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Rotaxanated Conjugated Sensory Polymers

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The utilization of rotaxanes, catenanes, and various supramolecular complexes in molecular machines and photonic devices has met considerable success in recent years.^{1–3} In these multicomponent systems, the imposed proximity between the interlocked subunits often generates unexpected and complex photophysical properties. As a result, supramolecular systems offer greater diversity than their single-molecule counterparts. Recently, our group reported a rotaxane exciplex, wherein a charge transfer complex formed in the excited state between the electronically complementary chromophores.⁴ We report herein our effort to extend the rotaxane into polymeric systems and to study their photophysical properties. The rotaxane groups are of interest as they create three-dimensional molecular recognition elements. When tethered to conjugated polymers, these systems will yield sensitive chemosensory responses.⁵

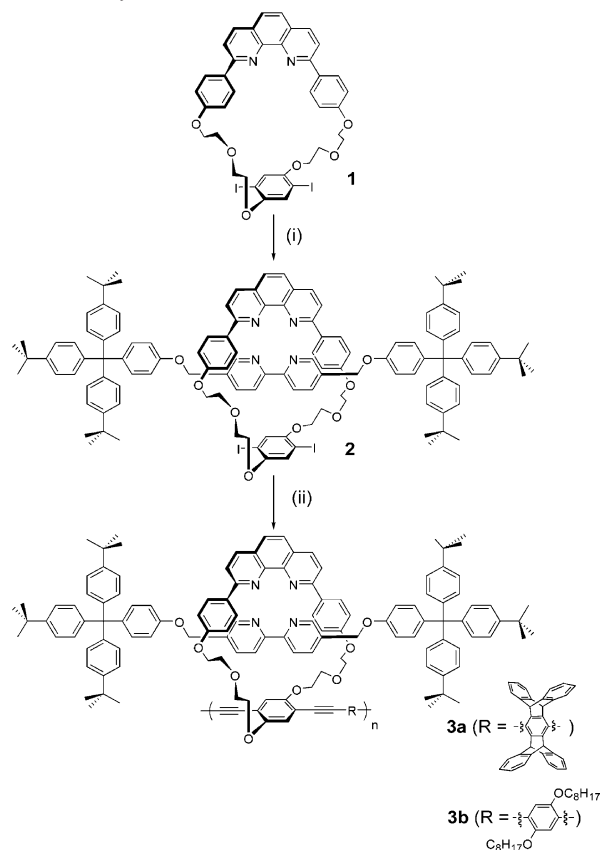
Scheme 1 shows the syntheses of rotaxane **2** and polymers **3a** and **3b**. Rotaxane **2** was synthesized in 83% yield using a Cu(I)-templated assembly of 5,5'-bis-bromomethyl-[2,2']bipyridyl and macrocycle **1**, a method pioneered by Sauvage,⁶ followed by Williamson etherification with tris(*p*-*tert*-butylphenyl)(4-hydroxyphenyl)methane. Replacing the ester bipyridyl-based thread in the previously reported rotaxanes with ether linkages greatly improved the stability of the complex. However, model compound **4** exhibited no emissive exciplex (Figure 1).

Microwave-assisted Sonogashira–Hagihara coupling of **2** with the corresponding aryl diacetylene afforded poly(*p*-phenylene ethynylene)s (PPEs) **3a** (dp ≈ 20) and **3b** (dp ≈ 30).^{7–9} Microwave irradiation dramatically reduced reaction time from 2 days to under an hour.

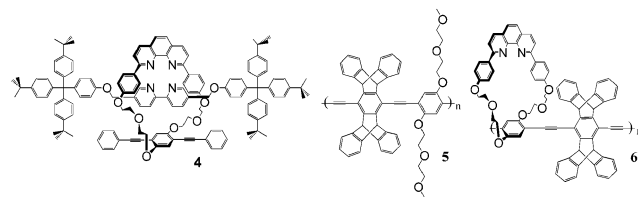
The absorption and emission maxima, excited-state lifetimes, and quantum yields of the metal-free polymers are typical of PPEs (Figure 2). The pendant bulky rotaxane groups enhanced the polymer solubility in organic solvents and prevented interchain aggregation, as evidenced by the absence of red shift in the polymer solid-state emission.

Phenanthroline and bipyridine groups are well-known hydrogen bond (H-bond) acceptors. To investigate the scope and spatial requirement of this interaction, we sought to test our polymers with well-known H-bond donors. In this regard, phenols, whose hydrogen bonding interactions with electron-deficient *N*-heteroaromatics have been extensively investigated, presented the ideal class of candidates.^{10,11}

Reversible binding of phenol to polymers **3a** and **3b** resulted in fluorescence quenching, both in solution and thin films. In addition, the residual polymer emission was slightly red-shifted by about 6 nm in the presence of phenol vapor. In thin films, polymer **3b** exhibited a more efficient response to phenol vapor than **3a**. We attributed this to the smaller and more flexible dialkoxybenzene

Scheme 1. Synthesis of Rotaxane PPEs^a

^a Conditions: (i) CuI; bpy(CH₂Br)₂; K₂CO₃, *p*-(*t*-BuC₆H₄)₃CC₆H₄OH; KCN. (ii) Pd(PPh₃)₄, R(C≡CH)₂, CuI, toluene/HNⁱPr₂, 65 °C; KCN.

Figure 1. Model compound **4** and control polymers **5** and **6**.

comonomer (compared to the rigid pentiptycene), which afforded higher porosity in polymer film morphology.

As expected, the polymer thin films responded to other H-bond donors such as *p*-nitrophenol and 2,2,2-trifluoroethanol (Figure 3). Analyte diffusion also plays a role in fluorescence quenching. As experiments with 4-*tert*-butylphenol reveal, increased steric demand of the analyte reduces its ability to penetrate into the polymer matrix. Consequently, fluorescence quenching becomes less effective. Exposing control polymers **5** and **6** to phenol vapors elicited negligible response. These results confirmed our hypothesis that

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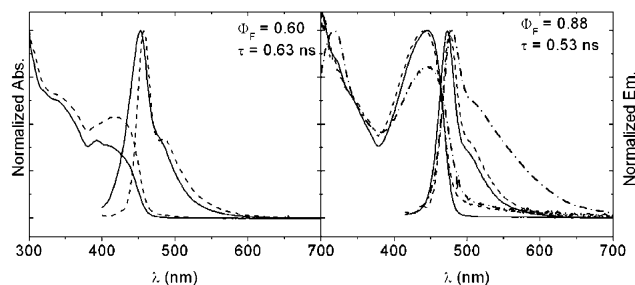


Figure 2. Absorption and emission spectra acquired at room temperature in CH_2Cl_2 (solid), thin film (dash), and zinc-doped thin film (line-dot). (Left) **3a**, $\lambda_{\text{exc}} = 385$ nm. (Right) **3b**, $\lambda_{\text{exc}} = 400$ nm. The quantum yields and lifetimes correspond to metal-free polymers in solution.

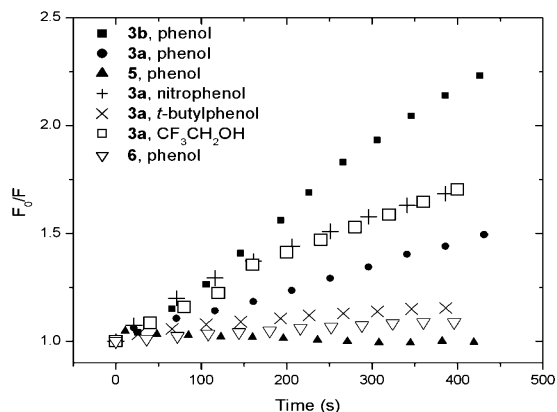


Figure 3. Fluorescence quenching of polymer thin films upon exposure to alcohol vapors (room temperature). For **3a** and **5** and **6**, $\lambda_{\text{exc}} = 400$ nm, fluorescence monitored at 455 nm. For **3b**, $\lambda_{\text{exc}} = 420$ nm, fluorescence monitored at 475 nm. Quenching in **3a** by acidic alcohols is representative.

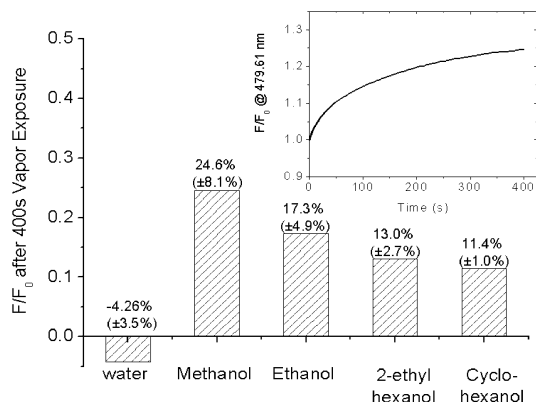


Figure 4. Fluorescence change in Zn-doped films of **3b** after 400-s exposure in saturated vapors at 25 °C. Inset: Relative fluorescence change of **3b** film in methanol vapor as a function of time. Results are representative.

the rotaxane groups were solely responsible for the interactions with acidic alcohols. Furthermore, NMR experiments indicated that hydrogen bonding, rather than complete proton transfer, was the dominant mechanism for the interactions.^{12,13}

In addition to hydrogen bonding, the tetrahedral pockets predispose the rotaxane repeat units to metal binding. A new absorption band centered at 318 nm appeared in the absorption spectra of thin films cast from a solution mixture of the polymers and zinc(II) perchlorate (Figure 2). Control experiments with **4** confirmed that metal binding caused the emergence of the new absorption band. Compared to polymers **3a** and **3b**, the doped films exhibited red-shifted and visibly weaker emission. Exposing the Zn-doped polymer thin films to alcohol reversibly modulated the effect of the metal centers and reversed the quenching by up to 25% (Figure

4). The hydrophobic environment of the rotaxanes made water molecules inaccessible to the metal ions. As a result, we observed minor but irreversible quenching from water vapor, most likely due to photobleaching. For Zn-doped **3b** thin films, methanol, the smallest primary alcohol, induced the greatest fluorescence change, while secondary alcohols such as cyclohexanol elicited less response. Doped films of **3a** also showed similar trends.

In conclusion, we have synthesized conjugated polymers with tethered rotaxane groups. The polymer fluorescence was greatly attenuated in the presence of phenols as a result of hydrogen bonding. On the contrary, exposing the Zn-doped polymers with alcohol vapor resulted in an increase in the emission. These results demonstrate the intricacy of macromolecular photophysics and present a fertile ground for future complex chemosensor development.

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Supporting Information Available: Detailed procedures for the synthesis of rotaxane monomer and polymers and quenching experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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