Scientists at the University of Cincinnati and PNNL are developing an innovative, fluorescence-based sensor for technetium (Tc) for monitoring the vadose zone and groundwater at the Hanford Site and elsewhere. Funded by DOE’s Environmental Management Science Program (EMSP), this research project has an overall goal to design and implement new sensor technology offering unprecedented levels of specificity needed to analyze the complex contaminant mixtures found at DOE sites. A prototype was tested successfully on Hanford tank waste containing ferrocyanide (http://www.er.doe.gov/Science_News/features_articles_2000/uncommon_sensor/Uncommon_sen.htm).

Subsurface contamination by Tc is of particular concern because of the extremely long life of its most common isotope $^{99}$Tc (half-life = 2 x 10$^5$ years) and the fast migration in soils exhibited by its most common chemical form, pertechnetate (TcO$_4^-$). The sensor has the capability for onsite monitoring, either by immersion in subsurface water for continuous monitoring or for immediate analysis of collected samples. The device combines electrochemistry, spectroscopy, and selective partitioning, which substantially improves selectivity. The key to adapting this sensor to detect TcO$_4^-$ lies in the development of unique chemistry within the chemically selective (Figure 1).

This research has led to the discovery of the first luminescence from trans-dioxo-technetium(V) complexes. The room- and low-temperature luminescence studies of trans-[TcO$_2$(L)$_4$]$^+$ (L = pyridine or picoline) and trans-[TcO$_2$(CN)$_4$]$^-3$ opens a new chapter in Tc chemistry, both in a fundamental and practical sense. The low temperature luminescence spectrum (Figure 2) for [TcO$_2$(pic)$_4$](BPh$_4$), with [ReO$_2$(pic)$_4$](BPh$_4$) shown as an overlay spectrum, and clearly shows a lower energy (~180-200 cm$^{-1}$) vibronic progression for analogous Re and Tc complexes. This important development allows us to develop a theoretical model that can be used to predict the optical behavior of Tc complexes in general.

This discovery also provides the first opportunity to directly compare fundamental luminescence properties of second- and third-row d$^2$ metal-oxo congeners. The analytical applications of the TcO$_2$ chromophore offer promise for design of dual-mode

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complexes that can correlate luminescence and radioimaging properties into a single agent. For the EMSP project’s purposes, luminescent Tc(V) complexes are a significant advance in the team’s design of a spectroelectrochemical sensor for detection of pertechnetate in the environment. An article featuring the sensor work was released on the October 8 web page of the Journal of the American Chemical Society and can be accessed at http://pubs3.acs.org/acs/journals/doilookup?in_doi=10.1021/ja054906m. The research team members are William R. Heineman and Carl J. Seliskar, University of Cincinnati; and Samuel A. Bryan and Timothy L. Hubler, PNNL.

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Figure 2. Low-temperature (8 K) luminescence spectra of microcrystalline [ReO₂(pic)₄](BPh₄) (blue) and [TcO₂(pic)₄](BPh₄) (red). Spectra are not normalized for excitation intensity differences.

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