Supramolecular Receptor Design: Anion-Triggered Binding of C_{60}**

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Self-assembled structures are widespread in nature and are a key feature of many biological small-molecule recognition motifs. Not surprisingly, therefore, considerable effort has been devoted to developing synthetic self-assembled receptor systems, multicomponent molecular hosts that are able to

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interact with, and bind to, specifically targeted substrates.[1,2] To date, systems based on metal coordination[3–8] and hydrogen-bond recognition[3,9–11] have received the greatest attention. Singularly lacking from the lexicon of known self-assembled receptor systems are those in which anion recognition plays a key structural or controlling role. Anion binding has, however, been used to template the formation of various large structures,[12–19] regulate the formation of a pseudo-rotaxane,[20] induce the translocation of a macrocycle in a molecular shuttle,[21] and stabilize the formation of several supramolecular host–guest complexes.[22,23]

Herein, we show how treatment of a solution of a tetrathiafulvalene-functionalized calixpyrrole with chloride anions in dichloromethane produces a bowl-like receptor that is able to encapsulate C_{60} in a 2:1 barrel-like manner. The use of a two-step molecular-recognition approach, which first involves an anion-triggered conformational change followed by binding of C_{60}, allows for the controlled assembly of five individual components (two chloride anions, two tetrathiafulvalene-functionalized calixpyrroles, and one C_{60} unit) and the production of a complex host–guest ensemble of well-defined structure and stoichiometry. The color of this ensemble (green in dichloromethane) differs dramatically from that of its constituents (yellow and magenta in the case of the tetrathiafulvalene-functionalized calixpyrrole and C_{60}, respectively), thus allowing its formation to be monitored visually. The present strategy differs fundamentally from previous approaches to assembled receptor design in that anion binding provides the key element of structural control. It thus defines a new approach to the generation of complex supramolecular assemblies.

The unique nature of C_{60} and other fullerenes[24,25] have made these species important targets for molecular receptor design. However, the need to match the shape of the receptor to the convex surfaces of fullerenes and to overcome the inherently weak associations that C_{60} and related species display in host–guest complexes has made this a particular challenge. To date, a number of "molecular containers", including cyclodextrins,[26] (benzotri(benzonorbornadienes)),[27] calixarenes,[28–31] calixnaphthalenes,[32] and cyclotriveratrylene,[33] have been used to achieve fullerene recognition. Porphyrins and metalloporphyrins,[34,35] which benefit from favorable van der Waals interactions with the π surface of fullerenes, have also been used to achieve C_{60} recognition, as have individual tetrathiafulvalene[36,37] (TTF) subunits in the solid state.[38] However, in all cases the receptor is a discrete entity (that is, the product of fermentation or synthesis), rather than a scaffold built up through self-assembly. The use of a self-assembled approach potentially confers a number of advantages, including savings in synthetic investment and the ability to effect control through the regulation of more than one supramolecular chemical event (e.g., the formation of the self-assembled receptor and, separately, fullerene recognition). As described below, the use of a tetrathiafulvalene-functionalized calix[4]pyrrole, TTF-calix[4]pyrrole **1** (Figure 1 A), allows this strategy to be implemented.

The synthesis of **1** (Figure 1 A) was carried out as described previously.[39,40] As is true for most other calix[4]-
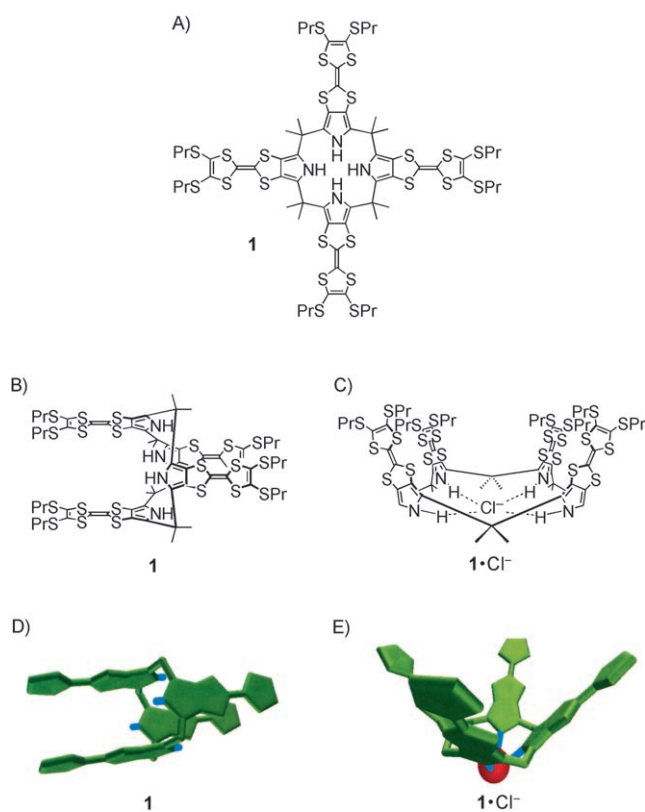

Figure 1. A) A 2D representation of **1**. B) A 3D representation of **1** in its 1,3-alternate conformation. C) A 3D representation of the chloride-bound receptor **1**·Cl⁻ in its cone conformation. D) A cartoon representation of **1** in its 1,3-alternate conformation. E) A cartoon representation of **1**·Cl⁻ in its cone conformation.

pyrroles, **1** exists (Figure 1 B) predominantly in the 1,3-alternate conformation in the absence of anions. However, in halogenated solvents **1** binds chloride anions very tightly— a binding constant (K_a) of $2.5 \times 10^6 \, \text{M}^{-1}$ has been reported[39,40] for the complexation of **1** with chloride ions in 1,2-dichloroethane (DCE) at 298 K, thus leading it to adopt (Figure 1 C) a bowl-like conformation. In the case of **1**, the resulting bowl-shaped receptor system possesses TTF-derived electron-rich "walls" and was thus expected to act as a receptor for electron-deficient spherical guests such as fullerene, for example.

Support for the notion that the electron-rich TTF-derived walls of **1** would stabilize interactions with the electron-deficient guest C_{60} came from an X-ray crystal structural study carried out on crystals[41] obtained from a mixture of tetrabutylammonium chloride, receptor **1**, and C_{60} in toluene. This structure revealed[42] an extraordinary cubic ensemble $[(\mathbf{1}\cdot\text{Cl})_6(C_{60})_8(\text{toluene})_5]^{6-}$ (Figure 2), in which eight C_{60} molecules define the corners of a cube and **1**·Cl⁻ units lie within each cube face locked in the bowl-shaped conformation. The chloride anions lie to the inside of the cube, which also encapsulates five toluene solvent molecules. All four TTF-derived subunits on each **1**·Cl⁻ unit interact with C_{60} molecules, and each C_{60} moiety lies within a threefold symmetric cavity defined by the electron-rich TTF subunits. In the solid state, the internal cavities of the bowl-shaped
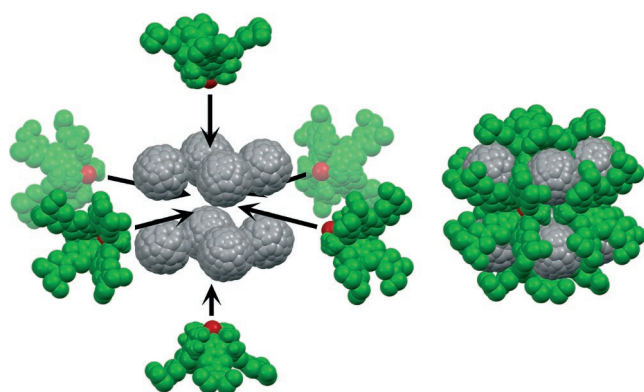
Figure 2. Enlarged view (right) of the $[(1 \cdot Cl)_6(C_{60})_8(toluene)_5]^{6-}$ ion, as determined by X-ray crystallography. As shown on the left, the C_{60} molecules (gray) define the corners of a cube and $1 \cdot Cl^-$ units (green/red) lie within each cube face, locked in the bowl-shaped conformation. The chloride anions (red) lie to the inside of the cube, which also encapsulates five toluene solvent molecules (not shown).

$1 \cdot Cl^-$ receptors are occupied by tetrabutylammonium cations. Characterization of this complex established the viability of the interactions between $1 \cdot Cl^-$ and C_{60}, although it seemed unlikely that the complex cubic ensemble would persist in solution. It was expected that more limited $1 \cdot Cl^-$ to C_{60} stoichiometries would be seen in solution, as concentrations are inherently lower and better controlled and long-range interensemble interactions are minimized.

For reasons of solubility, solution-state binding studies involving **1**, chloride anions (studied as the tetrabutylammonium salt), and C_{60} were carried out in dichloromethane. Both absorption and emission spectroscopy were used to monitor the putative binding events.

The absorption spectrum recorded in dichloromethane of **1** in its 1,3-alternate conformation (Figure 3 A) did not reveal (Figure 3 B, curve a) any visible absorption bands at $\lambda \geq$ 550 nm. Likewise, no significant absorption features were seen at $\lambda \geq 650$ nm in the absorption spectrum (Figure 3 B, curve b) of C_{60} in dichloromethane. These solutions, thus, appear yellow and magenta (Figure 3 C), respectively. The addition of five equivalents of tetrabutylammonium chloride to a solution of **1** in dichloromethane serves to shift the 1,3-alternate conformation to the cone conformation, thus producing the bowl-shaped receptor $1 \cdot Cl^-$ almost exclusively (Figure 3 A). Although this chloride-mediated conformational change is readily visualized by ^{1}H NMR spectroscopy,[39] it does not give rise to any appreciable change in the color of the solution; thus, solutions of the cone complex $1 \cdot Cl^-$ appear yellow (Figure 3 D), as do those of the neutral **1** in its 1,3-alternate conformation. However, when 0.5 equivalents of C_{60} (in dichloromethane) are added to the yellow solution of $1 \cdot Cl^-$, the solution turns green (Figure 3 E) essentially instantaneously. The absorption spectrum (Figure 3 B, curve c) of this solution showed a strong charge-transfer (CT) band centered around $\lambda_{max} = 725$ nm ($\varepsilon = 1900 \, M^{-1} cm^{-1}$). This diagnostic spectroscopic feature is most readily accounted for by the formation (Figure 3 A) of the well-ordered, multicomponent supramolecular ensemble $C_{60} \subset (1 \cdot Cl^-)_2$, wherein one C_{60} molecule is encapsulated by two bowl-shaped receptors (that
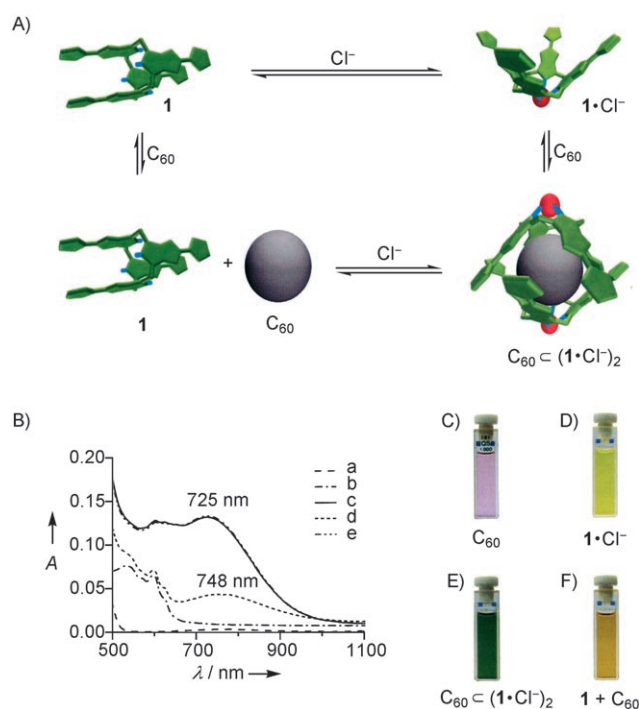

Figure 3. A) Mechanistic scheme for the proposed complex formation between **1** and C_{60} in the presence of chloride ions. B) Absorption spectra recorded in dichloromethane at 298 K of a) **1** (0.135 mM), b) C_{60} (0.0687 mM), c) $1 \cdot Cl^-$ + C_{60} (0.5 equiv), d) **1** + C_{60} (0.5 equiv), and e) **1** + C_{60} (0.5 equiv) and then nBu$_4$NCl (excess). C–F) Solutions in dichloromethane of C) C_{60}, D) $1 \cdot Cl^-$, E) $1 \cdot Cl^-$ + C_{60} (0.5 equiv), and F) **1** + C_{60} (0.5 equiv).

is, $1 \cdot Cl^-$) produced by the binding of the chloride anion to calix[4]pyrrole **1**. Presumably, the formation of this ensemble reflects an appropriate size and shape matching, as well as favorable CT interactions between the electron-rich TTF donor units and the electron-accepting C_{60} moiety. Analysis of the spectral features allows this CT interaction to be quantified in terms of a fairly pronounced electronic coupling element (V) of 2687/340 Å cm^{-1}.

A Job plot carried out[41] in dichloromethane between $1 \cdot Cl^-$ and C_{60} exhibits a maximum around 0.35, a finding that is consistent with the formation of the proposed 2:1 complex between $1 \cdot Cl^-$ and C_{60}. Addition of two equivalents of the yellow receptor **1** in its 1,3-alternate conformation (that is, in the absence of chloride anions) to a solution (magenta) of C_{60} in dichloromethane produced (Figure 3 A) a brown solution (Figure 3 F). This solution was characterized by the presence of a weak, broad absorption band centered around $\lambda_{max} =$ 748 nm ($\varepsilon = 500 \, M^{-1} cm^{-1}$) in the visible spectral region (Figure 3 B, curve d), a finding that is consistent with the presence of only a minimal intermolecular interaction[43] between C_{60} and **1** in its 1,3-alternate conformation. However, the addition of five equivalents of tetrabutylammonium chloride to this 2:1 mixture of **1** and C_{60} resulted in an immediate color change from brown to green and the appearance (Figure 3 B, curve e) of a strong CT absorption band centered at $\lambda_{max} = 725$ nm ($\varepsilon = 1900 \, M^{-1} cm^{-1}$). Such a finding provides support for the proposal that C_{60} is only encapsulated after **1** undergoes a change (Figure 3 A) from

the 1,3-alternate conformation to the corresponding chloride-bound cone conformation (that is, **1**·Cl⁻).

Force-field modeling of the proposed 2:1 complex (that is, $C_{60} \subset (\mathbf{1} \cdot Cl^-)_2$) that formed as the result of these two very different binding events (chloride binding and C_{60} encapsulation) was undertaken. For these calculations, the thiopropyl groups were replaced by thiomethyl groups for simplicity. Carried out in this way, a complexation energy of 7.4 kcal mol⁻¹ was derived using the Merck molecular force field (MMFF) and the generalized Born/surface area (GB/SA) solvent model[44] for chloroform. This value is in good agreement with the experimental result of 5.6 kcal mol⁻¹ (see below). The geometry was reoptimized[41] at the B3LYP/3-21G level,[45] and single-point calculations were performed with the larger 6-31G(d) basis set. As the B3LYP method underestimates the dispersion energy, it is not possible to obtain realistic complexation energies at this level. A natural bond orbital (NBO) population analysis indicated a charge transfer of 0.03 electrons to C_{60} from the TTF units. Although these calculations refer to the gas phase, they provide important support for the proposed interaction between the C_{60} guest and the electron-rich TTF "walls" of the calix[4]pyrrole "bowl".

A UV/Vis titration experiment (Figure 4B) was carried out to determine the binding constants (K_1 and K_2) that lead to the formation of the putative 2:1 complex between **1**·Cl⁻ and C_{60} (Figure 4A). In particular, the change in the intensity of the CT band ($\lambda_{max} = 725$ nm) was monitored as increasing quantities of **1**·Cl⁻ were added to a solution of C_{60} in dichloromethane at 298 K. A saturation point was reached after the addition of two equivalents of **1**·Cl⁻ to this latter solution of C_{60} (Figure 4B, curve d), with no perceptible changes being observed as additional equivalents of **1**·Cl⁻ were added (Figure 4B, curve e). The binding profile obtained in this way (Figure 4C) was subject to a standard nonlinear (2:1 host/guest) curve fitting analysis,[46] from which
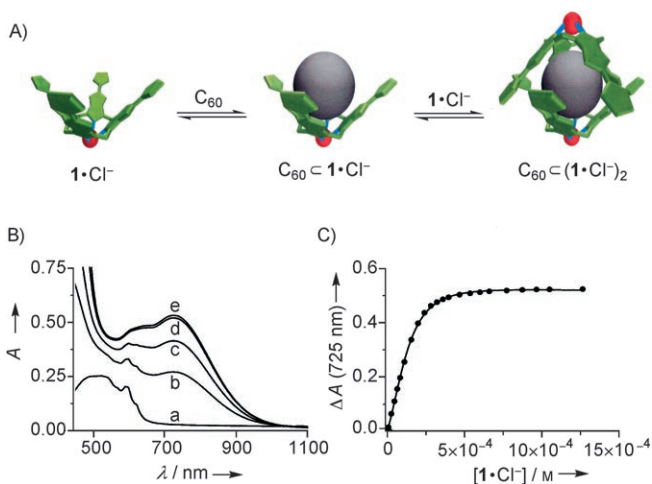
Figure 4. A) Equilibriums that lead to the formation of $C_{60} \subset \mathbf{1} \cdot Cl^-$ and $C_{60} \subset (\mathbf{1} \cdot Cl^-)_2$. B) Absorption spectra recorded in dichloromethane at 298 K of a) C_{60} (0.2 mM), b) C_{60} + **1**·Cl⁻ (0.5 equiv), c) C_{60} + **1**·Cl⁻ (1.0 equiv), d) C_{60} + **1**·Cl⁻ (2.0 equiv), and e) C_{60} + **1**·Cl⁻ (6.0 equiv). C) Changes in the CT band at 725 nm in the titration of C_{60} (0.2 mM) with **1**·Cl⁻ in dichloromethane at 298 K.

binding constants[47] $K_1 = 2.3 \times 10^3$ M⁻¹ and $K_2 = 1.3 \times 10^4$ M⁻¹—reflecting the formation of $C_{60} \subset \mathbf{1} \cdot Cl^-$ and $C_{60} \subset (\mathbf{1} \cdot Cl^-)_2$, respectively—were obtained. These values correspond to ΔG_1 and ΔG_2 values of -4.6 and -5.6 kcal mol⁻¹, respectively, at 298 K in dichloromethane.

Electrochemical measurements with C_{60}, **1**·Cl⁻, and $C_{60} \subset (\mathbf{1} \cdot Cl^-)_2$ in dichloromethane provided further support for the proposed binding events. In particular, the half-wave potential associated with the first reduction of the fullerene in $C_{60} \subset (\mathbf{1} \cdot Cl^-)_2$ was found to be shifted to a more negative potential (by -74 mV) relative to the first reduction of C_{60}. Such a finding is completely consistent with a partial shift of electron density from the electron-donating TTF subunits to the bound C_{60} guest. The unusually high shift seen for the C_{60} half-wave potential also serves to corroborate the strong electronic coupling within the $C_{60} \subset (\mathbf{1} \cdot Cl^-)_2$ self-assembled host–guest complex.

A gradual decrease in the C_{60} steady-state fluorescence spectral intensity ($\Phi = 2.0 \times 10^{-4}$) was also seen (Figure 5A)
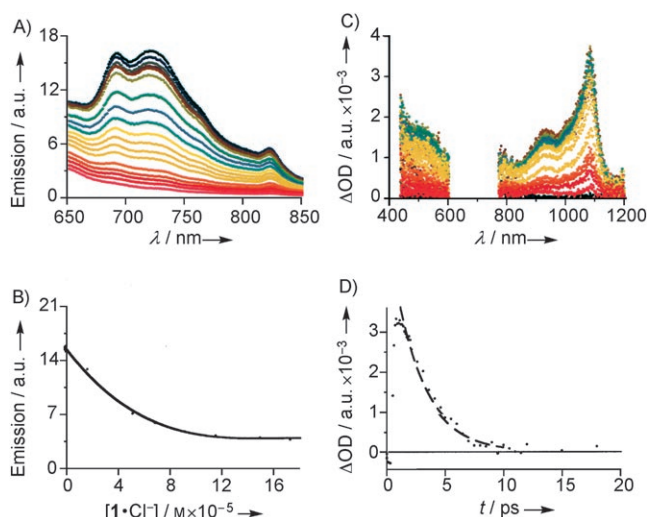
Figure 5. A) Steady-state fluorescence of a 5.38×10^{-5} M solution of C_{60} in dichloromethane upon adding variable concentrations of **1**·Cl⁻ (1.72×10^{-5} M to 2.87×10^{-4} M). B) Fluorescence intensity at 690 nm of $C_{60} \subset \mathbf{1} \cdot Cl^- / C_{60} \subset (\mathbf{1} \cdot Cl^-)_2$ in dichloromethane—the concentrations of **1**·Cl⁻ vary from 1.72×10^{-5} M to 2.87×10^{-4} M, whereas the concentration of C_{60} is constant at 5.38×10^{-5} M. C) Differential absorption spectra (visible) obtained upon femtosecond flash photolysis (740 nm) of $C_{60} \subset (\mathbf{1} \cdot Cl^-)_2$ in nitrogen-saturated dichloromethane with several time delays between 0 and 10 ps at room temperature; arrows indicate the evolution of differential changes. D) Time versus absorption profiles of the spectra shown above as recorded at 1080 nm.

when increasing quantities of **1**·Cl⁻ were added to solutions of C_{60} in dichloromethane. This decrease is attributed to an electron-transfer process that evolved from the singlet excited state of C_{60}. As in the case of the absorption-based studies, the change in intensity could be used to determine the binding constants for the formation of the successive $C_{60} \subset \mathbf{1} \cdot Cl^-$ and $C_{60} \subset (\mathbf{1} \cdot Cl^-)_2$ complexes. Data taken at 690 nm were plotted (Figure 5B) versus the concentration of **1**·Cl⁻.[48] Most importantly, the values obtained—$K_1 = 2.4 \times 10^3$ M⁻¹ (that is, for $C_{60} \subset \mathbf{1} \cdot Cl^-$) and $K_2 = 2.8 \times 10^4$ M⁻¹ (that is, for $C_{60} \subset$

($1\cdot Cl^-)_2$)—are in good agreement with those values determined using the UV/Vis titrations described above.

In addition, the fluorescence spectra recorded at the end of the titrations, that is, at the plateau value of each assay, were evaluated to assess the dynamics of the excited-state deactivation. A quenching factor of 17 ($\Phi = 1.1 \times 10^{-5}$) relative to bare C_{60} in the tightly organized $C_{60} \subset (1\cdot Cl^-)_2$ complex leads to an appreciably fast electron-transfer rate of $1.4 \times 10^{10}\,s^{-1}$ relative to the intrinsic decay of the singlet excited-state decay of C_{60} (that is, an intersystem-crossing rate of $8 \times 10^8\,s^{-1}$).

Transient absorption spectroscopy provided support for this proposed electron-transfer mechanism. In particular, femtosecond excitation into the CT absorption bands revealed features that correspond to the one-electron-reduced fullerene radical anion at 1080 nm[49] and the one-electron-oxidized TTF radical cation, a species that is known to absorb at 400 nm. Although the latter lies near the detection limit[41] of our femtosecond transient apparatus, it is clearly discernable (Figure 5 C). Mapping the radical-ion-pair formation rate to a first-order kinetic model, we determined a rather fast electron-transfer rate on the order of $10^{12}\,s^{-1}$, a value that is in good agreement with that obtained from an extrapolation of the steady-state fluorescence-quenching studies discussed above. Consistent with the proposed strong electron–donor interactions in $C_{60} \subset (1\cdot Cl^-)_2$, the resulting radical ion pair is short-lived with a lifetime of only 3.1 ps (Figure 5 D).[50]

In summary, we have demonstrated a step-by-step assembly of a complex calix[4]pyrrole-derived host–guest ensemble that contains two electron-rich TTF-functionalized calix[4]-pyrroles, an anion (that is, chloride), and an electron-deficient substrate (fullerene). In contrast to other self-assembled receptor systems, initial anion binding in the present ensemble serves as a "trigger" for the crucial reorganization of the calix[4]pyrrole receptor needed to produce a "cone" conformation, wherein multiple TTF units are appropriately arranged to allow for fullerene binding. The dramatic color change that accompanies the C_{60} binding event allows the recognition process to be followed readily, and thus the presence of this fullerene to be readily "sensed". As the size of the calixpyrrole receptor, may be varied (by the use of, for example, calix[5]pyrrole or calix[6]pyrrole) and the nature of the TTF substituents readily fine-tuned, this approach to elaborated receptor design could prove to be quite general, as may be the use of anion recognition as a triggering mechanism to generate complex supramolecular ensembles.

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[41] Details are available in the Supporting Information.

[42] The cubic cluster motif $[(\mathbf{1}\cdot Br)_6(C_{60})_8]^{6-}$ is found also in crystals obtained from a mixture of **1** and C_{60} with tetrabutylammonium bromide. Although the bulk crystal structures of the Cl^- and Br^- derivatives are quite different, the cubic cluster is apparently robust in the solid state.

[43] The nature of the interaction between **1** in its 1,3-alternate conformation and C_{60} is most likely such that C_{60} is complexed alongside one or more of the TTF units present in **1**.

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