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Dynamic Supramolecular Ruthenium-based Gels Responsive To Visible/NIR Light And Heat

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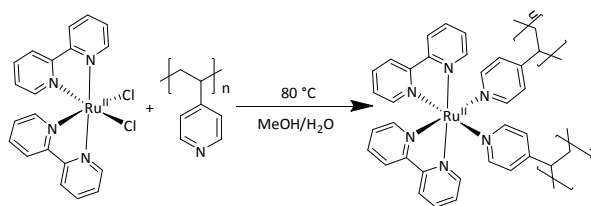
Abstract: A simple supramolecular crosslinked gel is reported with a photosensitive ruthenium bipyridine complex functioning as a crosslinker and poly(4-vinylpyridine) (P4VP) as a macromolecular ligand. Irradiation of the organogels in H₂O/MeOH with visible and near infrared (NIR) light (in a multi-photon process) leads to cleavage of pyridine moieties from the ruthenium complex breaking the cross-links and causing degelation and hence solubilisation of the P4VP chains. Real time (RT) photorheology experiments of thin films showed a rapid degelation in several seconds while larger bulk samples could also be photocleaved. Furthermore, the gels could be reformed or healed by simple heating of the system and restoration of the metal-ligand cross-links. The relatively simple dynamic system with a high sensitivity towards light in the visible and NIR region make them interesting positive photoresists for nano/micropatterning applications, as was demonstrated by writing, erasing and rewriting of the gels by single and multiphoton lithography.

The field of supramolecular polymers aims to use directional intermolecular forces^[1] to prepare dynamic materials. These so called "dynamers" are designed to undergo reorganization via reversible chemical reactions under the influence of external factors^[2]. The dynamicity can be incorporated either by reversible covalent or non-covalent bonding, such as defined hydrogen bonding moieties, or alternatively via ionic bonding or coordinating metal bonds^[2]. Metallopolymers can offer unique properties and a number of supramolecular systems have been developed based on dynamic ligand-metal interactions^[3]. Such materials have been investigated in a wide field of applications, for example the transduction of mechanical force into chemical reactions^[4], as well as in dynamic self-healing^[5] and optically

healable materials^[6]. Also a number of ruthenium-containing metallopolymers have been reported, with a particular focus on their use as stimuli responsive polymers^[7].

Meanwhile, photocleavable polymers, that is polymers which cleave or degrade in response to irradiation with certain wavelengths of light have been recently developed^[8]. Incorporation of known photocleavable protecting groups, also sometimes referred to as photocages,^[9] into macromolecular systems is one route to achieve this goal. Examples include the incorporation of coumarin^[10] or o-nitrobenzyl^[11] groups into polymeric materials^{[12],[10]} to achieve selective photodegradation.

While materials responsive to UV-light have long been established, there has been a recent shift in the field towards the use of photochemical processes which respond in the visible and near infrared (NIR) region^{[13],[11a]} due to the poor penetration of high energy UV-light as well as its incompatibility with biological environments.^[14] Also light-sensitive ruthenium-based complexes have been shown to be responsive to light with long wavelength^[15] for example for photodynamic therapy with deep tissue penetration. Various complexes based on a *cis*-[Ru^{II}(bpy)₂(L₁)(L₂)]²⁺ structure are established as photocages^[16] and show a rapid cleavage of ligands upon excitation with visible light, as well as two-photon process in the NIR region. Furthermore, such complexes have recently been incorporated into hydrogels to achieve degelation and enable microphotopatterning^[17] and the light-triggered release of enzymes^[18].



Scheme 1. Reaction scheme for the synthesis of Ru(bpy)₂Cl₂ and poly(4-vinylpyridine)

Herein we report the use of ruthenium bipyridine complexes as a crosslinker for the polymer poly(4-vinylpyridine) (P4VP) which acts as a macromolecular ligand, binding to the ruthenium centers and hence cross-linking the polymers. The procedure of the gel preparation was identical for all gels, just the concentration of the ruthenium complex was varied. Briefly, poly(4-vinylpyridine) (P4VP; $M_w \sim 60\,000\text{ g mol}^{-1}$) was

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crosslinked with $\text{Ru}(\text{bpy})_2\text{Cl}_2$ through complexation with the polymer bound pyridine ligands in a water/methanol ($v/v = 2/3$) mixture at 80°C for 16 hours (**Fehler! Verweisquelle konnte nicht gefunden werden.**) upon which gelation occurred (see SI for full experimental details). The ligand exchange at the ruthenium atom with P4VP can be observed by UV/vis spectroscopy (Figure 1), shown as an example for the gel with 5 mol% of the ruthenium complex. A thin layer of the gel (1 mm) was applied between two glass slides and measured in the UV/vis spectrometer. For comparison, the spectrum of $\text{Ru}(\text{bpy})_2\text{Cl}_2$ is included in Figure 1 with its characteristic MLCT transition observed at 491 nm. The complexation with the pyridine moieties to the ruthenium atom shifts the peak maximum to 461 nm with a shoulder at ~ 435 nm. The observed shift is typical for the MLCT peak of comparable ruthenium-pyridine complexes^[17,19]. Above ~ 600 nm no significant absorption is observed (see Figure S4).

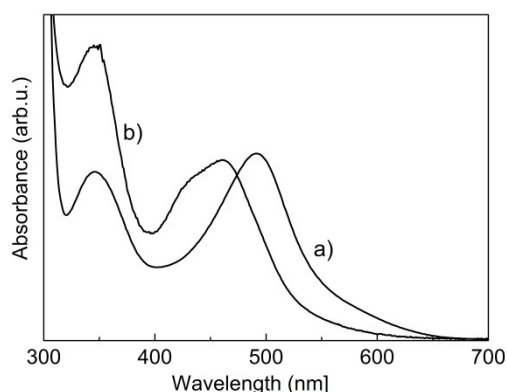


Figure 1. Absorption spectra of (a) $\text{Ru}(\text{bpy})_2\text{Cl}_2$ in water and (b) the ruthenium containing P4VP gel in water/methanol (5 mol % Ru)

In order to compare different crosslinker ratios, bulk gels with 5, 10, 15 and 20 mol% of $\text{Ru}(\text{bpy})_2\text{Cl}_2$ per pyridine unit were prepared (see SI). Accordingly, with higher ruthenium ratios the color of the obtained gel becomes darker and the gel more brittle. Additionally, the crosslinking ratio also impacts the gelation time. P4VP gels with 20 mol% of $\text{Ru}(\text{bpy})_2\text{Cl}_2$ are formed in about 15 minutes while standing at room temperature and gels with 5 mol% require up to 60 minutes until complete gelation.

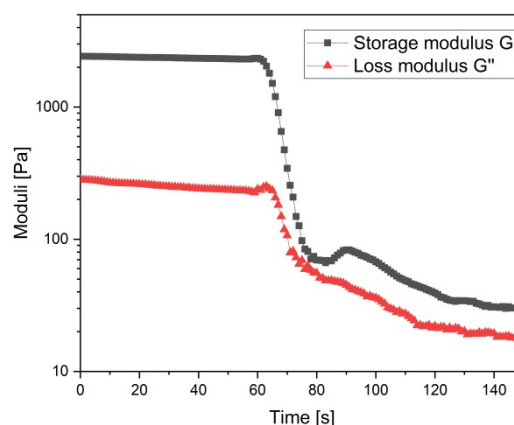
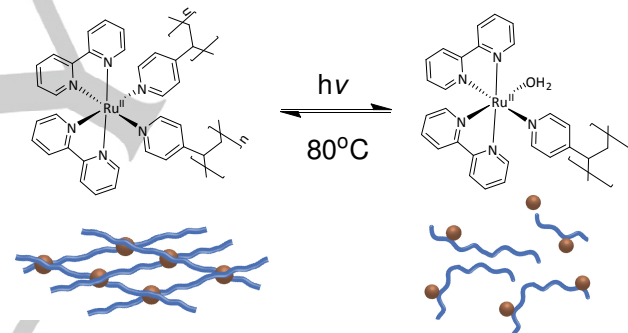


Figure 2. Polymer with 5 mol% ruthenium cross-linker (85.9 mg in 2.5 mL water/methanol ($v/v = 2/3$)). Light was switched on after 60 seconds. The significant decrease in modulus represents a reduced resistance to deformation, indicating a liquefaction of the gel caused by de-crosslinking upon irradiation.



Scheme 2. Dynamic reversible gels formed by binding of ruthenium to the P4VP macromolecular ligand.

All obtained gels remain solid in the dark for at least > 12 months. The sensitivity to light was investigated by photorheology for polymers with 5% ruthenium cross-linker content (Figure 2). Real-time (RT)-photorheology experiments in which thin films are exposed to a light source were directly measured on the rheometer plates^[20]. The storage modulus G' and the loss modulus G'' of the gels were measured in oscillation mode (1% deformation, 10 rad s^{-1} , for further details and explanations see SI). Upon irradiation (365 nm , 25000 mW cm^{-2}) an immediate and rapid decrease in moduli was observed, indicative of a de-crosslinking of the gel^[21] through cleavage of the pyridine moiety of the P4VP from the complex.

Degelation of the bulk samples was also investigated. Upon irradiation of the P4VP gel in a 10 mL pyrex culture tube with visible light $> 395 \text{ nm}$ the gel becomes liquid. The kinetics differ from the RT-rheology experiments due to the different light source used and different thickness and hence penetrability of the samples. As expected, the degree of crosslinking ratio also impacts the cleavage time due to the increased number of cross-links but predominantly due to the increased absorbance

of the incident light by the ruthenium chromophore. While the P4VP with 5 mol% Ru cross-linker becomes dissolved within 10 minutes, the sample with 15 mol% requires up to 60 minutes until the reaction mixture becomes liquid (see Figures S1-S3). Meanwhile for the P4VP gel with 20 mol% of $\text{Ru}(\text{bpy})_2\text{Cl}_2$ no degelation was observed, presumably due to higher absorption of light and hence the lower penetration of light into the system. The cleavage of the ligand can also be followed via UV/vis spectroscopy (Figure S4). Since only one of the pyridine ligands is cleaved in water^[17,22] the change in the absorption spectra is indicated through a slight shift of the MLCT band.

It was postulated that since the gelation reaction is initiated by an exchange of H_2O ligands in the ruthenium complex with pyridine ligands^[17], and since $[\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})(\text{py-P})]^{2+}$ (py-P = one pyridine group of P4VP) is known to be the product of the photoreaction, then the gelation reaction would be thermally reversible (Scheme 2). Simple heating of the sample in the (RT)-photorheology experiments indeed showed an increase in modulus (Figure S5), although heating of thin films caused some solvent evaporation, which may interfere with the read-out. The process was thus investigated on bulk samples with a rotational viscometer in a pyrex culture tube. The viscosity of the ~15 % P4VP $[\text{Ru}(\text{bpy})_2\text{Cl}_2]^{2+}$ mixture increased to a maximum of 12 800 mPas upon heating for 16 h hours at 80°C (Figure 3). Upon irradiation with visible light >395 nm the value decreases to near its initial value of around 320 mPas, suggesting a near complete degelation and hence solubilisation of the P4VP chains.

Interestingly the reversible gelation/degelation process could be repeated with a number of cycles, as shown for the gel with ~15 % Ru in Figure 3 and S5. The maximum viscosity of the gel appears to decrease with increasing number of cycles, suggesting a reduced extent of cross-linking as the system is reheated. It should however be stressed, that the viscosity experiments had to be carried out under ambient conditions. After 8 cycles gelation could not be achieved for this cross-linker concentration. This is presumably due to some oxidation of the ruthenium centres to Ru(III) over time. It is well known that Ru(II)-bpy complexes are efficient photo-reductants^[23]. The formed Ru(III) complexes are in general less prone to ligand exchange reactions and to our knowledge no analogous photo-substitution has been reported for Ru(III)-bpy complexes. Hence, the decreasing number of reactive ruthenium(II) centres available for crosslinking leads to a loss of gelation ability.

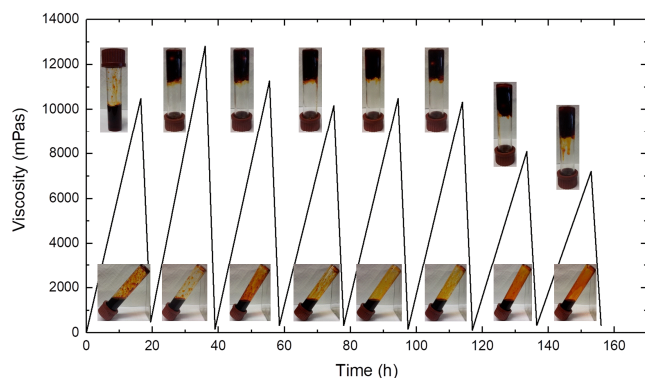


Figure 3. Rotational viscosity measurements of the ruthenium cross-linked P4VP (~15% Ru). The gelation/de-gelation cycle is as follows: (i) Complexation by heating at 80°C, (ii) gelation at r.t., (iii) measurement of viscosity, (iv) irradiation at $\lambda > 395$ nm, (v) measurement of viscosity.

Since it was anticipated that the photocleavage is locally restricted, a gel containing test tube was covered with aluminum foil leaving a strip of 1 cm uncovered. The tube was then exposed to visible light leading to the degelation and solubilisation of the P4VP chains (Figure S7). Upon subsequent immersion of the test tube in a water bath at 80 °C, a complete gel was obtained again, suggesting a potential use of the polymers as healable materials.

Furthermore, to demonstrate the potential for micropatterning, logos were written into gel portions (Figure 4) containing 5 mol% and 15 mol% of ruthenium crosslinker. These polymer samples were enclosed between two glass slides and properly sealed. The micropatterning could be achieved both by focused NIR-laser light at 1028 nm (2 mW 15% gel, 20 mW 5% gel) in a multi-photon process^[24,25], as well as by single-photon laser at single photon lithography (1PL) at 514 nm (2 μW 15% gel). To verify the micropatterning, images were acquired directly after writing with the same setup using an infinity corrected NIR air microscopy objective (50x/0.42). For imaging we used either an industrial camera for white light images or a single photon avalanche diode for backscattered images (see Figure S8). Upon smoothly heating the gel samples on a hot plate at 60°C for 1 hour, the logos were observed to disappear. Subsequently, the same area of the gel was rewritten using the same MPL and 1PL conditions. All acquired images were contrast enhanced.

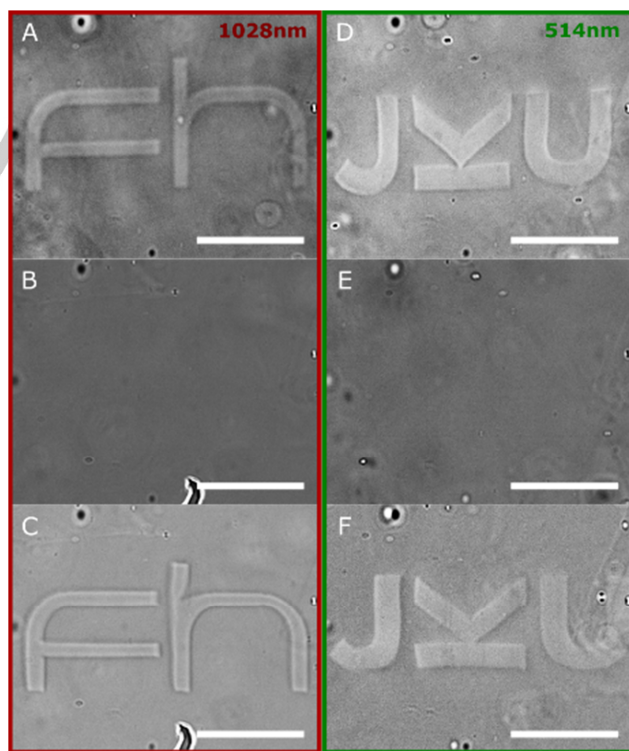


Figure 4. Contrasted white light images showing the writing, erasing and rewriting of the gels. (A) The 15 mol% hydrogel after writing the FH logo by

multiphoton photon lithography (MPL) at 1028 nm (B) After thermal healing treatment and (C) rewriting the same area by MPL. (D-F) The same process is repeated with single photon lithography (1PL) at 514 nm. All scale bars are 50 μm .

In summary, a simple crosslinked gel was prepared based on P4VP as a macromolecular ligand cross-linked with $\text{Ru}(\text{bpy})_2\text{Cl}_2$ complexes. Photocleavage of the metal-ligand bond upon irradiation broke the linkage between the macromolecules leading to degelation and hence solubilisation of the PV4P chains. RT-rheology experiments of thin films showed a rapid degelation in several seconds while larger bulk samples could also be photocleaved in several minutes, depending on the concentration of ruthenium and penetrability of light into the gels. Furthermore the system was shown to be reversible with the gel being reformed upon heating, a process which could be cycled a number of times. The gels were prepared by simple mixing and heating and the properties could be tuned by the ratio of crosslinker to polymer. The relative simplicity of the system combined with the high sensitivity of the systems to light in the visible and NIR region make them highly interesting novel materials for lithographic applications. In this context micropatterning of the gels was demonstrated by multiphoton and single photon lithography at 1028 and 514 nm respectively and it was shown that the gels could be positive photoresist erased, healed and rewritten on the same region of the gel. The multiphoton absorption for 1028 nm wavelength process however needs to be analysed in more details. The assumption of a multi-photon process is based on earlier findings¹.

Acknowledgements

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Keywords: photosensitive gels • metallopolymer • ruthenium • multi-photon absorption • self-healing

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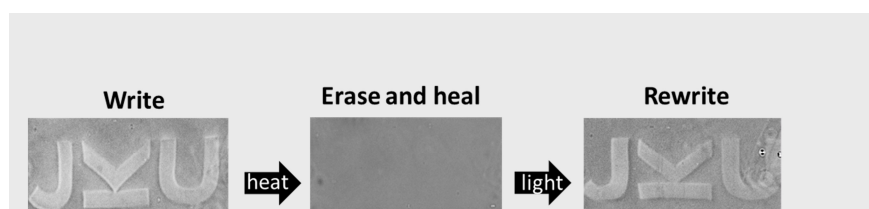
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Dynamic Supramolecular Ruthenium-based Gels Responsive To Visible/NIR Light And Heat



Polymer Etch a Sketch: A simple supramolecular crosslinked gel of polyvinylpyridine (P4VP) with a photosensitive ruthenium bipyridine crosslinker shows reversible gelation upon exposure to light and heat allowing writing, erasing and rewriting using one-photon or multi-photon lithography