Supramolecular Metallogels

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Light-Powered Self-Healable Metallosupramolecular Soft Actuators

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Abstract: *Supramolecular functional materials able to respond to external stimuli have several advantages over their classical covalent counterparts. The preparation of soft actuators with the ability to respond to external stimuli in a spatiotemporal fashion, to self-repair, and to show directional motion, is currently one of the most challenging research goals. Herein, we report a series of metallopolymers based on zinc(II)–terpyridine coordination nodes and bearing photoisomerizable diazobenzene units and/or solubilizing luminescent phenylene–ethynylene moieties. These supramolecular polymers act as powerful gelating agents at low critical gelation concentrations. The resulting multiresponsive organogels display light-triggered mechanical actuation and luminescent properties. Furthermore, owing to the presence of dynamic coordinating bonds, they show self-healing abilities.*

The preparation of smart soft materials able to respond to external stimuli and translate them into a well-defined, controllable, and reversible macroscopic action is one of the most fascinating and challenging current research goals.[1] The development of soft actuators able to mimic expansion–contraction functions, undergo directional motion, and self-repair is of paramount importance and is particularly difficult to achieve. Supramolecular chemistry, which employs components held together by weak intermolecular forces, is an ideal method to prepare such smart functional materials by means of a powerful bottom-up approach.[2]

The preparation of chemical species bearing functional moieties able to respond to an external stimulus, such as electrical input,[3] pH,[4] humidity,[5] redox,[6] pressure,[7] and light,[8] has led to the development of attractive materials that have shown expansion–contraction and self-healing properties.[9] In this respect, light is a powerful external stimulus because of the possibility to remotely trigger and spatiotemporally control the action with high precision.[10]

To date, reports on light-induced soft actuators are relatively scarce. This type of material is usually based on host–guest interactions, liquid-crystalline materials, crystals, or polymers containing photoswitchable units (such as diarylethene or azobenzene moieties) which can be switched either between two energy minima (bistable systems) or from the ground state to a light-promoted, far-from-equilibrium state with concomitant variation of the molecular geometry.[10,11]

Herein, we report the design and preparation of light-powered soft actuators based on metallosupramolecular polymers; a straightforward approach for the preparation of photoresponsive systems. The designed supramolecular materials are able to act as organogelators at low critical gelation concentrations (CGC). Thanks to the reversible and dynamic metal–ligand coordination bond, the photoresponsive organogels demonstrate the ability to self-heal. Finally, owing to the presence of photoresponsive moieties within the metallopolymer backbone, the prepared supramolecular gels display macroscopic and light-induced orientation-dependent volume reduction and syneresis under UV light exposure.

Our molecular design starts from the synthesis of ditopic ligands leading to supramolecular metallopolymers that can be easily obtained by simply mixing a metal salt and ligand in the desired ratio. Our ditopic ligands of choice are terpyridyl (tpy) moieties owing to the wide synthetic accessibility of 4′-substituted terpyridines,[12] the reversible coordination-bond formation between tpy and Zn^{II} ions (ligand scrambling), along with large equilibrium constants. The large equilibrium constants provide the thermodynamic driving force towards supramolecular polymerization.[13] Introduction of diazobenzene moieties into the backbone of the ditopic tpy ligands (**A**; see Scheme 1 for ligand structures), which is able to act as a photoinduced switch between a *trans* and a *cis* conformation, is expected to allow large molecular geometry variation as a consequence of the conformational change, that is, the light-triggered response. Furthermore, introduction of rigid π-conjugated small phenylene ethynylene (PE) moieties in the ditopic tpy, namely **B**, allowed modulation of the solubility and π–π stacking ability of the resulting supramolecular metallopolymeric organogelator. This approach readily facilitates the introduction of luminescence, thus yielding a multifunctional supramolecular organogel (Figure 1).[1e,13d] In this way, we prepared a small library of Zn-containing metallo-copolymers incorporating **A** and **B** ligands in different ratios, thus modulating (multi)functionality and the rheological properties of the resulting material.

The synthesis of the Zn-based metallopolymers is depicted in Scheme 1.[14] Ditopic ligands **A** and **B** were

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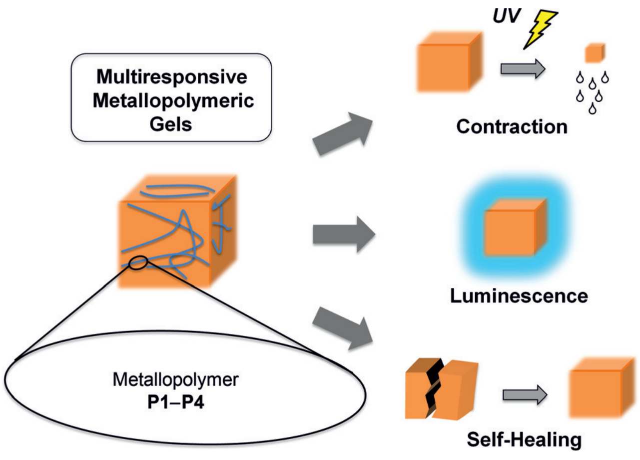


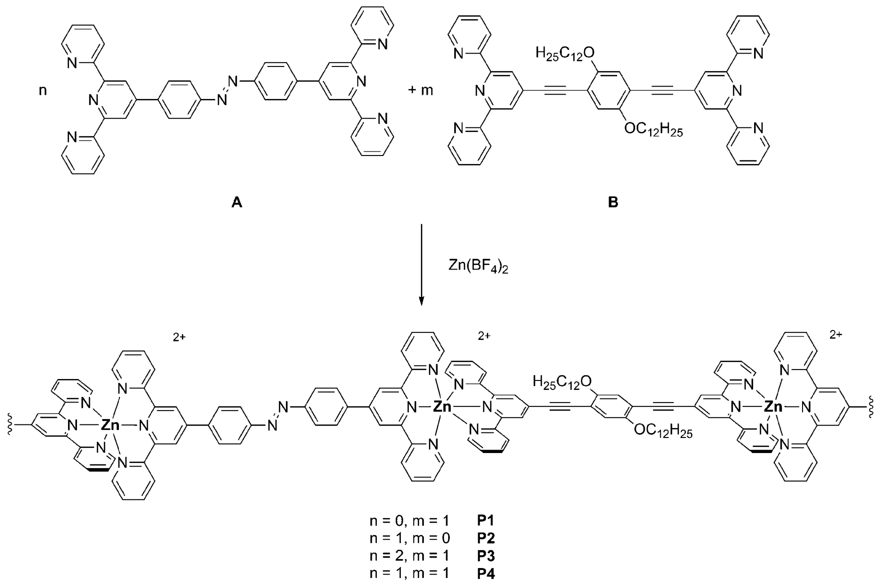
Figure 1. Schematic representation of the properties of the metallo-supramolecular polymers and their corresponding gels reported herein. These properties include light-powered actuation, photoluminescence, and self-healing. For the structures of metallopolymers **P1**–**P4**, see Scheme 1.

heated in the presence of $Zn(BF_4)_2$ at various stoichiometric ratios in chloroform. Homo-metallopolymers **P1** and **P2** (where **P1** contains just ligand **B**, and **P2** just ligand **A**) and metallo-copolymers **P3** and **P4** (with ligand ratios **A**:**B** of 2:1 and 1:1, respectively) were obtained as orange powders. Unfortunately, it was not possible to obtain information about the exact arrangement of the monomers (either random or alternated) along the polymer chains because of the large signal overlap in the NMR spectra (see the Supporting Information, Figure S1). We thus assume a random distribution in both copolymers on the basis of the dynamic nature of the Zn–tpy bonds (see the Supporting Information for further details).

To obtain deeper insight into the self-assembly processes yielding the metallo-copolymer, we titrated $Zn(BF_4)_2$ into a solution containing equimolar amounts of **A** and **B** and monitored the reaction by UV/Vis absorption spectroscopy (Figure S2, top).[13a,b] The intensity of the lowest-energy absorption band at $\lambda_{abs} = 450$ nm, ascribable to a transition with intraligand charge transfer (ILCT) character, was plotted as function of the Zn^{II}/ligand ratio (Figure S2, bottom).[13a,b,15] Two different regimes of absorbance increases could be detected until 1 equivalent of Zn^{II} had been added. Notably, after the addition of the first 0.5 equivalents, the slope of the plot became slightly less steep, most likely indicating preferential coordination of one ligand with respect to the other under the experimental conditions used. However, a randomization (ligand shuffling) along the polymer chains is expected to occur over a longer timescale as a consequence of the dynamic nature of the tpy–Zn coordination. After addition of the first equivalent of Zn^{II}, further addition until a total of 2 equivalents had been added led to further spectral changes as a consequence of the Zn-mediated depolymerization. Overall, these findings confirm the formation of a hetero-metallopolymer, where each of the Zn cations are complexed with two terpyridine moieties at a Zn:ligand ratio of 1:1.[13b]

Upon photoirradiation at $\lambda = 410$ nm into the ILCT band (a wavelength that is not expected to promote *trans*-to-*cis* isomerization on the basis of the UV/Vis absorption spectra) solutions of metallopolymers **P1**, **P2**, **P3**, and **P4** (10 μM in dimethylformamide (DMF)) displayed luminescence with emission maxima centered at $\lambda = 453$, 483, 455, and 454 nm, respectively, photoluminescence quantum yields (PLQY) up to 41 % for **P4**, and excited-state lifetimes between 2.5 and 2.9 ns (Figure S3 and Table S1). Similarly to what is detected in the electronic absorption spectra and by comparison with related Zn–tpy metallopolymers,[13a,b] such an emission is ascribed to the lowest-lying excited state with ILCT character involving the PE and the Zn–tpy moieties.

Finally, the *cis*/*trans* isomerization ability of metallopolymer **P3** containing diazobenzene photoswitching units has been evaluated in DMF solution at a concentration of 0.02 mg mL^{-1} upon irradiation at $\lambda_{exc} = 365$ nm (Figure S4). Isomerization to the *cis* conformation was achieved with a LED light source and the photostationary state (PSS) was reached after only 150 s. Interestingly, the *trans* form can be recovered in the same timescale by simply irradiating the sample under visible light at $\lambda_{exc} = 455$ nm (Figure S4, right).[16] Noteworthily, the photoinduced process could be repeated many times without any sizeable change in the UV/Vis absorption spectra (Figure S5), which confirms the possibility to independently address luminescence and photoisomerization processes within the system upon selecting a longer excitation wavelength ($\lambda_{exc} = 410$ nm



Scheme 1. Synthesis of homo-metallopolymers **P1** and **P2** and random metallo-copolymers **P3** and **P4**.

versus 365 nm, respectively). On the other hand, both luminescence and *trans*-to-*cis* isomerization are photoinduced upon excitation of the metallopolymer at $\lambda_{exc} = 365$ nm.

We found out that upon dissolution of the polymers in DMF and addition of a nonsolvent, such as CH_2Cl_2, EtOH, MeOH, AcOEt, or THF, **P3** and **P4** can act as powerful organogelators, most likely as a result of the establishment of extended interchain π–π interactions. In contrast, **P1** does not display any gelation abilities under similar conditions, whereas **P2** tends to precipitate because of the low solubility of the ligand moieties. Interestingly, the mechanical and gelation properties of the material can be tuned to a certain extent by simply varying the photoswitchable/solubilizing ligand ratio (that is, **A**:**B**) within the metallopolymer. **P4** displays poor gelating ability and the corresponding organogels appear soft to such an extent that they were difficult to handle at the macroscopic scale (data not shown). In particular, a stiffer gel with improved properties was obtained upon increasing the content of ligand **A** with respect to that of **B**. Using the reverse vial test, it was found that polymer **P3** had a CGC value as low as 0.12 wt.% in a solvent mixture of DMF:EtOH 1:20 v/v, meaning that it can be classified as supergelator. These findings indicate that the gelating properties and the stiffness of the resulting gel can be easily modulated upon variation of the ligand **A**:**B** ratio within the metallopolymers.

Moreover, the **P3** gel retains the photophysical properties detected for the polymer in solution (Table S1, Figure S3 (right), and Figure S6). Upon irradiation at $\lambda_{exc} = 410$ nm, the organogel displayed intense photoluminescence with maxima at $\lambda = 450$ and 543 nm, where the higher and lower energy emission bands can be attributed to the Zn^{II}–**B** fragment and to interchain π–π stacking interactions between PE moieties, respectively.

To more thoroughly investigate the mechanical properties of these novel materials, a series of rheological experiments was carried out on the **P3** organogel (prepared at 1.5 wt.% in DMF:EtOH 1:2 v/v). Using this system we studied: a) the dependency of the shear modulus (storage modulus G' and loss modulus G'') on frequency and b) the dependency of the G' and G'' values upon applied strain.[17] At low values of applied stress (0.5 % of strain), the modulus of the gel showed a linear response as function of the frequency (Figure S7), whereas a nonlinear behavior was detected by varying the shear stress (Figure S8). The yield point was found to be around 10 % of strain after which the G' value decreases rapidly leading to a gel–sol transition at around 60 % of strain ($G' < G''$ at strain greater than 60 %). This behavior indicates that at this applied stress value, the network of the gel is broken. Finally, the G' value exceeds the G'' value by around one order magnitude ($\tan\delta = G''/G' \approx 0.11$), although the gels display a rather soft nature.

The supramolecular polymer network includes reversible and dynamic bonds within the metallopolymeric chain that are prone to ligand exchange and reshuffling following metal–ligand de-coordination events,[13h,18] that is, gel-network breaking.

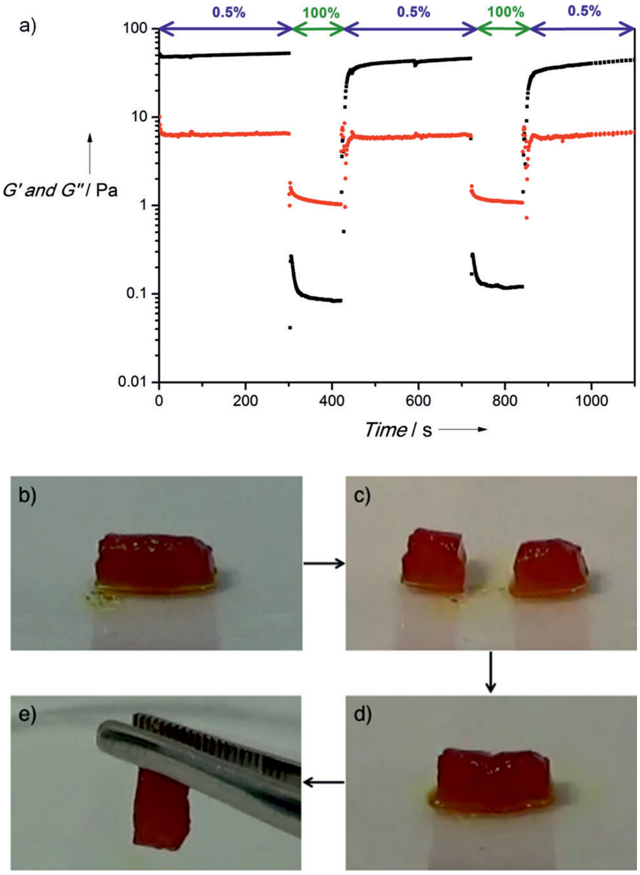


Figure 2. a) Rheological monitoring of the self-healing process, monitoring G' (black) and G'' values (red) of the **P3** organogel (1.5 wt.% in DMF:EtOH 1:2 v/v) using continuous-step strain measurements (10 °C). b–e) Frames taken from Movie S1 showing photographs of supramolecular gel **P3** b) before and c) after damage, d) after free standing for 1 min, e) after free standing for 15 min.

The self-healing properties of this novel supramolecular organogel comprising photoresponsive units has been investigated by carrying out a break test. We measured the rheological properties of the **P3** organogel (1.5 wt.%, DMF:EtOH 1:2 v/v) under small (0.5 %) and large strain (100 %) and the results are displayed in Figure 2a. Under 0.5 % strain, G' values were larger than G'' values by about one order of magnitude ($\tan\delta = 0.11$) resulting in a self-standing organogel, whereas the opposite behavior was detected under 100 % strain. Indeed, under such high strain, the G'' values were larger than the G' values, indicating that the organogel is now in the sol state ($\tan\delta = 12.3$). This dramatic change of values is most probably because of the interchain interactions and ligand–Zn bond breakage under these specific conditions. When returned to 0.5 % strain, the G' and G'' returned to their original values. The complete recovery of G' and G'' values after approximately 300 s confirmed the self-healing ability of the organogel (Figure 2a). Additionally, the macroscopic self-healing abilities of the gel were investigated and the results are displayed in Figure 2b–d (see also Movie S1 in the Supporting Information). The images show that pieces of the gel can undergo self-healing upon placing the broken faces of the gel into close contact for only 15 min.

The presence of photoresponsive moieties in the polymer backbone prompted us to study light-induced actuation on the macroscopic scale. Upon irradiation of the **P3** organogel (0.2 wt.% in DMF:EtOH 1:20 v/v) in a 1 × 1 cm quartz cuvette with a light source at $\lambda_{exc} = 365$ nm, a continuous macroscopic contraction of the gel is observed (Figure 3; see also Figure S9 and Movie S2). The gel contracts by a value as high as 85 % of its initial volume and the contraction is accompanied by a concomitant release of an excess of the solvent mixture (that is, a syneresis process, see the kinetic experiment in Figure S10). To unambiguously prove that it is a photomechanical action rather than a simple melting process, the concentration of the Zn ions in the expelled solution has been analyzed by means of ICP-MS and compared to the Zn ion concentration in the original gel. We found that in the excreted solution, the Zn^{II} ion concentration is 9 ppm, in contrast to the 112 ppm of Zn^{II} ions present into the original organogel, indicating that only a very small leakage of metallopolymer accompanies the large photomechanical actuation.

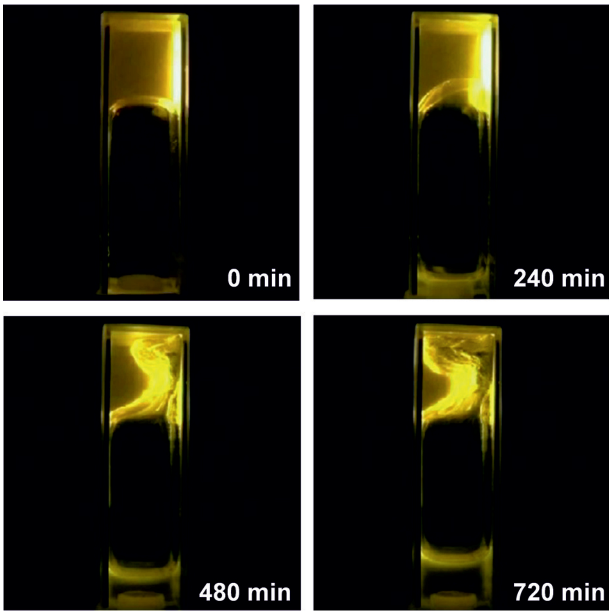


Figure 3. Contraction of the gel upon continuous UV photoirradiation ($\lambda_{exc} = 365$ nm) showing the macroscopic photomechanical response. The images are taken from Movie S2 at different time points (indicated in each box).

Thus, upon UV photoirradiation a *trans*-to-*cis* photoisomerization process takes place within the ligand **A** units, which induces a large variation of the molecular structure of the metallopolymer chains. We believe that the decreased flatness of the *cis* form of **A** in the metallopolymer units may decrease the π–π interchain interaction rendering π-stacking much less favorable. As a consequence, macroscopic collapse of the organogel occurs. Unfortunately, the photoisomerization process cannot be reversed by simply irradiating the contracted gel with visible light at $\lambda_{exc} = 450$ nm in the presence of a solvent mixture of DMF:EtOH 1:20 v/v because of the poor solubility of **P3** in a solvent system with such a high EtOH content. Nonetheless, we found that, upon solvent removal and dissolution in DMF, ligand **A** units present in the photoresponsive metallopolymer **P3** can be thermally isomerized back to the *trans* form and thus reused, while maintaining both the organogelation ability and photomechanical properties for up to several cycles (Figure S11).

In conclusion, we have reported the design and characterization of photoresponsive supramolecular metallopolymers, which bear photoisomerizable units and are able to act as supergelators in organic solvents. The so-prepared gels are luminescent as a consequence of the presence of π-conjugated emissive units in their backbone. Even more importantly, the organogels are able to quickly self-heal owing to the presence of dynamic and reversible Zn–tpy coordination bonds, and can act as light-triggered soft actuators. These compounds are the first examples of light-powered self-healable soft actuators based on supramolecular metallopolymers. Introduction of further functionalities able to promote gelation in aqueous media as well as redox- and pH-responsive moieties can now be envisaged by employing this modular and straightforward bottom-up synthetic method. These findings encourage investigation of high-performance multiresponsive materials based on metallosupramolecular polymers, with further improvements in terms of mechanical properties and the responsiveness of the materials still needed. Finally, by taking advantage of both luminescence and photomechanical properties of such organogels, their use in biomedical and bioengineering applications to locally promote light-induced actuation and drug release can be anticipated.

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