compound,[7] bulk solid materials containing the aromatic Al_4^{2-} ion have not been synthesized. Nevertheless, the current finding of aromaticity in the isoelectronic Hg_4^{6-} ion establishes a solid bridge between our gas-phase studies of aromatic clusters and bulk materials containing such species. It is a pleasant surprise that new insight can still be obtained into such an ancient and well-known material as the amalgam. It is possible that further development in the concept of aromaticity in metallic systems, through gas-phase clusters and model investigations, will lead to discovery of new classes of materials or new insights into the electronic structures and chemical bonding of complex materials.[13]

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Allosteric Fluoride Anion Recognition by a Doubly Strapped Porphyrin**

Masayuki Takeuchi, Takeshi Shioya, and Timothy M. Swager*

The design of anion receptors with high selectivity is challenging.[1–6] Most systems developed use complimentary binding sites with hydrogen-bonding groups, quaternary ammonium centers, Lewis acids, and cationic metal ions.[1–6] It is often difficult to control selectivity and sensitivity among anions because of their wide range of geometries, low charge to radii ratios, sensitivities to pH, and high solvation energies.[1a] Receptors for the smallest anion, fluoride, are of special importance for monitoring the fluoride metabolism in nature, the analysis of drinking water,[7] and the detection of chemical warfare agents.[8] We report herein a highly selective allosteric fluoride recognition system[9] by a doubly strapped porphyrin[10] **1** that contains two small hydrogen-bonding cavities that are not able to bind larger anions. It is also demonstrated that a conducting polymer based upon **1** displays both electrochemical and conductivity responses to fluoride ions and no response to chloride ions.

Compound **1** was prepared by condensation of strap moieties **2** with $\alpha\beta\alpha\beta$-tetrakis(2-aminophenyl)porphyrin **3** under high-dilution conditions (Scheme 1).[11, 12] By comparison with related strapped porphyrins containing four linkers, we estimate that the cofacial distance between the phenyls in the straps and the porphyrin is between 3–4 Å.[12] This distance creates a small pocket that is suitable for fluoride-ion binding (the radius of a fluoride anion in an octahedral environment is 1.19 Å[1a, 13]), but should exclude larger anions. The proximate location of the strap moieties to the porphyrin in **1** is confirmed by NMR spectroscopy in $CDCl_3$, which revealed significant upfield shifts of specific signals. The phenyl protons appear at $\delta = 4.24$ which is approximately 2.96 ppm upfield of the dicarboxylate strap precursor. The amide N–H protons resonate at $\delta = 7.68$, which is comparable to closely related phenyl-capped porphyrins which have an additional methylene between the amide carbonyl and the phenyl ether of the strap.[14] These values are very different from unstrapped porphyrins where the same resonances generally appear between $\delta = 5$ and 6.5[10, 15] and suggest that the amide N–H protons are constrained against the porphyrin core. The Soret band of **1** (5.00 μM) in dichloromethane is split into two bands of equal intensity at 404 and 423 nm, which indicate that the strap presents a significant perturbation. This

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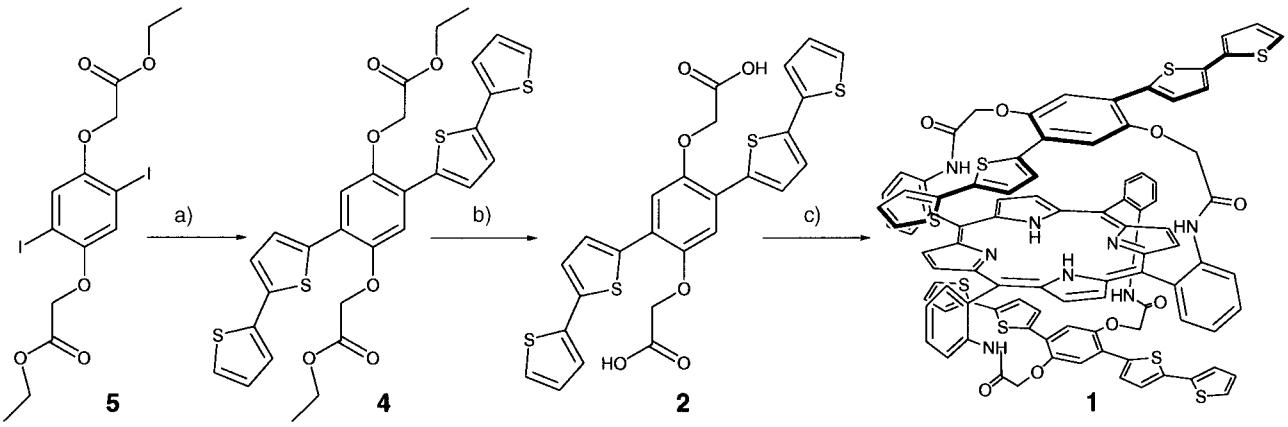

Scheme 1. a) 5-tributylstannyl-2,2′-bithiophene, $[PdCl_2(PPh_3)_2]$, 80 °C, 62 %, b) NaOH, THF/EtOH/H_2O, RT, 92 %, c) oxalyl chloride, **3**, pyridine, THF, high-dilution conditions, RT, 37 %.

splitting is caused by π–π interactions of the bis(dithienyl)-benzene moieties with the porphyrin.[14b, 16] The effect of solvent on the Soret bands is minimal. The spectral features were the same in THF and acetonitrile, but the Soret splitting was slightly less in DMSO (408(sh) and 424 nm).[17] These results suggest that the solvent can not occupy the cavity defined by the straps and the porphyrin.

Upon addition of fluoride anion (as a cesium or tetrabutylammonium (TBA) salt) to the solution of **1** (5.00 μM) in DMSO at 25 °C, the split Soret band shifted to a single band at 417 nm with a simultaneous red shift of the Q band (Figure 1).[18] The UV/Vis absorption spectra measured as a

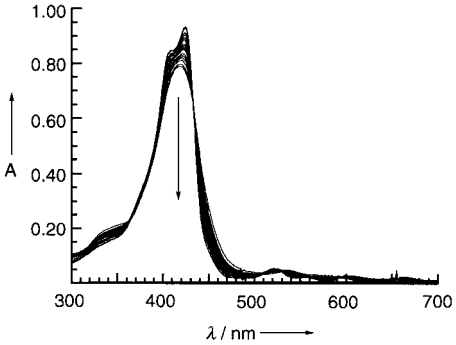

Figure 1. Absorption spectra of **1** on addition of TBAF.

function of fluoride concentration provided multiple isosbestic points visible at 364, 433, and 508 nm, which confirm that the reaction consists of only two species in equilibrium (Figure 1). No absorbance changes in either the Soret or Q band were observed upon exposure of **1** to larger anions including chloride, bromide, iodide, acetate, cyanide, and dihydrogen phosphate. Apparently only the smaller anion, fluoride, can fit in the hydrogen-bonding cavity of **1**. Noteworthy is that plots of the absorbance changes at 424 nm versus tetrabutylammonium fluoride (TBAF) concentration show a sigmoidal curve, which indicates that the binding of fluoride anion to **1** is cooperative (positive, homotropic allosterism; Figure 2). This cooperative guest binding was analyzed with the Hill equation [Eq. (1)].[19]

$$\lg(y/(1-y)) = n\lg[\text{guest}] + \lg K \qquad (1)$$

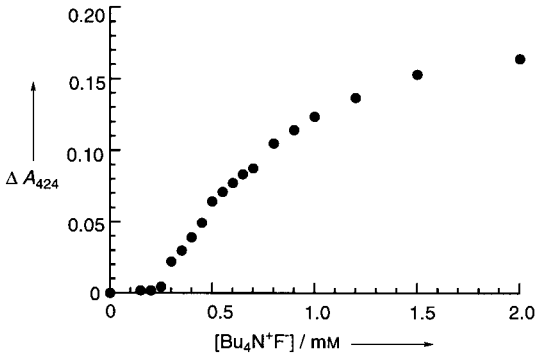

Figure 2. Plots of absorbance at 424 nm for **1** versus [TBAF].

K and n are the association constant and Hill coefficient, respectively, and $y = K/([\text{guest}]^{-n} + K)$. From the slope and the intercept of the linear plot, we obtained $\lg K = 6.6$ and $n = 2.0 \pm 0.1$ (correlation coefficient 0.997). We utilized Scatchard plots (see Supporting Information) to further characterize the binding. In these plots Hill coefficients (n) are correlated with the maximum values (y_{max}) with $n = 1/(1 - y_{max})$, and positive and negative allosterisms are expressed by the upward and downward curvatures, respectively.[19] Consistently the y_{max} values for fluoride revealed a maximum at 0.5 with upward curvature. Given the observed 1:2 binding stoichiometry we computed energy-minimized geometries of **1** and $\mathbf{1}(F^-)_2$.[20] As shown in Figure 3 these results suggest that the cavities in **1** are contracted, a result of favorable π–π interactions between the strap band and the porphyrin (π-stacking distance of 4.0 Å). The calculated structure with two bound fluorides causes an expansion of the cavity that

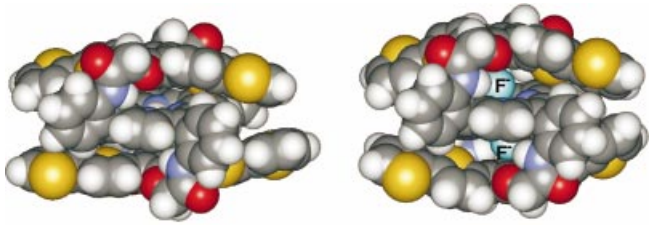

Figure 3. Energy-minimized structures of **1** (left) and $\mathbf{1}(F^-)_2$ (right). Yellow: sulfur, red: oxygen, blue: nitrogen, and light blue: fluoride.

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separates the planes of the porphyrin and the straps by 4.9 Å. This increase in distance is consistent with the transformation of the spilt Soret band into a single band and supports our assertion that the strap–porphyrin interactions are responsible the splitting. The computations place the fluoride 3.6 Å from the amide N–H protons and 2.3 Å from the pyrrole N–H protons. Typical H···F hydrogen bonds range from about 2.3–2.5 Å and hence we propose that ion–dipole interactions between amide N–H and fluoride assist the hydrogen bonding between pyrrole N–H and fluoride. Our experimental findings clearly indicate that binding of a first fluoride anion facilitates a second binding. To account for this effect, we suggest the possibility of bridging F···H···F interactions through the center of the macrocycle and that the first binding distorts the macrocycle from planarity and thereby favors the binding of the second fluoride ion (Scheme 2).

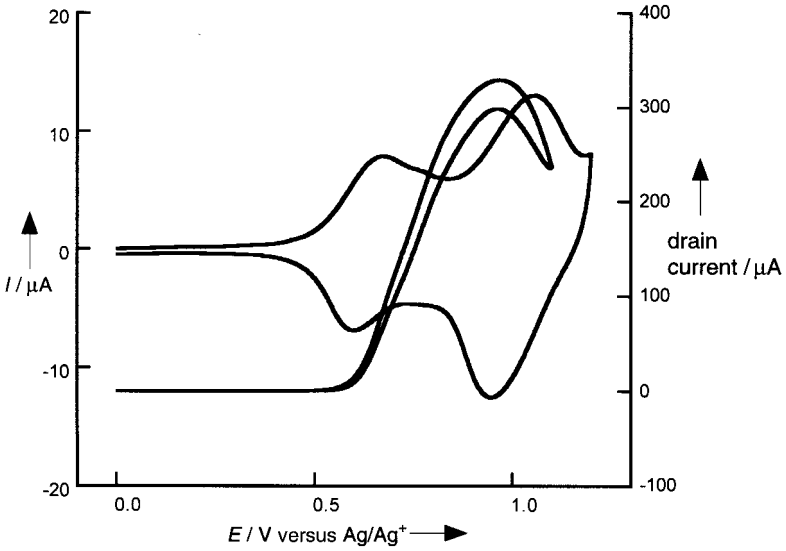


Figure 4. Cyclic voltammogram and conductivity profile using interdigitated microelectrodes (10 mV s^{-1}, offset potential of 40 mV) of a deposited film of poly**1** in CH_2Cl_2.

To demonstrate the high selectivity of **1** to the fluoride ion we examined the influence of a second coexisting halide ion on the UV/Vis spectrum of the **1**$(F^-)_2$ complex. The UV/Vis spectrum of **1**$(F^-)_2$ ([**1**] = 5.00 μM, [fluoride] = 2.00 mM) was essentially unaffected by the added halides up to concentrations of 200 mM. From these studies the affinity of **1** to fluoride is estimated to be at least 10^4 times higher than for other halogens. It is likely that both the allosterism and the cavity size make contributions to the fluoride selectivity toward other anions.

Compound **1** (0.05 mM in 0.1M $TBAPF_6$ in CH_2Cl_2) readily electropolymerized to give conducting films upon cycling (100 mV s^{-1}) electrodes between 0 and 1.1 V versus the Ag/Ag^+ couple. Films of poly**1** thick enough for in situ conductivity studies on interdigitated microelectrodes (Figure 4) were formed in 10 cycles and the maximum conductivity was determined to be 6 S cm^{-1}.[21, 22] The films are orange when neutral and green when oxidized. Poly**1** is highly cross-linked because of the presence of the four unsubstituted sites, α to the sulfur on the terminal thiophenes, that are active toward polymerization. The multiple sites for oxidative coupling are also responsible for the rapid growth of films. The cyclic voltammogram is a composite of the electrochemistry of the poly(bis(dithienyl)phenylene) and the porphyrin. The lower potential peak at ≈0.65 V, attributed to the conjugated polymer, also displays broad featureless electroactivity at higher potentials, a feature that is consistent with its highly conductive delocalized nature. Superimposed upon this electroactivity is a redox wave at about 1 V that is assigned to the porphyrin. This potential is consistent with those reported for other porphyrins.

Treatment of poly**1** with 0.3 mM F^- ion shifted the redox waves associated with the porphyrin (Figure 5) to lower potentials. Interestingly the electrochemical behavior of the conjugated polymer was largely unaffected. The negative shift

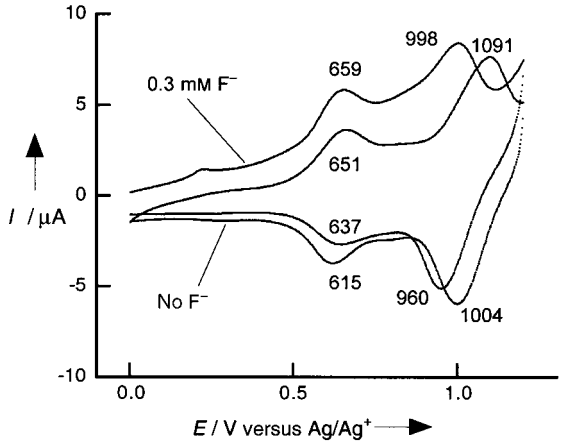
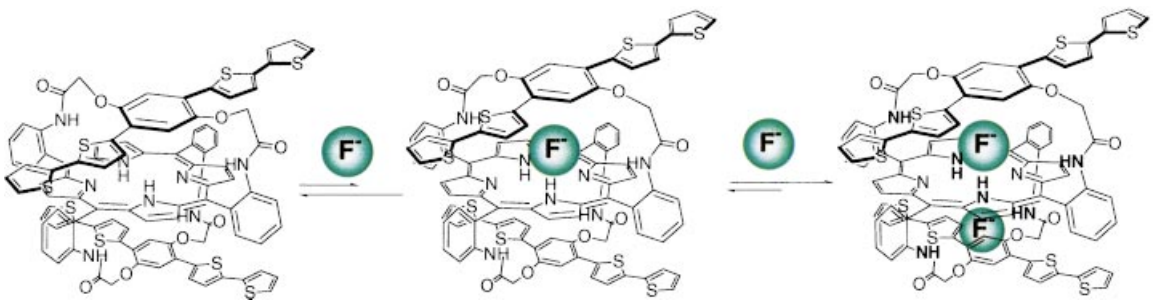


Figure 5. Cyclic voltammogram of poly**1** in 0.1M $TBAPF_6$ in CH_2Cl_2 with and without 0.3 mM F^- ion. The peak potentials (mV) are labeled in the plot.



Scheme 2. Sequential binding of the fluoride ions.

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of the redox potential of the porphyrin is consistent with the presence of an anion, which will stabilize proximate positive charge. Additionally, the insensitivity of the conjugated polymer is in accord with our model for fluoride-ion binding, Figure 3. In spite of the lack of interaction of the fluoride with the conjugated polymer the conductivity of the polymer is dramatically and irreversibly reduced (<50 fold reduction) upon fluoride-ion binding. The irreversible behavior can be attributed to the large binding constant, which will result in slow kinetics for the removal of the fluoride from the film. However, it is not clear why this system displays such a greatly reduced conductivity while the electrochemical response of the conjugated polymer appears unchanged. It is possible that the large effect is a result of the bulk transport properties of the conducting polymer being much more sensitive to the presence of fluoride than the electrochemical potential. We have previously found evidence for such effects in conducting polymers containing alkali metal ion receptors.[23] However, the irreversible nature of this effect precludes the elimination of other possibilities such as the formation of cracks in the films or large interfacial resistances in response to fluoride binding.

In conclusion, we have demonstrated that **1** is a novel scaffold for the selective fluoride sensing, and shows positive homotropic allosterism with Hill coefficients of 2.0. Moreover, **1** has been easily transformed into highly conducting polymer poly**1** ($6\ S\,cm^{-1}$) coatings on electrodes that show a composite electrochemical response of the polymer backbone and the porphyrin ring. Treatment of the polymer with fluoride ion produced a shift of the porphyrin electrochemistry and a large reduction in the materials conductivity. Such rational amalgamations of molecular-wire sensor schemes[24] and allosteric systems[9] represent a powerful design scheme for the construction of highly sensitive and selective sensory systems.

Experimental Section

General procedures: Reactions were carried out in oven-dried glassware using standard Schlenk techniques under an inert atmosphere of dry argon. ^{1}H NMR and UV/Vis spectra were recorded with a Varian UN-300 or Mercury 300 spectrometer and a Hewlett-Packard 8453 diode array spectrophotometer, respectively. Electrochemical measurements were performed using a computer controlled Autolab Model PGSTAT 20 potentiostat from Eco Chemie. A platinum coil was used as a counter electrode, and 5 micron spaced interdigitated microelectrodes purchased from ABTECH were used as working electrodes. Compound **5** was synthesized from the 2,5-diiodo-1,4-dihydroxybenzene and ethyl bromoacetate in DMF according to the reported method.[25]

Synthesis of **4**: Compound **5** (530 mg, 1 mmol), 5-tributylstannyl-2,2′-bithiophene (1.14 g, 2.5 mmol), and *trans*-$[PdCl_2(PPh_3)_2]$ (35 mg) were dissolved in dry DMF (40 mL) and the mixture was stirred overnight at 80 °C. The reaction mixture was poured into aqueous NH_4Cl solution (100 mL) and extracted with diethyl ether (150 mL). The ether layer was washed with brine (50 mL, three times) and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the yellow residue was purified by chromatography (silica gel, CH_2Cl_2/hexane 9/1) to produce **4** (380 mg, yield 62 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.34$ (t, $J = 7.2$ Hz, 6H), 4.32 (q, $J = 7.2$ Hz, 4H), 4.74 (s, 4H), 7.03 (m, 2H), 7.20 (m, 8H), 7.59 (d, $J = 3.6$ Hz, 2H); HR-MS (ESI): for $C_{30}H_{27}O_6S_4$ $[M+H]^+$ (calcd): 611.0690 (611.0680).

Synthesis of **2**: Compound **4** (200 mg, 0.33 mmol) was dissolved in THF/ethanol (15/1, 480 mL) solution and NaOH (130 mg; 10 equiv) in H_2O (5 mL) was added to the mixture. The reaction mixture was stirred for 24 h at room temperature and 1 M HCl solution (50 mL) and brine (50 mL) were added. The organic layer was extracted with diethyl ether (150 mL) and then dried over anhydrous $MgSO_4$. Evaporation to small volume afforded compound **2** as yellowish orange powder in 92 % yield. This compound was used for next reaction with no further purification. HR-MS (ESI): for $C_{26}H_{19}O_6S_4$ $[M+H]^+$ (calcd): 555.0064 (555.0074).

Synthesis of **1**: In a 500 mL flask equipped with a stir bar, dry THF (350 mL) and dry pyridine (5 mL) were introduced. In another flask, compound **2** (158 mg, 0.285 mmol) was treated with oxalyl chloride (1.5 mL, large excess) in dry THF (30 mL) containing 1 drop of DMF at 60 °C for 1 h to yield the diacidchloride derivative of **2**. After removal of THF and excess oxalyl chloride under vacuum, dry THF (40 mL) was added and this solution was loaded in two 20 mL syringes. A third syringe was loaded with a dry THF solution (20 mL) of compound **3**[15a, 26] (96 mg, 0.142 mmol). The simultaneous addition of the two reagents was driven by a syringe pump over 12 h, and the reaction mixture was stirred for an additional 24 h at room temperature. The solvent was removed by evaporation, then the red residue was purified by chromatography (silica gel, $CHCl_3$/acetone 98/2 and $CHCl_3$/ethyl acetate 95/5) to give **1** (90 mg, yield 37 %) as a brownish red powder. M.p. >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -3.47$ (s, 2H), 3.16 (d, $J = 16.7$ Hz, 4H), 4.15 (d, $J = 16.7$ Hz, 4H), 4.24 (s, 4H), 5.26 (d, $J = 3.9$ Hz, 4H), 6.74 (d, $J = 3.8$ Hz, 4H), 7.14–7.20 (m, 8H), 7.36 (d, $J = 3.7$ Hz, 4H), 7.67 (s, 4H), 7.72–7.79 (m, 8H), 8.52 (d, $J = 8.3$ Hz, 4H), 8.62 (dd, $J = 3.5$, 10.8 Hz, 8H); HR-MS (ESI) for $C_{96}H_{63}N_8O_8S_8$ $[M+H]^+$: (calcd): 1711.2558 (1711.2534); UV/Vis (DMSO): λ_{max} ($\lg\varepsilon$) = 408 (5.23), 424 (5.27), 521 (4.03), 555 (3.64), 598 (3.62), 653 nm (3.43).

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[16] The λ_{max} of **4** appears at 397 nm in dichloromethane. We could not obtain an accurate ε value for **4** because of its poor solubility in common organic solvents.

[17] Intermolecular aggregation can be ruled out because this split Soret band maintained a constant shape over the concentration range 0.5–50 μM.

[18] The titration using the fluoride salts introduced stoichiometric amounts of water which is known to interfere with fluoride complexation.[1] In this system, no absorbance changes in either the Soret or Q band was observed upon exposure of **1** to 5% (v/v) water. Moreover 40% of $\mathbf{1}(F^-)_2$ complex formed even when 3% (v/v) (1.67 M) of water was added to the complex solution ([**1**] = 5.00 μM, [fluoride] = 2.00 mM).

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[20] Conformations with low potential energy encountered during 100 ps MD (molecular dynamics) simulation at 300 K were selected. The system was minimized using the conjugate gradient and Newton–Raphson methods until convergence was attained for a gradient of 0.01 kcal mol^{-1} Å^{-1}. The force field used in this study was the ESFF.

[21] The surface coverage for conductivity values was determined using profilometery. The absolute conductivity values were determined using the methods of Zotti and co-workers: a) G. Zotti, G. Schiavon, *Synth. Met*. **1990**, *39*, 183; b) G. Schiavon, S. Sitran, G. Zotti, *Synth. Met.* **1989**, *32*, 209, and have been confirmed in our laboratory to be accurate within a factor of 2.[22]

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