Communication

Chloride Anion Controlled Molecular "Switching". Binding of 2,5,7-Trinitro-9-dicyanomethylenefluorene-C by Tetrathiafulvalene Calix[4]pyrrole and Photophysical Generation of Two Different Charge-Separated States

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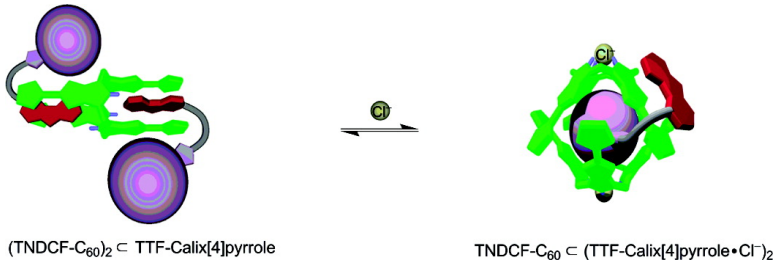

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Chloride Anion Controlled Molecular "Switching". Binding of 2,5,7-Trinitro-9-dicyanomethylenefluorene-C_{60} by Tetrathiafulvalene Calix[4]pyrrole and Photophysical Generation of Two Different Charge-Separated States

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A hallmark of living systems, either through intelligence or instinct, is an ability to differentiate between different pathways and outcomes based on environmental changes.[1] Such stimulus-based branching is also a key feature of advanced logic devices,[2] which produce different outputs based on a specific discrimination between different inputs.[3] While essential for life and a predicate to effecting artificial intelligence design, achieving this level of sophistication at the fundamental chemical level has proved exceptionally challenging[4] since it requires the development of systems that effect the differential recognition of various substrates. To date, such recognition and triggering have been demonstrated in multisite rotaxanes,[5] molecular grids,[6] self-regulating systems,[7] and certain elementary logic devices,[8] to name a few. However, we are unaware of any examples where differential selection between highly disparate substrates is controlled via an anionic triggering element. In this communication, we describe (Figure 1) a snake-like trinitrodicyanomethylene-fluorene-C_{60}[9] (TNDCF-C_{60}, **2**) derivative that can bind to a tetrathiafulvalene (TTF)-modified calix[4]pyrrole derivative[3b] **1** via two limiting recognition modes. The choice of these modes is determined by the presence or absence of added chloride anion and is correlated with (*i*) a switching in the conformation of the calix[4]pyrrole **1**, (*ii*) the formation of two different charge transfer (CT) complexes, and (*iii*) a change in the optical signature of the system as a whole. Since these latter substrate-dependent changes may be monitored both by the naked eye and more quantitatively by flash photolysis studies, this system functions as an environmentally responsive supramolecular "switching device", wherein "on" and "off" are controlled by the chloride anion concentration, the "leads" are the bifunctional substrate **2**, and the effect of on−off switching is manifested in the observable changes in the spectroscopic properties.

As is true for most other calix[4]pyrroles, receptor[3b] **1** exists predominantly in the 1,3-alternate conformation in the absence of anions (Figure 1).[10] In this conformation, the receptor **1** binds preferentially near-planar electron-deficient aromatic guests[3b] that are capable of forming stabilizing CT and hydrogen bonding interactions with the receptor by forming a sandwich-like complex with a receptor/guest stoichiometry of 1:2.[3b] However, in halogenated solvents, **1** binds chloride anions very tightly—a binding

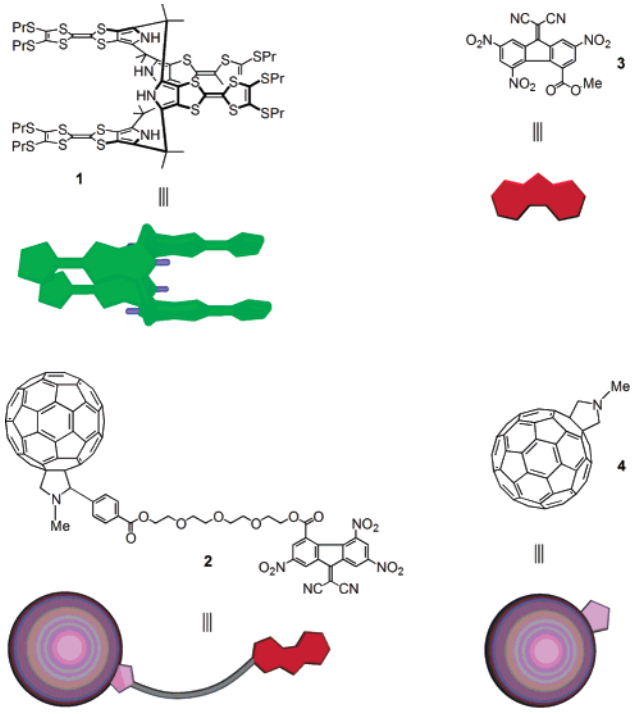

Figure 1. Line drawing of TTF-calix[4]pyrrole **1**, shown as a three-dimensional representation, and a cartoon representation of **1** in its 1,3-alternate conformation, and line drawings of TNDCF-C_{60} **2**, MTNDCM **3**, and NMF **4** and their corresponding cartoon representations.

constant (K_a) as high as 2.5×10^6 M^{-1} has been reported[3b,11] for the complexation of **1** with chloride ions in $ClCH_2CH_2Cl$ at 298 K—leading it to adopt a cone conformation (Figure 2A, **1**·Cl^-). In this cone conformation, the receptor **1**·Cl^- binds preferentially electron-deficient spherical guests, such as fullerene,[12] by encapsulating the guest in a 2:1 ratio. These anion-triggered differences in selectivity are reflected in easy-to-visualize color differences. This has led us to consider that receptor **1** could function as a kind of rudimentary anion-dependent supramolecular switching device. In an effort to explore this possibility, the bifunctional TNDCF-C_{60} substrate **2** was prepared.[9] This system contains two different binding motifs, a spherical fullerene head and a near-planar aromatic

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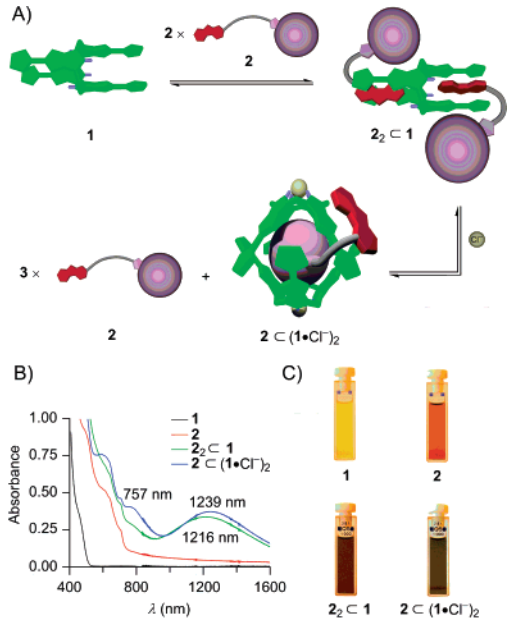

Figure 2. (A) Mechanistic scheme illustrating the proposed binding of the bifunctional substrate **2** to, and partial release from, receptor **1** observed in the absence and presence of chloride anions (studied as the tetrabutylammonium salt), respectively, under conditions where the substrate/receptor ratio is 2:1. (B) Absorption spectra recorded in CH_2Cl_2 at 298 K. (C) Pictures of CH_2Cl_2 solutions of receptor **1** (0.133 mM), guest **2** (0.267 mM), the complex $\mathbf{2}_2\subset\mathbf{1}$, and the complex $\mathbf{2}\subset(\mathbf{1}\cdot Cl^-)_2$.

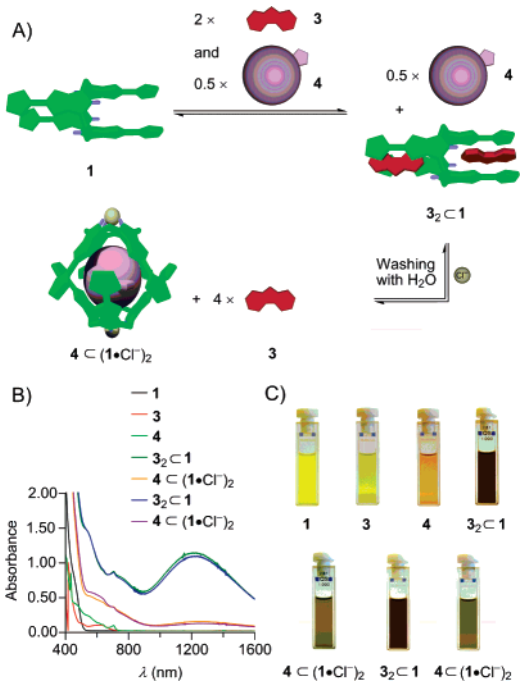

Figure 3. (A) Mechanistic scheme of the proposed complexation events involving receptor **1** and guests **3** and **4** observed in the absence and presence of chloride anions, respectively. (B) Absorption spectra recorded in CH_2Cl_2 at 298 K. (C) Pictures of CH_2Cl_2 solutions of receptor **1** (0.4 mM), guest **3** (0.8 mM), guest **4** (0.2 mM), the complex $\mathbf{3}_2\subset\mathbf{1}$, the complex $\mathbf{4}\subset(\mathbf{1}\cdot Cl^-)_2$, the complex $\mathbf{3}_2\subset\mathbf{1}$ after washing with water, and finally the complex $\mathbf{4}\subset(\mathbf{1}\cdot Cl^-)_2$ after the addition of a second aliquot of chloride anion.

TNDCF tail; it was thus expected to interact with receptor **1** in a chloride anion dependent manner.

The interactions between receptor **1** and, separately, the dyad TNDCF-C_{60} **2** and the two reference compounds (Figure 1), methyl 2,5,7-trinitrodicyanomethylene-fluorene-4-carboxylate[9] (MTNDCM, **3**) and *N*-methylfullero-pyrrolidine[13] (NMF, **4**), were investigated in solution using absorption, ^{1}H NMR, and emission spectroscopies.

The absorption spectra (Figure 2B) of receptor **1** in its 1,3-alternate conformation recorded in CH_2Cl_2 did not reveal any visible absorption bands at $\lambda > 550$ nm, and the solution appears yellow (Figure 2C). TNDCF-C_{60} **2** showed (Figure 2B) absorptions in the region from 400 to 800 nm;[14] dilute CH_2Cl_2 solutions of this compound thus appear light brown (Figure 2C). Addition of 2 equiv of the guest **2** to a CH_2Cl_2 solution of **1** in its 1,3-alternate conformation resulted in an immediate color change from yellow to dark brown (Figure 2C), a change ascribed to the formation of $\mathbf{2}_2\subset\mathbf{1}$. The absorption spectrum (Figure 2B) of this solution showed a strong CT band ($\epsilon = 2500$ M^{-1} cm^{-1}) centered at $\lambda_{max} = 1216$ nm corresponding to the CT interactions expected to occur between the electron-rich TTF units in receptor **1** and the electron-deficient TNDCF moiety of guest **2** within $\mathbf{2}_2\subset\mathbf{1}$. The addition of 2 equiv of tetrabutylammonium chloride (TBACl) to a solution of the complex $\mathbf{2}_2\subset\mathbf{1}$ results in a chloride-mediated conformational change (Figure 2A) of the receptor **1** into its cone conformation $\mathbf{1}\cdot Cl^-$. This change in conformation happens essentially instantaneously and is observed as a color change from dark brown to a more greenish color (Figure 2C). The absorption spectrum (Figure 2B) showed an increase in the absorption for the CT band centered at $\lambda_{max} = 757$ nm,[15] corresponding to the complexation of the C_{60} moiety of the guest **2** by 2 equiv of receptor **1** in its cone conformation (i.e., $\mathbf{1}\cdot Cl^-$) and the formation of the supramolecular complex $\mathbf{2}\subset(\mathbf{1}\cdot Cl^-)_2$. A small intensity increase and a bathochromic shift in the band corresponding to the CT interaction ($\lambda_{max} = 1239$ nm, $\epsilon = 2800$ M^{-1} cm^{-1}, Figure 2B) between the receptor **1** and the TNDCF moiety of the bidentate receptor **2** are also noteworthy. Even though the TNDCF part of **2** is no longer encapsulated "within" receptor **1**, it is still held in close proximity to the TTF units—by the glycol linker—and this side-by-side interaction, it is believed,[16] gives rise to the pronounced CT band centered at $\lambda_{max} = 1239$ nm. Since such putative secondary effects do not affect the visible portion of the spectrum, the dramatic change in response to substrate **2** (i.e., binding of the C_{60} head rather than the TNDCF tail) elicited by Cl^- may be followed easily by monitoring the change in color of the solution. Further support for the proposed switching events came from ^{1}H NMR spectroscopic analyses.[14]

In order to investigate the effect of the individual chemical "leads", namely, the TNDCF and C_{60} subunits present in **2**, an experiment was carried out wherein this bifunctional substrate **2** was replaced by a combination of MTNDCM **3** and NMF **4**. Specifically, addition of 2.0 molar equiv of **3** and 0.5 equiv of **4** to a CH_2Cl_2 solution of receptor **1** (Figure 3A) resulted in an immediate color change from yellow to brown (Figure 3B,C). Such a change is consistent with the formation of a complex, $\mathbf{3}_2\subset\mathbf{1}$, wherein receptor **1** is in its 1,3-alternate conformation. The absorption spectrum of this presumed complex displayed CT bands centered at $\lambda_{max} = 525$, 720, and 1220 nm ($\epsilon = 3700$, 2000, and 2800 M^{-1} cm^{-1}, respectively) and is thus in agreement with what is seen in the case of $\mathbf{2}_2\subset\mathbf{1}$ (cf. Figure 2). Addition of 2 equiv of chloride anions to this solution results in a conformational change of the receptor **1** from the 1,3-alternate to its cone conformation $\mathbf{1}\cdot Cl^-$. As a consequence, the 2:1 complex $\mathbf{3}_2\subset\mathbf{1}$ breaks up and is replaced by the 1:2 complex $\mathbf{4}\subset(\mathbf{1}\cdot Cl^-)_2$ (Figure 3A). This switching event is readily observed as a color change (Figure 3C) from brown to green. In more quantitative terms, the absorption spectrum (Figure 3B) reveals a huge decrease in the three absorption bands ($\lambda_{max} =$ 525, 720, and 1220 nm) associated with $\mathbf{3}_2\subset\mathbf{1}$ and a concomitant appearance of an absorption band at $\lambda_{max} = 735$ nm (Figure 3B),[15] corresponding to the 1:2 complex $\mathbf{4}\subset(\mathbf{1}\cdot Cl^-)_2$.

To show that the conformation of the receptor can be controlled via the presence or absence of a chloride anion, the CH_2Cl_2 phase containing a mixture of **1**, **3**, and **4** was washed with water. Such a washing serves to remove the chloride anions from **4**⊂(**1**·Cl^-)$_2$ and shift the conformation of the receptor **1** from the cone-like form back to the corresponding 1,3-alternate conformation. As a result, the complex **3**$_2$⊂**1** is re-established in preference to **4**⊂(**1**·Cl^-)$_2$, a conversion that is reflected in an observable change in the absorption spectrum (Figure 3B). Addition of a new aliquot of chloride anions to the CH_2Cl_2 phase serves to regenerate the green color, as would be expected given the presumed re-formation of the bischloride fullerene complex, **4**⊂(**1**·Cl^-)$_2$ (cf. Figure 3B). These experiments thus provide additional support for the notion that the differential recognition properties of receptor **1** can be controlled by adding or removing chloride anions and that the specific chemical "lead" (i.e., the nature of the guest) has a demonstrable effect on the optical "output" from the overall "device" (i.e., the color of the solution).[17]

Using standard absorption-based titration techniques, the binding constants[14] (K_1 and K_2) for the 2:1 complex between **1**·Cl^- and the C_{60} moiety of guest **2** were determined to be 2.8×10^3 (C_{60} moiety of **2**⊂**1**·Cl^-) and 1.3×10^4 M^{-1} (C_{60} moiety of **2**⊂(**1**·Cl^-)$_2$) in CH_2Cl_2 at 298 K.

These absorption-based binding studies were complemented by fluorescence quenching based analyses. Here, it was appreciated that the various CT interactions between the TTF donor groups of **1** and the electron-accepting moieties (i.e., the TNDCF and C_{60} subunits) present in **2** would lead to a quenching of the fluorescence. Indeed, when a CH_2Cl_2 solution of **2** is titrated[14] with increasing quantities of **1** in the absence of chloride, a gradual decrease in the fluorescence intensity of the TNDCF moiety present in **2** is seen. By monitoring the change in intensity of the fluorescence maximum at 540 nm as a function of the concentration of **1**, binding constants, $K_1 = 7.8 \times 10^5$ M^{-1} and $K_2 = 3.7 \times 10^3$ M^{-1}, corresponding to the binding of **1** to **2** and **2**⊂**1**, respectively, could be derived. Similar fluorescence quenching studies, this time plotting[14] the change in intensity at 710 nm versus the concentration of **1**·Cl^- (formed by addition of TBACl; vide supra), allowed the binding constants for the successive formation of **2**⊂(**1**·Cl^-) and **2**⊂(**1**·Cl^-)$_2$ to be determined. Gratifyingly, the values obtained, $K_1 = 8.3 \times 10^3$ M^{-1} and $K_2 = 1.2 \times 10^4$ M^{-1}, respectively, are in agreement with those obtained from the absorption-based studies discussed above.

Selective excitation of the 2:1 complex **2**$_2$⊂**1** could be effected by irradiation at 775 or 1200 nm. The resulting transient absorption spectra revealed the radical anion bands of the one-electron-reduced TNDCF moiety of **2** at 535 and 870 nm. Subjecting the decay traces to a first-order kinetic analysis afforded a 2.4 ps lifetime for the underlying radical ion pair state. We also confirmed that an electron transfer (ET) mechanism governs the excited state deactivation in the complex **2**⊂(**1**·Cl^-)$_2$. In this case, selective femtosecond excitation may be effected by irradiation at 730 nm (Figure S13A), which corresponds to the CT absorption band. The resulting transients revealed features at 1020 and 400 nm that clearly match the one-electron-reduced radical anion of C_{60} and the one-electron-oxidized radical cation of TTF, respectively.[18] Fitting these transients to a first-order kinetic equation (Figure S13B) gave rise to a lifetime of 3.7 ps for the metastable radical ion pair state.

In conclusion, we have shown that the dynamic nature of the receptor TTF-calix[4]pyrrole **1** can be utilized to follow the complexation of the bifunctional substrate **2** containing both a C_{60} subunit and a TNDCF moiety under conditions that allow for preferential control. In the presence of chloride anion, binding of the C_{60} head is preferred, whereas complexation of the TNDCF tail is dominant in the absence of this anion. This differential binding process is reflected in easy-to-visualize color changes and may be followed readily by both static and time-resolved absorption spectroscopy. System **1** thus shows the essential features of an environmentally responsive, supramolecular switching device.

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Supporting Information Available: Spectroscopic characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) See Supporting Information.

(15) This situation is characteristic for a C_{60} moiety encapsulated by 2 equiv of **1**·Cl^- in CH_2Cl_2, which produces a CT band at $\lambda_{max} = 725$ nm ($\epsilon = 2800$ M^{-1} cm^{-1}) in the case of pristine C_{60}; see ref 12.

(16) The existence of side-by-side interactions was also supported by ^{1}H NMR investigations[14] carried out on **2**⊂(**1**·Cl^-)$_2$ in $CDCl_3$.

(17) These experiments, specifically, the huge relative decrease in the magnitude of the CT bands at $\lambda_{max} = 525$ and 1220 nm for experiments involving **3** and **4** as compared to experiments carried out with guest **2**, also provide support for the notion that tethering the two moieties in **2** via a covalent linker serves to enhance the CT band seen in Figure 2B. This is because such a linkage means that the TNDCF moiety of **2** remains in close proximity to the receptor **1**·Cl^-, even though the primary binding process occurring under these conditions involves complexation of the C_{60} head of **2**.

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