158. Potassium Cryptate of a Macrobicyclic Ligand Featuring a Reducible Hexakis(phenylthio)benzene Electron-Acceptor Site

by **Marcel Mayor** and **Jean-Marie Lehn***

Laboratoire de Chimie Supramoléculaire, Institut Le Bel, Université Louis Pasteur, CNRS URA 422, 4, rue Blaise Pascal, F-67000 Strasbourg

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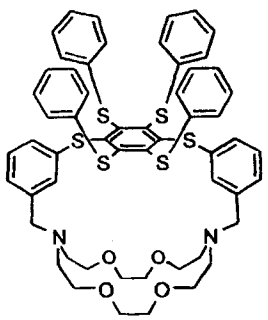
The synthesis and structural characterization of the macrobicyclic ligand **1** containing a reducible hexakis(phenylthio)benzene electron-acceptor site is described. It is based on the condensation of the tetraoxa-diazamacrocycle **3** with a suitably functionalized derivative **4** of hexakis(phenylthio)benzene. Complexation of a potassium cation by **1** gives the corresponding cryptate **2**, with a stability constant of *ca.* 4000 M^{-1} as determined by ^{1}H-NMR titration in CD_3CN. The reduction potential of the hexakis(phenylthio)benzene electron-acceptor site in **2** is shifted by 170 mV towards more positive values with respect to that in **1** by complexation of potassium.

Introduction. – Numerous macrocyclic ligands were synthesized over the last 30 years, and their cation coordination properties have been studied [1–3]. In particular, macropolycyclic ligands have been shown to form highly stable and selective inclusion complexes, cryptates, with a variety of metal ions. Of particular interest among them are those containing reducible electron-acceptor sites, which make possible the neutralization of the charge of the complexed cation by introduction of the required number of electrons onto the acceptor site(s). The resulting neutral species, termed *cryptatium*, may be described either as a radical ion pair or as a sort of molecular 'expanded atom'. A first member of the *cryptatium* family was obtained by electroreductive crystallization of a macrobicyclic tris(bipy) sodium cryptate [4]. Electrochemical neutralization of the corresponding complexes gave also calcio- and lanthano-cryptatium species [5].

As, on one hand, the reduction potential of the ligand is affected by the positive charge of the complexed cation, and, on the other hand, the binding strength of the cation depends on the reduction state of the acceptor site in the ligand, the two features are interdependent so that one may be used to monitor or to tune the other. Thus, antraquinone-functionalized polyether macrocycles have been used as redox switchable cation-transport system as well as redox-cation sensors [6].

Our aim was to explore the use of other electroreducible groups for cryptatium formation in order to extend the cryptatium family and to further explore the generation of 'molecular expanded metals' along these lines. Poly(phenylthio)-substituted aromatic systems are well-known for their host-guest chemistry [7]. Recently, they were shown to display remarkably low reduction potentials [8]. Therefore, such units appeared to be suitable candidates as reducible electron-acceptor sites in ligands.

We herein describe the synthesis and physical properties of the macrobicyclic ligand **1**, containing a hexakis(phenylthio)-substituted benzene unit as electron-acceptor site, and its potassium cryptate **2**.



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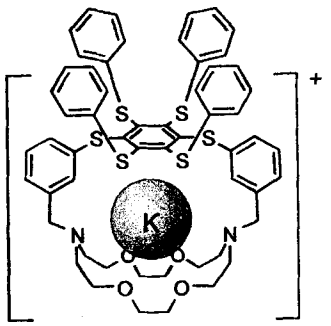

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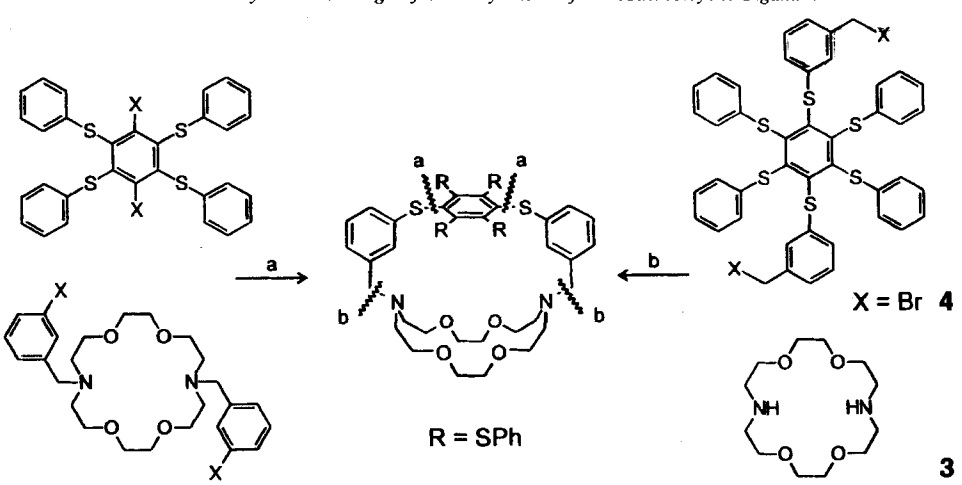
Synthesis of the Macrobicyclic Ligand 1. – Two strategies were considered for the synthesis of ligand **1** (*Scheme 1*). *Pathway a* was based on the attachement of *meta*-substituted benzyl groups to the N-sites of the tetraoxa-diaza macrocycle **3** [9] followed by reaction with the corresponding *para*-disubstituted tetrakis(phenylthio)benzene unit. This pathway seemed very promising, as both building blocks, *i.e.*, 1,4-dihalo-2,3,5,6-tetrakis(phenylthio)benzene and 4,13-bis(3-halobenzyl)-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane, were available in one step and in good yields, but the attempts to transform the halogens on either one of the two building blocks into SH groups failed. Substitution of the halogens by mercaptoalkyl-sodium salts was successful, but subsequent deprotection could not be achieved.

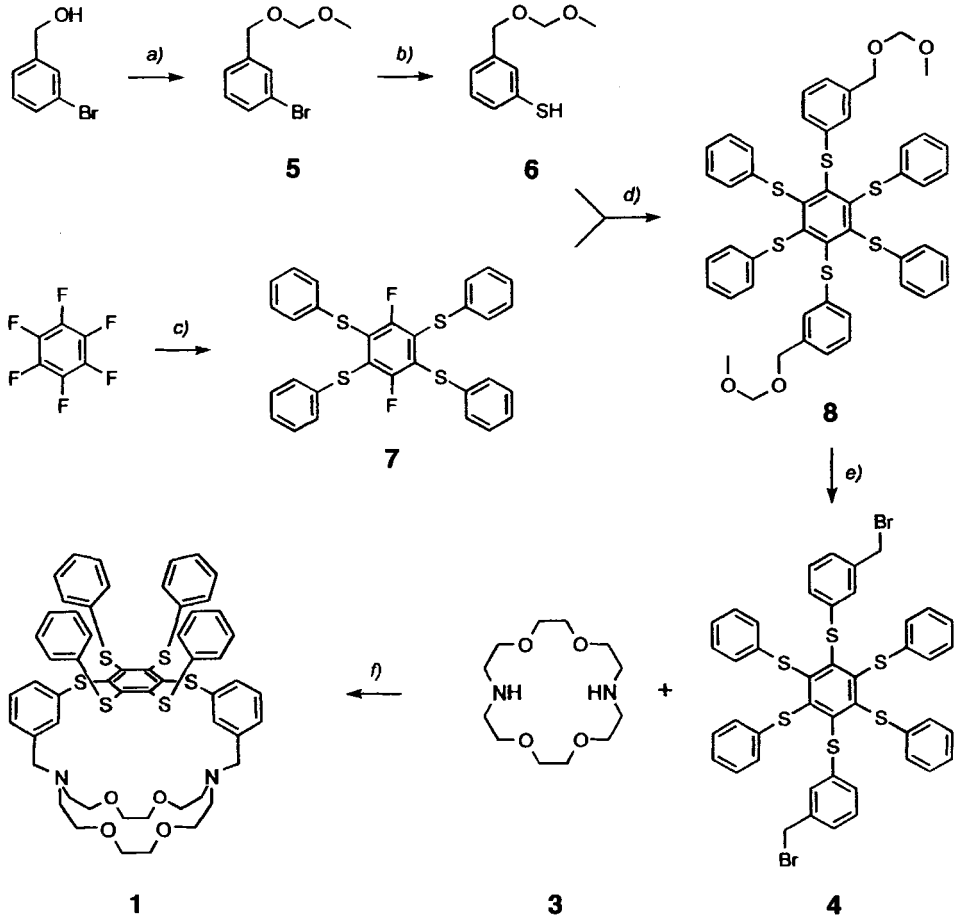
Pathway b was based on the condensation of the macrocycle **3** with a suitably functionalized derivative **4** of hexakis(phenylthio)benzene. Even though this pathway had more steps, it turned out to be successful and is depicted in *Scheme 2*.

The OH function of commercial 3-bromobenzyl alcohol was protected by reaction with $ClCH_2OMe$ in $EtN(i\text{-}Pr)_2$ at room temperature to give **5** in 91% yield. Introduction

Scheme 1. *Synthetic Strategies for the Synthesis of the Macrobicyclic Ligand* **1**



Scheme 2. *Synthesis of the Macrobicyclic Ligand* **1**



a) $ClCH_2OMe$, $EtN(i\text{-}Pr)_2$, r.t.; 91%. *b*) 1. *t*-BuLi, THF, −78°. 2. 'S', −40° to r.t.; 65%. *c*) NaSPH, DMI, EtOH, 80°; 48%. *d*) 1. NaH, THF; 2. DMI; 40°; 45%. *e*) HCl, PBr_3, $CHCl_3$, r.t.; 82%. *f*) MeCN, $CaCO_3$, reflux; 35%.

of the SH function was achieved by treatment of **5** with 2 equiv. of *t*-BuLi in THF at −78°, followed by quenching at −40° with sulfur affording the (methoxy)methyl-(MOM)-protected 3-mercaptobenzyl alcohol **6** in 65% yield after column chromatography [10].

1,4-Difluorotetrakis(phenylthio)benzene (**7**) was obtained by nucleophilic aromatic substitution of four F-atoms by PhS^- anions. The desired 2,3,5,6-substitution pattern was expected, by analogy with the results reported for (isopropyl)mercaptyl anions [11]. Treatment of hexafluorobenzene with 4 equiv. of thiophenol-sodium salt in 1,3-dimethylimidazolidin-2-one (DMI)/EtOH (1:1) at 80° yielded **7** (48%).

A key step in the synthesis was the introduction of the two additional functionalized thiophenols on the central benzene core. The choice of F as leaving group was crucial in

order to compete with PhS itself as leaving group in the nucleophilic substitution reaction. A procedure similar to that described by *MacNicol et al.* [12] afforded the hexakis-(phenylthio)benzene containing two protected benzyl-alcohol functions **8**. Compound **6** was converted into its sodium salt by treatment with NaH in THF. After evaporation of the solvent, the latter was reacted with **7** in DMI at 40° to give the functionalized hexakis(phenylthio)benzene **8** in 45% yield.

Deprotection of the OH function of **8** with HCl followed by treatment with Br_3P in $CHCl_3$ at room temperature gave the dibromo derivative **4** (82% yield)[1]).

The second key step was the bridging of the macrocycle **3** with **4**. High-dilution conditions were employed in order to favor the intramolecular ring closure. An equimolar solution of **3** and **4** was added over a period of 3 days to a refluxing suspension of $CaCO_3$ in MeCN. The macrobicyclic ligand **1** was isolated in 35% yield by column chromatography as a yellow compound. It is fairly soluble in organic solvents such as $CHCl_3$, CH_2Cl_2, MeCN, or toluene, which allowed its characterization by ^{1}H- and ^{13}C-NMR, and FAB-MS.

The spectral and analytical data agree with the proposed structure for **1**. The ^{1}H-NMR spectra of **1** in $CDCN_3$ (*Fig. 1*) presents in the high-field region two *triplets* ($J = 6$ Hz) at 2.85 and 3.58 ppm for $O-CH_2-CH_2-N$, a *singlet* at 3.56 ppm for $O-CH_2-CH_2-O$, and a *singlet* at 3.80 ppm for the $PhCH_2$ protons. At lower field, apart from the signal for aromatic protons between 6.8 and 7.3 ppm, a broad signal at 6.78 ppm worth two protons may be attributed to the aromatic protons between the benzylic and the phenylthio connection, pointing inside the binding cavity.

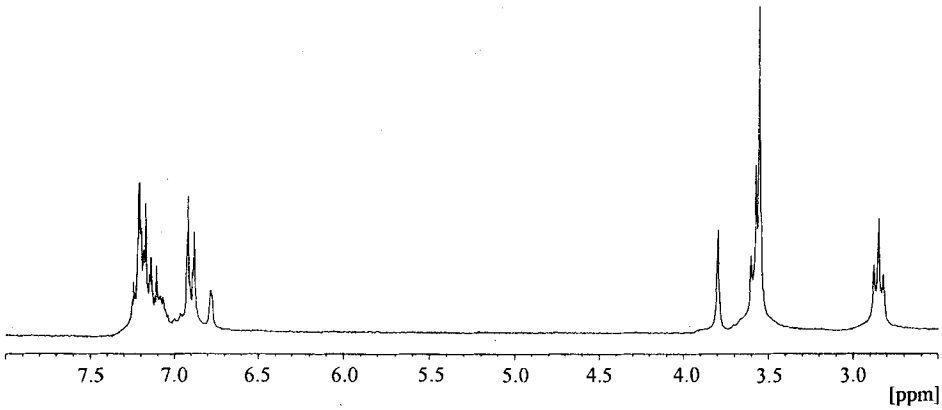


Fig. 1. *200-MHz ^{1}H-NMR Spectrum of the macrobiyclic ligand* **1** *in CD_3CN at 20°*

Potassium Complexation Properties. – The potassium-binding properties of **1** were studied by analyzing the ^{1}H-NMR spectral changes occurring on titration with KPF_6[2]). Addition of excess KPF_6 produced major shifts in the ^{1}H-NMR spectra for the $O-CH_2-CH_2-O$ *singlet* (0.14 ppm downfield), for the broad signal at 6.78 ppm

[1]) In a small-scale reaction, treatment of **8** with HBr in $CHCl_3$, gave **4** in quantitative yield.

[2]) ^{1}H-NMR Titrations were performed following the procedure of *Rebek* and coworkers [13]. K_a values were estimated using least-square fitting program.

(0.2 ppm upfield), and for the *singlet* of the four PhCH_2 protons (0.06 ppm upfield). All the other signals shift to smaller extent (< 0.05 ppm). Titration of a $4.17 \cdot 10^{-3}$ M solution of **11** with a $2.34 \cdot 10^{-5}$ M solution of KPF_6 in CD_3CN allows evaluation of the association constant $K_a(K^+)$. *Fig. 2* shows the ^{1}H-NMR shifts of the corresponding protons as a function of $[K^+]$. The data sets for the three signals yield good correlation with calculated curves using a 1:1 binding model. The calculated association constants are in good agreement: 4010 M^{-1} for the aromatic signal, 4120 M^{-1} for the $-CH_2-CH_2-$ signal, and 4550 M^{-1} for the PhCH_2 signal giving an average value of *ca.* 4200 M^{-1}.

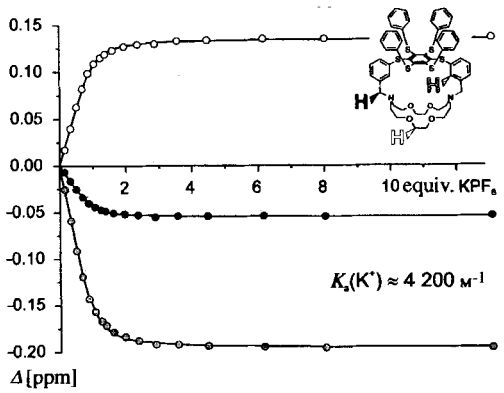


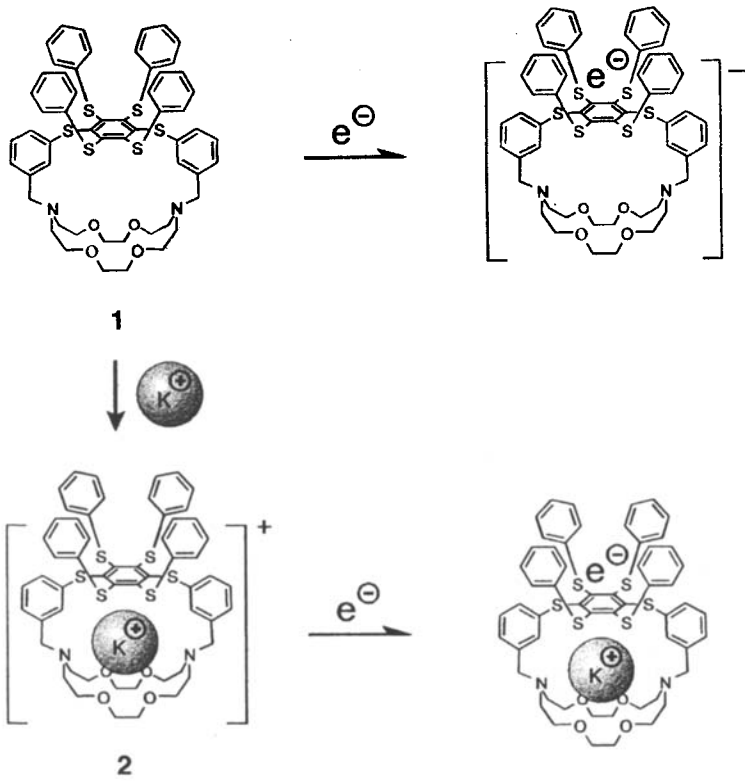
Fig. 2. *^{1}H-NMR Shifts observed for* **1** *on titration with KPF_6 in CD_3CN at 20°.* The dots represent the experimental data. *Top*: O–CH_2–CH_2–O signal at 3.56 ppm; *middle*: benzylic CH_2 signal at 3.8 ppm; *bottom*: aromatic H signal at 6.78 ppm. The solid lines are the calculated curves for $K_a(K^+) = 4200\ M^{-1}$.

The ^{1}H-NMR spectra of **1** in CD_3CN presents a temperature dependence for the N–CH_2–CH_2–O protons. At low temperature, an *AB* pattern ($J \approx 14$ Hz) is observed which coalesces into a broad signal at 263 K and gives a *triplet* at 283 K. By addition of excess KPF_6 (42 equiv.), the potassium cryptate **2** is formed. The low-temperature spectrum of **2** presents an *AB* system ($J \approx 14$ Hz) for the N–CH_2–CH_2–O protons and a broad signal for the N–CH_2–CH_2–O protons. The *AB* pattern coalesces into a broad signal at 303 K and gives a *triplet* at 323 K. The higher coalescence temperature for **2** compared to the free ligand **1** indicates, as one may expect, an increased hindrance of motion by the complexed potassium.

Electrochemical Properties. – Of particular interest are the redox properties of **1** and of its potassium cryptate **2**. The binding of a K^+ cation to form **2** places a positive charge close to the reducible hexakis(phenylthio)benzene subunit and may be expected, thereby, to increase its electron-accepting character [6]. The potassium cryptate **2** should be reducible at less negative potential and yield a neutral *cryptatium* species, while reduction of the ligand **1** itself forms a negatively charged species (*Scheme 3*).

The electrochemical properties of **1** and of its potassium cryptate **2** were investigated by cyclic voltammetry in MeCN solution with Bu_4NPF_6 (0.1 M) as supporting electrolyte. The ligand **1** ($5 \cdot 10^{-3}$ M) was not oxidized up to + 1.2 V *vs.* SCE but showed a reversible reduction at a formal potential ($(E_a + E_c)/2$) of −1.8 V *vs.* SCE. The parent compound

Scheme 3. *Comparison of the Reductions of Ligand* **1** *and Its Potassium Cryptate* **2**. Due to the positive charge of K^+, **2** should be a better electron acceptor than **1**.



of the reducible subunit, hexakis(phenylthio)benzene, is reduced at −1.73 V *vs.* SCE under the same conditions. The slightly more negative reduction potential of **1** may be due to the bridging substitutents on two phenylthio groups. It has been shown that the reduction potential of hexakis(phenylthio)benzenes depends on substituents in *para*-position on the phenylthio substituents [8]. By addition of excess (6 equiv.) KPF_6, the potassium cryptate **2** was formed *in situ*. Compound **2** showed a reversible reduction at a formal potential of −1.63 V *vs.* SCE. The complexation of potassium causes a rather large shift of + 170 mV (*Fig. 3*), demonstrating also the potential of **1** as redox sensor for potassium.

The values are determined by comparison to ferrocene, which was measured under the same conditions *vs.* SCE (0.38 V *vs.* SCE). The criterion applied for reversibility was 1.0 ± 0.5 for the ratio of the differences between peak potential (E_p) and the half-peak potential ($E_{p/2}$) of the compound and ferrocene in the same measurement and no shift of the half-wave potential with varying scan rates.

Conclusion. – The new ligand **1**, based on a macrocyclic diamine bridged by a reducible hexakis(phenylthio)benzene subunit, forms a potassium cryptate displaying increased electron-accepting properties. Cyclic-voltammetry experiment showed a + 170-mV shift

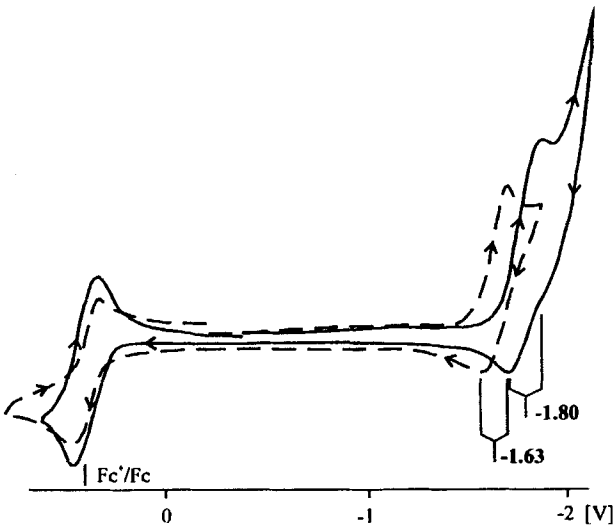


Fig. 3. *Cyclic voltammogram of the macrobicyclic ligand* **1** (—) *and cryptate* **2** (- - -) ($5 \cdot 10^{-3}$ M) *with ferrocene as internal reference, in 0.1M* Bu_4NPF_6*/MeCN solution, scan rate 100 mV/s*

of the reduction potential of the hexakis(phenylthio)benzene subunit by the complexed potassium. Further investigations are focused on electrocrystallization of the neutral *cryptatium* species, formed by electrochemical reduction of the potassium cryptate **2**.

The present results indicate that poly(phenylthio)-containing aromatic compounds are suitable candidates for incorporation as reducible entities onto molecular devices. Such is the case for reducible molecular wire-type rigid rods containing such groups [14].

Experimental Part

General. All reaction vessels were flame-dried under Ar. The reactions were carried out under Ar using commercial reagents. THF: distilled over Na. MeCN: distilled over CaH_2. Column chromatography (CC): commercial-grade solvents, distilled; silica gel *Geduran SI 60* from *Merck*. TLC: *Macherey-Nagel* pre-coated TLC plates *SIL G-50* UV_{254}, visualization by UV or $KMnO_4$. IR: *Perkin-Elmer-FT-IR-1600*; in cm^{-1}. ^{1}H-NMR: *Bruker-AC-200* (200 MHz); δ in ppm rel. to the solvent signal: $CDCl_3$: (δ(H) 7.24); CD_3CN: (δ(H) 1.94), J in Hz. ^{13}C-NMR: *Bruker-AC-200* (50 MHz); δ in ppm rel. to the solvent signal: $CDCl_3$: (δ(C) 77.00); CD_3CN: (δ(C) 1.30), J in Hz. The mass spectra were performed at the Laboratoire de Spectrométrie de Masse, Strasbourg; in *m/z* (%).

3-Bromobenzyl Methoxymethyl Ether (**5**). 3-Bromobenzyl alcohol (2.5 g, 13.4 mmol) in $EtN(i\text{-}Pr)_2$ (18 ml) was cooled to 0°. $ClCH_2OMe$ (2.14 g, 26.6 mmol) was added dropwise. The mixture was stirred for 1.5 h at 0° and for 15 h at r.t., then poured into sat. NH_4Cl soln. (40 ml) and extracted with Et_2O (3 × 10 ml). Evaporation of the solvent and CC (silica gel, Et_2O/hexane 1:1) gave **5** (2.8 g, 91%). Colorless liquid. IR (film): 2991 *w*, 2944 *m*, 2884 *m*, 2842 *w*, 2821 *w*, 1598 *w*, 1571 *m*, 1473 *m*, 1428 *m*, 1401 *w*, 1377 *m*, 1209 *m*, 1150 *s*, 1105 *s*, 1071 *s*, 1048 *s*, 997 *m*, 953 *m*, 919 *m*, 884 *w*, 861 *w*, 778 *s*, 698 *m*, 672 *m*. ^{1}H-NMR ($CDCl_3$): 3.39 (*s*, 3 H); 4.54 (*s*, 2 H); 4.68 (*s*, 2 H); 7.1–7.3 (*m*, 2 H); 7.40 (*m*, 1 H); 7.52 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 55.09; 67.96; 95.52; 122.28; 125.92; 129.70; 130.40; 140.17. EI-MS: 232 (9), 230 (9, M^+), 200 (7), 199 (6), 198 (8), 197 (5), 183 (5), 172 (62), 171 (95), 170 (27), 169 (100), 157 (9), 121 (9), 119 (31), 92 (7), 91 (87), 90 (16), 89 (33), 78 (7), 77 (11), 76 (6), 63 (17), 62 (5). Anal. calc. for $C_9H_{11}BrO_2$: C 46.78, H 4.80; found: C 46.79, H 4.80.

3-Mercaptobenzyl Methoxymethyl Ether (**6**). Ether **5** (5 g, 21.6 mmol) was solved in THF (80 ml), bubbled with Ar, and cooled to −80°. *t*-BuLi (1.5M in pentane; 28 ml, 42 mmol) was added. The mixture was allowed to warm to −35°, followed by the addition of sulfur (0.69 g, 21.5 mmol). After 15 h stirring at r. t., NaOH soln. (1M, 150 ml)

was added. The org. solvents were removed, and the aq. soln. was washed with Et_2O (50 ml) and CH_2Cl_2 (50 ml). After treatment with AcOH, the crude product was extracted with Et_2O (2 × 50 ml). Evaporation of the solvent and CC (Et_2O/hexane 1:5) gave **6** (2.6 g, 65%). Colorless liquid. IR (film): 2990*w*, 2943*m*, 2884*m*, 2842*w*, 2822*w*, 2561*w*, 1595*m*, 1576*m*, 1474*m*, 1429*m*, 1401*w*, 1377*m*, 1212*m*, 1149*s*, 1105*s*, 1081*m*, 1048*s*, 1000*m*, 919*m*, 780*m*, 707*m*, 686*m*. ^{1}H-NMR ($CDCl_3$): 3.41 (*s*, 3 H); 3.49 (*s*, 1 H); 4.53 (*s*, 2 H); 4.70 (*s*, 2 H); 7.05–7.25 (*m*, 3 H); 7.28 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 55.21; 68.44; 95.57; 124.84; 128.38; 128.93; 130.92; 138.85. EI-MS: 185 (5), 184 (55, M^+), 154 (7), 137 (5), 125 (9), 124 (88), 123 (100), 122 (13), 121 (26), 119 (11), 111 (8), 109 (9), 91 (78), 89 (7), 79 (13), 78 (16), 77 (24), 69 (8), 65 (8), 63 (8).

1,2-Difluoro-2,3,5,6-tetrakis(phenylthio)benzene (**7**). Thiophenol sodium salt (3.45 g, 26.1 mmol) was dissolved in EtOH (30 ml). Hexafluorobenzene (1.15 g, 6.2 mmol) in DMI (1,3-dimethylimidazolidin-2-one; 30 ml) was added, and the mixture was stirred for 75 h at r.t. The precipitate was filtered and washed with EtOH (10 ml). Recrystallization of the filtrate from hot toluene yielded **7** (1.62 g, 2.96 mmol, 48%). Pale ivory crystals. IR (KBr): 1580*m*, 1476*m*, 1440*m*, 1392*m*, 1379*m*, 1331*w*, 1174*w*, 1080*w*, 1022*w*, 1022*m*, 999*w*, 851*s*, 738*s*, 696*s*, 687*s*, 649*m*, 604*m*. ^{1}H-NMR ($CDCl_3$): 7.22 (*m*, 20 H). ^{13}C-NMR ($CDCl_3$): 126.95; 128.86 (*d*, J = 19); 129.04; 129.37; 134.60; 159.18 (*d*, J = 252). FAB-MS: 546 (100, M^+), 391 (47), 328 (16), 252 (28). Anal. calc. for $C_{30}H_{20}F_2S_4$: C 65.91, H 3.69; found: C 65.71, H 3.71.

1,4-Bis{3-[(Methoxymethoxy)methyl]phenylthio}-2,3,5,6-tetrakis(phenylthio)benzene (**8**). NaH (0.25 g, 10.42 mmol) was suspended in THF (10 ml), and a soln. of **6** (1.5 g, 8.14 mmol) in THF (10 ml) was added. After H_2 evolution subsided, the solvent was evaporated. Compound **7** (0.9 g, 3.66 mmol) in DMI (30 ml) was added to the residue. The mixture was stirred for 4 d at 40°, poured into sat. NaCl soln. and extracted with toluene (3 × 10 ml). Evaporation of the solvent and CC (toluene/CH_2Cl_2 3:2) yielded **8** (1.44 g, 1.64 mmol; 45%). Yellow dye. IR (film): 3055*w*, 2928*w*, 2882*w*, 1580*m*, 1476*s*, 1438*m*, 1376*w*, 1270*w*, 1210*w*, 1148*s*, 1103*m*, 1077*m*, 1045*s*, 1024*m*, 999*w*, 918*w*, 779*w*, 737*s*, 699*m*, 687*s*. ^{1}H-NMR ($CDCl_3$): 3.43 (*s*, 6 H); 4.53 (*s*, 4 H); 4.70 (*s*, 4 H); 6.85–7.35 (*m*, 28 H). ^{13}C-NMR ($CDCl_3$): 55.32; 68.48; 95.49; 125.44; 126.07; 127.17; 128.01; 128.08; 128.16; 128.86; 128.97; 137.64; 137.83; 138.78; 148.12. FAB-MS: 877 (19), 876 (44), 875 (85, M^+), 874 (100), 783 (10), 411 (14), 290 (19). Anal. calc. for $C_{48}H_{44}O_4S_6$: C 65.72, H 5.06; found: C 65.49, H 5.04.

1,4-Bis[3-(bromomethyl)phenylthio]-2,3,5,6-tetrakis(phenylthio)benzene (**4**). Compound **8** (1.2 g, 1.37 mmol) was dissolved in $CHCl_3$ (50 ml) and bubbled with HCl for 5 min. PBr_3 (2 ml) was added, and the mixture was stirred for another 5 min at r.t. MeOH (10 ml) was added to destroy the remaining PBr_3. Evaporation of the solvent and CC (EtO_2/hexane 1:1) yielded **4** (1.02 g, 82%). Yellow dye. IR (film): 3055*w*, 1580*m*, 1476*s*, 1438*m*, 1265*m*, 1225*m*, 1204*w*, 1078*m*, 1023*m*, 998*w*, 890*w*, 783*w*, 736*s*, 686*s*, 624*w*, 556*w*. ^{1}H-NMR ($CDCl_3$): 4.34 (*s*, 4 H); 6.85–7.30 (*m*, 28 H). ^{13}C-NMR ($CDCl_3$): 32.99; 126.14; 126.65; 127.94; 128.05; 128.19; 128.87; 128.93; 129.08; 137.53; 138.03; 138.23; 148.30. FAB-MS: 917 (13), 916 (29), 915 (50), 914 (83), 913 (68, M^+), 912 (100), 911 (32), 910 (41), 868 (8). Anal. calc. for $C_{44}H_{32}Br_2S_6$: C 57.89, H 3.53; found: C 58.06, H 3.46.

10,11,37,38-Tetrakis(phenylthio)-23,26,31,34-tetraoxa-8,13-dithio-1,20-diazapentacyclo[18.8.8.2^{9,12}.1^{3,7}.1^{14,18}]-tetraconta-3(40),4,6,9(10),11,14(15),16,18(39),37-nonaene (**1**). To a suspension of $CaCO_3$ (7.38 g, 73.4 mmol) in MeCN (150 ml) at reflux, a H_2O-cooled (*ca.* 10°) soln. of **4** (0.79 g, 0.87 mmol) and 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (0.23 g, 0.88 mmol) in MeCN was added over a period of 3 d. After refluxing another day, the suspension was filtered. Evaporation of the solvent and CC (silica gel, AcOEt/EtOH 2:1) gave **1** containing some silica as impurity, which was removed by resolvation in $CHCl_3$ and filtration: 0.31 g (35%) of **1**. Yellow dye. IR (KBr): 3051*w*, 2863*m*, 1654*w*, 1637*w*, 1580*m*, 1476*s*, 1438*m*, 1383*w*, 1353*w*, 1267*m*, 1198*w*, 1109*s*, 1078*m*, 1023*m*, 998*w*, 926*w*, 852*w*, 791*w*, 740*s*, 699*m*, 687*s*, 492*w*. ^{1}H-NMR (CD_3CN): 2.85 (*t*, J = 6, 8 H); 3.56 (*s*, 8 H): 3.58 (*t*, J = 6, 8 H); 3.80 (*s*, 4 H); 6.78 (br. *s*, 2 H); 6.85–7.25 (*m*, 26 H). ^{13}C-NMR (CD_3CN): 53.34; 57.15; 69.88; 70.59; 127.16; 128.06; 128.33; 128.52; 129.91; 130.28; 130.37; 138.55; 138.62; 138.96; 148.80. FAB-MS: 1017 (30), 1016 (27), 1015 (54), 1014 (66), 1013 (100, M^+), 508 (26), 507 (38), 369 (18), 262 (35). Anal. calc. for $C_{56}H_{56}N_2O_4S_6$: C 66.37, H 5.57, N 2.76; found: C 66.29, H 5.66, N 2.78.

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