Rationally-Designed Redox-Active Materials for the Separation of Isomers

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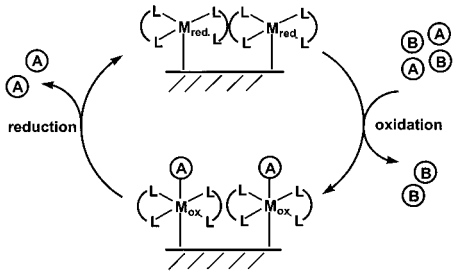
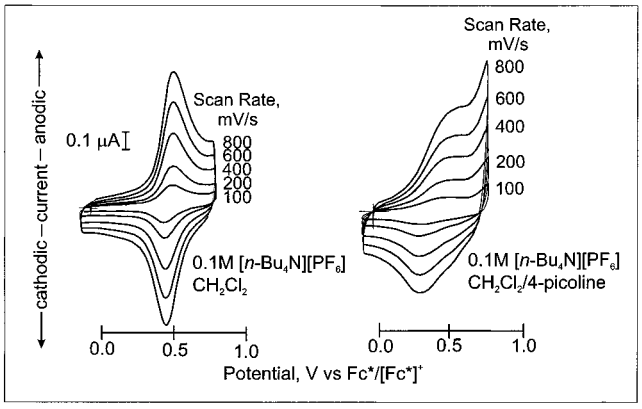
Herein we describe a new method for separating mixtures of small coordinating molecules that relies upon a polymeric transition metal-based redox-switch. The concept involves the observations that: (1) transition metal complexes in general, upon metal-centered oxidation, tend to coordinate additional ligands to satisfy electron deficiencies at the metal centers, and conversely, upon metal-centered reduction, they tend to release ligands; (2) while Cu(I) compounds are typically four-coordinate, Cu(II) complexes are usually five- or six-coordinate;[1] (3) many Cu−amine complexes possess relatively low oxidation potentials,[1] which do not result in oxidation of the small molecules to be separated; (4) the molecular recognition properties of these metal centers can be easily tailored through a choice of substitutionally inert ancillary ligands; and (5) high surface area polymers can be obtained from a variety of available bipyridine (bpy) precursors.[2] Taken together these observations allow one to design electrode-surface-confined polymeric complexes that can recognize and selectively coordinate one component of a mixture in one oxidation state and release it in the other, thereby providing a way of separating the mixture, Scheme 1.

The first step of a three-step separation cycle in our new scheme is metal-centered oxidation of a polymer-supported complex poly−$[M_{red}(L_2)_2]$, which induces preferential coordination of **A**-type molecules due to favorable steric or electronic interactions between **A**-type molecules and the complex. The next step is separation of **B**-type molecules from the complex poly−$[M_{ox}(L_2)_2$-**A**], which is facilitated by the polymeric nature of the complex. The final step is metal-centered reduction of poly−$[M_{ox}(L_2)_2$-**A**], which releases **A**-type molecules and regenerates poly−$[M_{red}(L_2)_2]$. Significantly, incomplete separation of the components of the mixture can be addressed simply by repeating this cycle of uptake and release until the desired purity of the components is reached.

Koval et al. have reported an important related but different method for separating gaseous alkene/alkane mixtures, which is based on selective uptake and release of an alkene with mixtures of uncharacterized Cu(I)/Cu(II) salts with labile aqua or vinyl sulfonate ligands.[3] Although very impressive and useful with respect to the separation of coordinating gaseous molecules from noncoordinating ones, the ill-defined nature of the Cu metal centers and their substitutionally labile ligands do not allow one to rationally design materials for separating a specific set of components with comparable but different properties of ligation to the metal center.

Scheme 1





In view of the aforementioned observations, we investigated the redox-induced separation of binary mixtures of pyridine and picolines by using the known complex $[Cu^{I}(bpy)_2]PF_6$ (**1**)[4] under homogeneous conditions. No reaction occurred when **1** was treated with 100 equiv of pyridine or 2-, 3-, or 4-picoline in CH_2Cl_2 as evidenced by ^{1}H NMR spectroscopy, but chemical oxidation of **1** with $FcPF_6$ [Fc = $\{Fe(\eta^5\text{-}C_5H_5)_2\}^+$] in the same solvent in the presence of just 5−20 equiv of any of these compounds resulted in their uptake to afford the five-coordinate blue-green paramagnetic complexes $[Cu^{II}(bpy)_2L][PF_6]_2$ (**2a**, L = pyridine; **2b**, L = 2-picoline; **2c**, L = 3-picoline; **2d**, L = 4-picoline). For comparison, chemical oxidation of **1** in MeCN, THF, or CH_2Cl_2 afforded the known four-coordinate complex $[Cu^{II}(bpy)_2][PF_6]_2$ (**3**).[5] Paramagnetic compounds **2a**−**d** were characterized by elemental analyses and their reactivities, which are consistent with the proposed formulations.[6] In addition, the solid-state structure of **2a** was determined by a single-crystal X-ray diffraction study and is consistent with our structural formulation for it in solution.[7] Significantly, reduction of **2a**−**d** with Fc* [Fc* = $Fe(\eta^5\text{-}C_5Me_5)_2$] cleanly regenerated complex **1** and released 1 equiv of the expected pyridine or picoline as evidenced by ^{1}H NMR spectroscopy, thus completing the cycle of uptake and release.

Reversible uptake and release of small coordinating molecules with **1** also was effected via electrochemical means. The cyclic voltammogram of **1** in CH_2Cl_2 (a weakly coordinating solvent) exhibited a reversible wave at +520 mV,[8] which is assigned to the $[Cu(bpy)_2]^+/[Cu(bpy)_2]^{2+}$ redox couple. When the electro-

(1) *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1987; Vol. 5.

(2) (a) Kajita, T.; Leasure, R. M.; Devenney, M.; Friesen, D.; Meyer, T. J. *Inorg. Chem.* **1998**, *37*, 7, *4782*. (b) Bommarito, S. L.; Lowery-Bretz, S. P.; Abruña, H. D. *Inorg. Chem.* **1992**, *31*, 495.

(3) (a) Suzuki, T.; Noble, R. D.; Koval, C. A. *Inorg. Chem.* **1997**, *36*, 136. (b) Terry, P. A.; Noble, R. D.; Swanson, D.; Koval, C. A. *Am. Inst. Chem. Eng.* **1997**, *43*, 1709.

(4) Munakata, M.; Kitagawa, S.; Asahara, A.; Masuda, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1927.

(5) Formation of **3** was confirmed by elemental analysis (Anal. Calcd for $C_{20}H_{16}N_4CuP_2F_{12}$: C, 36.10; H, 2.43; N, 8.42. Found: C, 36.27; H, 2.40; N, 8.40) and a single-crystal X-ray diffraction study.

(6) **2a**: Anal. Calcd for $C_{25}H_{21}N_5CuP_2F_{12}$: C, 40.33; H, 2.85; N, 9.40. Found: C, 40.01; H, 2.58; N, 9.10. **2b**: Anal. Calcd for $C_{26}H_{24}N_5CuP_2F_{12}$: C, 41.09; H, 3.18; N, 9.22. Found: C, 40.89; H, 3.12; N, 9.11. **2c**: Anal. Calcd for $C_{26}H_{24}N_5CuP_2F_{12}$: C, 41.09; H, 3.18; N, 9.22. Found: C, 39.85; H, 3.03; N, 9.10. **2d**: Anal. Calcd for $C_{26}H_{24}N_5CuP_2F_{12}$: C, 41.09; H, 3.18; N, 9.22. Found: C, 39.95; H, 3.07; N, 9.15.

(7) Used for characterization purposes only (see Supporting Information); to be published at a later date.

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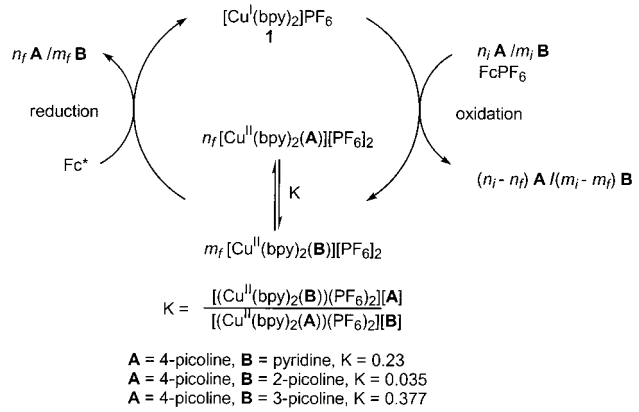
Scheme 2



chemical measurements were performed in CH_2Cl_2 containing pyridine (20−40 equiv), the reversible wave became irreversible with the oxidative peak potential shifting from +380 mV (20 equiv of pyridine) to +300 mV (40 equiv of pyridine) upon increasing concentration of pyridine. The irreversibility of this processes is consistent with the proposed oxidatively induced uptake reaction.

Chemical oxidation of **1** in CH_2Cl_2 in the presence of binary mixtures of 4-picoline and either pyridine or 2- or 3-picoline results in the formation of thermodynamic mixtures of two five-coordinate complexes $[Cu^{II}(bpy)_2(\mathbf{A})][PF_6]_2$ and $[Cu^{II}(bpy)_2(\mathbf{B})][PF_6]_2$ (**A** = 4-picoline; **B** = 2- or 3-picoline or pyridine, Scheme 2). When the two Cu complexes were separated and isolated from solvent and excess pyridine and picolines and subsequently reduced, compound **1** was regenerated along with a mixture of **A** and **B**. In all cases, the mixtures were enriched in 4-picoline (**A**). In each case, the ratio of **A** to **B** (n_f to m_f, Scheme 2 and Figure 1) after one redox separation cycle is different from the ratio of **A** to **B** before separation (n_i and m_i) and is determined by the equilibrium constant *K*, Scheme 2. The equilibrium constants for the reaction defined by eq 1

$$[Cu^{II}(bpy)_2(\mathbf{A})][PF_6]_2 + \mathbf{B} \leftrightarrows [Cu^{II}(bpy)_2(\mathbf{B})][PF_6]_2 + \mathbf{A} \quad (1)$$

were determined by ^{1}H NMR spectroscopy to be $K = 0.035$ for **B** = 2-picoline, 0.377 for **B** = 3-picoline, and 0.23 for **B** = pyridine. Generally, the efficacy of the separation is inversely proportional to *K* (Figure 1).

The separation of 4-picoline from 2-picoline is straightforward due to the vastly different ligating ability of these molecules for the Cu(II) complex, which is primarily a steric phenomenon. The remarkable feature of this switch is its ability to differentiate 3- and 4-picoline, which have very similar physical and chemical properties (i.e., boiling temperature; 144 °C for 3-picoline and 145 °C for 4-picoline). Separation of 3- and 4-picoline has received considerable attention in the literature, and several elaborate separation methods including dissociation extractive crystallization,[9a] distillation in the presence of host compounds,[9b] reactive distillation,[9c] inductive adsorption,[9d] and clathrate formation[9e] have been reported and patented.

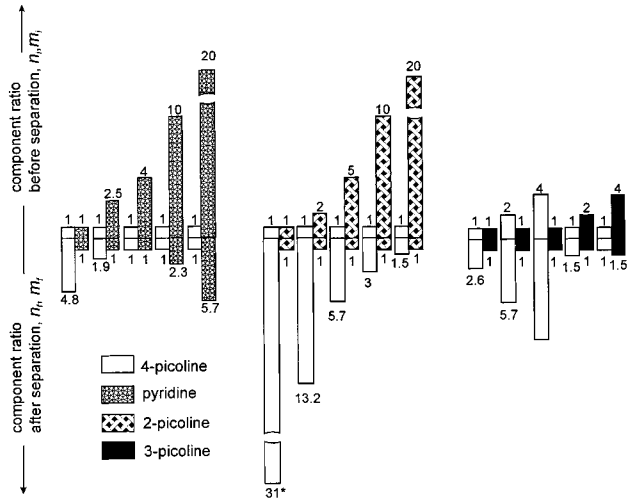


Figure 1. Bar plots reflecting efficacy of separation of binary mixtures of 4-picoline and pyridine or 2-picoline or 3-picoline. ∗ The ratio of 31:1 is calculated on the basis of the equilibrium constant, *K*; no 2-picoline was observed by ^{1}H NMR spectroscopy.

To demonstrate proof-of-concept of our proposed separation protocol based upon a polymeric redox-switch, a polymeric analogue of **1** was prepared as a thin film on the surface of a gold electrode. This was accomplished by electrochemically polymerizing 4,4′-$(CH_2Br)_2$-2,2′-bpy according to literature methods.[10] The resulting insulating film was soaked in a solution of $[Cu(MeCN)_4]PF_6$ in acetonitrile (0.01 M) to afford a redox-polymer, $[\{Cu(4,4'\text{-}(CH_2)_2\text{-}2,2'\text{-}bpy)_2\}PF_6]_n$ (**4**), as evidenced by cyclic voltammetry, Scheme 1. The cyclic voltammetry of **4** in CH_2Cl_2 shows a reversible wave at ∼+500 mV (Scheme 1, left inset) and remains unchanged even after 1000 cycles, signifying the robust nature of the polymer in both oxidation states. Upon addition of 4-picoline, the reversible wave shifts to a lower potential ($E_{pa} = \sim$+400 mV, Scheme 1, right inset) and becomes irreversible, which is consistent with the homogeneous voltammetry of **1** (vide supra) and suggests analogous stereochemistry and similar redox-induced transformations for **4** in the presence of 4-picoline. Significantly, polymeric complex **4** was used to completely separate (within the HPLC detection limit) a mixture of 2- and 4-picolines ($\sim 10^{-9}$ mol)[11] in just one cycle of electrochemically induced uptake and release.

These experiments, along with the abundance of pyridine-derived ligands, strongly suggest that this approach can be used as a general one for designing materials to separate many two-component mixtures. Efforts to evaluate this assertion are underway, including the development of analogous chiral redox-active materials that can be designed to separate enantiomers.

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Supporting Information Available: Detailed synthesis of complexes **2**−**4**, complete description of the separation procedures, and X-ray structural information on **2a** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Unless otherwise noted, the electrochemical data are referenced vs Fc*/$[Fc^*]^+$; 0.1 M *n*-$[Bu_4N]PF_6$ was used as a supporting electrolyte.

(9) (a) Gaikar, V. G.; Mahaparta, A.; Sharma, M. M. *Ind. Eng. Chem. Res.* **1989**, *28*, 199. (b) Takumi, H.; Koga, M.; Toda, F. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1996**, *277*, 439. (c) Duprat, F.; Gau, G. *Can. J. Chem. Eng.* **1991**, *69*, 1327. (d) Duprat, F.; Gassend, R.; Gau, G. *Ind. Eng. Chem. Res.* **1988**, *27*, 831. (e) Toda, F. U.S. Patent 649,783, 1996.

(10) Sharon, G.; Strouse, G. F.; Meyer, T. J.; Sullivan, B. P. *Inorg. Chem.* **1992**, *30*, 2942.

(11) All separations have been done on a very small scale and have not been evaluated or optimized with respect to throughput.