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A Novel Optical Sensor for Metal Ions Based on Ground-State Intermolecular Charge-Transfer Complexation

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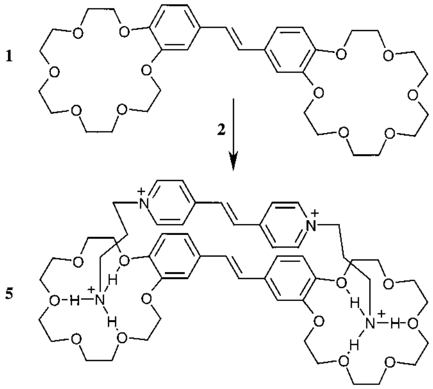
ABSTRACT



A derivative of dipyridylethylene 2 was synthesized in order to study intermolecular coordination between the 18-crown-6 ether units of bis-crown stilbene 1 and the NH_3^+ groups of 2. In acetonitrile solution, the formation of a supramolecular complex is evidenced by a considerable upfield shift of the ^{1}H NMR signals from the aromatic and olefinic protons. Emission quenching and the appearance of a new absorption band in the visible spectral region indicate the formation of a charge-transfer complex. The addition of Ba^{2+} to a solution of the complex leads to significant fluorescence enhancement and to the disappearance of the charge-transfer absorption band.

Crown ether derivatives containing unsaturated fragments attract much attention because of their utility as optical sensors for alkali and alkaline-earth metal cations.[1−3] Various functional units whose spectroscopic behavior is controlled by photophysical phenomena, such as charge-transfer excited states, photoinduced electron or energy transfer, or excimer formation have been employed to create optical sensors.[2] In this Letter, we present a novel sensor based on ground-state intermolecular charge-transfer complexation between bis-crown stilbene **1** and dialkylammonium dipyridylethylene **2** via self-assembly in acetonitrile.

Bis(18-crown-6) stilbene **1** was obtained from 4′-formylbenzo-18-crown-6 ether in 21% yield.[4] Compounds **2** and **3** were synthesized as depicted in Scheme 1. *trans*-1,2-Bis(4-

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[2] de Silva, P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515.

[3] Alfimov, M. V.; Gromov, S. P. *Applied fluorescence in chemistry, biology, and medicine*; Rettig, W., Strehmel, B., Schrader, S., Seifert, H., Eds.; Springer-Verlag: Berlin, 1999; p 161.

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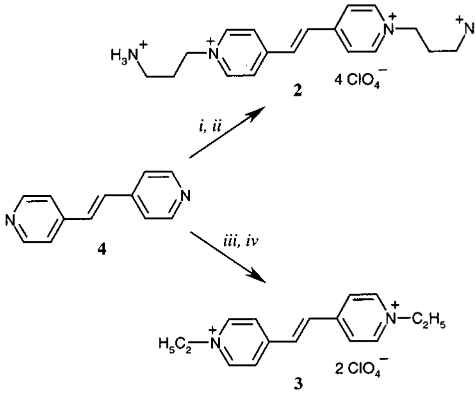
Scheme 1. Preparation of Bis-Quaternary Salts **2** and **3**[a]



pyridyl)ethylene **4** was converted in two steps into *N*,*N*′-di-(3-ammoniumpropyl)dipyridyliumylethylene tetraperchlorate, which was purified by recrystallization from aqueous ethanol in 30% yield. The main byproduct was the product of monoalkylation of **4**. *N*,*N*′-Diethyldipyridyliumylethylene diperchlorate **3** was prepared as a reference compound in 64% yield. The newly synthesized compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy as well as by elemental analysis.[5]

Figures 1 and 2 show absorption and emission spectra of acetonitrile solutions of **1**, **2**, and their 1:1 mixture. Compounds **1** and **2** exhibit structured absorption and emission bands. The maxima of the most intensive transitions in the absorption and emission spectra are around 336 and 386 nm for **1** and around 322 and 369 nm for **2**. Fluorescence quantum yields for **1** and **2** in air-equilibrated acetonitrile solutions are ca. 0.3 and 0.02, respectively.

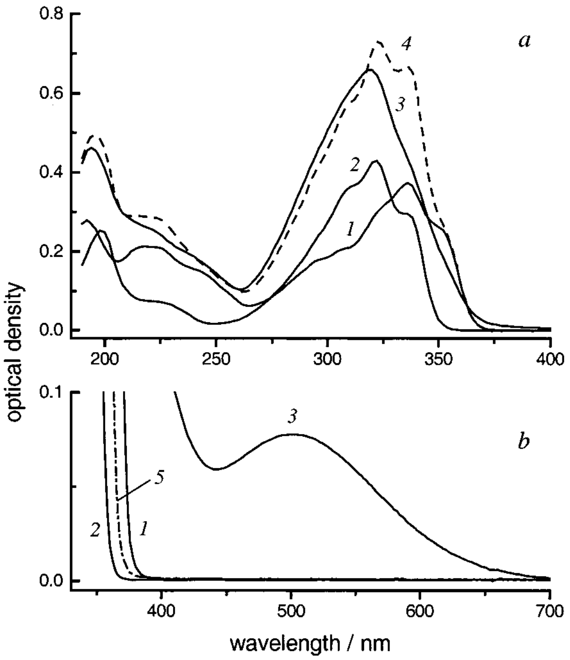


Figure 1. Absorption spectra of **1** (*1*), **2** (*2*), and their 1:1 mixture (*3*) in acetonitrile; concentrations of the reactants are 1.0×10^{-5} (*a*) and 2.0×10^{-4} mol dm^{-3} (*b*). Curve *4* is the sum of the spectra *1* and *2*. Curve *5* is the spectrum of the 1:1 mixture recorded after addition of 5.0×10^{-4} mol dm^{-3} $Ba(ClO_4)_2$.

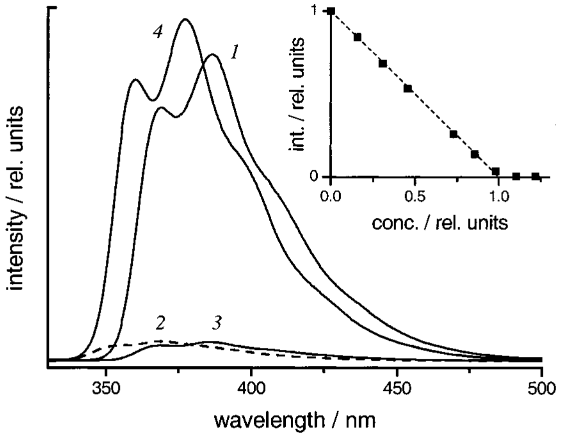
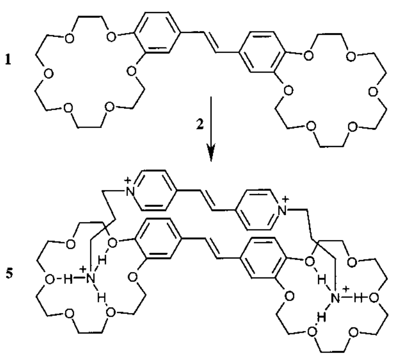


Figure 2. Emission spectra of **1** (*1*), **2** (*2*), and their 1:1 mixture (*3*) in acetonitrile; excitation at 274 nm. Concentrations of the reactants are 4.0×10^{-6} mol dm^{-3}. Curve *4* is the spectrum of the 1:1 mixture recorded after addition of 5.0×10^{-5} mol dm^{-3} $Ba(ClO_4)_2$. Inset: intensity of the emission of **1** (1.0×10^{-5} mol dm^{-3}, excitation at 363 nm) as a function of the concentration of **2**.

The significant difference between the spectrum of the 1:1 mixture and the sum of the spectra of the components (Figure 1a) indicates that compounds **1** and **2** form a complex. The spectrum of the complex has a long-wavelength tail extending into the visible region. The spectrophotometric data obtained from a concentrated solution of **1** and **2** (Figure 1b) reveal that the complex has a weak, broad absorption band with a maximum near 500 nm which is reminiscent of the charge-transfer (CT) band of donor−acceptor complexes. Formation of the complex also results in significant quenching of the emission from each of the components, suggesting that CT interactions between electron donor **1** and electron acceptor **2** enhance internal conversion and radiationless decay.

The data of fluorescence titration presented in the inset of Figure 2 indicate the 1:1 stoichiometry for complexation between **1** and **2** in dilute solution. Fitting these data to a 1:1 complexation model provides the lower boundary for the complex stability constant, log $K > 7$.

Generally, molecules in ground-state CT complexes are weakly bound and no spectral evidence for these complexes can be obtained in dilute solution.[6,7] In fact, no emission quenching was observed for solutions of **1** containing reference compound **3** at concentrations of $\sim 1 \times 10^{-5}$ mol dm^{-3}. The high stability of the CT complex formed between **1** and **2** is evidently due to the cooperative intermolecular coordination of two NH_3^+ groups of **2** with two 18-crown-6 ether units of **1**, as proposed in complex **5**.



This cooperative coordination also explains the fact that the stability constant for complexation between **1** and **2** is several orders of magnitude higher than those for complexation of 18-crown-6 with t-$C_4H_9NH_3^+ClO_4^-$ (log $K = 3.47$) and for complexation of benzo-18-crown-6 with $NH_4^+SCN^-$ (log $K = 4.07$) in the same solvent.[8]

Complexation is also demonstrated by considerable changes in ^{1}H NMR chemical shifts for the aromatic and olefinic protons of **1** and **2** (Figure 3). In the case of a 1:1 mixture of **1** and **2**, most of the protons are shifted upfield by 0.15−0.35 ppm, suggesting that **1** and **2** form complex **5** in which the conjugated systems are placed one under other. NOESY cross-peaks between the signals from the protons of **1** and **2** moieties proved the existence of complex **5**.

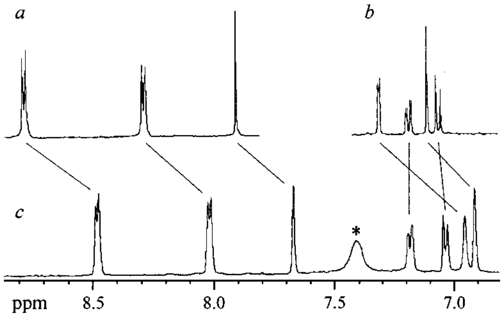


Figure 3. Aromatic proton regions of the ^{1}H NMR spectra of **2** (*a*), mixture of **1** with 10 equiv of $MeNH_3^+ClO_4^-$ (*b*), and 1:1 mixture of **1** and **2** (*c*) (CD_3CN, 60 °C, concentrations of **1** and **2** are 6×10^{-3} mol dm^{-3}). The straight lines show the changes in the proton chemical shifts. The peak marked by an asterisk corresponds to the NH_3^+ groups.

The addition of $Ba(ClO_4)_2$ to a solution of the **1**−**2** CT complex induced disappearance of the long-wavelength absorption band (Figure 1b) and significant emission enhancement (Figure 2). This optical response is very likely to arise from disruption of the CT complex structure because of the competing complexation of Ba^{2+} with the crown ether groups of **1**. The resulting emission spectrum was similar to that obtained from a solution of Ba^{2+} complexes of **1**. In addition, the absorption spectra of 1:1 mixtures of **1** and **2** recorded after addition of $Ba(ClO_4)_2$ correlates well to the sum of the spectra of **2** and a Ba^{2+} complex of **1**.

These results demonstrate that the ground-state CT complex formed by **1** and **2** is a promising example of the supramolecular system which is able to produce a strong optical response upon interaction with metal cations.

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(5) **2**: mp 293−295 °C (dec); δ_H (CD_3CN, 50 °C) 8.75 (d, $J = 6.8$ Hz, 4 H), 8.27 (d, $J = 6.8$ Hz, 4 H), 7.90 (s, 2 H), 6.45 (br s, 6 H), 4.63 (m, 4 H), 3.15 (m, 4 H), 2.41 (m, 4 H); δ_C (DMSO-d_6, 28 °C) 150.71 (s, 2 C), 145.31 (d, $J = 191.1$ Hz, 4 C), 134.22 (d, $J = 168.5$ Hz, 2 C), 125.79 (d, $J = 172.1$ Hz, 4 C), 57.68 (t, $J = 147.6$ Hz, 2 C), 35.89 (t, $J = 143.4$ Hz, 2 C), 28.65 (t, $J = 130.2$ Hz, 2 C). Anal. Calcd for $C_{18}H_{28}Cl_4N_4O_{16}$: C, 30.96; H, 4.04; N, 8.02. Found: C, 30.75; H, 4.28; N, 7.91. **3**: mp 295−296 °C (dec); δ_H (CD_3CN, 60 °C) 8.74 (d, $J = 6.8$ Hz, 4 H), 8.22 (d, $J = 6.8$ Hz, 4 H), 7.85 (s, 2 H), 4.62 (q, $J = 7.3$ Hz, 4 H), 1.68 (t, $J = 7.3$ Hz, 6 H); δ_C (DMSO-d_6, 27 °C) 150.40 (s, 2 C), 144.97 (d, $J = 192.0$ Hz, 4 C), 134.01 (d, $J = 161.2$ Hz, 2 C), 125.49 (d, $J = 172.6$ Hz, 4 C), 56.12 (t, $J = 146.2$ Hz, 2 C), 16.15 (q, $J = 129.3$ Hz, 2 C). Anal. Calcd for $C_{16}H_{20}Cl_2N_2O_8$: C, 43.75; H, 4.59; N, 6.38. Found: C, 43.72; H, 4.45; N, 6.22.

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