Rotaxane-Based Mechanophores Enable Polymers with Mechanically Switchable White Photoluminescence

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Supporting Information

ABSTRACT: Three mechanoresponsive polyurethane elastomers whose blue, green, and orange photoluminescence can be reversibly turned on by mechanical force were prepared and combined to create a blend that exhibits deformation-induced white photoluminescence. The three polyurethanes contain rotaxane-based supramolecular mechanoluminophores based on π-extended pyrene, anthracene, or 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) lumino- phores, respectively, and 1,4,5,8-naphthalenetetracarboxylic diimide as an electronically matched quencher. Each polymer shows instantly reversible, strain-dependent switching of its photoluminescence intensity when stretched and relaxed, as deformation leads to a spatial separation of the luminophore and quencher. The present study shows that the photoluminescence color can easily be tailored by variation of the luminophore and also by combining several mechanophores in one material and demonstrates that adaptability is a key advantage of supramolecular approaches to create mechanoresponsive polymers.

INTRODUCTION

Mechanophores that change their photophysical properties upon activation by mechanical force are now widely studied, because embedding such moieties into polymers is one of the most promising ways to achieve mechanochromic polymers.1−3 Mechanochromic (luminescent) polymers can signal mechanical stresses and visualize material damage ahead of structural failure.4−23 Conventional mechanophores that are activated by the mechanically induced scission of covalent bonds suffer from several limitations, which are directly related to their general operating mechanism. First, the activation requires a relatively high activation energy, as the process involves the cleavage of covalent chemical bonds that are supposed to be stable in the absence of mechanical force.4,11,16,21,22 Second, the process is usually irreversible,5,7,10 or the return reaction requires activation energy or is slow,9,15−17 which results in limited reversibility. Third, the mechanical stimuli-induced cleavage reaction can typically also be caused by thermal treatment or light irradiation, which makes the process unspecific. To overcome the disadvantages of conventional mechanophores, we recently developed a supramolecular rotaxane-based mechanoluminophore that was composed of a cyclic compound containing a luminophore and a dumbbell-shaped molecule containing an electronically matched quencher and two stopper groups.24 A linear polyurethane containing the rotaxane-based supramolecular mechanoluminophore exhibited instantly reversible ON/OFF switching of its photoluminescence. The activation process does not involve any bond cleavage, but relies simply on the spatial separation of the luminophore and the quencher. Consequently, the activation energy is low;24 the process is fully and instantly reversible, specific to mechanical force, and cannot be triggered by light or heat. We note that mechanophores that do not require scission of covalent bonds for activation and change their photoluminescence properties are still limited.19,24,26

Here, we show another significant advantage of the supramolecular approach to mechanophores, i.e., that the optical signal produced can readily be tailored in a simple and rational manner without otherwise changing the mechanores- ponses of the mechanophore in a given polymer, even though the molecular-level activation energies may be slightly different.27 Thus, blue-, green- and orange-light-emitting rotaxane-based supramolecular mechanoluminophores were created on the basis of our previous design24 by varying only...
the luminophore incorporated in the cyclic moiety (Figure 1). In the unactivated state, the luminophores are located close to the quencher, and therefore, their photoluminescence is suppressed, while upon application of mechanical force, they are drawn away from the center of the axle, and strong photoluminescence of each of the luminophores studied is turned on. Consequently, films of polyurethanes that contain the mechanophores individually show instantly reversible ON/OFF switching of the corresponding emission. As targeted, their mechanoresponsive characteristics were, with the exception of the emission color, identical. Blending the three polyurethanes allowed access to a white-light-emitting material that shows instantly reversible mechanically switchable emission.

White-light-emitting crystals and solids, as well as “soft” materials such as supramolecular polymers, physical gels, organic–inorganic hybrid gels, micelles, inclusion complexes, solvent-free liquid particles, and DNA-based materials, have recently attracted considerable attention. Some of these materials are responsive and change their color from white to other colors in response to light irradiation, pH changes, addition of molecules, or mechanical stimuli. In these systems, the responsiveness originates from chemical changes of the luminophores and/or variations of the supramolecular structures, which in turn changes the relative contribution of the emission of different species contributing to broad-band emission. Interestingly, however, to the best of our knowledge, no white-light-emitting soft materials have been reported to exhibit a mechanically induced ON/OFF switching.

## RESULTS AND DISCUSSION

The cyclic building blocks containing the three different luminophores utilized in this study and the corresponding rotaxanes are depicted in Figure 2. The cyclic compounds 1, 2, and 3 feature 1,6-disubstituted pyrene, 9,10-disubstituted anthracene, and a π-extended 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) groups as the emitter, respectively. The 9,10-bis(phenylethynyl)-anthracene was used as the green emitter instead of 4,7-bis(phenylethynyl)-2,1,3-benzothiadiazole in our previous study because of the higher quantum efficiency. The three luminophores are well-studied and were selected on account of their ability to cover a broad range of the visible emission spectrum, and facile integration into a 1,5-disubstituted naphthalene crown ether, which is often used in neutral donor–acceptor rotaxanes. As in our recent study, an electron-poor 1,4,5,8-naphthalenetetracarboxylic diimide (NpI) was used as the matching quencher. The NpI also templated the rotaxane synthesis, which was achieved via 1,3-dipolar cycloaddition between alkylene and azide groups in precursors of the rodlike molecule in the presence of the cyclic luminophores (see the Supporting Information for details). The rotaxanes Rot-1, Rot-2, and Rot-3 thus produced feature two tetraphenylethylene units featuring three tert-butyl groups as stoppers that prevent the cyclic luminophores from sliding off. In each rotaxane, two hydroxy groups were introduced at the end of the luminophore and one of the stopper groups, enabling the covalent integration into polymer molecules. The rotaxane formation was confirmed by the quenching of the emitters’ photoluminescence (see below) and also by the observation of the expected shifts of the 1H NMR signals of the aromatic protons of the interlocked motifs (Figures S1–S3).

Absorption and photoluminescence measurements were carried out to characterize the optical properties of the three cyclic compounds and the corresponding rotaxanes (Figure 3). The absorption and emission spectra of chloroform solutions of both 1 and 2 show vibronic structures. The absorption band of 1 appears between 350 and 450 nm, whereas 2 absorbs between 400 and 500 nm. The emission spectrum of pyrene
derivative 1 displays two emission peaks at 430 and 450 nm, while the anthracene derivative 2 shows two emission peaks at 497 and 526 nm and a shoulder around 560 nm. In chloroform solutions, both 1 and 2 exhibit high photoluminescence quantum yields of 0.94 and 0.91, respectively. The DCM derivative 3 displays a broad absorption band between 300 and 550 nm in a mixture of hexane and chloroform (3:2 v/v). In contrast to compounds 1 and 2, the photoluminescence spectrum of 3 is broad (λmax = 605 nm), void of vibronic features, and the quantum yield is only 0.27. A superimposition of the photoluminescence spectra of 1–3 shows that they cover the entire visible wavelength region. Indeed, a mixed solution containing the three luminophores in a molar ratio of 1:6:10 in a hexane/chloroform mixture (3:2 v/v) exhibits white photoluminescence under excitation at 365 nm. Upon rotaxane formation, i.e., in Rot-1, Rot-2, and Rot-3, the photoluminescence of the three emitters is completely quenched, while the absorption spectra show slight red-shifts (Figure 3, dotted lines), which is indicative of electronic ground-state interactions between the luminophores and the NpI.

After confirmation that the rotaxanes Rot-1, Rot-2, and Rot-3 show no photoluminescence in solution, these mechanophores were separately incorporated into linear, segmented polyurethanes (Rot-1-PU, Rot-2-PU, and Rot-3-PU) by way of polyaddition reactions that involved poly(tetrahydrofuran), 4,4′-methylenebis(phenylisocyanate), and 1,4-butanediol. On the basis of our earlier study, the rotaxane content was chosen to be ca. 0.45 wt %, and on account of this low concentration mechanically induced photoluminescence immediately disappeared when the mechanical stress was released, and this instantly reversible ON/OFF switching of the photoluminescence was repeatable without significant change over many cycles. The results show clearly that aside from the different photoluminescence colors the three rotaxanes behave similarly and that applied mechanical forces are transduced to the mechanophores where they induce the temporary separation of the luminophores and NpI moiety. We note that the fact that the mechanoresponse of the three polymers is comparable does not necessarily reflect that the molecular activation energies of the three rotaxanes are indeed the same, as mechanophores with different molecular response may result in very similar macroscopic responses when incorporated into polymers. However, the data unambiguously demonstrate that our molecular design strategy based on the shuttling function of rotaxane structures is robust and versatile.

We monitored the changes of the emission spectra during deformation of films of Rot-1-PU, Rot-2-PU, and Rot-3-PU to obtain more details about their mechanoresponsive luminescence behavior. As shown in Figure S5, all polyurethane films exhibit a gradual increase of the emission intensity when uniaxially stretched, and in each system the emission spectral shapes remain the same; only the intensity varies. The film of Rot-1-PU displays two emission peaks at 430 and 448 nm, which mirror the vibronic structure of the emission spectrum of 1 in chloroform. Because the concentration of the rotaxane-
intensity increases with the applied strain, and the behavior is also observed for a peak observed at 432 nm is decreased. The same tendency was upon gradually stretching the samples to the strain indicated (left) and subsequent relaxation from the maximum strain of 600% (right).

Based mechanoluminophores in the solid polymers is approximately $1.5 \times 10^{-3}$ M, self-absorption significantly affects the emission spectra, and the relative intensity of the peak observed at 432 nm is decreased. The same tendency was also observed for a Rot-2-PU film, which shows emission maxima at 495 and 521 nm. In the case of the orange-emissive Rot-3-PU, a broad emission with a maximum located at 600 nm is observed, also matching the spectral features of 3 in solution. It is noteworthy that, even in the absence of any mechanical stress, films of Rot-1-PU, Rot-2-PU, and Rot-3-PU show very faint photoluminescence (Figure 5), although almost complete quenching was observed in solution (Figure 3). The fact that the photoluminescence was also almost completely quenched in THF, the solvent used to process the films (Figure S11), indicates that the residual photoluminescence observed in the solid materials originates from a small fraction of the rotaxanes in which the emitter is positioned away from the quencher, either on account of kinetic trapping or because the limited molecular mobility makes the shuttling process slow.

As shown in Figure 5, in all polymer films the emission intensity increases with the applied strain, and the behavior is reversible, although in the first elongation and relaxing cycle some hysteresis of the emission intensity is observed, which mirrors our earlier findings with another polyurethane-embedded rotaxane and is related to irreversible rearrangements of the hard phase at high strain. When cyclic tests were also performed beyond the first cycle, all polymers show reversible photoluminescence ON/OFF switching (Figure S12). After the cyclic tests, the samples were redissolved, and the fact that the emission spectra recorded mirror those of directly dissolved materials confirms that no dethreading of the cyclic luminoephores occurred during processing or deformation (Figure S13). Overall, the three rotaxane-containing polyurethanes show a comparable correlation between applied strains and incremental and decremental variation of the emission intensities.

Finally, we blended the three mecanoresponsive polyurethanes and produced a mechanically responsive white-light-emitting elastomer. Through empirical mixing experiments, a weight ratio of 8:16:5 of Rot-1-PU:Rot-2-PU:Rot-3-PU was identified as the best composition to generate white light. It is noteworthy that, at the wavelength used here to excite the blend films (365 nm, see below), the molar extinction coefficient of compound 2 ($\epsilon = 0.24 \times 10^4$ L mol$^{-1}$ cm$^{-1}$) is much smaller than those of compounds 1 ($\epsilon = 2.7 \times 10^4$ L mol$^{-1}$ cm$^{-1}$) and 3 ($\epsilon = 2.0 \times 10^4$ L mol$^{-1}$ cm$^{-1}$) (Figure 3), which explains the large amount of Rot-2-PU that was necessary to achieve white emission. Clearly, the blending approach proved beneficial in the color optimization in contrast to the methods to prepare materials by chemically integrating all three rotaxanes into the same polymer.

Films of the blended material (Rot-Mix-PU) show, like the individual polymers, instantly, reversible photoluminescence switching behavior (Figure 6a and Figure S14, Movie S4).

Under a strain of $\lambda = 600\%$, bright white photoluminescence appears under excitation of 365 nm, while faint photoluminescence was observed for the as-prepared sample. As expected, the initial state recovers after the mechanical stress is released. The CIE coordinates for Rot-1-PU, Rot-2-PU, Rot-3-PU, and Rot-Mix-PU films under strain of $\lambda = 600\%$ were calculated to be (0.15, 0.08), (0.23, 0.54), (0.55, 0.43), and (0.30, 0.31), respectively (Figure 6b), and indicate that Rot-Mix-PU exhibits almost ideal white photoluminescence when uniaxially stretched.
The emission spectral changing behavior was monitored for Rot-Mix-PU upon tensile deformation (Figure 6c and Figure S15). As-prepared film shows faint photoluminescence in the absence of any mechanical stress. The intensities of the emission bands associated with the three luminophores clearly increase when the strain of the film is increased. The spectral shapes associated with the blue- and green-emitting mechanophores are slightly different from those observed in films of Rot-1-PU and Rot-2-PU, respectively, where self-absorption effects in the short-wavelength region that decrease the emission intensities of the peaks corresponding to the 0→0 transitions are more prominent. By contrast, the absorption of the Rot-Mix-PU film covers the wavelength for blue and green emission and shows all features of the emission peaks of the pyrene- and anthracene-based luminophores in solution. We also note that the ratio of the three polymers that afforded white emission in the solid state is different from the composition that afforded a white-emitting solution (Figure S4). Notably, the Rot-Mix-PU films require a much lower content of the red-light-emitting Rot-3-PU and a larger content of Rot-1-PU, which appears to indicate that a combination of self-absorption effect and energy transfer from Rot-1-PU to Rot-2-PU, and from Rot-2-PU to Rot-3-PU, occurs in the solid films. Indeed, while straining Rot-1-PU films to a strain of 600% leads to an increase of the emission intensity of ca. 1600% (λ_em = 430 nm), an increase of only ca. 1000% was observed for the Rot-Mix-PU film at 430 nm. On the other hand, Rot-Mix-PU shows almost the same contrast related to the emission band of Rot-3-PU (ca. 700% at 600 nm). As shown in Figure S16, the Rot-Mix-PU film also shows good reversibility of the emission intensity in all three regions upon cyclic testing. Moreover, after 20 cycles of stretching the sample to a strain of 600% and subsequent relaxation, the emission spectrum (Figure S17a), and the CIE coordinates of Rot-Mix-PU (Figure S17b), remained unchanged, and no changes could be observed when the sample was exposed to another 20 cycles of stretching to a strain of 800% and subsequent relaxation (Figure S18). These results suggest that all three rotaxanes are mechanically robust and do not dethread, even under repeated exposure of the blend to large strains.

**CONCLUSIONS**

In conclusion, we developed the first white-light-emitting polymer that exhibits instantly reversible ON/OFF photoluminescence switching upon stretching and relaxation. The dynamic photophysical properties were achieved by incorporating blue-, green-, and orange-light-emitting supramolecular mechanophores based on interlocked rotaxane motifs. The present study highlights one of the advantages of rotaxane-based supramolecular mechanophores, i.e., that the photoluminescence color of such motifs can easily be tailored by replacing the luminophore and optionally combining several mechanophores in one material. While it might in principle be possible to create a multilayer assembly that emits white light under very specific conditions by stacking films of the three different polymers reported here, we note that, because of the different absorption spectra of the three layers, internal absorption effects (of both absorbed and emitted light) will have caused the emitted color to depend on the excitation direction and angle. The here-reported blends are symmetric, and off-white hues are only observed under very oblique angles (Movie S5). While it has yet to be investigated to what extent the molecular activation energies of the three rotaxanes are comparable, their response to macroscopic forces is the same in the soft polyurethanes investigated here, which bodes well for the chemical integration of multiple such mechanophanes at strategically selected positions of the same polymer (e.g., backbone and cross-links) to monitor stress distributions at the molecular level in situ. In addition, the supramolecular mechanoluminophores studied here appear to be activated by very small mechanical forces, which renders them useful for mechanobiology experiments, which are currently ongoing.

**ASSOCIATED CONTENT**

3** Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.9b00173.

Experimental procedure and additional data (PDF)

Movie S1: mechanoresponsive luminescent behavior upon cyclic stretching of Rot-1-PU film (MP4)

Movie S2: mechanoresponsive luminescent behavior upon cyclic stretching of Rot-2-PU film (MP4)

Movie S3: mechanoresponsive luminescent behavior upon cyclic stretching of Rot-3-PU film (MP4)

Movie S4: mechanoresponsive luminescent behavior upon cyclic stretching a white-light-emitting polyurethane film made from the blend Rot-Mix-PU, showing reversible photoluminescence switching behavior (MP4)

Movie S5: mechanoresponsive luminescent behavior upon cyclic stretching a white-light-emitting polyurethane film made from the blend Rot-Mix-PU, with off-white hues only observed under very oblique angles (MP4)

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**Notes**

The authors declare no competing financial interest.

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