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Enhanced Cation Transport Property of Polymeric "*Armed Macrocycles*"

Hiroshi Tsukube,* Tadashi Iwachido, Tatsuo Shimotani,† Tatsuya Dando,† and Michio Zenki†
Department of Chemistry, College of Liberal Arts & Science, Okayama University, Okayama 700
† Department of Chemistry, Faculty of Science, Okayama University of Science, Ridai-cho, Okayama 700

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Synopsis. Poly(diazacrown ether)s with dihydroxyalkylene bridges exhibited enhanced transport ability for alkali metal cations via three-dimensional complexation, though poly(armed azamacrocycle)s did little.

"Armed macrocycles" represent a family of potential cation binders and are characterized by a parent macrocyclic ligand and a cation-ligating functionalized sidearm. In this class of compounds, a donor group on the flexible sidearm can provide further coordination with a guest cation trapped in the parent macroring and such a three dimensional and dynamic complexation often offered specific cation transport phenomenon.[1] Since polymeric macrocycles have broad applicability especially in metal-sensing and separation,[2] there is the expectation that the incorporation of the armed macrocycle into a polymer system will enhance the usefulness. Here, we report cation-binding and transport properties of several polymeric armed macrocycles **1**—**4**, **6**, and **7** (Fig. 1). Among them, poly(diazacrown ether)s **1**—**4** with dihydroxyalkylene bridges offered enhanced carrier activity toward alkali metal cations. They are the first examples of polymeric armed macrocycles mediating effective cation transport.

We characterized four types of poly(macrocycles) with hydroxyalkylene bridges (Fig. 1): diazacrowns **1**—**3**,[3] benzocrown **4**, cyclam **6**, and dioxocyclam **7**. These were obtained by polycondensation of the corresponding diamine precursors with 1,2 : 7,8-diepoxyoctane.[4] Cation transport experiments were carried out in a chloroform liquid membrane[5] and initial transport rates obtained are summarized in Table 1.

Polymeric armed macrocycles **1**—**4** having diazacrown rings effectively transported some alkali metal cations across a liquid membrane, while polymers **6** and **7** having cyclam and dioxocyclam rings did little. This indicates that the nature of macroring greatly influences carrier activity of the polymeric armed macrocycle. Since polyester **5** with diaza-18-crown-6 ring showed lower transport rates than polymer **2**, the hydroxyethyl sidearm enhanced the carrier activity of poly(diaza-18-crown-6) more effectively than the ester sidearm. A combination of parent macroring and functionalized sidearm should be chosen carefully when the polymeric armed macrocycle is designed.

Table 1. Cation Transport Profiles of Polymeric Armed Macrocycles

Polymer	Transport rate × 10^6/ mol h^{-1}							
	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Ba^{2+}
1	0.3	1.4	0.3	*	*	*	*	*
2	*	1.1	2.7	0.3	0.3	*	*	*
3	*	0.3	0.7	*	*	*	*	*
4	*	1.6	0.9	*	*	*	*	*
5	*	*	1.4	*	*	*	*	*
6	*	*	*	*	*	*	*	*
7	*	*	*	*	*	*	*	*

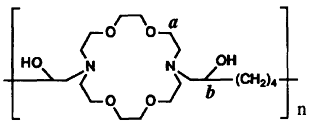
* below limit of detection ($<0.3\times10^{-6}$ mol h^{-1}).

Cation-binding behaviors of polymeric armed macrocycles **2**, **5**, and **7** were investigated by ^{13}C NMR spectroscopy. Table 2 summarizes guest-induced changes in chemical shifts of selected signals for macroring and sidearm carbons. Addition of $KClO_4$ to the solution of polymer **2** caused significant shifts of the crown ring and sidearm carbon signals, probably indicating that the –OH group on the sidearm effectively coordinated with K^+ cation trapped in the diazacrown ring.

Table 2. Guest-Induced Changes in ^{13}C NMR Chemical Shifts of Polymeric Armed Macrocycles

Polymer	Carbon[b]	Chemical shift[a]/ ppm		
		None	$+Na^+$	$+K^+$
2	*a*	86.2	(85.8)	85.3
	b	84.9	(84.7)	84.5
5	*a*	86.0	85.1	84.5
	b	190.2	190.2	190.2
7	*a*	57.9	57.9	57.9
	b	84.9	84.9	84.9

(Conditions) Polymer, 0.025 unit mmol; Guest perchlorate, 0.025 mmol/DMF-D_2O (4 : 1), 0.5 mL. ( ): These signals were broadened. a) Chemical shift indicated was determined by using the peak of the DMF carbonyl carbon (δ_C 180.00 ppm) as reference. b) See structural formulae shown below.



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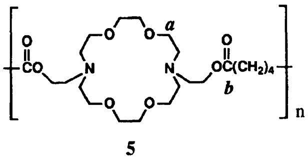

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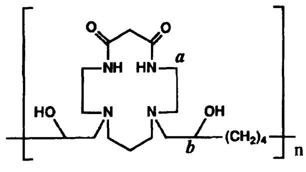

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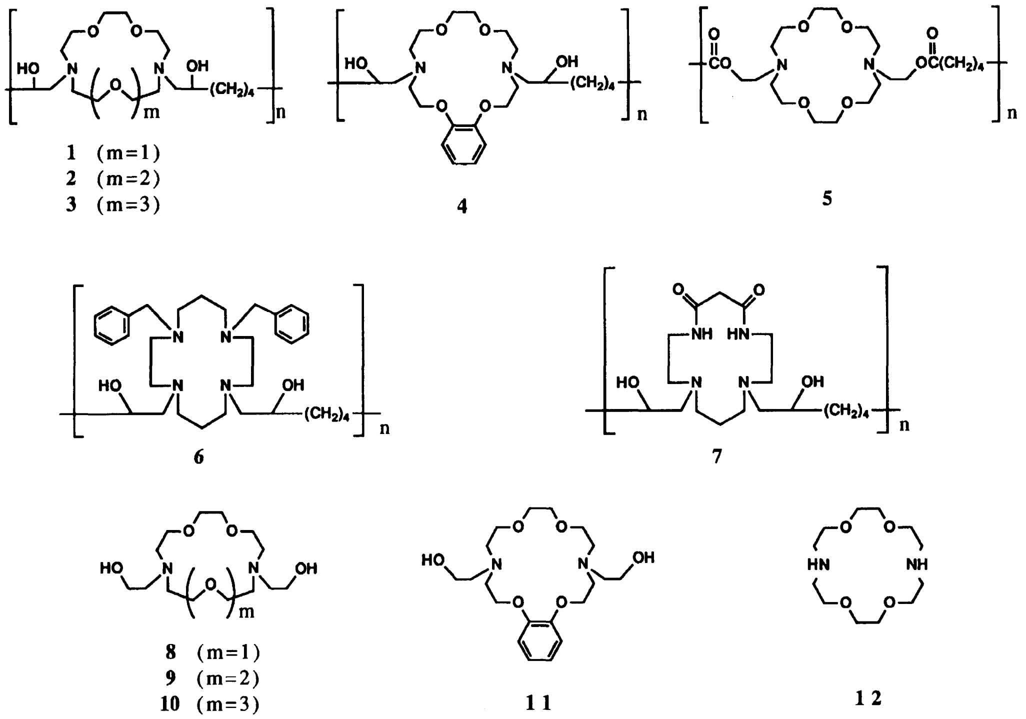

Fig. 1. Polymeric armed macrocycles and their monomer analogs.

Since $NaClO_4$ salt induced similar but modest spectral changes, K^+ ion was nicely accommodated in a three-dimensional manner. This may explain the large transport rate for K^+ ion. Polymer **5** showed a contrast. $KClO_4$ or $NaClO_4$ salt induced significant shifts of the crown ring carbons, whereas only slight changes were observed for signal of carbonyl carbon on the sidearm. Thus, this was thought to form complexes with K^+ and Na^+ cations as did simple crown ethers. A spectrum of polymer **7** was rarely changed in the presence of these metal salts, and the dioxocyclam polymer was ineffective.

Complexations with alkali metal cations of monomer analogs **8**—**12** were assessed on a semiquantitative level using FAB MS competition technique.[6] Table 3 summarizes relative peak intensities of [macrocycle+metal]$^+$ ions which reflect the relative metal-binding affinities. Typically, diaza-18-crown-6 **9** having hydroxyethyl sidearms bound K^+ cation more tightly than other alkai metal cations, while its benzo-derivative **11** favored Na^+ cation. Since these binding selectivities are similar to those observed in polymer-mediated cation transport system, the combination of hydroxyethyl sidearm and diazacrown ring may offer ligand geometries suitable for effective inclusion and transport of alkali metal cations even in the polymer backbone. A variety of armed macrocycles exhibiting specific metal binding and transport abilities has been presented.[7] Thus, new polymeric armed macrocycles can be developed for metal-sensing and separation, based on the host-guest chemistry of armed macrocycles.

Table 3. Relative Peak Intensities of [Macrocycle+Metal]$^+$ Ions in FAB MS

Macrocycle	Li^+	Na^+	K^+	$Rb^{+a)}$	Cs^+
8	16	100	19	3	0
9	1	50	100	17	0
10	4	8	100	0	0
11	2	100	33	0	0
12	b)	58	100	47	19

a) Addition of peak heights corresponding to isotopes ^{85}Rb and ^{87}Rb. b) This peak was overlapped with peak corresponding $(glycerol)_2\cdot Rb^+$.

Experimental

Materials. Polymers **2**, **5**, monomer analogs **8**, **9**, and unsubstituted benzodiaza-18-crown-6 were prepared as reported earlier.[4,8,9]

1,11-Dibenzyl-1,4,8,11-tetraazacyclotetradecane, a precursor of polymer **6**, was synthesized by BH_3-reduction of 1,11-dibenzyl-1,4,8,11-tetraazacyclotetradecane-5,7-dione[5] (85%; oil): ^1H NMR (90 MHz, $CDCl_3$, Me_4Si) δ=1.77 (4H, $2\times CH_2C\underline{H}_2CH_2$), 2.18—2.79 (16H, $8\times NCH_2$), 3.52 (4H, $2\times CH_2Ph$), 7.28 (10H, $2\times Ph$); IR ν_{max} ($CDCl_3$) 1600 cm^{-1}; HRMS. Found: m/z 380.2929. Calcd for $C_{24}H_{36}N_4$: M, 380.2939.

N,*N'*-Bis(2-hydroxyethyl)diazacrowns **10** and **11** were prepared by hydroxyethylation of corresponding diamines.

7,19-Bis(2-hydroxyethyl)-1,4,10,13,16-pentaoxa-7,19-diazacyclohenicosane **10** (84%, oil); ^1H NMR (90 MHz, $CDCl_3$, Me_4Si) $\delta=2.63$ (4H, $2\times C\underline{H}_2OH$), 2.79 (12H, $6\times NCH_2$), 3.50—3.71 (22H, $10\times OCH_2+2\times OH$); IR ν_{max}

($CDCl_3$) 3400 and 1090 cm^{-1}; HRMS. Found: m/z 394.2683. Calcd for $C_{18}H_{38}N_2O_7$: M, 394.2679.

7,16-Bis(2-hydroxyethyl)-2,3-benzo-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane **11** (90%, oil); ^{1}H NMR (90 MHz, $CDCl_3$, Me_4Si) $\delta=2.63$—3.09 (16H, $2\times C\underline{H}_2OH+6\times NCH_2$), 3.49—3.66 (10H, $2\times CH_2OCH_2+2\times OH$), 4.09 (4H, $2\times C\underline{H}_2Ph$), 6.86 (4H, Ph); IR $\nu_{\max}$ ($CDCl_3$) 3400, 1600, and 1080 cm^{-1}; HRMS. Found: m/z 398.2388. Calcd for $C_{20}H_{34}N_2O_6$: M, 398.2417.

Polymers **1**, **3**, **4**, **6**, and **7** were prepared from corresponding diamine precursors and 1,2 : 7,8-diepoxyoctane.$^{4)}$ Their main structures were confirmed as shown in Fig. 1 by ^{1}H NMR spectra in which intensity of each signal was satisfactory within ±15% deviation. The molecular weights were estimated as 2000—5000 by GPC (eluted by THF; calibrated with polystyrene standard samples).

Poly[(1,4,10-trioxa-7,13-diazacyclopentadecane-7,13-diyl)-(2,7-dihydroxyoctamethylene)] **1** (95%, oil): ^{1}H NMR (90 MHz, $CDCl_3$, Me_4Si) $\delta=1.39$ (8H, $CH_2CH_2CH_2CH_2$), 2.05—2.95 (12H, $6\times NCH_2$), 3.36—3.70 (14H, $6\times OCH_2+2\times CH$); IR $\nu_{\max}$ ($CDCl_3$) 1105 cm^{-1}.

Poly[(1,4,10,13,16-pentaoxa-7,19-diazacyclohenicosane-7,19-diyl)(2,7-dihydroxyoctamethylene)] **3** (95%, oil): ^{1}H NMR (90 MHz, $CDCl_3$, Me_4Si) $\delta=1.39$ (8H, $CH_2CH_2CH_2CH_2$), 2.20—2.90 (12H, $6\times NCH_2$), 3.40—3.80 (22H, $10\times OCH_2+2\times CH$) IR $\nu_{\max}$ ($CDCl_3$) 1098 cm^{-1}.

Poly[(2,3-benzo-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-diyl)(2,7-dihydroxyoctamethylene)] **4** (100%, oil): ^{1}H NMR (90 MHz, $CDCl_3$, Me_4Si) $\delta=1.39$ (8H, $CH_2CH_2CH_2CH_2$), 2.16—3.15 (12H, $6\times NCH_2$), 3.40—3.70 (10H, $2\times CH_2OCH_2+2\times CH$), 4.04 (4H, $2\times CH_2OPh$), 6.84 (4H, Ph); IR $\nu_{\max}$ ($CDCl_3$) 1595 and 1130 cm^{-1}.

Poly[(4,8-dibenzyl-1,4,8,11-tetraazacyclotetradecane-1,11-diyl)(2,7-dihydroxyoctamethylene)] **6** (90%, powder): ^{1}H NMR (90 MHz, $CDCl_3$, Me_4Si) $\delta=1.36$ (8H, $CH_2CH_2CH_2CH_2$), 1.72 (4H, $2\times CH_2C\underline{H}_2CH_2$), 2.08—3.02 (20H, $10\times NCH_2$), 3.30—3.90 (6H, $2\times CH_2Ph+2\times CH$), 4.16 (2H, $2\times OH$), 7.24 (10H, 2×Ph); IR $\nu_{\max}$ ($CDCl_3$) 1602 cm^{-1}.

Poly[(5,7-dioxo-1,4,8,11-tetraazacyclotetradecane-1,11-yl)(2,7-dihydroxyoctamethylene)] **7** (90%, powder): ^{1}H NMR (90 MHz, CD_3OD, CD_3OD) $\delta=1.46$ (8H, $CH_2CH_2CH_2CH_2$), 1.66 (2H, $CH_2C\underline{H}_2CH_2$), 2.30—2.73 (12H, $6\times CH_2N$), 3.17 (2H, $COCH_2CO$), 3.30—3.40 ($2\times C\underline{H}_2NH$, overlapped with CD_3OD signals), 3.61 (2H, 2×CH); IR $\nu_{\max}$ (CD_3OD) 1650 cm^{-1}.

Transport Experiments. The polymer, dissolved in chloroform (0.0372 unit-mmol/12 mL), was place in the base of a U-tube glass cell (2.0 cm, i.d.),$^{5)}$ and two aqueous phases (Aq I: $MClO_4$, 0.500 mmol/H_2O, 5mL; Aq II: H_2O, 5 mL) were placed in the arms. The membrane phase was stirred at ambient temperature. The transport rates were calculated from initial rates of appearance of guest cations and cotransported ClO_4^- anion. Reproducibilities were confirmed as 15% or better.

FAB MS Experiments. An aqueous solution of a macrocycle (0.01 M) and five metal chlorides (0.05 M, each) was mixed with twofold volume of glycerol. FAB mass spectra were recorded with a JEOL DX300 instrument, and the peak heights were averaged over at least 12 scans.

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