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► To cite this version:

Georgiana Surpateanu, Catalin N. Lungu, Sophie Fourmentin, David Landy, Gheorghe Surpateanu, et al. A competitive sensing system based on cyclobis(paraquat-p-phenylene) and a new β -cyclodextrin-tetrathiafulvalene derivative. *Supramolecular Chemistry*, 2009, 21 (05), pp.372-378. 10.1080/10610270802017673 . hal-00513529

HAL Id: hal-00513529

<https://hal.science/hal-00513529>

Submitted on 1 Sep 2010

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

Journal:	<i>Supramolecular Chemistry</i>
Manuscript ID:	GSCH-2007-0135.R1
Manuscript Type:	Full Paper
Date Submitted by the Author:	15-Feb-2008
Complete List of Authors:	surpateanu, Georgiana; ULCO, Laboratoire de Synthèse Organique et Environnement LUNGU, Catalin; ULCO, Laboratoire de Synthèse Organique et Environnement Fourmentin, Sophie; LSOE, MREI Landy, David; Université du Littoral Côte d'Opale, Laboratoire de Synthèse Organique et Environnement Surpateanu, Gheorghe; ULCO, Laboratoire de Synthèse Organique et Environnement avarvari, Narcis; Université d'Angers
Keywords:	β -cyclodextrin, Tetrathiafulvalene, cyclobis(paraquat-p-phenylene), Charge transfer complex, Inclusion



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3 **A competitive sensing system based on cyclobis(paraquat-*p*-phenylene) and a new**
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6 **β -cyclodextrin-tetrathiafulvalene derivative**
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34 We report the synthesis of 4,5-di(ethylthio)-4'-[6-deoxy- β -cyclodextrin-6-yl-
35 aminocarbonyl]-tetrathiafulvalene (β -CD-DET-TTF) and its inclusion abilities toward
36 cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺) and 1-naphthol. The structure of the
37 synthesized compound has been established by mass spectrometry and ¹H NMR spectra
38 combined with a theoretical MM3 and AM1 study. The sensor affords a charge transfer
39 (CT) complex with the CBPQT⁴⁺ and is able to include 1-naphthol in the cyclodextrin
40 cavity. The complexes were characterized experimentally by UV-VIS spectroscopy and
41 simulated by a MM3 docking procedure. The sensing ability of the β -CD-DET-
42 TTF/CBPQT⁴⁺ complex towards 1-naphthol has been investigated by a competitive
43 spectral method.
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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, and this 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) has proven their ability to include a large variety of organic compounds [6,7]. Thus, such derivatives might lead to molecule-sensing systems [8-13]. Especially, we have developed a new class of fluorescent sensors towards volatile organic compounds (VOC), 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 (β -CD-EDT-TTF) together with its sensing ability toward 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 characterization 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 (CBPQT⁴⁺).

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] by 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 synthesized upon monodecarboxylation of the diester precursor **2'**, prepared according to literature method [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.

Insert Scheme 1

The compound crystallizes 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 R22(8) motif [33], is observed (Figure 1). Then, the corresponding acid chloride **2**, conventionally prepared upon reaction of **2''** with oxalyl chloride, has been reacted with the 6-deoxy-6-amino- β -cyclodextrin **1** [34] in dry DMF, under argon, thus affording the mixed β -CD-DET-TTF derivative **3** (Scheme 2).

Insert Figure 1

Insert Scheme 2

Note that the reaction of TTF-acid chlorides with various primary amines has been previously described [35,36]. The chemical structure of **3** has been established by NMR and mass spectra. The presence in the ^1H 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.

Then we investigated the inclusion properties of our redox active CD **3** towards the 1-naphthol alone or in the presence of the CBPQT^{4+} , an electron acceptor compound able to promote CT with the TTF [37]. It is worth noting that within the system $\beta\text{-CD-DET-TTF/CBPQT}^{4+}/1\text{-naphthol}$ one can expect a competition between the inclusion of the 1-naphthol in the CD cavity or in 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-COSMO semiempirical quantum methods and MM3 molecular mechanic model in Cache library [38]. The most stable conformations of $\beta\text{-CD-DET-TTF}$ **3**, CBPQT^{4+} and 1-naphthol are shown in figure 2.

Insert Figure 2

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3 The docking of 1-naphthol with respect to the locked β -CD unit (Figure 3) or
4
5 unlocked CBPQT⁴⁺ inner cavity has been performed using three dummy atoms, in such
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7 a way that the molecule of 1-naphthol crosses the rings while making a continuous
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9 rotation. Moreover, two regiochemical ways E1 and E2 have been considered.
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15 **Insert Figure 3**
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20 The most stable conformations of the inclusion complexes CBPQT⁴⁺/1-naphthol,
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22 β -CD-DET-TTF/1-naphthol, β -CD-DET-TTF/CBPQT⁴⁺ and β -CD-DET-
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24 TTF/CBPQT⁴⁺/1-naphthol, along with their computed complexation energies ΔE are
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26 shown in figure 4. ΔE represents the difference between the potential energy on the
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28 inclusion complex and the sum of their individual components in the optimized ground
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30 state.
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36 **Insert Figure 4**
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44 It is worth noting that, according to the calculations, both β -CD and CBPQT⁴⁺
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46 form stable inclusion complexes with the 1-naphthol, the CBPQT⁴⁺/1-naphthol one
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48 being more stable by about 6.4 kcal mol⁻¹ than the β -CD-DET-TTF/1-naphthol.
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51 The inclusion of β -CD-DET-TTF in CBPQT⁴⁺ is also favoured (figure 4), even
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53 more than the two previous complexes. When 1-naphthol is added to this β -CD-DET-
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55 TTF/CBPQT⁴⁺ complex, its inclusion in the free cyclodextrin cavity may be envisaged,
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57 but the corresponding complexation energy is really weaker than in absence of
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3 CBPQT⁴⁺. Thus, one could think that 1-naphthol, if used in excess, will probably
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6 displace the TTF unit, rather than interact with the cyclodextrin cavity.
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10 *Inclusion of 1-naphthol*

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15 The evaluation of the hosts' inclusion ability towards 1-naphthol has been carried out by
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17 UV-VIS spectroscopy combined with the well known direct titration method. For a 1:1
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19 molar ratio, the calculation of the formation constant K_f was developed as follows:
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$$26 \quad K_f = \frac{[\text{HOST/GUEST}]}{[\text{HOST}] * [\text{GUEST}]} \quad 27 \quad (1)$$

$$28 \quad K_f = \frac{[\text{HOST/GUEST}]}{([\text{GUEST}]_T - [\text{HOST/GUEST}]) - ([\text{HOST}]_T - [\text{HOST/GUEST}])} \quad 29 \quad (2)$$

$$30 \quad [\text{HOST/GUEST}] = -\frac{1}{2} \sqrt{\left[\left(\frac{1}{K_f} + [\text{HOST}]_T + [\text{GUEST}]_T \right)^2 - 4[\text{HOST}]_T [\text{GUEST}]_T \right]} \quad 31$$

$$32 \quad + \frac{1}{2} \left(\frac{1}{K_f} + [\text{HOST}]_T + [\text{GUEST}]_T \right) \quad 33 \quad (3)$$

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where K_f and T stand for formation constant and total respectively. For a given value of K_f the $[\text{HOST/GUEST}]$ concentration is known, thus allowing the calculation of the molecular absorptivity of the inclusion compound. An algorithmic treatment was then

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3 applied to minimize the difference of the spectral characteristics over the various
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5 solutions.
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8 The absorbance of the host was recorded in function of different concentrations
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10 of the added guest. In the first series of experiments, our aim was to emphasize the
11
12 formation of a CT complex between the CBPQT⁴⁺ and the 1-naphthol in water solution
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14 (Figure 5). The λ_{\max} for the CT complex is at 490 nm and the obtained stability constant
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16 is $K_f = 8029 \text{ M}^{-1}$. This formation constant is significantly higher than the one obtained
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18 for β -CD-DET-TTF/1-naphthol (107 M^{-1}), as expected in the molecular modelling
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20 study. Thus, it also confirms that a competition between the two cavities for the
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22 inclusion of 1-naphthol would be in favour of CBPQT⁴⁺.
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30 **Insert Figure 5**

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34 Then, we investigated the formation of the CT complex β -CD-DET-
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36 TTF/CBPQT⁴⁺ 5 upon adding increasing amounts of CBPQT⁴⁺ in a 0.1 mM aqueous
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38 solution of β -CD-DET-TTF (Figure 6).
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44 **Insert Figure 6**

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48 It is obvious from the titration curve that the maximum in absorbance at $\lambda_{\max} =$
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50 770 nm is reached for a 1:1 ratio β -CD-DET-TTF/CBPQT⁴⁺, in accordance with the
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52 formation of an inclusion complex. No further evolution is observed upon adding
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54 additional CBPQT⁴⁺ salt. The experimental formation constant of the CT complex
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56 reaches a value of $K_f = 27889 \text{ M}^{-1}$. The stronger affinity of this complex, if compared to
57
58 naphthol inclusion compounds, was also suggested by our theoretical calculations.
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3 Furthermore, in a competition experiment, a solution of 1-naphthol 0.5 mM was
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5 added to the CT complex β -CD-DET-TTF/CBPQT⁴⁺ **5** (formed from 0.1 mM solutions
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7 of each component in water). While a resulting concentration of 1-naphthol equal to 0.1
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9 mM leads to few variations, the absorption spectrum (Figure 7) obtained for 1-naphthol
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11 0.5 mM, shows a dramatic decrease in the CT band at $\lambda_{\text{max}} = 770$ nm.
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18 Insert Figure 7

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22 The shoulder at $\lambda = 490$ nm in the competition curve is also indicative of the
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24 formation of the inclusion complex CBPQT⁴⁺/1-naphthol. It demonstrates that the 1-
25
26 naphthol very likely displaces the initial CT complex to form a new one through
27
28 inclusion in the CBPQT⁴⁺ unit, rather than affording an inclusion into the CD cavity.
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30 This hypothesis is in agreement with the relative stabilities of the corresponding
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32 inclusion complexes (vide supra).
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39 CONCLUSIONS

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43 The synthesis and characterization of a new water soluble β -CD-DET-TTF derivative
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45 has been reported. The formation of a CT complex with the CBPQT⁴⁺ acceptor, as an
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47 inclusion compound, has been evidenced by UV-VIS spectroscopy. The relative
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49 energies of the most stable conformers of inclusion complexes between the modified
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51 CD, CBPQT⁴⁺ ring and 1-naphthol have been evaluated through theoretical calculations.
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53 The results indicate that the inclusion of the 1-naphthol into the CBPQT⁴⁺ ring is
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55 favoured over that into the CD cavity. Accordingly, a competition experiment followed
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57 by UV-VIS spectroscopy demonstrated the expulsion of the TTF from the CBPQT⁴⁺
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3 ring to allow the formation of the CT complex CBPQT⁴⁺/1-naphthol. This result
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5 suggests that the water soluble CT complex β -CD-DET-TTF/CBPQT⁴⁺ could be used as
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8 an efficient sensor towards aromatic guests prone to give inclusion complexes with the
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10 CBPQT⁴⁺ ring.
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12 13 14 15 Experimental section

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20 ¹H NMR spectra were recorded with a Bruker AM 400 spectrometer with
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22 tetramethylsilane (TMS) as internal standard. Chemical shift values δ are reported in
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24 ppm and coupling constants J are in Hertz. The following abbreviations have been used:
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26 s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), C (cyclodextrin). Mass
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28 spectra were measured using a Platform II Micromass Apparatus. IR spectra were
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30 recorded on a Perkin Elmer instrument. Chromatographic separation was carried out on
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32 Sephadex G15.
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39 Syntheses

40 41 42 43 **4,5-di(ethylthio)-4'-hydroxycarbonyl-tetrathiafulvalene 2''**

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45 4,5-di(ethylthio)-4',5'-di(methoxycarbonyl)-tetrathiafulvalene **2'** (5.1 g, 11.6 mmol)
46
47 and LiBr (18.16 g, 0.21 mol) were stirred in DMF (200 ml) under smooth heating (85
48
49 °C). After three hours (reaction monitored by TLC), brine (100 ml) was added. The
50
51 mixture was extracted 3 times with ethylacetate, the organic phase washed 3 times with
52
53 brine, dried over MgSO₄ and concentrated under vacuum. The red oil was filtered on
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55 silica gel (eluent CH₂Cl₂), and then concentrated under vacuum to yield about 4 g (91%
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60 yield) of an orange oil, representing the intermediate monoester compound. This oil was

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3 dispersed in 1,4-dioxane (200 ml), and a solution of LiOH.H₂O (2.1 g, 50 mmol) in
4 water (25 ml) was added under stirring. After stirring for 15 hours, HCl 5 M (10.5 ml,
5 52.5 mmol) was added and the solution stirred for 15 minutes. Diethylether (150 ml)
6 and water (60 ml) were added followed by HCl 5M until the pH of the aqueous phase
7 reached 1.5-2. The mixture was decanted, the aqueous phase washed 3 times with
8 diethylether, the organic phases mixed, dried over MgSO₄, and finally evaporated under
9 vacuum to afford the acid **2''** as a violet powder. Yield 3.4 g (90 %). Suitable crystals
10 for X-Ray diffraction were grown by slow evaporation of an acetone solution of **2''**. ¹H
11 NMR (DMSO-d₆): δ = 7.69 (s, 1H, CH), 2.83 (q, 4H, CH₂, J = 7.45 Hz), 1.31 (t, 6H,
12 CH₃, J = 7.45 Hz). Anal. calcd. for C₁₁H₁₂O₂S₆: C, 35.84; H, 3.28. Found: C, 35.72; H,
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32 **4,5-di(ethylthio)-4'-chlorocarbonyl-tetrathiafulvalene 2**

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34 To a solution of **2''** (2.0 g, 5.42 mmol) in THF (150 ml) and pyridine (6 μl), oxalyl
35 chloride (1.5 ml, 17.1 mmol) was added drop wise. The mixture was heated (45 °C)
36 under stirring for two hours, and then evaporated to dryness. Washing with a small
37 volume of pentane (10 ml) and drying under vacuum afforded the compound **2** as a
38 violet powder. Yield 1.8 g (86 %). ¹H NMR (CDCl₃): δ = 7.80 (s, 1H, CH), 2.91 (q,
39 4H, CH₂, J = 7.40 Hz), 1.35 (t, 6H, CH₃, J = 7.40 Hz). Anal. calcd. for C₁₁H₁₁ClOS₆: C,
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34.13; H, 2.86. Found: C, 34.35; H, 2.75.

53 **4,5-di(ethylthio)-4'-[6-deoxy-β-cyclodextrin-6-yl-aminocarbonyl]-** 54 55 56 **tetrathiafulvalene 3**

57
58 In a 100 ml round-bottomed flask 0.567 g (0.5 mmol) 6-deoxy-6-aminocyclodextrin **1**
59 was dissolved in dry DMF (40 ml). Then, 0.193 g (0.5 mmol) solid 4,5-(diethylthio)-4'-
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3 chlorocarbonyl-tetrathiafulvalene **2** was gradually added under stirring. To the stirred
4
5 reaction mixture pyridine (0.08 ml) in DMF (5 ml) was added over a period of 15
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7 minutes. Stirring under argon and warming (65 °C) of the reaction mixture were
8
9 continued for 12 hours. After cooling the mixture was poured drop wise into acetone
10
11 (100 ml). The resulting precipitate was collected and washed with acetone. The crude
12
13 solid was dissolved in distilled water (50 ml), filtered, and then concentrated to provide
14
15 10 ml of solution which was purified on a Sephadex G-15 column to give the compound
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17 **3** as a yellow orange powder. Yield 52%. IR (KBr, cm⁻¹): 3392, 1636 (νC=O), 1387,
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19 1154, 1027. ¹H NMR (DMSO-d₆): δ 7.97 (m, 1H, NH), 6.81 (s, 1H, =CH), 5.91–5.75
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21 (m, 14 H, –OH-2C, –OH-3C), 4.90–4.75 (m, 7H, H-1C), 4.57–4.40 (m, 8H, –O–
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23 CH₂C–, –OH-6C), 3.81–3.15 (m, 40H, H-2C, H-4C, H-3C, H-5C, H-6CA,B), 2.87
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25 (q, 4H, CH₂, J = 7.20 Hz), 1.23 (t, 6H, CH₃, J = 7.20 Hz). MS (ES⁺, cone 40) m/z (%):
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27 1506 (M + 23) (20%), 1157 (CD-6-yl-NH + 23) (80%), 1185 (CD-6-yl-NH-CO + 23)
28
29 (100%). Anal. calcd. for C₅₃H₈₁NO₃₅S₆, 3H₂O: C, 41.37; H, 5.70; S, 12.50. Found: C,
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31 41.29; H, 5.88; S, 12.32.
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41 *UV-VIS spectroscopy*

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46 Spectra were recorded at 25 °C using a Perkin Elmer Lambda 2S double beam
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48 spectrometer and a quartz cell with optical path length of 1 cm. The control of
49
50 temperature was realized by the use of a thermostated bath linked to the cell holder
51
52 (accuracy: ± 0.1 °C). The compounds were dissolved in phosphate buffer at pH 5.8. All
53
54 spectra were used in the derivative form in order to avoid the influence of diffraction on
55
56 the titration experiment.
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Molecular modelling

Compound **3** and 1-naphthol were built starting from data provided by the Cambridge Structural Data Base Center. The structural manipulations on β -CD were made using the CAChe library on 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 (IPDS), operating with a Mo-K α 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 F² [42]. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations but not refined. All the heavy atoms have been refined anisotropically. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center 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 (e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

Financial support from the CNRS, University of Angers and University of Dunkerque is gratefully acknowledged.

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3 Figure Captions
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8 Scheme 1: Synthesis of 4,5-diethylthio-4'-chlorocarbonyl-tetrathiafulvalene **2**.
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12 Figure 1: Centrosymmetric dyads in the crystal structure of **2**'. Selected distances (Å)
13 and angles (°): C3–C4 1.342(4), C11–O1 1.237(4), C11–O2 1.290(4), O1•••O2 (-2-x, 1-
14 y, 1-z) 2.65, O1–H2–O2 175.9.
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22 Scheme 2: Synthesis of 4,5-di(ethylthio)-4'-[6-deoxy-β-CD-cyclodextrin-6-yl-
23 aminocarbonyl]-tetrathiafulvalene (β-CD-DET-TTF) **3**.
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29 Figure 2: Docking and regiochemical ways for the inclusion of 1-naphthol into the CD
30 cavity.
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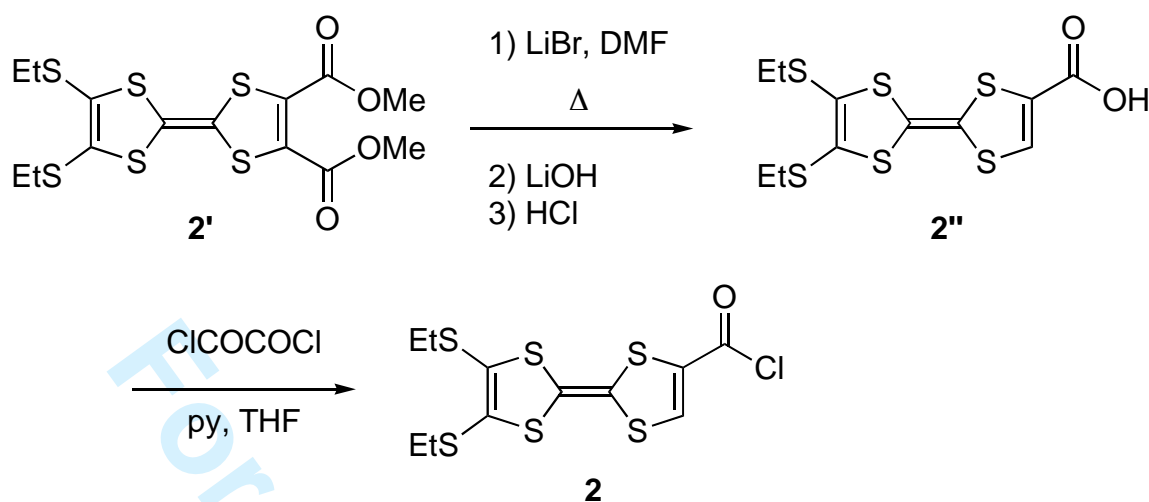
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36 Figure 3: Optimized conformations of β-CD-DET-TTF (a) **3**, CBPQT⁴⁺ (b) and 1-
37 naphthol (c).
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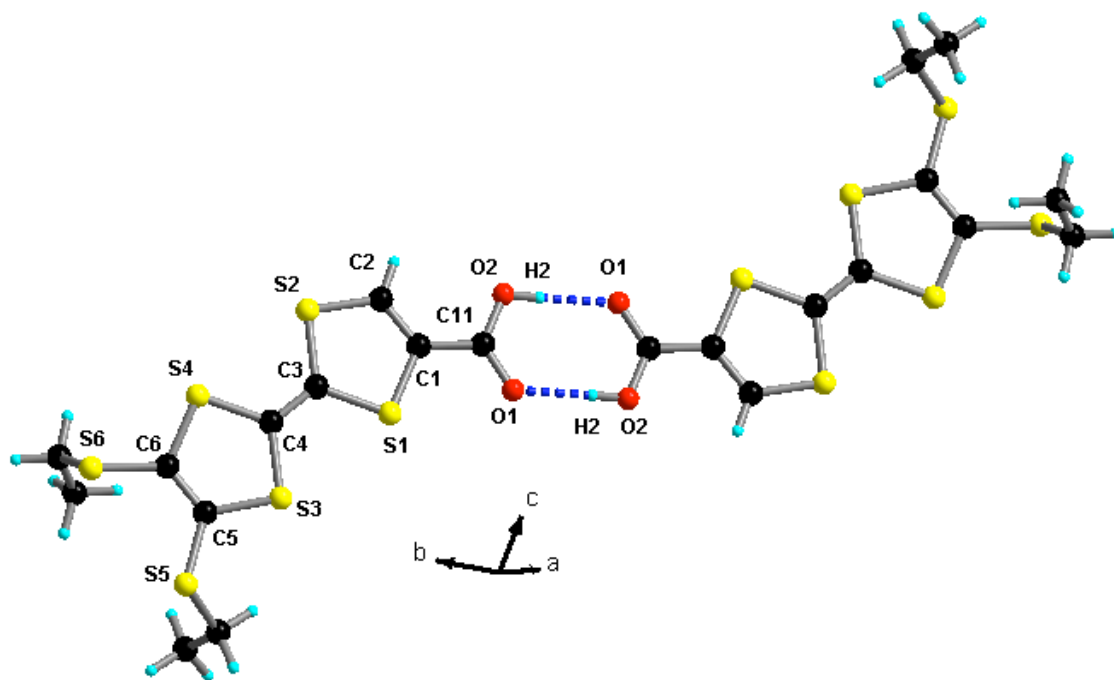
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43 Figure 4: Optimized conformations of CBPQT⁴⁺/1-naphthol (a), β-CD-DET-TTF/1-
44 naphthol (b), β-CD-DET-TTF/CBPQT⁴⁺ (c) and β-CD-DET-TTF/CBPQT⁴⁺/1-naphthol
45 (d) inclusion complexes along with the corresponding energies.
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53 Figure 5: Absorbance of the charge transfer between CBPQT⁴⁺ (0.3 mM) and 1-
54 naphthol (0.1 mM) in aqueous solution (a) in comparison with CBPQT⁴⁺ (0.3 mM)
55 alone (b).
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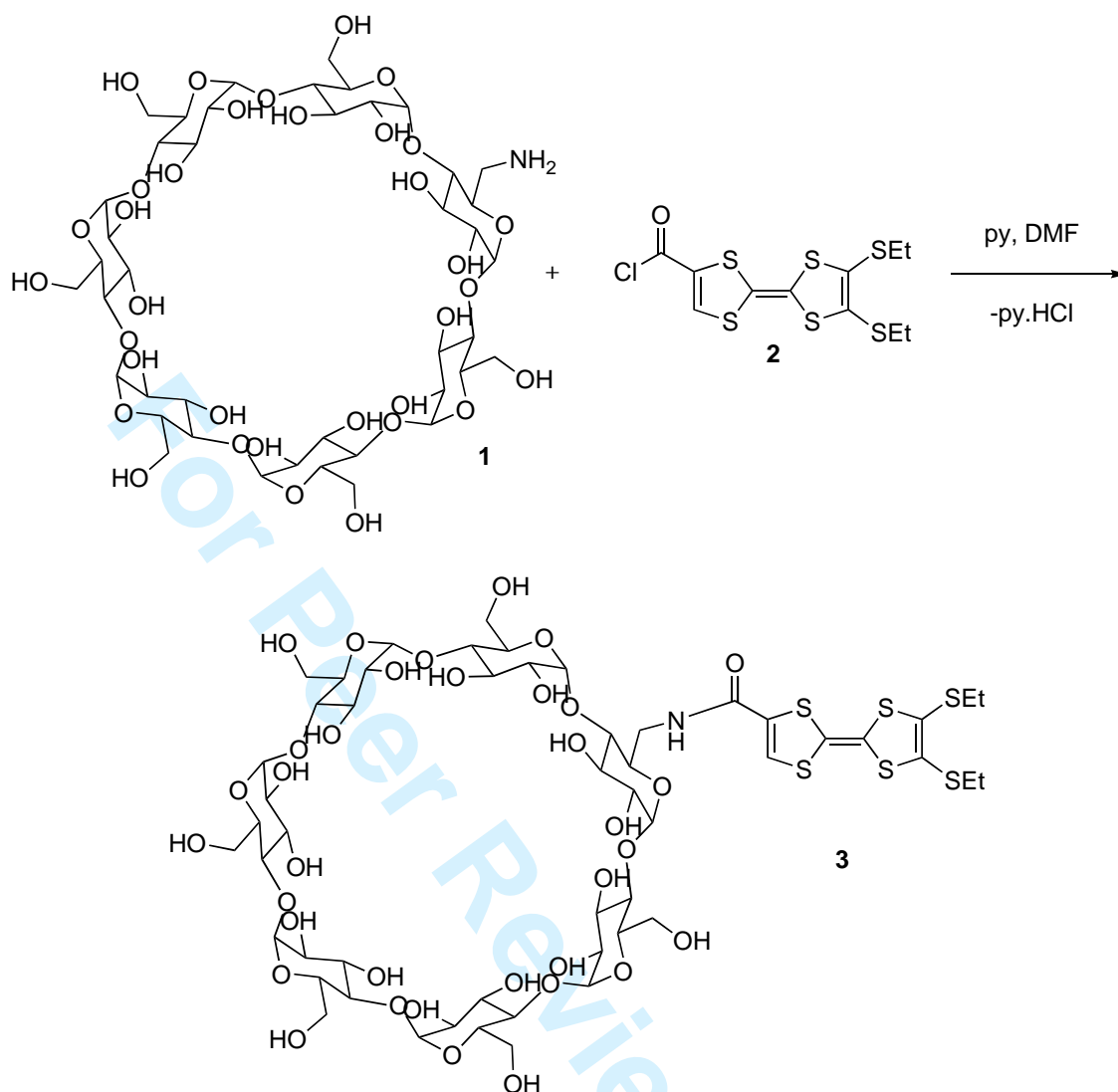
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3 Figure 6: Variation of the charge transfer absorbance in aqueous solution between β -
4 CD-DET-TTF 0.1 mM and CBPQT⁴⁺ at various concentrations: 0.1 mM (a), 0.05 mM
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8 (b), 0.025 mM (c) and 0.0175 mM (d).
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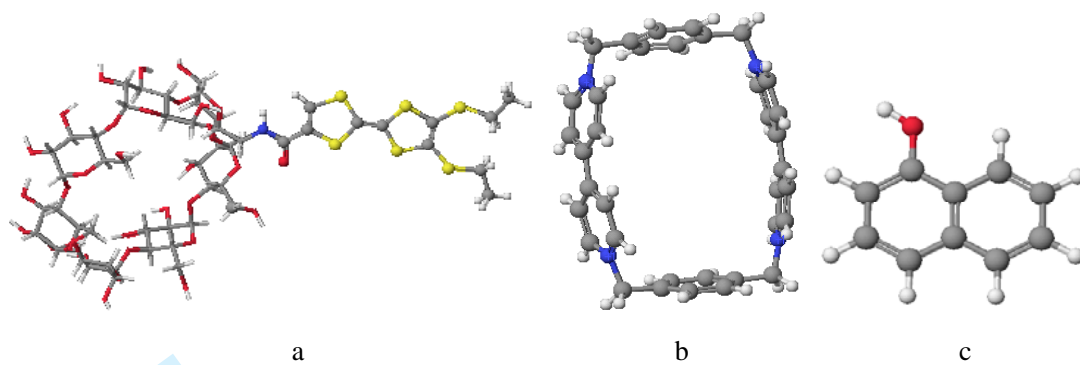
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12 Figure 7: Absorbance of the β -CD-DET-TTF /CBPQT⁴⁺ (0.1 mM) charge transfer alone
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14 (a) and in the presence of 1-naphthol (0.5 mM) (b).
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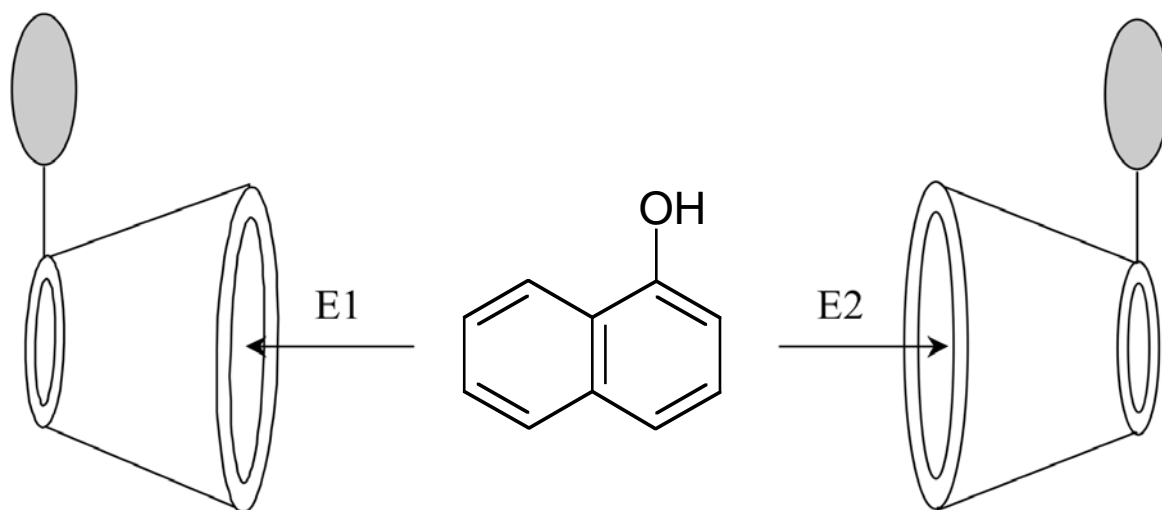


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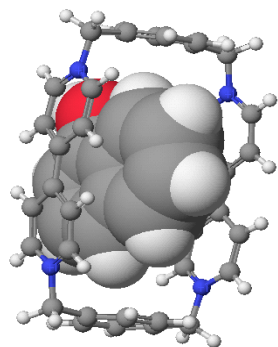




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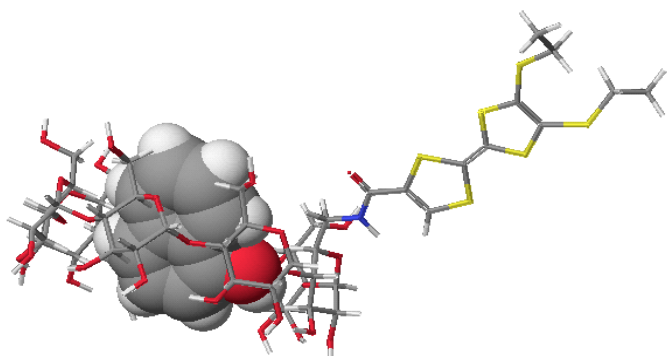


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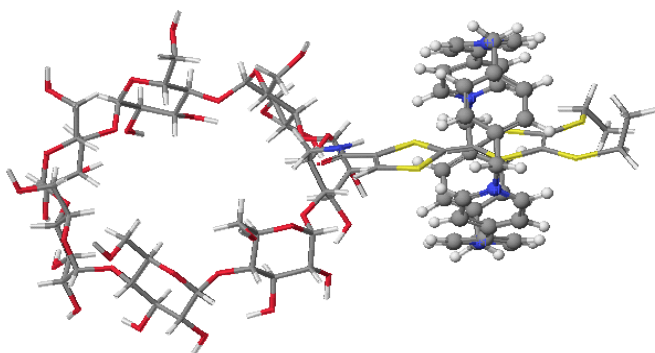
$\Delta E = -33.7$ kcal/mol

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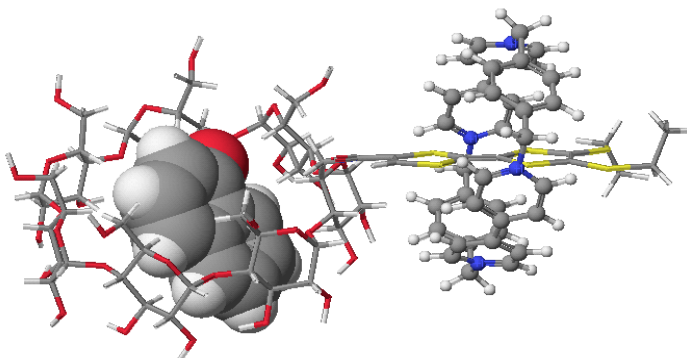
$\Delta E = -27.4$ kcal/mol

b



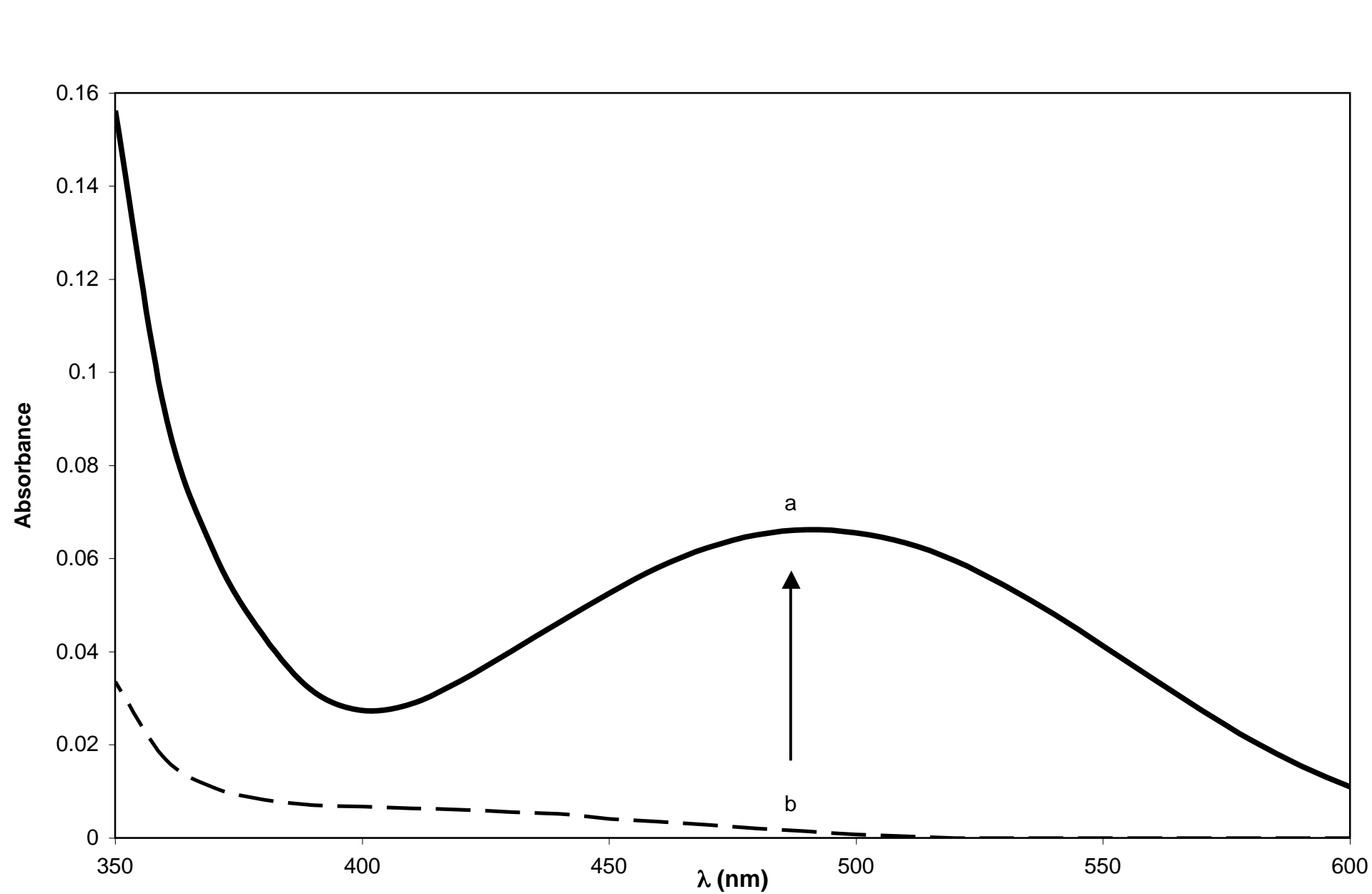
$\Delta E = -81.7$ kcal/mol

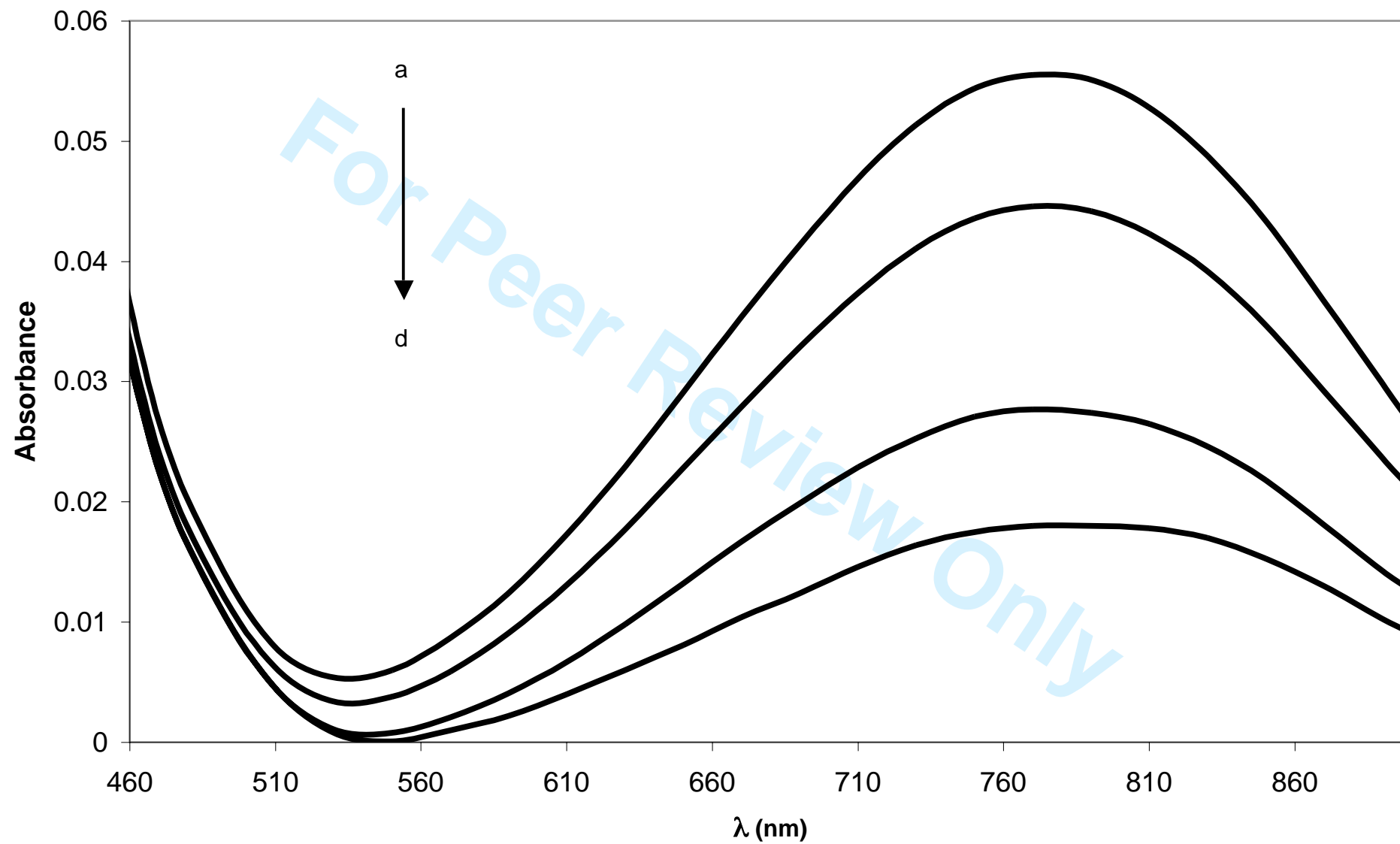
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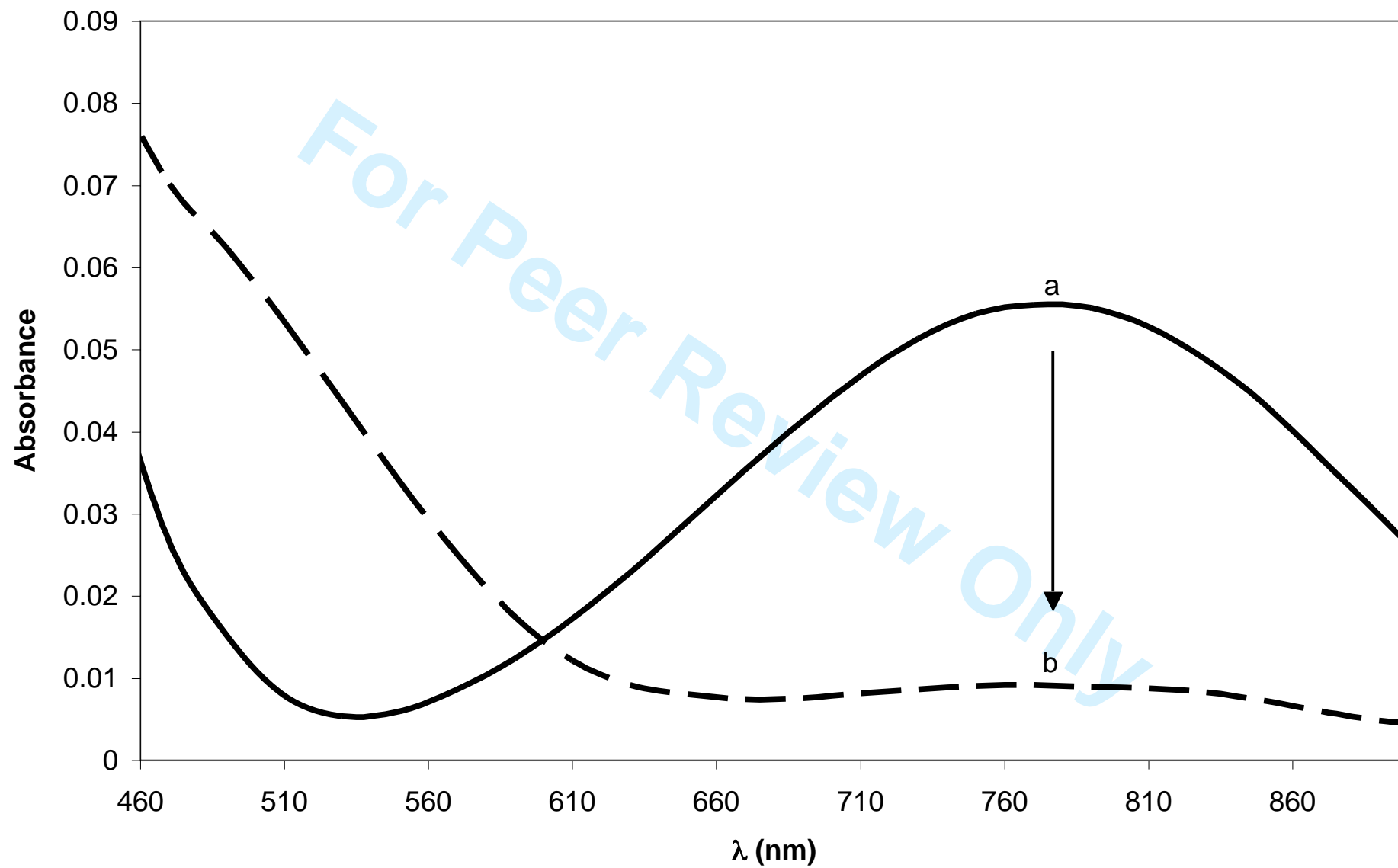


$\Delta E = -14.7$ kcal/mol

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

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14 The synthesis and characterization of a new water soluble β -CD-DET-TTF derivative able to formed a charge
15 transfer complex with the cyclobis(paraquat-*p*-phenylene) acceptor is reported. The water soluble CT complex β -
16 CD-DET-TTF/CBPQT⁴⁺ could be used as an efficient sensor towards aromatic guests prone to give inclusion
17 complexes with the CBPQT⁴⁺ ring.
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