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A Rotaxane Exciplex

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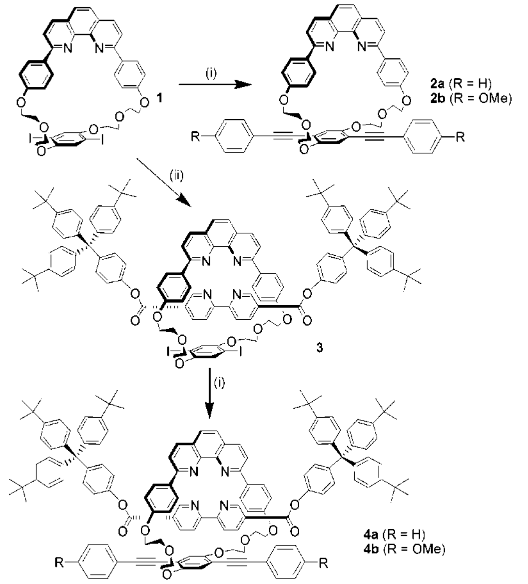
The creation of molecular-scale photonic devices requires supramolecular logic elements.[1−3] Although the study of supramolecular photochemistry is still in its infancy, it is clear that it offers much greater diversity than single-molecule systems. These components may permit access to complex photophysical processes, such as vectorial energy transfer, energy migration, and optical switching.[4] Fundamental studies of supramolecular photochemistry are also relevant to biological studies of vision and photosynthesis.[5,6]

Intramolecular exciplexes formed between tethered donor and acceptor moieties have been investigated extensively.[7,8] These studies are important for understanding energy transport and molecular dynmaics, as well as designing new chemical sensors. Luminescent intramolecular exciplexes between molecular components that are not covalently bound to one another have not been developed.[9,10] Herein, we report the observation of an emissive exciplex formed between two components of a rotaxane, an unusual optical phenomenon.

Making use of methods developed by Sauvage,[11] rotaxane **3** was prepared in 81% yield from a Cu(I)-templated esterification of tris(*p-tert*-butylphenyl)(4-hydroxyphenyl)-methane with 5,5′-(2,2-bipyridine)diacid chloride in the presence of the phenanthroline-based macrocycle **1** as illustrated in Scheme 1.[12] The demetalated rotaxane **3** was characterized by ^{1}H and ^{13}C NMR spectroscopy, FAB MS, IR, and UV−vis spectroscopy. The single-crystal X-ray structure of **3** confirmed the proposed structure (Figure 1), with a thread noncovalently bound inside the macrocycle. Notably, the diiododialkoxyphenyl ring lies parallel to the plane of the pyridine ring containing N(3) (3° between the planes), with the N atom positioned directly over the center of the aromatic ring. The phenyl-bipyridine cofacial separation is 3.50 Å, consistent with a weak $\pi-\pi$ interaction between the aromatic rings. This observation in the solid-state packing of **3** underlines the propensity of the aromatic rings of the thread and the macrocycle to weakly interact.

Scheme 1[a]



[a] (i) *p*-RC$_6$H$_4$C≡CH, CuI, toluene/HN^{i}Pr$_2$, 65 °C; KCN. (ii) CuI; bpy(COCl)$_2$; EtN^{i}Pr$_2$, *p*-(^{t}BuC$_6$H$_4$)$_3$CC$_6$H$_4$OH; KCN.

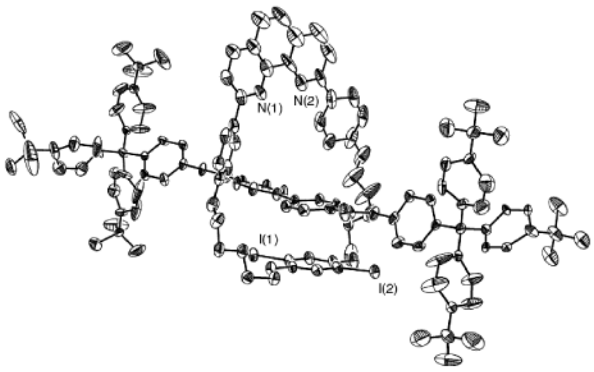


Figure 1. Molecular structure of rotaxane **3** with thermal ellipsoids shown at the 30% probability level.

Macrocycles **2** and rotaxanes **4** were prepared by Pd(0)-catalyzed cross-coupling of **1** and **3**, respectively, with phenylacetylene (**2a**, **4a**) or 4-methoxyphenylacetylene (**2b**, **4b**).[13] We investigated the photophysical properties of **2** and **4** in solution.

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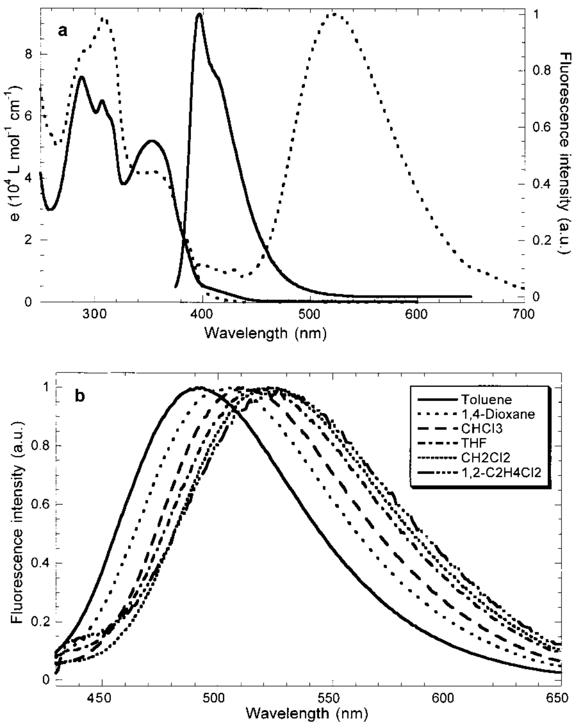

Figure 2. (a) Absorption and normalized fluorescence spectra of **2a** (—) and **4a** (···). (b) Normalized fluorescence spectra of **4a** in various solvents.

Figure 2a shows the absorption and luminescence spectra of **2a** and **4a**. Macrocycle **2a** displays an absorption edge ($\pi-\pi^*$) near 350 nm and a fluorescent peak at 396 nm (monoexponential, $\tau = 1.5$ ns in CH_2Cl_2; $\Phi_F = 0.66$). The similarity of these values to those of 1,4-bis(phenylethynyl)-2,5-dimethoxybenzene ($\tau = 1.5$ ns; $\Phi_F = 0.88$) suggest that the source of luminescence in **2a** is likely the phenylacetylene chromophore.

Surprisingly, the introduction of a bipyridyl-based thread through macrocycle **2** dramatically affected the optical properties of the molecule. Rotaxane **4a** displayed no fluorescent band at 396 nm, but instead a new broad, featureless peak at 520 nm (fwhm = 104 nm; $\Phi_F = 0.02$ in CH_2Cl_2). Lifetime measurements of this rotaxane indicated a longer lifetime for the redshifted band (monoexponential, $\tau = 3.7$ ns in CH_2Cl_2),[14] as expected for an exciplex. The broad, featureless nature of the peak is also consistent with exciplex emission since the ground state shows no vibrational structure.[15] Moreover, the band is highly solvatochromic, increasing in wavelength with increasing solvent permittivity; the peak shifted from 491 nm in toluene to 527 nm in 1,2-dichloroethane (Figure 2b). The absence of significant new absorption in the rotaxane compared with the individual components indicates that the exciplex is an excited-state species only. As the fluorescence intensity versus concentration was linear between 3×10^{-6} and 1×10^{-5} M, the new band arises from a unimolecular process and not intermolecular aggregation.

Thus, rotaxane **4a** displays a new emission band assigned to an intramolecular exciplex. The exciplex is likely formed between the electron-rich phenylacetylene group and the electron-deficient bipyridine diester. Indeed, modification of the phenylacetylene chromophore with methoxy groups (rotaxane **4b**) results in a red-shift of the excimer peak to 544 nm in CH_2Cl_2 ($\Phi_F = 0.008$).

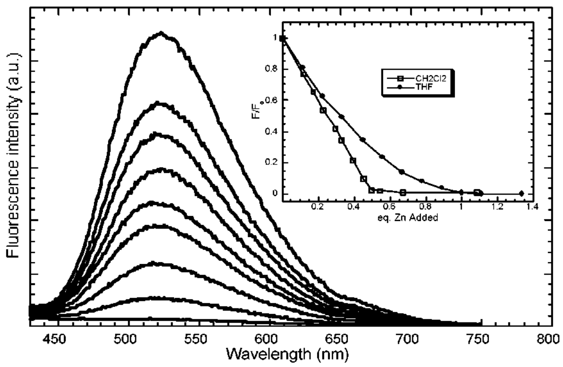

Figure 3. Fluorescence spectra of **4a** ([**4a**] = 6.64×10^{-6} M in CH_2Cl_2) showing the intensity decrease with increasing concentration of Zn(II) ($\lambda_{exc} = 358$ nm). (Inset) A plot of the relative fluorescence (F/F_o) vs 1 equiv of Zn(II) when a solution of **4a** in CH_2Cl_2 or THF is titrated with Zn(II).

Rotaxane **4a** offers a tetradentate pocket for the binding of metals, and may function as a sensitive cation detector. Indeed, upon binding alkali, alkali-earth, or first row transition metals, the fluorescence of **4a** is quenched. This is consistent with the participation of the bipyridine in the exciplex emission, which is no longer able to interact with the phenylene−ethynylene oligomer when a cation is in the pocket. Titration of a solution of **4a** in CH_2Cl_2 or THF with zinc(II) triflate in MeCN resulted in the diminution of the exciplex band, Figure 3. In the case of **4a** in CH_2Cl_2, the relative fluorescence (F/F_o) decreases linearly with Zn(II) addition, until 0.5 equiv of Zn(II) have been added. This suggests that a bimolecular quenching event (e.g. coordination of the bpy from two molecules to a single Zn(II)) is initially responsible for the quenching. This species may form when two rotaxane molecules with their threads fully extended to one side of the macrocycle coordinate to a metal ion. In THF, the fluorescence is gradually quenched until 1.0 equiv of Zn(II) has been added. Curvature in the titration curve indicates that a more complex phenomenon, possibly competition between unimolecular and bimolecular quenching events, is present.

The fluorescence quenching of rotaxane **4a** may be attributed to energy- or electron transfer from the excited state to the coordinated phenanthroline or bipyridine.[16] Upon binding a metal or proton, the excited states of the ligands, which contain increased electron density on the nitrogen atoms, are perturbed. The $\pi-\pi^*$ transition is red-shifted, where it overlaps with the fluorescence of the bis(phenylethynyl)dialkoxybenzene chromophore. The fluorescence of macrocycle **2a** (396 nm) without the bipyridine thread is also quenched upon binding alkali and transition metals.

In conclusion, rotaxanes **4** are multichromophoric systems that display intramolecular exciplexes between the thread and the macrocycle. Knowledge of this photoprocess may be useful in the design of new photochemical or photophysical devices.

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Supporting Information Available: Experimental details, crystallography details, and table of bond lengths, bond angles, and atomic coordinates for **3** (PDF). An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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