

## exTTF as a Building Block for Fullerene Receptors. Unexpected Solvent-Dependent Positive Homotropic Cooperativity

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Photo- and electroactive donor–acceptor dyads and triads,<sup>1</sup> molecular rectifiers,<sup>2</sup> cation sensors,<sup>3</sup> and bistable molecular shuttles and catenanes<sup>4</sup> based on tetrathiafulvalene (TTF) have all been reported, illustrating the versatility of this electron donor unit in a wide range of research areas.<sup>5</sup> In contrast, and although it has been known for more than 15 years,<sup>6</sup> the applications of its  $\pi$ -extended analogue, 2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9H)-ylidene]-1,3-dithiole (exTTF), have thus far been somewhat limited.<sup>7</sup> For instance, exTTF has scarcely been used as a building block in supramolecular chemistry,<sup>8</sup> despite its suggestive curved shape.

We wish to report the first exTTF-based receptor for fullerene, **2**, and its unexpected solvent-dependent complexation behavior toward C<sub>60</sub>.

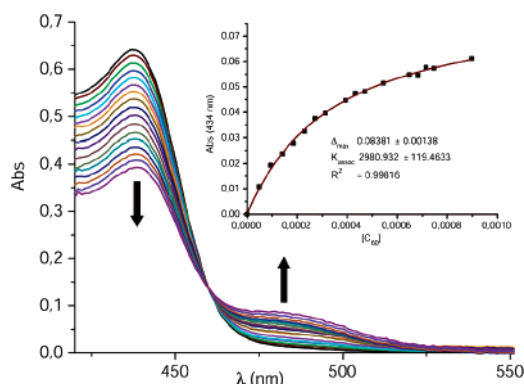
Porphyrins and other planar aromatic systems are known to interact favorably with fullerenes—mainly via dispersion forces—both in solution and in the solid state.<sup>9</sup> This has been exploited in the synthesis of a wide range of receptors. A bivalent, tweezer-like design in which two units of the recognizing fragment are connected covalently by means of an adequate spacer has been particularly fashionable in this area<sup>10</sup> since generally the interaction with a single recognizing unit is not sufficient for efficient complexation.<sup>11</sup>

We envisaged the relatively large, concave aromatic surface of exTTF to be a good match for the convex exterior of fullerenes and expected it to establish favorable van der Waals and  $\pi$ – $\pi$  interactions with it.

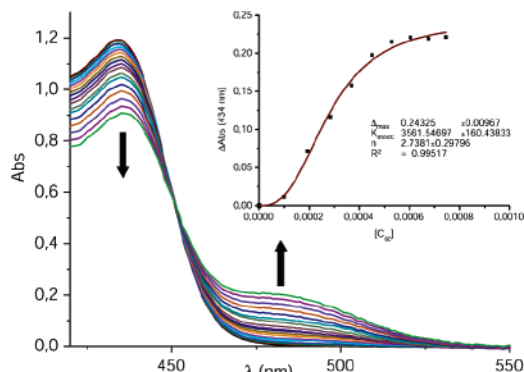
Preliminary molecular modeling studies suggested that an isophthalic ester would be well suited as a spacer between two exTTF fragments. Since receptor **2** was conceived as a proof-of-principle example of exTTF-based receptors for fullerene, its design was also strongly biased by a criterion of simplicity and synthetic ease. Alcohol **1** is readily obtained from 2-(hydroxymethyl)-anthraquinone,<sup>12</sup> while isophthaloyl chloride is a cheap, commercially available starting material. A simple condensation reaction afforded receptor **2** in 96% yield (Scheme 1).

UV–vis titrations of **2** with C<sub>60</sub> were carried out in chlorobenzene and CHCl<sub>3</sub>/CS<sub>2</sub> mixtures. Figure 1 shows the electronic absorption spectral changes of receptor **2** ( $2.01 \times 10^{-5}$  M) upon addition of C<sub>60</sub> ( $4.06 \times 10^{-3}$  M) in chlorobenzene at ambient temperature. Depletion of the maximum at 434 nm is accompanied by the emergence of a new transition ( $\lambda_{\text{max}} = 483$  nm) which is assigned to the **2**•C<sub>60</sub> complex. The appearance of an isosbestic point at 459 nm is suggestive of 1:1 stoichiometry, which was confirmed by Job plot analysis (see Supporting Information). The variation in absorption at 434 nm fits well to a 1:1 binding isotherm (Figure 1, inset) affording a binding constant of  $(2.98 \pm 0.12) \times 10^3$  M<sup>-1</sup>.

Interestingly, the complexation behavior of **2** in CHCl<sub>3</sub>/CS<sub>2</sub> proved to be significantly different. The changes in absorption of **2** (CHCl<sub>3</sub>,  $2.32 \times 10^{-5}$  M) upon addition of C<sub>60</sub> (CS<sub>2</sub>,  $4.06 \times 10^{-3}$  M) are depicted in Figure 2.

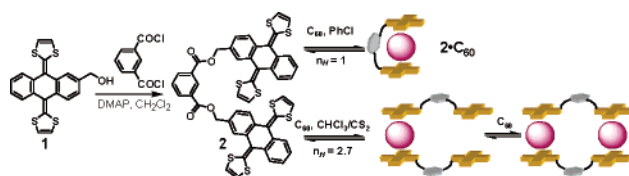


**Figure 1.** Absorption spectral changes of receptor **2** (chlorobenzene, 298 K,  $2.31 \times 10^{-5}$  M) upon addition of fullerene (chlorobenzene, 298 K,  $4.05 \times 10^{-3}$  M). The absorption spectra of fullerene have been subtracted. The inset shows the fit of  $\Delta$ Abs (434 nm) to a 1:1 binding isotherm.

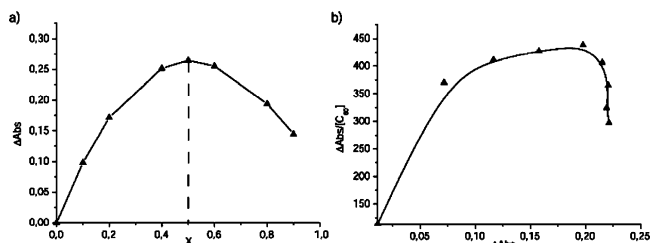


**Figure 2.** Absorption spectral changes of receptor **2** (CHCl<sub>3</sub>, 298 K,  $2.32 \times 10^{-5}$  M) upon addition of fullerene (CS<sub>2</sub>, 298 K,  $4.05 \times 10^{-3}$  M). The absorption spectra of fullerene have been subtracted. The inset shows the fit of  $\Delta$ Abs (434 nm) to the Hill equation.

### Scheme 1. Synthesis of Receptor **2** and Its Complexation with C<sub>60</sub>



Similarly to that observed in chlorobenzene, the maximum at 434 nm decreases as a new band ( $\lambda_{\text{max}} = 482$  nm) increases, forming a distinctly clear isosbestic point at 451 nm, which points to the formation of a 1:1 complex in this solvent system, too. This stoichiometry is also supported by Job plot analysis (Figure 3a). However, in this case, the binding curve is sigmoidal in shape, which is generally regarded as the criterion for cooperativity. The concave-upward Scatchard plot (Figure 3b) is also in agreement



**Figure 3.** (a) Job plot for **2** upon increasing molar fraction of  $C_{60}$  in  $CHCl_3/CS_2$  at a fixed overall concentration of  $2.31 \times 10^{-5}$  M. (b) Scatchard plot of the data shown in Figure 2.

with a positive cooperative binding event.<sup>13</sup> Indeed, the changes in absorption can be fitted to the Hill equation very satisfactorily ( $R^2 = 0.995$ ), yielding a Hill coefficient of  $n_H = 2.7 \pm 0.3$  and an apparent binding constant of  $(3.56 \pm 0.16) \times 10^3 M^{-1}$ . Although it is often considered a direct indication of the number of available binding sites on the receptor, the Hill coefficient is best thought of as an interaction coefficient reflecting the extent of cooperativity, with a maximum value equal to the number of binding sites.<sup>13</sup> Thus, a value of  $n_H > 2$  rules out the formation of the expected pincer-like  $2 \cdot C_{60}$  complex since it features two binding sites only. This, together with the 1:1 stoichiometry, strongly suggests the formation of a supramolecular tetramer<sup>14</sup> in which two units of  $C_{60}$  are sandwiched between two molecules of receptor **2**, as depicted in Scheme 1. Unfortunately, all attempts to obtain single crystals of the complex from  $CHCl_3/CS_2$  mixtures have been unsuccessful so far. The marked cooperative effect toward formation of the tetramer is self-evident considering its structure (Scheme 1). Binding of a first fullerene molecule greatly facilitates binding of a second one by preorganizing the two free exTTF fragments.

In  $CHCl_3/CS_2$ , the high entropic cost of formation of the tetramer must be compensated for by a significant increase in solvation energy when compared to the  $2 \cdot C_{60}$  dimer. The molecular basis and the structural requirements for this solvent-controlled change in binding mode are currently being investigated, both experimentally and theoretically.

In summary, we have described the first exTTF-based receptor for fullerene, **2**, based on a synthetically straightforward tweezer-like design. Despite its structural simplicity, **2** binds fullerene efficiently in both chlorobenzene and  $CHCl_3/CS_2$  mixtures, which substantiates the validity of exTTF as a new building block for fullerene receptors and suggests that binding constants comparable to those obtained for porphyrin-based receptors could be obtained by incorporating preorganization in the design.<sup>10a</sup>

Moreover, receptor **2** shows a unique solvent-controlled positive homotropic cooperative binding behavior. Negative and positive cooperative binding events are ubiquitous in Nature,<sup>15</sup> and their regulation lies at the heart of many signal transduction processes. Other synthetic receptors that show cooperative behavior have been reported previously,<sup>16</sup> which generally show either negative<sup>16c</sup> or positive heterotropic<sup>16d</sup> cooperativity. Positive homotropic<sup>17</sup> cooperativity is much more infrequent in artificial systems, and, to date, exercising control over it remains a major challenge.<sup>18</sup> In particular, the different binding modes of receptor **2** might find use in the controlled self-assembly of supramolecular exTTF- $C_{60}$  donor-acceptor ensembles.<sup>19</sup>

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**Supporting Information Available:** Experimental details, equations, and supplementary figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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