MW. Calcd for $C_{20}H_{18}O$: 274.1358. Found: 274.1360.

2-(Bromomethyl)naphthalene (9). 2-Methylnaphthalene (1.71 g, 12.0 mmol), *N*-bromosuccinimide (2.30 g, 12.9 mmol), and benzoyl peroxide (0.1 g) were refluxed 7 days in CCl_4 (50 mL). The solution was filtered and the solvent removed to yield the crude 2-(bromomethyl)naphthalene (**9**) (2.56 g): ^{1}H NMR (CCl_4) δ 4.58 (s, 2 H, ArCH_2Br), 7.05-7.70 (m, 7 H, Ar*H*).

2-(3′-Butenyl)naphthalene (5). Freshly prepared, crude bromide **9** (2.56 g) in THF (15 mL) solution was added dropwise to a THF solution of allylmagnesium chloride (50 mL of 0.90 M, 45 mmol). The solution was refluxed 12 h, and then the excess Grignard reagent was quenched by the addition of 10% H_2SO_4 (40 mL). The butene **5** was extracted into ether (40 mL) and dried over $MgSO_4$. After solvent removal, the product was vacuum distilled [bp 85 °C (0.20 mm Hg)] to yield 1.59 g of clear liquid **5**, pure by GC analysis: MS (GC-MS) *m/e* (RA) 183 (M + 1, 3.3), 182 (M^+, 16), 142 (12), 141 (M - C_3H_7, 100); ^{1}H NMR ($CDCl_3$) δ 2.35 (q, *J* = 7 Hz, 2 H, -CH_2-), 2.80 (t, *J* = 7 Hz, ArCH_2-), 4.90 (s, 1 H, *cis*-C*H*), 5.05 (d, *J* = 8 Hz, 1 H, *trans*-C*H*), 5.60-6.10 (m, 1 H, -C*H*=), 7.10-7.80 (m, 7 H, Ar*H*). MW. Calcd for $C_{14}H_{14}$: 182.1096. Found: 182.1090.

1-Bromo-2-(bromomethyl)naphthalene (10). 1-Bromo-2-methylnaphthalene (9.20 g, 41.6 mmol, Aldrich), *N*-bromosuccinimide (8.60 g, 48.3 mmol), and benzoyl peroxide (0.1 g) were refluxed in CCl_4 (400 mL) for 6 days. The chilled (-5 °C) solution was filtered through glass wool and the solvent distilled to yield the crude 1-bromo-2-(bromomethyl)naphthalene (**10**) (13.3 g): ^{1}H NMR (CCl_4) δ 4.80 (s, 2 H, -CH_2Br), 7.30-7.70 (m, 5 H, Ar*H*), 8.25 (d, *J* = 10 Hz, 1 H, Ar*H*-8).

1-Bromo-2-(3′-butenyl)naphthalene (6). The crude bromide **10** (13.3 g) in THF (30 mL) solution was added dropwise with stirring to a THF solution of allylmagnesium chloride (400 mL of 0.90 M) and the resulting mixture refluxed 2 h. The product **6** was worked up by addition of 10% H_2SO_4 (80 mL), extracted with diethyl ether, and dried over $MgSO_4$. Removal of solvent followed by vacuum distillation [bp 110 °C (6×10^{-2} mmHg)] yielded clear liquid **6**, pure by GC analysis (8.01 g, 30.7 mmol, 74% yield from 1-bromo-2-methylnaphthalene): ^{1}H NMR ($CDCl_3$) δ 2.50 (q, *J* = 8 Hz, 2 H, -CH_2-), 3.05 (t, *J* = 8 Hz, 2 H, ArCH_2), 4.90 (s, 1 H, *cis*-C*H*), 5.15 (d, *J* = 9 Hz, 1 H, *trans*-CH), 5.70-6.30 (m, 1 H, -C*H*=), 7.50-8.00 (m, 5 H, ArH), 8.30 (d, *J* = 10 Hz, 1 H, Ar*H*-8); ^{13}C NMR ($CDCl_3$) 34.0 (-CH_2-), 36.9 (ArCH_2-), 115.2 (=CH_2), 123.6, 125.7, 127.1, 127.2, 127.3, 127.9, 128.0, 132.5, 133.1 (aryl carbons), 137.6 (-CH=), 139.1 (ArCCH_2-). MW. Calcd for $C_{14}H_{13}Br$: 260.0201 (M^+), 262.0181 (M + 2). Found: 260.0209 (M^+), 262.0186 (M + 2).

1-Methylbenz[*e*]indan (4). 1-Bromo-2-(3′-butenyl)naphthalene (**6**) (1.41 g, 5.40 mmol) was treated with *n*-BuLi (4.8 mL of 2.0 M solution, 2 equiv) while stirring in diethyl ether (150 mL) at -78 °C for 2 h. The solution was then warmed to 23 °C for 28 h. The reaction mixture was quenched with methanol (20 mL), washed twice with a 10% NaOH solution (30 mL), and dried over $MgSO_4$. Removal of solvent yielded the crude, 1-methylbenz[*e*]indan (**4**) (0.95 g), which contained ca. 10% 2-(3′-butenyl)naphthalene. Chromatography (pentane/5% $AgNO_3$ on silica) of the crude product yielded clear, liquid **4**, pure by GC analysis (0.760 g, 4.18 mmol, 77.4% yield): ^{1}H NMR ($CDCl_3$) δ 1.45 (d, *J* = 8 Hz, 3 H, -CH_3), 1.70-2.10 (m, 1 H, H_a), 2.20-2.60 (m, 1 H, H_b), 2.70-3.30 (m, 2 H, -CH_2-), 3.50-3.90 (m, 1 H, methine), 7.20-7.90 (m, 6 H, Ar*H*); MS (GC-MS) *m/e* (RA) 183 (M + 1, 4.5), 182 (M^+, 22.5), 180 (M - 2, 2), 168 (13), 167 (M - CH_3, 100), 165 (23), 152 (19). MW. Calcd for $C_{14}H_{14}$: 182.1096. Found: 182.1084.

6-(3′-Butenyl)-1,4-dihydronaphthalene (11). Compound **11** was isolated (by preparative GC) from the reaction mixture that resulted from the treatment of **5** with the Na-K/tetraglyme/THF ether cleavage system: ^{1}H NMR ($CDCl_3$) δ 2.30 (q, *J* = 7 Hz, 2 H, ArCH_2CH_2-), 2.65 (t, *J* = 7 Hz, 2 H, ArCH_2-), 3.35 (d, *J* = 1.5 Hz, 4 H, ArCH_2CH=), 4.85 (s, 1 H, *cis*-C*H*), 5.05 (d, *J* = 10 Hz, 1 H, *trans*-C*H*), 5.55-6.05 (m, 1 H, -C*H*=CH_2), 5.90 (t, *J* = 1.5 Hz, 2 H, ArCH_2C*H*=), 7.05-7.85 (m, 3 H, Ar*H*); MS (GC-MS) *m/e* (RA) 185 (M + 1, 2.0), 184 (M^+, 12.5), 144 (13), 143 (M - C_3H_5, 100), 129 (10), 128 (5).

9b,5-Dihydro-1-methylbenz[*e*]indan (12). Compound **12** was also obtained from the reaction mixture of the room-temperature cleavage of **3** by preparative GC and spectroscopically characterized: ^{1}H NMR ($CDCl_3$) δ 1.25 (d, *J* = 8 Hz, 3 H, CH_3), 1.50-2.30 (m, 2 H, -CH_2-), 2.40-2.80 (m, 2 H, -CH_2-), 2.90-3.30 (m, 1 H), 3.35 (d, *J* = 8 Hz, 2 H, ArCH_2-), 3.55 (d, *J* = 10 Hz, 1 H, ArC*H*-), 6.35 (t, *J* = 8 Hz, 1 H, ArCH_2C*H*=), 7.20-7.90 (m, 4 H, Ar*H*); MS (GC-MS) *m/e* (RA) 185 (M + 1, 3.2), 184 (M^+, 18.5), 170 (14), 169 (M - CH_3, 100), 167 (10), 129 (20), 128 (11).

6-(3′-Butenyl)-1,4-dihydro-5-phenoxynaphthalene (13) and 6-(3′-Butenyl)-1,2,3,4-tetrahydronaphthalene (14). Compounds **13** and **14** were tentatively identified by their GC-MS. Quantitation was performed assuming similar compounds **13** and **14** had the same GC response factor as **3** and **5**, respectively. Compound **13**: MS (GC-MS) *m/e* (RA) 277 (M + 1, 4.5), 276 (M^+, 20.2), 236 (18), 235 (M - C_3H_5, 100), 233 (15), 115 (10), 78 (20). Compound **14**: MS (GC-MS) *m/e* (RA) 186 (M^+, 18.0), 146 (12.5), 145 (M - C_3H_5, 100), 144 (8), 143 (23), 130 (8), 129 (12), 115 (9).

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Cation Transport Using Anthraquinone-Derived Lariat Ethers and Podands: The First Example of Electrochemically Switched "On/Off" Activation/Deactivation

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Abstract: Anthraquinone undergoes one- and two-electron reduction to form either radical anions or dianions. When a crown-ether-type macrocycle or a polyethyleneoxy side chain is attached, the reduced aromatic and the oxygen donor groups cooperate to bind the cation. Binding of Li^+ or Na^+ is greater when anthraquinone is reduced because there is a charge–charge interaction between it and the cation. This property has been used to facilitate transport. Thus, reduction at the source phase enhances cation binding, and oxidation in the receiving phase induces cation release. Activation/deactivation was effected electrochemically. The ligands studied in a bulk CH_2Cl_2 phase were 1-((9,10-dioxo-1-oxanthracenyl)methyl)-15-crown-5, **1**; 1-((9,10-dioxo-1-oxanthracenyl)methyl)-18-crown-6, **2**; 1-(2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethoxy)anthracene-9,10-dione, **3**; 1-(2-(2-(2-(2-octadecyloxyethoxy)ethoxy)ethoxy)ethoxy)anthracene-9,10-dione, **4**. The first example of an electrochemically activated (reduction) and deactivated (oxidation) cation transport system based on anthraquinone ligands is demonstrated.

The ability of synthetic ionophores such as crown ethers and cryptands to bind and transport cations has fascinated the chemical community almost since the introduction of these molecules.[1,2] Most of these studies have utilized liquid membrane systems, and

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much of this work has been reviewed by Izatt and co-workers.[3] Although bulk liquid membranes poorly approximate a lipid bilayer, studies in these systems have been necessary due to experimental difficulties and because of the lack of understanding of transport involving synthetic membranes when such studies were begun. Although transport across bulk liquid membrane systems is known to be influenced by factors such as stirring rate, interface area, cell geometry, etc., complexation and decomplexation rates are knwon to be extremely important in lipid bilayers.[4]

The importance of switching as a means to control the rate of cation transport has been recognized for some time. Shinkai and co-workers and others[5] have developed novel photoswitchable cryptands that exhibited different binding properties when in the ground state or photoactivated. Lehn[6] demonstrated that transport by cryptands could be enhanced by protonation of the ligand at the receiving phase interface. Izatt and co-workers[7] have shown similar properties for calixarene carriers which can be "activated" by deprotonation at the source phase and "deactivated" by protonation at the receiving phase. In all of these cases, a high-binding state is used for complexation while release of the cation is effected by switching the carrier to a low or lower binding state at the receiving phase.

Our own approach to ligand switching involved electrochemical reduction of a weakly binding lariat ether.[8] When reduced to the radical anion, the binding of typical alkali metal cations was enhanced by as much as 10^6. Release of the cation could be effected by oxidation which returned the ligand to its neutral, low-binding state. The obvious application of electrochemical switching requires reduction at the source phase followed by oxidation at the receiving phase. Indeed, we have successfully demonstrated the enhancement of transport by electrochemical activation of a lariat ether.[9] In our case, the second requirement of our switching definition, namely oxidation of the activated carrier, was not demonstrated. Recently, the deactivation of a ligand was demonstrated by Saji, although in the latter case, the ligand was a neutral carrier rather than an activated one.[10] We now report the first example of cation transport in which both activation and deactivation of the ligand are carried out electrochemically.

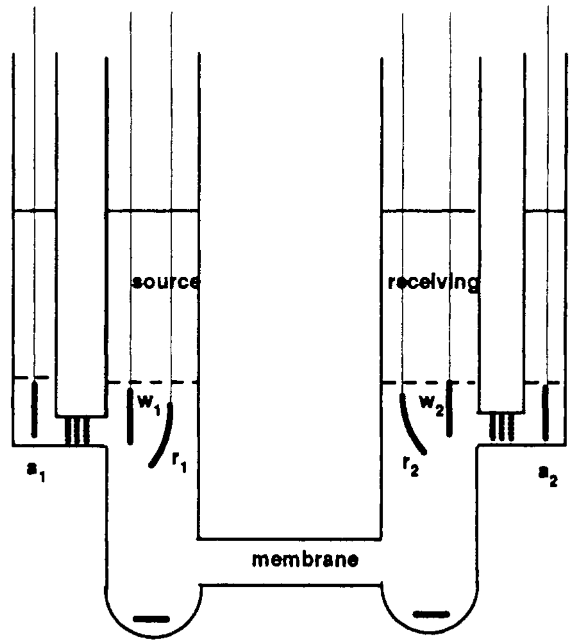
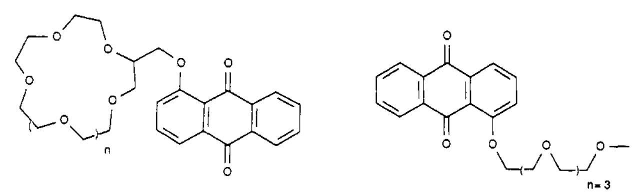


Figure 1. Diagram of transport cell showing the two 3-Pt-electrode configurations (a_1, w_1, r_1, for reduction and a_2, w_1, r_2 for oxidation) source phase = 0.1–1.0 M $MClO_4$ in H_2O; receiving phase = distilled, deionized water; membrane phase = 0.5–2.0 mM ligand and 0.1 M TBAP in CH_2Cl_2. Note that auxiliary electrodes are separated from their corresponding working electrodes and reference electrodes by fine porosity glass filters.

Results and Discussion

Ligand Syntheses. Four ligands were required for the present study. They are 1-((9,10-dioxo-1-oxanthracenyl)methyl)-15-crown-5, **1**; 1-((9,10-dioxo-1-oxanthracenyl)methyl)-18-crown-6, **2**; 1-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)anthracene-9,10-dione, **3**; and 1-(2-(2-(2-*n*-octadecyloxyethoxy)ethoxy)ethoxy)-anthracene-9,10-dione, **4**. All four compounds were prepared by reaction of the appropriate alcohol [a hydroxymethyl crown or $R(OCH_2CH_2)_4OH$] with 1-chloroanthraquinone in the presence of sodium hydride. This transformation is formally a nucleophilic aromatic substitution reaction although the mechanism is currently unclear. We will report shortly in a separate paper results of a study on this reaction. The reaction conditions which produce compounds **1** and **3** have been previously described.[8g] Compounds **2** and **4** were prepared in a fashion analogous to the preparations of **1** and **3** (Experimental Section). The structures are shown below.



1, n = 1 **3**, R = CH_3

2, n = 2 **4**, R = $C_{18}H_{37}$

Apparatus. The transport experiments were conducted using an H-cell similar to that previously described[9] but modified to a symmetrical form to accommodate the second electrode set (see Figure 1). Working and counter electrodes consisted of Pt foil (4 cm^2) connected with Pt wires. The wires going through the water phases were protected with Teflon tubing. Reference electrodes were also Pt wires. The bulk liquid membrane used in the transport experiments described here consisted of 40 mL of 0.5–2 mM ligand in CH_2Cl_2 carrier solution which also contained 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The source phase consisted of 5.0 mL of a 0.1–1.0 M solution of alkali metal perchlorate salt in water. The

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Table I. Transport Rate Constants for Electrochemically Switched Lariat Ethers[a]

carrier	cation	neutral[b] (h^{-1})	reduced	pumped
1	Na^+	6.9×10^{-2}	1.3×10^{-1}	3.4×10^{-1}
2	Na^+	9.7×10^{-2}	1.4×10^{-1}	2.3×10^{-1}
3	Na^+	2.1×10^{-2}	1.4×10^{-2}	5.4×10^{-2}
3	Li^+	1.3×10^{-4}	1.4×10^{-3}	
4	Li^+	1.5×10^{-4}	3.1×10^{-3}	
4	Li^+ (1 M)	1.3×10^{-4}	3.2×10^{-3}	
	Na^+ (4 mM)	9.9×10^{-4}	4.0×10^{-4}	

[a] See text and Experimental Section for a description of terms and details of the experiments. [b] Rate constants given in h^{-1} (second order) to normalize results for different carrier concentrations needed for Li^+ and Na^+ transport experiments.

receiving phase was 10.0 mL of pure water. Surface interphase areas were 1.7 cm^2. The concentration of the alkali metal was monitored by using atomic absorption spectrophotometry. Aliquots were removed from the receiving phase at regular intervals (see Experimental Section). Throughout the entire experiment, the rotation rate for both stirring bars was maintained at ca. 400 rpm.

Conduct of the Experiments. Each experiment comprised three stages. In the first stage, transport was conducted with the apparatus described above and shown in Figure 1, in the absence of any applied potential. This stage corresponds directly to the typical transport experiments conducted in numerous laboratories using neutral ionophores. The time of this stage was usually 24 h. The second stage required controlled potential coulometric reduction of the carrier ligand (complete reduction required ca. 15 min). The reduction was accomplished by using a single potentiostat (Figure 1). Cation transport was monitored for another 8 h. The final stage utilized simultaneous application of controlled potentials with two separate potentiostats. The potential of the working electrode at the source interface was controlled in order to effect reduction of the ligand while that at the receiving interface was controlled for oxidation of the reduced carrier complex. Three rates were thus obtained in each experimental run. These rates are shown in Table I as, respectively, "neutral", "reduced", and "pumped". The latter term refers to enhanced cation transport rates mediated by an electrochemical gradient present across the bulk liquid membrane.

Transport Results. The rate constants for all three stages of each experiment as described above for the four different ligand systems are shown in Table I.

Our preliminary report of this work utilized ligand **3**, and in that case no appreciable Li^+ transport was observed over the shorter duration of those studies.[9] During the 24-h period of stage one (neutral ligand) used in the present study, Li^+ transport by **3** had a rate constant of 1.3×10^{-4} h^{-1}. In both stages two and three of the present study, cation transport rates were higher than observed in stage one for this and other ligands studied. For example, carrier **1** essentially doubles its transport rate for Na^+ upon reduction and nearly triples it over the reduced rate when in the pumped mode. The net rate increase from neutral to pumped is 5-fold.

For carrier **2**, in the presence of Na^+, the overall increase is lower, only slightly over 2-fold. This result corresponds to the binding order exhibited by compounds **1** and **2**. Since **2** contains an 18-membered macroring, it binds Na^+ more strongly than does **1**. This is, in turn, reflected by faster Na^+ transport in the neutral state, 9.7×10^{-2} vs 6.9×10^{-2} h^{-1}, respectively for **2** vs **1**. When both **1** and **2** are reduced, the corresponding Na^+ transport rates are essentially equal. These results suggest that the previously observed[8d] leveling effect is in operation. Lithium cation is usually weakly bound by neutral ligands, and K^+ is usually strongly bound by them. When the sidearm is reduced, Li^+ binding increases dramatically; K^+ binding increases less. In the end, binding for both species is often similar. In the present case, overall binding by different ligands may be similar even though relative contributions from the macroring and reduced sidearms are different in each case. When "pumped", **1** is more efficient than **2**. Again, this is consistent with the lower binding affinity of **1** for Na^+ at the receiving interface, which results in enhanced transport.

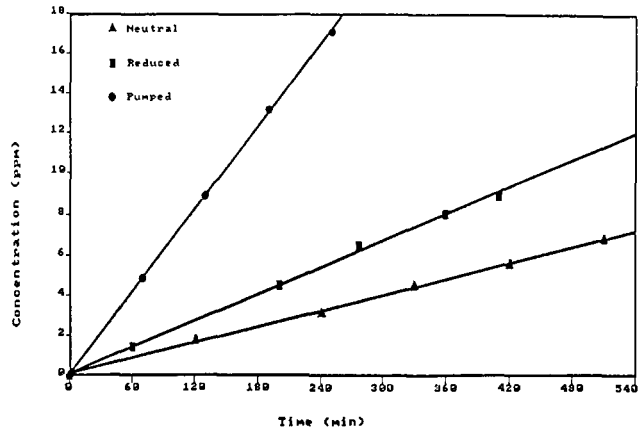

Figure 2. Typical concentration vs time profile (receiving phase) for the three stages of Na^+ transport by ligand **1**: triangles = neutral, squares = reduced, and circles = pumped.

It is interesting that both **3** and **4**, when reduced, exhibit decreased Na^+ transport rates. There is evidence from spectroelectrochemical studies[13] and from ESR[14] that this may result from a very large binding enhancement caused by a shift in the disproportionation equilibrium from the anion radical to the dianion upon addition of Na^+ and Li^+. Since the cation binding strength (K_{eq}) is defined by the ratio $k_{complex}/k_{release}$, if binding becomes very strong, cation release rates can become very slow. Upon "pumping," the rate increases, even beyond that observed for the neutral case, as expected. Another interesting, although not unexpected, observation comes from the Li^+ transport results. Neutral transport is slower than that for Na^+ (about 10-fold), a reflection of the lower binding affinity. In all cases involving Li^+, reduction leads to a 10–20-fold increase in the transport rate. Pumping experiments with Li^+ have met with great experimental difficulty. Besides the disproportionation phenomena mentioned above, we have observed that the reduced carrier is partially being extracted into the Li^+-containing donor phase. The latter leads to depletion of carrier in the membrane by the time of commencing stage 3.

The differences in transport rates for Na^+ by **1** in the neutral, reduced, and pumped stages are illustrated in Figure 2. It is clear not only that substantial differences in rates occur but also that the processes are well-behaved under all three sets of conditions.

As anticipated, a competition experiment (last entry in Table I) between Li^+ and Na^+ involving **1** as a carrier showed a favored Na^+ transport in the neutral case (9.9×10^{-4} vs 1.3×10^{-4} h^{-1}) even though Na^+ was only 4 mM in the donor phase, while Li^+ was 1 M. Interestingly, transport rates were reversed in the reduced state, with Li^+ being favored by a factor of 8.

Conclusion

We have demonstrated that electrochemically mediated transport can be controlled by reduction of an anthraquinone carrier molecule at an electrode near the source phase and oxidation of the anthraquinone–metal complex at a second electrode near the receiving phase. For the bulk, model membrane system, these carriers are well-behaved, and their properties can be understood in terms of previous results on reducible lariat ether and podand systems. Experiments are currently in progress to simulate the electrochemical pump successfully demonstrated here with

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(12) Due to the fact that the reference electrodes were Pt, the reduction and oxidation potentials were not exactly constant. Thus, when the pumped experiment was attempted by using controlled potentials at both sides, the currents did not exactly balance out. It was then decided to use controlled current electrolysis near the receiving phase to oxidize the reduced ligand back to its neutral state.

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chemical redox agents in transport experiments conducted in a lipid bilayer membrane.

Experimental Section

^1H NMR were recorded on a Varian EM 360A NMR spectrometer or on a Hitachi Perkin-Elmer R-600 high resolution NMR spectrometer in $CDCl_3$ solvents and are reported in ppm (δ) downfield from internal Me_4Si. ^{13}C NMR were recorded on a Varian XL 100 NMR spectrometer or as noted above. IR spectra were recorded on a Perkin-Elmer 298 or a Perkin-Elmer 599 infrared spectrophotometer and were calibrated against the 1601-cm^{-1} band of polystyrene. Melting points were determined on a Thomas Hoover apparatus in open capillaries and are uncorrected. TLC analyses were performed on aluminum oxide 60 F-254 neutral (type E) with a 0.2 mm layer thickness or on silica gel 60 F-254 with a 0.2 mm layer thickness. Preparative chromatography columns were packed with activated aluminum oxide (MCB 80–325 mesh, chromatographic grade, AX 611) or with Kieselgel 60 (70–230 mesh). Chromatotron chromatography was performed on a Harrison Research Model 7924 chromatotron with 2 mm circular plates prepared from Kieselgel 60 PF-254.

All reactions were conducted under dry N_2 unless otherwise noted. Molecular distillation temperatures refer to the oven temperature of a Kugelrohr apparatus. Combustion analyses were performed by Atlantic Microlab, Inc., Atlanta, GA, and are reported as percents.

Alkali metal perchlorates were obtained from Aldrich Chemical Co. and recrystallized twice from distilled, deionized water prior to use. TBAP was obtained from Fluka Chemical Co. and was recrystallized from ethyl acetate prior to use. The dichloromethane used as bulk membrane was Aldrich HPLC grade, glass distilled, and was used as received.

For the "reduced" stage, a BAS electrochemical analyzer was used as the controlled potential source in the bulk electrolysis mode. Reduction potentials were determined by cyclic voltammetry[8] and set accordingly in the present experiments (−0.9 to −1.0 V). Differences between acetonitrile and methylene chloride solvents were negligible. Reduction was carried out coulometrically until all of the carrier was converted into the radical anion.

For the "pumped" stage, in addition to the BAS on the reduction side of the cell, a PAR 173 potentiostat/galvanostat was connected to the second three-electrode configuration by using the working electrode as the oxidation electrode. This time, the potentiostat/galvanostat was set for controlled-current, bulk electrolysis in such a way as to match the current generated by the BAS on the reduction side. A balanced system was thus obtained, maintaining the equilibrium between the amount of neutral carrier being reduced and the amount of reduced carrier being oxidized.[12] Due to the nature of the two potentiostats used, a small potential difference of 0.09 V was intrinsically maintained between the two working electrodes (I = 900 uA; R_L = 100).

Since some water electrolysis was observed during these experiments, analysis of the water phases indicated basic and acidic pH values at the reduction and oxidation sides, respectively. In order to test whether or not this affected the transport rates, an experiment was set in which both source and receiving aqueous phases were kept essentially neutral with Tris buffer (Sigma). Transport rates were observed not to be affected by pH.

Aliquots (2 mL each) were removed approximately every hour for all three stages of each run and replaced by 2 mL of pure water (or buffer). Concentration changes were taken into account for the final plots and calculations. All samples were analyzed by atomic absorption (Perkin-Elmer Model 403). All transport rate constants reported here are the average obtained from at least three independent experiments.

1-((9,10-Dioxo-1-oxanthracenyl)methyl)-15-crown-5, 1, was prepared from 2-(hydroxymethyl)-15-crown-5 (20 mmol) and 1-chloroanthraquinone (20 mmol) in the presence of NaH (30 mmol) and THF as previously described.[8g] Compound **1** was obtained in 40% yield as a yellow solid, mp 100–102 °C.

1-((9,10-Dioxo-1-oxanthracenyl)methyl)-18-crown-6, 2. 2-(Hydroxymethyl)-18-crown-6[11] (2.52 g, 8.56 mmol) in dry THF (5 mL) was slowly added to a vigorously stirred suspension of NaH (60% in oil, 0.51 g, 12.8 mmol) in THF (5 mL) under N_2. After stirring for 30 min, 1-chloroanthraquinone (2.08 g, 8.56 mmol) was added as a solid, and the flask was rinsed with THF (10 mL). The mixture was stirred for 5 h at ambient temperature and concentrated in vacuo. The residue was partitioned between $CHCl_3$ (100 mL) and H_2O (50 mL), and the aqueous phase was extracted with $CHCl_3$ (25 mL). The combined organic phases were washed (brine), dried ($MgSO_4$), and evaporated. Column chromatography (silica gel 60, elution with $CHCl_3$/hexanes, 3:2, then 2% i-PrOH/$CHCl_3$) gave **2** (1.54 g, 36%) as a yellow solid (mp 86–88 °C): ^1H NMR ($CDCl_3$) 3.68–4.26 (m, 25 H), 7.29–8.31 (m, 7 H); IR (KBr) 1670, 1590, 1275, 1110, 715 cm^{-1}. Anal. Calcd for $C_{27}H_{32}O_9$: C, 64.78; H, 6.46. Found: C, 64.89; H, 6.41.

1-(2-(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)ethoxy)anthracene-9,10-dione, 3, was prepared as previously described[8g] and obtained in 65% yield as a yellow powder, mp 70–72 °C.

Tetraethylene Glycol Monooctadecyl Ether. To a suspension of NaH (60% oil dispersion, 1.10 g, 27.5 mmol) in THF (10 mL) was added tetraethylene glycol (10.33 g, 53.2 mmol). This mixture was stirred under reflux for 30 min. A solution of 1-bromooctadecane (6.00 g, 18.0 mmol) in THF (15 mL) was added slowly and then stirred for overnight. The reaction mixture was concentrated in vacuo. The residue was added to CH_2Cl_2 and washed with H_2O. Column chromatography (alumina, CH_2Cl_2 then 2% MeOH/CH_2Cl_2) gave 4.8 g (59%) of a white solid: mp 41–42 °C; ^1H NMR 0.70–1.50 (m, 35 H, methylene) 2.75 (br, 1 H, OH), 3.30–3.80 (m, 18 H, OCH_2).

1-(2-(2-(2-(2-Octadecyloxyethoxy)ethoxy)ethoxy)ethoxy)-anthracene-9,10-dione, 4. To a vigorously stirred suspension of NaH (60% oil dispersion, 0.29 g, 7.25 mmol) in THF (10 mL) was added slowly a solution of tetraethylene glycol monooctadecyl ether (2.15 g, 4.81 mmol) in THF (10 mL). After stirring for 30 min under reflux, 1-chloroanthraquinone (1.28 g, 5.28 mmol) in THF (20 mL) was added and stirred for 10 h under reflux. The reaction mixture was concentrated, and the residue was added to CH_2Cl_2 and washed with H_2O (twice) and then with brine. The organic phases were dried (over $MgSO_4$), filtered, and concentrated. Column chromatography (silica gel, 2% MeOH/CH_2Cl_2) followed by recrystallization (CH_2Cl_2/hexane then EtOH) gave 2.73 g (79%) as a yellow solid: mp 68–69 °C; ^1H NMR 0.80–1.75 (m, 35 H, $(CH_2)_{16}CH_3$), 3.25–4.45 (m, 20 H, OCH_2), 7.20–8.35 (m, 7 H, ArH); IR (KBr) 2940, 2865, 1685, 1600, 1320, 1270, 1140, 1100 cm^{-1}. Anal. Calcd for $C_{40}H_{60}O_7$: C, 73.57; H, 9.28. Found: C, 73.41; H, 9.31.

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