

Project 90301

The Supramolecular Chemistry of Selective Anion Recognition for Anions of Environmental Relevance

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RESULTS TO DATE: This report summarizes work performed in FY 2004, the second year of the current three-year renewal period.

Work carried out at ORNL since the inception of the project has served to demonstrate that the calix[4]pyrroles from the co-P.I.'s laboratory at the Univ. of Texas strongly enhance the extraction of sulfate by tricaprylmethylammonium nitrate or chloride in the presence of excess nitrate and chloride. Similar results were found in the case of the tetraamide macrocycles synthesized in the Bowman-James laboratory (Univ. of Kansas). Effort at the Univ. of Texas thus focused on generating new pyrrole-amide macrocycles that might combine the most favorable aspects of the calixpyrroles and the tetraamides. This culminated in the synthesis of several new receptors, which provided a "matched set" from whence insights into anion recognition could be inferred. As can be inferred from the data summarized in Table 1, small adjustments in the structure allow for a fine-tuning of the anion binding properties in favor of sulfate recognition, or in the case of injudicious modifications, selectivities that favor completely different classes of anionic substrates.

Although further work is necessary, on the basis of this first set of well-controlled comparative data, it is tentatively concluded that a combination of subunit rigidity combined with a high degree of overall macrocycle flexibility favors sulfate and that systems that either too "floppy" or too constrained will favor other tetrahedral anions or halide anions, respectively.

In addition to the work on new classes of pyrrole amide receptors, efforts have continued to study further the anion binding properties of calix[4]pyrroles. Here, a very exciting discovery was made, namely that these species can serve as ion pair receptors, binding not only an anion but a counter cation as well. This finding, which has important implications in terms of extraction-type applications, is animating the study of other electronically modified calix[n]pyrroles ($n = 4$ and 5). Of particular interest are systems that have been subject to electronic modification, since, as in the case of the simple calix[4]pyrroles, data from the ORNL team provides support for the notion that these species will prove highly effective as sulfate anion extractants. Other recent data from ORNL has led to the suggestion that cyclo[n]pyrroles ($n = 8$) may also be extremely useful as sulfate anion extractants.

DELIVERABLES: 1. Sessler, J. L.; Katayev, E.; Pantos, G. D.; Ustynyuk, Y. A. "Synthesis and study of a new diamidodipyrromethane macrocycle. An anion receptor with a high sulfate-to-nitrate binding selectivity," *Chem. Commun.* 2004, 1276-1277. Featured in *C & E News*: "Macrocycle for Nuclear Waste," *Chemical Engineering News*, June 7, 2004, p. 8.

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3. Sessler, J. L.; Katayev, E.; Pantos, D. G.; Scherbakov, P.; Reshetova, M. D.; Khurstalev, V. N.; Lynch, V. M.; Ustynyuk, Y. A. "Fine Tuning the Anion Binding Properties of 2,6-Diamidopyridine Dipyrromethane Hybrid Macrocycles," *J. Am. Chem. Soc.* 2005, 127, 11442-11446.

4. Custelcean, R.; Moyer, B. A.; Sessler, J. L.; Cho, W.-S.; Gross, D.; Bates, G. W.; Brooks, S. J.; Light, M. E.; Gale, P. A. *Angew. Chem. Int. Ed.* 2005, 44, 2537-2542; *Angew. Chem.* 2005, 117, 2513-2518. Featured on the cover.

5. Sessler, J. L.; Katayev, E. A.; Pantos, G. D.; Reshetova, M. D.; Khrustalev, V. N.; Lynch, V. M.; Ustynyuk, Y. A. ?Anion Induced Synthesis and Combinatorial Selection of Polypyrrolic Macrocycles,? *Angew. Chem.*, in press.

6. Moyer, B. A.; Delmau, L. H.; Fowler, C. J.; Ruas, A.; Bostick, D. A.; Sessler, J. L.; Llinares, J. M.; Hossain, A.; Kang, S. O.; Bowman-James, K. *Supramolecular Chemistry of Environmentally Relevant Anions.*, submitted.