Research Article

Characterization of Anthraquinone-Derived Redox Switchable Ionophores and Their Complexes with Li^+ , Na^+ , K^+ , Ca^{2+} , and Mg^{2+} Metal Ions

Vaishali Vyas, Pankaj Raizada, and Uma Sharma

School of Studies in Chemistry and Biochemistry, Vikram University, Madhya Pradesh, Ujjain 456010, India

Correspondence should be addressed to Vaishali Vyas, vaishalivyas10@yahoo.co.in

Received 13 February 2011; Accepted 12 April 2011

Academic Editor: Rubin Gulaboski

Copyright © 2011 Vaishali Vyas et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Anthraquinone derived redox switchable ionophores 1,5 bis (2-(2-(2-ethoxy) ethoxy) ethoxy)anthracene-9,10-dione (V_1) and 1,8-bis(2-(2-(2-ethoxy)ethoxy)ethoxy) anthracene—9,10-dione (V_2) have been used for isolation, extraction and liquid membrane transport studies of Li^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+} metal ions. These isolated complexes were characterized by melting point determination, CV and IR, ^1H NMR spectral analysis. Ionophore V_2 shows maximum shift in reduction potential (ΔE) with $\text{Ca}(\text{Pic})_2$. The observed sequence for the shifting in reduction potential (ΔE) between V_2 and their complexes is V_2 calcium picrate (42 mV) > V_2 potassium picrate (33 mV) > V_2 lithium picrate (25 mV) > V_2 sodium picrate (18 mV) > V_2 magnesium picrate (15 mV). These findings are also supported by results of extraction, back extraction and transport studies. Ionophore V_2 complexed with KPic and showed much higher extractability and selectivity towards K^+ than V_1 . These synthetic ionophores show positive and negative cooperativity towards alkali and alkaline earth metal ions in reduced and oxidized state. Hence, this property can be used in selective separation and enrichment of metal ions using electrochemically driven ion transport.

1. Introduction

Electrochemical molecular recognition is a fast expanding research area at the interface of electrochemistry and supramolecular chemistry. One of the earliest examples of electrochemical recognition of cations was reported by Saji [1] in 1986. Boulas et al. [2] have recently published an extensive review of the electrochemical properties of a wide range of supramolecular systems. Besides the conventional supramolecular systems, switchable ionophore is one of the most important classes of supramolecular host, due to their applications in the field of electrochemically driven membrane transport, drug delivery, catalysis, and so forth [3–5]. Switchable ionophores contain both a conventional cation complexation unit with well investigated cation binding properties such as polyethylene glycols, crown ether, and cryptand, and a switch-functionalized molecule..

Redox switchable ionophores have been synthesized by incorporation of a variety of redox active centers such as thiadiazole heterocycle, thiol derivatives, ferrocene, nitro

benzene, and quinones into macrocyclic structural frameworks based on crown ethers, cryptands, and calixarenes, which are selective and electrochemically responsive to specific alkali metal cations [6]. Redox active ionophores have obvious applications in the design of sensor systems [7] and electrochemically driven ion transport [8, 9]. Anthraquinone system is an interesting one for the study of reducible and switchable ionophores [10]. Delgado et al. have reported two armed podands based on anthraquinone ring system [11].

In this work new anthraquinone-derived redox switchable ionophores V_1 and V_2 (Figure 1) have been synthesized [12, 13] by condensation of 1,5 and 1,8 dichloroanthraquinone with diethyleneglycolmonoethylether, respectively, in which oxygen of polyethylene glycol chains providing binding site for metal ions and anthraquinone acts as a redox switchable moiety. The affinity of these synthetic ionophores towards Li^+ , Na^+ , K^+ , Ca^{2+} , and Mg^{2+} metal cations has been checked by isolation, extraction, and transport studies.

FIGURE 1: Used ionophores in the present study

2. Experimental

2.1. Chemicals. Lithium picrate, sodium picrate, potassium picrate, calcium picrate, and magnesium picrate were prepared. The solvents used were obtained from Qualigens, dried, and distilled before use. For the cyclic voltammetric studies 1×10^{-3} M stock solution of sample was prepared in dimethyl formamide (DMF) and 1 M KCl and Britton Robinson (BR) buffer 6.5 pH was used as supporting electrolyte. All reagents and solvents were of analytical grade (Merck and Sigma).

2.2. Instruments. Boss 165 melting point apparatus was used for melting point determination of ionophores and complexes. IR spectra were recorded on FTIR spectrophotometer (Perkin-Elmer BX 70836) at School of Studies in Chemistry and Biochemistry, Vikram University, Ujjain. ^1H NMR spectral analysis has been carried out using ^1H NMR spectrophotometer—Bruker DRX-300, 300 MHz from CDRI Lucknow. BASI Epsilon electrochemical system (Bio-analytical System, USA) was used for cyclic voltammetric studies.

2.3. Method for Preparation of Metal Salts. Lithium, sodium, and potassium picrates were prepared [14] by mixing a warm solution of picric acid in ethanol with a warm aqueous solution of NaOH/KCl in 1:1 molar ratio with constant stirring. The solution was concentrated on a water bath and hot filtered. The filtrate on cooling gave yellow crystals of the picrates, which were filtered on a vacuum pump using a Buckner funnel and recrystallized from ethanol.

Calcium and magnesium picrates were prepared by the same procedure as mentioned for alkali metal picrates using $\text{CaCO}_3/\text{MgCO}_3$ and picric acid in 1:2 molar ratio. All the prepared metal salts were characterized by their m.p. determination.

2.4. Method for Extraction Studies. For extraction studies [15] equal volume of (10 mL) aqueous solution of metal salt (lithium picrate, sodium picrate, potassium picrate, calcium picrate, and magnesium picrate) and ionophore solution in chloroform was vigorously stirred in a 50 mL beaker for 4 h on magnetic stirrer. The amount of metal ions in aqueous phase was initially determined. After 4 h the amount of metal ions in the depleted aqueous phase was determined using flame photometer for Li^+ , K^+ , Ca^{2+} , and Mg^{2+} and was

detected by titrimetric method. The amount of metal ions extracted by ionophore was determined by the difference in amount of metal ions before and after extraction. For back extraction studies, aliquots from the loaded organic phase were withdrawn and subsequently back extracted for about 4 h with the same volume of the stripping which is double distilled water. After 4 h the back extracted amount of metal ions was determined.

2.5. Method for Bulk Liquid Membrane Transport Studies. Transport experiments [16] were performed in a “U” shape glass cell. The organic solution of ionophore in chloroform was placed at the bottom of the “U” tube to serve as liquid membrane, 10 mL of aqueous solution of metal salt was placed in one limb of the “U” tube to serve as the feed phase (F. P.), and 10 mL of double distilled water was placed in the other limb of the “U” tube to serve as the stripping phase (S. P.). The membrane phase was stirred by magnetic stirrer for 24 h. Samples of both feed phase and stripping phase were analyzed after 24 h by using flame photometer for Li^+ , K^+ , Ca^{2+} , and Mg^{2+} and were estimated by titrimetric method.

Extraction and transport studies have been carried out in oxidized as well as reduced state of the ionophores. For the reduction of ionophores NaOH and Zn metal was used as reducing agent.

2.6. Method for Isolation Studies. The complexes were prepared [17] by mixing different proportions of alkali and alkaline earth metal salts with ionophores in solvent series like methanol, ethylacetate, isopropanol, acetonitrile, tetrahydrofuran, carbon tetrachloride, and dichloromethane. The mixture was then slightly warmed on a water bath and allowed to evaporate at room temperature. Crystallization generally occurs within two-three days and shiny crystals were obtained. The crystals were vacuum-filtered and recrystallized from the same solvent from which they had been isolated. The characterization of isolated compounds was carried out by melting point determination and confirmed by CV and spectral analysis (IR, ^1H NMR).

2.7. Cyclic Voltammetric Studies. Voltammetric measurements were performed with a BASI Epsilon electrochemical system. A conventional three-electrode system was used consisting of an Ag/AgCl/KCl reference electrode, a glassy carbon electrode as a working electrode, and a graphite rod as auxiliary electrode. The whole measurements were automated and controlled through the programming capacity of the apparatus. All the solutions examined by electrochemical technique were purged for 10 min with purified nitrogen gas after which a continuous stream of nitrogen was passed over the solutions during the measurements.

3. Results and Discussion

Isolation studies have been carried out to know the affinity of anthraquinone-derived ionophores toward Li^+ , Na^+ , K^+ , Ca^{2+} , and Mg^{2+} metal ions. The results of extraction and transport studies have been reported [12, 13] and used

TABLE 1: Properties of isolated complexes of alkali and alkaline earth metal salts with anthraquinone-derived ionophore V₂.

Ionophores	Complex	Solvent	M.P. (°C)	Elemental analysis (%)			
				C%	H%	N%	M%
V ₂			45	C: 66.09	6.83	—	—
				F: 66.04	6.72	—	—
	V ₂ LiPic	Methanol	160	C: 48.41	3.82	8.91	1.47
				F: 48.45	3.80	8.85	1.43
	V ₂ NaPic	Methanol	125	C: 46.82	3.69	8.62	4.70
				F: 47.10	3.69	8.31	4.73
	V ₂ KPic	Methanol	130	C: 51.96	4.60	5.68	5.27
				F: 50.47	4.62	5.61	5.25
	V ₂ Ca(Pic) ₂	Methanol	145	C: 47.10	3.71	8.67	4.13
				F: 46.75	3.69	8.63	4.11
	V ₂ Mg(Pic) ₂	Methanol	110	C: 47.89	3.78	8.82	2.52
				F: 47.53	3.71	8.79	2.57

TABLE 2: IR spectral data of alkali and alkaline earth metal complexes with ionophore V₂.

Ionophore	Complex	Selected IR absorption bands in ionophore and respective shift in complexes (cm ⁻¹)
V ₂		2873 (C–H), 1676 (C=O), 1264, 1162, 1127, 1097 (CH ₂ –O–CH ₂)
	V ₂ LiPic	2881 (C–H), 1675 (C=O), 1270, 1160, 1130, 1078 (CH ₂ –O–CH ₂)
	V ₂ NaPic	2873 (C–H), 1679 (C=O), 1270, 1161, 1130, 1074 (CH ₂ –O–CH ₂)
	V ₂ KPic	1674 (C=O), 1266, 1161, 1074 (CH ₂ –O–CH ₂)
	V ₂ Ca(Pic) ₂	1675 (C=O), 1271, 1164, 1133, 1080 (CH ₂ –O–CH ₂)
	V ₂ Mg(Pic) ₂	1633 (C=O), 1270, 1163, 1129, 1079 (CH ₂ –O–CH ₂)

here as support to compare the affinity of these synthetic ionophores toward Li⁺, Na⁺, K⁺, Ca²⁺, and Mg²⁺ metal ions.

Ionophore V₂ complexed with lithium picrate, sodium picrate, potassium picrate, calcium picrate, and magnesium picrate. Hence, this synthetic ionophore does not complex selectively because flexible ether chains can adapt itself to cations of different size [18]. These isolated complexes have been characterized by m.p., CV, IR, and ¹H NMR spectral and elemental (CHN) analysis.

Results of elemental analysis are shown in Table 1. IR spectral data of ionophores and their isolated complexes are shown in Table 2. It is observed that the characteristic IR bands of V₂ at 1264 cm⁻¹, 1162 cm⁻¹, 1127 cm⁻¹ (CH₂–O–CH₂), and 1097 cm⁻¹ (Ar–O–R) are shifted to 1271 cm⁻¹, 1164 cm⁻¹, 1133 cm⁻¹, and 1080 cm⁻¹ in calcium picrate V₂ complex. Characteristic IR band of V₂ for C=O at 1676 cm⁻¹ is shifted to 1675 cm⁻¹, 1679 cm⁻¹, 1674 cm⁻¹, 1675 cm⁻¹, and 1633 cm⁻¹ in V₂ lithium picrate, V₂ sodium picrate, V₂ potassium picrate, V₂ calcium picrate, and V₂ magnesium picrate, respectively, this shift is evidence for participation of quinone oxygen in complexation [19].

The results of IR spectral analysis are also supported by ¹H NMR spectral data, which is tabulated in Table 3. ¹H NMR peaks of ionophore V₂ at δ 1.19–1.23 (CH₃), δ 3.48–4.35 (CH₂–O–CH₂), and δ 7.28–8.17 (Ar–H) are shifted to

δ 1.11–1.27 (CH₃), δ 3.47–4.62 (CH₂–O–CH₂), and δ 7.52–8.20 (Ar–H) in V₂ lithium picrate complex. Maximum shifts in ¹H NMR peaks at δ 1.03–1.08, δ 3.35–4.29, and δ 7.57–8.13 are observed in V₂ potassium picrate complex, while V₁ potassium picrate complex has not been isolated.

From Table 4 it can be observed that the reduction potentials of 1,5 dichloroanthraquinone, 1,8 dichloroanthraquinone, and ionophores V₁ and V₂ are –667 mV, –690 mV, –718 mV, and –735 mV. Increase in reduction potential of ionophores as compared to that of corresponding anthraquinone was observed due to the presence of polyethyleneglycol chains. The reduction potential of isolated complexes of ionophore V₂ with lithium picrate, sodium picrate, potassium picrate, calcium picrate, and magnesium picrate is –710 mV, –717 mV, –702 mV, –693 mV, and –720 mV, respectively. Decrease in reduction potential [20] in complexes as compared to that of corresponding ionophores was observed as a result of electrostatic interactions of donor oxygen atoms with metal ion. Cyclic voltammograms of V₁ with 1,5 dichloroanthraquinone and ionophores V₂ are shown in Figures 2 and 3, respectively. Ionophore V₂ shows maximum shift in reduction potential (ΔE) with Ca(Pic)₂ due to its high charge density. Figure 4 shows the cyclic voltammogram of V₂ calcium picrate complex. The observed sequence for the shifting in reduction

TABLE 3: ^1H NMR spectral data of alkali and alkaline earth metal complexes with ionophore V_2 .

Ionophore	Complex	^1H NMR absorption bands [$(\delta \text{ ppm})$]
V_2		1.19–1.231 (CH_3), 3.48–4.35 ($\text{CH}_2\text{--O--CH}_2$), 7.28–8.17 (Ar–H)
	V_2LiPic	1.11–1.27 (CH_3), 3.47–4.62 ($\text{CH}_2\text{--O--CH}_2$), 7.52–8.20 (Ar–H)
	V_2NaPic	1.12–1.26 (CH_3), 3.48–4.61 ($\text{CH}_2\text{--O--CH}_2$), 7.48–8.17 (Ar–H)
	V_2KPic	1.03–1.08 (CH_3), 3.35–4.29 ($\text{CH}_2\text{--O--CH}_2$), 7.57–8.13 (Ar–H)
	$\text{V}_2\text{Ca}(\text{Pic})_2$	1.11–1.16 (CH_3), 3.47–4.62 ($\text{CH}_2\text{--O--CH}_2$), 7.52–8.20 (Ar–H)
	$\text{V}_2\text{Mg}(\text{Pic})_2$	1.11–1.16 (CH_3), 3.49–4.65 ($\text{CH}_2\text{--O--CH}_2$), 7.47–8.17 (Ar–H)

TABLE 4: Cyclic voltammetric data of redox switched ionophores and their complexes.

Reactant	Ionophore	Complex	Reduction potential E (mV)	Shifting of reduction potential in complex ΔE (mV)
1,5-DichloroAQ	V_1		–667	
			–718	
1,8-DichloroAQ	V_2		–690	
			–735	
		V_2LiPic	–710	25
		V_2NaPic	–717	18
		V_2KPic	–702	33
		$\text{V}_2\text{Ca}(\text{Pic})_2$	–693	42
		$\text{V}_2\text{Mg}(\text{Pic})_2$	–720	15

potential (ΔE) between V_2 and their complexes is V_2 calcium picrate (42 mV) > V_2 potassium picrate (33 mV) > V_2 lithium picrate (25 mV) > V_2 sodium picrate (18 mV) > V_2 magnesium picrate (15 mV) and the same sequence is observed in extraction studies as shown in Figure 5.

The observed trend for extraction and transport (Figures 5 and 6) of alkali and alkaline earth metal cations by ionophores V_1 and V_2 is $\text{Ca}^{2+} > \text{Li}^+ > \text{K}^+ > \text{Mg}^{2+}$ and $\text{Ca}^{2+} > \text{K}^+ > \text{Li}^+ > \text{Mg}^{2+}$, respectively. Ionophores V_1 and V_2 show good extraction and transport ability for Ca^{2+} due to its high charge density. It is observed that V_2 is a better extractant and carrier for K^+ as compared to V_1 .

The transport ability of these ionophores has been increased in their reduced state because the anion and dianion are formed [21] as a result of reduction, and ionophores act as better carrier, which is clearly evident from Figure 6. In oxidized state, ionophore V_1 shows no transport but V_2 transports detectable amount of metal ions because the closer proximity of side chains provides a large number of binding sites.

The results of back extraction studies are shown in Figure 7. The back extraction was preferred to check the decomplexation of metal salt-carrier complex. Ionophores V_1 and V_2 exhibit better back extraction efficiency in their reduced state, and K^+ and Ca^{2+} are more efficiently back extracted by V_2 .

In ionophores V_1 and V_2 the two side arms were placed on the rigid anthraquinone framework in such a way that they were on opposite side in V_1 and the same side in V_2 . From the results of isolation, extraction, back extraction, and

FIGURE 2: Cyclic voltammograms: (A) 1,5-dichloroanthraquinone (–667 mV), (B) ionophore V_1 (–718 mV). Scan rate 100 (mV/s), and switching potential from 1100 mV to –1500 mV.

transport studies of these ionophores it can be observed that the ionophore V_1 does not form complex with potassium picrate and shows poor extraction and carrier ability for the same, while V_2 shows good affinity towards potassium picrate as shown in Figure 8, this can be explained by the pseudo cavity conformation formed by two diethyleneglycol chains in closer proximity, which provides six donor oxygen atoms in its binding site and this conformation suits as per the ionic radii of K^+ .

FIGURE 3: Cyclic voltammograms of ionophore V_2 (-735 mV). Scan rate 100 (mV/s) and switching potential from 1100 mV to -1500 mV.

FIGURE 4: Cyclic voltammogram of complex of V_2 with Ca(Pic)_2 . Scan rate 100 (mV/s) and switching potential from 1100 mV to -1500 mV.

FIGURE 5: Extraction of metal ions using ionophores V_1 and V_2 .

In these redox switchable synthetic ionophores anthraquinone moiety is responsible for increasing (positive cooperativity) and decreasing (negative cooperativity) their affinity towards an appropriate guest. Negative cooperativity has been less explored than the positive, though this property

FIGURE 6: Transport of metal ions using ionophores V_1 and V_2 .

FIGURE 7: Back extraction of metal ions using ionophores V_1 and V_2 .

FIGURE 8: Extraction, back extraction, and transport of K^+ by ionophores V_1 and V_2 .

may be more interesting for applications, such as selective separation and enrichment of metal ions for sample preparation through electrochemically driven ion transport because which are more difficult to separate with other techniques.

Acknowledgments

The authors are thankful to UGC for financial support under major research project. Professor Rajeev Jain, Chemistry

Department, Jiwaji University, Gwalior, is also acknowledged for valuable discussion. They would like to thank Professor Ashok Sharma and Professor Pratibha Sharma, School of Chemical Sciences, D. A. V. V. Indore for CV analysis and CDIR Lucknow for spectral analysis.

References

- [1] T. Saji, "Electrochemically switched cation binding in penta-*taoxa* [13] ferrocene-*phane*," *Chemistry Letters*, vol. 15, no. 3, pp. 275–276, 1986.
- [2] P. L. Boudry, M. Gómez-Kaifer, and L. Echegoyen, "Electrochemistry of Supramolecular Systems," *Angewandte Chemie—International Edition*, vol. 37, no. 3, pp. 216–247, 1998.
- [3] B. L. Feringa, Ed., *Molecular Switches*, John Wiley & Sons, Chichester, UK, 2001.
- [4] H. J. Schneider and A. Yatsimirsky, *Principles and Methods in Supramolecular Chemistry*, John Wiley & Sons, New York, NY, USA, 2000.
- [5] M. Takeuchi, M. Ikeda, A. Sugasaki, and S. Shinkai, "Molecular design of artificial molecular and ion recognition systems with allosteric guest responses," *Accounts of Chemical Research*, vol. 34, no. 11, pp. 865–873, 2001.
- [6] P. D. Beer, P. A. Gale, and G. Z. Chen, "Electrochemical molecular recognition: pathways between complexation and signalling," *Journal of the Chemical Society*, no. 12, pp. 1897–1909, 1999.
- [7] J. Janata, "Chemical sensors," *Analytical chemistry*, vol. 12, no. 15, pp. 33R–44R, 1990.
- [8] L. E. Echegoyen, H. K. Yoo, V. J. Gatto, G. W. Gokel, and L. Echegoyen, "Cation transport using anthraquinone-derived lariat ethers and podands: the first example of electrochemically switched "on/off" activation/deactivation," *Journal of the American Chemical Society*, vol. 111, no. 7, pp. 2440–2443, 1989.
- [9] T. Saji and I. Kinoshita, "Electrochemical ion transport with ferrocene functionalized crown ether," *Journal of the Chemical Society, Chemical Communications*, no. 9, pp. 716–717, 1986.
- [10] B. J. Ryu, E. J. Cho, and K. C. Nam, "Synthesis and metal binding properties of anthraquinone bridged with coumarin," *Bulletin of the Korean Chemical Society*, vol. 28, no. 9, pp. 1585–1587, 2007.
- [11] M. Delgado, D. A. Gustowski, H. K. Yoo, V. J. Gatto, G. W. Gokel, and L. Echegoyen, "Contrasting one- and two-cation binding behavior in syn- and anti-anthraquinone bibrachial podand (BiP) mono- and dianions assessed by cyclic voltammetry and Electron Paramagnetic Resonance spectroscopy," *Journal of the American Chemical Society*, vol. 110, no. 1, pp. 119–124, 1988.
- [12] V. Vyas, A. Vani, S. Dubey, M. Mimrot, and U. Sharma, "Effect of side arm variation in anthraquinone-derived lariat ethers on uptake of Li^+ , K^+ , Ca^{2+} and Mg^{2+} metal ions," *Main Group Metal Chemistry*, vol. 31, no. 6, pp. 283–288, 2008.
- [13] V. Vyas, P. Raizada, and U. Sharma, "Design and synthesis of anthraquinone derived ionophores and their extraction and transport ability for Li^+ , K^+ , Ca^{2+} and Mg^{2+} metal ions," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 80, pp. 139–144, 2010.
- [14] M. Bhatnagar, A. Awasthy, and U. Sharma, "Stoichiometric complexes of some main group metal ions (Li^+ , Na^+ , K^+ , Ca^{2+}) with redox-switched lariat ethers," *Main Group Metal Chemistry*, vol. 27, no. 3, pp. 163–168, 2004.
- [15] P. Joshi, N. Joshi, and U. Sharma, "Extraction and carrier-facilitated transport of amino acids using synthetic non-cyclic receptors through bulk liquid membrane," *Indian Journal of Biochemistry and Biophysics*, vol. 43, no. 5, pp. 323–326, 2006.
- [16] A. Awasthy, M. Bhatnagar, J. Tomar, and U. Sharma, "Design and synthesis of redox-switched lariat ethers and their application for transport of alkali and alkaline-earth metal cations across supported liquid membrane," *Bioinorganic Chemistry and Applications*, vol. 2006, Article ID 97141, 4 pages, 2006.
- [17] M. Bhatnagar, J. Tomar, and U. Sharma, "Isolation and characterization of complexes of alkali and alkaline earth metal cations with synthetic podands," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 77, no. 1, 2007.
- [18] M. Bhatnagar, A. Awasthy, and U. Sharma, "Redox chemical switching of cation transport in liquid membrane system," *Main Group Metal Chemistry*, vol. 31, no. 3-4, pp. 203–209, 2008.
- [19] J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, Germany, 1995.
- [20] L. Sun, J. Von Gersdorff, J. Sobek, and H. Kurreck, "Novel biomimetic models for photosynthesis: porphyrins covalently linked to redox-active crown ether quinones," *Tetrahedron*, vol. 51, no. 12, pp. 3535–3548, 1995.
- [21] D. A. Gustowski, M. Delgado, V. J. Gatto, L. Echegoyen, and G. W. Gokel, "Electrochemical switching in anthraquinone-substituted carbon-pivot lariat ethers and podands: chain length effects in geometric and electronic cooperativity," *Journal of the American Chemical Society*, vol. 108, no. 24, pp. 7553–7560, 1986.