing the photoluminescent response.⁸¹ For R = i-Pr, a shift in emission spectrum is also observed.⁸³

