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A competitive sensing system based on cyclobis(paraquat-*p*-phenylene) and a new β-cyclodextrin-tetrathiafulvalene derivative

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We report the synthesis of 4,5-di(ethylthio)-4′-[6-deoxy-β-cyclodextrin-6-yl-aminocarbonyl]-tetrathiafulvalene (β-CD-DET-TTF) and its inclusion abilities towards cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) and 1-naphthol. The structure of the synthesised compound has been established by mass spectrometry and ^1H NMR spectra combined with a theoretical MM3 and AM1 study. The sensor affords a charge transfer (CT) complex with the $CBPQT^{4+}$ and is able to include 1-naphthol in the cyclodextrin cavity. The complexes were characterised experimentally by UV–vis spectroscopy and simulated by a MM3 docking procedure. The sensing ability of the β-CD-DET-TTF/$CBPQT^{4+}$ complex towards 1-naphthol has been investigated by a competitive spectral method.

Keywords: β-cyclodextrin; tetrathiafulvalene; cyclobis(paraquat-*p*-phenylene); charge transfer complex; inclusion

Introduction

The detection of chemical and biological compounds has been increasingly studied in order to develop analysis systems, without any modification of the analytes (*1–5*). Within this scope, the non-covalent capture of the products may be useful, and in this field, chemically modified cyclodextrins (CDs) have proven their ability to include a large variety of organic compounds (*6*, *7*). Thus, such derivatives might lead to molecule-sensing systems (*8–13*). In particular, we have developed a new class of fluorescent sensors towards volatile organic compounds, by coupling a β-cyclodextrin fragment (β-CD) with indolizine units (*14–19*). On the other hand, the sensing of anions or metallic cations may be realised by means of electrochemical sensors based on tetrathiafulvalene (TTF) and various receptors such as crown ethers, calixarenes or calyxpyrroles (*20–25*). The interaction and the coupling between CD and TTF derivatives have been described in some works (*26–30*). In a recent paper, we described the synthesis of 4,5-ethylenedithio-4′-[6-deoxy-β-cyclodextrin-6-yl-aminocarbonyl]-tetrathiafulvalene together with its sensing ability towards 1-adamantanol (*31*). Moreover, the TTF oxidation state may be further used to modulate host–guest interactions with cyclophane. We report herein the synthesis and characterisation of a new water soluble sensor consisting of a charge transfer (CT) complex between 4,5-di(ethylthio)-4′-[6-deoxy-β-cyclodextrin-6-yl-aminocarbonyl]-tetrathiafulvalene (β-CD-DET-TTF) and the tetrachloride salt of cyclobis(paraquat-*p*-phenylene) ring ($CBPQT^{4+}$).

Results and discussion

Synthesis

In order to increase the solubility of the TTF derivative, we decided to substitute the ethylenedithio ring of the previously described electroactive β-CD (*31*) with two thioethyl substituents. The product was obtained upon reaction of the 6-deoxy-6-amino-β-cyclodextrin **1** with a TTF chlorocarbonyl compound. Accordingly, the corresponding DET-TTF-COCl intermediate has been synthesised upon monodecarboxylation of the diester precursor **2′**, prepared according to literature (*32*), followed by treatment of the carboxylic acid **2″** with oxalyl chloride (Scheme 1). The structure of the acid **2″** was confirmed by a single-crystal X-ray study.

The compound crystallises in the triclinic system, space group *P*-1, with one independent molecule in the unit cell. The formation of centrosymmetric dyads through a pair of intermolecular O1···O2 hydrogen bonds, leading to the establishment of the classical $R_2^2(8)$ motif (*33*), is observed (Figure 1). Then, the corresponding acid chloride **2**, conventionally prepared upon the reaction of **2″** with oxalyl chloride, has been reacted with 6-deoxy-6-amino-β-cyclodextrin **1** (*34*) in dry dimethylformamide (DMF), under argon, thus affording the mixed β-CD-DET-TTF derivative **3** (Scheme 2).

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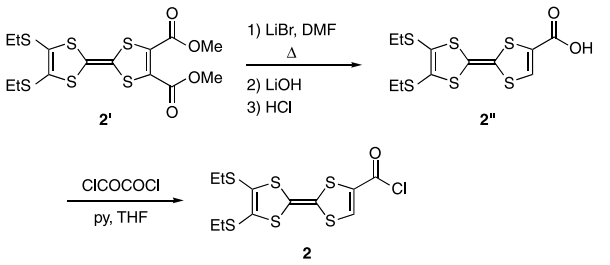


Scheme 1. Synthesis of 4,5-diethylthio-4′-chlorocarbonyl-tetrathiafulvalene **2**.

Note that the reaction of TTF-acid chlorides with various primary amines has been described previously (*35*, *36*). The chemical structure of **3** has been established by NMR and mass spectra. The presence in the ^{1}H NMR spectrum of the typical pattern for the ethyl groups, along with the CD protons, undoubtedly proves the proposed structure. As noticed before, the small size of the covalent link between the TTF moiety and the CD unit very likely prevents the self-inclusion of the TTF framework in the cavity of CD.

We then investigated the inclusion properties of our redox-active CD **3** towards 1-naphthol alone or in the presence of $CBPQT^{4+}$, an electron acceptor compound able to promote CT with TTF (*37*). It is worth noting that within the β-CD-DET-TTF/$CBPQT^{4+}$/1-naphthol system, one can expect a competition in the inclusion of 1-naphthol into the CD cavity or the $CBPQT^{4+}$ ring, depending on the stability of the TTF/$CBPQT^{4+}$ CT complex.

Molecular modelling

The most stable conformer structures have been found by a multifunctional search on the level of all exocyclic single bonds, by means of AM1 and AM1- conductor like screening model (COSMO) semi-empirical quantum methods and MM3 molecular mechanic model in the Cache library (*38*). The most stable conformations of β-CD-DET-TTF **3**, $CBPQT^{4+}$ and 1-naphthol are shown in Figure 2.

The docking of 1-naphthol with respect to the locked β-CD unit (Figure 3) or unlocked $CBPQT^{4+}$ inner cavity has been performed using three dummy atoms, in such a way that the molecule of 1-naphthol crosses the rings while making a continuous rotation. Moreover, two regiochemical ways E1 and E2 have been considered.

The most stable conformations of the inclusion complexes $CBPQT^{4+}$/1-naphthol, β-CD-DET-TTF/1-naphthol, β-CD-DET-TTF/$CBPQT^{4+}$ and β-CD-DET-TTF/$CBPQT^{4+}$/1-naphthol, along with their computed complexation energies ΔE are shown in Figure 4. ΔE represents the difference between the potential energy of the inclusion complex and the sum of its individual components in the optimised ground state.

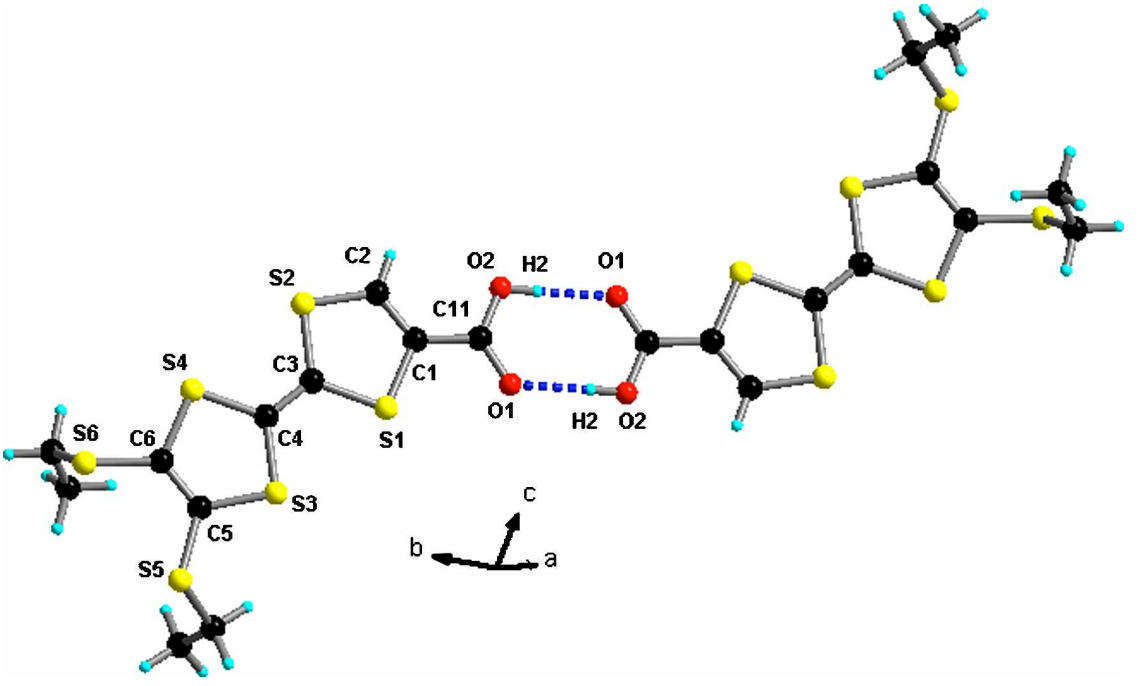
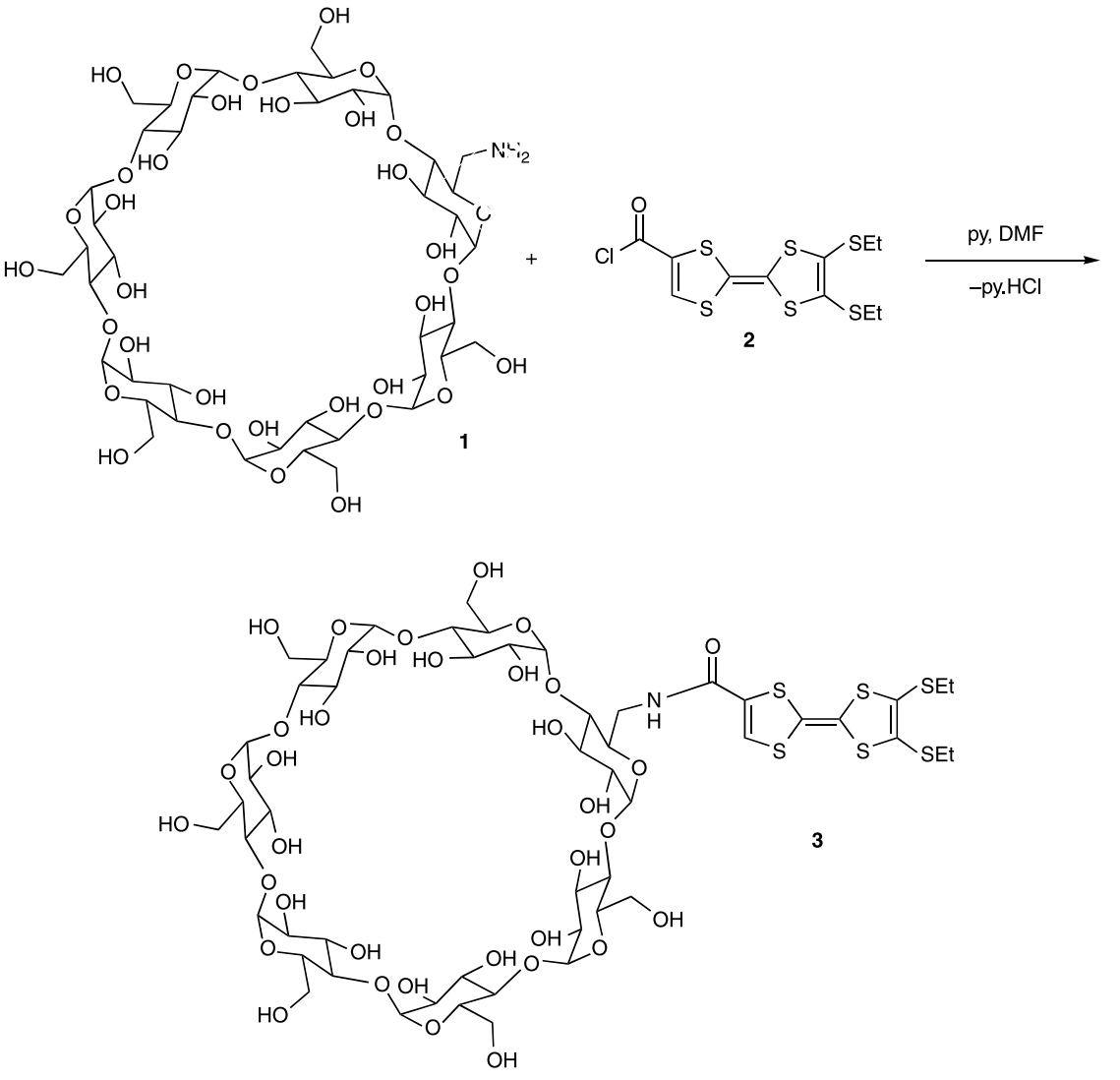


Figure 1. Centrosymmetric dyads in the crystal structure of **2″**. Selected distances (Å) and angles (°): C3—C4, 1.342(4); C11—O1, 1.237(4); C11—O2, 1.290(4); O1···O2 (−2 − *x*, 1 − *y*, 1 − *z*) 2.65 and O1—H2—O2, 175.9.



Scheme 2. Synthesis of 4,5-di(ethylthio)-4′-[6-deoxy-β-CD-cyclodextrin-6-y1-aminocarbonyl]-tetrathiafululene (β-CD-DET-TTF) **3**.

It is worth noting that, according to calculations, both β-CD and $CBPQT^{4+}$ form stable inclusion complexes with 1-naphthol, the $CBPQT^{4+}$/1-naphthol being more stable by about 6.4 kcal mol^{-1} than the β-CD-DET-TTF/1-naphthol.

The inclusion of β-CD-DET-TTF in $CBPQT^{4+}$ is also favoured (Figure 4), even more than the two previous complexes. When 1-naphthol is added to this β-CD-DET-TTF/$CBPQT^{4+}$ complex, its inclusion in the free cyclodextrin cavity may be envisaged, but the corre-

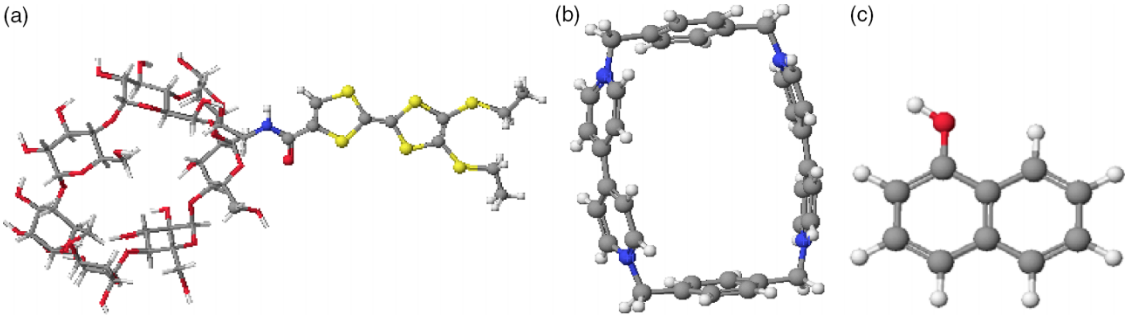


Figure 2. Optimised conformations of (a) β-CD-DET-TTF **3**, (b) $CBPQT^{4+}$ and (c) 1-naphthol.

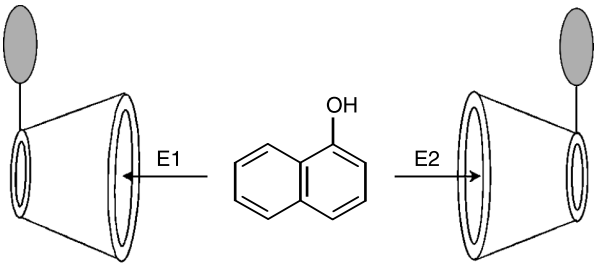


Figure 3. Docking and regiochemical ways for the inclusion of 1-naphthol into the CD cavity.

sponding complexation energy is really weaker than that in the absence of $CBPQT^{4+}$. Thus, one could think that 1-naphthol, if used in excess, will probably displace the TTF unit, rather than interacting with the cyclodextrin cavity.

Inclusion of 1-naphthol

The evaluation of the hosts' inclusion ability towards 1-naphthol has been done by UV–vis spectroscopy combined with the well-known direct titration method. For a molar ratio of 1:1, the calculation of the formation constant K_f was developed as follows:

$$\text{HOST} + \text{GUEST} \rightleftharpoons \text{HOST/GUEST}$$

$$K_f = \frac{[\text{HOST/GUEST}]}{[\text{HOST}]^*[\text{GUEST}]} \quad (1)$$

obtained for β-CD-DET-TTF/1-naphthol ($107\,M^{-1}$), as expected in the molecular modelling study. Thus, it also confirms that a competition between the two cavities for the inclusion of 1-naphthol would be in favour of $CBPQT^{4+}$.

We then investigated the formation of the CT complex β-CD-DET-TTF/$CBPQT^{4+}$ **5** upon adding increasing amounts of $CBPQT^{4+}$ in a 0.1 mM aqueous solution of β-CD-DET-TTF (Figure 6).

It is obvious from the titration curve that the maximum in absorbance at $\lambda_{max} = 770$ nm is reached for a 1:1 ratio of β-CD-DET-TTF/$CBPQT^{4+}$, in accordance with the formation of an inclusion complex. No further evolution is observed upon adding additional $CBPQT^{4+}$ salt. The experimental formation constant of the CT complex reaches a value of $K_f = 27{,}889\,M^{-1}$. The stronger affinity of this complex, when compared with naphthol inclusion compounds, was also suggested by our theoretical calculations.

Furthermore, in a competition experiment, a solution of 0.5 mM 1-naphthol was added to the CT complex β-CD-DET-TTF/$CBPQT^{4+}$ **5** (formed from 0.1 mM solutions of each component in water). While a resulting concentration of 1-napthol equal to 0.1 mM leads to few variations, the absorption spectrum (Figure 7) obtained for 0.5 mM 1-naphthol, shows a dramatic decrease in the CT band at $\lambda_{max} = 770$ nm.

The shoulder at $\lambda = 490$ nm in the competition curve is also indicative of the formation of the inclusion complex $CBPQT^{4+}$/1-naphthol. It demonstrates that 1-naphthol very likely displaces the initial CT complex

$$K_f = \frac{[\text{HOST/GUEST}]}{([\text{GUEST}]_T - [\text{HOST/GUEST}]) - ([\text{HOST}]_T - [\text{HOST/GUEST}])} \quad (2)$$

$$[\text{HOST/GUEST}] = -\frac{1}{2}\sqrt{\left[\left(\frac{1}{K_f} + [\text{HOST}]_T + [\text{GUEST}]_T\right)^2 - 4[\text{HOST}]_T[\text{GUEST}]_T\right]} + \frac{1}{2}\left(\frac{1}{K_f} + [\text{HOST}]_T + [\text{GUEST}]_T\right), \quad (3)$$

where K_f and T represent the formation constant and total, respectively. For a given value of K_f, the [HOST/GUEST] concentration is known, thus allowing the calculation of the molecular absorptivity of the inclusion compound. An algorithmic treatment was then applied to minimise the difference of the spectral characteristics over the various solutions.

The absorbance of the host was recorded as a function of different concentrations of the added guest. In the first series of experiments, our aim was to emphasise the formation of a CT complex between $CBPQT^{4+}$ and 1-naphthol in water solution (Figure 5). The λ_{max} for the CT complex is 490 nm and the obtained stability constant is $K_f = 8029\,M^{-1}$. This formation constant is significantly higher than that

to form a new one through inclusion into the $CBPQT^{4+}$ unit, rather than affording an inclusion into the CD cavity. This hypothesis is in agreement with the relative stabilities of the corresponding inclusion complexes (*vide supra*).

Conclusions

The synthesis and characterisation of a new water soluble β-CD-DET-TTF derivative has been reported. The formation of a CT complex with the $CBPQT^{4+}$ acceptor, as an inclusion compound, has been evidenced by UV–vis spectroscopy. The relative energies of the most stable conformers of inclusion complexes between the modified CD, $CBPQT^{4+}$ ring and 1-naphthol have been evaluated

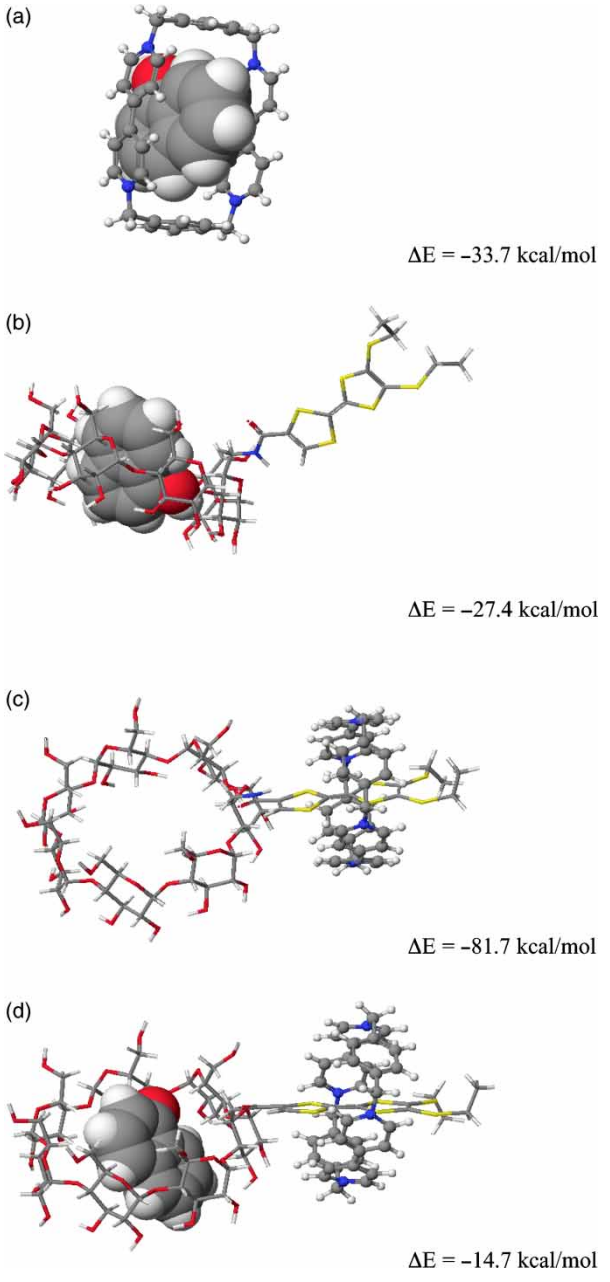


Figure 4. Optimised conformations of (a) CBPQT^{4+}/1-naphthol, (b) β-CD-DET-TTF/1-naphthol, (c) β-CD-DET-TTF/CBPQT^{4+} and (d) β-CD-DET-TTF/CBPQT^{4+}/1-naphthol inclusion complexes along with the corresponding energies.

through theoretical calculations. The results indicate that the inclusion of the 1-naphthol into the CBPQT^{4+} ring is favoured over that into the CD cavity. Accordingly, a competition experiment followed by UV–vis spectroscopy demonstrated the expulsion of TTF from the CBPQT^{4+} ring to allow the formation of the CT complex CBPQT^{4+}/1-naphthol. This result suggests that the water soluble CT complex β-CD-DET-TTF/CBPQT^{4+} could be used as an efficient sensor towards aromatic guests prone to give inclusion complexes with the CBPQT^{4+} ring.

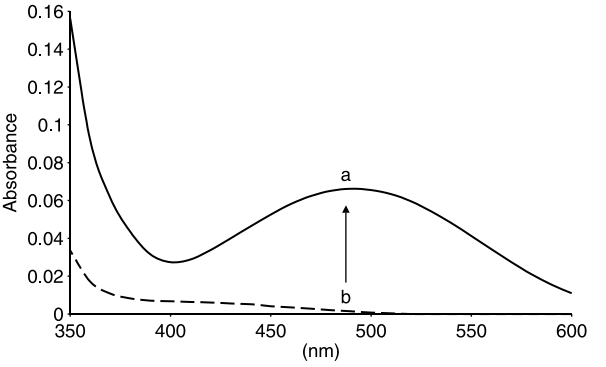


Figure 5. Absorbance of the charge transfer between CBPQT^{4+} (0.3 mM) and 1-naphthol (0.1 mM) in aqueous solution (a) in comparison with CBPQT^{4+} (0.3 mM) alone (b).

Experimental section

^{1}H NMR spectra were recorded using a Bruker AM 400 spectrometer with tetramethylsilane as the internal standard. Chemical shift values δ are reported in ppm

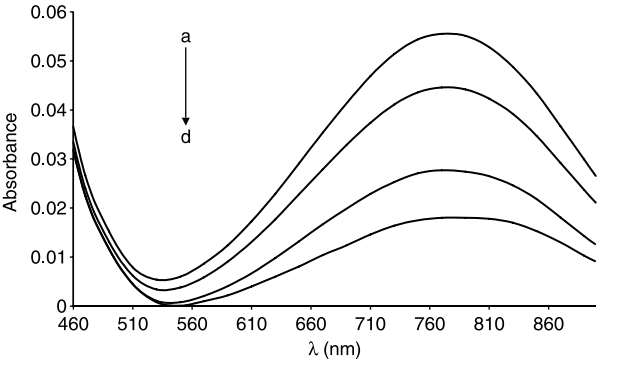


Figure 6. Variation of the charge transfer absorbance in aqueous solution between 0.1 mM β-CD-DET-TTF and CBPQT^{4+} at various concentrations: (a) 0.1 mM, (b) 0.05 mM, (c) 0.025 mM and (d) 0.0175 mM.

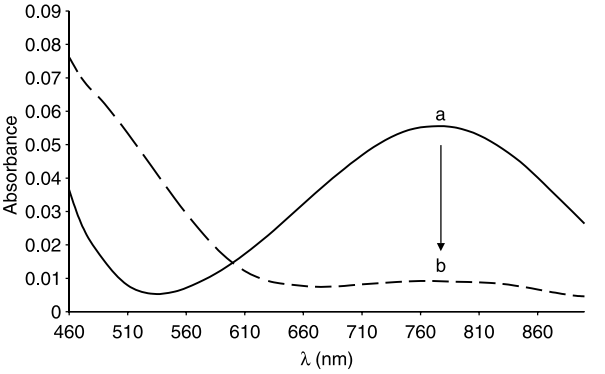


Figure 7. Absorbance of the β-CD-DET-TTF/CBPQT^{4+} (0.1 mM) charge transfer alone (a) in the presence of 1-naphthol (0.5 mM) (b).

and coupling constants J are in Hertz. The following abbreviations have been used: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and C (cyclodextrin). Mass spectra were measured using a Platform II Micromass Apparatus. IR spectra were recorded on a Perkin Elmer instrument. Chromatographic separation was carried out on Sephadex G15.

Syntheses

4,5-Di(ethylthio)-4′-hydroxycarbonyl-tetrathiafulvalene ***2″***

4,5-Di(ethylthio)-4′,5′-di(methoxycarbonyl)-tetrathiafulvalene **2′** (5.1 g, 11.6 mmol) and LiBr (18.16 g, 0.21 mol) were stirred in DMF (200 ml) under uniform heating (85°C). After 3 h (reaction monitored by TLC), brine (100 ml) was added. The mixture was extracted three times with ethylacetate, the organic phase washed three times with brine, dried over $MgSO_4$ and concentrated under vacuum. The red oil was filtered on silica gel (eluent CH_2Cl_2), and then concentrated under vacuum to yield about 4 g (91% yield) of an orange oil, representing the intermediate monoester compound. This oil was dispersed in 1,4-dioxane (200 ml), and a solution of $LiOH.H_2O$ (2.1 g, 50 mmol) in water (25 ml) was added under stirring. After stirring for 15 h, 5 M HCl (10.5 ml, 52.5 mmol) was added and the solution was stirred for 15 min. Diethyl ether (150 ml) and water (60 ml) were added followed by 5 M HCl until the pH of the aqueous phase reached 1.5–2. The mixture was decanted, the aqueous phase washed three times with diethyl ether, the organic phases mixed and dried over $MgSO_4$, and finally evaporated under vacuum to afford the acid **2″** as a violet powder. Yield 3.4 g (90%). Suitable crystals for X-ray diffraction were grown by slow evaporation of an acetone solution of **2″**. ^{1}H NMR (DMSO-d_6): $\delta = 7.69$ (s, 1H, CH), 2.83 (q, 4H, CH2, $J = 7.45$ Hz), 1.31 (t, 6H, CH3, $J = 7.45$ Hz). Anal. calcd for $C_{11}H_{12}O_2S_6$: C, 35.84; H, 3.28. Found: C, 35.72; H, 3.18.

4,5-Di(ethylthio)-4′-chlorocarbonyl-tetrathiafulvalene ***2***

To a solution of **2″** (2.0 g, 5.42 mmol) in tetrahydrofuran (THF) (150 ml) and pyridine (6 μl), oxalyl chloride (1.5 ml, 17.1 mmol) was added dropwise. The mixture was heated (45°C) under stirring for 2 h, and then evaporated to dryness. Washing with a small volume of pentane (10 ml) and drying under vacuum afforded compound **2** as a violet powder. Yield 1.8 g (86%). ^{1}H NMR ($CDCl_3$): $\delta = 7.80$ (s, 1H, CH), 2.91 (q, 4H, CH2, $J = 7.40$ Hz), 1.35 (t, 6H, CH3, $J = 7.40$ Hz). Anal. calcd for $C_{11}H_{11}ClOS_6$: C, 34.13; H, 2.86. Found: C, 34.35; H, 2.75.

4,5-Di(ethylthio)-4′-[6-deoxy-β-cyclodextrin-6-yl-aminocarbonyl]-tetrathiafulvalene ***3***

In a 100 ml round-bottomed flask, 0.567 g (0.5 mmol) 6-deoxy-6-aminocyclodextrin **1** was dissolved in dry DMF (40 ml). Then, 0.193 g (0.5 mmol) solid 4,5-(diethylthio)-4′-chlorocarbonyl-tetrathiafulvalene **2** was gradually added under stirring. To the stirred reaction mixture pyridine (0.08 ml) in DMF (5 ml) were added over a period of 15 min. Stirring under argon and warming (65°C) of the reaction mixture were continued for 12 h. After cooling, the mixture was poured dropwise into acetone (100 ml). The resulting precipitate was collected and washed with acetone. The crude solid was dissolved in distilled water (50 ml), filtered, and then concentrated to provide 10 ml of solution which was purified on a Sephadex G-15 column to give compound **3** as a yellow orange powder. Yield 52%. IR (KBr, cm^{-1}): 3392, 1636 (νC═O), 1387, 1154, 1027. ^{1}H NMR (DMSO-d_6): δ 7.97 (m, 1H, NH), 6.81 (s, 1H, ═CH), 5.91–5.75 (m, 14H, —OH—2C, —OH—3C), 4.90–4.75 (m, 7H, H—1C), 4.57–4.40 (m, 8H, —O—CH2C—, —OH—6C), 3.81–3.15 (m, 40H, H—2C, H—4C, H—3C, H—5C, H—6CA,B), 2.87 (q, 4H, CH2, $J = 7.20$ Hz), 1.23 (t, 6H, CH3, $J = 7.20$ Hz). MS (ES +, cone 40) m/z (%): 1506 (M + 23) (20%), 1157 (CD-6-yl-NH + 23) (80%), 1185 (CD-6-yl-NH-CO + 23) (100%). Anal. calcd for $C_{53}H_{81}NO_{35}S_6$, $3H_2O$: C, 41.37; H, 5.70; S, 12.50. Found: C, 41.29; H, 5.88; S, 12.32.

UV–vis spectroscopy

Spectra were recorded at 25°C using a Perkin Elmer Lambda 2S double beam spectrometer and a quartz cell with an optical path length of 1 cm. The control of temperature was realised by the use of a thermostated bath linked to the cell holder (accuracy, ±0.1°C). The compounds were dissolved in a phosphate buffer at pH 5.8. All spectra were used in the derivative form in order to avoid the influence of diffraction on the titration experiment.

Molecular modelling

Compound **3** and 1-naphthol were built starting from data provided by the Cambridge Structural Data Base Centre. The structural manipulations on β-CD were made using the Cache library on a PC Computer (*38*). The study of compound **3** was performed by applying a general procedure of multiconformational search with the MM3 force field (*39–41*). The potential energy variation (ΔE) depending on the variation of the dihedral angles (defined between the TTF and cyclodextrin moieties) is recorded with rotational increments of 15°.

X-ray crystallography

Data were collected on a Stoe Imaging Plate System, operating with a Mo Kα X-ray tube with a graphite monochromator. The structure was solved (SHELXS-97)

by direct methods and refined (SHELXL-97) by full-matrix least-square procedures on F^2 (*42*). Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations, but were not refined. All the heavy atoms have been refined anisotropically. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 648244 (CIF file). Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (email: deposit@ccdc.cam.ac.uk).

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