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A Supramolecular Microfluidic Optical Chemosensor

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Abstract: A supramolecular microfluidic optical chemosensor (μFOC) has been fabricated. A serpentine channel has been patterned with a sol−gel film that incorporates a cyclodextrin supramolecule modified with a Tb^{3+} macrocycle. Bright emission from the Tb^{3+} ion is observed upon exposure of the μFOC to biphenyl in aqueous solution. The signal transduction mechanism was elucidated by undertaking steady-state and time-resolved spectroscopic measurements directly on the optical chemosensor patterned within the microfluidic network. The presence of biphenyl in the cyclodextrin receptor site triggers Tb^{3+} emission by an absorption-energy transfer-emission process. These results demonstrate that the intricate signal transduction mechanisms of supramolecular optical chemosensors are successfully preserved in microfluidic environments.

Introduction

Microfluidic (μF) devices are emerging as an important technology for chemo- and bioanalytical applications.[1] The miniaturization offered by μF devices allows for the analysis of fluid samples to be performed on a chip, leading to advantages such as reduced sample volume, increased reaction speed, and the possibility of massive parallelism.[1−8] One method for rapidly prototyping μF networks involves conformally contacting a micromolded elastomeric polymer such as poly(dimethylsiloxane) to a glass or quartz substrate, thus forming enclosed microchannels.[9,10] To date, optical analysis on μF platforms has been performed by direct spectroscopic detection methods. The advantage of this approach is that signal transduction is easy to implement within the constraints imposed by the μF environment. The simplicity of the detection method, however, has inherent limitations; these include difficulties associated with selectively distinguishing analyte (usually because an optical signature must be identified from a multicomponent spectral envelope) and the measurement of an optical signal against a bright background, to name a few. Such limitations may be overcome when analytes are detected by specially tailored supramolecular chemosensors[11−15] in which a noncovalent molecular recognition event at a receptor site is communicated by physical or chemical means to a reporter site, which produces a measurable optical signal. This "3R" sensing scheme of recognize, relay, and report typically relies on the chemical and physical compatibility between the analyte and the crafted supramolecular binding site, relay mechanisms involving intricate energy or electron transfer and specially tailored photophysical properties of the reporter site.

Following the 3R approach, we have created a cyclodextrin (CD) supramolecule appended with a Tb^{3+} macrocycle (**1** in Figure 1) for the optical detection of polyaromatic hydrocarbons in aqueous solutions.[16,17] Molecular recognition of the aromatic hydrocarbon in the CD bucket is signaled by the appearance of green luminescence from the encrypted Tb^{3+} ion. Detailed mechanistic investigations show signal transduction to proceed via an absorption-energy transfer-emission (AETE) mechanism in which excitation energy absorbed by the bound analyte is transferred from its long-lived triplet excited state to the Tb^{3+} reporter site.[18] The appearance of green luminescence against a dark background enables polyaromatics to be detected at submicromolar concentrations with no need for amplification. In view of the benefits gained in selectivity and sensitivity, the

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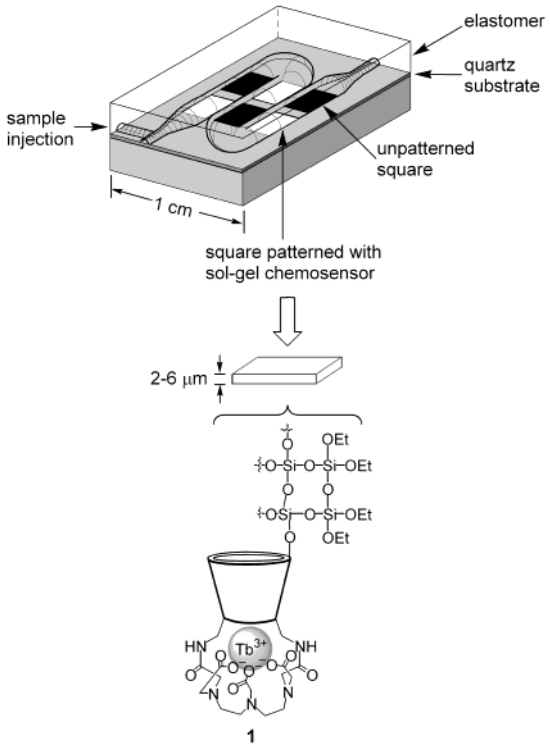

Figure 1. A microfluidic optical chemosensor fabricated in a serpentine channel configuration. The white, sol−gel squares contain the supramolecular chemosensor (**1**), a cyclodextrin strapped by a DTPA macrocycle in which a Tb^{3+} ion resides. The conical bucket schematically represents the cyclodextrin receptor site.

incorporation of supramolecular optical chemosensors onto μF platforms presents the opportunity for the discovery of new sensing applications. The design of such devices, however, demands that the functional requirements of the supramolecular optical chemosensor are retained within a μF environment. The host matrix of the μF chemosensor must permit analyte to access and recognize the supramolecule binding site without hindering selectivity or specificity and without perturbing the stereoelectronic factors that control the relay and reporting steps of the signal transduction mechanism. Accordingly, we sought to ascertain whether optical supramolecular chemosensor function could be preserved in a μF platform. Here we report methods to immobilize chemosensor **1** within inorganic and organic polymer host matrixes and show by steady-state and transient laser spectroscopy that the 3R sensing strategy may be implemented on a patterned μF device, thus allowing us to construct the first supramolecular microfluidic optical chemosensor (μFOC).

Experimental Section

General Methods. ^{13}C and ^{1}H NMR and 2-D total correlation spectra (TOCSY)[19] were obtained at the MIT Department of Chemistry Instrumentation Facility using VARIAN Inova-500 MHz NMR spectrometers with dual broadband RF hosting an Oxford Instruments Ltd. superconducting magnet. TOCSY was run at the set temperature of 25 °C with a mixing time of 60 ms. Data were processed using a Sun Ultra 5 workstation. Polymer molecular weights were determined with a Hewlett-Packard 1100 series HPLC equipped with a PL gel mixed-C column (5 μm) using THF as the mobile phase at a rate of 1.0 mL/min. Gel permeation chromatography (GPC) measurements were made relative to monodispersed polystyrene standards purchased from Polymer Laboratories. Spin casting was carried out on a Lavall Technologies WS-400-6NPP\Lite spin coater.

Materials. Lanthanide-modified CD chemosensor **1** was prepared according to published procedures.[16] Starting reagents and solvents for synthesis were reagent grade or better and were used as received from Aldrich Chemical Co. Samples of the chemosensor gave satisfactory analyses, which were performed at H. Kolbe Mikroanalytisches Laboratorium. The starting material, *m*-nitrophenyl acrylate, was prepared by the dropwise addition of 5.0 g (55.0 mmol, 1.0 equiv) of acryloyl chloride to a stirring solution of 2.5 g of KOH and 3.5 g (25.0 mmol, 0.5 equiv) of *m*-nitrophenol in 250 mL of water at 0 °C. The precipitate formed after 10 min of continued stirring and was filtered and recrystallized from ether to afford long off-white needles of the product. ^{13}C NMR (d_6-DMSO) δ/ppm: 165.5, 151.8, 149.6, 136.1, 131.6, 129.7, 127.9, 121.7, 118.0.

Quartz substrates were modified by deposition from aqueous alcohol solutions onto substrates cleaned according to the RCA SC-1 method.[20] A 95%-ethanol/5%-water solution was adjusted to pH 5.0 with acetic acid, and 3-acryloxypropyltrimethoxysilane (United Chemical Technologies, Inc.; Bristol, PA) was added with stirring to yield a 2% final concentration. Five-minute reaction times were allowed for hydrolysis and silanol formation. The quartz slides were coated with the resulting solution for a period of 2 min, and then rinsed by dipping in ethanol; the treated slides were cured for 24 h at room temperature before use.

CD chemosensor **1** was immobilized in an acryloyl polymer film by adapting previously reported procedures[21] to achieve the site-directed functionalization of the secondary rim of **1** with a vinyl acrylate moiety. Chromatographically purified samples of **1** (0.10 g, 6.7×10^{-2} mmol, 1.0 equiv) in 10 mL of pH 11 carbonate buffer were combined with 0.012 g (6.7×10^{-2} mmol, 1.0 equiv) of *m*-nitrophenyl acrylate in acetonitrile in air. The clear solution immediately turned bright yellow upon shaking, indicating the presence of *m*-nitrophenolate in solution. Shaking was continued for 5 min after which enough 0.1 M HCl was added to neutralize the solution, causing the solution to turn colorless. Water was removed by rotary evaporation to yield a pale yellow solid. The acryloyl-modified product of **1** was purified on a G-15 Sephadex (Aldrich Chemical Co.) size exclusion column to give purified product in 24% yield. ^{1}H NMR (D_2O) δ/ppm: 2.5−4.0 (m, 84H), 4.9 (m, 7H), 6.0 (m, 3H). ^{13}C NMR (D_2O) δ/ppm: 176.8, 172.3, 168.0, 132.4, 127.3, 102.0, 84.5, 81.5, 73.2, 72.3, 60.5, 57.7, 57.3, 56.5, 53.2, 52.3, 49.4, 41.8, 39.1. Anal. Calcd for $C_{59}H_{93}N_5O_{42}$: C, 45.88; H, 6.07; N, 4.53; O, 43.51. Found: C, 45.73; H, 6.12; N, 4.23; O, 43.80.

Acryloyl-modified **1** was polymerized by dissolving 80 mg of the compound in 10 mL of H_2O to which a methanol solution of 0.1% 2,2′-azobis(isobutyronitrile) was added. The resulting solution was freeze−pump−thawed four times and filled with N_2 prior to radical initiation, which was induced by heating to 50 °C. Solvent was removed by rotary evaporation after 24 h to give the water-soluble solid product. (M_n = 44 000, M_w = 83 000). ^{13}C NMR (D_2O) δ/ppm: 176.8, 172.3, 168.0, 102.0, 84.5, 81.4, 73.2, 72.2, 69.7, 65.5, 64.0, 60.5, 57.9, 55.4, 53.6, 51.3, 49.1, 47.5, 46.8, 40.9, 29.6. ^{1}H NMR (D_2O) δ/ppm: 2.5 (t, 2H), 2.9−3.8 (m, 109H), 4.9 (m, 7H). Acryloyl polymers of **1** were introduced onto a quartz substrate by performing the identical polymerization reaction on the surface of a quartz platform surface modified with vinyl acrylate.

Chemosensor was immobilized in sol−gel films by following the methods of Bright and Prasad et al.[22] A partially hydrolyzed sol was prepared by stirring tetraethyl orthosilicate TEOS (Aldrich Chemical Co.), ethanol, and 0.1 N HCl (1.5:2:0.5) in a closed container in air for 5 h. To 100 μL of this sol, 100 μL of a 0.025−0.032 M aqueous

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solution of **1** was added while stirring; mixing was continued in a closed container for an additional 45 min. Aliquots of the CD-doped sol (~20 μL for a 1 cm^2 quartz substrate) were introduced onto the surface of a clean quartz substrate (RCA SC-1), which was then sealed in an airtight container for 72 h to allow the sol to gel and age. Unbound CD was removed from monoliths by washing with spectroscopic grade water. Profilometry measurements (Tencor Alpha-Step 200; KLA-Tencor Corp., San Jose, CA) showed that film thicknesses of 2−6 μm were obtained from this procedure. Thinner films (1 μm thickness) were achieved by spin casting sol−gel films at 2000 rpm for 30 s.

Chemosensor-coated quartz substrates (ESCO Products, Oak Ridge, NJ) were patterned using deep UV exposure in an AZ327 developer after application of Hoechst Celanese (Somerville, NJ) AZ1512 positive photoresist. Dip-etching was accomplished by employing a buffered HF solution, and photoresist was subsequently removed in an 80 °C Act 1 photoresist stripper (ACT, Inc., Allentown, PA). The thicknesses of the coated surfaces were measured by profilometry.

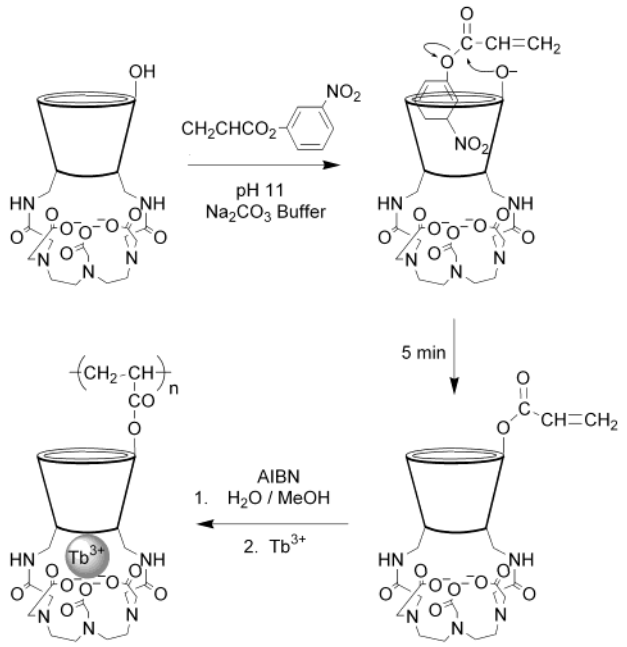
Physical Methods. Steady-state emission spectra were recorded on a high-resolution instrument that has been previously described.[18] Terbium ion luminescence, produced upon excitation with 273 nm wavelength light from a Hg−Xe lamp, was captured with a R943-02 Hamamatsu (Bridgewater, NJ) photomultiplier tube interfaced to a Stanford Research Instruments (Palo Alto, CA) SR400 gated photon counter. Spectra were corrected for detector response. All measurements were performed at 25(2) °C. Quartz substrates, modified with sol−gel films of **1** (3 μm films unless otherwise specified), were exposed to solutions of varying concentrations of biphenyl in water; the maximum concentration of analyte was limited by its solubility (5×10^{-5} M). Samples were mounted 45° to the incident beam to enable front-face detection; a machined holder allowed the quartz substrate to be reproducibly positioned. Excitation light was eliminated with 450 and 470 nm long pass filters. Spectroscopic measurements on the μF prototype were performed by flowing aqueous solutions of analyte through the capillary channels of the μF device.

Time-resolved data were collected on a nanosecond laser instrument utilizing a Coherent (Auburn, CA) Infinity XPO tunable laser (fwhm = 7 ns) as the source. The Infinity Nd:YAG laser system consisted of an internal diode pumped, Q-switched oscillator, which provided the seed pulse for a dual rod, single lamp, amplified stage. Sequential second and third harmonics of 532 and 355 nm radiation were generated from the Nd:YAG 1064 nm fundamental via Type I polarization and frequency mixing in tuned BBO crystals. The resultant 355 nm third harmonic was subsequently passed thorough Type I tunable XPO and second harmonic cavities capable of producing the required 273 nm excitation wavelength. Emitted light from the sample passed through f/4 collimating and f/4 focusing lenses onto the entrance slit of an Instruments SA (Edison, NJ) Triax 320 monochromator. The signal wavelengths were dispersed by a grating possessing a blaze wavelength of 500 nm and 300 grooves/cm and detected with a Hamamatsu R928 PMT. The output from the PMT was fed into a LeCroy (Chestnut Ridge, NY) 1 GHz 9384CM digital oscilloscope, which was triggered from the Q-switch sync output of the laser. Monochromator operation, data storage, and data manipulation were managed by National Instruments driver software (Labview) incorporated into programs written at MIT. Communication between a Dell Optiplex GX-1 computer and the instrumentation was achieved through an IEEE-488 (GPIB) interface. Excited-state kinetics data were obtained by signal averaging (1000 pulses at 20 Hz) Tb^{3+} emission at 546 nm.

Results and Discussion

The construction of a μFOC requires the immobilization of the optical chemosensor in a support that is compatible with lithographic patterning protocols. Scheme 1 presents a site-directed functionalization strategy that leads to the successful incorporation of **1** into organic host matrixes. A vinyl acrylate

Scheme 1



group is introduced under mild conditions onto the secondary rim of the CD bucket. The reaction is conveniently monitored by following the vinyl resonances, which appear in a spectrally uncongested region of both ^{1}H and ^{13}C NMR spectra of **1**. For the former spectrum, the vinyl and CD protons integrate as 3H and 90H, respectively. The ^{13}C NMR spectrum is more distinguishing with the appearance of three doublets, which we ascribe to the carbonyl (168.0 ppm) and the two vinylic carbons (132.4 and 127.3 ppm) of the acryloyl substituent. The crucial step in the synthetic protocol is the inclusion of the polymer precursor, *m*-nitrophenyl acrylate, within the CD to direct functionalization to a single secondary hydroxyl group. The limiting capacity of the CD cavity to incorporate only one conformationally restricted *m*-nitrophenyl acrylate precursor is responsible for functionalization at a single site. Mono functionalization is crucial to the overall performance of the μFOC since the entrance of the CD is the least sterically encumbered, thus providing maximum access of analyte to the receptor site of the immobilized supramolecule. Polymerization of acryloyl-modified **1** by the free-radical initiator 2,2′-azobis(isobutyronitrile) affords a polymer possessing the pendant supramolecular chemosensor. Disappearance of the vinyl ^{13}C resonances at 127.3 and 132.4 ppm is indicative of complete polymerization. A concomitant growth of resonances at 45−70 ppm for the polymer chain carbons was observed over the course of the reaction.[23] The corresponding alkyl ^{1}H resonances at 3.3 and 2.5 ppm were identified in the 2-D ^{1}H NMR spectrum.

Whereas a well-characterized functionalized polymer was obtained from the procedures of Scheme 1, attempts to immobilize the polymer onto quartz substrates resulted in low and inconsistent surface coverages. For this reason, we turned our efforts to alternative supports. Specifically, we investigated sol−gel films as a support of **1** owing to their superior properties in regard to optical sensing applications.[24−28] Sol−gels are optically transparent throughout the ultraviolet spectral region, and

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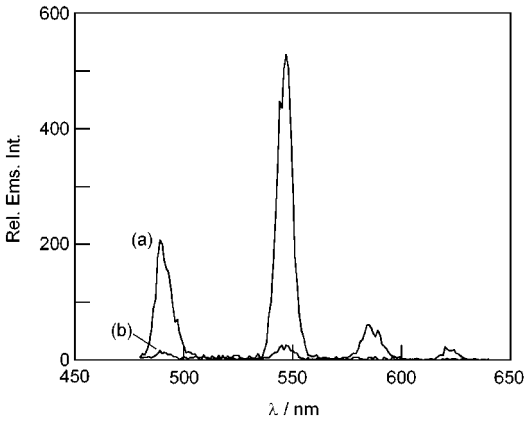

Figure 2. Emission from a patterned thin film of the microfluidic device shown in Figure 1 in contact with (a) a 50 μM aqueous solution of biphenyl and (b) an aqueous solution in the absence of analyte. The intensity of the luminescence of spectrum a is $\times$45-fold that of spectrum b.

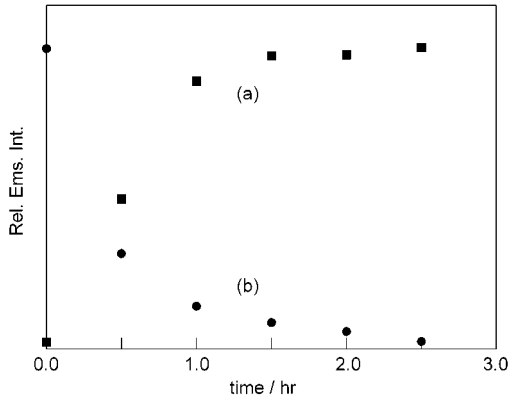

Figure 3. The time evolution of Tb^{3+} emission from a patterned thin film (6 μm in thickness) of the microfluidic device shown in Figure 1 after (a) exposure to a 50 μM aqueous solution of biphenyl followed by (b) a methanol rinse to remove biphenyl from film. Signal reproducibility is maintained over repeated cycles.

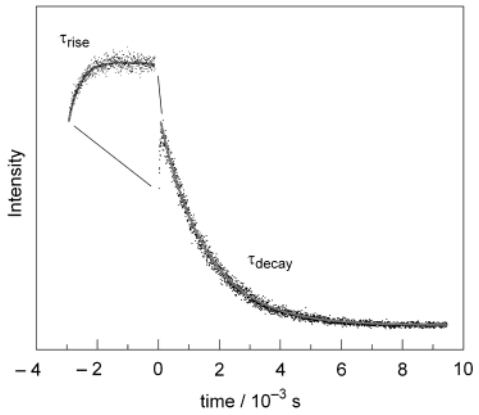

Figure 4. The growth and subsequent decay of Tb^{3+} luminescence (λ_{det} = 546 nm) from **1** upon the excitation of biphenyl with a Nd:YAG nanosecond laser (λ_{exc} = 273 nm). The time axis for the magnified rise time trace is from 0 to 3 $\times$ 10^{-5} s. The solid lines display the exponential fits of the data from which the rise time and decay rate constants were derived.

monoliths can be made with varying porosity to permit analyte to diffuse to and from an irreversibly immobilized chemosensor active site. In addition, numerous casting methodologies permit films of various thicknesses to be readily synthesized.

One millimeter squares of sol−gel films of **1**, photolithographically patterned within the serpentine channel of the μF platform shown in Figure 1, exhibit excellent optical responses to polyaromatics. Whereas weak Tb^{3+} emission is observed from the direct irradiation (λ_{exc} = 273 nm) of thin films (patterned squares of 3 μm thickness containing 4.8 nmoles of **1**), the luminescence intensity of Tb^{3+} is significantly enhanced when analyte is flowed through the μF network of Figure 1. As shown in Figure 2, a $\times$45-fold enhancement of the Tb^{3+} luminescence intensity is triggered when a 50 μM solution of biphenyl contacts the patterned microstructure. Sol−gel films containing only Tb^{3+} ion or the Tb^{3+} macrocycle (not appended to CD) exhibit no variation in luminescence intensity upon addition of biphenyl. Equivalent concentrations of analyte added to aqueous solutions of **1** generate significantly smaller enhancements (e.g., $\times$8-fold enhancement for [biphenyl] = 50 μM), suggesting that analyte more strongly associates to the CD bucket of **1** when immobilized in sol−gel films. The Tb^{3+} luminescence enhancement proves to be concentration-dependent, increasing monotonically with the concentration of biphenyl; detection of biphenyl at 5 μM is easily achieved. The detection response varies approximately linearly with the concentration of **1** in sol−gel monoliths. For example, the enhancement in luminescence intensity is $\times$8, $\times$27, and $\times$45 upon exposing films containing 1.2, 3.6, and 4.8 nmols of **1** to aqueous solutions of [biphenyl] = 50 μM. We estimate from the extrapolation of these data to the limits of our detector response that analyte can be detected reliably with μFOC platforms patterned with 700 nm thick films. The detection response is reversible and reproducible (Figure 3), though cycle times are slow ($\sim$1 h when purging with methanol/aqueous solutions). Increased response times ($\sim$10 min) are observed for spin-cast films owing to the decreased film thickness (1 μm thickness). The μFOC platform exhibits considerable structural and optical integrity; the signal response of **1** is maintained over a period of greater than 3 months with little degradation of the signal response (<10% change in signal intensity).

The signal transduction mechanism for the μFOC was investigated by undertaking steady-state and time-resolved luminescence spectroscopic measurements directly on patterned squares in contact with aqueous solutions of analyte. An AETE process was confirmed by examining the emission characteristics of the μFOC as the wavelength of the excitation light was scanned. The intensity of the green luminescence from Tb^{3+} tracked the absorption profile of biphenyl and not the Tb^{3+} ion itself, unequivocally establishing that the Tb^{3+} emission is excited by light passing through biphenyl. The kinetics of the AETE mechanism were ascertained by focusing the excitation laser pulse of a nanosecond transient laser system onto the μFOC. The singlet excited state of biphenyl, produced upon absorption of the exciting photon, decays within the 7 ns laser pulse. As shown in Figure 4, the Tb^{3+} luminescence appears at significantly longer times; a monoexponential fit of the rise time of the Tb^{3+} emission yields a first-order rate constant of 4.0 $\times$ 10^4 s^{-1}. The incommensurate time scales between the decay of the singlet excited state of biphenyl and the appearance of Tb^{3+} luminescence signifies the participation of biphenyl's triplet

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excited state in mediating the overall AETE process. The initially prepared $^1\pi\pi^*$ excited state of biphenyl decays to its corresponding $^3\pi\pi^*$ excited state, from which energy transfer to the $^5D_4$ emitting state of the Tb^{3+} occurs. A fit of the decay curve of Figure 4 establishes that the green luminescence emanating from the Tb^{3+} excited state decays with a lifetime of 1.5 ms. Such long decay lifetimes are observed only when the O−H oscillators of H_2O are excluded from the Tb^{3+} coordination sphere by the DTPA strap of **1**.

Chemosensor **1** operates by one of the most intricate optical signal transduction pathways reported to date. That such a mechanism is preserved in the μF network of Figure 1 bodes well for the general development of supramolecular μFOC devices. As the architectural elements in which optical chemosensors function move toward the micro- and even nanoscale,[29] sensitivity will be compromised because fewer active sites will be available to produce a signal. Accordingly, attendant to the dimensional reduction inherent to μFOC design will be the need to increase the intensity of the signal response. Current efforts are focused on utilizing sensory amplification[30,31] and conjugated fluorescence polymers[32] as gain media for the μFOC shown in Figure 1. Signal amplification should allow even further reduction of μFOC length scales (including a reduction in optical chemosensor film thickness), enabling the development of higher-performance μFOC devices.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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