

Supramolecular Threaded Complexes from Fullerene–Crown Ether and π -Extended TTF Derivatives

Beatriz M. Illescas,^[a] José Santos,^[a] Marta C. Díaz,^[a] Nazario Martín,^{*[a]} Carmen M. Atienza,^[b] and Dirk M. Guldi^{*[b]}

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A series of π -extended TTFs (exTTFs) bearing one (**8**, **16**, **19**) or two (**14**) dibenzylammonium units have been threaded through a dibenzo-24-crown-8 (DB24C8) ring covalently linked to a C₆₀ sphere. Whereas **8** and **14** were prepared in a multistep synthetic procedure involving Sonogashira cross-coupling reactions affording rigid donors, exTTFs **16** and **19** were prepared by direct esterification reactions leading to more flexible systems. Complexation experiments carried out by ¹H NMR titration and fluorescence studies show the for-

mation of stable supramolecular dyads with binding constants ranging from 10³ to 10⁴ M⁻¹. Although the UV/Vis and CV studies reveal the lack of interaction between the electroactive species (C₆₀ and exTTF) in the ground state, fluorescence data indicate the presence of an electronic interaction in the excited state.

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Introduction

The design of new molecular materials able to harvest and transform solar energy into chemical or electrical power has been intensively studied over the last years.^[1] Such bio-inspired artificial systems mimic the photoinduced electron transfer process occurring during photosynthesis, which results in an efficient formation of the corresponding radical ion pair species.^[2] The assembly of an electron donor (D) and an electron acceptor (A) provides the necessary pathway that allows photoinduced electron transfer to occur. In this sense, fullerene C₆₀ has been successfully used as the acceptor moiety in the construction of model photosynthetic systems due to its remarkable photophysical, electrochemical and chemical properties.^[3]

The covalent linkage of the two electroactive donor and acceptor fragments by means of flexible or rigid spacers has been, by far, the most studied approach. A wide variety of electron donor units, such as porphyrins,^[4] organometallic complexes, such as ferrocenes^[5] or Ru^{II}bipyridine,^[6] carotenes,^[7] aniline derivatives,^[8] π -conjugated oligomers,^[9] phthalocyanines^[10] and tetrathiafulvalenes (TTFs)^[11,12] have been covalently linked to C₆₀ through different chemical protocols.

Since photoinduced electron transfer between the donor and C₆₀ may take place through space, both moieties can also be connected by means of non-covalent interactions. Thus, C₆₀-based supramolecular donor–acceptor dyads have also been widely studied.^[13]

Our groups have intensively worked in the preparation and study of covalent TTF–C₆₀ dyads, especially, in the study of systems bearing π -extended-TTF (exTTF) as the donor fragment.^[11] Contrary to other donor fragments such as porphyrins, π -conjugated oligomers, etc, both TTF and exTTF undergo a strong gain of aromaticity upon oxidation. Furthermore, in comparison to the parent TTF, exTTF has proved to have exceptional properties for the stabilization of the charge-separated states generated upon light irradiation. Thus, the radical ion pair lifetimes of exTTF–C₆₀ dyads were two orders of magnitude higher than those reported for the analogue TTF–C₆₀ systems.^[11,12]

Although there are many examples in the literature involving supramolecular aspects of TTF chemistry,^[14] exTTF has been much less studied in this context, and only a few examples have been reported. Bryce et al.^[15] described crown-annelated derivatives of exTTF **1** and **2** (Figure 1) and exploited their chromophoric and strong π -electron donor properties in the spectrophotometric and voltammetric sensing of metal cations.

Very recently in our group, exTTF has been used as a building block for the preparation of efficient fullerene receptors of type **3**. Strikingly, such exTTF based tweezers show a unique solvent-controlled positive homotropic cooperative binding behaviour.^[16] Previously, we had reported on the synthesis of a π -extended TTF dimer crown ether **4**

[a] Departamento Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain
Fax: +34-91-394-4103
E-mail: nazmar@quim.ucm.es

[b] Institute of Physical and Theoretical Chemistry and Interdisciplinary Center for Molecular Materials, University of Erlangen, 91058 Erlangen, Germany
Fax: +49-913-185-28307
E-mail: dirk.guldi@chemie.uni-erlangen.de

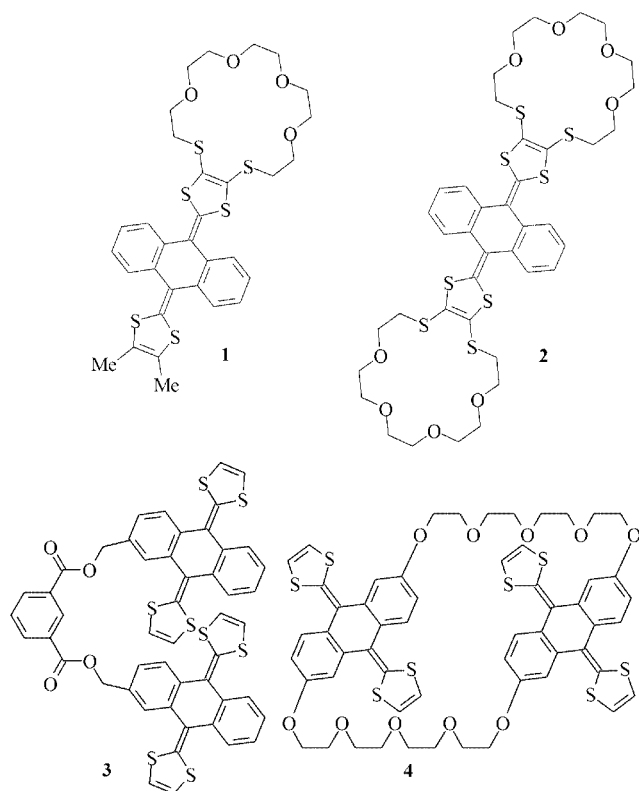


Figure 1. Representative exTTF derivatives exploited in supramolecular chemistry.

and its supramolecular complexation with a fullerene derivative bearing a secondary ammonium salt. An association constant (K_a) of 50 M^{-1} in $\text{CDCl}_3/\text{CD}_3\text{CN}$ was obtained for

this supramolecular ensemble via ^1H NMR titration experiments and complementary fluorescence measurements.^[17]

It is known that the ammonium–crown ether interactions are relatively weak and, consequently, the binding constants are usually low.^[18] However, when additional recognition elements are present, the stability of the complexes is dramatically increased. Thus, the intramolecular π -stacking between the two chromophores is responsible for the high stability of the self-assembled systems in supramolecular porphyrin–fullerene conjugates.^[13c,19] In this sense, exTTF has a concave aromatic surface expected to match the convex exterior of [60]fullerene and, therefore, to establish favourable van der Waals and π - π interactions with it.^[16] These additional recognizing aspects should favour the self assembly of complementary exTTF ammonium salts with fullerene crown ethers.

In a step toward the construction of more efficient non-covalent exTTF- C_{60} dyads, we report here on the self assembly of a series of exTTF-based secondary ammonium salts with fullerene C_{60} endowed with a DB24C8 crown ether appendage (Figure 2).

Results and Discussion

Synthesis

The multistep preparation of the novel exTTFs **8**, **14**, **16** and **19** suitably functionalized with a dibenzylamine moiety is depicted in Schemes 1 to 4.

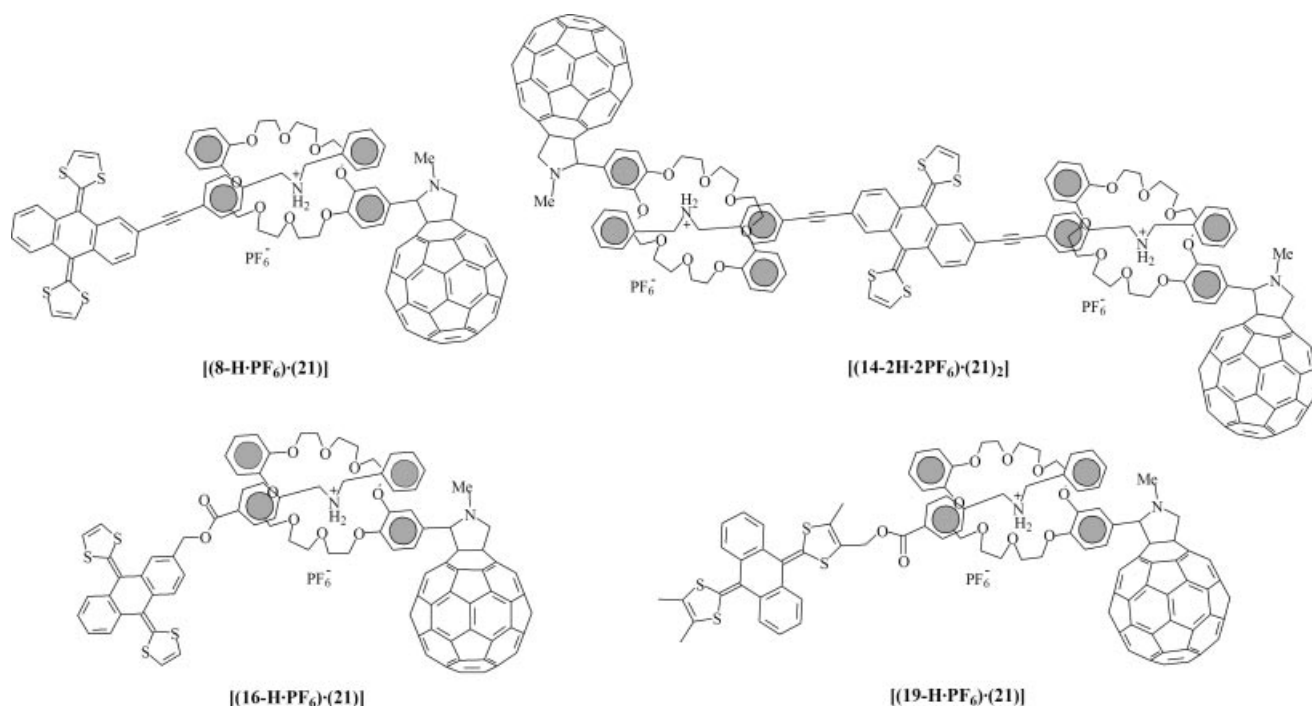
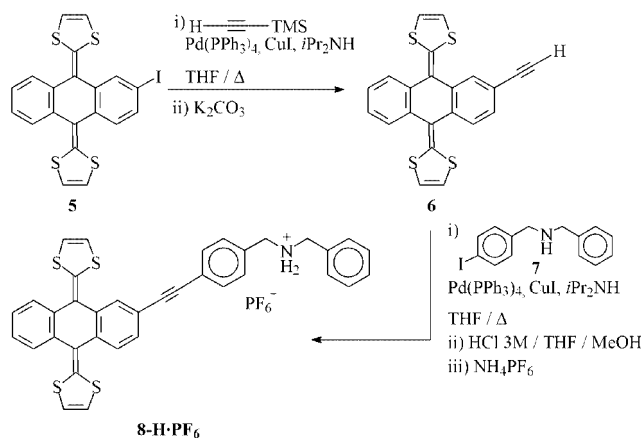


Figure 2. Supramolecular complexes prepared by threading the electron donor into the crown ether-containing [60]fullerene.



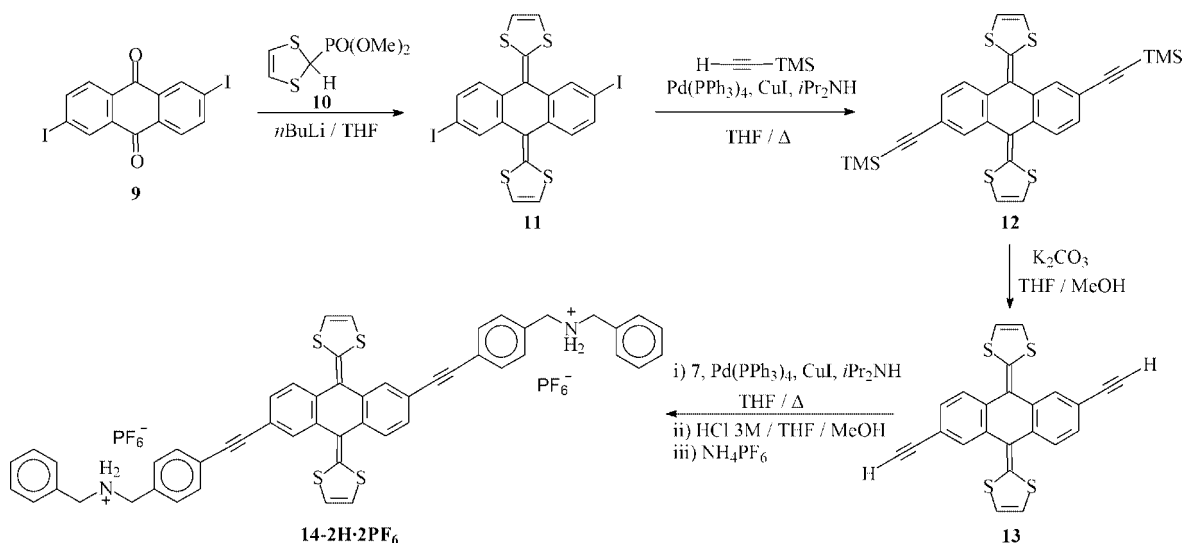
Scheme 1.

Scheme 1 outlines the synthesis of **8-H·PF₆** in which a rigid alkynyl spacer is introduced between the exTTF moiety and the dibenzylammonium unit. exTTF **6** was obtained by a Sonogashira coupling reaction of 2-iodo-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (**5**)^[20] with ethynyl(trimethyl)silane in the presence of Pd(PPh₃)₄, CuI and diisopropylamine, followed by desilylation with K₂CO₃. A further Sonogashira reaction of **6**, carried out under the same experimental conditions, with *N*-benzyl-*N*-(4-iodobenzyl)amine (**7**), obtained in turn by condensation

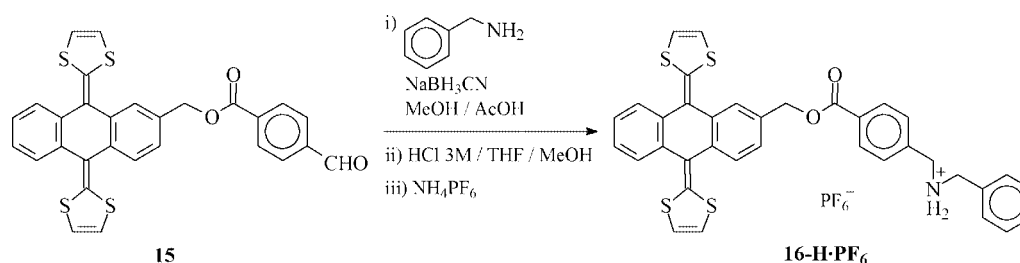
of benzylamine and 4-iodobenzaldehyde under reductive conditions (NaBH₃CN),^[21] led to amine **8** in moderate yield (49%). Finally, according to a typical protocol,^[22] protonation of this compound with 3 M HCl (aq.) yielded the salt **8-H·PF₆** after counterion exchange with saturated aqueous NH₄PF₆.

The preparation of double hexafluorophosphate salt **14-2H·2PF₆** was carried out following a similar synthetic procedure in several steps, as shown in Scheme 2. Compound **11** was synthesized from 2,6-diiodo-9,10-anthraquinone (**9**), which in turn was prepared by a double Sandmeyer reaction from commercially available 2,6-diamino-9,10-anthraquinone.^[23] Subsequent twofold reaction of quinone **9** with the phosphorus-stabilized carbanion generated by treatment of **10**^[24] with *n*-butyllithium, gave exTTF **11**. A Sonogashira coupling reaction of **11** with ethynyl(trimethyl)silane in the presence of Pd(PPh₃)₄, CuI and diisopropylamine, followed by desilylation, afforded exTTF **13** in a good overall yield (62%). Finally, the palladium/copper catalyzed cross-coupling reaction combining **13** and two equivalents of *N*-benzyl-*N*-(4-iodobenzyl)amine (**7**) gave **14-2H·2PF₆** in a moderate yield after carrying out protonation and counterion exchange.^[22]

The ammonium salt **16-H·PF₆** was prepared in a multistep synthetic procedure from the previously reported aldehyde **15**.^[11h] The reductive amination of this aldehyde



Scheme 2.



Scheme 3.

with benzylamine using sodium cyanoborohydride afforded the corresponding secondary amine **16** (Scheme 3). According to the above-mentioned procedure, it was protonated and the counterion was exchanged to give **16-H·PF₆** as an orange solid in 59% overall yield.

The ammonium salt **19-H·PF₆** was prepared starting from the hydroxymethyl-exTTF derivative **17**,^[25] as depicted in Scheme 4. The esterification reaction of **17** with an equimolar amount of 4-formylbenzoic acid in the presence of DMAP and DCC, led to the formyl-containing ester **18**. Further protonation (3 M HCl/THF/MeOH) and counterion exchange (NH₄PF₆) of the corresponding secondary amine **19**, obtained by reductive amination, afforded **19-H·PF₆** as an orange solid in moderate yield (see Experimental Section).

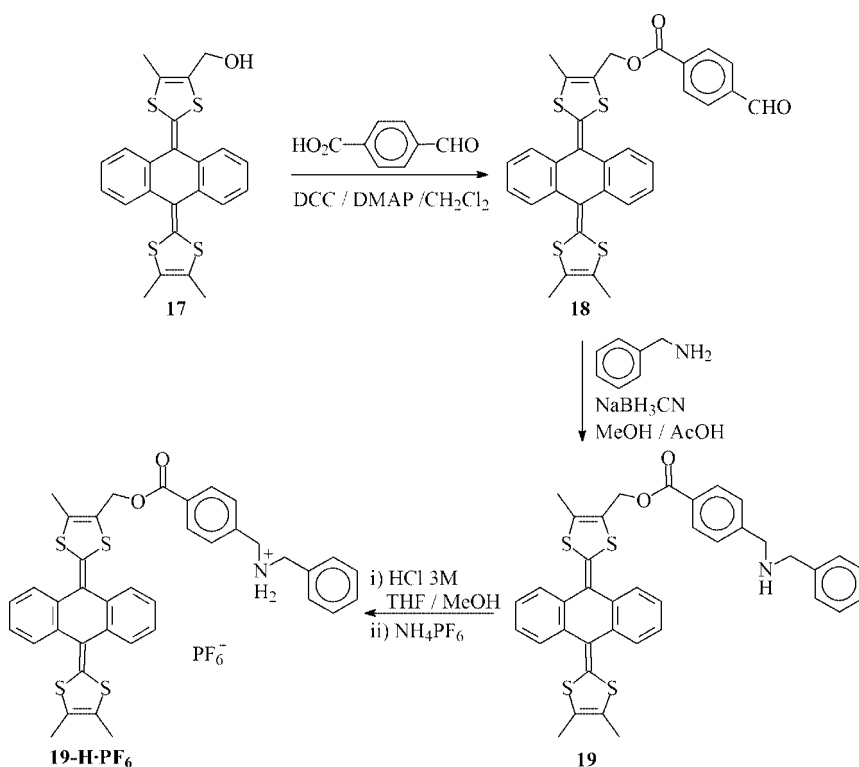
The new exTTF derivatives have been characterized by FTIR, MS, ¹H and ¹³C NMR spectroscopy. Owing to their lack of solubility, the ¹³C NMR spectra of the exTTF salts

(**8-H·PF₆**, **14-2H·2PF₆**, **16-H·PF₆** and **19-H·PF₆**) could not be recorded. A remarkable downfield shift of the signals corresponding to the dithiole ring protons was observed in the ¹H NMR spectra of the ammonium salts in comparison to the corresponding neutral amines. Thus, while these protons are observed at $\delta \approx 6.2$ – 6.3 in the amines (**8**, **14**, **16**), they appear at $\delta \approx 7.2$ – 7.9 in the respective salts (see Experimental Section).

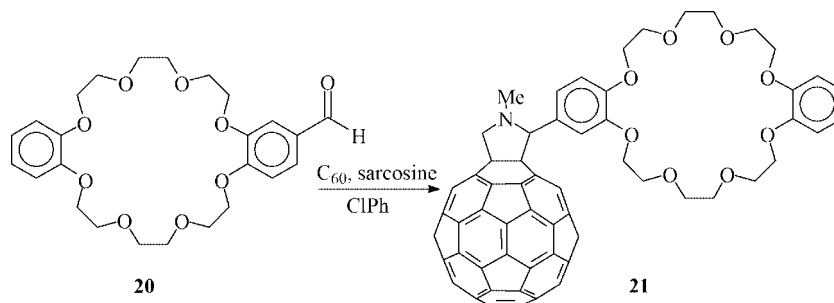
Crown ether fullerene derivative **21** was obtained (Scheme 5) as a brown solid in 44% yield by a cycloaddition reaction of C₆₀ with the azomethine ylide generated in situ from (2-formyl)dibenzo[24]crown-8 (**20**)^[26] and sarcosine.

Complexation Studies

We have investigated the ability of the exTTF derivatives **8-H·PF₆**, **14-2H·2PF₆**, **16-H·PF₆** and **19-H·PF₆** to form



Scheme 4.



Scheme 5.

supramolecular complexes with crown ether fullerene **21** (Figure 2). The first evidence for complexation was obtained when comparing the ^1H NMR spectra of the free species with those of mixtures of the corresponding salt and **21**. Thus, upon titration of one equivalent (or two for **14-2H-2PF₆**) of **21**, significant resonance shifts are observed. The most dramatic changes mainly involve both the ammonium protons and the benzylic protons of the ammonium salt. This fact reveals that complexation has taken place by threading the exTTF-containing ammonium salt through the DB24C8 moiety of compound **21**.

The association constant for the formation of complex $[(16\text{-H-PF}_6)\cdot(21)]$ has been evaluated by ^1H NMR binding titration experiments (500 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$, 298 K) upon addition of a solution of **21** in CDCl_3 into a solution of **16-H-PF₆** in CD_3CN (Figure 3). Changes in chemical shifts induced upon complexation are particularly visible for the aromatic protons of the exTTF units together with the shifting of the ammonium signal. The most important downfield shift of the ammonium protons ($\Delta\delta = 0.17$ ppm) has been used for the calculation of the association constant by fitting to a 1:1 binding isotherm, affording a value of $K_a = 2.2 \times 10^3 \text{ M}^{-1}$.^[27]

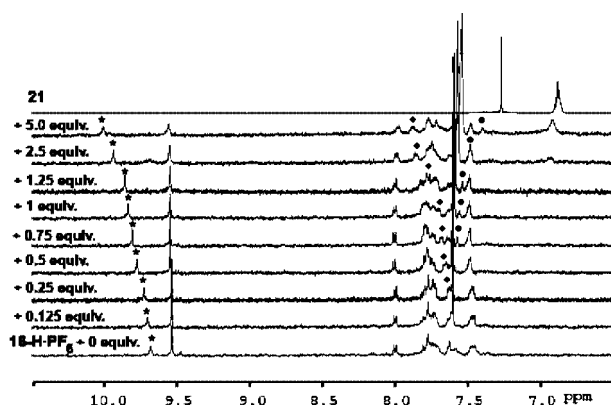


Figure 3. Partial ^1H NMR of 1 mM **16-H-PF₆** (bottom) upon addition of increasing amount of **C₆₀** crown ether derivative **21** (top).

The UV/Vis spectrum of a dilute solution of **16-H-PF₆** in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ did not change significantly upon addition of an equimolar amount of the fullerene derivative **21**, thus indicating negligible electronic interactions between the chromophores in the ground state. This observation is consistent with the electrochemical results discussed in the following section.

The low solubility of exTTF salts (**8-H-PF₆**, **14-2H-2PF₆**) on the one hand and the high instability of **19-H-PF₆** in solution on the other, prevented the NMR titration experiments with these compounds.

In complementary work, the crown ether complexation, that is, interactions between fullerene **21** and the exTTF based ammonium salts [i.e., **8-H-PF₆**, **14-2H-2PF₆**, **16-H-PF₆**, **19-H-PF₆**] were assayed by means of fluorescence experiments. The basis for these assays is the prominent electron donor–acceptor interactions as they prevail pre-

dominantly with photoexcited **C₆₀** and ground state exTTF. In this light, we expected that the crown ether complexation would exert a notable impact on the singlet excited state deactivation of the photoexcited fullerene. In particular, the fullerene fluorescence of **21** ($2.05 \times 10^{-5} \text{ M}$) was monitored in the absence and presence of variable concentrations of the different ammonium salts (i.e., typically in the range between 1.90×10^{-6} and $1.49 \times 10^{-5} \text{ M}$). The experimental findings reveal that the fullerene fluorescence intensities decreased exponentially as the ammonium salts were added (Figure 4). It is interesting to note that blank experiments using **C₆₀** itself instead of **21** resulted in a quenching of the fluorescence lower than 5%, thus confirming the intramolecular character of fluorescence deactivation in these complexes. The following quantum yields were determined: 5.8×10^{-4} (1:1, **21/8-H-PF₆**), 4.9×10^{-4} (1:1, **21/16-H-PF₆**), 2.2×10^{-4} (2:1, **21/14-2H-2PF₆**) and 4.7×10^{-4} (1:1, **21/19-H-PF₆**) (Figure 4).

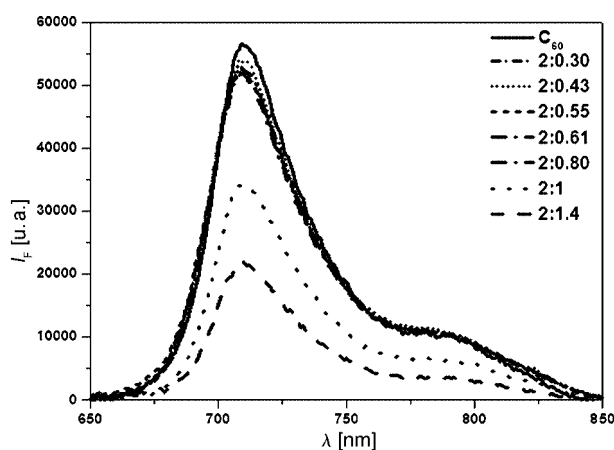


Figure 4. Room temperature fluorescence spectra of **21** ($2.05 \times 10^{-5} \text{ M}$) in a mixture of $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$, 1:1 upon adding variable concentration of **14-2H-2PF₆** (1.90×10^{-6} – 1.49×10^{-5}); λ_{exc} : 345 nm.

In each individual assay, the fluorescence intensities were corrected by a background spectrum, which was recorded just using matching ammonium salts concentrations. In the next, the quenching of the fullerene fluorescence was used to analyze the association constants for the underlying crown ether complexations [i.e., **21** with **8-H-PF₆**, **14-2H-2PF₆**, **16-H-PF₆**, **19-H-PF₆**] through the following relationship:

$$\frac{I_F}{I_o} = 1 - \frac{1}{2c_D} \left[\frac{1}{K_S} + c_o + c_D - \sqrt{\left(\frac{1}{K_S} + c_o + c_D - 4c_o c_D \right)} \right]$$

Using the fluorescence maxima at 709 nm, the following binding constant values were obtained: $1.4 \times 10^4 \text{ M}^{-1}$ $\{[(14\text{-}2\text{H-}2\text{PF}_6)\cdot(21)]_2\}$, $1.3 \times 10^3 \text{ M}^{-1}$ $\{[(16\text{-H-PF}_6)\cdot(21)]\}$ and $8.6 \times 10^2 \text{ M}^{-1}$ $\{[(19\text{-H-PF}_6)\cdot(21)]\}$.

Supramolecular complexation was also evidenced by electrospray mass spectrometry (ESI-MS). The spectrum of an equimolar mixture of **16-H-PF₆** and **21** displayed the

peak corresponding to the 1:1 complex after loss of the hexafluorophosphate counteranion.

Electrochemical Studies

The redox properties of the individual components and the [2]pseudorotaxanes were determined by cyclic voltammetry (CV). The measurements were carried out at room temperature in dichloromethane/acetonitrile (1:1) using glassy carbon (GC) as the working electrode, standard Ag/AgCl as the reference electrode and tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. The data are collected in Table 1, together with those measured for exTTF **16** as a reference.

Table 1. Redox potentials (in volts vs. Ag/AgCl) of exTTF-based ammonium salts and supramolecular complexes at 100 mV s⁻¹.

Compound	$E^{1,ox}$	$E^{1,red}$	$E^{2,red}$	$E^{3,red}$
16	0.11			
8-H·PF₆	0.19			
14-2H·2PF₆	0.25			
16-H·PF₆	0.12			
19-H·PF₆	0.02			
21		-0.82	-1.22	-1.77
[(8-H·PF₆)·(21)]	0.20	-0.81	-1.20	-1.78
[(14-2H·2PF₆)·(21)]₂	0.27	-0.83	-1.25	-1.78
[(16-H·PF₆)·(21)]	0.18	-0.82	-1.22	-1.78
[(19-H·PF₆)·(21)]	0.09	-0.88	-1.18	-1.77

Unlike the parent TTF, exTTF **16** exhibits only one two-electron, quasireversible oxidation wave to form a dication, which has been confirmed by Coulombimetric analysis.^[28] The coalescence of the two one-electron processes into one two-electron process reveals that the presence of the quinonoid structure between the two 1,3-dithiole rings leads to unstable, highly distorted, nonplanar radical cations.^[29]

In agreement with the above data, exTTF ammonium salts exhibit only one oxidation wave to form the dication species, showing, however, a slightly poorer oxidation potential than the neutral amines (Table 1). This fact could be explained by electrostatic repulsion between the charges generated upon oxidation and the charge already present in the ammonium salts. It is worth mentioning that the presence of the methyl groups on the dithiole rings in exTTF results in a significant cathodic shift of the oxidation potential value of **19-H·PF₆** (Table 1) due to their positive inductive effect, which increases the electron donor ability of this compound. This stronger electron-donor character resulted, however, in a higher instability of this compound (**19-H·PF₆**) in solution, thus accounting for the unsuccessful ¹H NMR titration results.

The voltammogram of the fullerene crown ether **21** shows three quasireversible reduction waves, which correspond to the first three reduction steps of the fullerene moiety. As expected, these reduction potentials appear at more negative values than those of C₆₀ due to the saturation of a double bond in the fullerene skeleton.^[30]

Upon addition of the exTTF ammonium salts, neither these waves nor the oxidation values of the exTTFs changed

significantly, revealing that complexation does not influence strongly the electroactive properties of the components, and suggesting that the electroactive units are not spatially close enough to allow measurable electronic interactions between them (Figure 5).

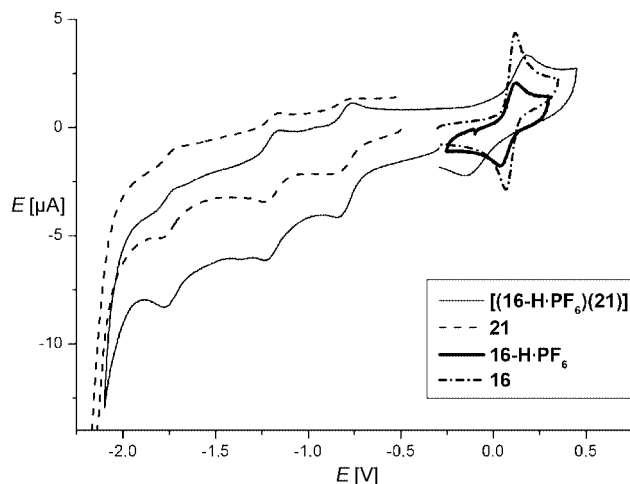


Figure 5. Cyclic voltammograms (sweep rate 100 mV s⁻¹) of **16**, **16-H·PF₆**, **21**, **[(16-H·PF₆)·(21)]** in CH₂Cl₂/CH₃CN.

Conclusions

In summary, we have synthesized a new series of π -extended tetrathiafulvalenes (exTTFs) covalently connected to a dibenzylammonium moiety through an alkynyl rigid spacer (**8**) or a more flexible ester group (**16**, **19**). A twofold Sonogashira reaction on the diiodo-substituted exTTF (**11**) has allowed us to obtain an exTTF (**14**) endowed with two dibenzylammonium units. The resulting exTTFs (**8**, **14**, **16** and **19**) are suitably functionalized to be threaded into a DB24C8 ring which, in turn, is linked to the efficient electron acceptor [60]fullerene through a pyrrolidine ring following Prato's protocol.

The stability of the resulting supramolecular ensembles has been determined for the complex **[(16-H·PF₆)·(21)]** by ¹H NMR binding titration experiments (500 MHz, CDCl₃/CD₃CN, 298 K) because of its better solubility in comparison with those complexes bearing the alkynyl moiety, which showed a remarkably lower solubility, thus preventing the ¹H NMR titration experiments. Interestingly, a binding constant of $2.2 \times 10^3 \text{ M}^{-1}$ was determined, which indicates the relatively high stability of these complexes. This value was confirmed by fluorescence experiments ($1.3 \times 10^3 \text{ M}^{-1}$) which allowed us to determine the binding constants for the double complex **[(14-2H·2PF₆)·(21)]₂** as well as that for **[(19-H·PF₆)·(21)]** which resulted to be $1.4 \times 10^4 \text{ M}^{-1}$ and $8.6 \times 10^2 \text{ M}^{-1}$ respectively.

Although ESI-MS evidenced the supramolecular complexation, UV/Vis and CV measurements revealed negligible electronic communication between the donor (exTTF) and acceptor (C₆₀) moieties in the ground state. The redox potential values of the exTTF units in the complexes ap-

peared slightly anodically shifted in comparison with the neutral amines, probably due to the presence of the positive charge in the complex, thus hindering the generation of new charges in the oxidation process.

Finally, the quenching of the fluorescence observed upon adding the ammonium salt of exTTFs to the crown ether connected to the fullerene (**21**) suggest an electron transfer from the donor (exTTF) to the acceptor (C_{60}) unit, thus mimicking the photosynthetic process. A thorough photo-physical study is currently under investigation.

Experimental Section

General: All solvents were dried and distilled according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, kieselgel 60, 230–240 mesh or Scharlau 60, 230–240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminum-backed Merck Kieselgel 60 F254 plates. Melting points were determined on a Gallenkamp apparatus. NMR spectra were recorded with Bruker AC-200, Bruker Avance 300 or Bruker AMX 500 spectrometers at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet; br. = broad. FT-IR spectra were recorded with a Perkin–Elmer 781 or Nicolet–Magna IR 5550 spectrometers. UV/Vis spectra were recorded with a Varian Cary 50 spectrophotometer. Mass spectra were recorded with an HP 5989A spectrometer or a Bruker Reflex III spectrometer with a nitrogen laser operating at 337 nm. Cyclic voltammetry was performed using an Autolab PGStat 30. These measurements were made in a double-walled cell (Metrohm EA 876–20). A glassy carbon working electrode (Metrohm 6.0804.010) was used after being polished with alumina (0.3 μ) for 1 min, and platinum wire was used as the counter electrode. A Ag/Ag⁺ electrode was used as a reference. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte, and dry dichloromethane/acetonitrile, 1:1 was used as the solvent. The samples were purged with argon prior to measurement. The scan rate was 100 mV/s.

2-Ethynyl-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (6): To a solution of the iodo derivative **5** (1.35 g, 2.7 mmol) in dry THF (50 mL), trimethylsilylacetylene (288 mg, 2.9 mmol), Pd(PPh₃)₄ (154 mg, 0.13 mmol), CuI (25 mg, 0.13 mmol) and diisopropylamine (816 mg, 8.0 mmol) were added. The reaction was refluxed under argon for 12 h. After cooling to room temperature, ethyl acetate (50 mL) was added to the solution. The organic layer was washed sequentially with a saturated NH₄Cl solution (50 mL), water (2 $\times$ 50 mL) and brine (2 $\times$ 50 mL), and then dried with MgSO₄. The solvent was removed under reduced pressure, and the crude product was purified by silica gel flash chromatography using hexane/dichloromethane (3:1) as the eluent, providing the TMS protected alkynyl TTF derivative as a red solid in 54% yield (686 mg). ¹H NMR (200 MHz, CDCl₃): δ = 7.76 (d, J = 1.5 Hz, 1 H), 7.70–7.63 (m, 2 H), 7.59 (br. s, 1 H), 7.37 (dd, J = 8.1, 1.5 Hz, 1 H), 7.32–7.23 (m, 2 H), 6.28 (s, 4 H), 0.27 (s, 9 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 136.7, 136.6, 135.5, 135.4, 135.2, 129.5, 128.2, 126.1, 126.0, 125.0, 124.9, 124.8, 121.7, 121.2, 120.5, 117.3, 117.1, 105.4, 94.3, 0.04 ppm. m/z (EI) = 476 (M⁺). IR (KBr): $\tilde{\nu}_{\max}$ = 2343, 1598, 1406, 1280, 1220, 1159, 1093, 1004, 925, 800, 655, 619, 567, 505, 459, 445, 434 cm^{−1}. UV (CH₂Cl₂): $\lambda_{\max}$ = 437,

373, 256 nm. A solution of this exTTF derivative (135 mg, 0.3 mmol) in THF/MeOH (1:1, 20 mL) and K₂CO₃ (40 mg, 0.3 mmol) was stirred at room temperature for 6 h. The mixture was then extracted with CH₂Cl₂ (3 $\times$ 25 mL), and the combined organic layers were washed with water (2 $\times$ 50 mL) and dried with MgSO₄. The residue was purified by flash chromatography on silica gel using hexane/CH₂Cl₂ (3:1) as the eluent to give **8** (114 mg, 100%) as a yellow solid. ¹H NMR (200 MHz, CDCl₃): δ = 7.82 (d, J = 1.6 Hz, 1 H), 7.72–7.64 (m, 3 H), 7.41 (dd, J = 8.0, 1.6 Hz, 1 H), 7.32–7.28 (m, 2 H), 6.33–6.32 (m, 4 H), 3.03 (s, 1 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 135.02, 129.4, 128.3, 126.0, 124.8, 119.2, 117.2, 117.1, 83.7, 77.1 ppm. MS (EI): m/z = 404 (M⁺). IR (KBr): $\tilde{\nu}_{\max}$ = 3255, 2122, 1546, 1406, 1280, 1247, 1004, 925, 856, 655, 642 cm^{−1}. UV (CH₂Cl₂): $\lambda_{\max}$ = 436, 371, 246 nm.

N-Benzyl-N-(4-iodobenzyl)amine (7): To a stirred solution of 4-iodobenzaldehyde (746 mg, 5 mmol) and benzylamine (536 mg, 5 mmol) in methanol/acetic acid 99:1 (60 mL), sodium cyanoborohydride (471 mg, 7.5 mmol) was added in portions over 30 min. The resulting mixture was stirred at room temperature for 20 h, and then poured into NaHCO₃ solution (250 mL). The aqueous layer was then extracted with ethyl acetate (3 $\times$ 50 mL), and the combined organic extracts were washed with brine (3 $\times$ 50 mL) and dried with Na₂SO₄. The solvent was removed under reduced pressure, and the product was purified by chromatography on a silica gel column using hexane/ethyl acetate (1:1) as the eluent, giving **7** as an oil (297 mg, 92%). ¹H NMR (300 MHz, CDCl₃): δ = 7.58 (d, J = 8.1 Hz, 2 H), 7.29–7.16 (m, 5 H), 7.02 (d, J = 8.1 Hz, 2 H), 3.71 (s, 2 H), 3.66 (s, 2 H), 1.99 (s, 1 H, NH) ppm. MS (ESI): m/z = 322 (M⁺). IR: $\tilde{\nu}_{\max}$ = 3400, 2922, 1550, 1253, 1217, 1009, 630 cm^{−1}. UV (CH₂Cl₂): $\lambda_{\max}$ = 276, 234 nm.

N-Benzyl-N-(4-{[9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl]ethynyl}benzyl)amine (8): To a solution of the deprotected alkyne **6** (444 mg, 1.1 mmol) in dry THF (50 mL), benzyl(4-iodobenzyl)amine **7** (323 mg, 1 mmol), Pd(PPh₃)₄ (58 mg, 0.05 mmol), CuI (10 mg, 0.05 mmol) and distilled diisopropylamine (1 mL) were added. The solution was refluxed under argon for 20 h. After cooling to room temperature, ethyl acetate (50 mL) was added to the solution. The organic layer was washed sequentially with a saturated NH₄Cl solution (50 mL), water (2 $\times$ 50 mL) and brine (2 $\times$ 50 mL), and then dried with MgSO₄. The solvent was removed under reduced pressure, and the crude product was purified by silica gel flash chromatography with dichloromethane as the eluent, providing **8** as a yellow solid (287 mg, 48%). M.p. 161–163 °C. ¹H NMR (200 MHz, CDCl₃): δ = 7.84 (d, J = 1.2 Hz, 2 H), 7.73–7.63 (m, 4 H), 7.53–7.28 (m, 8 H), 7.16 (d, J = 8.4 Hz, 2 H), 6.33 (s, 2 H), 6.32 (s, 2 H), 3.54 (s, 2 H), 3.49 (s, 2 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 137.18, 137.11, 135.94, 135.71, 135.65, 132.62, 132.57, 132.16, 129.54, 129.09, 129.00, 128.94, 128.89, 128.86, 128.65, 128.60, 128.54, 128.29, 127.62, 127.49, 127.45, 126.52, 126.50, 125.43, 125.35, 122.39, 122.12, 121.69, 121.12, 117.74, 117.71, 117.66, 117.62, 90.09, 53.50 ppm. HRMS (MALDI-TOF): calcd. for [C₃₆H₂₅NS₄]⁺ 599.0864; found 599.0892. IR (KBr): $\tilde{\nu}_{\max}$ = 3437, 1545, 1454, 1406, 802, 756, 650, 640 cm^{−1}. UV (CH₂Cl₂): $\lambda_{\max}$ = 441, 376, 309, 272 nm.

Ammonium Salt 8-H-PF₆: Aqueous HCl (3 N) was added with stirring to a solution of compound **8** (100 mg, 0.17 mmol) in MeOH/THF (1:1, 60 mL) until the pH was just less than 1. After stirring for 3 h, the resulting suspension was concentrated in vacuo. The residue was dissolved in MeNO₂ (200 mL), and saturated aqueous NH₄PF₆ (50 mL) was added. The phases were partitioned, and the organic phase was washed with sat. aqueous NH₄PF₆ (50 mL) and water (4 $\times$ 100 mL), dried with MgSO₄, and filtered. The solvent

was removed under reduced pressure to give the ammonium salt as a red solid (700 mg, 94%). M.p. 296 °C (dec.). ^1H NMR (300 MHz, CD_3CN): δ = 9.55 (s, 2 H), 7.90–7.24 (m, 20 H), 4.19–4.14 (m, 4 H) ppm. m/z (ESI) = 599 ($\text{M} - \text{HPF}_6$) $^+$. IR (KBr): $\tilde{\nu}_{\text{max}}$ = 3436, 2926, 2854, 2341, 1635, 1402, 833, 559 cm^{-1} . UV (CD_3CN): λ_{max} = 423, 379, 276, 270 nm.

2,6-Diiodo-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (11): *n*-Butyllithium (BuLi) (1.6 M in hexane; 0.7 mL, 1.1 mmol) was added via syringe into a stirred solution of the phosphonate **10**^[24] (212 mg, 1 mmol) in dry THF (100 mL) at -78°C under argon. After 30 min at -78°C , anthraquinone **9** (115 mg, 0.25 mmol), dissolved in dry THF (100 mL), was added via syringe into the solution of phosphonate carbanion. The mixture was stirred for 1 h at -78°C , and then warmed to 20°C overnight. After evaporation of the solvent, the residue was diluted with water (100 mL) and extracted with dichloromethane (3×75 mL). The combined organic extracts were sequentially washed with water (2×75 mL), brine (1×75 mL) and dried with MgSO_4 . After removing the solvent in vacuo, the residue was purified by column chromatography on silica gel with hexane/dichloromethane (9:1) as the eluent to afford **11** as a yellow solid (131 mg, 82%). M.p. 252–254 °C. ^1H NMR (200 MHz, CDCl_3): δ = 7.99 (d, J = 1.7 Hz, 2 H), 7.60 (dd, J = 8.1, 1.7 Hz, 2 H), 7.41 (d, J = 8.1 Hz, 2 H), 6.35 (s, 4 H) ppm. ^{13}C NMR (50 MHz, CDCl_3): δ = 146.1, 142.2, 139.7, 139.2, 134.1, 132.0, 128.7, 127.8, 127.2, 119.5, 117.1, 114.2 ppm. MS (EI): m/z = 632 (M^+), 506 ($\text{M}^+ - \text{I}$), 380 ($\text{M}^+ - 2\text{I}$). IR (KBr): $\tilde{\nu}_{\text{max}}$ = 2924, 2852, 2183, 1545, 1516, 1452, 1394, 756, 646, 623, 501 cm^{-1} . UV (CH_2Cl_2): λ_{max} = 430, 366, 238 nm.

2,6-Bis(trimethylsilyl)ethynyl-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (12): To a solution of diiodo exTTF **11** (942 mg, 1.49 mmol) in Et_3N (40 mL), $\text{Pd}(\text{OAc})_2$ (33.4 mg, 0.15 mmol), PPh_3 (78.2 mg, 0.3 mmol) and trimethylsilylacetylene (0.64 mL, 4.48 mmol) were added under argon. The reaction was heated at 90°C for 26 h. The mixture was diluted with ethyl acetate (50 mL), washed with brine (3×50 mL) and dried with MgSO_4 . The solvent was removed in vacuo, and the resulting residue was purified by flash chromatography on silica gel using hexane/ethyl acetate (9:1) as the eluent to afford **12** (429 mg, 75%) as a yellow solid. M.p. 179–181 °C. ^1H NMR (300 MHz, CDCl_3): δ = 7.76 (d, J = 1.5 Hz, 2 H), 7.65 (d, J = 8.2 Hz, 2 H), 7.38 (dd, J = 8.2, 1.5 Hz, 2 H), 6.31 (s, 4 H), 0.27 (s, 18 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 136.7, 136.6, 135.5, 135.4, 135.2, 129.5, 128.2, 126.1, 126.0, 124.5, 124.9, 124.8, 121.7, 121.2, 120.5, 117.3, 117.2, 117.1, 105.4, 94.3, 0.1 ppm. MS (EI): m/z = 572 (M^+). IR (KBr): $\tilde{\nu}_{\text{max}}$ = 2343, 1598, 1406, 1280, 1220, 1159, 1093, 1004, 925, 800, 655, 619, 567 cm^{-1} . UV (CH_2Cl_2): λ_{max} = 450, 382, 273 nm.

2,6-Diethynyl-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (13): To a solution of **12** (543 mg, 0.95 mmol) in THF/MeOH, 1:1 (30 mL), K_2CO_3 (272 mg, 1.97 mmol) was added. The reaction was stirred at room temperature for 6 h. The solution was extracted with CH_2Cl_2 (3×25 mL) and the combined organic layers were washed with water (2×50 mL) and dried with MgSO_4 . The residue was purified by flash chromatography on silica gel using hexane/ CH_2Cl_2 (2:1) as the eluent to give **13** (407 mg, 100%) as a yellow solid. M.p. 201 °C (dec.). ^1H NMR (200 MHz, CDCl_3): δ = 7.80 (d, J = 1.8 Hz, 2 H), 7.64 (d, J = 8.0 Hz, 2 H), 7.40 (dd, J = 8.0, 1.8 Hz, 2 H), 6.31 (s, 4 H), 3.11 (s, 2 H) ppm. ^{13}C NMR (50 MHz, CDCl_3): δ = 135.0, 129.4, 128.3, 125.9, 124.8, 119.2, 117.2, 117.1, 83.7, 77.1 ppm. MS (EI) m/z = 428 (M^+). IR (KBr): $\tilde{\nu}_{\text{max}}$ = 3255, 2122, 1546, 1406, 1280, 1247, 1004, 925, 856, 655, 642 cm^{-1} . UV (CH_2Cl_2): λ_{max} = 449, 381, 262 nm.

***N*-Benzyl-*N*-(4-{[6-(4-{(benzylamino)methyl}phenyl)ethynyl]-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl]ethynyl}-**

benzyl)amine (14): To a solution of the deprotected alkyne **13** (428 mg, 1 mmol) in dry THF (50 mL), the iodo derivative **7** (1.22 g, 3 mmol), $\text{Pd}(\text{PPh}_3)_4$ (115 mg, 0.1 mmol), CuI (19 mg, 0.1 mmol) and distilled diisopropylamine (1 mL) were added. The solution was refluxed under argon for 24 h. After warming to room temperature, ethyl acetate (50 mL) was added to the solution. The organic layer was washed sequentially with a saturated NH_4Cl solution (50 mL), water (2×50 mL) and brine (2×50 mL), and then dried with MgSO_4 . The solvent was removed under reduced pressure, and the crude product was purified by silica gel flash chromatography using ethyl acetate as the eluent, providing **14** as an orange solid (229 mg, 28%). M.p. 260 °C (dec.). ^1H NMR (200 MHz, CDCl_3): δ = 7.85 (d, J = 1.2 Hz, 2 H), 7.73–7.63 (m, 4 H), 7.55–7.43 (m, 8 H), 7.37–7.29 (m, 12 H), 6.34 (s, 4 H), 3.82 (m, 8 H) ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 140.11, 137.53, 136.53, 136.37, 132.68, 130.76, 130.41, 130.12, 130.01, 129.59, 129.24, 129.09, 128.58, 126.30, 123.80, 121.52, 120.74, 118.87, 118.67, 117.94, 90.56, 90.29, 52.79, 52.39 ppm. HRMS (MALDI-TOF): calcd. for $[\text{C}_{52}\text{H}_{38}\text{N}_2\text{S}_4]^+$ 818.1912; found 818.1865. IR (KBr): $\tilde{\nu}_{\text{max}}$ = 3437, 2924, 2852, 1630, 1500, 1458, 1400, 1120, 698, 542 cm^{-1} . UV (CH_3CN): λ_{max} = 448, 385, 311, 246 nm.

Ammonium Salt 14-2H-2PF₆: Aqueous HCl (3 N) was added with stirring to a solution of compound **14** (100 mg, 0.12 mmol) in MeOH/THF, 1:1 (80 mL) until the pH was below 1. After stirring for 3 h, the resulting suspension was concentrated in vacuo. The residue was dissolved in MeNO_2 (250 mL), and saturated aqueous NH_4PF_6 (75 mL) was added. The phases were partitioned, and the organic phase washed with sat. aqueous NH_4PF_6 (75 mL) and water (4×100 mL), dried with MgSO_4 and filtered. The solvent was removed under reduced pressure to give the ammonium salt as an orange solid (121 mg, 90%). ^1H NMR (300 MHz, CD_3COCD_3): δ = 9.95 (s, 4 H), 8.16 (s, 2 H), 8.03–7.99 (m, 2 H), 7.83–7.38 (m, 24 H), 4.64–4.53 (m, 8 H) ppm. MS (ESI): m/z = 818 ($\text{M} - 2\text{HPF}_6$) $^+$. IR (KBr): $\tilde{\nu}_{\text{max}}$ = 3437, 2926, 2361, 2343, 2208, 1618, 1458, 843, 559 cm^{-1} . UV (CD_3CN): λ_{max} = 425, 329, 239, 198 nm.

[9,10-Bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl]methyl 4-[(Benzylamino)methyl]benzoate (16): To a stirred solution of aldehyde **15**^[11h] (70 mg, 0.13 mmol) and benzylamine (14 mg, 0.13 mmol) in methanol/acid acetic 99:1 (20 mL), sodium cyanoborohydride (12.2 mg, 1.5 mmol) was added in portions over 30 min. The resulting mixture was stirred at room temperature for 4 h and poured into a NaHCO_3 solution (25 mL). The aqueous layer was then extracted with ethyl acetate (50 mL), and the combined organic extracts were washed with brine (40 mL) and dried with Na_2SO_4 . The solvent was removed under reduced pressure, and the product was purified by chromatography on a silica gel column with dichloromethane/ethyl acetate (7:3) as the eluent, giving **16** as a yellow solid (63 mg, 62%). M.p. > 300 °C (dec.). ^1H NMR (200 MHz, CDCl_3): δ = 8.02 (d, J = 8.1 Hz, 2 H), 7.73–7.61 (m, 4 H), 7.38–7.19 (m, 10 H), 6.22 (s, 2 H), 6.20 (s, 2 H), 5.35 (s, 2 H), 3.80 (s, 2 H), 3.74 (s, 2 H) ppm. ^{13}C NMR (50 MHz, CDCl_3): δ = 166.3, 144.5, 135.7, 135.3, 135.2, 133.7, 130.0, 128.5, 128.4, 128.3, 127.4, 126.0, 125.6, 125.1, 125.0, 124.9, 124.6, 121.8, 121.7, 117.2, 117.1, 66.5, 52.7, 52.6 ppm. HRMS (MALDI-TOF): calcd. for $[\text{C}_{36}\text{H}_{27}\text{NO}_2\text{S}_4]^+$ 633.0919; found 633.0903. IR (KBr): $\tilde{\nu}_{\text{max}}$ = 3447, 1716, 1653, 1628, 1543, 1508, 1269, 1103, 754, 646 cm^{-1} . UV (CH_2Cl_2): λ_{max} = 431, 366, 240 nm.

Ammonium Salt 16-H-PF₆: Aqueous HCl (3 N) was added with stirring to a solution of compound **16** (100 mg, 0.16 mmol) in MeOH/THF, 1:1 (60 mL) until the pH was just less than 1. After stirring for 3 h, the resulting suspension was concentrated in vacuo. The residue was dissolved in MeNO_2 (200 mL), and saturated aqueous

NH_4PF_6 (50 mL) was added. The phases were partitioned, and the organic phase washed with sat. aqueous NH_4PF_6 (50 mL) and water (4×100 mL), dried with MgSO_4 and filtered. The solvent was removed under reduced pressure to give the ammonium salt as an orange solid (118 mg, 95%). M.p. 216 °C (dec.) ^1H NMR (300 MHz, CD_3CN): δ = 9.52 (s, 1 H), 9.51 (s, 1 H), 8.04 (d, J = 8.2 Hz, 2 H), 7.86–7.70 (m, 9 H), 7.60 (d, J = 8.2 Hz, 2 H), 7.49–7.46 (m, 7 H), 5.51 (s, 2 H), 4.33–4.24 (m, 4 H) ppm. MS (ESI): m/z = 633 ($\text{M} - \text{HPF}_6$) $^+$. IR (KBr): $\tilde{\nu}_{\text{max}}$ = 3437, 1716, 1635, 1431, 1275, 1124, 1084, 868, 845, 744, 559, 484 cm^{-1} . UV (CH_3CN): λ_{max} = 470, 399, 374, 264 nm.

{(2Z)-2-[10-(4,5-Dimethyl-1,3-dithiol-2-ylidene)anthracen-9(10H)-ylidenel-5-methyl-1,3-dithiol-4-yl]methyl 4-Formylbenzoate (18): To a suspension of 4-formylbenzoic acid (83 mg, 0.55 mmol) in CH_2Cl_2 (10 mL), DCC (126 mg, 0.61 mmol) and DMAP (74 mg, 0.61 mmol) were added. The mixture was stirred for 20 min at room temperature, and then a solution of the hydroxy derivative **17** (250 mg, 0.55 mmol) in CH_2Cl_2 (10 mL) was added. After stirring for 20 h, the solvent was removed in vacuo yielding a residue, which was purified by column chromatography (SiO_2 , hexane/ethyl acetate, 8:2). Compound **18** was obtained as a yellow solid (161 mg, 50%). M.p. 185 °C. ^1H NMR (300 MHz, CDCl_3): δ = 10.1 (s, 1 H), 8.20 (d, J = 8.3 Hz, 2 H), 7.95 (d, J = 8.3 Hz, 2 H), 7.68–7.59 (m, 4 H), 7.32–7.26 (m, 4 H), 5.10 (d, J_{AB} = 12.9 Hz, 1 H), 4.99 (d, J_{AB} = 12.9 Hz, 1 H), 2.12 (s, 3 H), 1.92 (s, 6 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 192.1, 165.5, 139.7, 135.6, 135.3, 134.9, 133.8, 131.7, 130.9, 130.8, 130.3, 129.9, 126.4, 126.3, 126.2, 126.1, 125.8, 125.7, 125.6, 125.2, 123.0, 121.2, 120.4, 59.3, 13.9, 13.5 ppm. MS (ESI): m/z = 584 (M^+). IR (KBr): $\tilde{\nu}_{\text{max}}$ = 2920, 2850, 1726, 1707, 1522, 1444, 1267, 1201, 1097, 756 cm^{-1} . UV (CHCl_3): λ_{max} = 436, 367, 306, 254, 239 nm.

{(2Z)-2-[10-(4,5-Dimethyl-1,3-dithiol-2-ylidene)anthracen-9(10H)-ylidenel-5-methyl-1,3-dithiol-4-yl]methyl 4-[(Benzylamino)-methyl]benzoate (19): To a stirred solution of aldehyde **18** (76 mg, 0.13 mmol) and benzylamine (14 mg, 0.13 mmol) in methanol/acid acetic 99:1 (20 mL), sodium cyanoborohydride (12.2 mg, 1.5 mmol) was added in portions over 30 min. The resulting mixture was stirred at room temperature for 14 h, and then poured into a NaHCO_3 solution (25 mL). The aqueous layer was then extracted with ethyl acetate (50 mL), and the combined organic extracts were washed with brine (40 mL) and dried with Na_2SO_4 . The solvent was removed under reduced pressure, and the product was purified by chromatography on a silica gel column using dichloromethane/ethyl acetate (9:1) as the eluent, giving **19** as a yellow solid (34 mg, 38%). M.p. 130–132 °C. ^1H NMR (500 MHz, CD_3COCD_3): δ = 8.00–7.96 (m, 2 H), 7.67–7.63 (m, 4 H), 7.57–7.53 (m, 2 H), 7.41–7.39 (m, 2 H), 7.37–7.31 (m, 6 H), 7.27–7.23 (m, 2 H) ppm. ^{13}C NMR (125 MHz, CD_3COCD_3): δ = 205.62, 165.81, 135.68, 135.66, 135.45, 135.43, 130.10, 130.07, 129.87, 129.84, 129.33, 128.55, 128.53, 128.48, 127.04, 126.98, 126.50, 126.47, 126.31, 126.28, 125.73, 125.71, 125.68, 125.60, 122.39, 121.50, 121.19, 121.12, 58.46, 57.01, 55.21, 53.07, 52.63, 12.90, 12.46 ppm. MS (EI): m/z = 675 (M^+). IR (KBr): $\tilde{\nu}_{\text{max}}$ = 3447, 1716, 1653, 1628, 1543, 1508, 1269, 1103, 754, 646 cm^{-1} . UV (CH_2Cl_2): λ_{max} = 431, 366, 240 nm.

Ammonium Salt 19-H- PF_6 : Aqueous HCl (3 N) was added with stirring to a solution of compound **19** (108 mg, 0.16 mmol) in MeOH/THF (1:1, 60 mL) until the pH was just less than 1. After stirring for 3 h, the resulting suspension was concentrated in vacuo. The residue was dissolved in MeNO_2 (200 mL), and saturated aqueous NH_4PF_6 (50 mL) was added. The phases were partitioned, and the organic phase was washed with sat. aqueous NH_4PF_6 (50 mL) and water (4×100 mL), dried with MgSO_4 and filtered. The solvent

was removed under reduced pressure to give the ammonium salt as an orange solid (122 mg, 93%). M.p. 211 °C (dec.). ^1H NMR (300 MHz, CD_3COCD_3): δ = 8.17 (d, J = 8.0 Hz, 2 H), 8.04–8.01 (m, 4 H), 7.83–7.79 (m, 6 H), 7.55–7.54 (m, 2 H), 7.44–7.42 (m, 3 H), 6.15 (s, 2 H), 4.59 (s, 2 H), 4.47 (s, 2 H), 3.33 (s, 3 H), 3.13 (s, 6 H) ppm. HRMS (MALDI-TOF): calcd. for $[\text{C}_{39}\text{H}_{33}\text{NO}_2\text{S}_4]^+$ 675.1389; found 675.1406. IR (KBr): $\tilde{\nu}_{\text{max}}$ = 3439, 2924, 2852, 1628, 1387, 1099, 839, 557 cm^{-1} . UV (CH_3CN): λ_{max} = 431, 396, 373, 313, 259 nm.

DB24C8 Fullerene 21: A solution of C_{60} (106 mg, 0.15 mmol), (2-formyl)dibenzo[24]crown-8 (**20**)^[26] (70 mg, 0.15 mmol) and sarcosine (65 mg, 0.73) in chlorobenzene (50 mL) was refluxed for 16 h. The solvent was removed under reduced pressure, and the crude material was carefully purified by chromatography on a silica gel column using toluene/ethyl acetate (1:1) as the eluent. Further purification was accomplished by repetitive precipitation and centrifugation by using cyclohexane as solvent (81 mg, 44%). M.p. 241–243 °C. ^1H NMR (300 MHz, CDCl_3): δ = 7.42–7.37 (m, 2 H), 6.93–6.83 (m, 5 H), 4.98 (d, J = 9.4 Hz, 1 H), 4.86 (s, 1 H), 4.24 (d, J = 9.4 Hz, 1 H), 4.17–4.13 (m, 8 H), 3.93–3.91 (m, 8 H), 3.84–3.82 (m, 8 H), 2.81 (s, 3 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 149.35, 147.73, 147.71, 147.24, 146.88, 146.74, 146.68, 146.63, 146.57, 146.55, 146.51, 146.37, 146.34, 146.19, 145.96, 145.94, 145.90, 145.76, 145.72, 145.69, 145.65, 145.57, 145.11, 145.05, 144.80, 143.57, 143.40, 143.10, 143.01, 142.99, 142.96, 142.64, 142.58, 142.55, 142.45, 142.31, 142.25, 142.10, 141.98, 140.58, 140.53, 140.26, 140.10, 136.95, 136.14, 121.85, 121.83, 114.49, 83.72, 71.78, 71.75, 71.69, 71.66, 70.35, 70.30, 70.17, 69.89, 69.84, 69.78, 69.63, 69.36, 40.42 ppm. HRMS (MALDI-TOF): calcd. for $[\text{C}_{87}\text{H}_{38}\text{NO}_8]^+$ 1224.2592 ($\text{M}^+ + \text{H}$); found 1224.2611. IR (KBr): $\tilde{\nu}_{\text{max}}$ = 3010, 2925, 2856, 2779, 2360, 1504, 1461, 1419, 1257, 1215, 1128, 756 cm^{-1} . UV (CH_2Cl_2): λ_{max} = 432, 309, 256 nm.

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