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Photo-reversible Pb^{2+}-complexation of insoluble poly(spiropyran methacrylate-*co*-perfluorohydroxy methacrylate) in polar solvents

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The first demonstration of photo-reversible Pb^{2+}-complexation of an insoluble spiropyran-carrying copolymer in aqueous solutions is presented.

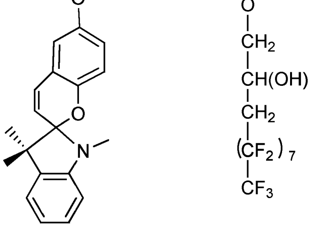
The attractive features of photochromic spiropyrans have prompted a number of studies to investigate the derivatives of these compounds and their metal-binding characteristics.[1,2] Upon irradiation with UV and visible lights, spiropyrans isomerize between the closed and open forms,[3] in which the open form is comparatively more polar. Metal ions can influence this isomerization process by associating with the open form through the consequently electron-rich oxygen atom. In contrast, visible light produces high concentrations of the closed form, and thus hinders metal-binding. Spiropyrans, therefore, show potential in providing photo-reversible metal-complexation. However, strong polar solvents, such as water and alcohols, can thermally stabilize the metal-complexed open form significantly, resulting in an irreversible metal-complexation. In these polar solvents, visible light is not sufficient to transform the metal-complexed open form to its closed form. Reversible photo-induced switching of metal-complexation in aqueous solutions was first demonstrated by Collins and coworkers by utilizing quinolinospiropyran,[4] in which the enhancement of thermodynamic stability of the closed form of spiropyrans was crucial in promoting the photo-reversiblity of metal-complexation in polar solvents. Recently, we have reported on photo-reversible metal-complexations for polar fluoroalcohols.[5] To the best of our knowledge, there are no published accounts of photo-reversible metal-complexations that involve an insoluble spiropyran-carrying copolymer in aqueous solutions. Insoluble materials are attractive for metal-ion adsorption, such as adsorbents or sensors of metals, because of their relative ease of use. Herein, we describe the photo-reversible Pb^{2+}-complexation for a synthetic spiropyran methacrylate (SPMA) in polar solvents (mixtures of methanol and water). Furthermore, we present the first demonstration of reversible photo-induced Pb^{2+}-complexation of an insoluble copolymer consisting of SPMA and perfluorooctylhydroxy methacrylate (FHMA),[6] P(SPMA-FHMA) (Scheme 1), in aqueous solutions.

Synthesis of SPMA was carried out by the reaction between 1′,3′,3′-trimethyl-6-hydroxyspiro(2*H*-1-benzopyran-2,2′-indoline) and methacryloyl chloride in toluene. Subsequently, the radical polymerization of SPMA in toluene was performed under a nitrogen atmosphere at 60 °C with 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator to afford poly(spiropyran methacrylate), P(SPMA), ($M_w = 1.5 \times 10^5$, $M_w/M_n = 2.1$). Similarly, P(SPMA-FHMA) was synthesized from SPMA and FHMA in acetonitrile under nitrogen atmosphere at 60 °C with AIBN for 12 hours. The ratio of SPMA in P(SPMA-FHMA) was 15 mol%, as determined by elemental analysis.

As shown in Fig. 1(A), the absorption spectrum of a solution of SPMA in CH_3OH–H_2O (9 : 1 v/v) in the dark exhibited a purplish-blue band ($\lambda_{max} = 560$ nm) that is attributable to the open form of SPMA. Solutions of SPMA in toluene or THF did not exhibit any absorption bands in the visible regions. Our results indicate that the open form of SPMA was stabilized in polar environments. Addition of a tenfold molar excess of $Pb(ClO_4)_2$ into the solution resulted in the appearance of a yellow band ($\lambda_{max} = 435$ nm) in the dark, as shown in Fig. 1(B), along with the disappearance of the 560 nm band. These changes in the absorption spectra suggest the generation of a different open form of SPMA, which could be the Pb^{2+}-complex. Subsequently, as shown in Fig. 1(C), the yellow band disappeared upon irradiation with visible light (>420 nm). The 435 nm band appeared again in the dark, and attained the same absorbance as spectrum (B) in the equilibrium.

The photo-reversible isomerization of SPMA in a CD_3OD–D_2O (9 : 1 v/v) solution containing Pb^{2+} ions was similarly observed using ^1H NMR spectroscopy; in this case, the photo-responding reversible isomerization corresponded to the changes in the *gem*-CH_3 signals of SPMA (1.14 and 1.27 ppm in the closed form, and 1.82 ppm in the open form). Using the values of concentrations of the open form of SPMA, as determined from ^1H NMR measurements in the dark, the molar absorption coefficient of the open form was calculated as 2.0×10^4 ($dm^3\,mol^{-1}\,cm^{-1}$ at 435 nm). Stabilization of the open form of SPMA in polar solvents did not prevent the photo-induced ejection of the complexed Pb^{2+} ions.

Although purplish-blue P(SPMA) was insoluble in methanol and water, the polymer became soluble after addition of



Scheme 1 P(SPMA-FHMA).

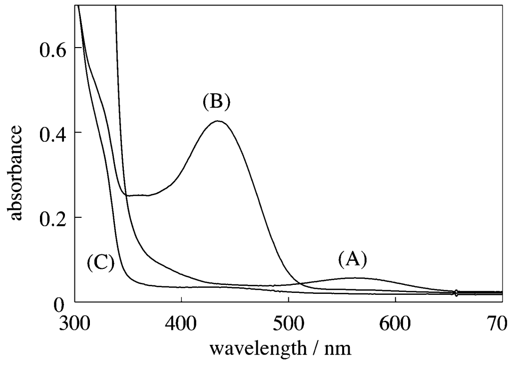


Fig. 1 Absorption spectra of a CH_3OH–H_2O (9:1 v/v) solution of SPMA. (A): [SPMA] = 0.5 mM, (B): [SPMA] = 0.1 mM, $[Pb(ClO_4)_2]$ = 1.0 mM, (C): same solution as (B), measured under visible light irradiation.

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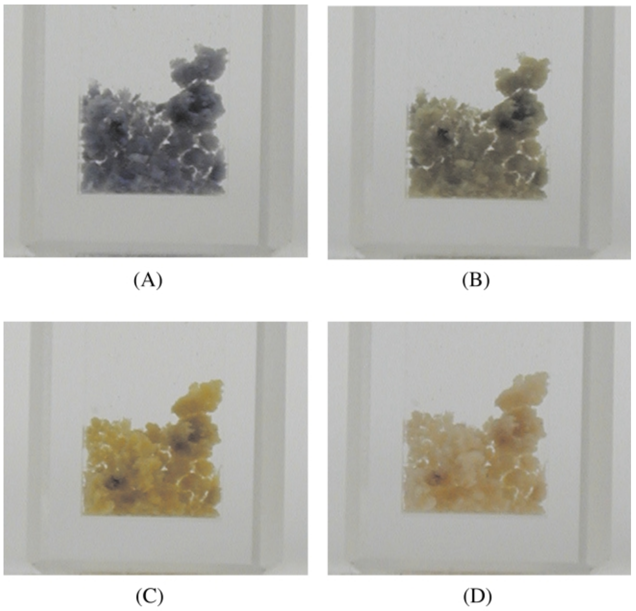
$Pb(ClO_4)_2$. The resulting solution showed an absorption band (λ_{max} = 435 nm), which was identical to spectrum (B) in Fig. 1. In contrast, P(SPMA-FHMA) was completely insoluble in methanol and water, even after complexation with Pb^{2+} ions. The color of the solid P(SPMA-FHMA) in H_2O–CH_3OH (8 : 2 v/v) changed as follows: 1) it existed as purplish-blue in the dark, as shown in Fig. 2(A); 2) upon addition of Pb^{2+} ions, started turning yellow, initially at the surfaces of the solid, as shown in Fig. 2(B); 3) after diffusion of the Pb^{2+} ions into the solid, turned completely yellow, as shown in Fig. 2(C); 4) upon irradiation of visible light, although the interior was still yellow, the surface of the solid turned white, as shown in Fig. 2(D). The white color of the solid is attributable to the closed form of the SPMA portion (15 mol%) and the FHMA portion (85 mol%) of P(SPMA-FHMA). Moreover, the solid turned yellow again in the dark. Removal of the ejected Pb^{2+} in the solution upon irradiation with visible light resulted in the purplish-blue solid of P(SPMA-FHMA) in the dark as observed in Fig. 2(A).

To determine the ejection of Pb^{2+} ions, square-wave voltammetry of the Pb^{2+}-complex of SPMA or P(SPMA-FHMA) solutions in CH_3OH–H_2O (9 : 1 v/v), in the presence of 0.1 M $LiClO_4$, were carried out using amalgamated Au in a conventional three-electrode electrochemical cell. Voltammetry of SPMA in the dark or under visible light did not yield any waves within the −0.2 to −0.8 V region (*vs*. Ag/AgCl). P(SPMA-FHMA) was insoluble in the solvent. Next, in the absence of SPMA or P(SPMA-FHMA), our studies showed the cathodic wave of free Pb^{2+} ions (−0.35 V *vs*. Ag/AgCl), which was consistent with the results of Weber and co-workers.[7] Exposure of the solution to visible light had no effects on the voltammogram prior to the addition of SPMA or P(SPMA-FHMA). Increases in the concentration of SPMA in solution caused the Pb^{2+}(free)-cathodic wave (−0.35 V) to decrease in intensity, as shown in Fig. 3(a), and moreover, also caused the appearance of another Pb^{2+}-cathodic wave (−0.60 V *vs*. Ag/AgCl). Conversely, under irradiation of visible light, the intensity of the cathodic wave of the free Pb^{2+} ions (−0.35 V) increased with simultaneous decrease of the other wave (−0.60 V). The Pb^{2+} (free)-cathodic wave decreased again in the dark. These results are indicative of Pb^{2+}-complexation with SPMA, which corresponds with the photoisomerization of SPMA (the closed form ⇄ the open form). Incomplete ejection of Pb^{2+} ions into the solution (41%) from the metal-complexed open form SPMA should be the result of insufficient exposure of the solution to visible light. The results of our photochemical studies of Pb^{2+} ions in the presence of P(SPMA-FHMA) are illustrated in Fig 3(b). The Pb^{2+}(complexed)-cathodic wave (−0.60 V) was not observed during the process of the complexation, nor during the photo-induced ejection of Pb^{2+} ions; however, the intensity of the Pb^{2+}(free)-cathodic wave (−0.35 V) changed reversibly in response to visible light irradiation. Our results suggest that P(SPMA-FHMA) remained insoluble upon complexation with Pb^{2+} ions. Exposure of only the surface of solid P(SPMA-FHMA) to visible light correspondingly caused the ejection of only a portion of Pb^{2+} ions (13%).


(A) (B)

(C) (D)

Fig. 2 Color changes of solid P(SPMA-FHMA) in H_2O–CH_3OH (8 : 2 v/v): (A) in the dark, (B) 15 s after addition of $Pb(ClO_4)_2$, (C) a minute after addition of $Pb(ClO_4)_2$, (D) for a minute under visible light irradiation.

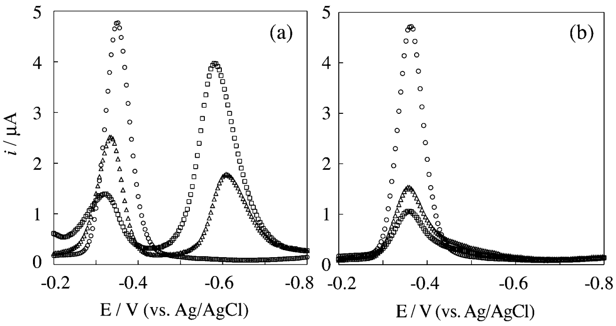


Fig. 3 Cathodic reduction of Pb^{2+} ions in a CH_3OH–H_2O (9 : 1 v/v) containing (a) SPMA and (b) P(SPMA-FHMA). [Pb^{2+}] = 0.04 mM (○); after addition of SPMA (2.0 mM) or P(SPMA-FHMA)[8] (□); the same solution measured after visible light irradiation (△).

In conclusion, this report demonstrates the first photo-reversible Pb^{2+}-complexation from an insoluble copolymer, P(SPMA-FHMA), in aqueous solutions.[9] Modifications of these systems designed to improve the photo-reversibility in aqueous solution, for example, efficient exposure of solid P(SPMA-FHMA) to visible light, and a degradation test with repeated irradiation of light, are currently under investigation.

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8 The 50-fold molar excess of P(SPMA-FHMA) in the SPMA unit of P(SPMA-FHMA) to Pb^{2+} ions was added in the solution.

9 In addition to Pb^{2+}, the photo-reversible metal-complexation by P(SPMA-FHMA) was examined using UV–visible spectroscopy for Zn^{2+}, Cu^{2+}, Ni^{2+}, and Mn^{2+}.