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Redox responsive molecular tweezers with tetrathiafulvalene units: synthesis, electrochemistry, and binding properties

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ABSTRACT

Several new molecular tweezers with tetrathiafulvalene (TTF) arms as well as mono-TTF derivatives bearing 3,5-di-tert-butylbenzylthio groups to provide enhanced solubility were prepared starting from a bis-cyanoethyl-protected tetrathiafulvalene derivative. The X-ray crystallographic analysis of **3** and **7a** showed highly distorted TTF groups and absence of close TTF–TTF contacts in the crystalline state. Comparative cyclic voltammetry (CV) measurements demonstrated that through space distance-dependent TTF–TTF interactions take place in the TTF-containing molecular tweezers, leading to electronic pairing with formation of mixed valence $[TTF]_2^{2+\bullet}$ species and splitting of the first oxidation wave. TTF-containing molecular tweezers were successfully tested as receptors for several electron-deficient substances.

1. Introduction

The discovery of organic conductors[1] and charge–transfer (CT) complexes[2] based on tetrathiafulvalenes (TTFs) triggered intensive studies of this heterocyclic system. Initial research efforts focused mainly on applications in the field of materials chemistry, making tetrathiafulvalene one of the most important building blocks for organic molecular electronics.[3] Later, due to their electron-donating properties and possibility of reversible stepwise oxidation forming stable radical cation and dication species, tetrathiafulvalenes found use in macromolecular,[4] supramolecular,[5] and other areas of chemistry. The versatile chemistry of tetrathiafulvalenes[6] allows the construction of various functional architectures, such as TTF-based chiral dimers,[7] dendrimers,[8] cyclophanes, and cages.[9] In interlocked supramolecular systems, such as catenanes and rotaxanes, tetrathiafulvalenes efficiently play a role as molecular motors, triggering positional displacement of supramolecular components upon oxidation/reduction.[10]

Non-cyclic compounds with cavities, commonly called molecular tweezers or clips,[11,12] have been already successfully employed as molecular hosts for binding of flat molecules in solution as well as in solid state, typically forming sandwich-like host–guest complexes with them. Despite the broad development of TTF chemistry, only a few TTF-containing rigid molecular tweezers[13] or structures preferring to adopt a tweezers-like conformation in solid state (either neutral[14a] or oxidized[14b,c]) have been reported so far. Very recently, several TTF-containing calixpyrroles[15] were shown to be efficient guest binders for electron-deficient guests, such as tetracyanoquinodimethane and derivatives of 2,4,7-trinitro-9-fluorenylidenemalononitrile, due to the electron-donating properties of tetrathiafulvalene units.

2. Results and discussion

2.1. Molecular design

In this paper we describe the preparation and characterization of a series of highly soluble tetrathiafulvalene derivatives bearing 3,5-di-*tert*-butylbenzylthio groups. Several of these compounds have structural features characteristic of molecular tweezers, with tetrathiafulvalene arms attached to benzene and naphthalene scaffolds. This design is similar to the one used before for the construction of molecular tweezers built on the basis of the dioxa[2.2]orthocyclophane[12] or dithia[2.2]orthocyclophane skeletons.[16] Interestingly in these systems, the introduction of redox active TTF groups in molecular tweezers opens the possibility to control their conformational and binding preferences by redox stimuli. Previously we have shown[16] that molecular tweezers with two TTF arms covalently linked to a benzene backbone via a dithia[2.2]orthocyclophane spacer (Fig. 1) prefer the *closed* conformation in neutral and mono-

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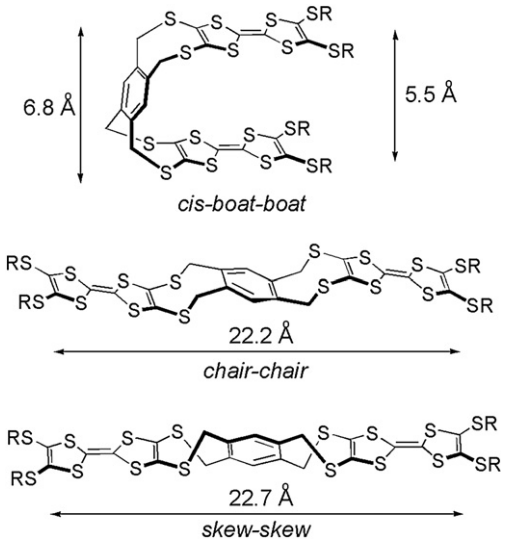


Figure 1. Selected low potential energy conformations with approximate dimensions of molecular tweezers with benzene scaffold. Dimensions are based on molecular modeling results.

oxidized states, but undergo conformational transition to the *open* conformation upon complete oxidation due to the *Coulombic* repulsion between the two doubly charged TTF moieties. This observation has paved the way to the employment of such architectures as appealing systems for host–guest binding: an affinity to electron-deficient guests, which is expected in the non-oxidized state, can be turned off by oxidation of the TTF-containing host.

In this work, we have optimized the solubility and geometry of TTF-containing molecular tweezers for binding electron-deficient flat molecular guests as a step further in our research on TTF-containing systems. Thus, receptors with benzene and naphthalene backbones and accordingly different TTF–TTF distances and properties have been prepared and investigated.

2.2. Synthesis and properties

The initial goal of our study was to render high solubility to thioalkyl TTF derivatives in non-polar organic solvents, yet avoiding the use of long alkyl chains as solubilizing groups due to their potential interference with binding substrates. Thus, we have chosen 3,5-di-*tert*-butylbenzylthio moiety as solubilizing group, being inspired by the remarkable application records of analogous 3,5-di-*tert*-butylphenyl groups for the solubilization of otherwise low soluble planar systems, such as porphyrin derivatives.[17]

The synthesis of TTF-containing tweezers started with the preparation of thione **1** from 3,5-di-*tert*-butylbenzylbromide[17a] and bis(tetraethylammonium)-bis(1,3-dithiole-2-thione-4,5-dithiol)zincate **2**[18] (Scheme 1). Thione **1** was then used for the synthesis of 2,3-bis(2-cyanoethylthio)-tetrathiafulvalene **3** in a phosphite-mediated coupling with the oxo-derivative **4**. As expected, compound **3** showed good solubility in various non-polar organic solvents (alkanes, chloroalkanes, and aromatics). 2-Cyanoethylthio-protected tetrathiafulvalene **3** can serve as a versatile building block for the preparation of various highly soluble TTF derivatives: by treatment with one or two equivalents of caesium hydroxide mono- or dithiolates can be generated and subsequently alkylated.[19]

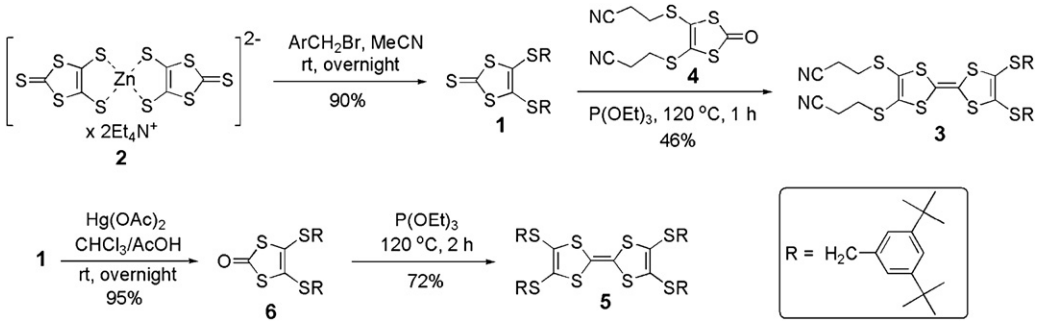
Symmetric tetrakis(3,5-di-*tert*-butylbenzylthio)-tetrathiafulvalene **5** was prepared in two steps from **1** by transchalcogenation with mercuric acetate into the corresponding oxo-derivative **6** followed by phosphite-mediated homo-coupling to yield **5**. Compound **5** displayed almost unlimited solubility in alkanes, aromatic, and chlorinated solvents, but crystallized in a fridge from concentrated (60–80%) hexane solution. NMR experiments in $CDCl_3$ did not imply any significant self-aggregation of **5** up to ca. 10% concentration.

Tetrathiafulvalene derivatives **7a**,**b** and TTF-containing molecular tweezers **8a**–**c** (Scheme 2) were prepared by reaction of TTF dithiolates generated in situ from 2,3-bis(2-cyanoethylthio)tetrathiafulvalenes **3** and aromatic methylene bromides **9a**, **9b**,[20] **10a**,[21] **10b**,[20] and **10c**,[22] following the previously reported synthetic protocols.[16,23] Purification by column chromatography in dichloromethane/petroleum ether mixtures afforded pure products in 63–81% yields. The new TTF derivatives are bright yellow (sometimes with orange hint) solids with high solubility in non-polar organic solvents, such as dichloromethane, toluene, and even alkanes.

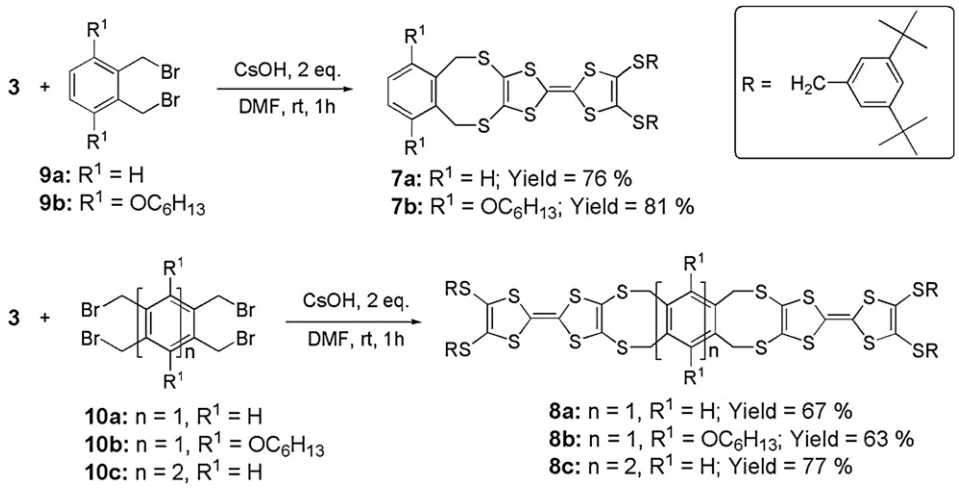
All new tetrathiafulvalene derivatives were characterized by means of NMR (^{1}H and ^{13}C), MS (high resolution EI, ESI, or MALDI), and UV/Vis spectroscopy. In the ^{1}H NMR spectra of compounds **7a**,**b** and **8a**–**c** the methylene protons of the eight-membered dithia rings appeared as a singlet, suggesting fast conformational equilibration at room temperature. The UV/Vis spectra (CH_2Cl_2, 293 K) of the new tetrathiafulvalenes featured the typical absorption pattern for tetrathio-substituted TTF derivatives[23,24] with absorption bands at λ_{max} ca. 300 and 330 nm, as well as a shoulder at ca. 400 nm.

2.3. Crystallographic study

X-ray structures of the TTF derivatives **3** and **7a** showed significantly non-planar TTF moieties (Figs. 2 and 3) featuring the boat-like distortions. Their central C_2S_4 groups are planar, whereas both five-membered rings are folded along their S···S vectors and tilted inwards toward each other. In compound **3**, the dihedral angles between the least-squared planes A (S1, S2, C1, C2, S3, S4) and B (S1, S2, C3, C4) and A and C (S3, S4, C5, C6) are ca. 30.83° and 12.58°, respectively. The distortion of the TTF moiety is even more remarkable in **7a**, where the dihedral angles between the least-squared planes A (S1, S1^i, C1, C2, S2, S2^i) and B (S1, S1^i, C3, C3^i) and A and C (S2, S2^i, C4, C4^i) reach ca. 27.57° and 30.44°, respectively. Such a significant distortion is caused only by weak intermolecular interactions with other molecules in the crystal lattice and not by covalent bonding, for



Scheme 1. Synthesis of 3,5-di(*tert*-butylbenzylthio)tetrathiafulvalene derivatives **3** and **5**.



Scheme 2. Synthesis of 3,5-di(*tert*-butylbenzylthio)tetrathiafulvalene derivatives **7** and **8**.

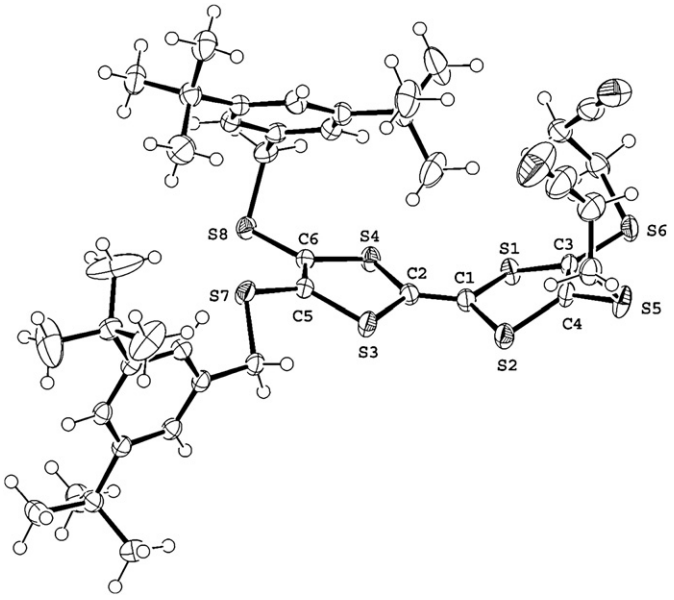


Figure 2. ORTEP plot of **3** (50% probability of thermal ellipsoids). Minor positions of the disordered atoms are omitted.

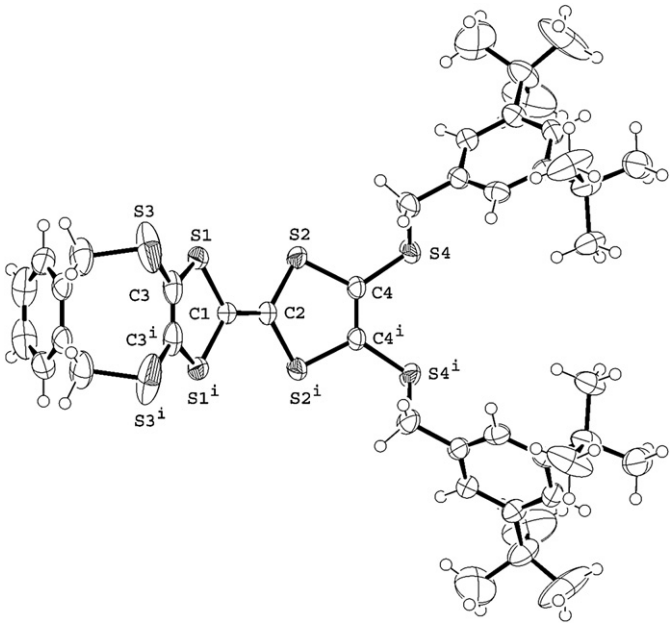


Figure 3. ORTEP plot of **7a** (50% probability of thermal ellipsoids).

example, due to incorporation of the TTF moiety into a cyclophane backbone,[25] demonstrating remarkable flexibility of the TTF group.

The presence of the bulky 3,5-di-*tert*-butylbenzyl groups in both structures did not give a possibility for the normally observed TTF–TTF stacking, in which planar TTF molecules are separated by ca. 3.6 Å from each other. The long-range lattice order is governed by the weak dispersion interactions involving *tert*-butyl groups and aromatic rings, which separate TTF units from each other. (Figs. 4 and 5) No close contacts between the sulfur atoms could be observed.

Thus, analysis of the X-ray structures evidenced notable flexibility of the TTF moiety, which allows adopting their conformation to make it suitable for tight packing in the solid state. The same flexibility can be also advantageous for molecular recognition processes, allowing the receptor to adopt the best conformation for the guest binding, as well as close TTF–TTF contacts in compounds with the benzene scaffold.

2.4. Electrochemistry

The cyclic voltammograms of mono-TTF derivatives show the classical redox behavior of TTF, displaying two quasi-reversible electrochemical processes on the cathodic scan, the first one at $E^1_{1/2}$=0.30–0.40 V (vs Ag/AgCl, Table 1) leading to the TTF radical cation, and the second one at $E^2_{1/2}$=0.60–0.70 V giving the dication, as it is known from literature.[3] On the other hand, the cyclic voltammograms of molecular tweezers **8a** and **8b**, which are constructed on the benzene scaffold, feature a splitting of the first oxidation wave into two relatively well-defined waves with $\Delta E^1_{1/2} \approx 0.14$ V (Table 1 and Fig. 6), indicating the one-electron sequential formation of the mono-(radical cation) and the bis-(radical cation).[26]

This fact suggests the electronic stabilization of the first-formed radical cation by the π electrons of the neighboring TTF moiety, thus leading to a reduction of the potential with formation of mixed valence $[TTF]_2^{+\bullet}$ species, and to an increase of the second mono-electronic oxidation step to $[TTF]_2^{2(+\bullet)}$ in molecular tweezers **8a** and **8b**, as a result of the proximity of the first-formed radical cation. In contrast, molecular tweezer **8c**, built onto the naphthalene scaffold, does not show any splitting of the first oxidation wave (Fig. 6) but an electrochemical behavior similar to tetraarylthiotetrathiafulvalene

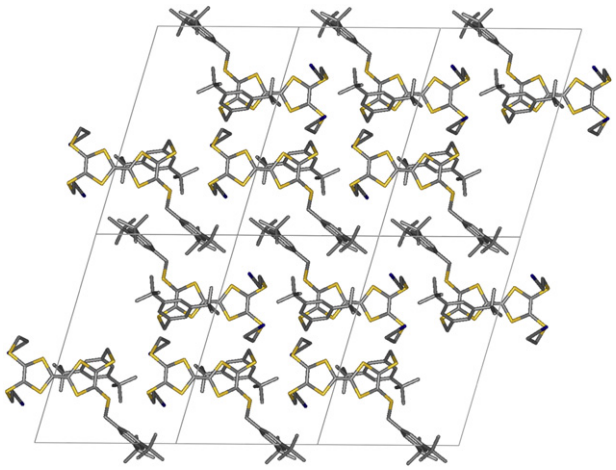


Figure 4. Crystal packing of **3**, projection along the *a* axis. Hydrogen atoms are omitted for clarity.

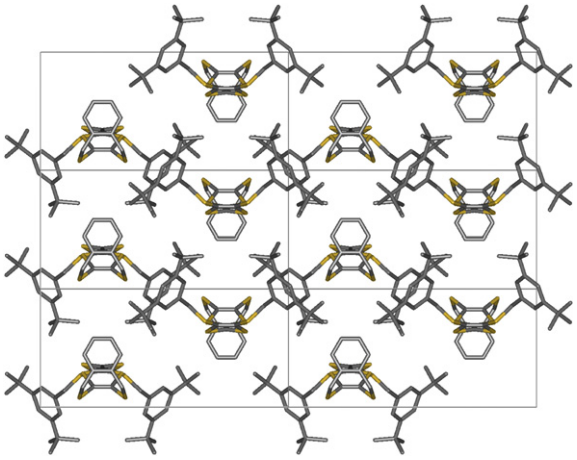


Figure 5. Crystal packing of **7a**, projection along the *c* axis. Hydrogen atoms are omitted for clarity.

Table 1
Electrochemical data of TTF derivatives[a]

Compound	$E^{ox1}_{1/2}$ (V)	$E^{ox1'}_{1/2}$ (V)	$E^{ox2}_{1/2}$ (V)	E^{ox3} (V)
3	0.36		0.68	–
5	0.33		0.66	1.90
7a	0.33		0.69	1.86
7b	0.33		0.68	1.31, 1.94
8a	0.26	0.40	0.66	1.89
8b	0.27	0.43	0.67	1.90
8c	0.34		0.66	1.86

[a] Data were obtained using a one-compartment cell in CH_2Cl_2/0.1 M Bu_4NPF_6, Pt as the working and counter electrodes. Values given at room temperature vs Ag/Ag^+, scan rate 200 mV/s.

derivative **5**. This fact implies that in molecular tweezers **8a**,**b** TTF–TTF interaction takes place exclusively through space, and in **8c** this interaction does not seem to be possible as a consequence of the long TTF–TTF distance, independently of the tweezers' conformation. Intermolecular nature of the splitting due to tweezers' dimerization[13c] seems quite unlikely due to the following reasons: (a) splitting was observed only for the tweezers with the benzene scaffold, in which close TTF–TTF contacts upon conformational distortion are possible; (b) the splitting shows a well-defined doublet, whereas for a dimer more complex pattern can be expected.[13c] (c) Measurements with different scan rates did not lead to significant changes of the voltammograms.

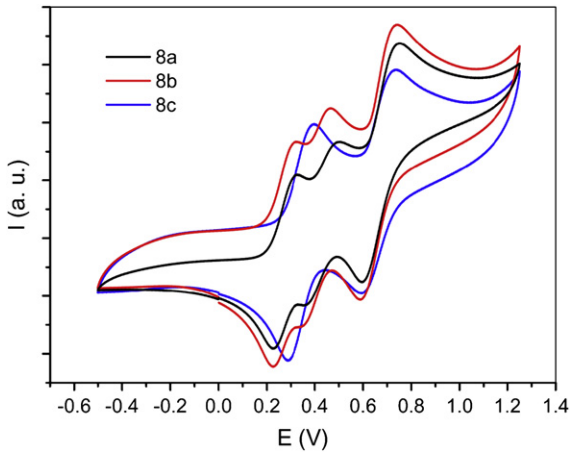


Figure 6. Cyclic voltammograms of molecular tweezers **8a**, **8b** and **8c**. (CH_2Cl_2/0.1 M Bu_4NPF_6, scan rate 200 mV/s).

The reversible two-electron process for **8a**–**c** leading to the formation of the tetracations can be observed at around 0.66 V, a similar value recorded for TTF **5**. No splitting of this wave could be detected for **8a**–**c**, indicating that the two TTF chromophores are at large distance and no more in electronic communication with each other.[27] Finally, the cyclic voltammograms of these derivatives are completed in most cases with one additional oxidation wave at around 1.90 V, probably arising from the 3,5-di-*tert*-butylbenzyl substituents (Table 1).

2.5. Binding studies

Unlike previously reported molecular tweezers, which either had limited solubility or sterically hindering groups near the binding site,[16] the new compounds lacked these disadvantages and were suitable for molecular recognition studies. Thus, molecular recognition properties were tested for molecular tweezers **8a** and **8c**, built onto a benzene and naphthalene backbone and thus with different TTF–TTF spans, as well as for the reference compound **7a**. Binding studies were performed by means of NMR binding titrations in chloroform using tetracyanoquinodimethane (TCNQ), 2,4,7-trinitro-9-fluorenylidenemalononitrile (TNF),[28] and tetracyanobenzene (TCNB) (Fig. 7) as guest compounds. As expected, NMR spectra showed fast host–guest exchange. Both molecular tweezers **8a**,**c** showed binding with TNF (K_a=16 M^{-1} and K_a=22 M^{-1} for **8a** and **8c**, respectively), whereas only **8c** showed weak binding with TCNB (K_a=6 M^{-1}).[29] In binding experiments with TCNQ, the broadening and disappearance of the NMR resonance of the TCNQ protons were observed for quite low host concentrations (<1 mM) with both **8a** and **8c**, implying generation of paramagnetic species due to formation of a charge–transfer (CT) complex. In the IR spectra of TCNQ with **8a** and **8c** weak CT absorption bands could be detected at ca. 760 and 850 nm, respectively, although at 5–10 times higher concentrations of a host. Rough estimation based on donor and acceptor oxidation/reduction potentials[30] indicated that the degree of CT for complexes of TCNQ

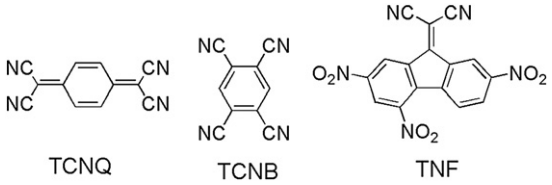


Figure 7. Structures of guests used for molecular recognition studies.

with hosts **8** should be rather small. Thus, other reasons for the signal broadening, such as dynamic host–guest exchange with a timescale similar to the one of NMR, cannot be fully ruled out. Dilution studies with **7a** and **8a**,**b** did not reveal any self-association of the molecular host at the concentrations used for binding titrations. Additional host–guest binding studies using other solvents and guest compounds are currently under way.

Binding studies have thus showed the feasibility of the molecular design used in our molecular tweezers systems, with two TTF moieties aligned in parallel fashion, although relatively low binding constants imply that significant tuning of the receptor structure is necessary to improve the binding efficiency. Thus, molecular tweezers bearing pyrrolo-[31] and alkyl-substituted tetrathiafulvalenes, which are know for their better electron-donating[3] and binding[32] properties than thioalkyl-substituted TTFs, are planned to be tested as hosts for electron-deficient guests.

3. Conclusions

In summary, the attachment of 3,5-di-*tert*-butylbenzylthio groups to TTF has been shown to be an efficient strategy to obtain soluble tetrathiafulvalene derivatives. It was used to render solubility to several novel TTF derivatives; some of those with architectures of molecular tweezers. Two new tetrathiafulvalene derivatives were characterized using X-ray, showing significant distortion of the TTF moieties due to the hindering influence of the bulky 3,5-di-*tert*-butylbenzyl groups, which prevent efficient TTF–TTF stacking. Cyclic voltammetry measurements evidenced that only distance-dependent through space TTF–TTF interactions are possible in the TTF-containing molecular tweezers. Finally, TTF-containing molecular tweezers were successfully tested as receptors for several electron-deficient substances, and, although the binding constants were relatively low, this result is promising. Further synthetic efforts are aimed to the construction of analogous receptors with improved binding properties using more electron rich pyrrolo-TTF and alkyl-TTF arms instead of thioalkyl-TTFs.

4. Experimental section

4.1. General

Reagent grade chemicals and solvents were used without further purification unless otherwise stated. All reactions were carried out under the atmosphere of dry N_2. Chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane using the residual solvent peak as internal reference: $CDCl_3$ (7.26 ppm for ^1H, 77.23 ppm for ^{13}C). ^1H and ^{13}C NMR spectra were recorded with a *Bruker Avance DPX-200* spectrometer. EIMS spectra were measured on a *Finnigan MAT 8200* spectrometer, ESI-MS spectra were measured on a *BrukermicrOTOF* spectrometer using direct injection method, MALDI-MS spectra were measured on a *Perseptive (Applied Bioystems) Voyager DE Pro* spectrometer. UV/Vis measurements were performed on a *Varian Cary 50 Conc* spectrophotometer. IR spectra were recorded on a *Perkin–Elmer Paragon 500* FTIR spectrometer. Analytical thin layer chromatography (TLC) was performed on 0.2 mm silica gel aluminum cards with F-254 fluorescent indicator. Flash chromatography (FC) was carried out using 230–440 mesh (particle size 36–70 μm) silica gel.

4.2. Synthetic procedures

*4.2.1. 4,5-Bis(3,5-di-tert-butylbenzylthio)-1,3-dithiole-2-thione (**1**).* To a solution of bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5-dithiol)zincate **2** (1.38 g, 1.92 mmol) in MeCN (30 mL) a solution of 1-bromomethyl-3,5-di-*tert*-butylbenzene (2.30 g, 8.12 mmol) in MeCN (30 mL) was added dropwise. The reaction mixture turned brown and then gradually changed its color to yellow-green. The reaction was stirred overnight, and then evaporated to dryness. The residue was dissolved in CH_2Cl_2/petroleum ether (1:3, 40 mL), and the undissolved material was filtered off. After evaporation of the solvent, the product was purified by flash chromatography (CH_2Cl_2/petroleum ether, 1:4–1:3) to give the product as a viscous yellow syrup, which crystallized upon cooling yielding a bright yellow solid (2.086 g, 3.46 mmol, 90%). Mp: 76.5–78.5 °C. R_f=0.28 (CH_2Cl_2/petroleum ether, 1:4). ^1H NMR (200 MHz, $CDCl_3$): δ=1.30 (36H, s), 3.96 (4H, s), 7.05 (4H, d, J=2.0 Hz), 7.33 (2H, t, J=2.0 Hz) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ=31.55; 34.86, 41.77, 121.98, 123.40, 134.78, 137.98, 151.27, 211.45 ppm. HRMS (EI): m/z calcd for $C_{33}H_{46}S_5$ (M^+) 602.22031, found 602.22177.

*4.2.2. 2,3-Bis(2-cyanoethylthio)-6,7-bis(3,5-di-tert-butylbenzylthio)-tetrathiafulvalene (**3**).* A suspension of **1** (1.66 g, 2.76 mmol) and **4** (0.795 g, 2.9 mmol) in $P(OEt)_3$ (5 mL) was degassed by a freeze–pump–thaw cycle, and then heated with stirring at 120 °C for 2 h. The reaction mixture gradually turned from yellow to bright yellow-orange, and a precipitate appeared. The solvent was removed under high vacuum; the residue was suspended in MeOH (20 mL) and the undissolved material, mostly consisting of 2,3,6,7-tetrakis(2-cyanoethylthio)tetrathiafulvalene, was filtered off. Methanol was then removed under vacuum, and the residue was first subjected to crude chromatography (CH_2Cl_2) using a short SiO_2 plug, and then the product was additionally purified by flash chromatography (petroleum ether/EtOAc, 7:3). Compound **3** crystallized upon concentration of the solvent affording bright yellow crystalline powder (1.08 g, 1.26 mmol, 46%). Mp: 119–120 °C. R_f=0.34 (CH_2Cl_2). ^1H NMR (200 MHz, $CDCl_3$): δ=1.31 (36H, s), 2.75 (4H, t, J=7.0 Hz), 3.10 (4H, t, J=7.0 Hz) 3.85 (4H, s), 7.09 (4H, d, J=2.0 Hz), 7.31 (2H, t, J=2.0 Hz) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ=18.74, 31.15, 31.39, 34.66, 41.06, 106.91, 114.27, 117.42, 121.43, 123.08, 127.71, 129.51, 135.34, 150.75 ppm. IR (KBr): ν_{max}=2251 (C≡N) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (ε)=310 (16,300), 331 (16,900), 393 (2950 $dm^3\,mol^{-1}\,cm^{-1}$) nm. HRMS (EI): m/z calcd for $C_{42}H_{54}N_2S_8$ (M^+) 842.20527, found 842.20639.

*4.2.3. 4,5-Bis(3,5-di-tert-butylbenzylthio)-1,3-dithiole-2-one (**6**).* Compound **1** (388 mg, 0643 mmol) was dissolved in $CHCl_3$ (7.5 mL) and $Hg(OAc)_2$ (410 mg, 1.29 mmol) was added to it, followed by AcOH (2.5 mL). The reaction mixture was stirred overnight, and then the white precipitate was filtered off using Celite. The resulting organic phase was washed with saturated $NaHCO_3$ solution, the aqueous phase was extracted two times with CH_2Cl_2. The combined organic phase was dried ($MgSO_4$) and evaporated to dryness affording an almost colorless syrup that crystallized upon standing in a fridge. The product was additionally purified by flash chromatography (CH_2Cl_2/petroleum ether, 1:2) yielding colorless crystalline material (357 mg, 0.608 mmol, 95%). Mp: 87.5–89 °C. R_f=0.37 (CH_2Cl_2/petroleum ether, 1:2). ^1H NMR (200 MHz, $CDCl_3$): δ=1.28 (36H, s), 3.92 (4H, s), 7.05 (4H, d, J=2.0 Hz), 7.31 (2H, t, J=2.0 Hz) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ=31.62; 34.98, 41.76, 121.92, 123.43, 129.12, 135.14, 151.29, 190.33 ppm. HRMS (EI): m/z calcd for $C_{33}H_{46}OS_4$ (M^+) 586.24315, found 586.24240.

*4.2.4. 2,3,6,7-Tetrakis(3,5-di-tert-butylbenzylthio)tetrathiafulvalene (**5**).* A suspension of compound **6** (333 mg, 0.567 mmol) in $P(OEt)_3$ (3 mL) was degassed by a freeze–pump–thaw cycle, then heated with stirring at 120 °C for 2 h. The reaction mixture gradually turned from colorless to yellow-orange. The solvent was removed under high vacuum, the oily residue was subjected to flash chromatography (CH_2Cl_2/petroleum ether, 1:4) affording compound **5** as a yellow-orange oil, which crystallizes upon standing (232 mg, 0.203 mmol, 72%). Mp: 63–65 °C. R_f=0.44 (CH_2Cl_2/petroleum ether, 1:3). ^1H NMR (200 MHz, $CDCl_3$): δ=1.30 (72H, s), 3.86 (8H, s), 7.10

(8H, d, J=2.0 Hz), 7.29 (4H, t, J=2.0 Hz) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ=31.67; 35.01, 41.44, 111.01, 121.77, 123.45, 129.36, 135.71, 151.15 ppm. UV–vis (CH_2Cl_2): λ_{max} (ε)=309 (17,500), 332 (16,800), 396 (3090 dm^3 mol^{-1} cm^{-1}) nm. HRMS (EI): m/z calcd for $C_{66}H_{92}S_8$ (M^+) 1140.49648, found 1140.49887.

4.3. Synthesis of compounds 7 and 8, general procedure

TTF derivative **3** (0.2 mmol) was dissolved in dry DMF (20 mL) and degassed by a freeze–pump–thaw cycle; then CsOH (0.42 mmol, 0.84 mL) was added as a 0.5 M solution in MeOH at 0 °C. The mixture was allowed to warm to rt and stirred for 30 min, turning from orange to dark brown-red in color. Aromatic bromomethyl derivative **9** (0.2 mmol) or **10** (0.1 mmol) was dissolved in dry THF (3 mL), and the solution was degassed by a freeze–pump–thaw cycle. The THF solution was added in one portion to the previously prepared DMF solution at −20 °C, then the mixture was allowed to warm gradually to rt. The reaction mixture turned orange-yellow, sometimes a yellow precipitate formed. The reaction was allowed to stir for additional 30 min at rt, and then was evaporated to dryness. The residue was purified by flash chromatography on silica gel.

*4.3.1. 2-[4,5-Bis(3,5-di-tert-butylbenzylthio)-1,3-dithiol-2-ylidene]-5H,10H-1,3-dithiolo[4,5-c][2,5]benzodithiocine (**7a**).* Two consecutive flash chromatographies (CH_2Cl_2/petroleum ether, 1:3; then cyclohexane/EtOAc, 20:1) afforded the product as a yellow syrup (128 mg, 0.152 mmol, 76%), which crystallized upon trituration with a small volume of hexane giving a bright yellow crystalline powder. Mp: 219–221 °C. R_f=0.55 (cyclohexane/EtOAc, 19:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.28 (36H, s), 3.76 (4H, s), 4.30 (4H, s), 7.04 (4H, d, J=1.8 Hz), 7.21–7.34 (4H, m), 7.28 (2H, t, J=1.8 Hz) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ=31.64, 35.00, 38.69, 41.48, 111.86, 112.29, 121.73, 123.41, 128.89, 129.64, 130.24, 130.78, 134.82, 135.78, 151.15 ppm. UV–vis (CH_2Cl_2): λ_{max} (ε)=295 (15,200), 335 (18,500), 400 sh (2600 dm^3 mol^{-1} cm^{-1}) nm. HRMS (EI): m/z calcd for $C_{44}H_{54}S_8$ (M^+) 838.19913, found 838.20284.

*4.3.2. 2-[4,5-Bis(3,5-di-tert-butylbenzylthio)-1,3-dithiol-2-ylidene]-5H,10H-6,9-dihexyloxy-1,3-dithiolo[4,5-c][2,5]benzodithiocine (**7b**).* Two consecutive flash chromatographies (CH_2Cl_2/petroleum ether, 1:3; then cyclohexane/EtOAc, 25:1) afforded the product as a yellow syrup (169 mg, 0.162 mmol, 81%), which crystallized upon trituration with a small volume of hexane giving a bright yellow crystalline powder. Mp: 125–126 °C. R_f=0.67 (cyclohexane/EtOAc, 19:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.94 (6H, t, J=6.4 Hz), 1.27 (36H, s), 1.33–1.58 (12H, m), 1.73–1.87 (4H, m), 3.75 (4H, s), 3.95 (4H, t, J=6.4 Hz), 4.35 (4H, s), 6.79 (2H, s), 7.04 (4H, d, J=1.8 Hz), 7.27 (2H, t, J=1.8 Hz) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ=14.35, 22.90, 26.09, 29.64, 31.63, 31.80, 32.02, 34.98, 41.50, 69.50, 111.90, 112.50, 112.80, 121.72, 123.41, 125.27, 129.60, 130.94, 135.80, 150.74, 151.14 ppm. UV–vis (CH_2Cl_2): λ_{max} (ε)=318 (17,900), 331 (19,800), 400 sh (2500 dm^3 mol^{-1} cm^{-1}) nm. HRMS (EI): m/z calcd for $C_{56}H_{78}O_2S_8$ (M^+) 1038.37676, found 1038.37727.

*4.3.3. 2,10-Bis[4,5-bis(3,5-di-tert-butylbenzylthio)-1,3-dithiol-2-ylidene]-5H,7H,13H,15H-bis[1,3]dithiolo[4,5-b:4′,5′-b′]benzo[1,2-f:4,5-f′]bis[1,4]dithiocine (**8a**).* Two consecutive flash chromatographies (CH_2Cl_2/petroleum ether, 1:2; then cyclohexane/EtOAc, 10:1) afforded the product as a yellow syrup (107 mg, 0.0668 mmol, 67%), which crystallized upon trituration with a small volume of hexane giving a bright yellow crystalline powder. Mp: 260–270 °C (decomp.). R_f=0.29 (cyclohexane/EtOAc, 19:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.26 (72H, s), 3.75 (8H, s), 4.29 (8H, s), 7.04 (8H, d, J=1.8 Hz), 7.09 (2H, s), 7.26 (4H, t, J=1.8 Hz) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ=31.64, 34.98, 38.19, 41.53, 111.84, 114.24, 121.73, 123.42, 129.48, 129.70, 132.85, 135.28, 135.71, 151.12 ppm. UV–vis (CH_2Cl_2): λ_{max} (ε)=292 (35,600), 335 (36,000), 396 sh (5800 dm^3 mol^{-1} cm^{-1}) nm. HRMS (ESI) m/z calcd for $C_{82}H_{102}S_{16}$ (M^+) 1598.3507, found 1598.3517; calcd for (MCl^-) 1633.2867, found 1633.3255.

*4.3.4. 2,10-Bis[4,5-bis(3,5-di-tert-butylbenzylthio)-1,3-dithiol-2-ylidene]-5H,7H,13H,15H-6,14-dihexyloxy-bis[1,3]dithiolo[4,5-b:4′,5′-b′]benzo[1,2-f:4,5-f′]bis[1,4]dithiocine (**8b**).* Two consecutive flash chromatographies (CH_2Cl_2/petroleum ether, 1:2; then cyclohexane/EtOAc, 12:1), afforded the product as a yellow syrup (113 mg, 0.0627 mmol, 63%), which crystallized upon trituration with a small volume of hexane giving a yellow-orange crystalline powder. Mp: 133–135 °C. R_f=0.48 (cyclohexane/EtOAc, 19:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.98 (6H, t, J=6.8 Hz), 1.25 (72H, s), 1.38–1.61 (12H, m), 1.83–1.97 (4H, m), 3.75 (8H, s), 4.12 (4H, t, J=6.6 Hz), 4.34 (8H, s), 7.04 (8H, d, J=1.8 Hz), 7.25 (4H, t, J=1.8 Hz) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ=14.41, 22.91, 25.89, 30.49, 31.63, 32.01, 32.59, 34.98, 41.55, 110.52, 115.62, 121.72, 123.46, 129.45, 129.85, 130.55, 135.71, 151.09, 152.23 ppm. UV–vis (CH_2Cl_2): λ_{max} (ε)=304 (38,200), 332 (35,800), 396 sh (5800 dm^3 mol^{-1} cm^{-1}) nm; HRMS (MALDI, matrix: DHB): m/z calcd for $C_{94}H_{126}O_2S_{16}$ (M^+) 1798.5289, found 1798.5431.

*4.3.5. 2,11-Bis[4,5-bis(3,5-di-tert-butylbenzylthio)-1,3-dithiol-2-ylidene]-5H,8H,14H,17H-bis[1,3]dithiolo[4,5-b:4′,5′-b′]naphtho[2,3-f:6,7-f′]bis[1,4]dithiocine (**8c**).* Due to its low solubility, compound **10c** was added to the reaction mixture as a powder. Flash chromatography (CH_2Cl_2; then cyclohexane/EtOAc, 9:1) with gradual addition of CH_2Cl_2 until the entire fraction containing the product was collected. After concentration of the solution, the product was obtained as an amorphous yellow-orange powder (128 mg, 0.0775 mmol, 77%). Mp: 200–210 °C (decomp.). R_f=0.44 (cyclohexane/EtOAc, 19:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.25 (72H, s), 3.73 (8H, s), 4.43 (8H, s), 7.02 (8H, d, J=1.8 Hz), 7.26 (4H, t, J=1.8 Hz), 7.67 (4H, s) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ=31.62, 34.98, 39.46, 41.47, 111.71, 112.71, 121.72, 123.39, 129.49, 131.01, 132.95, 133.79, 135.72, 151.12 ppm. UV–vis (CH_2Cl_2): λ_{max} (ε)=292 sh (43,600), 330 (37,900), 396 sh (6800 dm^3 mol^{-1} cm^{-1}) nm. HRMS (ESI): m/z calcd for $C_{86}H_{104}S_{16}$ $(M+H)^+$ 1649.3742, found 1649.3730; calcd for $(M+Cl)^-$ 1683.33.63, found 1683.3375.

4.4. X-ray crystallography

Crystallographic measurements were performed on a Siemens-P4 diffractometer with a graphite monochromated Mo Kα radiation (λ 71.073 pm) and the low-temperature device LT2. The structure was solved by direct methods and refined by full matrix least-squares technique on F^2 using SHELX[33] program package. All non-H-atoms were refined anisotropically, the positions of hydrogen atoms were calculated as a 'riding' model.

Crystallographic data (excluding structure factors) for the structures **3** and **7a** in this paper have been deposited with the Cambridge Crystallographic Data Centre under deposition numbers 747,600 and 747,601, respectively. Copy of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk). Abbreviated crystallographic data are given below.

Compound **3**. $C_{42}H_{54}N_2S_8$, MW=843.35, triclinic, P-1 (#2), a=1027.30 pm, b=1222.8 pm, c=1900.2 pm, α=73.520°, β=80.290°, γ=86.090°, V=2.2556 nm^3, Z=2, T=173 K, μ=0.427 mm^{-1}, ρ=1.242 Mg m^{-3}, GOF on F^2=1.019, R_1=0.0451, wR_2=0.1205 [$I>2\sigma(I)$]. Crystals were grown by slow evaporation of a cyclohexane solution.

Compound **7a**. $C_{44}H_{54}S_8$, MW=839.35, monoclinic, $P2_1/m$ (#11), a=929.40 pm, b=1869.80 pm, c=1363.8 pm, α=90°, β=105.860°, γ=105.860°, V=2.2798 nm^3, Z=2, T=173 K, μ=0.421 mm^{-1},

ρ=1.223 Mg m^{-3}, GOF on F^2=1.029, R_1=0.0525, wR_2=0.1381 [$I>2\sigma(I)$]. Crystals were grown by slow evaporation of a $CHCl_3$/heptane solution.

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Supplementary data

NMR and UV spectra of the new compounds, CV plots with description of CV measurements, full crystallographic data, and binding plots with description of binding experiments. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.10.052.

References and notes

1. Wudl, F.; Wobschall, D.; Hufnagel, E. J. *J. Am. Chem. Soc.* **1972**, *94*, 670–672.
2. Ferraris, J.; Cowan, D. O.; Walatka, V., Jr.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948–949.
3. Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891–4945.
4. Bryce, M. R. *J. Mater. Chem.* **2000**, *10*, 589–598.
5. Nielsen, M. B.; Lomholt, C.; Becher, J. *Chem. Soc. Rev.* **2000**, *29*, 153–164.
6. (a) Krief, A. *Tetrahedron* **1986**, *42*, 1209–1252; (b) Segura, J. L.; Martín, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 1372–1409; (c) Fabre, J. M. *Chem. Rev.* **2004**, *104*, 5133–5150; (d) Gorgues, A.; Hudhomme, P.; Sallé, M. *Chem. Rev.* **2004**, *104*, 5151–5184; (e) Canevet, D.; Sallé, M.; Zhang, G.; Zhang, D.; Zhu, D. *Chem. Commun.* **2009**, 2245–2269.
7. (a) Gómez, R.; Segura, J. L.; Martín, N. *Org. Lett.* **2000**, *2*, 1585–1587; (b) Gómez, R.; Segura, J. L.; Martín, N. *J. Org. Chem.* **2000**, *65*, 7566–7574; (c) Zhou, Y.; Zhang, D.; Zhu, L.; Shuai, Z.; Zhu, D. *J. Org. Chem.* **2006**, *71*, 2123–2130; (d) Delogu, G.; Fabbri, D.; Dettori, M. A.; Sallé, M.; Le Derf, F.; Blesa, M.-J.; Allain, M. *J. Org. Chem.* **2006**, *71*, 9096–9103.
8. (a) Devonport, W.; Bryce, M. R.; Marshallsay, G. J.; Moore, A. J.; Goldenberg, L. M. *J. Mater. Chem.* **1998**, *8*, 1361–1372; (b) Bryce, M. R.; Devonport, W.; Goldberg, L. M.; Wang, C. *Chem. Commun.* **1998**, 945–951; (c) González, A.; Segura, J. L.; Martín, N. *Tetrahedron Lett.* **2000**, *41*, 3083–3086.
9. Jeppesen, J. O.; Nielsen, M. B.; Becher, J. *Chem. Rev.* **2004**, *104*, 5115–5131.
10. (a) Pease, A. R.; Jeppesen, J. O.; Stoddart, J. F.; Luo, Y.; Collier, C. P.; Heath, J. R. *Acc. Chem. Res.* **2001**, *34*, 433–444; (b) Becher, J.; Jeppesen, J. O.; Nielsen, K. *Synth. Met.* **2003**, *133–134*, 309–315; (c) Moonen, N. N. P.; Flood, A. H.; Fernández, J. M.; Stoddart, J. F. *Top. Curr. Chem.* **2005**, *262*, 99–132.
11. (a) Chen, C.-W.; Whitlock, H. W., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 4921–4922; (b) Zimmerman, S. C.; VanZyl, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 7894–7896; (c) Rowan, A. E.; Elemans, J. A. A. W.; Nolte, R. J. M. *Acc. Chem. Res.* **1999**, *32*, 995–1006; (d) Klärner, F.-G.; Kahlert, B. *Acc. Chem. Res.* **2003**, *36*, 919–932; (e) Harmata, M. *Acc. Chem. Res.* **2004**, *37*, 862–873; (f) Petitjean, A.; Khoury, R. G.; Kyritsakas, N.; Lehn, J.-M. *J. Am. Chem. Soc.* **2004**, *126*, 6637–6647; (g) Colquhoun, H. M.; Zhu, Z. *Angew. Chem., Int. Ed.* **2004**, *43*, 5040–5045; (h) Pardo, C.; Sesmilo, E.; Gutiérrez-Puebla, E.; Monge, A.; Elguero, J.; Fruchier, A. *J. Org. Chem.* **2001**, *66*, 1607–1611.
12. (a) Kurebayashi, H.; Sakaguchi, M.; Okajima, T.; Haino, T.; Usui, S.; Fukazawa, Y. *Tetrahedron Lett.* **1999**, *40*, 5545–5548; (b) Kurebayashi, H.; Haino, T.; Fukazawa, Y. *Tetrahedron Lett.* **2000**, *41*, 477–480; (c) Kurebayashi, H.; Haino, T.; Usui, S.; Fukazawa, Y. *Tetrahedron* **2001**, *57*, 8667–8674; (d) Iwamoto, H.; Takahashi, N.; Maeda, T.; Hidaka, Y.; Fukazawa, Y. *Tetrahedron Lett.* **2005**, *46*, 6839–6842; (e) Iwamoto, H.; Hidaka, Y.; Fukazawa, Y. *Tetrahedron Lett.* **2008**, *49*, 277–280.
13. (a) Chiang, P.-T.; Cheng, P.-N.; Lin, C.-F.; Liu, Y.-H.; Lai, C.-C.; Peng, S.-M.; Chiu, S.-H. *Chem.—Eur. J.* **2006**, *12*, 865–876; (b) Cheng, K.-W.; Lai, C.-C.; Chianga, P.-T.; Chiu, S.-H. *Chem. Commun.* **2006**, 2854–2856; (c) Chiang, P.-T.; Chen, N.-C.; Lai, C.-C.; Chiu, S.-H. *Chem.—Eur. J.* **2008**, *14*, 6546–6552.
14. (a) Tachikawa, T.; Izuoka, A.; Sugawara, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1227–1229; (b) Tachikawa, T.; Izuoka, A.; Sugawara, T. *Solid State Commun.* **1993**, *88*, 207–209; (c) Fujiwara, H.; Arai, E.; Kobayashi, H. *J. Mater. Chem.* **1998**, *8*, 829–831.
15. (a) Poulsen, T.; Nielsen, K. A.; Bond, A. D.; Jeppesen, J. O. *Org. Lett.* **2007**, *9*, 5485–5488; (b) Nielsen, K. A.; Sarova, G. H.; Martín-Gomis, L.; Fernández-Lázaro, F.; Stein, P. C.; Sanguinet, L.; Levillain, E.; Sessler, J. L.; Guldi, D. M.; Sastre-Santos, Á.; Jeppesen, J. O. *J. Am. Chem. Soc.* **2008**, *130*, 460–462; (c) Nielsen, K. A.; Martín-Gomis, L.; Sarova, G. H.; Sanguinet, L.; Gross, D. E.; Fernández-Lázaro, F.; Stein, P. C.; Levillain, E.; Sessler, J. L.; Guldi, D. M.; Sastre-Santos, Á.; Jeppesen, J. O. *Tetrahedron* **2008**, *64*, 8449–8463.
16. Azov, V. A.; Gómez, R.; Stelten, J. *Tetrahedron* **2008**, *64*, 1909–1917.
17. (a) Plater, M. J.; Aiken, S.; Bourhill, G. *Tetrahedron* **2002**, *58*, 2405–2413; (b) Cho, H. S.; Jeong, D. H.; Cho, S.; Kim, D.; Matsuzaki, Y.; Tanaka, K.; Tsuda, A.; Osuka, A. *J. Am. Chem. Soc.* **2002**, *124*, 14642–14654; (c) Bonifazi, D.; Accorsi, G.; Armaroli, N.; Song, F. Y.; Palkar, A.; Echegoyen, L.; Scholl, M.; Seiler, P.; Jaun, B.; Diederich, F. *Helv. Chim. Acta* **2005**, *88*, 1839–1884.
18. Wang, C.; Batsanov, A. S.; Bryce, M. R.; Howard, J. A. K. *Synthesis* **1998**, 1615–1618.
19. (a) Simonsen, K. B.; Svenstrup, N.; Lau, J.; Simonsen, O.; Mørk, P.; Kristensen, G. J.; Becher, J. *Synthesis* **1996**, 407–418; (b) Svenstrup, N.; Rasmussen, K. M.; Hansen, T. K.; Becher, J. *Synthesis* **1994**, 809–812.
20. Röhrich, J.; Müllen, K. *J. Org. Chem.* **1992**, *57*, 2374–2379.
21. Ried, W.; Bodem, H. *Chem. Ber.* **1956**, *89*, 2328–2331.
22. Rivera, J. M.; Martin, T.; Rebek, J., Jr. *J. Am. Chem. Soc.* **2001**, *123*, 5213–5220.
23. González, M.; Illescas, B.; Martín, N.; Segura, J. L.; Seoane, C.; Hanack, M. *Tetrahedron* **1998**, *54*, 2853–2866.
24. Moses, P. R.; Chambers, J. Q. *J. Am. Chem. Soc.* **1974**, *96*, 945–946.
25. (a) Röhrich, J.; Wolf, P.; Enkelmann, V.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1377–1379; (b) Simonsen, K. B.; Thorup, N.; Becher, J. *Synthesis* **1997**, 1399–1404; (c) Nielsen, M. B.; Thorup, N.; Becher, J. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1305–1308.
26. (a) Jørgensen, M.; Lerstrup, K. A.; Bechgaard, K. *J. Org. Chem.* **1991**, *56*, 5684–5688; (b) Blanchard, P.; Svenstrup, N.; Becher, J. *Chem. Commun.* **1996**, 615–616; (c) Spanggaard, H.; Prehn, J.; Nielsen, M. B.; Levillain, E.; Allain, M.; Becher, J. *J. Am. Chem. Soc.* **2000**, *122*, 9486–9494; (d) Le Derf, F.; Levillain, E.; Trippé, G.; Gorgues, A.; Sallé, M.; Sebastian, R.-M.; Caminade, A.-M.; Majoral, J.-P. *Angew. Chem., Int. Ed.* **2001**, *40*, 224–227; (e) Bouguessa, S.; Hervé, K.; Golhen, S.; Ouahab, L.; Fabre, J.-M. *New J. Chem.* **2003**, *27*, 560–564; (f) Lyskawa, J.; Sallé, M.; Balandier, J.-Y.; Le Derf, F.; Levillain, E.; Allain, M.; Viel, P.; Palacin, S. *Chem. Commun.* **2006**, 2233–2235; (g) Frei, M.; Diederich, F.; Tremont, R.; Rodríguez, T.; Echegoyen, L. *Helv. Chim. Acta* **2006**, *89*, 2040–2057.
27. The splitting of the second oxidation wave has been also observed for TTF-containing cyclophanes only when the TTF moieties were forced to stay in close proximity to each other: (a) Takimiya, K.; Imamura, K.; Shibata, Y.; Aso, Y.; Ogura, F.; Otsubo, T. *J. Org. Chem.* **1997**, *62*, 5567–5574; (b) See Ref. 25c.
28. For examples of TCNQ and TNF complexes with TTFs in solid state, see: (a) Moore, A. J.; Bryce, M. R.; Batsanov, A. S.; Heaton, J. N.; Lehmann, C. W.; Howard, J. A. K.; Robertson, N.; Underhill, A. E.; Perepichka, I. F. *J. Mater. Chem.* **1998**, *8*, 1541–1550; (b) Batsanov, A. S.; Bryce, M. R.; Chesney, A.; Howard, J. A. K.; John, D. E.; Moore, A. J.; Wood, C. L.; Gershtenman, H.; Becker, J. Y.; Khodorkovsky, V. Y.; Ellern, A.; Bernstein, J.; Perepichka, I. F.; Rotello, V.; Gray, M.; Cuello, A. O. *J. Mater. Chem.* **2001**, *11*, 2181–2191.
29. See Supplemetary data for details of the binding studies.
30. Saito, G.; Ferraris, J. P. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2141–2145.
31. (a) Jeppesen, J. O.; Takimiya, K.; Jensen, F.; Brimert, T.; Nielsen, K.; Thorup, N.; Becher, J. *J. Org. Chem.* **2000**, *65*, 5794–5805; (b) Jeppesen, J. O.; Becher, J. *Eur. J. Org. Chem.* **2003**, 3245–3266.
32. Nielsen, M. B.; Jeppesen, J. O.; Lau, J.; Lomholt, C.; Damgaard, D.; Jacobsen, J. P.; Becher, J.; Stoddart, J. F. *J. Org. Chem.* **2001**, *66*, 3559–3563.
33. (a) Sheldrick, G. M. *SHELXS97: Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997; (b) Sheldrick, G. M. *SHELXL97: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.