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Ligand-Functionalized Block Copolymer Materials for the Demetallization of Crude Oil

Jonathan L. Sessler, PI
Dept. of Chemistry
The Univ. of Texas at Austin
Austin, TX 78712

Introduction

Funds from the ACS PRF grant have been used to support in part the educational development and research progress of two graduate students, Rob Fimognari and Matt Moore. It has also provided partial support for a postdoctoral fellow, Xiaofan Ji. The overarching goal for all three project participants has been to join ion receptors with polymeric backbones. To date, good progress has been made by Rob and Xiaofan; however, Matt did not end up with a publishable contribution to the project. This report will thus summarize briefly what has been accomplished by Xiaofan and, to a lesser extent, Rob. In any case, it is important to appreciate that both students receiving partial support under the aegis of this grant have had a chance for professional growth and development. These opportunities have included the chance to work with postdocs, attend seminars, and meet with visiting speakers, and interact with faculty other than the PI. The career of the PI has also been impacted positively in that the PRF funds have allowed us to branch out and try something quite new in a group that has largely been focused on macrocycle design, synthesis, and biological testing.

Pyridine Carboxylate Polymers

The research work supported by the PRF and carried out by Rob has involved the creation of ROMP-based polymers that bear ligands selective for copper. As mentioned in last year's report, Rob successfully synthesized and characterized the resulting polymer and showed it was selective for Cu(II) over Ni(II). The structure of the free polymer, chelated form, and representative competition data are shown in Figure 1. The work itself has now been published (*Inorg. Chem.* **2018**, *57*, 392−399).

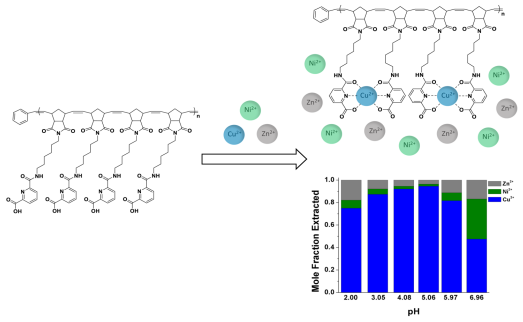

Figure 1. ROMP-based material suitable demonstrating selective capture of Cu(II) over Ni(II).

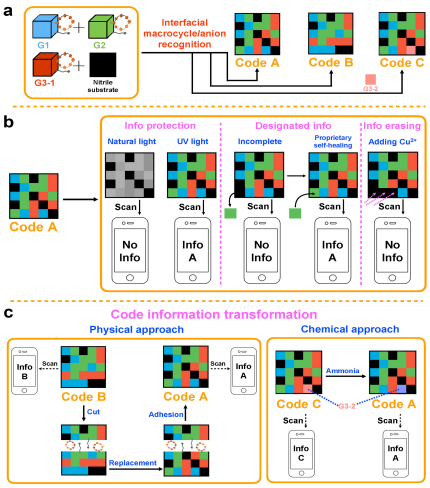

Figure 2. Cartoon representations: **a** Formation of 3D color codes via the interfacial adhesion of individual domains made up of hydrogels **G1**, **G2**, and **G3** (**G3-1** and **G3-2**). **b** Information protection, designated information, and information erasing of **Code A**. **c** Transformation of encoded information by physical and chemical approaches.

3D Color Codes

The research work supported by the PRF and carried out by Xiaofan has involved the creation of a new class of self- and hetero-healing hydrogels containing built-in fluorophores. The result of this "stickiness" is system that can be physically manipulated to produce color codes suitable for reading using a readily downloadable 'app'. The basic design is shown in Figure 2. The actual materials that comprise the constitute gels that may be reprogramed by both chemical and physical means to allow different information to be read out. The nature of the soft materials involved, the codes can be used as wearable materials allowing modulation-amenable information to be read out in a way that is not possible by use of non-dynamic physical attributes, such as finger prints. A first report on this PRF-sponsored hydrogel project has been published (*Adv. Mater.* **2018**, *30*, 170548); gratifyingly, this work was highlighted by *Nature*: ***Jelly blocks that send a message***: https://www.nature.com/articles/d41586-018-01139-6).

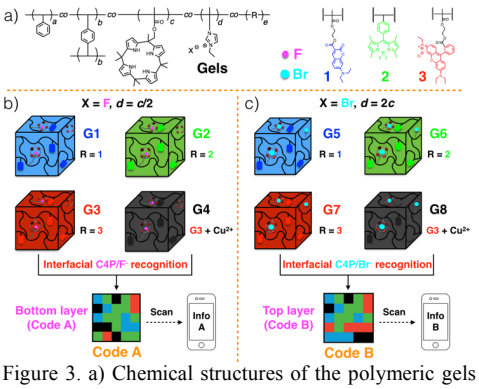

Figure 3. a) Chemical structures of the polymeric gels and the incorporated fluorescent elements. Cartoon representations of: b) **G1-G4** and the formation of 3D colour **Code A** via interfacial C4P/imidazolium-F^- interactions; c) **G5-G8** and the formation of 3D colour **Code B** via interfacial C4P/imidazolium-Br^- anion interactions.

Double Layer 3D Color Code

Very recently, we developed a double layer 3D color code, allowing direct recognition of the chloride anion using a smart phone. The actual materials that comprise the constitute gels are shown in Figure 3. We think this work is exciting because the developed materials provide a proof-of-principle demonstration of what we think could emerge as a totally new and readily generalizable approach

to the on-site analyte detection. The strategy is appealing because it does not rely on elaborate instrumentation. Typically, analyte detection is effected by spectroscopic means, which relies on the availability of laboratory instrumentation. This can be problematic in terms of cost and accessibility. In contrast, the approach we wish to report relies on a two-layer polymeric gel 3D code system; it permits the on-site detection of the chloride anion and a physiologically relevant concentration. The top layer of a two-layer 3D code that can be delaminated and thus effectively removed by exposure to a chloride anion source. This results in a differential information response that may be read out by means of a smart phone under conditions of UV illumination.

Macrocycle-Containing Polymeric Network

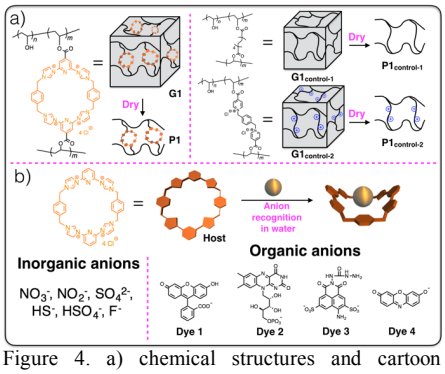

Figure 4. a) chemical structures and cartoon representations of the polymeric materials used in this study and b) proposed macrocycle-anion binding interactions that are operative in aqueous environments.

Industrialization and agriculture have made potentially hazardous anions ubiquitous that can have a serious impact on water quality and can affect human health. Anion-responsive supramolecular hydrogels might be useful in removing toxic anions from aqueous environments. While a number of elegant anion-responsive supramolecular hydrogels have been reported in the contest of anion sensing, to our knowledge such systems have yet to be exploited in the context of water purification. We reported a supramolecular hydrogel-based approach to water purification that relies on the use of a tetracationic anion receptor and which involves a simple two-step sequence of anion absorption, followed by physical separation. The simplicity of the present approach leads us to suggest that strategies such as those detailed here could have an important role to play in water purification. The structure of the polymer networks and the water purification process are shown in Figure 4. This work has been published] (*J. Am. Chem. Soc.* **2018**, *140*, 2777–2780), and highlighted by *C&EN News*: https://cen.acs.org/articles/96/web/2018/03/Hardy-hydrogel-cleans-water.html.

Thermoresponsive Calix[4]pyrrole Amphiphilic Polymer

We then developed a thermoresponsive calix[4]pyrrole amphiphilic polymer which allows for the removal of cesium anion salts from an aqueous source phase without the use organic solvents, as required by more traditional liquid-liquid extraction-based approaches. Liquid-liquid extraction is a venerable technique that is being explored for the removal of potentially harmful ion from aqueous environments. We reported a thermal-responsive amphiphilic polymer bearing pendent C4P receptors that allows cesium anion salts to be captured and removed from water without the need for organic solvents. This purification sequence involves 1) the capture of anion salts from aqueous media in the form of self-assembled micelles, 2) warming to induce micelle precipitation, and 3) removal of the anion-bound micelles from the aqueous medium via filtration.

Since it avoids the use of organic solvents, we suggest that this strategy could have a role to play in the development of potential new water purification processes. We specifically demonstrate its utility in the area of cesium halide salt removal. Cesium carries about 90% of the radioactivity in nuclear waste and is a huge threat in the case of nuclear disasters, such as the Fukushima meltdown. While classic extractants work in the case of cesium nitrate salts, they fail in the case of less hydrophobic salts, such as the CsCl, that would be found in the case of an untoward release of radioactive material. We thus think this work is of interest on both the fundamental and practical levels. The structure of the polymer networks, along with the water purification process, is shown in Figure 5. A manuscript describing this chemistry has been submitted to *Chemistry – A European Journal*.

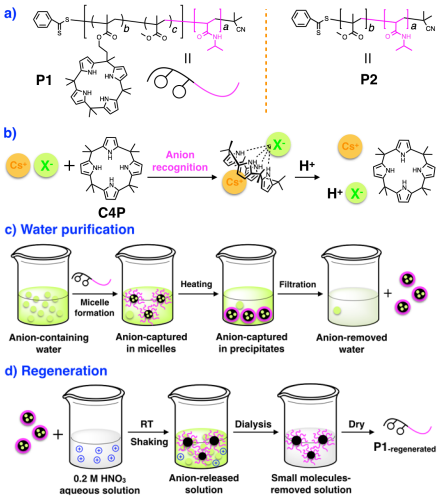

Figure 5. a) Chemical structures and cartoon representations of the polymeric materials used in this study. b) Schematic representation of the receptor anion + counter cation ion-pairing and acid-induced disassembly. Cartoon representations of c) anion removal from water by use of polymer **PI** containing C4P receptors, and d) sequence used to regenerate **P1**.

Conclusion and Future Plans

This PRF-supported foray into the world of receptor-functionalized materials has allowed us to launch a new research direction in the lab. As funding and other resources permit, further work will be carried out. This may permit us to go beyond anions and cations and the use of polar media. This is expected to allow us to address the tremendous challenges of crude oil purification and demetallization.