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Electrochemical properties of 3,5-diphenylaniline units encapsulated within a crown ether. Effects of the macrocycle's aromatic functionality and ring size

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ABSTRACT

This Letter describes a series of [2]rotaxanes featuring a 3,5-diphenylaniline terminus in their dumbbellshaped component and crown ethers as the macrocyclic component, prepared through imine formation and hydrogen bond—guided self-assembly. Electrochemical studies of these [2]rotaxanes revealed that the oxidation potential of the aniline moiety when positioned within the cavity of a crown ether was shifted negatively relative to that of the corresponding dumbbell-shaped compound, and that a crown ether possessing a small cavity and a large number of aromatic rings had a more negative effect on the oxidation potential of the aniline moiety than did a large-cavity crown ether featuring no aromatic rings. UV experiments showed that absorption band of the rotaxanes bearing small crowns shifted to longer wavelengths as compared to those of the rotaxanes having large crowns.

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Polyanilines have attracted much interest because of their applications as electrochromic devices, sensors, electromechanical actuators, and rechargeable batteries and for their use as hole-transporting materials in organic light emitting diodes.¹ One of the attractive features of polyanilines is that they are simple to synthesize in large quantities through oxidation of inexpensive aniline.

The properties of [2]rotaxanes containing π -conjugated systems in their dumbbell-shaped components are highly tunable through changes in the structure of their macrocyclic component; the degree of stabilization,² the electrochemical and/or photochemical properties,^{3,4} and the three-dimensional structures of π -conjugated moieties⁵ can all be regulated in the presence of encircling macrocyclic species, including cyclophanes,⁶ cyclodextrins,^{2b,c,7} cucurbiturils,^{2a,5b,8} and crown ethers.^{9,10}

Although the syntheses and characteristics of many [2]rotaxanes containing π -conjugated systems have been discussed, the effects of the size and functionality of the macrocyclic components on the properties of the dumbbell-shaped component are rarely examined sufficiently or systematically, possibly because the preparation of [2]rotaxanes featuring functionalized macrocycles is somewhat complex. In this study, we prepared a series of [2]rotaxanes comprising crown ether macrocyclic components (of various sizes and aromatic functionalities) and a diphenylanilineterminated dumbbell-shaped component to function as a small

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polyaniline unit. We used differential pulse voltammetry and UV to systematically investigate the effects of macrocyclic rings on the electrochemical and photochemical properties of π -conjugated system as a primary step of oligo- and polyanilines.

The crown ethers that we chose for this investigation were [24]crown-8 (24C8, **1a**), dibenzo[24]crown-8 (DB24C8, **1b**), dinaphtho[24]crown-8 (DN24C8, **1c**),¹¹ *p*-phenylenebenzo[26] crown-8 (DB26C8, **1d**),¹² trinaphtho[27]crown-9 (TN27C9, **1e**), and dinaphtho[30]crown-10 (DN30C10, **1f**),¹³ which contain 24-, 26-, 27-, and 30-membered rings and various aromatic units (Fig. 1, Scheme 1). Although we have previously synthesized the [2]rotaxanes **4a–c** and the dumbbell-shaped molecule **4g**,¹⁴ the methodology was not optimal: (i) acylation of the [2]rotaxane salts **3** afforded **4** in poor yields when hexafluorophosphate was used as the counter anion, meaning that counter ion exchange was necessary prior to acylation; (ii) the selectivity of the acylation reactions of the dialkylammonium moieties in the [2]rotaxanes **3** was poor. Therefore, we have modified our previous method to synthesize the [2]rotaxanes **4** more efficiently.

We synthesized the [2]rotaxanes **3a–f** from the aldehyde **2**, the crown ethers **1a–f**, and 3,5-diphenylaniline¹⁵ through thermodynamic covalent chemistry (reversible imine formation)^{16,17} and hydrogen bond–guided self-assembly (secondary dialkylammonium ion/crown ether complexation).¹⁸ Reduction of the imine units and subsequent spontaneous salt formation in the air gave the [2]rotaxanes **3a–f** as bicarbonate salts. Selective N-acylation of the dialkylammonium moieties afforded the corresponding [2]rotaxanes **4a–e** and the dumbbell-shaped

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4a: ring = 24C8 75% (24%)*
4b: ring = DB24C8 72% (57%)*
4c: ring = DN24C8 84% (65%)*
4d: ring = DB26C8 80% (74%)*
4e: ring = TN27C9 70% (15%)*
4f: ring = DN30C10 (0%)*
4g: no ring
*() warp 5t N warp wood oo a back

*(): when Et_3N was used as a base

2) 3,5-diphenylaniline
 3) NaBH₄ (85% for 3 steps)

Scheme 1.

4g

molecule **4g**. Exchanging Et_3N for sodium *tert*-butoxide had a particularly large effect on improving the yield of the acylation

reaction for the [2]rotaxane **4a**,¹⁹ presumably because the hydrogen bonds in 3a were the strongest among all of the [2]rotaxanes **3a–f** and, therefore, a weak base (Et_3N) could not completely deprotonated **3a**. In contrast, the strong base (NaOBu^t) readily deprotonated the dialkylammonium center in the [2]rotaxane 3a, causing the 24C8 unit to interact only weakly with the dialkylamino group, which, therefore, attacked the electrophile (BOC₂O) selectively, causing the 24C8 unit to hydrogen bond weakly to the aniline unit, which has a relatively high Brönsted acidity and hydrogen bond donating ability. Changing the base from Et₃N to NaOBu^t also improved the yield of the acylation of 4e, in this case because of the low solubility of 3e in dichloroethane. Notably, we could not isolate the acylated [2]rotaxane 4f featuring the 30-membered-ring crown ether after tert-butoxycarbonylation, presumably because the diphenylaniline terminus was not sufficiently bulky to prevent dethreading at high temperature.²⁰

¹H NMR spectra of the [2]rotaxanes **4a**–**e** and the dumbbellshaped molecule 4g revealed evidence for the selective acylation of the dialkylamine moieties of the [2]rotaxanes 3a-f and, therefore, the movement of the crown ether units from the dialkylamine stations to the aniline stations. For example, in the ¹H NMR spectrum of the [2]rotaxane 4a (Fig. 2c), the signals of the benzylic protons H_c and H_d (of **3a**, Fig. 2b) have shifted to higher field, and similar to those of the dumbbell-shaped molecule 4g (Fig. 2a), attributable to the loss of deshielding effects even though the neighboring nitrogen atom has been acylated. Shielding effects of the aromatic moieties are also responsible for the upfield shifts of the signals of the aromatic protons H_a and H_b in **4a**. In addition, the signals of the protons H_e and H_g moved to lower field, a likely result of shielding by the aromatic rings of the macrocyclic component. Moreover, the aniline moiety appears to exist as a free base because the integration of its NH unit corresponded to a single proton. And the correlation of signals between crown protons and H_b in 3a and between crown protons and H_g in 4a was observed in NOESY spectra of **3a** and **4a**, respectively.²¹

Table 1 reveals the differential pulse voltammetric behavior of the [2]rotaxanes **4a–e** and the dumbbell-shaped molecule **4g**. These experiments were performed in MeCN using a glassy carbon electrode as the working electrode and LiClO₄ (0.5 M) as the supporting electrolyte. We observed oxidation processes for all of the [2]rotaxanes **4a–e** and the dumbbell-shaped molecule **4g**. The oxidation potentials of the aniline moieties in the [2]rotaxanes **4a–e** were significantly shifted to more negative values (by up to 0.257 V for **4c**) relative to that for **4g**.

Two possible interactions between the two components might be responsible for the negative shifts of oxidation potentials: π – π stacking and hydrogen bonding interactions in the rotaxanes **4**. For the [2]rotaxanes **4a–c**, which all possess 24-membered macrocyclic components, we observed an effect of the presence of aromatic moieties in the crown ether units on the oxidation potentials: the potential shifted to more-negative values upon increasing the number of aromatic rings in the crown ether unit (from zero in **1a**, to two in **1b**, to four in **1c**), suggesting that π – π stacking interactions primarily increased electron density of the aniline moieties in these cases.

Notably, however, we did not observe a similar effect for the aromatic rings in the [2]rotaxane **4d**, the crown ether component of which features one hydroquinone unit and one catechol unit; the oxidation potential for **4d** was close to those of **4a**, which features a 24C8 unit (i.e., no aromatic units). The ¹H NMR spectra (DMSO- d_6 , 353 K) of the [2]rotaxanes **4a**–**e** provide a clue regarding the position of the hydroquinone ring of **4d**; the signals for the protons H_e in **4a**–**c** and **4e** appear in the range from 4.67 to 4.96 ppm, whereas that in **4d** appears at 3.76 ppm. This high field shift for **4d** suggests a shielding effect of the hydroquinone ring



Figure 2. ¹H NMR spectra (500 MHz, DMSO-d₆, 353 K) of (a) the dumbbell-shaped molecule 4g, (b) the NH₂⁺-centered [2]rotaxane 3a, and (c) the acylated [2]rotaxane 4a.

 Table 1

 Oxidation potentials and absorption maxima of the [2]rotaxanes 4a-e and the dumbbell-shaped molecule 4g

Rotaxane	4a	4b	4c	4d	4e	4g
Ring	24C8	DB24C8	DN24C8	DB26C8	TN27C9	None
Oxidation potential ^a λ_{\max}^{b}	+0.306 ± 5	+0.218 ± 5	+0.200 ± 5	+0.311 ± 5	+0.331 ± 5	+0.457 ± 5
	348 ± 1 ^c	346 ± 1 ^c	346 ± 1 ^c	342 ± 1	342 ± 1	333 ± 1

^a ΔV values versus ferrocene. All experiments were performed twice and the average is shown in table. Substrates in acetonitrile containing supporting electrolyte LiClO₄ (0.5 M); recorded in acetonitrile containing LiClO₄ (0.5 M). Pulse amplitude 50 mV, pulse with 50 ms, scan rate 5 mV/s, pulse interval 0.3 s.

^b UV-vis spectra of rotaxanes and the dumbbell-shaped molecule (34 μ M) in 1% triethylamine-acetonitrile.

^c Ref. 14.

over the ArCHN unit; therefore, it does not effectively overlap the aniline moiety.

The oxidation potential of **4e** was more positive than that of **4a**. We suspect that hydrogen bonding was important to increase the electron density of aniline moieties. In the ¹H NMR spectra of all the [2]rotaxanes **4a**–**e**, the presence of concentration-independent signals for the NH units (in the range 4.98–5.72 ppm) supports the presence of hydrogen bonds between the aniline NH units and the crown ether moieties in their ground states. We suspect that the strength of the hydrogen bonds would follow the order **4a** > **4b** \approx **4c** > **4d** and **4e**, because 24-membered rings provide stronger hydrogen bonds^{12a} and because oxygen atoms of dialkyl ethers have higher basicity relative to those of alkyl aryl ethers. Therefore, the negative shifts in the oxidation potentials resulted from the combination of effects from π – π stacking and hydrogen bonding interactions.

The absorption maxima (λ_{max}) of rotaxanes **4a–e** and their dumbbell-shaped molecule **4g** are shown in Table 1. The wavelength shifts of rotaxanes revealed the shielding effects of macrocycles; noncovalent interactions between the aniline moiety and crown ethers seem to cause a decrease in the energy gaps between HOMO and LUMO orbitals. Interestingly, the λ_{max} values of rotaxanes **4a–c** are similar, although the oxidation potentials were influenced by the aromatic rings. The respective shielding effects of macrocycles on HOMO and LUMO orbitals display similar tendencies among these rotaxanes **4a–c**. Probably, the aromatic effects are canceled by the hydrogen bonding and/or dipole interactions. In contrast, the λ_{max} of rotaxanes **4d** and **4e**, which feature large crown ethers, are shorter than those of **4a–c**, although some effects could be achieved by the macrocycles. Therefore, we suspect that the long-wave shifting of aniline moiety in UV spectra resulted from the effectiveness of interactions, which depend on the ring size of macrocyclic components.

In summary, we have used reversible imine formation, hydrogen bonding between crown ethers and dialkylammonium ions, and selective acylation of dialkylammonium moieties to construct the five [2]rotaxanes **4a–e** featuring aniline moieties in their dumbbell-shaped units and crown ethers as their macrocyclic components. Differential pulse voltammetry and UV experiments of these [2]rotaxanes and the corresponding dumbbell-shaped molecule **4g** revealed negative shifts in the oxidation potentials and long-wave shifting of the aniline moieties when situated within crown ether cavities, influenced by both the nature of the aromatic units and the ring size of the crown ether components.

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Supplementary data

Supplementary data (NOESY spectra of [2]rotaxanes **3a** and **4a**, differential pulse voltammograms of the [2]rotaxanes **4a–e** and the dumbbell-shaped molecule **4g**, and UV spectra of [2]rotaxanes **4a–e** and the dumbbell-shaped molecule **4g**) associated with this article can be found, in the online version, at doi:10.1016/ j.tetlet.2010.11.043.

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