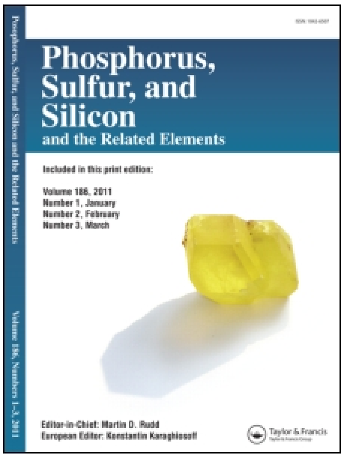

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Liu, Tian-Jun , Wang, Dong , Wang, W-Zhen and Xu, Guo-Zheng(1998) 'OPTICALLY ACTIVE SILACROWN ETHER PHOTOPHYSICAL BEHAVIORS AND COMPLEXATION WITH CATIONS AND VIOLOGEN BROMIDE', Phosphorus, Sulfur, and Silicon and the Related Elements, 140: 1, 237 — 244

To link to this Article: DOI: 10.1080/10426509808035746

URL: http://dx.doi.org/10.1080/10426509808035746

Phosphorus, Sulfur and Silicon, 1998, Vol. 140, pp. 237-244
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OPTICALLY ACTIVE SILACROWN ETHER. PHOTOPHYSICAL BEHAVIORS AND COMPLEXATION WITH CATIONS AND VIOLOGEN BROMIDE

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(Received 22 November, 1997 ; In final form 8 January, 1998)

Optically active silacrown ethers **7** and **8** were synthesized. The photophysical behaviors of the silacrown ethers and their complexation with cations and viologen bromide were investigated. **7** exhibits good lithium ion-complexation selectivity and very good ability to complex with viologen bromide.

INTRODUCTION

Since the discovery of macrocyclic polyethers by Petersen[1] some two decades ago, considerable attention has been focused on crown ethers and their analogues.[2] The synthesis of medium ring cyclic polyethers containing one or two silyl groups was first reported by Krieble and Burkhad as early as 1947.[3] However, since then only few investigations dealing with the synthesis[4] and properties[5] of macrocyclic poly(alkeneoxy)silanes, designed as silacrown ethers, have been published. Recently, Hosseini[6] reported the synthesis of large disilacrown ethers and indicated that the yields (5–30%) of the silacrown ether depended strongly on the bases used. On the other hand, Cram[7] reported that a chiral crown ether was prepared by introducing chiral 1,1'-binaphthyl group to macrocyclic polyethyleneglycol, but very few reports were on the photophysical behaviors of this binaphthol crown ether. Herein, we wish to report the synthesis

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of optically active silacrown ethers with chiral 1,1'-binaphthyl moiety and the investigations of their photophysical behaviors and the complexations with cations and ethyl viologen bromide.

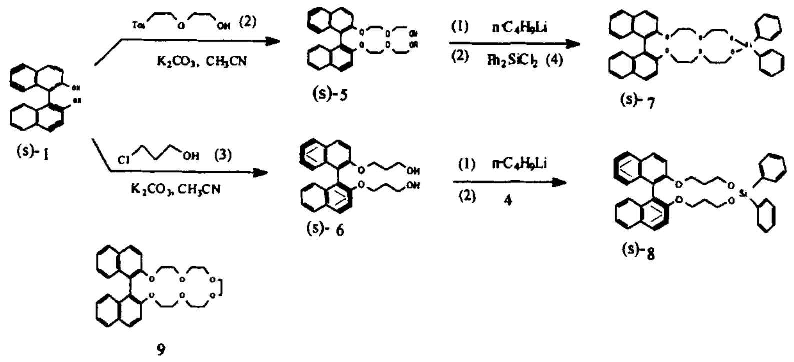
EXPERIMENTAL

Synthesis

The silacrown ethers **7** and **8** were prepared as Scheme 1. Starting from (S)-(-)-1,1'-binaphthol (**1**), the condensation with 2-(2-tosylethoxy)ethanol (**2**) and 3-chloropropan-1-ol (**3**) produced diols **5** and **6** in the yields 80% and 74% respectively. The cyclization of diol **5** with dichlorodiphenylsilane **4** was carried out with following procedure. To a solution of **5**(0.47g, 1mmol) in 10mL of THF, the solution of n-BuLi (0.7mL, C:1.5M in hexane) was added at 0°C, followed by stirring for 4h. A solution of **4** (0.25g, 1mmol) in 15mL of THF was added to the formed mixture. After stirring for 4h, the reaction temperature was increased to room temperature, followed by stirring for 12h. The solvent was removed by rotary evaporator. The residue was purified by flash chromatography on silica gel, giving a white solid **7**, 0.3g, yield 46% (overyield 37%). **8** was synthesized by the same procedure in yield 80% (overyield 59%).

7: $[\alpha]_D$:-37.4 (C,1.0, CH_2Cl_2). ν: 2920, 1615, 1420, 1265, 1090cm^{-1}, ^1H NMR, $\delta(CDCl_3)$: 3.30–4.24(m, 16H), 7.08–7.40(m, 14H), 7.65(m, 4H), 7.80(m, 4H). ^{13}C NMR, $\delta(CDCl_3)$: 62.77, 69.45, 69.67, 72.34, 115.83, 120.30, 123.52, 125.34, 126.17, 127.75, 127.80, 129.21, 129.80, 130.17, 132.84, 134.87, 154.35 ppm. ^{29}Si NMR, $\delta(CDCl_3)$: –38.90 ppm. *ms/z* (FAB): 643 (M^++1).

8: $[\alpha]_D$:-40.5 (C,1.0, CH_2Cl_2). ν: 3025, 2960, 1595, 1420, 1265, 1105cm^{-1}. ^1H NMR, $\delta(CDCl_3)$: 1.62–1.87(m, 4H), 3.47- 3.77(m, 4H), 4.05–4.44(m, 4H), 7.07–7.47(m, 14H), 7.60–7.64(m, 4H), 7.80–7.91(m, 4H) ppm. ^{13}C NMR, $\delta(CDCl_3)$: 39.98, 57.73, 63.28, 113.04, 122.89, 125.28, 126.03, 127.82, 128.66, 129.00, 130.25, 130.27, 132.65, 134.14, 134.32, 134.57, 134.73, 154.25 ppm. ^{29}Si NMR, $\delta(CDCl_3)$: –38.88 ppm. *ms/z* (FAB): 583 (M^++1).



SCHEME 1

Measurement and Instruments

The ^1H , ^{13}C and ^{29}Si NMR spectra were recorded by Varian 200MHz. The IR spectra were recorded by the Perkin-Elmer 400 FT-IR. FAB-MS was performed on KYKY-ZH-P-5 instrument. UV spectra were recorded by Hitachi 330 UV-Visible absorption spectrometer and fluorescent spectra by Hitachi-850 Fluorescent Spectrometer. Fluorescent lifetime was determined by Horiba Single-photon-counting equipment.

The association constants (Kass) were determined by following procedure: Based on the change of the absorptions with titration of the cation solution to the solution of the silacrown ether, the changes of corresponding optical density (ΔOD) were calculated. ΔOD is OD_0-OD, where OD_0 and OD are the optical density of the crown ether at free state and complex state respectively. In the light of Benesi-Hildebrand equation, plotting the $C_0/\Delta OD$ against the OD afforded a line, whose slope is 1/ Kass. C_0 is the concentration of the cation solution for titration.

RESULTS AND DISCUSSION

For the silacrown ethers **7** and **8**, the choice of diphenylsilyl group was made because diphenylsiloxy group is more stable to moisture than dimethylsiloxy group. The cyclization of **5** and **6** with **4** strongly depends on the bases used. In the presence of K_2CO_3, the cyclization reaction gave very small amount of the product, only observed on TLC. The use of Et_3N did not improve the yield at all, even prolonging reaction time to 30 hr. However, the use of n-BuLi increased the yields of **7** (46%) and **8** (80%) noticeably. One of the reasons giving better yield probably is the "template effect" of Li^+ on promoting the cyclization reactions, based on an idea of metal-assisted organization of linear molecules into crown ethers.[8]

The 1,1'-binaphthyl moiety can be considered as a chromic group. Introducing the rigid binaphthyl moiety into silacrwon ether molecule would provide some interesting photophysical properties. The wavelengths of absorption (λmax) and emission (λem), fluorescent quantum yield (ϕ) and fluorescent lifetime (τ) are summarized on Table I. It is shown that in comparison with **8,** λmax and λem of **7** are red-shifted. As reported,[9] the photophysical behaviors of binaphthylene and related compounds have a bearing on the rotation dynamics of binaphthyl groups around the connected single bond. The emission is the comprehensive result of the locally excited (LE) type of fluorescence and the twisted intramolecular charge transfer (TICT) type of fluorescence from the symmetry-breaking process[10]. The kinetics of charge transfer (K_{CT}) depends on the size of the groups and their steric conformration in ground state. The different dihedral angles between two naphthyl groups in **7** and **8** would lead to different K_{CT}. For binaphthylene type of molecule, although the spectra of LE and TICT overlap considerably, the TICT appears to be bathochromic slightly. Since the molecular structure of **7** is more flexible than that of **8**, the fluorescence of **7** is mainly from the contribution of TICT between two naphthyl groups instead of LE, leading to red-shift of the λmax and λem of **7** *via* **8**. On the other hand, Eisenthal[11] suggested that the naphthyl-naphthyl interaction energy in the ground state is small. Therefore, the difference between **7** and **8** in the dihedral angles of two naphthyl groups has influence slightly on the naphthyl-naphthyl interaction in the ground state. The absorptions at nearly same wavelength (Δλmax=6nm only) were observed for **7** and **8**. However, in excited state, the naphthyl-naphthyl interaction energy is bigger, the difference of **7** and **8** in the dihedral angle would cause a big difference in emission wavelengths (Δλem=16.3nm).

Table II lists the association constants (Kass) of silacrown ether **7** and **8** with some cations, which were determined by UV spectra. For **7**, the ability to complex with cations exhibits a following order: $Li^+ > Na^+ > K^+$, Mg^{++}. Obviously, **7** has very good lithium ion-complexation selectivity, while **8** has very weak ability to complex with given cations. In contrast, binaphthol crown ether **9**, same as **7** with six oxygen atoms in crown ether ring, has the potassium ion-cmplexation selectivity.[7] Apparently, although the ring size of crown ether did not change much: *ca.* 6.3–6.8 Å for **7** and *ca.* 6.5–7.0 Å for **9**, which are statistical values from 100 ps Molecular Modeling (NVT) running at 300K based on Dreiding force field,[11] the introduction of the diphenylsilyl group would result in more twisted conformation of **7** relative to **9**, leading to the better complexation with small size cation. The results are consistent with Inoue and Hakushi's observation about the cation-binding behaviors of crown ethers and their sila-analogues.[5]

TABLE I Photophysical data of silacrown ether **7** and **8**[a]

Compound	*λmax (nm)*	*λem (nm)*	ϕ	*τ (ns)*
7	336	367.8	0.30	3.59
8	332	356.8	0.53	4.86

a. in CH_3CN solution.

TABLE II Association constants (Kass) of **7** and **8** with cations* and **10**

silacrown ether	*Association constants (Kass)*				
	Li^+	*Na^+*	*K^+*	*Mg^{++}*	*V^{++} (10)*
7	10000	1300	68	76	29400
8	147	---	---	---	---

* solution of $M^+ClO_4^-$ in CH_3CN.

The complexation of silacrown ether **7** with molecule dication, ethyl viologen bromide **10** is very strong (Table II). As indicated by Gibson,[12] the crown complexes of viologen could be the rotaxane. Rotaxanes are compounds comprised of cyclic molecules penetrated by linear molecules, with no covalent bonds between the linear and cyclic components. In terms of the investigation, we suggested that the complex of **7** with viologen **10** should also be a rotaxane. As shown on Fig. 1, the rod-shaped diquanternary ammonium ion (the guest), carrying positive charge, is closely embraced by the oxygen atoms of silacrown ether (the host). In this rotaxane form, the twisted conformation of **7**, stemming from the introduction of diphenylsilyl group, does not influence the complexation with **10**.

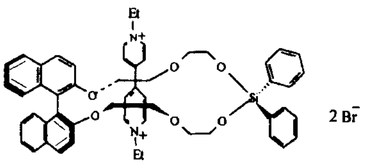


FIGURE 1 Complexation of 7 with viologen **10**

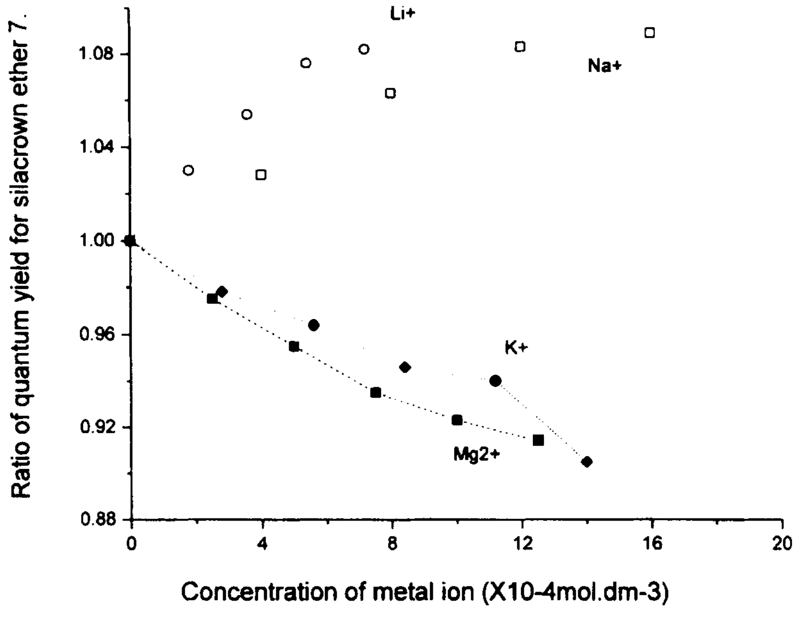


FIGURE 2 Plot of the ratio of fluorescent quantum yield against the concentration of doping metal ion

It is worthy to note that when the silacrown ethers complex with various cations, the absorption only shifts 2–5nm, but the fluorescent quantum yields change noticeably with the concentration of the cations. As shown on Fig. 2, the quantum yields enhances with the increase of the concentration of Li^+ and Na^+. In contrast, for K^+ and Mg^{++}, the quantum yields decrease with the concentration. It is suggested that in excited state, the π-π interaction between naphthyl groups would be weakened by the bigger size cations, such as K^+ and Mg^{++}.

CONCLUSION

The optically active silacrown ethers **7** and **8** were synthesized in good yields through the cyclization of diols 5 and **6**, derived from 1,1'-binaphthol, with dichlorodiphenyl silane in the presence of n-BuLi. The photophysical behaviors of silacrown ethers, such as absorption, emission and fluorescent spectra, as well as that of corresponding complexes with cations and viologen were investigated. The difference of the photophysical behaviors between **7** and **8** in excited state are bigger than that in ground state. The silacrown ether **7** exhibits very good lithium ion-complexation selectivity, as well as very good ability to complex with viologen.

Acknowledgements

We gratefully acknowledge the financial support by National Natural Science Foundation of China and Institute of Chemistry, Chinese Academy of Sciences.

References

[1] Petersen, C. J., *J. Am. Chem. Soc.*, **1967**, 89, 7017.

[2] Dietrich, B.; Viout, P.; Lehn, J. M., *Macrocyclic Chemistry,* VCH, Weinheim, **1993**; Vogtle, F., *Supramolecular Chemistry*, Wiley, **1991**.

[3] Krieble, R. H.; Burkhard, C. A., *J. Am. Chem. Soc.*, **1947**, 69, 2689.

[4] Sprung, M. M., *J. Org. Chem.*, **1958**, 23, 58; Arkles, B.; King, K.; Anderson, R.; Peterson, W., *Organometallics*, **1983**, 2, 454; Moran, M.; Inoue, Y.; Ma. Casado, C.; Cuadrado, I.; Losada, J., *Inorg. Chim. Acta*, **1991**, 185, 33.

[5] Ouchio, M.; Inoue, Y.; Kanzaki, T.; Hakushi, T., *Bull, Chem. Soc. Jan.*, **1984**, 57, 887.

[6] Oddon, G.; Hosseini, M. W., *Tetrahedron Letters*, **1993**, 34, 7413.

[7] Cram, D. J.; Cram, J. M., *Science*, **1974**, 183, 803.

[8] Kobuke, Y.; Kokubo, K.; Munakata, M., *J. Am. Chem. Soc.*, **1995**, 117, 12751.

[9] Friedel, R. A.; Orchin, M.; Reggel, L. *J. Am. Chem. Soc.* **1948**, 70, 199; Post, M. F. M.; Langelaar, J.; van Voorst, J. D. W., *Chem. Phys. Lett.* **1975**, 32, 59; Hochstrasser, R.M. *Can. J. Chem.* **1961**, 39, 459; Riley, M.J.; Lacey, A. R.; Sceats, M. G.; Gilbert, R. G., *Chem. Phys.* **1982**, 83, 72.

[10] Mataga, N.; Yao, H.; Okada, T.; and Rettig, W. *J. Phys.Chem.* **1989**, 93, 3383.

[11] Millar, D. P.; Eisenthal K. B., *J. Chem. Phys.*, **1985**, 83, 5076.

[12] Mays, S. L.; Olafson, B. D.; Goddard III, W. A., *J. Phys. Chem.*, **1990**, 94, 8897.
[13] Shen, Y. X.; Engen, P. T.; Berg, M. A. G.; Merola, J. S.; Gibson, H. W., *Macromolecules*, **1992**, 25, 2786.