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A Self-Assembled Supramolecular Optical Sensor for Ni(II), Cd(II), and Cr(III)

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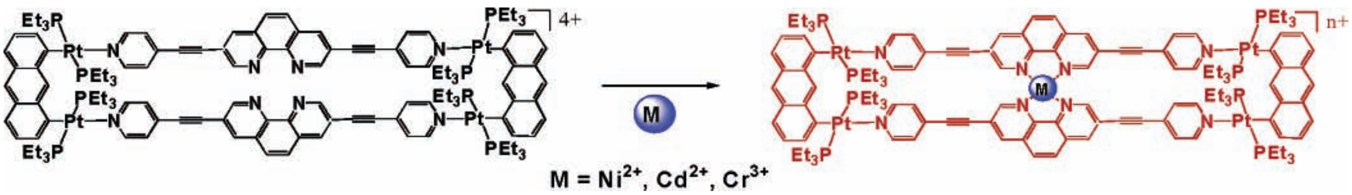
ABSTRACT



A new chromogenic supramolecular sensor for transition metals is reported. It is based on a newly designed phenanthroline-containing molecule that self-assembles via an organometallic "clip" into a supramolecular optical sensor for metals.

In recent years, chemical sensing has attracted the interest of many research groups.[1] One of the most important areas in contemporary sensor development is the design of functionalized molecules that trigger a measurable response upon exposure to specific analytes.[2] While the technology of electrical transducers in analytical instrumentation is relatively advanced, well characterized chemoselective materials are still needed.[1]

One of the more attractive approaches in this field involves the construction of optical sensor devises due to their potential for the rapid analysis of substrates.[3] Development of optical sensors for hazardous trace metals are of great interest in this area and will have applications in environmental and the biomedical fields.[4] Herein we report the design, synthesis, and evaluation of a supramolecular chromatic sensor that is sensitive to micromolar concentrations of Ni^{2+}, Cd^{2+}, and Cr^{3+}.

Supramolecular metal-organic assemblies could have a significant impact in the areas of molecular sensing, as they can combine the properties of their organic and inorganic components in order to design receptor sites for chemical sensing. Several examples using this approach have been previously reported.[5]

Recently, we reported that a 1,8-platinum-functionalized anthracene unit, which acts as a "molecular clip," allows for the preparation of complex supramolecular metallacyclophanes.[6] Herein we built upon this design and extend that

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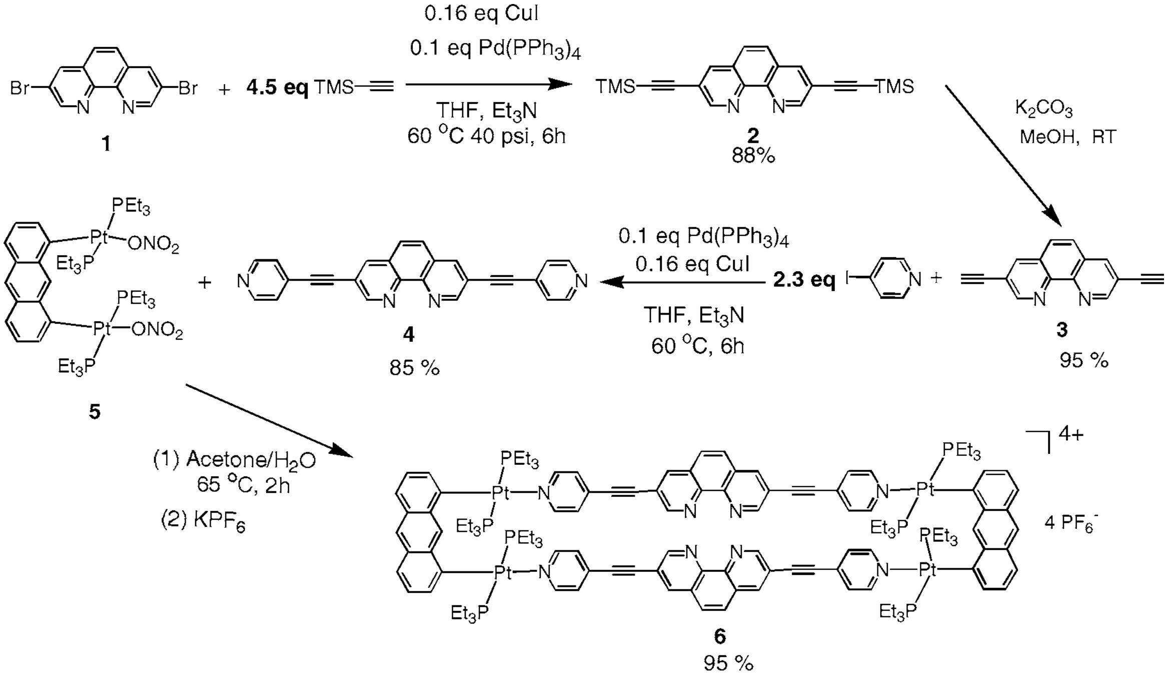
Scheme 1. Synthesis and Self-Assembly of Rectangular Chemosensor **6**



work by synthesizing a new functionalized ligand, namely, 3,8-bis-pyridin-4-ylethynyl[1,10]-phenanthroline (**BPP**), that upon self-assembly with the molecular clip generates a supramolecular rectangle that exhibits optical sensing functions toward various hazardous metals.

The ditopic pyridine linker **BPP** was prepared as shown in Scheme 1. The 3,8-dibromo-1,10-phenanthroline **1**[7] was coupled with (trimethylsilyl)acetylene in the presence of Pd(0)/CuI catalysts to give 3,8-bis-trimethylsilanylethynyl-[1,10]phenanthroline **2** (88%). This species was then treated with K_2CO_3 in methanol to give 3,8- diethynyl[1,10]phenanthroline **3**, as reported in the literature[8] (95%), which in turn, was coupled with 2.3 equiv of 4-iodopyridine in the presence of Pd(0)/CuI catalysts to provide the required ditopic pyridine linker **4** (85%) (Scheme 1).

The self-assembly of the rectangular chemosensor **6** is based upon a 1:1 stoichiometric combination of **4** and 1,8-bis(*trans*-Pt(PEt$_3$)$_2$(NO$_3$))anthracene **5**[6b] in an acetone/H_2O

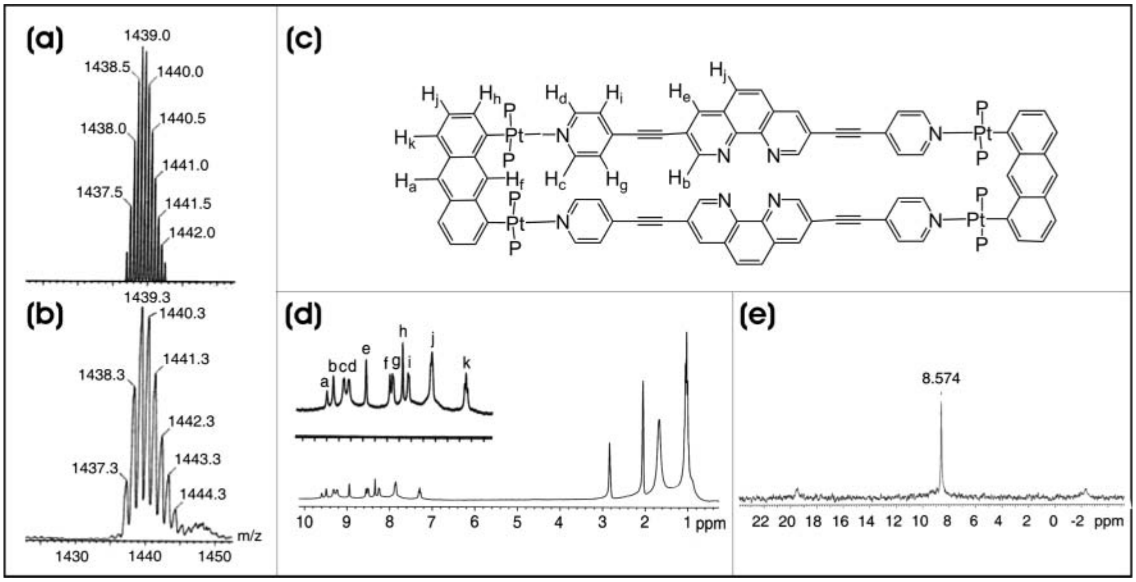


Figure 1. (a) Simulated isotope distribution for species [**6** + 2H$_2$O]$^{2+}$ {*m*/*z* = 1439.0}. (b) Experimental isotope distribution for [**6** + 2H$_2$O]$^{2+}$ {*m*/*z* = 1439.3}. (c) Molecular structure of **6**. (d) ^{1}H NMR spectra of **6** (e) ^{31}P{^{1}H} of **6**.

mixture and was isolated by precipitation with KPF_6 (yield 95%) (Scheme 1). Of particular diagnostic value for the structure of **6** are the $^{31}P\{^1H\}$ and ^1H NMR spectra. In the former, the formation of a single, highly symmetrical species is evident from the appearance of a sharp singlet peak with concomitant ^{195}Pt satellites, shifted 5.7 ppm upfield ($-\Delta\delta$) relative to **5** ($\Delta^1J_{PPt} = -2660$ Hz). For the ^1H NMR of **6**, two additional doublets appeared for the α- and *β*-pyridyl protons that also exhibit a downfield shift (0.2−0.6 ppm) due to the loss of electron density upon coordination, Figure 1. Further proof of complex **6** was obtained using elementary analysis[9] and electrospray ionization mass spectrometry (ESI/MS). In the mass spectrum of **6**, peaks (isotopically unresolved) attributable to the consecutive loss of hexafluorophosphate counterions $[\mathbf{6}\text{-}2PF_6]^{2+}\{m/z = 1566.5\}$, $[\mathbf{6}\text{-}3PF_6]^{3+}\{m/z = 995.6\}$, and $[\mathbf{6}\text{-}4PF_6]^{4+}\{m/z = 710.5\}$ were detected with good signal-to-noise ratio.

The supramolecular chemosensor **6** was also characterized with UV−vis absorption spectroscopy. Methanolic solutions of **6** exhibit several absorbance bands in the UV region, of which the most prominent are 350 nm ($\epsilon = 3200$), 280 nm (5200), 230 nm (5900). These bands are diagnostic for changes in the electronic structure of the macromolecule.

The addition of $Ni(II)(NO_3)_2{\cdot}6H_2O$ to a solution of **6** in methanol induced a dramatic change in the UV−vis spectrum (Figure 2). This optical response arises from the 1:1 complexation of **6** with the Ni^{2+} ions to generate the Ni complex **7**. Evidence from the job's method and ESI/MS support this conclusion. For example, a peak corresponding to $[\mathbf{7}\text{-}3PF6]^{3+}\{m/z = 1084.3\}$ is readily observed, see Supporting Information. The generation of an isosbestic point at 300 nm indicates that the complexation is clean and takes place without disturbing the supramolecular structure of **6**. Titration of **6** with other transition metal ions of environmental concern such as Cd^{2+} and Cr^{3+} showed a similar effect to that of Ni^{2+} and generated the corresponding Cd complex **8** and Cr complex **9**, see Supporting Information.

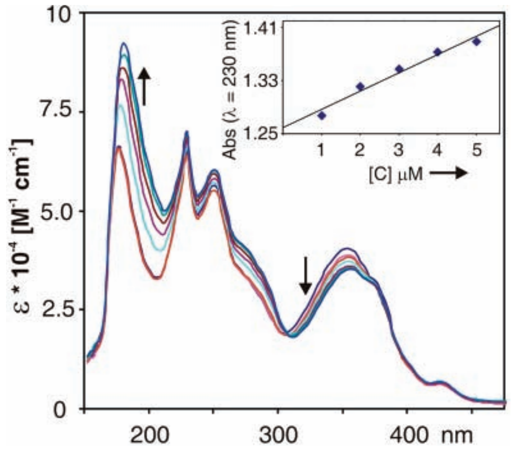


Figure 2. Titration of **6** in MeOH with $Ni(NO_3)_2{\cdot}6H_2O$.

The binding constants for **7**−**9** are shown in Table 1. The observed equilibrium constants for complexes **7**−**9** follow the same trend of affinity as those observed for free 1,10-phenanthroline with the same ions (i.e., for Ni^{2+} $K_1 = 8 \times 10^7$, Cd^{2+} $K_1 = 5 \times 10^5$, Cr^{3+} NA).[10] However, complex **6** provides a supramolecular complexity that endows the phenanthroline moiety with a preorganized architecture for metal binding as well as new optical properties.

Table 1. Binding Constants[a] for **6** with Ni^{2+}, Cd^{+2}, and Cr^{3+}

Ni complex **7**	$K = 2.01 \pm 0.05 \times 10^7$
Cd complex **8**	$K = 3.39 \pm 0.5 \times 10^4$
Cr complex **9**	$K = 7.53 \pm 0.4 \times 10^3$

[a] Equilibrium constants were obtained at 25 °C and 0.2 mM ionic strength in methanol.

In summary, we have prepared the functionalized ligand **5** that undergoes self-assembly to form the supramolecular rectangle **6** that allows for the rapid optical sensing of Ni(II), Cd(II), and Cr(III) ions in solution.

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Supporting Information Available: Experimental data for the binding of Cd^{2+} and Cr^{3+} with **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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