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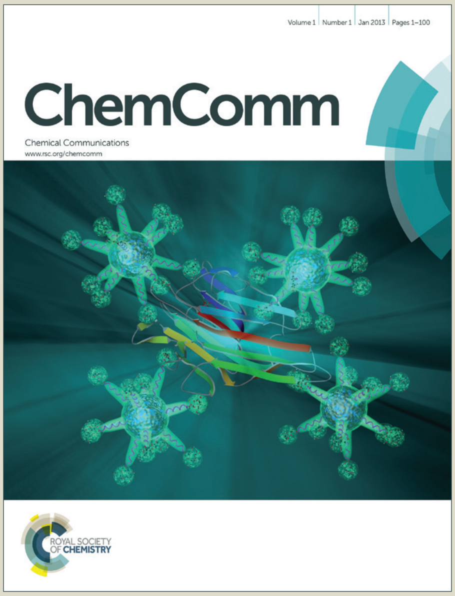

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pH-Responsive Inorganic-Organic Hybrid Supramolecular Hydrogels with Jellyfish-like Switchable Chromic Luminescence

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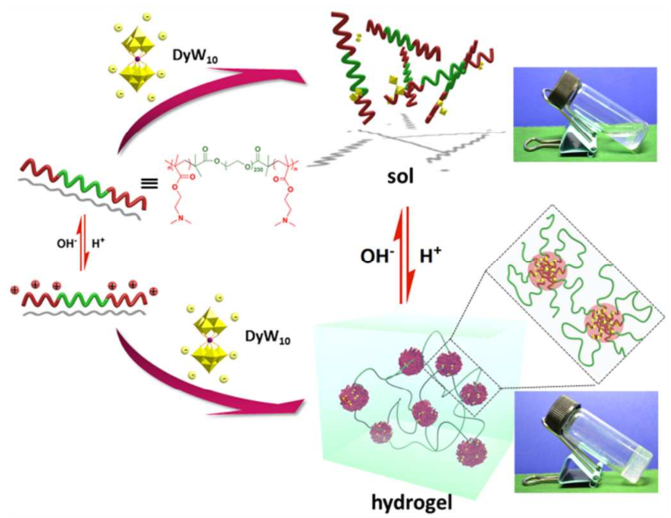
A unique type of novel supramolecular hybrid hydrogel based on the co-assembly of the anionic polyoxometalate and the cationic ABA triblock copolymer *via* electrostatic interaction was reported to resemble Jellyfish's switchable chromic luminescence. The hydrogel undergoes the reversible sol-gel transition in response to pH changes, and simultaneously exhibits an unprecedented luminescent chromism from weak green to strong white.

Stimuli-responsive gels have attracted extensive interest in the past decade because of their applications in a broad range of fields, including drug delivery, sensors, and molecular recognition.[1] Generally, adaptable gels have been designed to respond to external stimuli such as heat, light, chemical additives, pH or ionic strength in the surrounding medium.[2] As compared to low-molecular-weight gelators, polymer gelators endow gels with good mechanical properties as well as distinct dynamic nature, such as stimuli-responsive, shear-thinning, and self-healing.[3] For instance, Kros reported an azo based light-responsive hydrogel applied for light-controlled protein release through sol-gel switching.[4] Harada introduced ferrocene functionalized polymer and constructed a series of hydrogels which may be potential as self-healing materials, actuators or artificial muscles.[5] Other stimuli-responsive hydrogels composed of pH-responsive PAA and/or heat-responsive PNIPAAM, and *etc*, were also reported.[6] After the significant progress in the sol-gel transition of hydrogels in response to diverse stimuli has been made, however, little attention has been paid to changes of functions generated by this sol-gel process. Actually, in many living organisms there is a multi-element expression during structure/morphology changes induced by a single stimulus. For example, only during the routine breathing process, some jellyfish, of which hydrogel composes almost the whole body, exhibits the hydrogel membrane swelling/shrinkage concomitantly with on-off switchable fluorescence behavior.[7] Although sol-gel switching behaviors of synthetic polymer-based hydrogels are well known, an accompanying luminescent change is rarely reported.[8-9]

Herein, inspired by the biological hydrogels, we report a stimuli-responsive supramolecular hydrogel based on a polyoxometalate $Na_9[Dy(W_5O_{18})_2]$ (DyW_{10}) and a ABA triblock copolymer poly(N,N-dimethylaminoethyl methacrylate)$_{35}$-*b*-PEO_{230}-*b*-(N,N-dimethylaminoethyl methacrylate)$_{35}$ (PD_{35}-*b*-PEO_{230}-*b*-PD_{35}) with luminescence variation during the sol-gel transition in response to the pH change (Scheme 1). The polyoxometalate DyW_{10} is soluble in water and stays as a macroanion carrying 9 negative charges in water solution.[10] Poly(N,N-dimethylaminoethyl methacrylate) is a type of weak polyelectrolytes, and its protonation degree of the tertiary amino group is adjustable by pH. The hydrophilic copolymer PD_{35}-*b*-PEO_{230}-*b*-PD_{35} was synthesized by atom transfer radical polymerization (see ESI†).



Scheme 1 Schematic illustration of the reversible sol-gel transitions triggering by pH stimuli. The inserts are photographs of the sol and gel states of DyW_{10}/PD_{35}-*b*-PEO_{230}-*b*-PD_{35} mixtures with the total solid concentration of 12 wt%.

The DyW_{10}/PD_{35}-*b*-PEO_{230}-*b*-PD_{35} hybrid complex at a total solid concentration of 12.0 wt% was prepared by mixing the aqueous solutions of DyW_{10} and PD_{35}-*b*-PEO_{230}-*b*-PD_{35} together, where the molar ratio of tertiary amino groups of PDMAEMA to DyW_{10} is set as 11.0. As the PDMAEMA segments are weak polyelectrolytes with a *p*Ka of 7.4, a merely negligible part of the tertiary amino was protonated in the initial mixture with a pH of 9.3. Therefore, a viscous solution was obtained. However, after the addition of appropriated amount of HCl into solution to tune pH~4.0, the PDMAEMA segments became completely positively charged. The strong electrostatic interactions between the cationic PDMAEMA segments and the anionic DyW_{10} induce the coassembly, and consequently the gelation occurred spontaneously (Scheme 1). Moreover, through the addition of stoichiometric amounts of NaOH solution into the hydrogel, the transition from gel to sol can be observed due to the decrement of the protonation degree of the tertiary amino groups. The reversible protonation and deprotonation of the tertiary amino groups endowed the pH-responsiveness of the DyW_{10}/PD_{35}-*b*-PEO_{230}-*b*-PD_{35} complex.

Transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS) were used to explore the pH-responsive assembly behavior of the DyW_{10}/PD_{35}-*b*-PEO_{230}-*b*-PD_{35} complex. As revealed by TEM image, uniform spherical micelles were prevalently observed after the gelation, confirming the ordered coassembly (Fig. 1a). It is noteworthy that the extended PEO linkers are invisible under TEM because of their relatively low electron density, while the DyW_{10}/PD_{35}-*b*-PEO_{230}-*b*-PD_{35} micellar core is clearly visible with an average diameter of about 25 nm. In comparison, no ordered structures could be obtained at the sol state under TEM observation. Furthermore, as shown in Fig. S1a (ESI†), the enhancement of scattering intensity $I(q)$ of DyW_{10}/PD_{35}-*b*-PEO_{230}-*b*-PD_{35} mixture at low q values was observed *in situ* during the sol-gel transition, indicating of the formation of tight aggregates. Generalized indirect fourier transform analysis of SAXS measurement for the DyW_{10}/PD_{35}-*b*-PEO_{230}-*b*-PD_{35} gel indicates that the scattering objects, the micellar cores, have an globular, almost spherical shape with a R_g value of about 12 nm (Fig. S1b, ESI†), which is in good agreement with the TEM results. Therefore, a tentative model of the pH-responsive mixture was proposed as followed: Before the addition of HCl to pronate tertiary amino group of PD, intermolecular interaction between DyW_{10} and PD_{35}-*b*-PEO_{230}-*b*-PD_{35} is mainly weak *van der Waals* force, so that the mixture of DyW_{10}/PD_{35}-*b*-PEO_{230}-*b*-PD_{35} did not cause gelation, but appear to be a transparent, viscous fluid. Upon addition of acid to the mixture, the tertiary amino groups were completely protonated, and then electrostatically co-assembled with the macroanionic DyW_{10} to form the coacervate core, while the hydrophilic PEO blocks connect adjacent micelles to afford the crosslinked network, and therefore the DyW_{10}/PD_{35}-*b*-PEO_{230}-*b*-PD_{35} mixture changed from a viscous solution to a stable translucent hydrogel.

The DyW_{10}/PD_{35}-*b*-PEO_{230}-*b*-PD_{35} complex also demonstrates interesting luminescence variation during the sol-gel transition (Fig. 1b). It is known that the DyW_{10} only exhibits weak green emission in aqueous solution owing to the quenching of the DyW_{10} luminescence by radiationless deactivation of the $^4F_{9/2}$ excited state through coupling with O-H vibrations of the water molecules bound to DyW_{10} macroanions. However, the luminescent intensity of the DyW_{10} was enhanced largely after the gelation of DyW_{10}/PD_{35}-*b*-PEO_{230}-*b*-PD_{35} mixture (Fig. 1c) by the addition of acid. Similar to our previous reports,[11] we reasonably speculated that upon the addition of acid to induce hydrogelation, the water molecules coordinated to the DyW_{10} emission center in the sol state was replaced by the protonated tertiary amino groups closely coupled with the DyW_{10} center, and thus, the hydrophobic microenvironment inhibits the non-radiation processes and then obviously enhanced the emission intensity. As a control experiment, we monitored the luminescence property of pure DyW_{10} aqueous solution at pH = 7.2 and 4.4, and the results turned out there is hardly any observable luminescence and decay lifetime changes at different pH values (Fig S2, ESI†). Moreover, as illustrated in Fig. 1d, the decay lifetimes of DyW_{10} at the gel states, prolonged largely than that in the sol states, and comparable to that of DyW_{10} in the solid state (Fig S3, ESI†), further confirming that the luminophor DyW_{10} is located in relatively hydrophobic microenvironments.

Furthermore, an unprecedented luminescent chromism was observed during the sol-gel transition. A key feature of photoluminescent spectrum of DyW_{10} is that it has two characteristic emission bands, viz., $^4F_{9/2}\rightarrow{}^6H_{15/2}$ (blue emission, $\lambda_{em}^{max} = 476$ nm) and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ (yellow emission, $\lambda_{em}^{max} = 574$ nm) transitions and thus the apparent emission colour depends on the intensity ratio of the yellow/blue light ($I_{4F9/2\rightarrow 6H13/2}/I_{4F9/2\rightarrow 6H15/2}$). Although the apparent colour of Dy^{3+} luminophor has been predicted to be sensitive to the surrounding microenvironment long before, but no observation has been reported yet on its chromic property.[12,13] In the present work, the chromic luminescence of Dy^{3+} was achieved upon reversible supramolecular disassembly-assembly during the sol-gel transition. For the initial DyW_{10}/PD_{35}-*b*-PEO_{230}-*b*-PD_{35} solution where DyW_{10} are mostly surrounded by water molecules in a relatively asymmetrical microenvironment, the complex solution emits merely weak green light with an $I_{4F9/2\rightarrow 6H13/2}/I_{4F9/2\rightarrow 6H15/2}$ value of 0.53. After hydrogelation, the symmetric microenvironment of DyW_{10} was improved by lodging in the dense hydrophobic polymer matrix, and thus both emission intensities of the blue and yellow band were strikingly enhanced with $I_{4F9/2\rightarrow 6H13/2}/I_{4F9/2\rightarrow 6H15/2}$ ~1.05 which is comparable to that in DyW_{10} crystals.

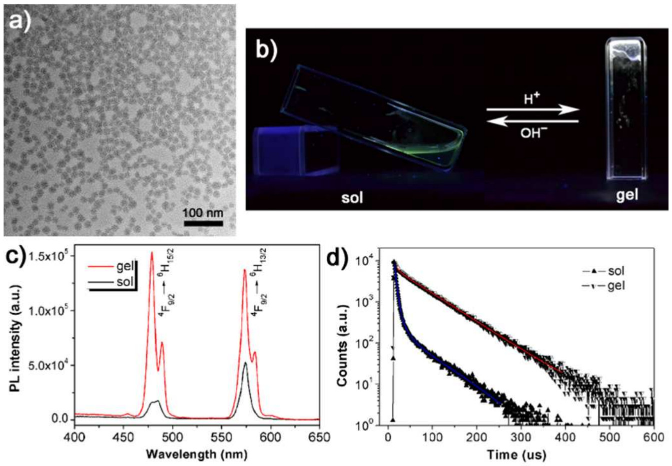


Fig. 1 (a) TEM images of DyW_{10}/PD_{35}-*b*-PEO_{230}-*b*-PD_{35} hybrid hydrogels. (b) Photographs of the luminescence variation (λ_{ex} = 254 nm) during the sol-gel transition of DyW_{10}/PD_{35}-*b*-PEO_{230}-*b*-PD_{35} mixtures with the total solid concentration of 12 wt% triggered by the addition of acid. (c) Luminescence spectra of DyW_{10}/PD_{35}-*b*-PEO_{230}-*b*-PD_{35} mixtures in the sol and gel states at an excitation wavelength of 280 nm, clearly indicating that the luminescence enhancement in the gel state. (d) Emission decay curves of DyW_{10}/PD_{35}-*b*-PEO_{230}-*b*-PD_{35} mixtures in the sol and gel states.

To study the viscoelastic and dynamic properties of the hybrid hydrogel, rheological measurements were performed. Frequency-dependent rheological characterizations performed in the linear viscoelastic region were shown in Fig. 2a. Although G' slightly varied with the range of applied angular frequency (ω), there is $G' > G''$ through the measured region, which clearly indentifies the solid-like behavior of the hydrogel. When a large-amplitude oscillatory (γ = 400%, ω = 2 rad/s) was applied, G' value decreased to about one tenth of its original value ~450 Pa and the tan δ (tan $\delta = G''/G'$) value increased from 0.33 to 2.7, indicative of collapse of the hydrogel to a quasi-liquid state. Interestingly, after the removal of the large strain, the quasi-liquid converted quickly to the hydrogel with more than 90% revovery of the original G' values in less than 30 s (Fig. 2b), demonstrating of the characteristic self-healing property of hybrid hydrogels. The dynamic nature of the hydrogel may be ascribed to the disassociation and reorganization of the coacervate core formed from cationic PDMAEMA segments and macroanionic DyW_{10} by electrostatic interaction. Nevertheless, unlike the hydrogel based on strong polyelectrolyte[11a,14], the fully recovery of the initial *G′* value is time-dependent, which may be ascribed to the weaker electrostatic interaction between the weak polyelectrolyte PDMAEMA and polyoxometalate than the strong polyelectrolytes, resulting in the slower reorganization of the electrostatic-based coacervate core. On the other hand, a macroscopical self-healing test was carried out by cutting the hydrogel in the vial by a needle, and it can heal within 3 minutes (Fig S4, ESI†), further confirming its self-healing features.

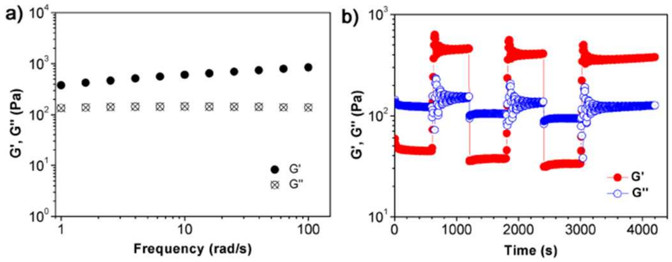


Fig. 2 Rheology properties (25 °C) of hybrid hydrogels. (a) The storage and loss moduli obtained from a frequency sweep performed at 0.8% strain, showing no crossover point through the experimental region. (b) *G′*and *G″* values of hydrogel in continuous step strain measurements. (ω = 2 rad/s, γ = 400% (600 s) → 0.8% (600 s) → 400% (600 s) → 0.8% (600 s) → 400% (600 s) → 0.8% (1200 s)). The hydrogel samples were prepared at a concentration of 12 wt%.

Conclusions

In summary, we successfully realized the reversible switchable sol-gel transition accompanying with simultaneous luminescence variation in a hybrid supramolecular hydrogel in response to pH changes. Moreover, the gel exhibits excellent self-healing properties, showing fast recovery even under 400% strain for at least three cycles of varying strains, owing to the dynamic nature of electrostatic interaction between the anionic DyW_{10} and the cationic triblock copolymer. In view of its intriguing properties, this hydrogel could potentially be used as adaptive and smart materials, such as multichannel detection, injectable sensors, and *etc*.

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Notes and references

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