Univocal Demonstration of the Electrochemically Mediated Binding of Pb²⁺ by a Modified Surface Incorporating a TTF-Based Redox-Switchable Ligand

Joël Lyskawa,[†,‡] Franck Le Derf,[†] Eric Levillain,[†] Miloud Mazari,[†] Marc Sallé,*[,†] Laetitia Dubois,[‡] Pascal Viel,[‡] Christophe Bureau,[‡] and Serge Palacin[‡]

Laboratoire CIMMA, UMR CNRS 6200, Université d'Angers, 2 Bd Lavoisier, F-49045 Angers Cedex, France, and CEA Saclay, DSM/DRECAM/SPCSI, Gif-sur-Yvette, F-91191, France

Received May 3, 2004; E-mail: marc.salle@univ-angers.fr

The control of heavy-metal concentrations in industrial effluents is of crucial importance for environmental reasons. High performance for metal removal is found with ion-exchange resins, but high volumes of polluted solutions are produced during their regeneration process. Smart materials promoting alternative regeneration modes are therefore of strong interest.

Redox-responsive ligands are known for their ability to electrochemically probe the binding of a given substrate and have been used in sensing applications.[1] Their molecular architecture associates an electroactive subunit to a ligating part, and the binding event is thus accompanied by a change in redox-potential. In the case of a metal cation recognition, the efficiency of the electroactive tetrathiafulvalene (TTF) framework has been recently demonstrated with crown-TTF derivatives.[2,3] The attractivity of TTF is ascribed to two successive reversible 1 e⁻ oxidations (to TTF•⁺ and TTF²⁺, at E^1_{ox} and E^2_{ox}, respectively). These ligands undergo a positive shift of E^1_{ox} upon metal cation complexation, since the proximity of the metal alters the oxidability of the TTF framework. It is noteworthy that the E^2_{ox} value remains generally constant whatever the amount of added metal. This observation is usually interpreted to result from the expulsion of the metal when reaching E^2_{ox}, because of increased repulsive electrostatic interactions between TTF²⁺ and the guest cation.[3] Such systems have been exploited for sensing purposes (i.e., *E^1_{ox} shift upon metal complexation*); surprisingly, no study has mentioned the use of the corollary property, building of a tunable material able to bind (TTF° state) or to expel the metal cation upon oxidation (TTF²⁺ state) (i.e., *decreasing of the binding constant upon electrochemical oxidation*).

Herein we report the preparation of a modified surface with a TTF-based redox-switchable ligand, its ability to remain at the solid−liquid interface, the recognition properties detected in homogeneous solutions, and the first univocal demonstration of an electrochemically mediated control of successive metal cation trapping and expulsion sequences.
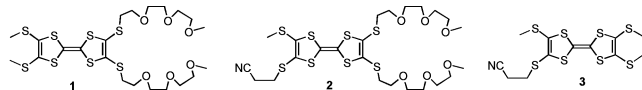
The synthesis[4] of TTF-podant **1** and **2** is inspired from the thiolato protection−deprotection method developed by Becher et al.[5] **1**, studied by cyclic voltammetry (CV), exhibits a shift of E^1_{ox} in the presence of Pb²⁺ with a good specificity for this metal (only small potential changes were observed with other cations such as Ag⁺, Sr²⁺, and Ba²⁺). The binding of the metal not only results in a very strong shift of E^1_{ox} but is accompanied by the concomitant appearance of a new redox system at +120 mV (Figure 1a), which
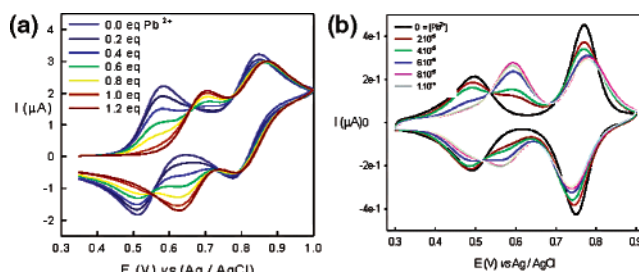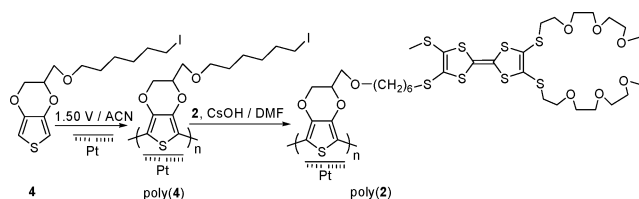
Figure 1. CV responses, ACN/DCM 1/1, with Pb²⁺ (Pb(ClO₄)₂), Bu₄NClO₄ (0.1 mol L⁻¹), Ag/AgCl: (a) [**1**], 10⁻³ mol L⁻¹, Pt (ø = 1 mm), 100 mV s⁻¹; (b) poly(**2**)-modified Pt electrode, Γ = 3.0 × 10⁻⁹ mol TTF cm⁻², ø = 1.6 mm, 10 mV s⁻¹.

Scheme 1

corresponds to the reversible oxidation of the **1**·Pb²⁺ complex. No additional change was observed for an excess of Pb²⁺ (>1 equiv). Such behavior is reminiscent of an elevated (K°/K•⁺) ratio of the binding constant, as well as of an optimal communication between the electroactive (TTF) and coordinating (podant) subunits. It is noteworthy that no change was observed for the E^2_{ox} value, which is again assigned to the Pb²⁺ expulsion. It has to be noted that such critical information cannot be obtained with the much more studied ferrocene-based ligands, in which the presence of only one redox system does not allow the expulsion of the metal to be controlled. The 1:1 stoichiometry of the complex was confirmed by ¹H NMR and UV−vis titrations, which also determined the binding constants (¹H NMR (CD₃CN), K° = 10⁴·⁹; UV−vis (DCM/ACN 1/1), K° = 10⁵·⁰). These values correctly converge to the one obtained from the electrochemical data and using the Digisim simulation program[3d] (K° = 10⁵·⁵).

On this basis, ligand **1** is an optimized candidate for the preparation of modified surfaces since (i) the synthesis is straightforward, (ii) **1** shows a good affinity for Pb²⁺, which is of great concern from the environmental point of view, and (iii) the K° value, and the intensity of the recognition event (ΔE^1_{ox}) are the highest ever observed for TTF-based ligands.

A further step toward applications lies in grafting **1** onto a solid surface. This could be realized very efficiently, using a postpolymerization functionalization strategy recently developed in our group (Scheme 1).[6] Ethylene-dioxythiophene (EDOT) derivative **4** was electropolymerized on a Pt electrode under potentiostatic conditions (E_{app} = 1.50 V). The poly(**4**)-modified surface was then
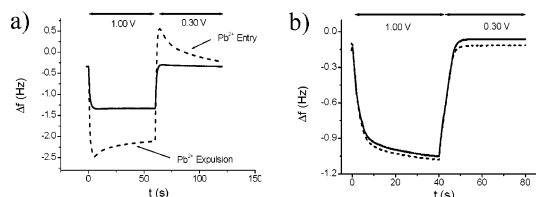
Figure 2. QCM responses, acetonitrile, Bu$_4$NClO$_4$ (0.05 mol L^{-1}): (—) without Pb^{2+}, (- - -) [Pb^{2+}] = 4 mmol L^{-1}; (a) poly(**2**) film; (b) poly(**3**) film.

Figure 3. Evolution of [Pb^{2+}] upon sequential poly(**2**) (- - -) or poly(**4**) (—) polarizations ($\Gamma = 2 \times 10^{-8}$ mol TTF cm^{-2}, surface = 180 cm^{-2}).

immersed in a DMF solution containing stoichiometric amounts of **2** ($C = 1 \times 10^{-2}$ mol L^{-1}) and CsOH (glovebox). Though the reaction was carried out in a heterogeneous medium, the displacement of the terminal iodine by the TTF thiolate is effective within a few minutes. The polymeric films have been characterized by XPS and X-ray energy dispersion spectrometry, which confirm the structures of poly(**4**) and poly(**2**). Additionally, SEM pictures demonstrate the spongelike morphology of poly(**2**), an important property for the mobility of species within the film.

Finally, the electrochemical behavior of poly(**2**) is characteristic of surface-confined redox phenomena, with two well-defined reversible oxidation peaks assigned to TTF oxidations (Figure 1b), and a linear relationship of the peak currents with scan rate.

The recognition ability of poly(**2**) for lead cation was shown by recording the CV response in the presence of increasing metal concentrations (Figure 1b). Remarkable similarities are found with the CV evolution observed in homogeneous medium (Figure 1a): (i) the appearance of a new redox system located at +100 mV and (ii) an unchanged potential value for the second redox system.[7] Moreover, the CV shape remains constant over tenths of potential cycles, which reflects the stability of the film across multiple successive complexation−expulsion sequences.

An additional illustration of this sequence as a function of the applied potential is given by the EQCM (electrochemical quartz crystal microbalance) analysis of poly(**2**) in the presence of Pb(ClO$_4$)$_2$ (Figure 2a). This method is very informative for probing mass-transport processes within thin films. To neglect the mass transport attributable to ClO$_4^-$, whose contribution is otherwise superimposed to Pb^{2+} movements, we applied static potentials of +1.00 V (TTF^{2+} state) and +0.30 V (TTF$°$ state). A first set of experiments was carried out without lead and showed a brutal decrease of the frequency on applying +1.00 V, corresponding to a mass increase, i.e., to the rapid entry of ClO$_4^-$. Upon reduction at +0.30 V, the frequency then increases sharply (mass decrease) to a plateau corresponding to the initial value (ClO$_4^-$ exit). When Pb^{2+} is present, one observes that once the very rapid perchlorate migration is finished at 1.00 V (or 0.30 V), Pb^{2+} migration can be detected during the oxidation process (1.00 V: slow increasing of Δf, Pb^{2+} expulsion), as well as during the reduction process (0.30 V: slow decreasing of Δf, Pb^{2+} binding). From these data, we have a picture of the complexation−expulsion sequence that occurs along one scan. The validity of these data is confirmed by a similar experiment led with a modified electrode prepared from TTF derivative **3**,[8] devoid of any binding part, for which the frequency evolution is insensitive to the presence of Pb^{2+} (Figure 2b).

Besides the above indirect evidence of the electrochemically mediated Pb^{2+} complexation, a univocal demonstration could be realized by a direct titration of residual Pb^{2+} in solution, by AA spectroscopy. For this purpose, a poly(**2**)-modified electrode of high specific area was prepared from a Pt grid (effective area: 180 cm^2), and polarization experiments were carried out with a Pb^{2+}-polluted solution. A first set of experiments was led by applying sequential potentials of +0.30 and +1.00 V, under magnetic stirring, and
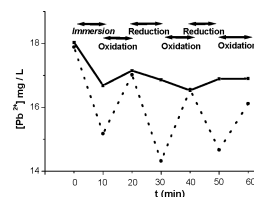
measuring the residual Pb^{2+} content in solution[9] (Figure 3). Immersion of the grid in the Pb^{2+} solution led to a decrease in [Pb^{2+}], which corresponds to the binding of the cation into the film. When a positive potential was applied for 10 min,[10] the surface polarization induced an increase in [Pb^{2+}] up to ca. the initial value. A critical interest for such a process lies in the degree of reversibility that can be illustrated by the sequential decreasing−increasing of [Pb^{2+}] observed upon the successive oxidation−reduction cycles. Furthermore, the central role of the TTF-based ligand in this electrochemically mediated process is demonstrated by the approximate constant value observed for [Pb^{2+}] as a function of the surface polarization state, in the case of a film devoid of TTF units (poly(**4**)) (Figure 3).

In summary, **1** exhibiting unprecedented electrochemical recognition properties among TTF-based ligands is described and is immobilized onto a solid surface. The recognition properties are remarkably conserved at a solid−liquid interface with poly(**2**). The demonstration of the modulation of the binding affinity of the modified surface, as a function of the potential applied, is given by EQCM analyses and by direct measurements of residual Pb^{2+} in solution by AA. Finally, the demonstration of the control of metal binding by triggering the surface polarization may suggest alternative solutions in ion-exchange resin technologies.

Supporting Information Available: Spectroscopic data, ^{1}H NMR, UV−vis, CV titrations, XPS analyses, and a SEM picture. This material is available free of charge via the Internet at http://pubs.acs.org.

References
(1) Kaifer, A. E.; Mendoza S. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E., MacNicol, D. D., Vögtle F., Eds.; Pergamon: Oxford, 1996; Vol. 1, pp 701−732. Boulas, P. L.; Gómez-Kaifer, M.; Echegoyen, L. *Angew. Chem., Int. Ed.* **1998**, *37*, 216−247. Beer, P. D.; Gale, P. A.; Chen, G. Z. *J. Chem. Soc., Dalton Trans.* **1999**, 1897−1909. Bernhardt, P. V.; Moore, E. G. *Aust. J. Chem.* **2003**, *56*, 239−258.
(2) Reviews on TTF applications: Segura, J. L.; Martín, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 1372−1409. Brondstet Nielsen, M.; Lomholt, C.; Becher, J. *Chem. Soc. Rev.* **2000**, *29*, 153−164.
(3) Le Derf, F.; Mazari, M.; Mercier, N.; Levillain, E.; Trippé, G.; Riou, A.; Richomme, P.; Becher, J.; Garín, J.; Orduna, J.; Gallego-Planas, N.; Gorgues, A.; Sallé, M. *Chem. Eur. J.* **2001**, *7*, 447−455. Le Derf, F.; Levillain, E.; Trippé, G.; Gorgues, A.; Sallé, M.; Sebastian, R. M.; Caminade, A. M.; Majoral, J. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 224−227.
(4) Synthesis of **1** and **2** will be published elsewhere.
(5) Simonsen, K. B.; Becher, J. *Synlett* **1997**, 1211−1220.
(6) Besbes, M.; Trippé, G.; Levillain, E.; Mazari, M.; Le Derf, F.; Perepichka, I. F.; Derdour, A.; Gorgues, A.; Sallé, M.; Roncali, J. *Adv. Mater.* **2001**, *13*, 1249−1252.
(7) Decrease in the i^2 peak intensity reflects kinetic effects in the film.[3b]
(8) **3** synthesized according to: Lau, J.; Simonsen, O.; Becher, J. *Synthesis* **1995**, 521−526.
(9) HClO$_4$ is added to the solution ($C = 1$ mmol L^{-1}) to stabilize Pb^{2+}.
(10) Constant charge of ca. 450 mC is exchanged during each 10 min step.

JA047411Q