configuration interactions is necessary to obtain a solution where the energies of the different geometries of the singlet excited state are stable. As the Cl number was increased the energies of the perpendicular geometries were less affected (lowered) compared with the \( E \) and \( Z \) ones.

The results are summarized in Figure 4. As regards the Franck–Condon transition energies the agreement with experimental data is fair. The structureless absorption and emission spectra of the mental data is fair. The structureless absorption and emission bigamous. The longest wavelength absorption maxima at 153 K from the emission spectra are 64, 66, and 72 kcal mol\(^{-1}\).

A prerequisite for an adiabatic mechanism is that there are no energy minima on the excited-state energy surface in the regions of 90° double bond twists. The calculated energy difference between \( 'Zp^* \) and \( 'ZZ^* \) (5.1 kcal mol\(^{-1}\)) and that between \( 'ZE^* \) and \( 'Ep^* \) (6.0 kcal mol\(^{-1}\)) are remarkably close to the experimentally determined energy barriers for the adiabatic isomerizations of \( 1 \) and \( 2 \) (4.6 kcal mol\(^{-1}\) for both).

For comparison the method of calculation applied to stilbene gives a distinct global minimum for a twisted structure starting from either cis- or trans-stilbene.

**Outlook.** The simple extension of the conjugated π-system of stilbene to a \( p \)-styrylstilbene changes the mechanism for the photoinduced \( Z/E \) isomerization from diabatic to mainly adiabatic processes. This together with previous findings by us and others of adiabatic singlet and triplet \( Z/E \) photoisomerizations encourage us to try to explore the scope and limitations as well as applications of this conceptually new photoreaction in molecules with extended linear or cyclic π-systems.

**Acknowledgment.** Financial support from the Swedish Natural Science Research Council and the Swedish Board of Technical Development is gratefully acknowledged. We also thank Prof. K. Müllen, Mainz, for discussions and a sample of 3,5-di-tert-butylbenzyltriphenylphosphonium bromide.

Phthalocyaninato Polysiloxanes Substituted with Crown Ether Moieties


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**Abstract:** We describe the synthesis and characterization of phthalocyaninato polysiloxanes substituted with 15-crown-5, 18-crown-6, and 21-crown-7 rings. The degree of polymerization of the polymer samples depends on the size of the crown ether rings and varies between 6 and 18 units. NMR spectroscopy reveals that the polysiloxanes have a rigid structure with staggered phthalocyaninato (Pc) units. The binding of alkali-metal ions to the polymers and their monomers is reported and discussed. Upon polymerization of the phthalocyaninato dihydroxysilanes the electronic conductivity increases from <10\(^{-9}\) to 10\(^{-3}\) S/m. The polymer substituted with 21-crown-7 rings conducts sodium ions.

Phthalocyanines (Pc’s) substituted with crown ether rings are currently receiving great interest. Recently, we reported that these molecules can be aggregated by addition of alkali-metal salts, which become complexed to the crown ether rings. Electrical measurements of the aggregated species revealed an increase in electrical conductivity that is 2–3 powers of 10 higher than that of the nonaggregated ones.

In this paper we report another method of aggregating phthalocyanines. This method, first described by Joyner and Kenney, involves the polyecondensation of a phthalocyaninato dihydroxysilane containing four crown ether rings. In this way a stacked quasi-one-dimensional arrangement of crowned Pc’s is achieved in which the central silicon atoms are bridged through O\(^{\#}\) ligands (Figure 1). These stacks are expected to transport electrons and ions in the stacking direction: electrons via the central Pc macrocycles and cations via the crown ether moieties. Such compounds when incorporated in vesicle bilayers could be used as synthetic models to mimic both electron and ion channels of natural transport systems.

| Table I. \(^{13}C\) Chemical Shifts of Se in Solution and in the Solid State*
<table>
<thead>
<tr>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{1}C_{1} )</td>
</tr>
<tr>
<td>( C_{2}C_{2} )</td>
</tr>
</tbody>
</table>

*In ppm relative to tetramethylsilane. Solution CDCl\(_3\). Solution CDOD.

Polysiloxanes are formed by the uncatalyzed polycondensation of phthalocyaninato dihydroxysilanes for 1–12 h at 440 °C under

\(^{1} \)University of Utrecht. \(^{2} \)Delft University of Technology. \(^{3} \)University of Nijmegen.

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Phthalocyaninato Polysiloxanes

Scheme I

**Figure 1.** Linear chain of "crowned" phthalocyanines.

This paper deals with the synthesis of phthalocyaninato silanols containing 15-crown-5, 18-crown-6, and 21-crown-7 rings and of their polycondensation products prepared by a metal salt catalyzed polycondensation. Spectroscopic characterization, alkali-metal binding data, and electrical properties of the prepared compounds are reported.
Results and Discussion

Synthesis. 4,5-Dicyanobenzo-crown ether (2a-c, Scheme I, Figure 1) was converted into the corresponding 1,3-dimino-1,3-dihydroisoindole derivative (3a-c) by reaction with sodium methoxide and ammonia in methanol (yield 83%). Sodium salts, complexed in the crown ethers of 3a-c, were removed by treatment with an ion exchange resin. Reaction of 3a-c with SiC14 in quinoline at elevated temperatures (130 °C) produced the phthalocyaninato dichlorosilanes 4a-c. These dichloro compounds are extremely air- and moisture-sensitive. Hydrolysis is rapid if the solvent is not rigorously anhydrous or when a sample is kept open to the air. Compounds 4a-c were readily hydrolyzed by water to give the dihydroxysilane compounds 5a-c (30% yield from the isoindole derivative). Polycondensation of 5a-c was induced by heating in quinoline at 200 °C in the presence of CaCl2 as catalyst. Reaction times of 2–5 h gave a mixture of dimeric and trimeric compounds which are soluble in organic solvents. These polymers are soluble in concentrated sulfuric acid, but under these conditions the crown ether moieties are destroyed. Calcium chloride, complexed to the polymers, was removed by repeated sonication with water. Polycondensation of 5a-c in quinoline without the catalyst, resulted in high molecular weight polymers as well, but much longer reaction times were required (~350 h). Under the reaction conditions employed, the 15-crown-5 derivative 5a gave higher molecular weight polysiloxanes than the 18-crown-6 5b and the 21-crown-7 5c derivatives (vide infra). The rate of polycondensation apparently depends on the size of the crown ether ring. Compounds 1a-c were obtained as dark blue/black powders which were stable up to 280 °C but which decomposed at higher temperatures.

NMR Spectroscopy. The 1H NMR spectra of the dihydroxysilanes 5a-c are similar to those of their free base derivatives. The proton spectrum of 5c (CD3OD, 200 MHz) is presented in Figure 2A. Signals for the crown ether protons appear between 3.7 and 4.8 ppm, while the aromatic protons afford a broad singlet at 9.4 ppm. The Si-OH protons are present in the TMS region at 0 ppm (not shown). The pattern of the crown

Figure 2. NMR spectra of 5c and of its oligomer (n = 3-4) in solution: (A) 200 MHz 1H NMR (CD3OD) spectrum of 5c, (B) 200 MHz 13C NMR (CD3OD) spectrum of 5c, (C) 400 MHz 1H NMR (CDCl3) spectrum of oligomeric 5c, (D) 400 MHz 13C NMR (CDCl3) spectrum of oligomeric 5c. Signals marked X are due to solvent.
ether signals is complex, due to the chemically inequivalent ether fragments.

The $^{13}$C NMR (CD$_3$OD) spectrum of 5c is given in Figure 2B. It shows four different aromatic carbon atoms and the carbon atoms of the crown ether rings. This spectrum is the result of an attached proton test (APT) experiment, which was used to assign the signals. In this APT experiment, carbon atoms of CH groups provide negative signals together with literature data to assign the signals. In this APT experiment, which was used to assign the signals, the atoms C$_{11}$, C$_{11}$, and C$_{11}$, C$_{11}$, of the Pc macrocycle have signals enriched with $^{13}$C at C$_{11}$ and C$_{11}$.

The remaining signal at 132 ppm is ascribed to C$_{22}$, C$_{22}$,.

In our spectra of 5c we find that the axially coordinated OH groups have a preorganized conformation than in the monomer. The spectrum of the oligomer does not significantly change with increasing temperature and this fact, combined with the observed splitting of the aromatic signals, indicates that the oligomeric compounds have rigid structures. Since addition of KSCN to the oligomeric compounds resulted in a further upfield expansion of the crown ether signals without changes in the aromatic signals, it would appear that complexation of an ion does not influence the staggered conformation of the Pc macrocycles.

The $^{13}$C CPMAS NMR spectra of polysiloxanes 1a–c are poorly resolved, and compared to the spectra of 5c, the signals are broad. Attempts to separate spinning side bands from the isotropic chemical shifts failed so far. An increase in temperature did not result in any appreciable change of the spectra.

The $^{29}$Si CPMAS NMR spectrum of 5c gave, as expected, one intense singlet at $\sim$110.8 ppm whereas polymers 1 gave two signals, a large multiplet at $\sim$115.1 ppm and a small singlet at $\sim$138.5 ppm. The polymer signals came from silicon in two very different environments, namely in Si–O–Si–O–Si fragments and in the end groups Si–O–Si–OH. From these spectra (with poor resolution) we were only able to make a rough estimate of the chain lengths of the polymer; the numbers yielded are similar to those obtained by IR spectroscopy (see below).

UV/Vis Spectroscopy. The electronic absorption spectra of monomers 5 and their polycondensation products are given in Figure 3. Monomers 5 show a Q band with maximum at 678 nm and two weaker bands at 650 and 612 nm. During the condensation process of monomeric 5 to the polycondensation products the degree of conversion can be estimated by following the changes of the bands in the absorption spectra; the monomeric band at 578 nm loses intensity and simultaneously there appears a new band at 640 nm that can be ascribed to the dimeric species of 5. After 3 h the band at 678 nm had almost disappeared. Prolonged reaction times resulted in the appearance of a new band at 634 nm which we attribute to a trimeric species. For 5a and 5b further condensation resulted in a precipitate of higher oligomers that is not soluble in organic solvents. Only for 5c did we obtain a soluble oligomer (m > 3), and this gave a broad maximum between 610 and 560 nm. Apparently, the solubility of these oligomeric compounds increases with increasing size of their crown ether subunits.

The polycondensation process can be followed by TLC as well (Al$_2$O$_3$, eluent CHCl$_3$/MeOH 1:1 (v/v)). Monomeric and dimeric...
species can be separated over Sephadex LH 60.

**Infrared Spectroscopy.** The polycondensation process of 5 to 1 can be readily followed by IR spectroscopy. The spectra of compounds 5 differ considerably from those of the unsubstituted silicon phthalocyanines.\(^{34}\) Unfortunately, most Pc skeleton and Si–OH vibrations, which are often used to estimate the chain length by end group analysis, are masked by the vibrations of the crown ether rings. In our condensed compounds the antisymmetric Si–O–Si stretch vibration, which is visible in unsubstituted phthalocyaninato polysiloxanes between 1000 and 1130 cm\(^{-1}\),\(^{3e}\) is dominated by the aliphatic ether bands. This IR method is therefore not expected to give accurate results for the degree of polymerization of our condensed materials.

Figure 4 shows the IR spectra of monomer 5a and its polymer 1a. The intensity of the absorption band at 870 cm\(^{-1}\), ascribed to the Si–OH stretch vibration,\(^{36}\) decreases during the polycondensation process and, simultaneously, a complex band between 900 and 840 cm\(^{-1}\) appears. The weak absorption at 820 cm\(^{-1}\), assigned to the antisymmetric O–Si–O stretch vibration,\(^{36}\) and the bands at 940 and 980 cm\(^{-1}\) disappear as well. Other notable changes upon polymerization are the increase in intensity of the bands at 760 and 1610 cm\(^{-1}\) and the disappearance of the band at 1520 cm\(^{-1}\); the intensity of bands at 1480, 1420, 1350, 1290, and 1210 cm\(^{-1}\) remain constant. An indication of the chain length of polymers 1a–c was obtained with use of relative intensities and intensity changes of the IR bands mentioned. The IR spectra of isolated mono-, di-, and trimeric derivatives of 5 were used as references, and for these derivatives the ratio of the absorbances were plotted versus molecular weight. The molecular weights of the polymers were subsequently derived by linear extrapolation. This method can only be applied to polymers with relatively short chain lengths. For samples prepared by heating for 70 h at 200 °C the degree of polymerization was calculated to be \(m = 14-18\) for 1a, \(m = 10-15\) for 1b, and \(m = 6-8\) for 1c. These results reveal that the length of the polymers depends on the size of the substituent. The formation of relatively high molecular weight polymers is favored when the substituent is small.

Alkali-Metal Binding. The association constants, \(K_a\), and the free energies of complexation, \(\Delta G^o\), of 5b and 5c and their corresponding soluble oligomers (\(m = 3-5\)) with various alkali-metal ions were determined by the picrate extraction method developed by Cram.\(^{6}\) This method is not applicable to 5a and its oligomers, because not only was 5a too soluble in water but also there was strong emulsion formation on addition of picrate. In Table II are presented the association constants (\(K_a\)) which were calculated assuming a 1:1 complex formation between crowns and cations. In Figure 5 the \(\Delta G^o\) values of the various complexes (calculated from \(K_a\)) are presented graphically.

For all alkali-metal ions except Cs\(^+\), compound 5b shows a binding profile similar to that of its copper derivative\(^{6d}\). Compound 5b is a good complexing agent for K\(^+\), because the 18-crown-6 ethers have a diameter that matches the diameter of this ion. The Rb\(^+\) and Cs\(^+\) ions are too large to be encapsulated in these crown ethers and they may, therefore, induce dimer formation of the phthalocyanines as was observed for the copper derivative of 5b.\(^{6e}\) UV/vis spectra, however, show that such dimer formation does not occur, probably because of steric hindrance by the axial OH groups. We can not exclude, however, the formation of a non-coplanar dimer.

Oligomeric 5c like 5b show a somewhat more selective binding profile toward alkali-metal ions than the monomer. The binding profile of 5c is similar to that of its copper derivative\(^{6a}\) and the 21-crown-7 rings prefer the larger Rb\(^+\) and Cs\(^+\) ions over the smaller ions. For oligomeric 5b and 5c a further increase in selectivity is to be expected for the higher molecular weight polymers. The reason that the oligomers show more selective binding than the monomers may be related to a difference in

---

**Figure 4.** Infrared spectra of 5a (A) and 1a (B).

**Figure 5.** Free energies of binding picrate salt to 5b (●) and of picrate salt to 1b (\(m = 3\) (A) (A). Free energies of binding of picrate salt to 5c (●) and of picrate salt to oligomer 1c (\(m = 4-5\)) (A) (B).
**Phthalocyaninato Polysiloxanes**

Table II. Association Constants of Alkali Metal Picrate Salt–Phthalocyanine Complexes

<table>
<thead>
<tr>
<th>host</th>
<th>cation of guest</th>
<th>$K_a$, $10^{-4}$ M$^{-1}$</th>
</tr>
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<tbody>
<tr>
<td>5b</td>
<td>Li$^+$</td>
<td>9.8</td>
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<td></td>
<td>K$^+$</td>
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<tr>
<td></td>
<td>Rb$^+$</td>
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</tr>
<tr>
<td></td>
<td>Cs$^+$</td>
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</tr>
<tr>
<td>1b</td>
<td>Li$^+$</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>Na$^+$</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>K$^+$</td>
<td>481</td>
</tr>
<tr>
<td></td>
<td>Rb$^+$</td>
<td>70.8</td>
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<tr>
<td></td>
<td>Cs$^+$</td>
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</tr>
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<td></td>
<td>Na$^+$</td>
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<td></td>
<td>Na$^+$</td>
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<td>K$^+$</td>
<td>39.7</td>
</tr>
<tr>
<td></td>
<td>Rb$^+$</td>
<td>249</td>
</tr>
<tr>
<td></td>
<td>Cs$^+$</td>
<td>315</td>
</tr>
</tbody>
</table>

*Trimer, $h_m = 4–5$.

Figure 6. Saturation levels of polymers 1a–c for Na$^+$. The conformation of the crown ether rings in the two systems. An isolated crown ether has a folded conformation, and this conformation becomes more planar upon binding a cation. Because of the packed structure of the oligomers, the crown ethers are already forced into a more planar conformation. Upon complexing an ion with a small diameter, the most favorable conformation for binding cannot be attained. This results in a lower $\Delta G^+$ value for the oligomers than for the free crown ether. Another aspect that may play a role in complexing ions in the oligomers is electrostatic repulsion. Preorganization of the crown ethers in the oligomers will facilitate complexation of K$^+$ to 1b and of Rb$^+$ and Cs$^+$ to 1c. However, because of the packed structure of the oligomers, electrostatic repulsion between the complexed ions may prevent complete saturation of the crown ethers.

Information on the saturation level of cations in the phthalocyaninato polysiloxanes 1a–c was derived from extraction experiments on the solid polymers using varying amounts of aqueous sodium picrate solutions. The results obtained were corrected for adsorption of the picrate salts to solid samples. To this end similar experiments were performed with solid H$_2$Pc. The results are presented in Figure 6. For both the 18-crown-6 and 21-crown-7 polymers, 1b and 1c, a saturation level of 0.34 was measured. The maximum (Na$^+$/CE) ratio of 1.0 is not reached in our polymers because of the above-mentioned electrostatic repulsion between the complexed cations. This is supported by results from similar measurements on rigid (iso)cyananes) with pendant crown ether moieties. For these polymers also a ratio to crown ether ratio lower than 1 was found even for ions with diameters that match the size of the crown ethers.

**Electronic Conductivity.** The electrical properties of phthalocyanines 5 and 1 were studied in the solid state by ac impedance spectroscopy. All spectra revealed one semicircular arc, indicating that the materials behave as a dielectric with a minor contribution of electronic conductivity. Seebeck measurements showed that compounds 1a–c are p-type electronic conductors. The impedance spectra of 1a–c could be fitted to the equivalent circuit $R_Q$, where $R_Q$ represents the bulk electronic resistance, and $Q$ is the constant phase element (CPE), with an impedance $Z = (k(i\omega)^\beta)^{-1}$. For all samples the CPE has a value for $\beta$ of about 0.9, and $k$ has, therefore, the character of a capacitance. Compounds 5a–c and their dimeric and trimeric derivatives could not be measured accurately by ac impedance spectroscopy, because these compounds had bulk resistances that were too high.

The electronic conductivity, $\sigma$, and the conductivity activation energy, $E_a$, calculated from the ln $\sigma$ vs $1/T$ plots are presented in Table III. As can be seen from this table, the electronic conductivity increases upon polymerization of the monomeric compounds 5. The higher molecular weight polymers 1a and 1b show larger values for $\sigma$ than the lower molecular weight polymer 1c. The explanation for this is that charge transport will be facilitated in longer chains of Pc units because the number of intermolecular barriers that the charge carriers have to cross, is reduced. The conduction activation energies of 1a–c differ only slightly in magnitude. The $E_a$ values may be dependent on the intrinsic charge formation activation energy, $\Delta E_f$, on the activation energy of intramolecular charge migration, $\Delta E_m$, and on the activation energy of intermolecular charge crossing, $\Delta E_{\text{inter}}$. In our case we are inclined to believe that the $E_a$ values are to be correlated with migration only. Previously, we showed that the sum of $\Delta E_f$ and $\Delta E_{\text{inter}}$ has values over 1 eV, and $\Delta E_m$ is independent on the distance between the stacks, which in turn is determined by the size of the crown ether rings. Indeed, Table III shows that the $E_a$ values decreases in the series 1c $\rightarrow$ 1b $\rightarrow$ 1a.

**Ionic Conductivity.** The occurrence of ionic conduction in compounds 1a–c was tested by using these polymers as a membrane in the concentration cell Na-analagam[1]Na picrate (30 mol %)-polymer complex[Hg(II)]. The open-circuit voltage (OCV) of this cell was measured at various time intervals of utilization in the discharge mode at 80 °C. For the 15-crown-5 polysiloxane 1a and the 18-crown-6 polysiloxane 1b, no decrease of the OCV was observed during a period of 72 h. This result indicates that compounds 1a and 1b are not able to transport sodium ions, the rationale being the strong complexation of sodium ions by these polymers. For the 21-crown-7 polymer 1c, the OCV decreased with time from a starting value of approximately 1.5 V. This initial value is not well defined because $\Delta E_m$ was calculated at 0 °C. After 24 h, the OCV was 1.28 V and in the following period of 95 h, the OCV decreased to 0.73 V. Subsequent replacement of the Na-analagam(1) electrode for Hg resulted in an OCV of ~0.22 V. These data reveal that the 21-crown-7 polymer 1c does conduct sodium ions. From the open-circuit-voltage (OCV), load-circuit-voltages (LCV), and load-current ($I_L$) data for the concentration cell in the discharge mode, a discharge curve LCV/OCV vs $I_L$ was constructed (Figure 7). From the linear part of this

Table III. Electronic Conductivities ($\sigma$) and Conduction Activation Energies ($E_a$)

<table>
<thead>
<tr>
<th>compound</th>
<th>$\sigma$, S m$^{-1}$</th>
<th>$E_a$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a–c</td>
<td>$&lt;10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>1a</td>
<td>$7 \times 10^{-12}$ (25 °C)</td>
<td>0.23</td>
</tr>
<tr>
<td>1b</td>
<td>$3 \times 10^{-12}$ (25 °C)</td>
<td>0.29</td>
</tr>
<tr>
<td>1c</td>
<td>$1 \times 10^{-8}$ (100 °C)</td>
<td>0.38</td>
</tr>
</tbody>
</table>


Figure 7. Normalized load-circuit voltages vs load currents for a concentration cell with a sodium picrate-I complex as membrane; \( T = 80 ^\circ\text{C} \)

plot, an \( R_D \) of \( 1.3 \times 10^7 \Omega \) was calculated. This \( R_D \) value is very high compared to that found for \( K^+ \) transport through a polymer of poly(isocyanide) containing 18-crown-6 rings.12 An appreciable cation transport is only expected for ions having low free energies of complexation, i.e., for ions having an ionometric diameter smaller compared to that of the crown ether.13,14 This is the case of sodium complexed in the 21-crown-7 polymer. 

Rdc

The polycation transport through a polymer is low. This feature can be explained by the structural difference of the two polymers. In the poly(isocyanide) the crown ether rings are stacked on top of each other and form extended channels whereas in 1, the Pc units have a staggered arrangement. This latter arrangement could result in distortion or even the complete absence of a channel structure, and therefore, ion transport may be hindered or even prevented. Better results for cationic conductivity are to be expected for Pc polymers containing crown ether rings larger than 21-crown-7. The present data reveal that the crown ether rings and their size do play a distinctive role in cationic conductivity.

Experimental Section

Infrared spectra were measured on Perkin-Elmer 283 and Perkin-Elmer 1800 instruments. UV/vis spectra were recorded on a Perkin-Elmer 555 spectrometer. Solution \( ^1H \) NMR and \( ^13C \) NMR spectra were recorded on Varian EM 360, Bruker WP 200, and Bruker AM 400 instruments. Tetramethylsilane was used as the internal standard. \( ^1H \), \( ^13C \), and \( ^15N \) spectra were recorded on Bruker AM 500 and Bruker CXP 300 spectrometers. Abbreviations used are as follows: s = singlet, d = doublet, t = triplet, q = quartet, b = broad, and sh = shoulder. FAB mass spectra were recorded on a VG ZAB 2F spectrometer. Elemental analyses were performed by the Elemental Analytical Section of the Institute for Applied Chemistry TNO, Zeist, The Netherlands.

Seebeck measurements were performed as described previously.15 Impedance spectra were recorded in the temperature range of 250-250 \( ^\circ\text{C} \) and analyzed as described earlier.16 Ionic conductivity experiments were performed using concentration cells of the type Na-namalag(1)Na picrate (30 mol %)-Hg(II). In the discharge mode, the dc resistance \( R_{dc} \) was determined from normalized load-circuit voltages (LCV/OCV) vs load-current densities \( (I) \), the relation between these parameters being

\[
\text{LCV} = \frac{R_D}{\text{OCV}} \times I + 1
\]

where \( \text{OCV} \) represents the open-circuit voltage of the concentration cell. The \( \text{OCV} \) is governed by the Nernst expression

\[
\text{OCV} = \frac{kT}{q} \ln \frac{\alpha_N(1)}{\alpha_N(II)}
\]

OCV and LCV were recorded with a Teletac Airtronic TE 924 elec-

trometer. Elemental analyses were performed by the Elemental Analy-

tical Section of the Institute for Applied Chemistry TNO, Zeist, The

Netherlands.

Polycation of 5a To Give 1a. A mixture of 0.25 g (0.19 mmol) of 5a in 20 mL of quinoline (freshly distilled from barium oxide) and a catalytic amount of \( \text{CaCl}_2 \) was heated under an atmosphere of \( N_2 \) at 200 \( ^\circ\text{C} \) for 70 h. The resulting dark blue/black powder was isolated by filtration and washed with using a sonicator at 50 \( ^\circ\text{C} \) with subsequently \( H_2O (3x) \), DMSO, pyridine, and \( \text{CHCl}_3 \). The product was dried over \( P_2O_5 \) under reduced pressure: yield 0.2 g (80%); \( TGA 280 ^\circ\text{C} \) dec. 

Analogous reaction with \( \text{C}_{63} \) was performed from 3a: yield 74%; mp 95 \( ^\circ\text{C} \); FAB MS \( m/e 380 (M + H)^+ \). IR (KBr) 3400 (NH), 3200 (N-H), 1680 (C=O), 1580 (C=N), 800 (N-H). Anal. Calcd for \( \text{C}_{63} \): C, 65.6; H, 5.6. Found: C, 65.4; H, 5.7.

Dihydroxy(4,5,4',5',4'',5'',4''',5''''-tetakis(1,4,7,10,13-pentaoxatridecylcyclohexadienyl)phthalocyaninato)silicon(IV) (5b). This compound was synthesized from 3b as described for 5a: yield 75%; mp 95 \( ^\circ\text{C} \); FAB MS \( m/e 380 (M + H)^+ \); IR (KBr) as for 3a; \( \text{H NMR} (\text{CDCl}_3) \Delta 3.6-4.4 (m, 20 H, CH2O), 7.3 (s, 1 H, NH), 7.4 (s, 2 H, ArH), 7.7-8.2 (br s, 3 H, NH) ppm. 

Dihydroxy(4,5,4',5',4'',5'',4''',5''''-tetakis(1,4,7,10,13,16-heaxaazadecamethylenyl)phthalocyaninato)silicon(IV) (5c). This compound was synthesized from 3c as described for 3a: yield 76%; mp 102 \( ^\circ\text{C} \); FAB MS \( m/e 380 (M + H)^+ \); IR (KBr) as for 3a; \( \text{H NMR} (\text{CDCl}_3) \Delta 2.9-3.4 (m, 18 H, CH2O), 7.5 (s, 2 H, ArH), 7.7-8.2 (br s, 3 H, NH) ppm. 

Dihydroxy(4,5,4',5',4'',5'',4''',5''''-tetakis(1,4,7,10,13,16-heaxaazadecamethylenyl)phthalocyaninato)silicon(IV) (5e). This compound was synthesized from 2e as described for 3a: yield 69%; TGA 280 \( ^\circ\text{C} \) dec. Anal. Calcd for \( \text{C}_{64} \): C, 57.5; H, 5.59; N, 8.39. Found: C, 58.8; H, 5.6; N 9.1 (different samples gave varying results with a maximum variation of about 1.5% for all elements).
An Annulation Method for the Synthesis of Highly Substituted Polycyclic Aromatic and Heteroaromatic Compounds

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Abstract: A general strategy for the synthesis of highly substituted polycyclic aromatic and heteroaromatic compounds has been developed. The new aromatic annulation is achieved simply by the irradiation of a dihaloethane solution of an acetylene derivative and a vinyl or aryl diazo ketone. Mechanistically, the reaction proceeds via the photochemical Wolff rearrangement of the diazo ketone to generate an aryl- or vinylketene, followed by a cascade of three pericyclic reactions. A variety of substituted phenols, naphthalenes, benzofurans, benzothiophenes, indoles, and carbazoles can be prepared by using the method. The application of the aromatic annulation to the total synthesis of the marine alkaloid hyellazole demonstrates the synthetic utility of the method.

The invention of efficient methods for the synthesis of substituted aromatic compounds has commanded the interest of chemists since the time of the earliest synthetic organic investigations in the 19th century. Classical approaches to aromatic chemistry relied heavily on electrophilic and nucleophilic substitution reactions. In recent years, directed metathesis reactions have joined the classical substitution methods as another vehicle for the introduction of substituents onto preexisting aromatic rings.

A second approach to highly substituted aromatic compounds involves the application of annulation methods: convergent strategies in which the aromatic system is assembled from acyclic precursors in a single step, with all (or most) substituents already in place. Annulation strategies enjoy several advantages over classical linear substitution strategies, especially when applied to the preparation of highly substituted target molecules. For example, annulation routes frequently avoid the regiochemical ambiguities associated with aromatic substitution reactions and provide access to substitution patterns that cannot be obtained via the more conventional routes. The intrinsic convergent nature of annulation strategies facilitates the efficient assembly of highly substituted aromatics that would require long, multistep routes using classical substitution methodology.

Particularly noteworthy aromatic annulations which have been developed recently include methods based on Diels-Alder chemistry,1 carbonyl condensation reactions,2 and transition-metal-mediated processes. Prominent among the last class of reactions are the cobalt-mediated [2 + 2 + 2] acetylene cycloadditions investigated by Vollhardt3 and the Dötz reaction of Fischer carbenecycles.4 We have recently shown that addition of vinylketenates