

#### Communication

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# Azobenzene-Bridged Expanded "Texas-sized" Box: A Dual-Responsive Receptor for Aryl Dianion Encapsulation

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**Abstract**: We report an expanded "Texas-sized" molecular box (**AzoTxSB**) that incorporates photo-responsive azobenzene bridging subunits and anion recognition motifs. The shape of this box can be switched through light induced  $E \leftrightarrow Z$ photoisomerization of the constituent azobenzenes. This allows various anionic substrates to be bound and released by using different forms of the box. Control can also be achieved using other environmental stimuli, such as pH and anion competition.

The encapsulation and controlled release of molecules in response to stimuli is a field of research that touches on both academic and industrial research interests.<sup>1</sup> Guest encapsulation can provide many advantages in range of application areas, and is often associated with improvements in efficiency, product stability, active ingredient compatibility, and better safety.<sup>2</sup> Classic approaches to encapsulation involve the selective inclusion of guests within discrete, shape-persistent macrocycles.<sup>3</sup> In many cases the associated host-guest recognition processes can often be modulated via application of various external stimuli. Typically, guest competition and pH/redox switching are used.<sup>4</sup> An attractive alternative involves controlling guest capture and release using light as the stimulus. To date, the photo-controlled uptake and release of guests has been achieved in numerous instances.<sup>5</sup> Generally, this has been done by exploiting in elegant fashion a variety of light-responsive guests. The use of photoresponsive host systems has been more limited.<sup>6</sup> This limitation is particularly noteworthy in the case of receptors capable of capturing anionic guests.7 Here, photo switchable nonmacrocyclic anion receptors, such as acyclic tweezers- and helical foldamer-based anion receptors, have allowed for important advances. For example, Flood and coworkers reported photodriven foldameric receptors that release anionic guests upon light excitation. They also described anion regulation and double-tosingle helix switching.7b, h Ballester and coworkers reported tetraazobenzene-extended calix[4]arenes that form photo-switchable dimeric capsules.8 Jeong and coworkers reported anion transporters with photoswitchable features.7e Feringa and coworkers developed an anion receptor that selectively binds CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, with an affinity that can be tuned via lightinduced E/Z isomerization.<sup>6b</sup> However, there remains a need for a photoresponsive system that can bind and release larger anionic guests, including organic species that can serve as proxies for anionic pollutants, pharmaceuticals, industrial feedstocks, plasticizers, and the like. Here, we report the synthesis of an

azobenzene-containing expanded "Texas-sized" box, AzoTxSB 1 (Scheme 1). This system is produced via a facile four-step synthetic procedure and is capable of recognizing various aryl dicarboxylates and releasing them upon photoirradiation. Anion release can also be achieved through changes in pH and via competition with tetrabutylammonium chloride (TBACl).

Inspired by the chemistry of the tetracationic cyclobis(paraquat-*p*-phenylene) CBPQT<sup>4+,9</sup> our group designed and prepared a tetracationic imidazolium-based macrocycle 1 in 2010 (**TxSB**; Scheme 1)<sup>10</sup>. To date, this and other "Texas-sized" boxes have been used to construct a wide range of stimuli responsive molecular and supramolecular constructs, many of which rely on anion recognition as a key structure-defining motif.<sup>11</sup> A range of important contributions have also come from studies of other extended box systems developed by the Stoddart group.<sup>6b,12</sup> While the latter group recently reported a photoresponsive system,<sup>6b</sup> to date the responsive behavior of our systems has largely been limited to chemical action (e.g., pH switching, substrate competition, etc.). We have now incorporated azobenzene subunits into the core **TxSB** structure to create the **AzoTxSB** (1).

The synthesis of **AzoTxSB** is summarized in Scheme 1. The key trimeric fragment, 2,6-di(1H-imidazol-1-yl) pyridine, and 1,4-bis-bromomethylazobenzene were prepared according to previous reports.<sup>10, 13</sup> Cyclization then gave the corresponding macrocycle in the form of its tetrabromide salt. Exposure to aqueous  $NH_4PF_6$  gave the corresponding tetrahexafluorophosphate salt, **AzoTxSB**, in 22% yield (based on cyclization and salt exchange).

**Scheme 1.** (a) Synthetic Route to Azobenzene "Texas-sized" Molecular Box AzoTxSB 1 and (b) Chemical Structures of Traditional "Texas-sized" Molecular Box (TxSB) and Small Molecular Guests Used in this Study.





AzoTxSB was designed to be an expanded version of the tetracationic "Texas-sized" box 1 (TxSB).<sup>10</sup> Compared to TxSB, AzoTxSB contains a larger central cavity as the result of incorporating bridging azobenzene subunits. A solid state structural analysis (Figure 1a) revealed that AzoTxSB is substantially elongated compared to TxSB. The distance between the centroids of the triaryl bridges is 14.43 Å the case of AzoTxB vs. 8.02 Å for TxSB. The breadth of the box, as measured by the average distance between the planes of the two sets of parallel azobenzene phenyl units, is 9.7 Å for AzoTxB vs. 8.61 Å for TxSB in its partial chair conformation.



**Figure 1.** (a) Single crystal structure of **E,E-AzoTxSB** showing one of the  $PF_6^-$  counter anions. Side view showing the partial chair conformation. Some of the counter anions and solvent molecules have been omitted for clarity. (b) DFT optimized structure of **Z,Z-AzoTxSB** and (c) **E,Z-AzoTxSB**.

The photoisomerization behavior of **AzoTxSB** was first studied by UV/Vis spectroscopy. A fresh prepared solution of **AzoTxSB** in DMSO shows an intense absorption band at 330 nm and a relative weak absorption feature at 438 nm. These characteristics are in agreement with the strong  $\pi$ - $\pi$ \* and weak n- $\pi$ \* absorption features expected for an azobenzene system (Figure S4, Supporting Information).<sup>6d,14</sup> Upon UV light irradiation (365 nm), the intensity of the band corresponding to the  $\pi$ - $\pi$ \* transition decreases sharply. At the same time, the intensity of the band corresponding to the n- $\pi$ \* absorption increases slightly. These observations are consistent with E→Z photoisomerization of the azobenzene subunits. Meanwhile, as normal for an azobenzene system, this isomerization can be reversed by exposure to visible light (420 nm).<sup>6d,14</sup>

The putative photoisomerization behavior of AzoTxSB was then studied by <sup>1</sup>H NMR spectroscopy. The spectrum of freshly prepared DMSO-d<sub>6</sub> solution of AzoTxSB (Figure 3c) is characterized by the presence of eight distinct resonances. This is consistent with the all-trans E,E-AzoTxSB stereoisomer dominating in the absence of light. After UV light irradiation (365 nm), the intensity of the H<sub>8</sub> proton resonance in the spectrum of E,E-AzoTxSB decreases and three additional sharp and wellresolved signals, corresponding to the same H<sub>8</sub> proton, are seen at 8.64 7.70, and 6.94 ppm. In light of literature precedent,<sup>6d</sup> these results lead us to suggest that UV-light-promoted  $E \rightarrow Z$ isomerization takes place and generates a mixture of three distinct stereoisomers, assigned as E,E-AzoTxSB (14.8%), E,Z-AzoTxSB (40.8%), and Z,Z-AzoTxSB (44.4%). Visible light Irradiation regenerates the initial spectrum. Clean interconversion between the photoisomers was seen over the course of several cycles (Figure S7).

Possible structures for the **E.Z-** and **Z,Z-AzoTxSB** were inferred from DFT calculations (Figure 1b, c).<sup>15</sup> On the basis of these analyses, we conclude that the size of the macrocyclic cavity decreases substantially upon azobenzene photoisomerization.

The thermal relaxation to the ground state starting from the Zrich **AzoTxSB** species produced upon photoirradiation was studied using thermal array <sup>1</sup>H NMR spectroscopy. The rates of decay were monitored at 313, 318, 323, and 328 K. The corresponding rate constants,  $k_1$  and  $k_2$ , and the thermodynamic parameters  $\Delta G^{\ddagger}$ ,  $\Delta H^{\ddagger}$ , and  $\Delta S^{\ddagger}$  (Figure 2, Figures S22–S31, Tables S1–S5) were calculated by fitting the data to a kinetic model allowing for two independent isomerization events (Eq S2–S6)) and the Eyring equation (Eq S4-S7). The activation barrier ( $\Delta G^{\ddagger}$ ) of **Z**,**Z**→**E**,**Z AzoTxSB** (80.4 kJ·mol<sup>-1</sup>) was found to be slightly lower than for the **E**,**Z**→**E**,**E AzoTxSB** process ( $\Delta G^{\ddagger} = 89.4$ kJ·mol<sup>-1</sup>) at 293 K (Figure 2).



Figure 2. Relative energies and thermal  $Z \rightarrow E$  isomerization activation energies of the three stereoisomers of AzoTxSB and E,E-AzoTxSB $\supset$ 2. Energies are plotted relative to the lowest energy conformation (E,E-AzoTxSB). The energy of E,E-AzoTxSB $\supset$ 2 accounts for the energy of free dianion 2.

DFT calculations led to the conclusion that the lowest energy molecular configuration of **Z,Z-AzoTxSB** is 38.67 kJ mol<sup>-1</sup> higher in energy than the **E,Z-AzoTxSB** isomer, which is in turn lies 57.38 kJ mol<sup>-1</sup> above the **E,E-AzoTxSB** (Figure 2). Such a result provides support for the notion that ring strain<sup>14</sup> does not

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play a significant role in defining the thermal isomerization parameters for AzoTxSB.

We next explored whether anionic organic guests could be encapsulated into the cavity of the macrocycle. The representative compounds 2—7 were chosen to test this possibility (Scheme 1b). <sup>1</sup>H NMR spectroscopic studies revealed chemical shift changes consistent with a binding interaction between **Azo-TxSB** and these guests (Figures S10-S19). In the case of dianion 2 (studied as its TBA salt) a <sup>1</sup>H NMR spectral analysis of a two equiv of 2 with AzoTxSB (2.00 mM) in DMSO-*d*<sub>6</sub> (Figure 3) provided evidence of fast exchange. Peaks corresponding to H<sub>7</sub>, H<sub>8</sub> of the host **AzoTxSB** and H<sub>a</sub>, H<sub>b</sub> of the guest are shifted upfield, while the signals for H<sub>2</sub>, H<sub>3</sub>, H<sub>4</sub>, H<sub>5</sub> and H<sub>6</sub> of the host are shifted downfield (Figure 3a-c). From a quantitative spectroscopic titration, the 1:1 association constant in DMSO-*d*<sub>6</sub> was determined to be  $(1.63 \pm 0.13) \times 10^6$  M<sup>-1</sup> (Figures 4b and S9).<sup>16</sup>



**Figure 3.** Partial <sup>1</sup>H NMR spectra (DMSO- $d_6$ ) of (a) **2**, (b) **E,E-AzoTxSB** $\supset$ **2**, (c) **E,E-AzoTxSB** before and (d) after photoirradiation (365 nm) and (e) followed by the addition of excess **2**, (f) after photoirradiation (420 nm) of (e).

Electrospray ionization mass spectrometry of equimolar mixtures of AzoTxSB with 2 revealed a peak at m/z = 539.2, corresponding to  $[AzoTxSB \supset 2 - 4PF_6]^{2+}$ , and a peak at m/z = 440.2, ascribable to  $[AzoTxSB \supset 2 - 4PF_6 + TBA]^{3+}$  (Figures 4a). While not a proof, such findings support the 1:1 binding stoichiometry proposed for AzoTxSB $\supset 2$ .

A possible structure for the AzoTxSB⊃2 complex was deduced on the basis of DFT calculations (Figure 4c).<sup>15</sup> This energyminimized structure provides support for the suggestion that the cavity provided by AzoTxSB is large enough to accommodate dianion 2 as guest and that, once bound, it is stabilized by C– H•••O hydrogen bonding interactions (Figure 4c and S34). This interpretation is consistent with the <sup>1</sup>H NMR spectral analysis (vide supra).

When **E,E-AzoTxSB** $\supset$ **2** was irradiated with UV light at 365 nm for 10 min, the induced  $E \rightarrow Z$  isomerization of the host leads to release of **2** from the host cavity. This conclusion was supported by an analysis of the <sup>1</sup>H NMR spectra, particularly the shifts in the resonances ascribed to protons H<sub>7</sub> and H<sub>8</sub> (Figure 3e). Little in the way of discernible peak shifts were seen for protons H<sub>7</sub> and H<sub>8</sub> (E,Z and Z,Z forms). Meanwhile, a downfield chemical shift was seen for proton H<sub>5</sub>. Based on these experimental observations, we conclude that neither **E,Z-AzoTxSB** nor **Z,Z-AzoTxSB** has an appreciable affinity for **2**, at least via complexation within the cavity. Exposure of the mixture produced upon UV illumination to light at 420 nm acts to reset the system back to the guest complexed **E,E-AzoTxSB** $\supset$ 2 enriched state. This switchable guest binding and release is shown schematically in Figure 5. Similar responsive behavior was inferred in the case of all other guests except for the relatively small guest 4 (cf. Supporting Information).



**Figure 4**. (a) Electrospray ionization mass spectrometric analysis of a 1:1 mixture proposed to produce **E,E-AzoTxSB** $\supset$ 2. (b) Global fit to a 1:1 binding model by nonlinear regression of the <sup>1</sup>H NMR spectral shifts seen for the H<sub>5</sub>, H<sub>6</sub>, H<sub>7</sub> and H<sub>8</sub> resonances when **E,E-AzoTxSB** is titrated with 2. (c) Energy optimized structure of AzoTxSB $\supset$ 2.



Figure 5. Schematic representation of the multi-responsive catchand-release of 2 by AzoTxSB, inlcuding photo-, pH- and anionresponsiveness. Geometry optimized molecular structures were used to create this image.

When **E,E-AzoTxSB** was added to a mixture of **2** and **4**, the observed chemical shift changes corresponded to those seen for **E,E-AzoTxSB** $\supset$ **2**, rather than to those of **E,E-AzoTxSB** $\supset$ **4**. On this basis we conclude that **2** is recognized preferentially by **AzoTxSB** (Figure S11a-c, Figure 5). However, when irradiated with UV light, guest **2** was released from the box while substrate **4** was incorporated into the box (Figure S11d-g, Figure 5).

Guest release and reformation of the complex  $AzoTxSB \supset 2$  could also be induced by adding in sequence trifluoroacetic acid

(TFA) and triethylamine (TEA) (Figures 5 and S10). Guest 2 is Raspberry-Like Colloids Based on Cucurbit [8] Uril Host-Guest Interactions. likewise released 2 by adding an excess of a competitive guest, such as TBACl (Figure S12).

In summary, we report an expanded "Texas-sized" box, AzoTxSB whose cavity shape can be controlled through photoirradiation. In the absence of UV light, this cationic macrocycle acts as an effective receptor for test aryl anions in DMSO- $d_6$ . Exposure to UV light then serves to effect guest release. Control over substrate binding can also be accomplished through chemical means. The present work extends the lexicon of anionic substrates whose binding can be controlled though lightbased stimuli and sets the stage for the design and preparation of more elaborate photoresponsive supramolecular systems.

#### ASSOCIATED CONTENT

Supporting Information: Experimental details and characterization data. Cif file for compound AzoTxSB (CCDC number: 1866348). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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The authors declare no competing financial interest.

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- energy cutoff of 400 eV. All structures were hosted in a cubic box with a side
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