

# Selective Transport of Alkali-Metal Cations through Liquid Membranes by Non-Cyclic Carriers

XU, Ming(徐明)    SONG, Kai(宋恺)    WU, Li-Zhu\*(吴骊珠)    ZHANG, Li-Ping(张丽萍)  
TUNG, Chen-Ho\*(佟振合)

*Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100101, China*

The emission spectra of a series of naphthalene end-labeled oligo-oxyethylene (N-P<sub>n</sub>-N) and their facilitated transport of cations across liquid membranes have been investigated. Alkali-metal cations enhance or inhibit the intramolecular excimer formation of N-P<sub>n</sub>-N remarkably, suggesting that the polyether chain of N-P<sub>n</sub>-N in solution complexes with the cations, and the orientation of the terminal chromophores depends on the cation size and the length of the polyether chain. These compounds are able to act as carriers to facilitate transport of alkali-metal cations through organic liquid membranes. The transport efficiencies are comparable with those of cyclic carriers such as crown ethers, and show remarkable selectivity.

**Keywords**    N-P<sub>n</sub>-N, excimer, ion extraction, cation transport

## Introduction

Transport of cations across an organic liquid membrane which separates two water phases has been extensively investigated.<sup>1,2</sup> The carriers are usually synthetic macrocyclic ligands such as crown ethers. Such macrocyclic ligands form stable complexes with metal cations at the interface of the source phase and often demonstrate a high degree of cation selectivity. The complexes thus formed go through the lipophilic membrane and release the cations into the receiving phase. In these respects, these macrocyclic ligands resemble the naturally occurring antibiotics which transport cations across cell membranes.<sup>3,4</sup> In addition, these ligands have potential in making separations among cations when introduced into

liquid membrane systems.<sup>5</sup> It is known that for cation transport an optimum stability of the cation-carrier complex exists above or below which the rate of transport decreases.<sup>6-8</sup> A carrier forming sufficiently low stable complex can not extract cations from the source phase into the membrane, while that forming very stable complex can not release the cations from the membrane into the receiving phase. Thus, the relationship between transport rate and association constant is bell-shaped.

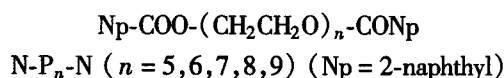
In contrast to macrocyclic ligands, use of non-cyclic compounds as carrier to transport cations through liquid membranes has not received much attention.<sup>9-12</sup> It has been established that oligo-oxyethylene molecules incorporating certain functional groups, such as carboxylic acid, hydroxyl group<sup>13,14</sup> and aromatic moieties<sup>15-18</sup> at the terminals of the molecules may also form complexes with metal cations. The conformation of these compounds changes drastically from a linear structure to a pseudocyclic one upon the complex formation. The intramolecular head-to-tail hydrogen bonds between the carboxylate and hydroxy groups in the case of carboxylic acid and hydroxy groups as the terminals, and the  $\pi$ - $\pi$  stacking interactions between the end-aromatic moieties in the case of aromatic groups as the terminals facilitate the formation of the pseudocyclic structure. Because these non-cyclic ether derivatives do not show a strong complexation ability with cations compared with that of crown ethers, their complexes should easily release the cations into the water phase. Thus, one might expect that oligo-

\* E-mail: chtung@ipc.ac.cn. Fax: 86-10-64879375

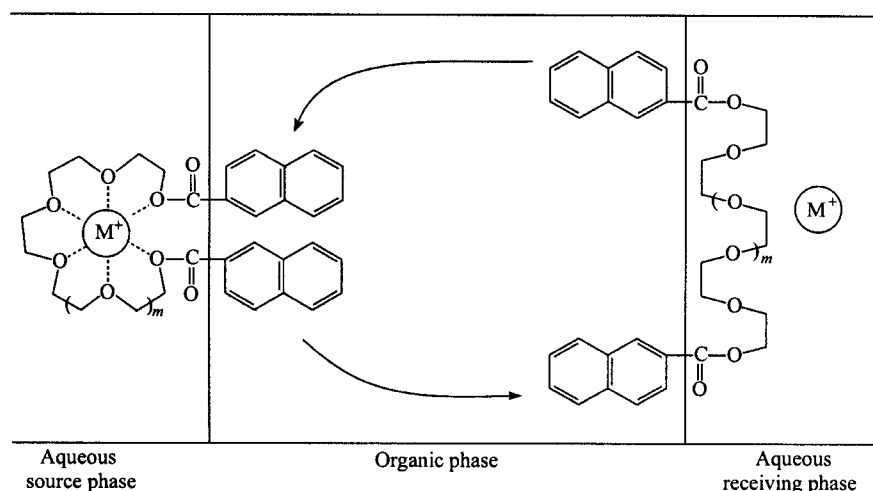
Received May 14, 2001; revised and accepted September 10, 2001.

Project supported by the Ministry of Science and Technology of China (Nos. G2000078104 and G2000077502) and the National Natural Science Foundation of China (Nos. 29602009, 20072038 and 29832040).

oxyethylene bearing appropriate aromatic groups at both terminals could act as good carriers for cation transport across a liquid membrane. We report that this is indeed the case for naphthalene end-labelled oligo-oxyethylenes. The molecules studied in this work have the following structures:



Scheme 1



## Experimental

### Materials and instruments

The preparation of N-P<sub>n</sub>-N has been described in the previous papers.<sup>17</sup> Analytical grade alkali-metal hydroxides, picric acid and dichloromethane were used without further purification. Distilled deionized water was used to prepare the source and receiving phase solution. Fluorescence spectra were run on a Hitachi EM 850 spectrofluorimeter. UV spectra were recorded with a Shimadzu UV-1601PC spectrometer.

### Fluorescence spectra, extraction procedure and cation transport measurements

The samples for fluorescence measurements were purged with nitrogen for at least 30 min before measurements were taken. The excitation wavelength was 280 nm. The spectra were fully corrected for instrumental re-

sponse. Through the examination of the fluorescence of naphthalene end-labeled oligo-oxyethylene N-P<sub>n</sub>-N in the presence of metal cations we obtained the evidence that the non-cyclic polyether chain complexes with the cations. These compounds could selectively extract metal cations from aqueous solution into organic phase, and were successfully used to transport cations through a liquid membrane (Scheme 1).

sponse.

To measure extraction equilibrium constants, the aqueous solutions were made up from standardized stock solutions of alkali-metal hydroxide and picric acid. Generally, picrate concentration was  $2.0 \times 10^{-4}$ — $2.0 \times 10^{-5}$  mol/L, and those of metal hydroxide were  $1.0 \times 10^{-3}$ — $0.1$  mol/L. The N-P<sub>n</sub>-N solution ( $4.0 \times 10^{-4}$  mol/L) in dichloromethane was also prepared. Equal volumes of the two solutions in screw-cap flasks were thoroughly agitated at  $25 \pm 1$  °C for at least 30 min to ensure that equilibration was reached. On standing phase separation was obtained. Equilibrium picrate concentrations in organic phase were determined with UV absorption.

The cation transport experiments were conducted in a U-tube. The diameter of the U-tube is *ca.* 1.4 cm. The membrane phase at the bottom was 12 mL of carrier solution in dichloromethane ( $4 \times 10^{-4}$  mol/L). In the source arm was placed 5 mL of the mixed solution of alkali-metal hydroxide (0.1 mol/L) and picric acid ( $2 \times$

$10^{-3}$  mol/L). The receiving phase is 5 mL of water. The area of the interface between the membrane and the aqueous phase is *ca.*  $1.54$  cm<sup>2</sup>. The whole apparatus was immersed in a thermostated water bath ( $25 \pm 1$  °C), and the membrane phase was stirred by a magnetic stirrer at 200 rpm. The transport experiments were started by addition of the cations as their picrate salts to the source phase. The transport flux was determined by measurement of the UV-absorption of the picrate at 355 nm in the receiving phase.

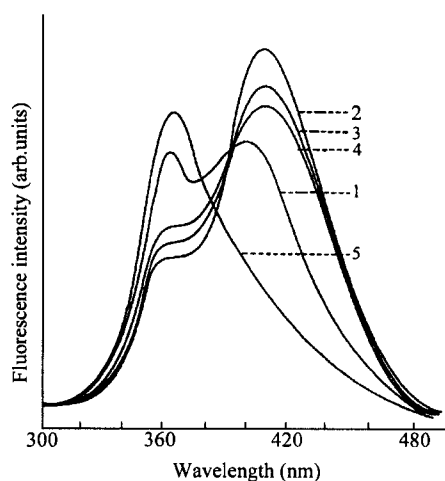
## Results and discussion

### Complexation of N-P<sub>n</sub>-N with metal cations

In order to provide evidence for complexation, the fluorescence of N-P<sub>n</sub>-N in methanol in the presence of cations was examined. Fig. 1 shows the fluorescence spectra of N-P<sub>5</sub>-N in methanol, which is typical of the other naphthalene end-labelled oligo-oxyethylene molecules in polar solvents. Both structureless monomer ( $\lambda_{\max} = 360$  nm) and excimer ( $\lambda_{\max} = 400$  nm) fluorescence emissions are observed in the absence of metal cations. At concentrations below  $1 \times 10^{-3}$  mol/L, the ratio of fluorescence intensities of excimer to monomer,  $I_D/I_M$ , is independent of concentration, suggesting that the excimer is intramolecular. The excitation spectra for the excimer and monomer emission are identical and the maxima correspond to that in the UV absorption spectrum. This indicates the absence of strong interactions between the naphthoate chromophores in the ground state.

The metal cation effects on the fluorescence of N-P<sub>n</sub>-N are strongly dependent on both the cation size and the chain length of N-P<sub>n</sub>-N. For N-P<sub>n</sub>-N with a short chain, an alkali-metal cation with a small radius enhances the excimer emission, whereas a large cation inhibits excimer formation. For example, progressive addition of LiCl, NaCl or KCl (radii of Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> are 0.076, 0.102 and 0.138 nm, respectively) to the solution of N-P<sub>5</sub>-N in methanol resulted in an increase in excimer emission at the expense of the monomer band, as shown in Fig. 1. All the spectra in Fig. 1 were obtained with the same spectrometer settings. In the presence of one of the alkali-metal chlorides ( $1 \times 10^{-4}$  mol/L), the fluorescence spectrum of N-P<sub>5</sub>-N is dominated

by excimer emission. This change is also accompanied by a 10 nm red-shift of  $\lambda_{\max}$  of the excimer emission. The excitation spectrum for excimer emission is evidently red-shifted compared with that for monomer emission. This is an indication of some interactions between the naphthoate chromophores in the ground state. Although many factors may influence excimer formation, the above observations suggest that in the presence of a salt, the polyether chain of N-P<sub>5</sub>-N complexes with the alkali-metal cation. As a result, the two terminal chromophores are in proximity and associate with each other, thus enhancing excimer formation.

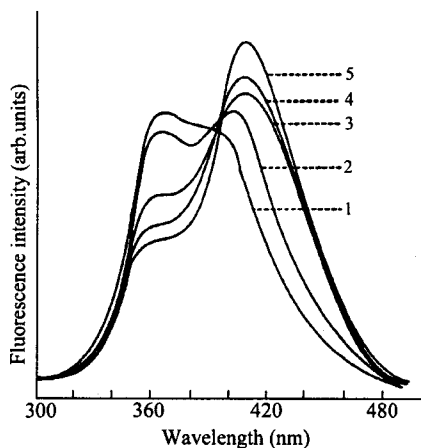


**Fig. 1** Fluorescence spectra of N-P<sub>5</sub>-N in methanol: (1) ion free; (2) in the presence of LiCl; (3) in the presence of NaCl; (4) in the presence of KCl; (5) in the presence of CsCl.  $[N-P_5-N] = 2 \times 10^{-5}$  mol/L;  $[MCl] = 1 \times 10^{-4}$  mol/L; excitation at  $\lambda_{\text{ex}} = 280$  nm. All of the spectra were obtained with the same spectrometer settings.

In contrast to Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup>, the alkali-metal cation with a large size inhibits excimer formation of N-P<sub>5</sub>-N. In the presence of  $1 \times 10^{-4}$  mol/L CsCl (radius of Cs<sup>+</sup> is 0.167 nm), N-P<sub>5</sub>-N in methanol exhibits strong monomer fluorescence (Fig. 1). The excimer emission is barely detectable. We proposed that the N-P<sub>5</sub>-N polyether chain complexes with Cs<sup>+</sup>. Since the small cavity of the pseudocycle can not match well with the large size of the cation, the two end groups of N-P<sub>5</sub>-N hardly associate with each other to form a sandwich pair. Thus, formation of intramolecular excimer is inhibited.

To support the above proposal, the effects of alkali-metal cations on the fluorescence emission of N-P<sub>n</sub>-N

with longer polyether chains were studied. Fig. 2 shows the fluorescence spectrum of N-P<sub>9</sub>-N in methanol. As with N-P<sub>5</sub>-N, this compound also shows monomer ( $\lambda_{\max} = 360$  nm) and intramolecular excimer ( $\lambda_{\max} = 400$  nm) fluorescences in the absence of metal cations. However, the ratio of fluorescence intensities of excimer to monomer,  $I_D/I_M$ , is slightly smaller than that for N-P<sub>5</sub>-N. Evidently, the longer polyether chain in N-P<sub>9</sub>-N reduces the probability of end-to-end encounters. Unlike N-P<sub>5</sub>-N, the large cation, Cs<sup>+</sup>, enhances the excimer emission remarkably, while the smaller cation, Li<sup>+</sup>, shows a relatively small effect on the fluorescence spectrum. Indeed, the large cavity of the pseudocycle of N-P<sub>9</sub>-N may match well with Cs<sup>+</sup>, and the two terminal naphthoate groups may associate with each other to form a sandwich pair.



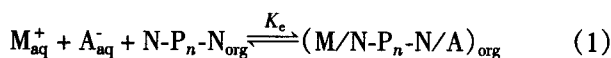
**Fig. 2** Fluorescence spectra of N-P<sub>9</sub>-N in methanol: (1) ion free; (2) in the presence of LiCl; (3) in the presence of NaCl; (4) in the presence of KCl; (5) in the presence of CsCl.  $[N-P_9-N] = 2 \times 10^{-5}$  mol/L;  $[MCl] = 1 \times 10^{-4}$  mol/L; excitation at  $\lambda_{\text{ex}} = 280$  nm.

To summarize, the non-cyclic oligo-oxyethylene derivatives form complexes with alkali-metal cations in solution, and the conformation of these compounds changes from a linear structure to a pseudocyclic one upon the complex formation.

#### *Extraction of metal cations from aqueous solution to organic membrane*

As mentioned above, the best carrier for the cation transport is a ligand that gives the moderately stable

rather than the very stable complex, because the very stable complex which may enhance the cation concentration in the organic membrane can not release metal cation efficiently from the complex, resulting in the low overall transport efficiency. To estimate the cation-transport ability of N-P<sub>n</sub>-N, we measured cation extraction equilibrium constants from aqueous solution into organic phase by N-P<sub>n</sub>-N. The equilibrium between an aqueous solution containing cation (M<sup>+</sup>) and picrate anion (A<sup>-</sup>), and an organic solution containing the carrier N-P<sub>n</sub>-N can be formulated<sup>19</sup> as



Where (M/N-P<sub>n</sub>-N/A) designates ion pairs (N-P<sub>n</sub>-N/ cations and picrate anions) in the organic phase. Thus, the cation extraction equilibrium constant is defined as

$$K_e = \frac{[(M/N-P_n-N/A)]_{\text{org}}}{[M^+]_{\text{aq}}[A^-]_{\text{aq}}[N-P_n-N]_{\text{org}}} \quad (2)$$

We prepared the aqueous solutions of alkali metal hydroxides and picric acid, and the N-P<sub>n</sub>-N solutions in dichloromethane. Equal volumes of the two solutions in screw-cap flasks were thoroughly agitated at  $25 \pm 1$  °C. On standing the phase clearly separated. The concentration of (M/N-P<sub>n</sub>-N/A) in organic phase was determined by UV absorption of the picrate. The measured cation extraction equilibrium constants with N-P<sub>n</sub>-N are listed in Table 1. These extraction equilibrium constants not only reflect strength of complexing but also involve the solubility of the various species in Eq. (1) in aqueous and organic phases. However, knowledge of the equilibrium constants permits predications of the ability of N-P<sub>n</sub>-N for cation transport.

The data in Table 1 indicate several interesting points. First, for a given cation, the cation extraction ability of N-P<sub>n</sub>-N increases remarkably with its polyether chain length. For example, the Na<sup>+</sup> and Rb<sup>+</sup> extraction equilibrium constants with N-P<sub>9</sub>-N are 24.4 and 106 times greater, respectively, than those with N-P<sub>5</sub>-N. Probably the complexation sites for N-P<sub>n</sub>-N with cations increase with the polyether chain length, thus resulting in the more stable complexes and greater concentration of the complexes in the organic phase. Second, N-P<sub>n</sub>-N show selectivity towards the extraction of the alkali-metal

cations. The remarkable inversion of the  $K^+/Rb^+$  extraction preference with N-P<sub>5</sub>-N, N-P<sub>6</sub>-N, N-P<sub>7</sub>-N *vs.* N-P<sub>8</sub>-N, N-P<sub>9</sub>-N demonstrates that the relative size of the cations and the cavities of the pseudocyclic polyether compounds is important in determining the efficiency of the cation extraction. Third, the cation extraction ability of the non-cyclic polyethers N-P<sub>*n*</sub>-N is comparable with

that of macrocyclic ethers. For example, the extraction equilibrium constants for potassium picrate and sodium picrate from aqueous solution to dichloromethane with dibenzo-18-crown-6 and dicyclohexyl-18-crown-6, reported in the literature,<sup>19</sup> are in the range of those with N-P<sub>*n*</sub>-N.

**Table 1** Picrate extraction equilibrium constants from aqueous solution into dichloromethane by N-P<sub>*n*</sub>-N ( $4 \times 10^{-4}$  mol/L) at 25 °C<sup>a</sup>

Carrier	Extraction equilibrium constant [ $(\text{mol/L})^{-2}$ ]				
	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>
N-P <sub>5</sub> -N	$3.6 \times 10$	$6.7 \times 10^2$	$3.9 \times 10^3$	$1.4 \times 10^3$	$8.8 \times 10^2$
N-P <sub>6</sub> -N	$7.9 \times 10$	$3.2 \times 10^3$	$7.6 \times 10^3$	$5.3 \times 10^3$	$2.7 \times 10^3$
N-P <sub>7</sub> -N	$2.5 \times 10^2$	$4.7 \times 10^3$	$1.8 \times 10^4$	$1.4 \times 10^4$	$5.8 \times 10^3$
N-P <sub>8</sub> -N	$3.6 \times 10^2$	$8.5 \times 10^3$	$5.4 \times 10^4$	$6.8 \times 10^4$	$1.7 \times 10^4$
N-P <sub>9</sub> -N	$5.2 \times 10^2$	$1.7 \times 10^4$	$8.4 \times 10^4$	$1.5 \times 10^5$	$3.7 \times 10^4$

<sup>a</sup> Picrate and alkali-metal hydroxide concentrations in aqueous solutions are  $2 \times 10^{-4}$ — $2 \times 10^{-5}$  mol/L and  $1 \times 10^{-3}$ — $0.1$  mol/L respectively.

#### Transport of alkali metal cations

The detail for the measurements of transport flux has been described in the Experimental Section. The metal picrate in the source phase moved into N-P<sub>*n*</sub>-N solution in dichloromethane with complex formation and was liberated to the aqueous receiving phase as described in Scheme 1. The rate of appearance of the salts in the receiving phase was monitored by the UV absorption of the picrate at 355 nm. Plots of the amounts of the metal picrates in the receiving phase as a function of transport time were linear. The slopes of the plots indicate the

transport rates in  $10^{-9}$  moles per hour. Since the area of the interface between the membrane and the aqueous phase is known, the cation transport fluxes were calculated and are given in Table 2. Deviation in the transport fluxes between different runs of the same system was < 10%. In a control experiment it is shown that no transport is detectable in the absence of a carrier. In addition, transport experiments with the standard 18-crown-6 were also carried out and established that our apparatus gives the results listed in Table 2 are in fair agreement with those in the literatures.<sup>20,21</sup>

**Table 2** Fluxes of alkali-metal cation transport by N-P<sub>*n*</sub>-N carriers

Carrier	Flux of cation transport $10^9$ ( $\text{mol/h} \cdot \text{cm}^2$ )				
	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>
N-P <sub>5</sub> -N	0.45	6.6	15.2	8.9	7.0
N-P <sub>6</sub> -N	1.3	13.1	26.9	22.7	12.3
N-P <sub>7</sub> -N	2.0	20.7	55.6	44.4	23.7
N-P <sub>8</sub> -N	4.0	35.6	98.5	105.6	49.9
N-P <sub>9</sub> -N	5.0	53.6	123.9	153.2	78.3
18-crown-6	5.3	15.5	51.0	43.7	26.3

Inspection of the data in Tables 1 and 2 reveals that the cation transport ability and the cation extraction ability for the non-cyclic polyethers N-P<sub>*n*</sub>-N are parallel. First, as in the case of cation extraction, for a given cation the transport ability of N-P<sub>*n*</sub>-N increases remarkably with the polyether chain length. Under identical

condition the Rb<sup>+</sup> transport flux for N-P<sub>9</sub>-N carrier is 17 times greater than that for N-P<sub>5</sub>-N. Second, the selectivity towards cation transport is similar to that for cation extraction. The N-P<sub>*n*</sub>-N with short polyether chains, N-P<sub>5</sub>-N to N-P<sub>7</sub>-N, selectively transport and extract K<sup>+</sup> among alkali-metal cations, while those with longer

polyether chains, N-P<sub>8</sub>-N and N-P<sub>9</sub>-N, selectively transport and extract Rb<sup>+</sup>. As mentioned above, cation transport process involves complex formation at the interface of the source phase, the diffusion of the complex through the organic phase and cation release at the interface of receiving phase, the enhanced factors in transport flux and extraction equilibrium constant by the increase in the strength of complex are not necessary to be the same. However, the above results indicate that the rate-determining step in cation transport by N-P<sub>n</sub>-N is complex formation rather than cation release. Evidently, the non-cyclic polyether does not form very stable complex with cations, and all of the data in Table 2 are located in the left side of the bell-shaped curve for the relationship between transport rate and association constant.

Table 2 also demonstrates that the cation transport ability of N-P<sub>n</sub>-N is comparable with that of macrocyclic ethers. For example, by using the same apparatus, the determined cation transport fluxes for the standard crown ether 18-crown-6 are in the range of those for N-P<sub>n</sub>-N. This suggests that the inexpensive and easily synthesized non-cyclic compounds N-P<sub>n</sub>-N can act as good carriers as crown ethers.

## References

- 1 Bradshaw, J. S.; Izatt, R. M. *Acc. Chem. Res.* **1997**, *30*, 338.
- 2 Ji, H. F.; Dabestani, R.; Brown, G. M.; Sachleben, R. A. *Chem. Commun.* **2000**, 833.
- 3 Pressman, B. C. In *Inorganic Biochemistry*, Vol. 1, Ed.: Elchhorn, G. L., American Elsevier, New York, **1973**, pp. 203—226.
- 4 Grell, E.; Funck, T.; Eggers, F. In *Membranes*, Vol. 3, Ed.: Eisenman, G., Marcle Dekker, New York, **1975**, pp. 1—126.
- 5 Schwind, R. A.; Gilligan, T. J.; Cussler, E. L. In *Synthetic Multidentate Macrocyclic Compounds*, Eds.: Izatt, R. M.; Christensen, J. J., Academic Press, New York, **1978**, pp. 289—308.
- 6 Kirch, M.; Lehn, J. M. *Angew. Chem., Int. Ed. Engl.*, **1975**, *14*, 555.
- 7 Lamb, J. D.; Christensen, J. J.; Oscarson, J. L.; Nielsen, B. L.; Asay, B. W.; Izatt, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 6820.
- 8 Izatt, R. M.; Dearden, D. V.; Brown, P. R.; Bradshaw, J. S.; Lamb, J. D.; Christensen, J. J. *J. Am. Chem. Soc.* **1983**, *105*, 1785.
- 9 Suzuki, Y.; Morozumi, T.; Nakamura, H.; Shimomura, M.; Hayashita, T.; Bartsh, R. A. *J. Phys. Chem. B.* **1998**, *102*, 7910.
- 10 Kawakami, J.; Komai, Y.; Ito, S. *Chem. Lett.* **1996**, 617.
- 11 Kawakami, J.; Sata, H.; Ebina, K.; Ito, S. *Chem. Lett.* **1998**, 535.
- 12 Itagaki, H.; Masuda, W.; Hirayanagi, Y. *Chem. Phys. Lett.* **1999**, *309*, 402.
- 13 Choy, E. M.; Evans, D. F.; Cussler, E. L. *J. Am. Chem. Soc.* **1974**, *96*, 7085.
- 14 Duax, W. L.; Smith, G. D.; Strong, P. D. *J. Am. Chem. Soc.* **1980**, *102*, 6725.
- 15 Vögtle, F.; Weber, E. *Angew. Chem., Int. Ed. Engl.* **1979**, 753.
- 16 Tung, C.-H.; Wu, L.-Z. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1381.
- 17 Tung, C.-H.; Wang, Y.-M. *J. Am. Chem. Soc.* **1990**, *112*, 6322.
- 18 Tung, C.-H.; Li, Y.; Yang, Z.-Q. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 947.
- 19 Frensdorff, H. K. *J. Am. Chem. Soc.* **1971**, *93*, 4684.
- 20 Lamb, J. D.; Christensen, J. J.; Izatt, S. R.; Bedke, K.; Astin, M. S.; Izatt, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 3399.
- 21 Rebek, Jr. J.; Wattlely, R. V. *J. Am. Chem. Soc.* **1980**, *102*, 4853.