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Immobilization of a Europium Salen Complex within Porous Organic Hosts: Modulation of Luminescence Properties in Different Chemical Environments

Jeremy T. Mitchell-Koch and A. S. Borovik*

Department of Chemistry, University of Kansas, Lawrence, Kansas 66045

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Reported herein is the synthesis and characterization of luminescent materials containing a Eu(III) complex ((Eu_2N,N'-bis[5-{4-vinylbenzyloxy}salicylideneethylenediamine])$_3$·2H_2O, **1**) immobilized within porous organic hosts using styrene groups for covalent linkages. Porous materials were prepared using template copolymerization methods to afford $\mathrm{P}^{\mathrm{EGDMA}}$−**1**, having a poly(methacrylate) host and $\mathrm{P}^{\mathrm{DVB}}$−**1**, which has a poly(divinylbenzene) host. A DMF solution of **1** displays a strong luminescent signal at $\lambda_{\mathrm{ex}} = 610$ nm; nearly identical emission spectra are obtained for suspension of $\mathrm{P}^{\mathrm{EGDMA}}$−**1** and $\mathrm{P}^{\mathrm{DVB}}$−**1** in DMF. A large Stokes shift is seen between the excitation ($\lambda_{\mathrm{ex}} = 370$ nm) and emission wavelengths, eliminating interference from the excitation source. Quenching is observed when organic solvents are introduced into DMF suspensions of the polymers and the effect is proportional to the amount of solvent present. This quenching effect is reversible with the emission signals of $\mathrm{P}^{\mathrm{EGDMA}}$−**1** and $\mathrm{P}^{\mathrm{DVB}}$−**1** being regenerated upon removal of the quenching molecule. Composition of the organic host is important in modulating the response and sensitivity of these materials to solvent binding. Highly aromatic porous hosts ($\mathrm{P}^{\mathrm{DVB}}$−**1**) show a greater luminescent response, as well as higher sensitivity toward aromatic compounds (i.e., benzene and toluene), when compared to that of a nonaromatic polymer ($\mathrm{P}^{\mathrm{EGDMA}}$−**1**). Nonaromatic compounds (methylene chloride) quench the emission signal linearly, but the sensitivity is not significantly different between hosts. These results show that changing the secondary coordination environment is a useful method for tuning selectivity of luminescent materials. This approach demonstrates the utility in preparing metal ion based luminescent materials for chemical detection.

Introduction

Luminescent materials are important in a variety of applications, including sensor and display technologies.[1,2] Metal-based luminophores immobilized within organic hosts is one method for preparation of these materials.[3] Lanthanide complexes, in particular, are a useful class of luminophores for incorporation into hosts because of their high luminescent quantum efficiencies, various energies of emission, and sensitivity to changes in their local environments.[4] For instance, immobilization of discrete europium complexes in a host matrix can, in principle, prevent self-quenching[5] and help regulate analyte/luminophore interactions.[1]

Template copolymerization is one effective method for immobilizing metal complexes in porous organic hosts.[6,7,8] This method is advantageous because it utilizes molecular precursors in the fabrication of materials, allowing control of various structural properties within the immobilized sites, which can lead to desirable functions.

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* To whom correspondence should be addressed. Phone: 785-864-4067. Fax: 785-864-5396. E-mail: aborovik@ku.edu.

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Our group has shown that metal complexes are useful in probing the structures of the immobilized sites and can act as centers for the reversible binding of analytes.[7g,9] These studies have shown that ~90% of the immobilized metal complexes are accessible for binding.[9g] We have extended our studies to include lanthanide complexes and reported herein is the immobilization of the highly luminescent complex, Eu_2(4-vinylbenzyloxy-salen)$_3$(X)$_2$ (**1**, X = MeOH, H_2O) within porous organic hosts. A luminescent signal is observed for the polymer when it is suspended in DMF. The signal is significantly reduced when exposed to organic solvents, such as benzene. The sensitivity of this quenching is dependent upon the porous organic host, with a poly(divinylbenzene) host being more sensitive than the methacrylate host, poly(EGDMA). These results suggest that the polymer-induced microenvironment around the immobilized metal complex has a role in controlling the luminescent properties of the material.

Experimental Section

Unless otherwise noted, solvents and reagents were used as received from Aldrich (Milwaukee,WI) or Fisher (Pittsburgh, PA). Solvents used for synthesis under an inert atmosphere were further purified using standard procedures. Ethylenediamine was distilled over potassium hydroxide pellets under dinitrogen immediately prior to use. Synthesis of the metal complex was carried out in a Vacuum Atmospheres (Hawthorne, CA) drybox under an argon atmosphere. Desert Analytics (Tucson, AZ) conducted all elemental analysis. 2-hydroxy-4-(4-vinylbenzyloxy)benzaldehyde and *N*,*N'*-bis[5-(4-vinylbenzyloxy)salicylideneethylenediamine] (4-vinylbenzyloxy-salen), (**2**) were prepared using previously published procedures.[9f]

Eu_2(4-vinylbenzyloxy-salen)$_3$(H_2O)$_2$ (1). Compound **2** (1.00 g, 1.87 mmol) was suspended in 100 mL of methanol. In a separate vessel, potassium hydride (0.150 g, 3.74 mmol) was reacted with excess methanol to generate potassium methoxide. This solution was added to the previous mixture and full dissolution occurred. A methanolic solution of europium(III) trifluoromethanesulfonate (0.750 g, 1.25 mmol) was then added and a yellow precipitate formed immediately. After 0.5 h of stirring, the volume was decreased by half under reduced pressure and allowed to stir overnight. The yellow product obtained by filtration of the reaction mixture was washed twice with 15 mL of methanol and dried under vacuum. Yield = 1.15 g (95.2%). FTIR (Nujol, cm^{-1}): ν (C=N) 1619 (s), 1598 (s). Anal. Calcd for Eu_2(4-vinylbenzyloxy-salen)$_3$(H_2O)$_2$, $C_{102}H_{94}Eu_2N_6O_8$: C, 63.09; H, 4.77; N, 4.41. Found: C, 63.07; H, 4.27; N, 4.42. MS (positive FAB): m/z = 1896.2 M$^+$. UV/Vis (DMF, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 345 (86 000).

P^{EGDMA}−1. The monomers, **1** (0.351 g, 0.179 mmol, 5 mol %) and ethylene glycol dimethacrylate (EGDMA) (0.660 g, 3.33 mmol, 93 mol %), were added to a thick-wall polymerization tube (Ace Glass) with azobisisobutyronitrile (AIBN) (0.0117 g, 0.0716 mmol, 2 mol %) as the free radical initiator. 1,2-Dichloroethane (DCE, 7 mL) was added as a porogen and the mixture was purged with N_2 and then sealed. The europium complex is sparingly soluble at room temperature and only upon heating does it dissolve completely in the DCE. The tube was immersed in an oil bath where the temperature was maintained at 60 °C. After 24 h the yellow monolithic polymer was removed from the polymerization tube and continuously extracted with DCE for 24 h. The resulting polymer was pulverized in a mortar and pestle and allowed to dry in air for 24 h (yield = 1.112 g). Anal. Calcd: Eu, 5.09. Found: Eu, 4.58 (300 μmol of Eu/g of polymer). BET surface area: 247 m^2/g. Average pore diameter: 55 Å. Density: 1.42 g/mL

P^{DVB}−1. DVB polymers were synthesized using the same procedure as for P^{EGDMA}−**1** with the following modifications. An additional monomer, styrene (0.0542 g, 0.520 mmol, 20 mol %) was added to a solution containing **1** (0.2547 g, 0.130 mmol, 5 mol %), divinyl benzene (DVB) (0.2474 g, 1.90 mmol, 73 mol %), and AIBN (0.0089 g, 0.054 mmol, 2 mol %) (yield = 0.5280 g). Anal. Calcd: Eu, 7.23. Found: Eu, 6.27 (410 μmol of Eu/g of polymer). BET surface area: 213 m^2/g. Average pore diameter: 43 Å. Density: 1.31 g/mL

Physical Methods. Infrared spectra were collected using a Mattson Genesis Series FT-IR spectrometer. UV−vis absorbance spectra were collected on a Varian Cary 50 spectrophotometer. Pore diameters and surface areas were determined with a Gemini surface area microanalyzer. All luminescence spectra were collected in a Photon Technology International (Lawrenceville, NJ) luminescence spectrometer QM-1 with PC control using Felix Software version 1.1. Bandwidth at fwhm for both excitation and emission were measured to be 5(1) nm. Excitation source intensity (70 W) and detector voltage (1000 V) were held constant for all experiments. Suspended polymer samples were prepared by weighing 50 mg of polymer into a triangular quartz fluorescence cuvette (NSG, Farmingdale, NY), adding the appropriate solvent or solvent mixtures, and then suspending the polymer by vigorously shaking the cell. All other sample solutions were analyzed using a standard 1-cm square quartz cell. Changes in the luminescent properties of P^{EGDMA}−**1** and P^{DVB}−**1** with organic analytes were done in the following manner. Solid polymer samples (50 mg) were transferred into a triangular quartz cuvette, which was then filled with the appropriate organic compound or a mixture of the compound and DMF. The cuvette and its contents were vigorously shaken immediately prior to collection of luminescence data. The samples were excited at λ_{ex} = 370 nm and emission data were collected between 500 and 700 nm.[10] The percentage (v/v) of quenching solvent relative to DMF was varied in order to construct a concentration-versus-response curve. Each sample was prepared with an unused 50-mg aliquot of polymer, and the plots shown in Figure 3 are the average of three independent experiments in which different samples of polymer were used. Density measurements of the polymers were made by suspensions in liquid mixtures of known density. In a typical experiment, several polymer particles were placed into a tared graduated cylinder and 1 mL of diethyl ether was added. Chloroform was then added dropwise until the particles were suspended. The total volume of the solvent and mass of the system were then measured and the density was determined.

Results and Discussion

Synthesis of Compound 1 and P-1. Archer and coworkers have synthesized and studied several different Eu(III) complexes with multidentate Schiff base ligands.[11] Their work showed that these compounds have high

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[10] The small experimental error shown in Figure 3b and c are likely attributed to the method of collection, which involves suspending the polymers via shaking. Different settling rates in various solvents could also affect luminescent intensities. However, densities of the solvents are similar (0.94 for DMF, 0.88 for benzene, and 1.33 for methylene chloride) and it seems unlikely that the settling rates differ significantly.

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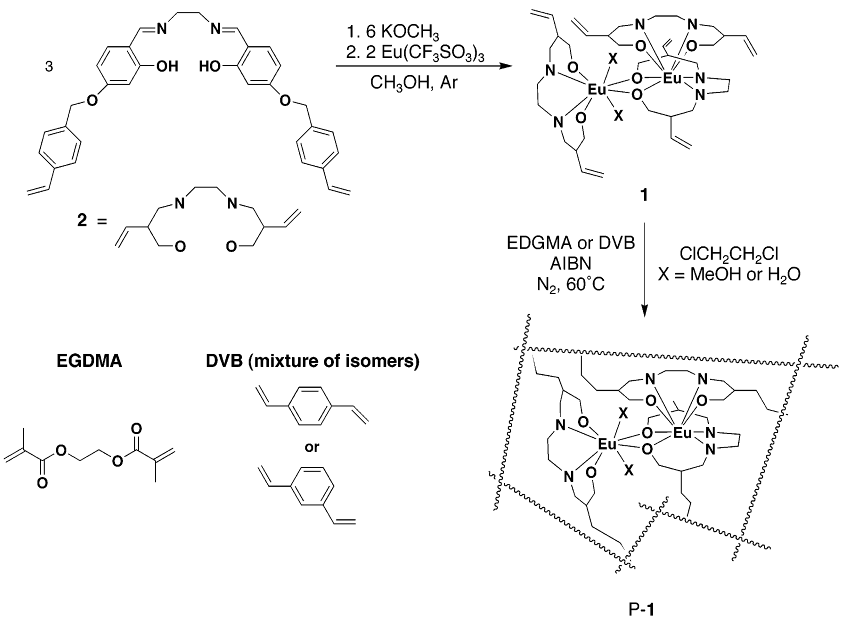
Scheme 1



quantum yields (≤ 0.60) and undergo intramolecular energy transfer (IMET) in a fashion similar to that of the well-documented β-diketonate complexes.[12] In these systems, the organic ligands coordinated to the metal center serve as the chromophore, whose properties included relatively large extinction coefficients and absorbance energies in the near UV region of the spectrum. Energy transfer to the 4f-manifold of orbitals on the europium ion occurs via intersystem crossing, which produces the luminescent properties. The low absorbance cross-section of lanthanide ions necessitates the use of the IMET pathway. We reasoned that different solvent molecules would alter the microenvironments around the Eu(III) Schiff base complexes immobilized within a porous host, which could perturb the IMET process and cause observable changes in the luminescence signals.

The europium template complex, **1**, was prepared using the procedure outlined in Scheme 1. This complex contains the tetradentate ligand ([**2**]$^{2-}$), which is salen (a diiminediphenol ligand) modified with 4-vinylbenzyloxy groups — these groups are necessary to covalently link **1** to a porous organic host. Because of the reactive nature of the 4-vinylbenzyloxy groups, the temperature used to synthesize **1** was lower than that of routes reported previously for related complexes.[11] Analytical and spectroscopic data are consistent with **1** being a dinuclear complex with a stoichiometry of three molecules of **2**, two water molecules, and 2 Eu(III) ions — that is, Eu$_2$(4-vinylbenzyloxyl-salen)$_3$(H$_2$O)$_2$. We proposed a structure where each Eu(III) ion has one fully coordinated, tetradentate ligand bonded and a third ligand molecule bridged between the two metal ions (Scheme 1). This proposal maximizes the number of donor atoms around the Eu(III) centers, yielding eight-coordinate metal centers, which is necessary to stabilize the Eu^{III} centers.[13] Moreover, bridging phenolates are common in coordination chemistry and have been observed in other metal complexes with diphenoldiimine ligands.[14] Note that a similar structure has been postulated for the analogous Eu(III) complex with unmodified salen.[11] Unfortunately, repeated attempts to obtain single crystals suitable for X-ray diffraction studies were unsuccessful.

Scheme 1 also shows the procedure used to immobilize **1** within porous polymeric hosts. For P^{EGDMA}−**1**, 5 mol % of **1** was used, with the remainder of the reaction mixture being 93 mol % EGDMA and 2 mol % AIBN. P^{DVB}−**1** was prepared similarly, except that 73 mol % DVB and 20 mol % styrene were used in making the host. The concentration of europium in P^{EGDMA}−**1** was 300 μmol/g of polymer, whereas for P^{DVB}−**1** it was 410 μmol/g of polymer. BET measurements revealed that particles of P^{EGDMA}−**1** and P^{DVB}−**1** had comparable average surface areas of 246 and 213 m^2/g, respectively. These materials are mesoporous solids, with particles of P^{EGDMA}−**1** having an average pore diameter of 55 Å, whereas those of P^{DVB}−**1** are 43 Å.

This copolymerization methodology produces network polymers having dispersed metal sites with **1** attached covalently to the polymer backbone. We have previous reported that the immobilized metal sites are sufficiently isolated within the host to prevent aggregation. Although isolated from each other, the metal complexes can interact with external species through the porous network of the host, with accessibilities to the immobilized metal sites reaching 90%. Furthermore, the similarities of spectroscopic properties between the **1** and P^{EGDMA}−**1**/P^{DVB}−**1** (vide infra) strongly suggests that the structure of the monomer Eu(III) complex is retained after polymerization, a result that is consistent with previous findings.

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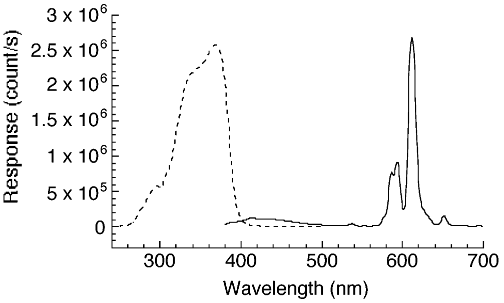

Figure 1. Emission (—) and excitation (- - -) spectra of **1** in DMF. Excitation data were collected at $\lambda_{em} = 610$ nm and emission data were measured at an excitation of $\lambda_{ex} = 370$ nm.

Absorbance and Luminescence Studies of 1. The spectroscopic properties of **1** in solution have been studied. Its absorbance spectrum recorded in DMF contains one peak at $\lambda_{max} = 345$ nm ($\epsilon = 86\,000$ M^{-1} cm^{-1}), which is assigned to ligand-centered transitions on the basis of its energy and similarities to the absorbance spectrum of **2** (Figure S1 in the Supporting Information). The emission and excitation spectra of **1** dissolved in DMF and collected at room temperature are shown in Figure 1. There are four main signals observed in the emission spectrum: two of lower intensity, nonbaseline resolved peaks at $\lambda_{em} = 585$ and 595 nm, a more intense signal at $\lambda_{em} = 610$ nm, and a weak band at $\lambda_{em} = 650$ nm. On the basis of previous studies of related complexes, these peaks are assigned to the following transitions: the $\lambda_{em} = 585$ nm peak is the forbidden $^5D_0 \rightarrow {}^7F_0$ transition, $\lambda_{em} = 595$ nm band is the $^5D_0 \rightarrow {}^7F_1$ transition, the $\lambda_{em} = 610$ nm peak is the $^5D_0 \rightarrow {}^7F_2$ transition, and emission from $\lambda_{em} = 650$ nm arises from the $^5D_0 \rightarrow {}^7F_3$ transition.[11] The excitation spectrum was measured at $\lambda_{em} = 610$ nm and the maximum intensity was found to be at a wavelength of 370 nm, consistent with this being a ligand-center excitation. This excitation wavelength was used in all subsequent luminescent spectra. **1** has limited solubility in many other solvents, such as benzene, toluene, and acetonitrile, which has prevented the detailed analysis of its absorbance and luminescence properties in these solvents.

Luminescence Studies of $\mathrm{P}^{\mathrm{EGDMA}}$–1. Figure 2 shows the luminescence properties of $\mathrm{P}^{\mathrm{EGDMA}}$–**1** suspended in DMF and benzene. Nearly identical features are observed between the luminescence properties of the **1** in a DMF solution and polymeric suspensions of $\mathrm{P}^{\mathrm{EGDMA}}$–**1** in DMF. Thus, the prominent features between 550 and 650 nm observed in the luminescence spectrum of **1** are also found in the spectrum of a DMF suspension of $\mathrm{P}^{\mathrm{EGDMA}}$–**1** (Figure 2a). In addition, the excitation spectrum of $\mathrm{P}^{\mathrm{EGDMA}}$–**1** suspended in DMF ($\lambda_{em} = 610$ nm) has a strong signal at 370 nm (Figure 2b). These results suggest that immobilization of **1** does not significantly change the properties of the complex. Note that there is a slight slope in the baseline for the spectrum of the $\mathrm{P}^{\mathrm{EGDMA}}$–**1** suspension. This is caused by excitation reflection off of the triangular cell used to collect the data. Similar spectroscopic features can be observed using related solvents, such as dimethyl acetamide (DMA).

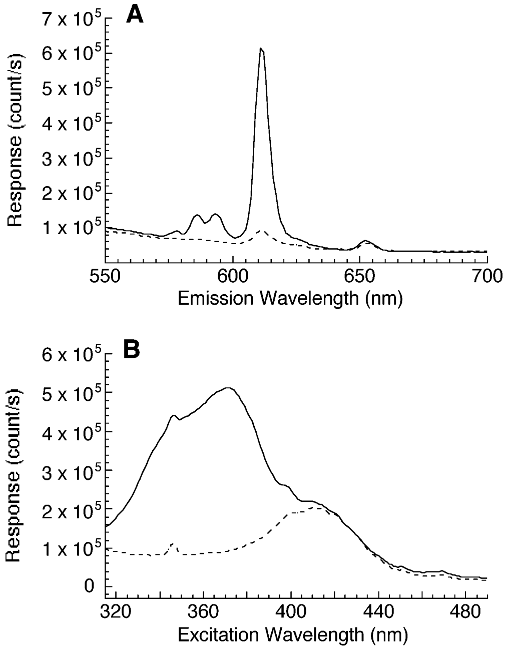

Figure 2. Emission spectra for $\mathrm{P}^{\mathrm{EGDMA}}$–**1** suspended in DMF (—) and benzene (- - -) (A) recorded at $\lambda_{ex} = 370$ nm. Excitation spectra for $\mathrm{P}^{\mathrm{EGDMA}}$–**1** suspended in DMF (—) and benzene (- - -) (B) recorded at $\lambda_{em} = 610$ nm.

Suspending $\mathrm{P}^{\mathrm{EGDMA}}$–**1** in other organic solvents causes a markedly different luminescent response. For instance, a significant decrease in the emission spectrum is observed for suspensions of $\mathrm{P}^{\mathrm{EGDMA}}$–**1** in benzene (Figure 2a), with the $^5D_0 \rightarrow {}^7F_n$ ($n = 0, 1, 2$) transitions at $\lambda_{em} = 585$, 595, and 610 nm being almost absent. Consistent with this finding is the loss of the $\lambda_{ex} = 370$ nm band in the excitation spectrum (Figure 2b). Note that similar loss of luminescence features is observed when $\mathrm{P}^{\mathrm{EGDMA}}$–**1** is suspended in acetonitrile, acetone, cyclohexane, and methylene chloride.

To further investigate this quenching response, luminescence spectra were collected for a suspension of $\mathrm{P}^{\mathrm{EGDMA}}$–**1** in mixtures with varying percentages of benzene/DMF. Figure 3a shows overlaid spectra displaying this experiment, and Figure 3b is a plot of luminescent intensity at $\lambda_{em} = 610$ nm versus % benzene added. A linear quenching response is observed for increasing percentage of benzene in the suspension solvent, demonstrating that the decrease in signal is proportional to the amount of benzene present. The same response is also observed with other solvents, an example of which is shown in Figure 3c for methylene chloride.[15]

The solvent-dependent luminescence intensity observed for P-**1** is in general agreement with results reported for other europium systems, but there are some notable differences. Solutions of Eu(III) salts show a solvent dependence on the relative intensity of different emission bands.[16] Interestingly, the $^5D_0 \rightarrow {}^7F_2$ transition is relatively weak in DMF, a solvent we observe to give a very intense transition in **1** and P-**1**. For Eu(III) β-diketones complexes emission is quenched by nonradiative exchange of energy from the metal center to X—H bonds of solvent.[17] Although protic solvents (e.g.,

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[15] Because these quenching responses are reproducible, it does not appear that light scattering from the polymeric particles affects the luminescent intensity to a significant extent.

[16] Bel'tyukova, S. V.; Kononenko, L. I.; Drobyazko, V. N.; Poluektov, N. S. *Zh. Prikl. Spektrosk.* **1977**, *26*, 466.

[17] (a) Zhao, X.; Fei, H. *J. Lumin.* **1988**, *40–41*, 286. (b) Voloshin, A. I.; Shavaleev, N. M.; Kazakov, V. P. *J. Lumin.* **2001**, *93*, 191.

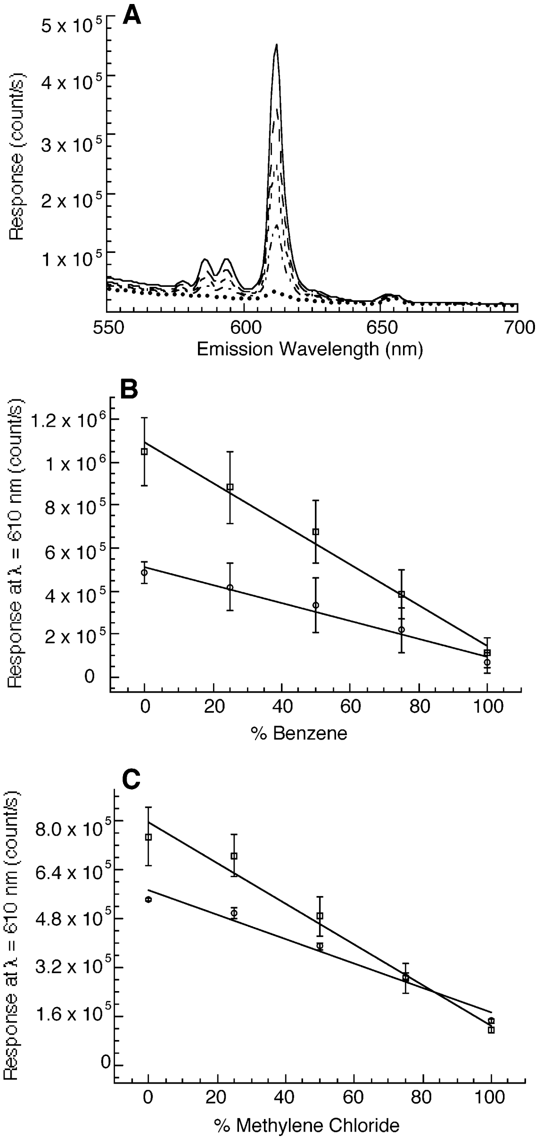

Figure 3. Overlay of emission spectra for $\mathrm{P}^{\mathrm{EGDMA}}$−**1**. Percent benzene, relative to DMF in the suspension solvent: 0% (—), 25% (— — —), 50% (- - -), 75% (-·-·-), 100% (···) (A). Spectra were collected at $\lambda_{\mathrm{ex}} = 370$ nm. Plots of emission response versus % benzene for $\mathrm{P}^{\mathrm{EGDMA}}$−**1** (○) and $\mathrm{P}^{\mathrm{DVB}}$−**1** (□) (B) and % methylene chloride (C) in DMF. In panel B slopes of the lines are −9460 and −4160 response/%benzene for $\mathrm{P}^{\mathrm{DVB}}$−**1** and $\mathrm{P}^{\mathrm{EGDMA}}$−**1**, respectively; in panel C slopes equal −6660 and −4010 response/%methylene chloride for $\mathrm{P}^{\mathrm{DVB}}$−**1** and $\mathrm{P}^{\mathrm{EGDMA}}$−**1**, respectively.

methanol and water) also quench the emission in P-**1**, we also observed diminished emission intensity when the materials are suspended in nonpolar solvents, such as benzene and dichloromethane. Moreover, the two solvents for which P-**1** displays the strongest intensity are dimethylformamide and dimethylacetamide — polar solvents that usually quench the emission signal in europium complexes. These differences from previously reported Eu(III) systems suggests that the primary and secondary coordination environments of **1** immobilized within the porous hosts has an effect on the solvent-dependent quenching of the luminescence intensity.

Figure 4 shows the results of reversibility studies carried out with $\mathrm{P}^{\mathrm{EGDMA}}$−**1**. The polymer was first suspended in DMF, a solvent known to promote luminescence, and an emission spectrum was collected. The polymer was isolated by collection on a glass filter frit, washed with acetone, and dried thoroughly. Resuspending the polymer in benzene caused the luminescent signal to be nearly quenched, as indicated by the almost complete loss of the emission band at $\lambda_{\mathrm{em}} = 610$ nm. Repeating the isolation procedure (vide supra) and suspending $\mathrm{P}^{\mathrm{EGDMA}}$−**1** again in DMF produced an emission spectrum nearly identical to that observed initially. This reversible luminescent behavior is reproducible over repeated (≥3) cycles.

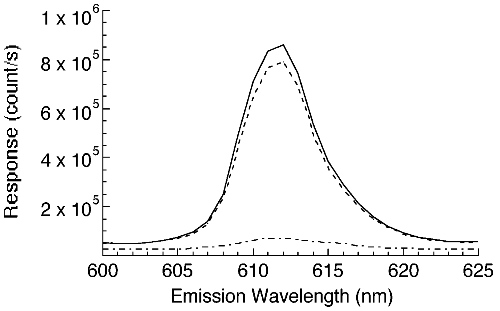

Figure 4. Emission spectra for the same sample of $\mathrm{P}^{\mathrm{EGDMA}}$−**1** suspended in DMF, (—), then benzene, (-·-·-), and finally DMF (- - -), showing the reversible luminescent properties. Spectra were recorded at room temperature and $\lambda_{\mathrm{ex}} = 370$ nm.

Although the exact nature of the quenching process is not yet known, these reversibility results indicate that weak interactions with the immobilized europium complex most likely lead to the loss of luminescent intensity in $\mathrm{P}^{\mathrm{EGDMA}}$−**1**. The solvent molecules may not be covalently bonded to **1** because simple cycles of filtration/washing/drying regenerate the luminescent signals. In addition, other noncoordinating solvents, such as methylene chloride and cyclohexane, also have this effect. Two possible explanations can account for these findings. One is that the quenching of the luminescent spectrum in $\mathrm{P}^{\mathrm{EGDMA}}$−**1** could arise from secondary coordination sphere effects, involving noncovalent interactions with the immobilized europium complex. A second possible explanation involves a solvent-sensitive inner sphere effect whereby a rearrangement of donor groups of **1** changes the primary coordination sphere of the europium centers.

Luminescence Studies of $\mathrm{P}^{\mathrm{DVB}}$−1. The above results suggest that the microenvironment of the immobilized europium complexes is important for the reversible changes in the luminescent properties for $\mathrm{P}^{\mathrm{EGDMA}}$−**1**. To further probe these effects, **1** was immobilized within the more aromatic porous host poly(divinylbenzene) to form $\mathrm{P}^{\mathrm{DVB}}$−**1**. Qualitatively, the luminescent behavior found for $\mathrm{P}^{\mathrm{DVB}}$−**1** is like that of $\mathrm{P}^{\mathrm{EDGMA}}$−**1**; that is, $\mathrm{P}^{\mathrm{DVB}}$−**1** shows the same reversible changes in its luminescence signal upon exposure to different organic solvents as $\mathrm{P}^{\mathrm{EDGMA}}$−**1**. However, $\mathrm{P}^{\mathrm{DVB}}$−**1** shows a 2-fold increase in sensitivity toward benzene compared to that of $\mathrm{P}^{\mathrm{EGDMA}}$−**1**, which is illustrated in the plot of emission response at $\lambda_{\mathrm{em}} = 610$ nm versus % benzene (Figure 3b and legend). A similar effect was observed when the solvent was toluene. This increase in sensitivity can be attributed to the highly aromatic microenvironment that surrounds the europium complexes in $\mathrm{P}^{\mathrm{DVB}}$−**1**, which would increase the access of benzene molecules to the immobilized sites. In contrast, $\mathrm{P}^{\mathrm{DVB}}$−**1** and $\mathrm{P}^{\mathrm{EGDMA}}$−**1** have similar sensitivities toward nonaromatic solvents, such as methylene chloride (Figure 3c).

Summary and Conclusions

We have demonstrated that the luminescent properties of the europium diiminediphenol complex **1**, immobilized within porous organic hosts, are reversibly modulated in the presence of several organic compounds at room temperature. The magnitude of the luminescent changes is dependent on the porous host, as illustrated by the increased sensitivity of P^{DVB}–**1** to aromatic compounds such as benzene and toluene.

Previous reports on the luminescent properties of Eu(III) diiminediphenol complexes were mostly done in the solid state, with solution studies often omitted. A possible reason for this is the low solubility of these complexes in common solvents, preventing a detailed analysis. We have observed similar problems with the monomer Eu(III) complex, **1**. A possible method to circumvent the low solubility is through the immobilization process described here. Immobilization of **1** within a porous host allows access of solvent molecules to the metal sites and permits investigations into the effects of external molecules on emission intensity.

The materials used in this studied were prepared using template copolymerization methods, which are often used in making molecularly imprinted polymers.[6,7] Although utilized mostly for materials in separation science[6,18] polymers made by this methodology have been used for sensors,[1a,8] with the template species typically serving as the analyte. Rather than analyze for the rebinding of a template compound, we have used the luminescent properties of the immobilized europium complexes in P^{EDGMA}–**1** and P^{DVB}–**1** to detect the binding of other molecules not present during the synthesis of the polymers. We have also taken advantage of the unique properties of the porous hosts to assist this process. The fact that performance of these materials is correlated strongly with the type of porous host indicates that the signaling of the binding event is coupled to the microenvironment of the immobilized site. The properties of the microenvironments of the immobilized sites can be readily adjusted by employing different cross-linking agents when generating the porous hosts. Therefore, further investigation of the effects of porous hosts, as well as the immobilized site structure, bodes well for the development of polymeric materials that are applicable to the detection of organic compounds.

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Supporting Information Available: Electronic absorption spectra in DMF for **2** and **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] For example see (a) Shea, K. J.; Spivak, D. A.; Sellergren, B. *J. Am. Chem. Soc.* **1993**, *115*, 3368. (b) Andersson, L.; Mosbach, K. *J. Chromatogr.* **1990**, *516*, 313.