Optical control over Pb²⁺ binding to a crown ether-containing chromene

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Naphthochromene 1 binds Pb²⁺ in the dark, and the complex is photodissociated by a novel mechanism.

Metal-ion chelation by crown ethers has been the subject of intense investigation by researchers[1] for over thirty years. Functionalization of crown ethers[2] leads to pH, redox, and photochemical control over metal-ion binding. Several reports of metal-ion chelation by crown ether groups coupled to photochromic azobenzenes,[2] spiropyrans,[3] and spirooxazines[4] have appeared in the literature. Binding strategies described include the 'butterfly'[2] configuration (*i.e.* a crown ether attached to each end of azobenzene) and use of ionic 'caps'.[2–4] We present here a crown ether-containing chromene that binds Pb²⁺ in the dark, with dissociation of Pb²⁺ upon irradiation with near-UV light. The process is photoreversible. We monitor Pb²⁺ binding by observing the changes in the cathodic reduction of Pb²⁺. To our knowledge, there are no published accounts of metal-ion binding using photochromic chromenes. In metal-binding azobenzenes,[2] spiropyrans,[3] and spirooxazines,[4] the binding affinity is controlled by light through its influence on the chelator's geometry and/or the large increase in donor strength of the pyran oxygen following cleavage of the spiro carbon–oxygen bond. In contrast, compound **1** functions by taking advantage of the decrease in electron donor strength on ligating heteroatoms that can also stabilize, by electron donation, the positive charge created following photolysis.

Compound **1** was synthesized from 1-phenyl-1-(3,4-benzo-1,4,7,10,13-pentaoxacyclopentadeca-3-ene)prop-2-yn-1-ol and β-naphthol under acidic conditions, and purified by re-crystallization (mp 83 °C). Perchlorate salts, benzo-15-crown-5, and methanol (MeOH) were used as received. Simultaneous photochemistry and square-wave voltammetry of solutions of Pb²⁺ and **1** [MeOH–H₂O (9:1)–5.0×10^{-2} mol dm⁻³ LiClO₄] were carried out at amalgamated Au in a 1 mm quartz cuvette. Square-wave voltammetry of solutions of Pb²⁺ and benzo-15-crown-5 was performed at amalgamated Au in a conventional three-electrode electrochemical cell, in the same medium used for the photoelectrochemistry.

We used the model compound benzo-15-crown-5 to study the effect of Pb²⁺ binding by a crown ether upon the voltammetry of Pb²⁺ (Fig. 1). In the absence of benzo-15-crown-5, we observed reduction of free Pb²⁺ (−346 mV *vs.* Ag/AgCl). Increasing the concentration of benzo-15-crown-5 in solution caused the Pb²⁺ reduction peak to shift and decrease in intensity, indicative of

binding of Pb²⁺ by benzo- 15-crown-5. We carried out competitive binding between Pb²⁺ and Na⁺, in the presence of an excess of Na⁺, to confirm that the decrease in the Pb²⁺ reduction wave upon addition of benzo-15-crown-5 was due to binding of Pb²⁺ by the crown ether. Addition of 7.0×10^{-2} mol dm⁻³ NaClO₄ to a solution containing 1.83×10^{-5} mol dm⁻³ Pb²⁺ and 1.0×10^{-2} mol dm⁻³ benzo-15-crown-5 yielded the reduction wave (*ca.* −420 mV, *vs.* Ag/AgCl) for free Pb²⁺ during voltammetry of this solution. Thus, the change in the voltammetry of Pb²⁺ observed in Fig. 1 was due to binding by the crown ether.

Compound **1** (λ_{max} = 284, 302, 346, 358 nm) yields a visible band (λ_{max} = 476 nm) during irradiation with 300–400 nm light. Photoswitching of **1** in the presence of Pb²⁺ (Fig. 2) reveals that **1** is fairly photostable. Voltammetry of **1** in the dark
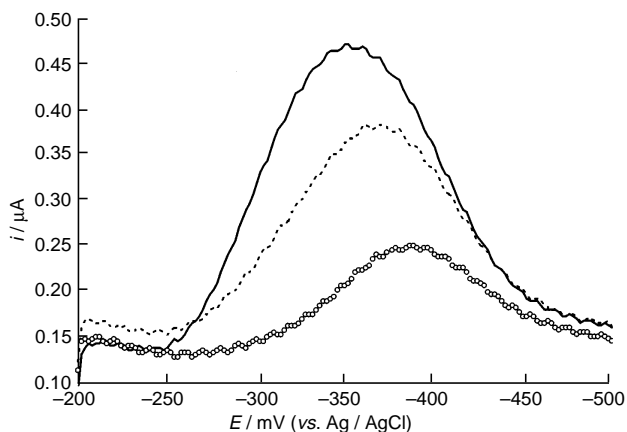

Fig. 1 Cathodic reduction of 4.0×10^{-5} mol dm⁻³ Pb²⁺ in MeOH–H₂O (9:1) containing 0.1 mol dm⁻³ LiClO₄ in the absence and presence of excess benzo-15-crown-5. (——) 4.0×10^{-5} mol dm⁻³ Pb²⁺; (---) 9.6×10^{-3} mol dm⁻³ benzo-15-crown-5 added; (ooo) 3.3×10^{-2} mol dm⁻³ benzo-15-crown-5 added.
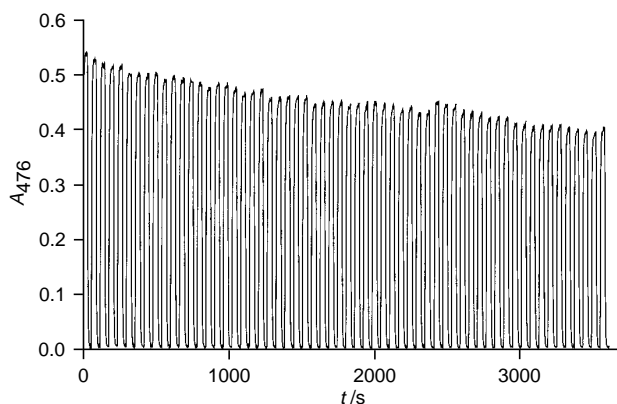
Fig. 2 Photoswitching of 4.93×10^{-4} mol dm⁻³ **1** in the presence of 5.39×10^{-3} mol dm⁻³ Pb²⁺, in MeOH–H₂O (9:1) containing 5×10^{-2} mol dm⁻³ LiClO₄. Each cycle consists of 30 s irradiation with 300–400 nm light, followed by 30 s irradiation with > 420 nm light.

1   **2**
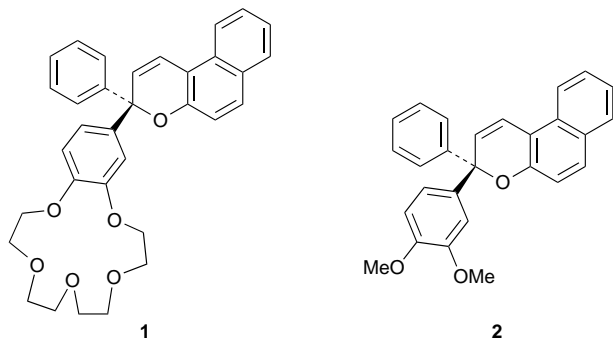
or during illumination yields no waves in the −300 to −1000 mV region. Fig. 3 illustrates the results of our photo-electrochemical studies of Pb²⁺ in the presence of **1**. In the dark, we do not see the wave at *ca.* −400 mV (*vs.* Ag) corresponding to reduction of free Pb²⁺. Instead, we observe a very broad wave at *ca.* −600 mV, indicating that the Pb²⁺ binds to the crown ether. Upon irradiation with 300–400 nm light, we obtain the wave (*ca.* −420 mV, *vs.* Ag) for reduction of free Pb²⁺, showing that the Pb²⁺–crown complex has dissociated due to photoisomerization of **1** (Scheme 1). Irradiation with > 420 nm light yields the same result observed in the dark, indicating the Pb²⁺ binds again to **1**. ¹H and ¹³C NMR spectroscopies† of **1** upon addition of Pb²⁺ (2 : 1 Pb²⁺ : **1** in CD₃CN) in the dark give further
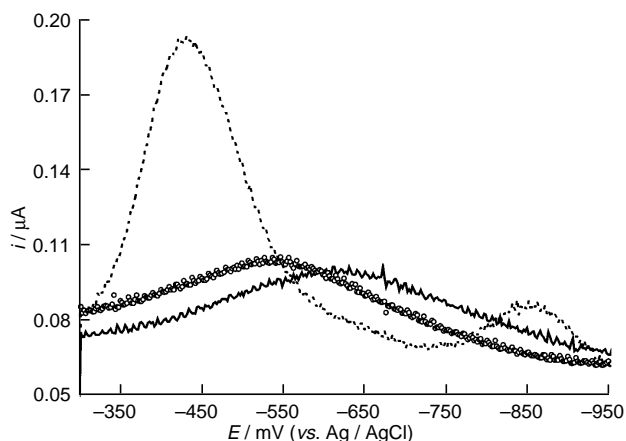
Fig. 3 Photoelectrochemistry of 5.8 × 10⁻⁵ mol dm⁻³ Pb²⁺ + 2 × 10⁻³ mol dm⁻³ **1** in MeOH–H₂O (9 : 1) containing 5 × 10⁻² mol dm⁻³ LiClO₄. (——) dark; (---) UV photolysis; (ooo) visible photolysis.
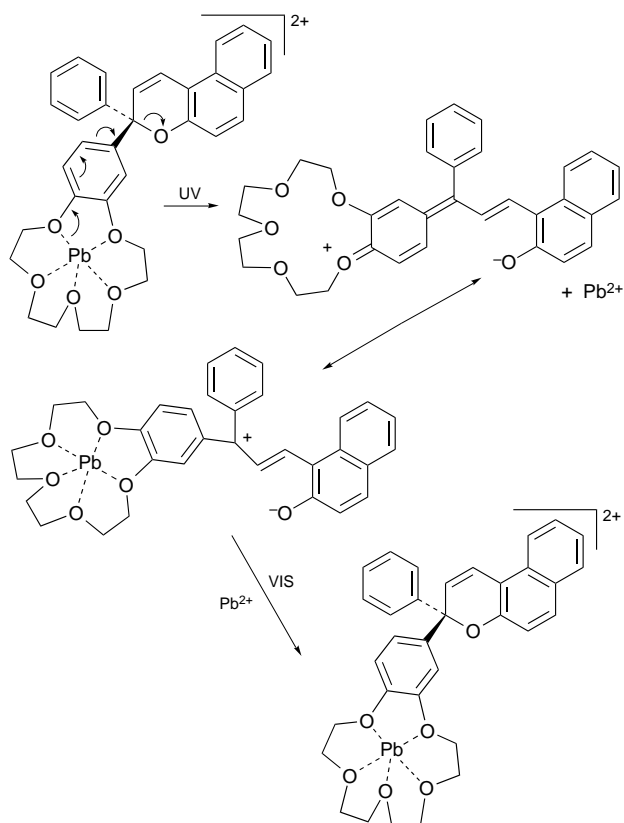
Scheme 1

evidence of binding by Pb²⁺. For ¹H NMR, the crown ether methylene proton resonances are in the region δ 3.73–4.33 with Pb²⁺ *cf.* δ 3.56–4.00 in the absence of Pb²⁺. Resonance shifting and line broadening occur in both ¹H and ¹³C NMR spectra of **1** in the presence of Pb²⁺.

Further evidence suggests that the Pb²⁺ binds to the crown ether moiety. In the dark, we observe the same trend for cathodic reduction of Pb²⁺ in the presence of a large excess of **1** (Fig. 3) as that in excess benzo-15-crown-5 (Fig. 1). In each case, the reduction potential of Pb²⁺ becomes more negative upon addition of the crown ethers. Control experiments involving the dimethoxylated analogue of **1** (*i.e.*, **2**) show no indication of Pb²⁺ binding. We observe no shift in the Pb²⁺ reduction peak potential upon addition of **2** in the dark. Also, ¹H and ¹³C NMR spectroscopies† reveal no changes in the chemical shifts and shapes of the resonances of **2** upon addition of Pb²⁺ in the dark, indicating that Pb²⁺ does not bind to **2**.

Unlike previously designed crowned photochromics,[2–4] in which UV photolysis enhances the cation-binding abilities of the ligands through the creation of additional binding sites or geometry changes, UV-induced photoisomerization of **1** causes open **1** to lose its cation-binding ability due to withdrawal of electron density from the crown ether moiety (Scheme 1). Kimura *et al.*[5] observe a similar occurrence for Na⁺ bound to a crowned malachite green leuconitrile. The difference between **1** and Kimura's[5] leuconitrile is that the coordination by **1** is photoreversible. There is a significant technical advantage to exerting optical control over metal-ion binding in this manner. The system using the photochromic chelator (*e.g.* sensor or extractor) functions in the dark, and only needs to be exposed to light, with consequent photodegradation, for brief periods of forced dissociation.

Footnote

† **1** ¹H NMR (500 MHz, CD₃CN, 298 K) δ 3.58 (t, 8 H, OCH₂), 3.71 (t, 4 H, OCH₂), 3.98 (t, 4 H, OMe), 6.42–8.00 (naphthopyran and phenyl, 16 H). ¹³C NMR (125 MHz, CD₃CN, 298 K) δ 69.5, 69.7, 69.9, 70.9, 71.4 (OCH₂), 83.0 (CPh₂), 113.7–151.3 (naphthopyran and phenyl).
2 ¹H NMR (500 MHz, CD₃CN, 298 K) δ 3.70 (s, 3 H, OMe), 3.72 (s, 3 H, OMe), remaining δ values same as those of **1** for naphthopyran and phenyl moieties. ¹³C NMR (125 MHz, CD₃CN, 298 K) δ 56.2 (OMe), 83.0 (CPh₂), 111.5–151.3 (naphthopyran and phenyl).

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