doi:10.1246/cl.2010.1192
Published on the web October 16, 2010

Removal of Perchlorate and Tetrafluoroborate Anions from Aqueous Solutions by a Self-assembled Cu(II) Molecular Capsule System Using Water-insoluble Cu(II) Source

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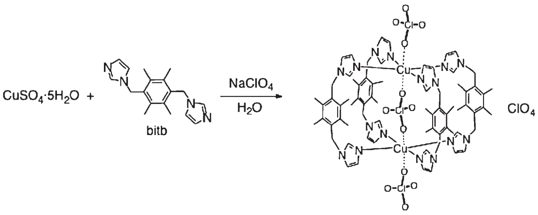
A self-assembled Cu–bitb molecular capsule system using basic copper(II) carbonate as a Cu^{2+} source removed perchlorate and tetrafluoroborate anions from aqueous solutions without contamination by Cu(II) ion.

Perchlorate (ClO_4^-) and tetrafluoroborate (BF_4^-) anions are known to interfere with the thyroid's uptake of iodide, which is an essential component of hormones made in the thyroid gland.[1] It is widely perceived that consumption of excess of these anions raises the possibility of serious effects on human health, particularly on growth of newborns and children. Although they are toxic, these anions are difficult to remove from aqueous solutions because of their high solubility in water and organic solvents.[2] At this point however, there are no metal ions that effectively precipitate these anions from water. Therefore, the development of new separation methods from aqueous solutions is an important and challenging subject in material science.

We have recently reported that 1,4-bis(imidazol-1-yl-methyl)-2,3,5,6-tetramethylbenzene (bitb) produces a self-assembled molecular capsule $[ClO_4 \subset Cu_2(bitb)_4(ClO_4)_2]ClO_4$ (**1**) (Scheme 1) on contact with ClO_4^- in aqueous media.[3] Due to insolubility in water, ClO_4^- is removed from aqueous solutions.

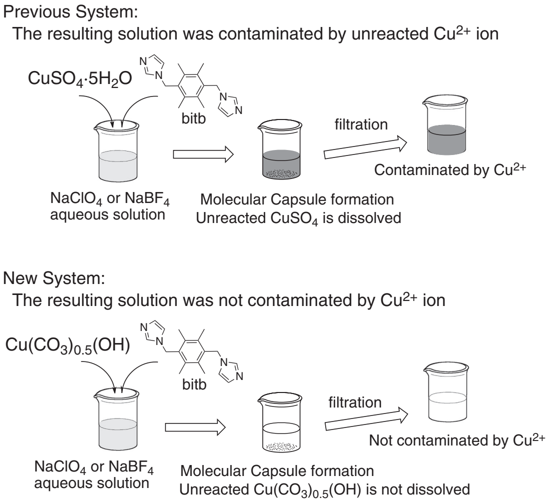
Although the ClO_4^- separation by encapsulations in Cu–bitb molecular cages might be useful as a new perchlorate separation method, this system still has a serious problem in that the resulting solution is contaminated by unreacted Cu^{2+} ion. That is, our previous method, which uses $CuSO_4{\cdot}5H_2O$ and bitb, seriously contaminates the resulting solution by Cu^{2+} ions that remain unreacted (Scheme 2).

Continuing work on this issue, we have tried to use $Cu(CO_3)_{0.5}(OH)$, i.e., basic copper(II) carbonate, and $Cu(OH)_2$ instead of $CuSO_4{\cdot}5H_2O$ as Cu^{2+} source to construct the Cu–bitb molecular capsule for anion separation. Because these Cu^{2+} sources and bitb are insoluble in water, the treated solution would not be contaminated by Cu(II) ion. We have found that the combination of $Cu(CO_3)_{0.5}(OH)$ and bitb is useful for selective removal of BF_4^- as well as ClO_4^- from aqueous solutions. Here, we report the new removal method for these anions from aqueous solutions without contamination by Cu(II) ion.



[$ClO_4 \subset Cu_2(bitb)_4(ClO_4)_2]ClO_4$ (1)

Scheme 1.



Scheme 2.

The molecular capsule $[BF_4 \subset Cu_2(bitb)_4(BF_4)_2]BF_4$ (**2**), which was obtained by treatment of $CuSO_4{\cdot}5H_2O$, bitb, and $NaBF_4$, is isomorphous to **1**.[4] The components of the added powder prepared for the experiments are represented by brackets, { }, in this paper. For example, when $Cu(CO_3)_{0.5}(OH)$ and two equivalents of bitb were added in an aqueous solution, the added materials are represented as $\{Cu(CO_3)_{0.5}(OH) + 2$ bitb$\}$.

The two combinations $\{Cu(CO_3)_{0.5}(OH) + 2$ bitb$\}$ and $\{Cu(OH)_2 + 2$ bitb$\}$ were examined, and the former showed useful activities for ClO_4^- and BF_4^- separations. Figure 1a shows the changes of concentration of ClO_4^- after addition of $\{Cu(CO_3)_{0.5}(OH) + 2$ bitb$\}$ or $\{Cu(OH)_2 + 2$ bitb$\}$ in $NaClO_4$ aqueous solution (1.0 mM) depending on time. The changes of the concentrations of anions were determined by using ion chromatography. When $Cu(CO_3)_{0.5}(OH)$ was used as a metal source, ClO_4^- anion was effectively reduced to about 0.3 mM within 2 h. On the other hand, addition of $\{Cu(OH)_2 + 2$ bitb$\}$ hardly reduced ClO_4^- anion, indicating that the counter anion of the Cu^{2+} sources remarkably affect the ClO_4^- separation activities.

Similar tendency was confirmed for BF_4^- separation as exhibited in Figure 1b. Addition of $\{Cu(CO_3)_{0.5}(OH) + 2$ bitb$\}$ in an aqueous solution of $NaBF_4$ (1.0 mM) reduced the

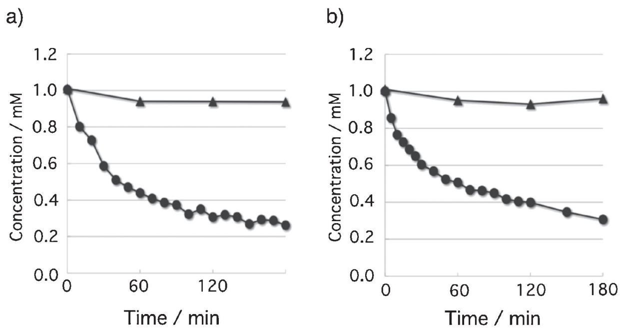


Figure 1. Changes of concentrations of ClO_4^- (a) and BF_4^- (b) anions in an aqueous solution of $NaClO_4$ or $NaBF_4$ (1.0 mM, 30 mL) after additions of mixed powder of $Cu(CO_3)_{0.5}(OH)$ (7.0 mg, 0.06 mmol) and bitb (35.4 mg, 0.12 mmol) (●) for each solution at 30 °C. Similar treatment was carried out by addition of $Cu(OH)_2$ (5.8 mg, 0.06 mmol) and bitb (35.4 mg, 0.12 mmol) (▲).

concentration of BF_4^- anion to about 0.4 mM within 2 h, while addition of $\{Cu(OH)_2 + 2$ bitb$\}$ hardly reduced the BF_4^- concentration under the same reaction conditions. These results demonstrate that $\{Cu(CO_3)_{0.5}(OH) + 2$ bitb$\}$ has higher activity for removal of ClO_4^- and BF_4^- from aqueous solutions than $\{Cu(OH)_2 + 2$ bitb$\}$.

When $\{CuSO_4{\cdot}5H_2O + 2$ bitb$\}$ was added to an aqueous solution containing equimolar $NaClO_4$ and $NaBF_4$, ClO_4^- was preferentially removed (Figure S1).[5] Because the molecular capsule is obtained by anion-templated self-assembly, this means that the molecular capsule $[Cu_2(bitb)_4]^{4+}$ has higher encapsulation selectivity to ClO_4^- than to BF_4^-. Similar tendency was observed for $\{Cu(CO_3)_{0.5}(OH) + 2$ bitb$\}$.

The light-purple powder obtained by treatment of $\{Cu(CO_3)_{0.5}(OH) + 2$ bitb$\}$ with excess $NaBF_4$ in an aqueous solution contains an absorption for **2** at around 530 nm in the reflectance spectrum (Figure S2).[5] This apparently demonstrates that the removal of BF_4^- anion from the aqueous solution is due to the formation of insoluble molecular capsule including BF_4^- within it.

We have shown that $\{CuSO_4{\cdot}5H_2O + 2$ bitb$\}$ removes ClO_4^- anion selectively from aqueous solutions.[3] This previous result prompted us to study whether addition of $\{Cu(CO_3)_{0.5}(OH) + 2$ bitb$\}$ can remove BF_4^- anions selectively or not. We chose BF_4^- as a target anion instead of ClO_4^-, because BF_4^- is more difficult to remove from aqueous solutions as mentioned above as well as removal of BF_4^- from aqueous solution by encapsulation in molecular capsule is unprecedented. Figure 2 summarizes the changes of concentrations of anions after 24 h from addition of $\{Cu(CO_3)_{0.5}(OH) + 2$ bitb$\}$ in an aqueous solution, containing 7 different salts (NaF, NaCl, $NaNO_2$, NaBr, $NaNO_3$, $NaBF_4$, and Na_2SO_4) all at the same concentration (1 mM). This shows the selective reduction of BF_4^- concentration, demonstrating that $\{Cu(CO_3)_{0.5}(OH) + 2$ bitb$\}$ selectively removes BF_4^- in the presence of the other anions.

One of the purposes of this study is the development of a new ClO_4^- and BF_4^- separation method without contamination of the resulting solutions by Cu(II) ion. Although the solutions remained colorless during the separation experiments, we have examined the concentration of Cu(II) ion in the resulting solution by inductively coupled plasma optical emission spectrometry.

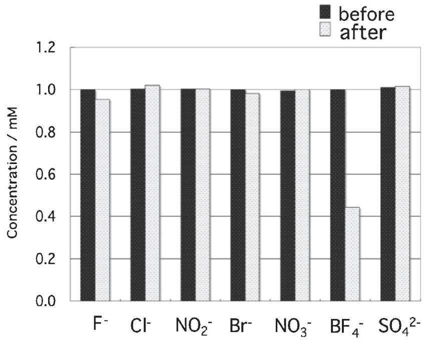


Figure 2. Changes of concentrations of anions before and after 24 h of additions of $Cu(CO_3)_{0.5}(OH)$ (24 mg, 0.20 mmol) and bitb (117 mg, 0.048 mmol) in an aqueous solution (30 mL) containing 1.0 mM of every sodium salt listed in the chart.

The detected concentrations of Cu(II) ion in the resulting solution after ClO_4^- and BF_4^- removal were 0.05 mg L^{-1} and less than 0.01 mg L^{-1} respectively. These values are smaller than the critical value set by Japanese law in waste water (3 mg L^{-1}) and even drinking water (1 mg L^{-1}), demonstrating that $\{Cu(CO_3)_{0.5}(OH) + 2$ bitb$\}$ can remove ClO_4^- and BF_4^- anions from aqueous solutions without significant contaminations by Cu(II) ion.

In summary, we have shown that BF_4^- as well as ClO_4^- are removed from aqueous solutions by addition of $\{Cu(CO_3)_{0.5}(OH) + 2$ bitb$\}$. The separation method based on the self-assembled formation of molecular capsules is interesting in that removal is not prevented by other general anions such as Cl^- and SO_4^{2-}, and that the resulting solution is not contaminated by Cu^{2+} ions.

This work was supported by a grant from New Energy and Industrial Technology Development Organization (NEDO) in Japan (No. 07A20008a). We thank Ms. K. Terasaki of Center for Instrumental Analysis for the assistance in elemental analysis of **2**.

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4 Complex **2** was obtained by treatment of $NaBF_4$, $CuSO_4{\cdot}5H_2O$, and 2 equivalents of bitb in a MeCN/water mixed solution. Anal. Calcd for $C_{72}H_{88}B_4Cu_2N_{16}F_{16}$: C, 52.35; H, 5.37; N, 13.57%. Found: C, 52.42; H, 5.29; N, 13.36%. Identification of the isostructure to complex **1** was carried out by determination of cell parameter; $a = 25.83(4)$, $b = 13.142(16)$, $c = 28.66(6)$ Å, $\beta = 114.704(12)°$, $V = 8839(26)$ Å^3.

5 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.