were not refined. The final refinements were carried out using full-matrix least-squares techniques for non-hydrogen atoms. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation. Crystal data: $C_{16}H_{12}Cu_2N_6O_{10}$, $M_r = 575.40$, orthorhombic, space group $P2_1/c$, $a = 4.693(3)$, $b = 19.849(2)$, $c = 11.096(2)$ Å, $\beta = 96.90(2)^\circ$, $V = 1026.1(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.862\,\mathrm{g\,cm^{-3}}$, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71069$ Å, $F(000) = 576$, $\mu(\mathrm{Mo_{K\alpha}}) = 21.43\,\mathrm{cm^{-1}}$, $T = 25\,^\circ\mathrm{C}$, $2\theta_{max} = 55.1^\circ$, 2447 reflections measured, 934 observed ($I > 2.00\sigma(I)$), number of parameters 155; $R = 0.062$, $R_w = 0.062$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-103110. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit @ccdc.cam.ac.uk).

Gas adsorption measurements: The adsorption isotherms of CH_4 gas were measured according to the reported procedure.[18, 24, 25] The apparatus was equipped with a Cahn R-100 electrobalance contained within a SUS steel pressure chamber which was connected with two separate lines for evacuation and adsorbate gas pressurization. Prior to adsorption measurement, in order to remove the solvated water molecules, the sample (50–80 mg) was dried under reduced pressure at 25 °C until no further weight loss was observed. The adsorbate CH_4 was dosed into the adsorption chamber, then the change of the weight of the sample was monitored. The entire adsorption isotherms were determined by increasing the adsorbate gas pressure to a maximum of 31 atm.

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Formation of Supramolecular Polymers from Homoditopic Molecules Containing Secondary Ammonium Ions and Crown Ether Moieties[**]

Nori Yamaguchi and Harry W. Gibson[*]

Chemists are extending the concept of self-organizing noncovalent interactions into the field of material science to control and engineer linear and network supramolecular polymers.[1] Such interactions permit reversibility in the polymeric materials at the molecular level to afford thermodynamically controlled suprastructures.[2] This factor is advantageous for producing polymers with the potential for commercial use, since kinetically induced defects in conventional covalently bonded polymers are irreversible.

Strong associations between self-organizing building blocks promote the construction of well-defined supramolecular polymeric materials with properties comparable to covalent polymers.[3] This prompted us to utilize a simple system with dibenzylammonium hexafluorophosphate and dibenzo-[24]crown-8 (DB24C8) units, between which the association constant is desirably high ($K_a = 2.7 \times 10^4\,\mathrm{M^{-1}}$ in [D$_3$]chloroform at 25 °C).[4] Association of homoditopic molecules that contain such complimentary units spontaneously leads to reversible chain extension in 1:1 stoichiometric solutions to form linear supramolecular polymers based on pseudorotaxane formation.

The synthetic methodologies employed for the homoditopic molecules are depicted in Scheme 1 and the constructions

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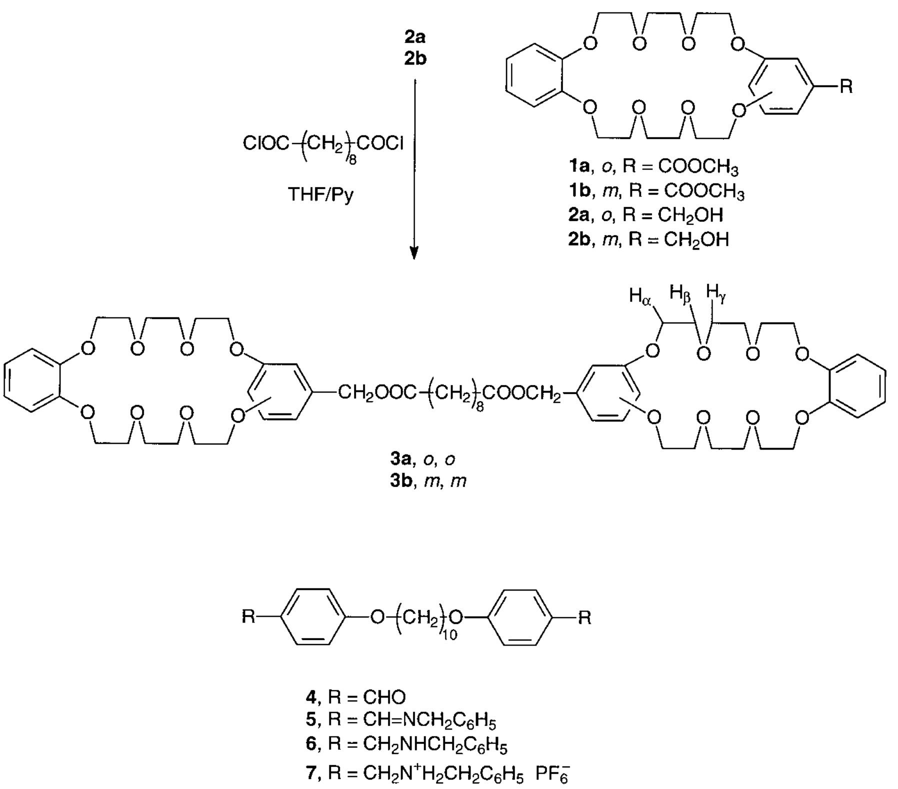
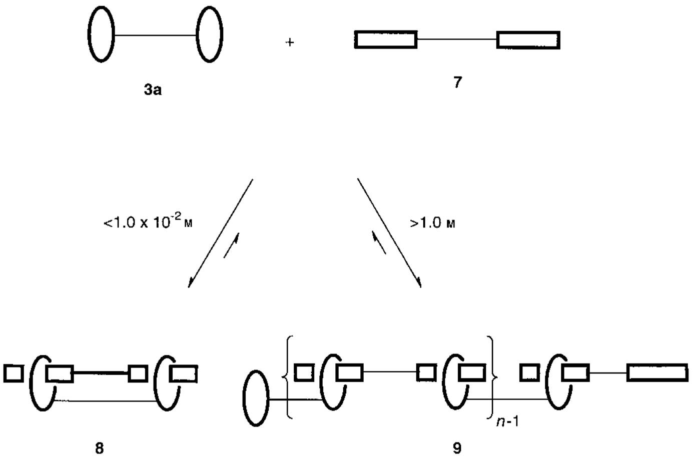


Scheme 1. Syntheses of **3a**, **3b**, and **7**.

of self-organized supramolecules are illustrated in Scheme 2. The ^1H NMR spectrum of an equimolar solution of **3a** and **7** in [D$_6$]acetone/[D$_3$]chloroform (1/1) at 22 °C showed three sets of signals for the benzylic protons of **7** (Figure 1 d).[5] Two of these can be attributed to the signals for complexed **7** while the other set corresponds to the signals for uncomplexed **7** based on the argument of slow exchange on the ^1H NMR time scale. The two sets of signals for complexed **7** arise from two different pseudorotaxane structures, the cyclic dimer **8** and linear chain **9**. The chemical shifts of the signals for complexed **7** in the 1:1 cyclic dimer **8** are unique from those in the linearly linked chain **9** as a consequence of the discrete geometry adopted by **8**. A series of 1.0×10^{-2} M solutions of **7** were prepared with nonstoichiometric amounts of **3a** (from 2.0×10^{-2} to 8.0×10^{-2} M) and the ^1H NMR spectra were recorded at 22 °C (Figure 2) so that the two sets of signals could be assigned properly. An increase in the concentration of **3a** with respect to **7** shifts the complexation equilibrium toward the formation of the 1:2 complex **7**:(**3a**)$_2$, which emulates the repeating sequence in **9**. Since the signals at $\delta = 4.53$ and 4.63 become more intense while the signals at $\delta = 4.45$ and 4.74 become less intense as the concentration of **3a** increases the former (inner) signals correspond to the benzylic protons of complexed **7** in the linearly linked chain **9** and the latter (outer) signals to those in the 1:1 cyclic dimer **8**.



Scheme 2. Illustration of the construction of the supramolecules **8** and **9** from **3a** and **7**.

The ^1H NMR spectra (Figure 1) recorded at different concentrations of equimolar solutions of **3a** and **7** in [D$_6$]acetone/[D$_3$]chloroform (1/1) at 22 °C revealed that both the ratio of **8**:**9** and the extent of aggregation in **9** are concentration dependent. At lower equimolar concentrations (less than 1.0×10^{-2} M) the ^1H NMR spectra revealed more intense signals for complexed **7** in the cyclic dimer **8** than

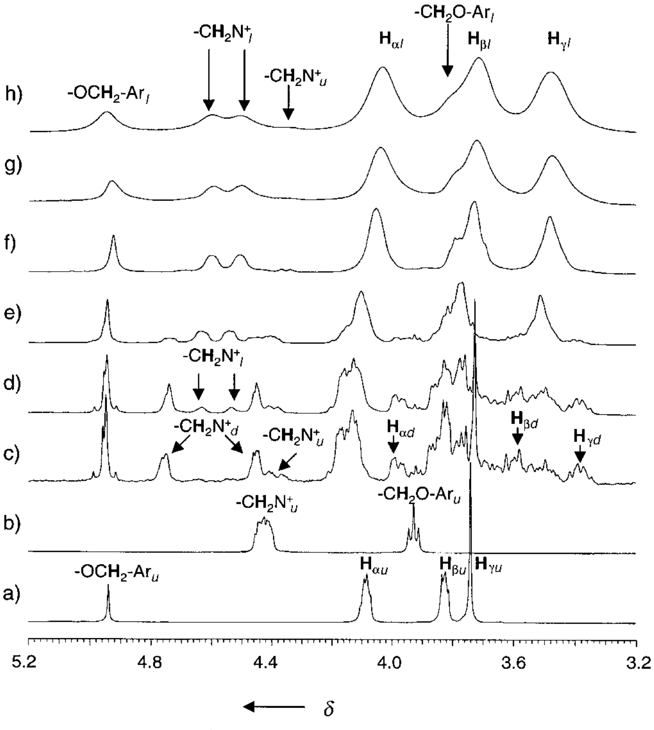


Figure 1. The stacked ^1H NMR spectra (400 MHz, [D$_6$]acetone/CDCl$_3$ (1/1), 22 °C) of solutions of **3a** and **7** at various concentrations: a) 1.0×10^{-2}/0 M, b) 0/1.0×10^{-2} M, and equimolar solutions c) 1.0×10^{-3} M, d) 1.0×10^{-2} M, e) 0.10 M, f) 0.50 M, g) 1.0 M, and h) 2.0 M. The three sets of signals are for uncomplexed **3a** and **7** (*u*), **8** (*d*), and **9** (*l*).

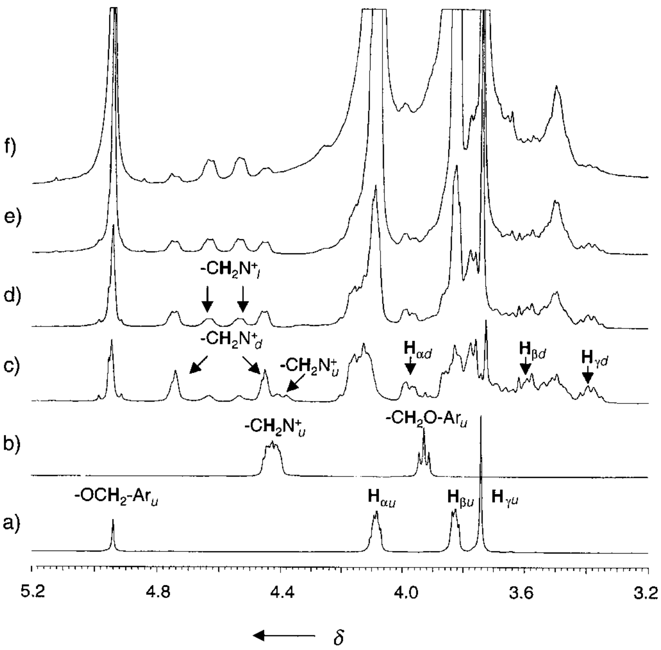


Figure 2. The stacked ^{1}H NMR spectra (400 MHz, [D$_6$]acetone/[D$_3$]chloroform (1/1), 22 °C) of solutions of **3a** and **7** at a) $1.0 \times 10^{-2}/0$ M, b) $0/1.0 \times 10^{-2}$ M, c) $1.0 \times 10^{-2}/1.0 \times 10^{-2}$ M, d) $2.0 \times 10^{-2}/1.0 \times 10^{-2}$ M, e) $4.0 \times 10^{-2}/1.0 \times 10^{-2}$ M, f) $8.0 \times 10^{-2}/1.0 \times 10^{-2}$ M . The three sets of signals are for uncomplexed **3a** and **7** (*u*), **8** (*d*), and **9** (*l*).

in the linear chain **9**. For instance, 72 and 66% of each homoditopic molecule are consumed to form the 1:1 cyclic dimer **8** in 1.0×10^{-3} and 1.0×10^{-2} M equimolar solutions at 22 °C, respectively (Table 1). The NOESY spectrum of the 1.0×10^{-3} M equimolar solution recorded at 22 °C showed a through-space interaction between the protons of the methylene units of corresponding homoditopic molecules **3a** and **7**, which indicated the presence of the 1:1 cyclic dimer **8**. In contrast, the signals for the 1:1 cyclic dimer are no longer observed (Figure 1h) at the highest equimolar concentration we examined (2.0 M), which indicated its absence.[6] Since the concentrations of the end groups in the supramolecular polymers **9** are readily determined by integration of the signal for uncomplexed **7** in the ^{1}H NMR spectra, one can estimate the average molecular weight of the linearly linked chain **9** at a given concentration (Table 1).[7] For instance, in the 1.0 M equimolar solution $M_n = 15$ kDa ($n = 7.5$), while the 2.0 M equimolar solution[8] gives an even higher molecular weight of 18 kDa ($n = 9.1$). Substantially broadened signals (Figures 1g and 1h) strongly support the formation of large supramolecular polymers **9** in solution.[9]

Table 1. Percentages of ammonium ion moieties in dimer **8** and supramolecular polymer **9**, and the average number of repeat units *n* in **9**.[a]

Equimolar conc. [M]	% **7** in **8** at 22/ – 40 °C	% uncomplexed **7** at 22/ – 40 °C	n[c] at 22/ – 40 °C	M_n[d] [kDa] at 22/ – 40 °C
2.0	0/ – [b]	5.5/ – [b]	9.1/ – [b]	18/ – [b]
1.0	3.4/ – [b]	6.4/ – [b]	7.5/ – [b]	15/ – [b]
0.50	12/15	7.9/5.1	5.6/8.3	11/16
0.10	23/27	20/5.4	1.9/6.8	3.8/13
0.01	66/81	16/4.3	1.1/2.2	2.2/4.4
0.001	72/94	20/2.3	0.70/1.3	1.4/2.6

[a] Calculated from the ^{1}H NMR spectra of equimolar solutions ([D$_6$]acetone/[D$_3$]chloroform, 1/1) of **3a** and **7** at various concentrations and temperatures. [b] The ^{1}H NMR spectra of the 2.0 and 1.0 M equimolar solutions recorded at lower temperatures exhibited severe signal broadening, which prevented accurate signal integration. [c] For the determination of *n* see reference [7]. [d] The number average molecular weight (M_n) of the aggregate was calculated from the following equation; $M_n = n \times 1980$ Da (repeat unit mass).

The plot of reduced viscosity η_{red} versus concentration of equimolar solutions of **3a** and **7** in chloroform/acetone (1/1) at 22 °C is nonlinear (Figure 3b), which reflects the increase in size of the supramolecular polymer **9** with concentration, as shown by the ^{1}H NMR data. In fact the viscosities of 1.0 and 2.0 M equimolar solutions were too high to measure by this method. On the other hand, a completely different solution viscosity profile was observed for equimolar solutions of **3b**, a constitutional isomer of **3a**, and **7** (Figure 3a). It should be noted that the ^{1}H NMR spectrum of an equimolar solution of **1b** and dibenzylammonium hexafluorophosphate in the same solvent system displayed no sign of complexation.[10] A straight line with a small slope (Figure 3a) is consistent with the ^{1}H NMR observation that there is no complexation between **3b** and **7** in solution. It also indicates that the ionic strength per se has a negligible effect on viscosity under these experimental conditions. Therefore, the sharp increase in viscosity at higher concentrations (Figure 3b) is reflective of the aggregation between **3a** and **7**, which produces structures of large hydrodynamic volume, namely, **9**.

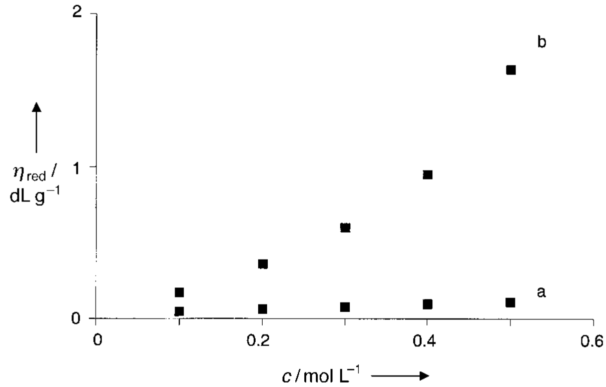


Figure 3. Reduced viscosity η_{red} as a function of concentration *c* in acetone/chloroform (1/1) at 22 °C for a) **3b** and **7** and b) **3a** and **7**.

Solid samples prepared by freeze-drying[11] the 1.0×10^{-2}, 0.10, and 0.50 M equimolar solutions of **3a** and **7** in acetone/chloroform (1/1) were analyzed by differential scanning calorimetry (DSC).[12] The M_n value of the supramolecular polymer **9** and the abundance of the 1:1 cyclic dimer **8** in each sample were estimated from low temperature ^{1}H NMR spectra (Table 1).[13] The DSC thermograms for the 0.10 and 0.50 M materials were entirely different from those observed for the pure, crystalline homoditopic molecules **3a** and **7**. As a result of self-organization amorphous polymers **9** with glass transition temperatures T_g above 50 °C were formed for the 0.10 and 0.50 M samples (57 and 59 °C, respectively). From end-group analysis the 0.10 and 0.50 M materials contained supramolecular polymers **9** of $M_n = 13$ and 16 kDa, respectively (Table 1). The polymers became rubberlike materials

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above T_g and thus they may be processable. A high degree of crystallinity was observed by optical microscopy in the case of the 1.0×10^{-2} M sample (81% cyclic dimer **8**, Table 1). Presumably, compactness and the semi-rigid nature of **8** allow stable packing in the crystal lattice.[14]

It is noteworthy that flexible, creasible, amorphous, and transparent films can be cast from 1:1 stoichiometric solutions of **3a** and **7**. Such properties can only result from entanglement of linearly connected macro-sized aggregates. Similarly, since a polymer structure of high molecular weight is necessary for fiber formation,[15] the scanning electron microscope images (Figure 4) of a rodlike fiber with a regular diameter of 10 μm drawn from a concentrated equimolar solution of **3a** and **7** in acetone/chloroform (1/1) indicate a high degree of the linear chain extension in **9**.

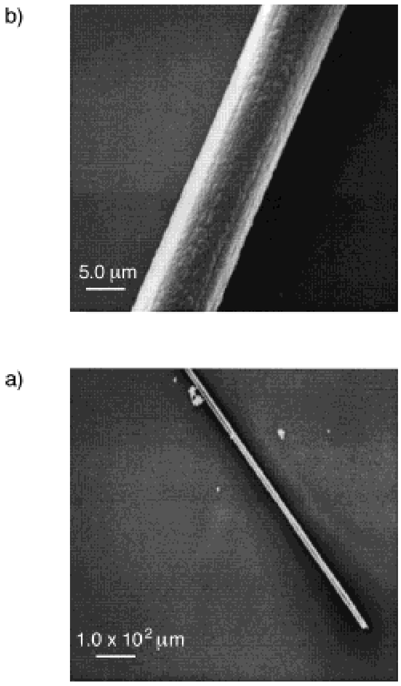

Figure 4. Longitudinal views of scanning electron micrographs of a fiber pulled from a concentrated (>2.0 M) acetone/chloroform (1/1) equimolar solution of **3a** and **7**; a) low resolution, b) high resolution.

In summary, the 1:1 cyclic dimer complex **8** is preferentially formed in dilute equimolar solutions ($<1.0\times10^{-2}$ M), while linear chain extension to **9** is observed almost exclusively in concentrated equimolar solutions (>1.0 M). The solution behavior of the self-organized supramolecules **9** was characteristic of large aggregates as demonstrated by the viscosity experiments. The solid state samples prepared by freeze-drying 0.10 and 0.50 M equimolar solutions showed that the supramolecules **9** are amorphous polymers. The preparation of films and fibers corroborates the polymeric nature of the self-organized suprastructures **9**.

Experimental Section

General procedure for **2a** and **2b**: Compounds **1a** and **1b**[16] were reduced with LAH in THF, followed by standard isolation and recrystallization from EtOH.

2a: 92% yield, m.p. 82–84 °C. ^{1}H NMR (400 MHz, $[D_3]$chloroform, 22 °C): $\delta = 3.83$ (8H, s), 3.91 (8H, t, $J = 4.4$ Hz), 4.13–4.17 (8H, m), 4.58 (2H, s), 6.82–6.90 (7H, m); MS (FAB): m/z: 478.3 $[M]^+$; HR-MS (FAB): calcd for $[M]^+$ $C_{25}H_{34}O_9$: 478.2203; found: 478.2200; elemental analysis calcd for $C_{25}H_{34}O_9$: C 62.73, H 7.17; found: C 62.61, H 7.15.

2b: 83% yield, m.p. 78–80 °C. ^{1}H NMR (400 MHz, $[D_3]$chloroform, 22 °C): $\delta = 3.72$ (8H, s), 3.81 (8H, m), 4.14 (8H, m), 4.58 (2H, d, $J = 6.4$ Hz), 6.52 (2H, d, $J = 1.6$ Hz), 6.61 (1H, t, $J = 1.6$ Hz), 6.88–6.93 (4H, m); MS (FAB): m/z: 478.3 $[M]^+$; HR-MS (FAB): calcd for $[M]^+$ $C_{25}H_{34}O_9$: 478.2203; found: 478.2183; elemental analysis calcd for $C_{25}H_{34}O_9$: C 62.73, H 7.17; found: C 62.58, H 7.17.

General procedure for **3a** and **3b**: Sebacoyl chloride was condensed with **2** (2.00 equiv) in pyridine (2.20 equiv) and anhydrous THF at 40°C, followed by standard isolation and recrystallization from EtOH.

3a: 80% yield, m.p. 120–122 °C. ^{1}H NMR (400 MHz, $[D_3]$chloroform, 22 °C): $\delta = 1.23$–1.27 (8H, m), 1.57 (4H, m), 2.31 (4H, t, $J = 8.0$ Hz) 3.83 (8H, s), 3.91 (8H, t, $J = 4.0$ Hz), 5.00 (4H, s), 6.82 (1H, d, $J = 8.0$ Hz), 6.85–6.91 (6H, m); MS (FAB): m/z: 1123.2 $[M{+}H]^+$; HR-MS (FAB): calcd for $[M]^+$ $C_{60}H_{82}O_{20}$: 1122.5399; found: 1122.5374; elemental analysis calcd for $C_{60}H_{82}O_{20}$: C 64.14, H 7.36; found: C 64.10, H 7.40.

3b: 90% yield, m.p. 78–80 °C. ^{1}H NMR (400 MHz, $[D_3]$chloroform, 22 °C): $\delta = 1.25$–1.29 (8H, m), 1.63 (4H, m), 2.33 (4H, t, $J = 8.0$ Hz), 3.72 (8H, s), 3.82 (4H, t, $J = 4.0$ Hz), 3.85 (4H, t, $J = 4.0$ Hz), 4.15 (8H, t, $J = 4.0$ Hz), 5.00 (4H, s), 6.48 (2H, d, $J = 1.6$ Hz), 6.66 (1H, t, $J = 1.6$ Hz), 6.87–6.92 (4H, m); MS (FAB): m/z: 1123.2 $[M{+}H]^+$; HR-MS (FAB): calcd for $[M]^+$ $C_{60}H_{82}O_{20}$: 1122.5399; found: 1122.5372; elemental analysis calcd for $C_{60}H_{82}O_{20}$: C 64.14, H 7.36; found: C 64.06, H 7.29.

5: Condensation of **4**[17] and benzylamine (2.00 equiv) in refluxing toluene afforded an off-white solid, 4.56 g, 88% yield, m.p. 105–107 °C. ^{1}H NMR (400 MHz, $[D_3]$chloroform, 22 °C): $\delta = 1.34$ (8H, s), 1.46 (4H, m), 1.79 (4H, m), 3.99 (4H, t, $J = 6.4$ Hz), 4.79 (4H, s), 6.92 (4H, d, $J = 8.8$ Hz), 7.24–7.34 (10H, m), 7.72 (4H, d, $J = 8.8$ Hz), 8.31 (2H, s); MS (FAB): m/z: 561.5 $[M{+}H]^+$; HR-MS (FAB): calcd for $C_{38}H_{44}N_2O_2$ ($[M{+}H]^+$): 561.3481; found: 561.3474; elemental analysis calcd for $C_{38}H_{44}N_2O_2$: C 81.39, H 7.91; found: C 81.28, H 7.86.

6: Reduction of **5** in MeOH with $NaBH_4$ (2.00 equiv) gave an off-white solid, 3.12 g, 93%, m.p. 64–66 °C. ^{1}H NMR (400 MHz, $[D_3]$chloroform, 22 °C): $\delta = 1.34$ (8H, s), 1.46 (4H, m), 1.78 (4H, m), 3.75 (4H, s), 3.80 (4H, s), 3.95 (4H, t, $J = 6.4$ Hz), 6.86 (4H, d, $J = 8.8$ Hz), 7.25 (4H, d, $J = 8.8$ Hz), 7.26–7.34 (10H, m); MS (FAB): m/z: 565.5 $[M{+}H]^+$; HR-MS (FAB): calcd for $C_{38}H_{48}N_2O_2$ ($[M{+}H]^+$): 565.3794; found: 565.3790; elemental analysis calcd for $C_{38}H_{48}N_2O_2$: C 80.81, H 8.57; found: C 80.68, H 8.47.

7: A solution of **6** in MeOH was treated with excess 2 M HCl. The solvent was removed to give an off-white solid, which was then suspended in acetone and aqueous NH_4PF_6 added until complete dissolution occurred. The solvent was evaporated and the resulting solid was washed thoroughly with H_2O to afford an off-white solid, 2.90 g, 87% yield, m.p. 150 °C (decomp). ^{1}H NMR (400 MHz, $[D_6]$acetone, 22 °C): $\delta = 1.34$ (8H, s), 1.45 (4H, m), 1.76 (4H, m), 4.01 (4H, t, $J = 6.4$ Hz), 4.58 (4H, s), 4.61 (4H, s), 6.99 (4H, d, $J = 8.8$ Hz), 7.45–7.58 (10H, m), 7.50 (4H, d, $J = 8.8$ Hz); MS (FAB): m/z: 711.6 $[M-PF_6]^+$; HR-MS (FAB): calcd for $C_{38}H_{50}N_2O_2PF_6$ ($[M-PF_6]^+$): 711.3514; found: 711.3528; elemental analysis calcd for $C_{38}H_{50}N_2O_2P_2F_{12}$: C 53.27, H 5.88; found: C 53.17, H 5.81.

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[5] Based on the assumption that the complexation at the ammonium ion moieties of **7** are independent of each other the association constant for pseudorotaxane formation between the ammonium ion moieties of **7** and DB24C8 in $[D_6]$acetone/$[D_3]$chloroform (1/1) at 22 °C was calculated as $3.5\times10^{2}\,\text{M}^{-1}$ by single point measurement (slow exchange) by using ^{1}H NMR spectroscopy.

[6] The NOESY spectra of 1:1 stoichiometric solutions of **3a** and **7** could not be recorded at concentrations greater than 1.0 M because of overloading of the analogue to digital converter.

[7] The average molecular weight of **9** was calculated on the assumption that the cyclic oligomers such as 2:2 and 3:3 complexes were absent. It is noteworthy that linear polymerization is highly favored over cyclization at high solution concentrations (for example, 1.0 M). For reviews on cyclization versus linear polymerization, see a) G. Odian, *Principles of Polymerization*, 3rd ed., Wiley, New York, **1991**, p. 73; b) S. C. Hamilton, J. A. Semlyen, *Polymer* **1997**, *38*, 1685–1691. Therefore, the assumption of the absence of the oligomeric cyclic complexes is valid in the more concentrated solutions. The percentage of ammonium ion units l in **9** is equal to 100 minus the percentage of ammonium ion units d in **8** ($l+d=100$) The ratio of the percentage of ammonium ion units l in **9** to the percentage of uncomplexed ammonium ion units u is equal to $2n$ (n = degree of aggregation). Thus, this equation yields $n=(100\,\% - d/2u)$. From the n value and the repeat unit mass (1980 Da) the number average molar mass M_n of **9** was calculated.

[8] A mixture of acetone/chloroform (1/1) was added to a flask containing **3a** (1.1233g) and **7** (0.8568 g) until complete dissolution occurred. The solution was slowly concentrated and vacuum dried to afford **9**, which was then diluted with acetone/chloroform (1/1) to 0.50 mL.

[9] Similar effects have been observed in a supramolecule assembled from a heteroditopic precursor. See N. Yamaguchi, D. S. Nagvekar, H. W. Gibson, *Angew. Chem.* **1998**, *110*, 2518–2520; *Angew. Chem. Int. Ed.* **1998**, *37*, 2361–2364.

[10] The ^{1}H NMR spectrum of a 1:1 stoichiometric solution of **1b** and dibenzylammonium hexafluorophosphate at 1.0×10^{-2} M in $[D_6]$acetone/$[D_3]$chloroform (1/1) did not show extra sets of signals from slow exchange or changes in the chemical shifts from fast exchange. The *m*-phenylene linkage prevents pseudorotaxane formation in solution.

[11] The solutions were frozen at −93 °C with an acetone–ethanol/liquid nitrogen bath and the solvents were removed under high vacuum to give yellow–orange solids.

[12] To eliminate sample history the freeze-dried samples were initially heated to 100 °C and cooled to 30 °C at the rate of 10 °C min^{-1}. They were then heated at 10 °C min^{-1} and the DSC thermograms were recorded.

[13] The ^{1}H NMR spectra of equimolar solutions of **3a** and **7** at 1.0×10^{-2}, 0.10, and 0.50 M in $[D_6]$acetone/$[D_3]$chloroform (1/1) were essentially unchanged from −40 to −60 °C. Below this temperature the ^{1}H NMR spectra of the solutions were unable to be recorded because of partial freezing of the solvents. Thus, M_n values of the freeze-dried (−93 °C) samples were estimated by simple integration of relevant signals of the spectra recorded at −40 °C.

[14] A similar dimeric cyclic species has recently been reported: P. R. Ashton, I. Baxter, S. J. Cantrill, M. C. T. Fyfe, P. T. Glink, J. F. Stoddart, A. J. P. White, D. J. Williams, *Angew. Chem.* **1998**, *110*, 1344–1347; *Angew. Chem. Int. Ed.* **1998**, *37*, 1294–1297.

[15] It must be noted that these fibers were formed in a manner analogous to that used for covalently bonded macromolecules (dry spinning: H. R. Allcock, F. W. Lampe, *Contemporary Polymer Chemistry,* 2nd ed., Prentice-Hall, New Jersey, **1990**, pp. 508–511) and not by gelation in a poor solvent, which has also yielded fibers by self-organization: a) C. F. van Nostrum, S. J. Picken, A.-J. Schouten, R. J. M. Nolte, *J. Am. Chem. Soc.* **1995**, *117*, 9957–9965; b) M. de Loos, J. van Esch, I. Stokroos, R. M. Kellogg, B. L. Feringa, *J. Am. Chem. Soc.* **1997**, *119*, 12675–12676; c) N. Kimizuka, S. Fujikawa, H. Kuwahara, T. Kunitake, A. Marsh, J.-M. Lehn, *J. Chem. Soc. Chem. Commun.* **1995**, 2103–2104. Linear hydrogen-bonded supramolecular aggregates have been formed into fibers from the molten state.[2f–h] For a review on fiber theory, see H. L. Needles, *Handbook of Textile Fibers, Dyes, and Finishes*, Garland STPM, New York, **1981**, pp. 1–27.

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Cleavage of Palladium Metallacycles by Acids: A Probe for the Study of the Cyclometalation Reaction**

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The cyclometalation reaction[1] constitutes one of the first known examples of C–H bond activation, which is a major achievement of organometallic chemistry.[2] Of particular interest is the cyclometalation of a pendant aromatic ring, a process that constitutes a good model for C–H activation and has in addition led to many useful synthetic applications.[3–6]

Despite the number of studies devoted to this transformation,[7] contemporary work continues to provide important mechanistic information.[1a] A recent account by Canty and van Koten has pointed out the formal relationship that may be established between the cyclometalation reaction and the protonation of M–CH_3 and M–C_6H_5 bonds,[8] as well as the possible intermediary role of arenonium ions in both processes.[8, 9] Here we provide experimental evidence in support

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