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Active Cross-Linkers

Active Cross-Linkers that Lead to Active Gels**

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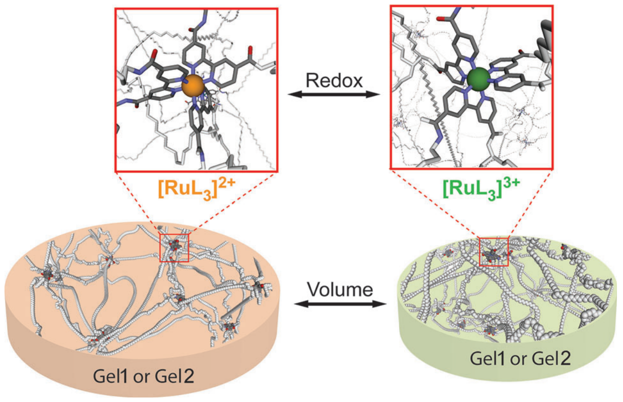
This communication describes the design, synthesis, and structure of the first ruthenium-complex-based hyper-cross-linker for creating a novel type of active gels as a chemomechanical soft material. Gels, which are soft materials composed of a three-dimensional (3D) network and a large amount of liquid, have found a wide range of applications, from biomedicine (for example, as a medium for tissue engineering[1]) to consumer products (for example, hair gels). Cross-linking, physically or covalently, is the fundamental and necessary attribute to produce a 3D network in a gel. Unlike supramolecular gels,[2] which are constructed through reversible, non-specific, and physical cross-linking, polymeric gels[3] usually rely on bifunctional cross-linkers (for example, bisacrylamide[4]) that become inactive after the formation of the covalent cross-links during the polymerization.

Whereas most cross-linkers in synthetic networks are less active, cross-linkers in biopolymer networks are active. For example, the cytoskeleton of muscle cells has myosin motors as the active cross-linkers to cross-link actin filaments.[5] Inspired by this process of converting chemical energy into mechanical motion, researchers have spent considerable efforts on using actin and myosins to create active gels in vitro to explore the structures and dynamics of these minimal active networks.[6] Encouraged by these developments, we developed an active cross-linker based on the tris(bipyridine) ruthenium complex ($[\mathrm{Ru(bipy)_3}]^{n+}$, $n = 2$ or 3) for the construction of novel polymer networks (Scheme 1). We made such a choice for several reasons: First, although active or functional molecules are increasingly used for making supramolecular gels,[7] such as self-healing soft materials,[7a,8] it is rather rare to generate polymeric gels by active cross-linkers.[8b,9] Second, $[\mathrm{Ru(bipy)_3}]^{n+}$, a well-known coordination compound,[10] has a long-lived excited state that has both oxidizing and reducing properties, which has attracted enduring research interests. Although its derivatives have served as photosensitizers,[11,12] electrochemiluminescent components,[13] the core of bacteria-sensing elements,[14] components for conducting polymers,[15] and as cores of star polymers,[16] the capacity of $[\mathrm{Ru(bipy)_3}]^{n+}$ as an active or hyper cross-linker has yet to be explored. Third, $[\mathrm{Ru(bipy)_3}]^{n+}$, in particular, also serves as a redox catalyst for a well-established chemical oscillator, namely the Belousov–Zhabotinsky (BZ) reaction.[17] The redox switch of the $[\mathrm{Ru(bipy)_3}]^{n+}$ complex has led to the development of a self-oscillating gel that swells in its oxidized state ($\mathrm{Ru^{III}}$) and shrinks in its reduced state ($\mathrm{Ru^{II}}$) during the BZ reactions.[18] However, in that type of gel, *N*,*N'*-methylenebis(acrylamide) (BIS)[19] is the cross-linker and the ruthenium(II/III) complex is the pendant of the cross-linked chains of poly(*N*-isopropylacrylamide).[4,20] Because of the stereochemical configuration of the $[\mathrm{Ru(bipy)_3}]^{n+}$ complex, its application as a cross-linker would result in an unprecedented molecular architecture for developing active gels as chemomechanical materials.



Scheme 1. Conceptual illustration of the active hyper cross-linker that gives rise to active gels, and the volumetric oscillation of the gels induced by the redox switch of the active hyper cross-linker **1** during the BZ reaction (side chains of the polymers are omitted for clarity).

Based on the above-described rationale, to evaluate the correlation between the molecular architecture and the chemomechanical behavior of a soft material, we used the $[\mathrm{Ru(bipy)_3}]^{n+}$ based active cross-linker **1** (Figure 1 a) and two distinct monomers, *N*-isopropylacrylamide (NIPAAm) and allylamine, for the polymerization that results in two active gels, Gel 1 and Gel 2, respectively. As shown in Scheme 1, both Gel 1 and Gel 2 employ the active cross-linker **1** as the cross-linker to construct the 3D polymeric network. During the BZ reaction, the cross-linkers switch between the reduced ($[\mathrm{RuL_3}]^{2+}$, L = *N*,*N'*-diallyl-(2,2'-bipyridine)-4,4'-dicarboxamide) and oxidized states ($[\mathrm{RuL_3}]^{3+}$), which causes Gel 1 and Gel 2 to shrink in the oxidized state and to swell in the reduced state. In contrast to Gel 1 and Gel 2, the gels Gel 3[18]

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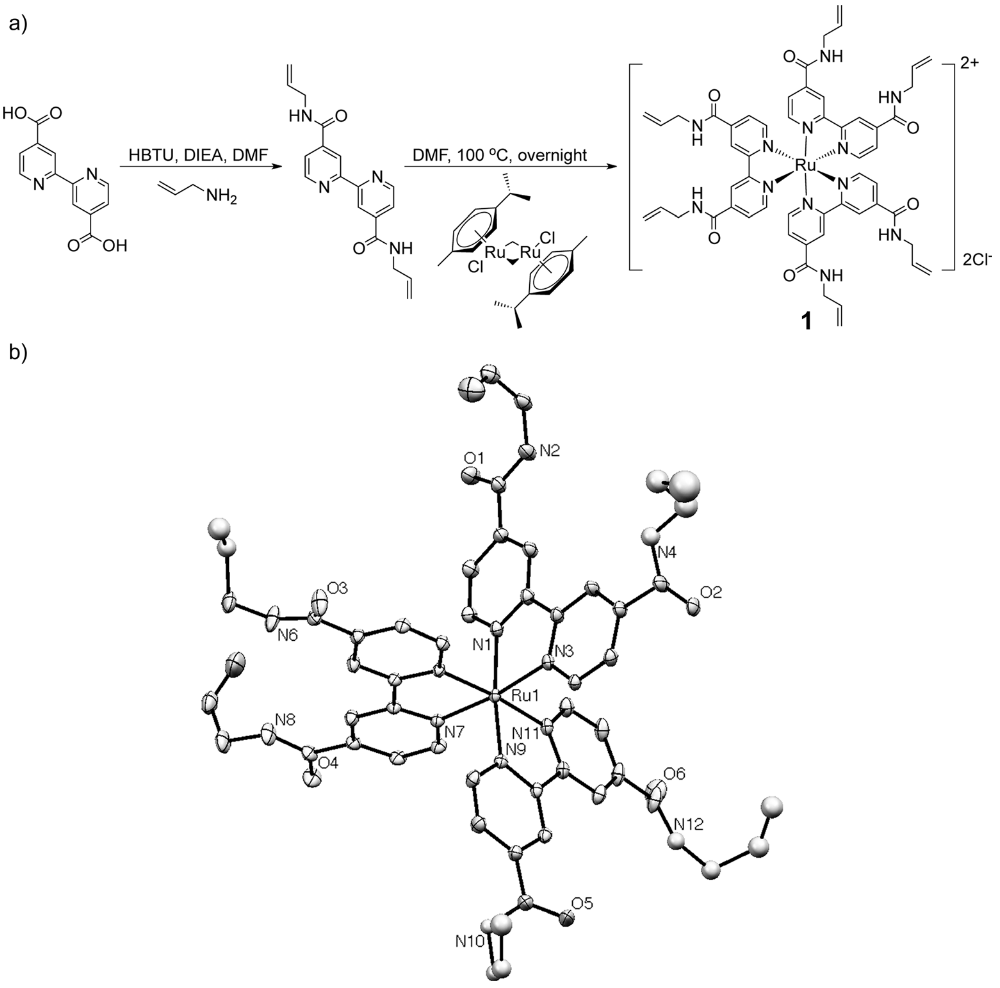

Figure 1. a) A simple route for synthesizing the active hyper cross-linker **1**. b) Crystal structure of the active hyper cross-linker **1**. Thermal ellipsoids set at 50% probability. For clarity, the Cl^- counterions and all hydrogen atoms have been omitted. DIEA = diisopropylethylamine, DMF = *N*,*N*-dimethylformamide, HBTU = O-(benzotriazol-1-yl)-*N*,*N*,*N'*,*N'*-tetramethyluronium hexafluorophosphate.

and Gel4 use $[Ru(bipy)_2L']^{n+}$ (L' = 4-methyl-4'-vinyl-2,2'-bipyridine, $n = 2$ or 3; Supporting Information, Scheme S1) as the pendants attached to the networks of poly(*N*-isopropylacrylamide) and poly(allylamine), respectively. Under the same conditions of the BZ reaction used for Gel1 and Gel2, Gel3 swells, and Gel4 exhibits little change in volume when the pendants are present in their oxidized state ($[Ru(bipy)_2L']^{3+}$). Such drastic contrasts in volume changes confirm that the molecular architecture determines the chemomechanical behavior of the active gels. Moreover, the transformation of a thermally insensitive polymer (such as poly(allylamine)) into a self-oscillatory material by using active cross-linkers, suggests that polymerization with active cross-linkers is an effective approach to generate active gels.

Figure 1 a shows a concise, two-step synthesis of the active cross-linker **1**. First, 4,4'-dicarboxyl-2,2'-bipyridine[21] was reacted with two equivalents of allylamine in the presence of coupling reagents to form *N*,*N'*-diallyl-(2,2'-bipyridine)-4,4'-dicarboxamide. Second, six equivalents of *N*,*N'*-diallyl-(2,2'-bipyridine)-4,4'-dicarboxamide reacted with one equivalent of dichloro(*p*-cymene)ruthenium(II) dimer[22] in DMF at 120 °C under N_2 for 12 h. After the reaction had reached completion, purification by column chromatography[23] and removal of the solvent afforded active cross-linker **1** as a red powder in a total yield of 52%. The UV/Vis spectrum of the active cross-linker **1** exhibits four absorption bands at 200, 250, 305, and 465 nm (Supporting Information, Figure S1). The 200 nm and 305 nm bands arise from ligand-centered (LC) π–π* transitions,[24] the remaining intense bands at 250 and 465 nm belong to metal-to-ligand charge-transfer (MLCT) d–π* transitions, and the shoulder at 350 nm reflects metal-centered (MC) transitions.[25] These peaks indicate that the active cross-linker **1** electronically resembles the $[Ru(bipy)_3]Cl_2$ complex, thus it should be able to function as the desired redox catalyst of the BZ reaction[17f,g] for the evaluation of the active cross-linker and the corresponding gels. Furthermore, we obtained a crystal structure of the cross-linker (Figure 1 b). The three bipyridine ligands around the Ru atom form a propeller-like trigonal arrangement. The coordination of the nitrogen atoms is close to octahedral. The results indicate that the active hyper cross-linker **1** retains a similar geometry to the known crystal structure of $[Ru(bipy)_3]^{2+}$.[26] Among the six *N*-allylacetamide groups, two of them, which are located on different bipyridine ligands, are rigid; the other four show small flexibilities. The stereochemical configuration of the active hyper cross-linker **1** makes it an inherent 3D cross-linker.

After characterizing the physiochemical and structural properties of the active cross-linker **1**, we used a photopolymerization process to fabricate the active gels. Based on the reported procedures,[27] we used prototype photomasks[28] to define the diameters of the gel disks as 300–500 μm and a polycarbonate mold to restrict the heights of the gels to 100–200 μm. We carried out the photo-initiated polymerization in an ice–water bath for a relatively short reaction time (10–30 min). Furthermore, by controlling the initial ratio of the monomers to the active cross-linker **1**, we ensured that gels with proper elasticity were obtained (Figures S2 and S3). For example, Gel 1, formed by the polymerization of the active cross-linker **1** and the monomer in a ratio of 0.004, achieves an optimal cross-linking density and undergoes a change in volume during the BZ reaction (see below). Whereas Gel 2 has the same molar ratio of active cross-linker **1** and monomer as Gel 1, the molar ratios of the monomer, ruthenium catalyst $[Ru(bipy)_2L']Cl_2$, and the cross-linker (BIS) are 1:0.015:0.012 for the syntheses of Gel 3 or Gel 4.

To understand the microstructure in the gels made using the active cross-linker **1**, we used confocal microscopy to image Gel 1 and Gel 2 at the reduced state as the active cross-linker **1**, in its reduced state, fluoresces strongly and stably upon excitation at 488 nm. Fluorescence images (Figure 2) indicate that Gel 1 and Gel 2 have different microstructures. For example, whereas Gel 1 shows largely homogeneous fluorescence (Figure 2 a) and some elliptical fluorescent dots (3.3 × 2.5 μm), Gel 2 exhibits a fluorescent porous network composed of interconnected micrometer-size clots (Figure 2 b). Furthermore, the 3D images (Figure 2 c and d) obtained from a Z-scan series of fluorescence confocal images of Gel 1 and Gel 2 further confirm that the cross-linkers are distributed more homogenously in Gel 1 than in Gel 2, despite the inhomogeneity of the cross-linkers in both Gel 1 and Gel 2. In comparison, the fluorescence images and the 3D images of Gel 3 and Gel 4 (Supporting Information, Figure S4) all show quite homogeneous fluorescence, which suggests that the $[Ru(bipy)_2L']^{2+}$ complexes, here used as pendants, distribute evenly in Gel 3 and Gel 4. Furthermore, Gel 1 (or Gel 3) and Gel 2 (or Gel 4) also exhibit different appearances. For example, Gel 1 (or Gel 3) is more transparent than Gel 2 (or Gel 4), a difference that likely originates from the different polymer backbones. These results indicate that although differences in monomer structure hardly influence the distribution of the pendants in Gel 3 and Gel 4, the monomers most likely contribute to the heterogeneous distribution of the cross-linkers in Gel 1 and Gel 2.

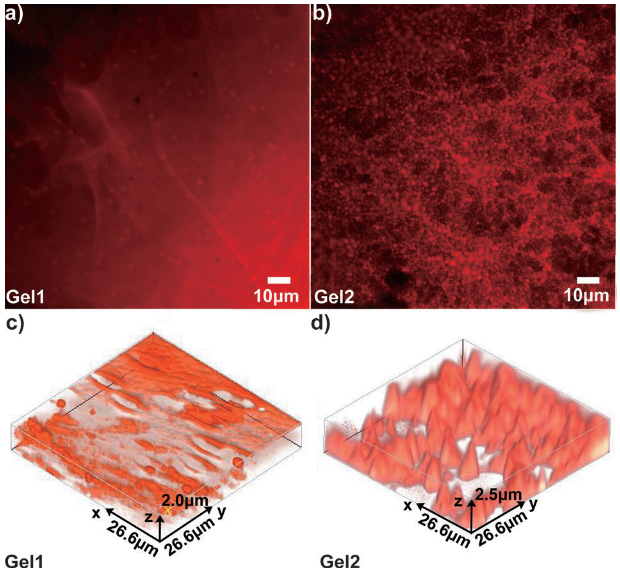

Figure 2. Confocal fluorescence images of a) Gel 1 and b) Gel 2, and the 3D images c) Gel 1 and d) Gel 2.

Indeed, the differences in the microstructures of the active gels result in different chemomechanical behavior during redox reactions (Figure 3). Upon oxidization by a cerium sulfate solution, both Gel 1 and Gel 2 shrink, but Gel 2 exhibits a bigger change in volume than Gel 1. The shrinkage of Gel 1 and Gel 2 in their oxidized states also makes them appear darker owing to increased UV/Vis absorption. Unlike Gel 1 and Gel 2, upon oxidation, Gel 3 swells, but Gel 4 hardly changes its volume. These results confirm that the use of the active cross-linkers not only leads to drastically different responses to redox switch from those of the gels containing $[Ru(bipy)_2L']^{n+}$ ($n = 2$ or 3) as pendants, but also allows polymers other than poly(*N*-isopropylacrylamide) to form active gels that exhibit chemomechanical behaviors (such as a change in volume upon a redox reaction).

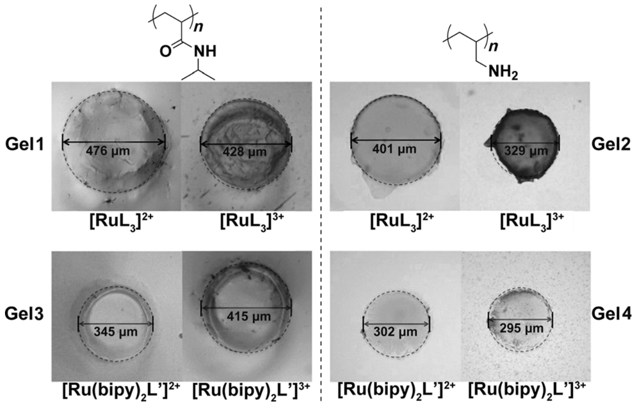

Figure 3. Optical images (top view) of Gel 1, Gel 2, Gel 3, and Gel 4 (the polymer chains are shown in the first row) in their reduced state (by treating with $Ce(NO_3)_3$) and oxidized state (by treating with a $Ce(SO_4)_2$ solution) at 24 °C. The dotted circles indicate the edges of the gels.

To further understand the correlation between molecular structure and the behavior of the active gels, we compared the volume change versus temperature at oxidized and reduced states of the gels (Figure 4 a–d). The relative diameters of all four gels, defined by dividing by the diameter of the gel at its minimum volume state, change in quite different manners. Gel 1, because of its thermoresponsive poly(NIPAAm) backbone,[4] swells upon decreasing the temperature in both its oxidized and reduced states and exhibits temperature-dependent phase transitions at about 28 °C and 24 °C for the reduced and oxidized states, respectively (Figure 4 a). In the range of temperatures tested, Gel 1, in its oxidized state, shrinks in a different ratio than its reduced state; above 30 °C, however, only a small difference in volume is observed for the two states (Figure 4 a). Unlike for Gel 1, the volume of Gel 2 is independent of a change in temperature, and a constant ratio is observed for the relative diameters of the oxidized and reduced states (Figure 4 b). In comparison to Gel 1, Gel 3,[18] which also contains poly(NIPAAm) backbones, swells in its oxidized state compared to its reduced state over the entire temperature range tested (Figure 4 c). Like Gel 1, Gel 3

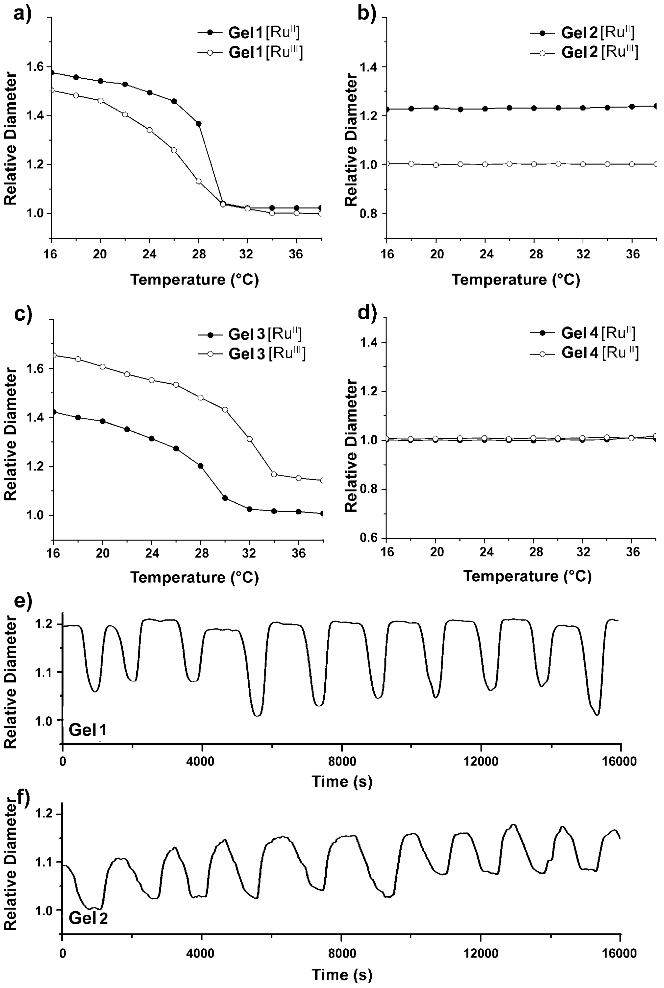

Figure 4. Volume changes of the active gels. The relative diameters (which reflect the equilibrium swelling ratio) of a) Gel 1, b) Gel 2, c) Gel 3,[18] and d) Gel 4 in their reduced (Ru^{II}) and oxidized (Ru^{III}) states, as a function of temperature. Mechanical oscillation profiles of e) Gel 1 and f) Gel 2 during the BZ reaction. Reaction conditions: malonic acid (0.4 M), BrO_3^- (0.2 M), HNO_3 (0.4 M), 10 °C and 15 °C for Gel 1 and Gel 2, respectively).

exhibits a temperature-dependent phase transition in its reduced and oxidized states, similar to results reported in the literature.[18] Unlike Gel 1, Gel 2, and Gel 3, the volume of Gel 4 is essentially independent of the redox state or temperature (Figure 4 d). Furthermore, although Gel 1 contains significantly fewer (1/5) Ru centers than Gel 3 does, the maximum difference in relative diameters for the reduced and oxidized states of Gel 1 reaches half of the difference for Gel 3, which implies a higher efficiency in chemomechanical conversion per redox center (Ru$^{II/III}$) when it serves as the cross-linkers rather than as the pendant group. Clearly, the same is true in the case of Gel 2 and Gel 4. These results further confirm the unique merits of an active cross-linker.

As the BZ reaction offers a convenient experimental setting[29] to further confirm that the active cross-linkers lead to active gels, we evaluated the chemomechanical behavior of Gel 1 and Gel 2 during the BZ reaction. As shown in Figure 4 e, Gel 1 oscillates with an average period of 1650 s and a maximum change in relative diameter of 18 %. Similarly, Gel 2 oscillates with an average period of 1550 s and a change in relative diameter of 12 % (Figure 4 f). Thus, the autonomous chemomechanical oscillations of Gel 1 and Gel 2 during the BZ reaction demonstrate that the use of active cross-linkers is a powerful approach to develop active gels.

The shrinkage of Gel 1 in the oxidized state (Figure 3) is a counterintuitive result because an increase in charge on the $[RuL_3]^{3+}$ complexes is expected to result in repulsion and to cause the gel to swell. However, scanning electron microscopy (SEM) of Gel 1 (Supporting Information, Figure S5) in its reduced and oxidized states exhibits the transition of a porous structure to a condensed structure upon oxidation of the $[RuL_3]^{2+}$ cross-linkers. This observation is consistent with an alternative interpretation: In the hyper-cross-linked system, the octahedral geometry of the active hyper cross-linker **1** leads to a genuine 3D network, in which the $[RuL_3]^{3+}$ cross-linker serves as the joint center of several polymer chains. As the $[RuL_3]^{3+}$ are highly restricted in movement within the hyper-cross-linked network, upon oxidation, the $[RuL_3]^{n+}$ cross-linkers attract extra counterions into the network. In fact, the influx of counterions increases the electrostatic interactions between the ions, which likely expels water molecules out of the network and eventually induces the collapse of the polymer network. Although other factors may contribute to the volume shrinkage, the results obtained by confocal imaging and SEM confirm that the active cross-linker play a critical role in the chemomechanical volume change of the active gels.

In conclusion, by designing and synthesizing the first octahedral ruthenium bipyridine complex that bears six polymerizable vinyl groups as the active cross-linkers, we have illustrated a new way to control molecular architecture for active materials, in which the active hyper-cross-linkers of the polymer network determine the material properties. This result suggests that the application of an active catalyst as the hyper-cross-linker of a polymer network may lead to a new way of making active soft materials.[30] Moreover, this work also increases the diversity of active materials, thus laying the foundation for combining counteracting components to construct sophisticated chemomechanical systems or materials.[31] Furthermore, this work offers a key building block for the construction of other new redox active polymers using the new octahedral ruthenium complex.

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[1] K. Y. Lee, D. J. Mooney, *Chem. Rev.* **2001**, *101*, 1869–1879.
[2] A. R. Hirst, B. Escuder, J. F. Miravet, D. K. Smith, *Angew. Chem.* **2008**, *120*, 8122–8139; *Angew. Chem. Int. Ed.* **2008**, *47*, 8002–8018.
[3] a) P. Calvert, *Adv. Mater.* **2009**, *21*, 743–756; b) Z. S. Liu, P. Calvert, *Adv. Mater.* **2000**, *12*, 288–291.
[4] H. G. Schild, *Prog. Polym. Sci.* **1992**, *17*, 163–249.

[5] a) I. Rayment, H. M. Holden, M. Whittaker, C. B. Yohn, M. Lorenz, K. C. Holmes, R. A. Milligan, *Science* **1993**, *261*, 58 – 65; b) Y. Harada, A. Noguchi, A. Kishino, T. Yanagida, *Nature* **1987**, *326*, 805 – 808.

[6] a) S. Köhler, V. Schaller, A. R. Bausch, *Nat. Mater.* **2011**, *10*, 462 – 468; b) A. K. Boal, H. Tellez, S. B. Rivera, N. E. Miller, G. D. Bachand, B. C. Bunker, *Small* **2006**, *2*, 793 – 803; c) S. Banerjee, M. C. Marchetti, *Soft Matter* **2011**, *7*, 463 – 473; d) P. Chen, V. B. Shenoy, *Soft Matter* **2011**, *7*, 355 – 358; e) Y. Tsuchiya, T. Komori, M. Hirano, T. Shiraki, A. Kakugo, T. Ide, J. P. Gong, S. Yamada, T. Yanagida, S. Shinkai, *Angew. Chem.* **2010**, *122*, 736 – 739; *Angew. Chem. Int. Ed.* **2010**, *49*, 724 – 727.

[7] a) M. M. Zhang, D. H. Xu, X. Z. Yan, J. Z. Chen, S. Y. Dong, B. Zheng, F. H. Huang, *Angew. Chem.* **2012**, *124*, 7117 – 7121; *Angew. Chem. Int. Ed.* **2012**, *51*, 7011 – 7015; b) Y. Kohsaka, K. Nakazono, Y. Koyama, S. Asai, T. Takata, *Angew. Chem.* **2011**, *123*, 4974 – 4977; *Angew. Chem. Int. Ed.* **2011**, *50*, 4872 – 4875; c) S. Tamesue, Y. Takashima, H. Yamaguchi, S. Shinkai, A. Harada, *Angew. Chem.* **2010**, *122*, 7623 – 7626; *Angew. Chem. Int. Ed.* **2010**, *49*, 7461 – 7464; d) O. Kretschmann, S. W. Choi, M. Miyauchi, I. Tomatsu, A. Harada, H. Ritter, *Angew. Chem.* **2006**, *118*, 4468 – 4472; *Angew. Chem. Int. Ed.* **2006**, *45*, 4361 – 4365; e) T. Oku, Y. Furusho, T. Takata, *Angew. Chem.* **2004**, *116*, 984 – 987; *Angew. Chem. Int. Ed.* **2004**, *43*, 966 – 969.

[8] a) K. Imato, M. Nishihara, T. Kanehara, Y. Amamoto, A. Takahara, H. Otsuka, *Angew. Chem.* **2012**, *124*, 1164 – 1168; *Angew. Chem. Int. Ed.* **2012**, *51*, 1138 – 1142; b) Y. Amamoto, J. Kamada, H. Otsuka, A. Takahara, K. Matyjaszewski, *Angew. Chem.* **2011**, *123*, 1698 – 1701; *Angew. Chem. Int. Ed.* **2011**, *50*, 1660 – 1663; c) Q. Wang, J. L. Mynar, M. Yoshida, E. Lee, M. Lee, K. Okuro, K. Kinbara, T. Aida, *Nature* **2010**, *463*, 339 – 343.

[9] a) Y. B. Xiong, J. J. Liu, Y. J. Wang, H. Wang, R. M. Wang, *Angew. Chem.* **2012**, *124*, 9248 – 9252; *Angew. Chem. Int. Ed.* **2012**, *51*, 9114 – 9118; b) Z. Shafiq, J. X. Cui, L. Pastor-Perez, V. San Miguel, R. A. Gropeanu, C. Serrano, A. del Campo, *Angew. Chem.* **2012**, *124*, 4408 – 4411; *Angew. Chem. Int. Ed.* **2012**, *51*, 4332 – 4335; c) J. L. Sorrells, R. Shrestha, W. L. Neumann, K. L. Wooley, *J. Mater. Chem.* **2011**, *21*, 8983 – 8986; d) P. A. Bertin, T. J. Meade, *Tetrahedron Lett.* **2009**, *50*, 5409 – 5412; e) N. Bruns, K. Pustelny, L. M. Bergeron, T. A. Whitehead, D. S. Clark, *Angew. Chem.* **2009**, *121*, 5776 – 5779; *Angew. Chem. Int. Ed.* **2009**, *48*, 5666 – 5669; f) A. P. Esser-Kahn, M. B. Francis, *Angew. Chem.* **2008**, *120*, 3811 – 3814; *Angew. Chem. Int. Ed.* **2008**, *47*, 3751 – 3754.

[10] a) V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, *Chem. Rev.* **1996**, *96*, 759 – 833; b) G. A. Crosby, W. G. Perkins, D. M. Klassen, *J. Chem. Phys.* **1965**, *43*, 1498 – 1503; c) J. V. Caspar, T. J. Meyer, *J. Am. Chem. Soc.* **1983**, *105*, 5583 – 5590; d) K. M. Maness, R. H. Terrill, T. J. Meyer, R. W. Murray, R. M. Wightman, *J. Am. Chem. Soc.* **1996**, *118*, 10609 – 10616.

[11] a) J. N. Demas, A. W. Adamson, *J. Am. Chem. Soc.* **1971**, *93*, 1800 – 1801; b) T. J. Meyer, *Acc. Chem. Res.* **1989**, *22*, 163 – 170.

[12] K. Kalyanasundaram, M. Gratzel, *Coord. Chem. Rev.* **1998**, *177*, 347 – 414.

[13] N. E. Tokel, A. J. Bard, *J. Am. Chem. Soc.* **1972**, *94*, 2862 – 2863.

[14] D. Grünstein, M. Maglinao, R. Kikkeri, M. Collot, K. Barylyuk, B. Lepenies, F. Kamena, R. Zenobi, P. H. Seeberger, *J. Am. Chem. Soc.* **2011**, *133*, 13957 – 13966.

[15] S. S. Zhu, R. P. Kingsborough, T. M. Swager, *J. Mater. Chem.* **1999**, *9*, 2123 – 2131.

[16] a) J. J. S. Lamba, C. L. Fraser, *J. Am. Chem. Soc.* **1997**, *119*, 1801 – 1802; b) J. E. Collins, C. L. Fraser, *Macromolecules* **1998**, *31*, 6715 – 6717; c) J. E. McAlvin, C. L. Fraser, *Macromolecules* **1999**, *32*, 6925 – 6932.

[17] a) T. Bansagi, V. K. Vanag, I. R. Epstein, *Science* **2011**, *331*, 1309 – 1312; b) Z. Noszticzius, J. Bodiss, *J. Am. Chem. Soc.* **1979**, *101*, 3177 – 3182; c) J. Masełko, H. L. Swinney, *J. Chem. Phys.* **1986**, *85*, 6430 – 6441; d) V. K. Vanag, A. M. Zhabotinsky, I. R. Epstein, *Phys. Rev. Lett.* **2001**, *86*, 552 – 555; e) V. K. Vanag, I. R. Epstein, *Phys. Rev. Lett.* **2001**, *87*, 228301; f) K. P. Zeyer, F. W. Schneider, *J. Phys. Chem. A* **1998**, *102*, 9702 – 9709; g) F. Bolletta, V. Balzani, *J. Am. Chem. Soc.* **1982**, *104*, 4250 – 4251.

[18] R. Yoshida, T. Takahashi, T. Yamaguchi, H. Ichijo, *J. Am. Chem. Soc.* **1996**, *118*, 5134 – 5135.

[19] R. Yoshida, *Adv. Mater.* **2010**, *22*, 3463 – 3483.

[20] a) G. H. Chen, A. S. Hoffman, *Nature* **1995**, *373*, 49 – 52; b) J. Eliassaf, *J. Appl. Polym. Sci.* **1978**, *22*, 873 – 874; c) T. G. Park, A. S. Hoffman, *Biotechnol. Prog.* **1994**, *10*, 82 – 86.

[21] a) G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch, D. G. Whitten, *J. Am. Chem. Soc.* **1976**, *98*, 2337 – 2338; b) P. J. Giordano, C. R. Bock, M. S. Wrighton, L. V. Interrante, R. F. X. Williams, *J. Am. Chem. Soc.* **1977**, *99*, 3187 – 3189.

[22] M. Zhou, G. P. Robertson, J. Roovers, *Inorg. Chem.* **2005**, *44*, 8317 – 8325.

[23] a) Y. Zhang, N. Li, J. Delgado, N. Zhou, R. Yoshida, S. Fraden, I. R. Epstein, B. Xu, *Soft Matter* **2012**, *8*, 3056 – 3061; b) Y. Zhang, N. Li, J. Delgado, Y. Gao, Y. Kuang, S. Fraden, I. R. Epstein, B. Xu, *Langmuir* **2012**, *28*, 3063 – 3066.

[24] O. Poizat, G. Buntinx, M. Ventura, M. F. Lautie, *J. Phys. Chem.* **1991**, *95*, 1245 – 1253.

[25] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. Vonzelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85 – 277.

[26] a) K. S. Low, J. M. Cole, X. Zhou, N. Yufa, *Acta Crystallogr. Sect. B* **2012**, *68*, 137 – 149; b) F. Pointillart, C. Train, F. Villain, C. C. d. Moulin, P. Gredin, L.-M. Chamoreau, M. Gruselle, G. Aullon, S. Alvarez, M. Verdaguer, *J. Am. Chem. Soc.* **2007**, *129*, 1327 – 1334.

[27] a) Y. N. Xia, G. M. Whitesides, *Angew. Chem.* **1998**, *110*, 568 – 594; *Angew. Chem. Int. Ed.* **1998**, *37*, 550 – 575; b) D. J. Beebe, J. S. Moore, J. M. Bauer, Q. Yu, R. H. Liu, C. Devadoss, B. H. Jo, *Nature* **2000**, *404*, 588 – 590.

[28] D. Qin, Y. N. Xia, G. M. Whitesides, *Adv. Mater.* **1996**, *8*, 917 – 919.

[29] a) A. F. Taylor, M. R. Tinsley, F. Wang, K. Showalter, *Angew. Chem.* **2011**, *123*, 10343 – 10346; *Angew. Chem. Int. Ed.* **2011**, *50*, 10161 – 10164; b) T. Ueki, M. Watanabe, R. Yoshida, *Angew. Chem.* **2012**, *124*, 12157 – 12160; *Angew. Chem. Int. Ed.* **2012**, *51*, 11991 – 11994.

[30] a) R. A. Siegel, *J. Pharmacokinet. Biop.* **1988**, *16*, 667 – 672; b) S. Maeda, Y. Hara, R. Yoshida, S. Hashimoto, *Angew. Chem.* **2008**, *120*, 6792 – 6795; *Angew. Chem. Int. Ed.* **2008**, *47*, 6690 – 6693.

[31] R. B. Thompson, V. V. Ginzburg, M. W. Matsen, A. C. Balazs, *Science* **2001**, *292*, 2469 – 2472.