Dyes and Pigments 92 (2011) 668–673

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

# Anion complexation by calix[4]arene–TTF conjugates

Karolína Flídrová [a], Marcela Tkadlecová [b], Kamil Lang [c], Pavel Lhoták [a,*]

[a] Department of Organic Chemistry, Prague Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic
[b] Department of Physical Chemistry, Prague Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic
[c] Institute of Inorganic Chemistry of the Academy of Sciences of the Czech Republic, v.v.i., 250 68 Řež, Czech Republic

ARTICLE INFO

*Article history:*
Received 22 April 2011
Received in revised form
27 May 2011
Accepted 1 June 2011
Available online 12 June 2011

*Keywords:*
Calix[4]arene
Tetrathiafulvalene
Anion recognition
Receptor
NMR titration
UV/vis spectroscopy

ABSTRACT

Calix[4]arenes bearing tetrathiafulvalene (TTF) moieties appended to the upper rim *via* the amidic functions were synthesized and used for $^1$H NMR and UV/Vis complexation studies towards selected anions. It was found that the complexation affinity towards $H_2PO_4^-$ dramatically depends on the substitution pattern of the calixarene moiety. As a result, the proximally disubstituted derivative has a complexation constant by two orders of magnitude higher than the distally disubstituted analogue. The differences between proximal and distal receptors were also documented by their behaviour during the oxidation of the attached TTF units.

© 2011 Elsevier Ltd. All rights reserved.

## 1. Introduction

Calix[4]arenes [1] are frequently used in the design and construction of new artificial receptors. The tuneable shapes of the molecules due to four different basic conformations together with highly advanced and well established derivatization chemistry make these molecules ideal candidates for the applications as building blocks and molecular scaffolds in supramolecular chemistry.

The fundamental importance of anions in various biological systems is well recognized. Not surprisingly, the anion recognition plays an important role in supramolecular chemistry as documented in many review articles and books published recently [2]. Albeit many approaches can be used, including the electrostatic interactions of anions with positively charged receptors, the neutral organic receptors offering hydrogen bonding interactions are especially useful in the design. The amidic groups or urea/thiourea moieties [2] can be efficiently applied for anion binding as these functional groups are capable of highly directional hydrogen bonding interactions. Correspondingly, their incorporation into calixarene/thiacalixarene skeletons can lead to highly preorganised structures [3] with interesting complexation abilities towards specific anion [4].

During our ongoing research into anion recognition [5] we have constructed many amide/urea-based receptors bearing *p*-nitrophenyl or porphyrins as chromophoric units. Their presence enables the sensing of anions *via* the changes of their spectroscopic properties. In this paper, we report the synthesis and complexation behaviour of novel anion receptors based on upper-rim substituted calix[4]arenes bearing the amidic function as a recognition unit and the TTF moiety [6] as a colour spectroscopic marker.

## 2. Experimental

Melting points are uncorrected and were determined using a Boetius Block apparatus (Carl Zeiss Jena, Germany). The NMR spectra were recorded at 300 MHz ($^1$H) and at 75 MHz ($^{13}$C). Elemental analyses were measured on Elementar vario EL (Elementar, Germany) instruments. The mass spectra were measured using the ESI technique on a Q-TOF (Micromass) spectrometer or the MALDI-TOF technique on an HP G2030A spectrometer (Hewlett Packard) with delayed extraction option. The IR spectra were measured on an FT-IR spectrometer Nicolet 740 in $CHCl_3$ and/or in KBr. The purity of the substances and the courses of reactions were monitored by TLC using TLC aluminum sheets with Silica gel 60 $F_{254}$ (Merck). The preparative TLC chromatography was carried out on 20 × 20 cm glass plates covered by Silica gel 60 $GF_{254}$ (Merck) or

* Corresponding author. Tel.: +420 220445055; fax: +420 220444288.
*E-mail address:* lhotakp@vscht.cz (P. Lhoták).

0143-7208/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2011.06.001

$Al_2O_3$ type G (Fluka). The column chromatography was performed using Silica gel 60 (Merck).

### 2.1. Nitration of 25,26,27,28-tetrapropoxycalix[4]arene – preparation of compounds **2a**–**2c**

25,26,27,28-tetrapropoxycalix[4]arene **1** (2.0 g, 3.37 mmol) was dissolved in 200 ml of dichloromethane and 5.73 g of sodium nitrate (67.47 mmol), 7.7 ml of glacial acetic acid (134.93 mmol), and 5.2 ml of trifluoroacetic acid (67.46 mmol) were added subsequently. The mixture was vigorously stirred at room temperature for 4.5 h and the reaction was monitored by TLC. The reaction mixture was quenched by water (300 ml), organic layer was separated, and water layer was extracted twice with dichloromethane. The combined organic layers were washed with saturated aqueous solution of $NaHCO_3$ (3 × 150 ml), water (2 × 150 ml), and were dried over $MgSO_4$. Solvent was evaporated *in vacuo* and a crude mixture was purified by column chromatography on silica gel ($CH_2Cl_2$:hexane 3:2). It was obtained 0.54 g (25%) of mononitro derivative **2a**, 0.49 g (21%) of distal dinitro derivative **2c**, and 0.45 g (19%) of proximal dinitro derivative **2b** in the form of yellowish powders.

#### 2.1.1. Compound **2a**

$^1$H NMR ($CDCl_3$, 300 MHz, 298 K): $\delta$ 7.10 (s, 2H, ArH), 6.95 (d, 2H, $J$ = 7.3 Hz, ArH), 6.92 (d, 2H, $J$ = 4.7 Hz, ArH), 6.83 (t, 2H, $J$ = 7.3 Hz, ArH), 6.21 (br s, 3H, ArH), 4.45 (d, 2H, $J$ = 13.8 Hz, $ArCH_2Ar$, ax.), 4.41 (d, 2H, $J$ = 13.8 Hz, $ArCH_2Ar$, ax.), 3.80–4.01 (m, 6H, $-OCH_2-$), 3.71 (t, 2H, $J$ = 7.0 Hz, $-OCH_2-$), 3.19 (d, 2H, $J$ = 13.5 Hz, $ArCH_2Ar$, eq.), 3.14 (d, 2H, $J$ = 11.7 Hz, $ArCH_2Ar$, eq.), 1.82–1.94 (m, 8H, $OCH_2CH_2-$), 0.80–0.95 (m, 12H, $-CH_3$).

#### 2.1.2. Compound **2b**

$^1$H NMR ($CDCl_3$, 300 MHz, 298 K): $\delta$ 7.50 (s, 2H, ArH), 7.45 (s, 2H, ArH), 6.50–6.62 (m, 6H, ArH), 4.55 (d, 1H, $J$ = 14.7 Hz, $ArCH_2Ar$, ax.), 4.47 (d, 2H, $J$ = 14.1 Hz, $ArCH_2Ar$, ax.), 4.42 (d, 1H, $J$ = 13.5 Hz, $ArCH_2Ar$, ax.), 3.73–4.04 (m, 8H, $-OCH_2-$), 3.32 (d, 1H, $J$ = 14.1 Hz, $ArCH_2Ar$, eq.), 3.28 (d, 2H, $J$ = 13.8 Hz, $ArCH_2Ar$, eq.), 3.18 (d, 1H, $J$ = 13.8 Hz, $ArCH_2Ar$, eq.), 1.81–1.93 (m, 8H, $-OCH_2CH_2-$), 0.92–1.02 (m, 12H, $-CH_3$).

#### 2.1.3. Compound **2c**

$^1$H NMR ($CDCl_3$, 300 MHz, 298 K): $\delta$ 7.42 (s, 4H, ArH), 6.74 (m, 6H, ArH), 4.45 (d, 4H, $J$ = 13.8 Hz, $ArCH_2Ar$, ax.), 3.81–3.93 (m, 8H, $-OCH_2-$), 3.22 (d, 4H, $J$ = 13.5 Hz, $ArCH_2Ar$, eq.), 1.83–1.96 (m, 8H, $-OCH_2CH_2-$), 0.92–1.04 (m, 12H, $-CH_3$).

All data are in agreement with Ref. [7].

### 2.2. Preparation of 5-amino-25,26,27,28-tetrapropoxycalix[4]arene **3a**

A suspension of mononitro derivative **2a** (0.54 g, 0.85 mmol) and 0.95 g (4.22 mmol) of $SnCl_2 \cdot 2H_2O$ in absolute ethanol (50 ml) was refluxed for 12 h. The reaction mixture was cooled to r.t. and poured into the mixture of aqueous ammonia (20 ml, 35%) and water (20 ml). The mixture was extracted with dichloromethane (4 × 50 ml), organic phase was washed with water (2 × 50 ml) and dried over $MgSO_4$. The evaporation of solvent yielded slightly pink powder (0.42 g, 82%) which was used in the next step without further purification. $^1$H NMR ($CDCl_3$, 300 MHz, 298 K): $\delta$ 6.51–6.67 (m, 9H, ArH), 5.95 (s, 2H, ArH), 4.45 (d, 2H, $J$ = 13.2 Hz, $ArCH_2Ar$, *ax.*), 4.38 (d, H, $J$ = 13.5 Hz, $ArCH_2Ar$, *ax.*), 3.80–3.89 (m, 6H, $OCH_2$), 3.73 (t, 2H, $J$ = 7.6 Hz, $-OCH_2-$), 3.16 (d, 2H, $J$ = 13.5 Hz, $ArCH_2Ar$, *eq.*), 3.01 (d, 2H, $J$ = 13.5 Hz, $ArCH_2Ar$, *eq.*), 1.82–1.93 (m, 8H, $-OCH_2CH_2-$), 0.93–1.00 (m, 12H, $CH_3$).

All data are in agreement with Ref. [8].

### 2.3. Preparation of 5,11-diamino-25,26,27,28-tetrapropoxycalix[4]arene **3b**

5,11-dinitro-25,26,27,28-tetrapropoxycalix[4]arene **2b** (0.39 g, 0.57 mmol) was suspended in 50 ml of absolute ethanol, 1.81 g (8.01 mmol) of $SnCl_2 \cdot 2H_2O$ was added and the mixture was refluxed overnight. Cooled reaction mixture was poured into solution of ammonia (10% in water) and extracted with $CH_2Cl_2$ (4 × 50 ml). Combined organic layers were washed with water (2 × 50 ml) and dried over $MgSO_4$. The evaporation of solvent gave slightly pink powder (0.28 g, 75%) which was used in the next step without further purification. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 6.56–6.67 (m, 6H, ArH), 6.01 (d, 2H, $J$ = 2.9 Hz, ArH), 5.95 (d, 2H, $J$ = 2.6 Hz, ArH), 4.46 (d, 1H, $J$ = 13.2 Hz, $ArCH_2Ar$, ax.), 4.38 (d, 2H, $J$ = 13.5 Hz, $ArCH_2Ar$, ax.), 4.30 (d, 1H, $J$ = 13.2 Hz, $ArCH_2Ar$, *ax.*), 3.83 (t, 4H, $J$ = 7.0 Hz, $-OCH_2-$), 3.72 (t, 4H, $J$ = 7.6 Hz, $-OCH_2-$), 3.15 (d, 1H, $J$ = 13.2 Hz, $ArCH_2Ar$, eq.), 3.03 (d, 2H, $J$ = 13.2 Hz, $ArCH_2Ar$, eq.), 2.91 (d, 1H, $J$ = 13.5 Hz, $ArCH_2Ar$, eq.),1.80–1.96 (m, 8H, $-OCH_2CH_2-$), 0.92–1.01 (m, 12H, $CH_3$).

All data are in agreement with Ref. [8].

### 2.4. Preparation of 5,17-diamino-25,26,27,28-tetrapropoxycalix[4]arene **3c**

A suspension of distal dinitrocalixarene **2c** (0.49 g; 0.72 mmol) and 2.27 g (10.08 mmol) of tin chloride dihydrate in absolute ethanol (80 ml) was refluxed for 12 h. After cooling the reaction mixture was poured into solution of ammonia (20 ml, 35%) in water (20 ml) and was washed with dichloromethane (4 × 60 ml). The organic phase was washed with water (2 × 60 ml) and dried over $MgSO_4$. The solvent was removed under reduced pressure to yield slightly pink powder (0.46 g, 97%) which was used in the next step without further purification. $^1$H NMR ($CDCl_3$, 300 MHz, 298 K): $\delta$ 6.71 (d, 4H, $J$ = 7.01 Hz, ArH), 6.61 (t, 2H, $J$ = 6.5 Hz, ArH), 5.94 (s, 4H, ArH), 4.39 (d, 4H, $J$ = 13.5 Hz, $ArCH_2Ar$, ax.), 3.83 (t, 4H, $J$ = 7.6 Hz, $-OCH_2-$), 3.63 (t, 4H, $J$ = 7.3 Hz, $-OCH_2-$), 3.03 (d, 4H, $J$ = 13.5 Hz, $ArCH_2Ar$, eq.), 1.80–1.96 (m, 8H, $-OCH_2CH_2-$), 0.89–1.01 (m, 12H, $-CH_3$).

All data are in agreement with Ref. [8].

### 2.5. Preparation of tetrathiafulvalene-2-carbonyl chloride **7**

TTF-2-carboxylic acid **6** (1.26 g, 5.07 mmol) was dissolved in a mixture of dried benzene (50 ml) and acetonitrile (20 ml). Then, 0.6 ml (6.59 mmol) of oxalyl chloride and catalytic amount (2 drops) of dried DMF were added. The reaction mixture was stirred for 2 h at room temperature while the colour turned dark violet. The solvents were carefully removed under a reduced pressure, and resulting product was used immediately for further reaction step without any purification and characterization because of low stability.

### 2.6. Preparation of calix[4]arene-TTF conjugate **4a**

A solution of a freshly prepared tetrathiafulvalene-2-carbonyl chloride **7** (0.31 g, 1.16 mmol) in dried THF (10 ml) was added dropwise to the solution of amino derivative **3a** (0.42 g, 0.69 mmol) and triethylamine (0.32 ml, 2.31 mmol) in 20 ml of dried THF. The reaction mixture was stirred at room temperature overnight (18 h), the solvent was evaporated under a reduced pressure, and the residue was purified by column chromatography on alumina using a $CH_2Cl_2$–hexane mixture as an eluent.

#### 2.6.1. Analytical data for **4a**

Bright orange crystals (75% yield), mp 126–129 °C, eluent = $CH_2Cl_2$:hexane 1:1 (v/v). $^1$H NMR (DMSO-$d_6$, 300 MHz, 298 K): $\delta$ 9.82

(s, 1H, NH), 7.65 (s, 1H, TTF), 6.94 (s, 2H, TTF), 6.74 (s, 2H, ArH), 6.63 (d, 3H, $J = 7.9$ Hz, ArH), 6.42–6.54 (m, 6H, ArH), 4.33 (d, 4H, $J = 12.9$ Hz, $ArCH_2Ar$, ax.), 3.68–3.81 (m, 8H, $OCH_2$), 3.16 (d, 2H, $J = 12.9$ Hz, $ArCH_2Ar$, eq.), 3.07 (d, 2H, $J = 12.9$ Hz,), 1.79–1.92 (m, 8H, $OCH_2CH_2$–), 0.92–1.01 (m, 12H, $CH_3$); $^{13}$C NMR (DMSO-$d_6$, 75 MHz, 298 K): $\delta$ 157.1, 156.8, 154.2, 135.9, 135.8, 135.1, 131.9, 130.9, 129.0, 128.9, 128.7, 127.9, 122.2, 121.6, 121.0, 119.4, 114.7, 107.2, 104.9, 31.3, 23.5, 23.4, 10.6, 10.4; TOF-ESI MS *m/z* for $C_{47}H_{51}NO_5S_4$ calculated: 838.19, found: 860.27 $[M + Na]^+$ (100%), 876.25 $[M + K]^+$ (15%); IR (KBr) $\nu_{max}$ ($cm^{-1}$): 3324 (NH), 1637 (C═O).

### 2.7. Preparation of calix[4]arene-TTF conjugate **4b**

A solution of a freshly prepared **7** (0.32 g, 1.21 mmol) in dried THF (20 ml) was added dropwise to the solution of **3b** (0.42 g, 0.67 mmol) and triethylamine (0.20 ml, 1.46 mmol) in 20 ml of dried THF. The reaction mixture was stirred at room temperature overnight (18 h), the solvent was evaporated under a reduced pressure, and the residue was purified by column chromatography on alumina using a $CH_2Cl_2$–hexane mixture as an eluent.

#### 2.7.1. Analytical data for **4b**

Orange crystals (64%), mp 171–175 °C, eluent = $CH_2Cl_2$:hexane 1:1 (v/v). $^1$H NMR (DMSO-$d_6$, 300 MHz, 298 K): $\delta$ 9.84 (s, 2H, NH), 7.75 (s, 2H, TTF), 7.00 (s, 2H, ArH), 6.96 (s, 2H, ArH), 6.78 (s, 4H, TTF), 6.61 (d, 4H, $J = 7.3$ Hz, ArH), 6.57 (t, 2H, $J = 7.0$ Hz, ArH), 4.21–4.39 (m, 4H, $ArCH_2Ar$, ax.), 3.64–3.80 (m, 8H, $OCH_2$), 2.19–3.02 (m, 4H, $ArCH_2Ar$, eq.), 1.76–1.89 (m, 8H, $OCH_2CH_2$), 0.93–1.04 (m, 12H, $CH_3$) $^{13}$C NMR (DMSO-$d_6$, 75 MHz, 298 K): $\delta$ 157.6, 156.8, 153.3, 135.4, 135.0, 134.8, 132.8, 128.9, 128.7, 126.4, 122.6, 121.0 120.7, 112.9, 106.8, 76.9, 31.2, 23.8, 11.0. TOF-ESI MS *m/z* for $C_{54}H_{54}N_2O_6S_8$ calculated 1083.55, found 1105.28 $[M + Na]^+$ (100%), 1121.25 $[M + K]^+$ (10%); IR (KBr) $\nu_{max}$ ($cm^{-1}$): 3306 (NH), 1639 (CO).

### 2.8. Preparation of calix[4]arene-TTF conjugate **4c**

A solution of a freshly prepared **7** (0.050 g, 0.20 mmol) in dried THF (10 ml) was added dropwise to the solution of compound **3c** (0.050 g, 0.08 mmol) and triethylamine (0.04 ml, 0.24 mmol) in 10 ml of dried THF. The reaction mixture was stirred at room temperature overnight (16 h), the solvent was evaporated under a reduced pressure, and the residue was purified by column chromatography on alumina using a $CH_2Cl_2$–hexane mixture as an eluent.

#### 2.8.1. Analytical data for **4c**

Bright orange crystals (73%), mp 200–204 °C, eluent = $CH_2Cl_2$:-hexane 3:1 (v/v). $^1$H NMR (DMSO-$d_6$, 300 MHz, 298 K): $\delta$ 9.82 (s, 2H, NH), 7.63 (s, 2H, TTF), 7.07 (s, 4H, TTF), 6.74 (s, 4H, ArH), 6.43–6.54 (m, 6H, ArH), 4.33 (d, 4H, $J = 13.2$ Hz, $ArCH_2Ar$, ax.), 3.85 (t, 4H, $J = 6.7$ Hz, $OCH_2$), 3.76 (t, 4H, $J = 6.7$ Hz, $OCH_2$), 3.14 (d, 4H, $J = 12.9$ Hz, $ArCH_2Ar$, eq.), 1.80–1.93 (m, 8H, $OCH_2CH_2$), 0.91–1.03 (m, 12H, $CH_3$); $^{13}$C NMR (DMSO-$d_6$, 75 MHz, 298 K): $\delta$ 156.8, 155.5, 153.9, 135.9, 134.6, 134.2, 132.8, 128.4, 126.5, 122.7, 121.5, 121.0, 120.7, 112.9, 110.2, 77.5, 77.4, 31.2, 23.7, 23.5, 11.1, 10.7; TOF-ESI MS *m/z* for $C_{54}H_{54}N_2O_6S_8$ calculated 1083.55, found 1105.19 $[M + Na]^+$ (100%), 1121.12 $[M + K]^+$ (10%); IR (KBr) $\nu_{max}$ ($cm^{-1}$): 3303 (NH), 1628 (CO).

### 2.9. Binding experiments

The complexation ability of **4a**–**4c** towards selected anions (benzoate, $H_2PO_4^-$, $HSO_4^-$) was measured by standard $^1$H NMR titration experiments in DMSO-$d_6$ using constant receptor concentration (0.1–2.0 mM) and increasing concentrations of appropriate anions to obtain different anion/receptor ratios (0.5–15). All anions were used as tetrabutylammonium salts to avoid possible inclusion of cationic species into the cavity of calix[4]arene. Binding UV/vis experiments were performed at room temperature (25 °C). The recorded sets of the absorption spectra were globally analysed using the Specfit program (v. 3.0, Spectrum Software Associates).

## 3. Results and discussion

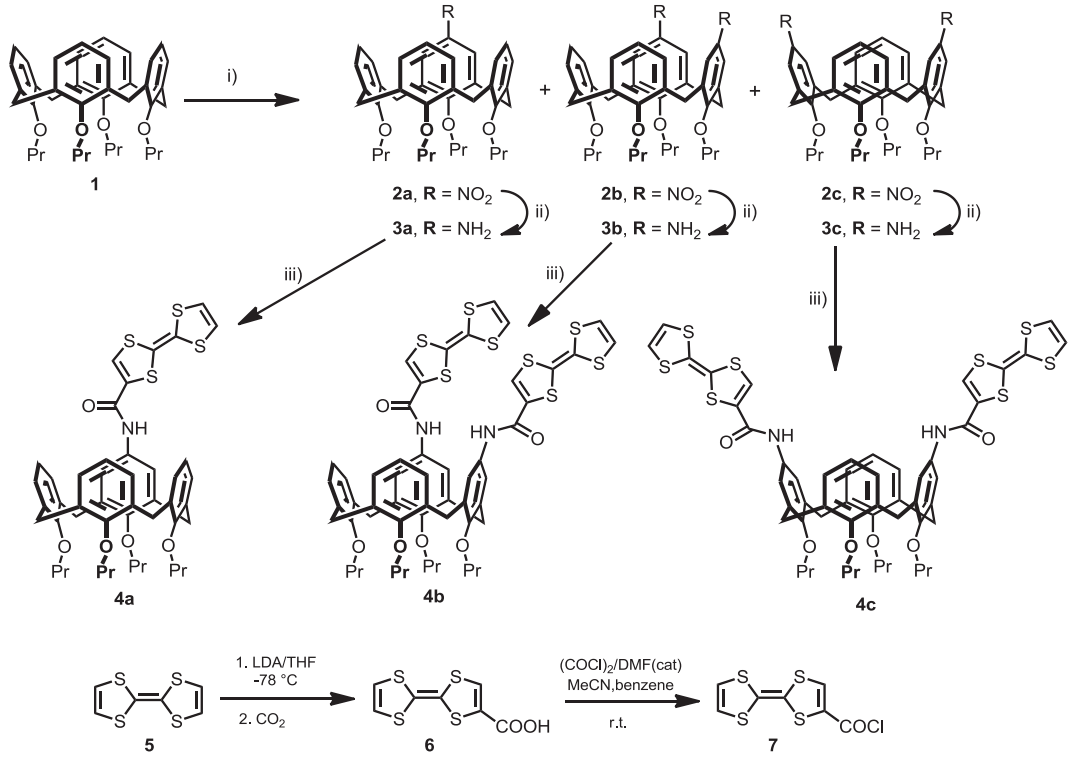
The synthesis of novel anion receptors started by the nitration of 25,26,27,28-tetrapropoxycalix[4]arene **1** immobilised in the *cone* conformation (Scheme 1). The use of $NaNO_3$ in a TFA/acetic acid mixture [7] at room temperature led to a crude reaction mixture containing mono- and two dinitro substituted products. Chromatographic separation on a silica gel column gave individual regioisomers in acceptable yields: **2a** (25%), **2b** (19%), **2c** (21%). Subsequent reduction with $SnCl_2 \cdot 2H_2O$ in refluxing ethanol led smoothly to aminosubstituted derivatives [8] **3a**, **3b** and **3c** in 82%, 75%, and 97% yield, respectively. TTF-carboxylic acid **6** was prepared according to the published procedure [10] using deprotonation of TTF with LDA in a THF solution and a subsequent reaction with dry ice. Free acid **6** was then converted to corresponding acyl chloride **7** (oxalyl chloride) and condensed with amino derivatives **3a**–**3c**. The calixarene–TTF conjugates were obtained in good yields – **4a** (75%), **4b** (64%), **4c** (73%).

The structures of receptors **4a**–**4c** were confirmed by the $^1$H NMR analysis. Thus, compound **4c** possesses two doublets of methylene bridges (4.33 and 3.14 ppm) with a typical geminal interaction constant ($J = 13$ Hz) corresponding to distally disubstituted calix[4]arene derivatives. Unfortunately, the expected splitting pattern of methylene bridges in **4b** collapsed into unresolved multiplets. The identity of **4b** is based on the correct splitting in parent amino derivative **3b** where six doublets at 4.46 (1H), 4.38 (2H), 4.30 (1H), 3.15 (1H), 3.03 (2H), and 2.91 (1H) ppm perfectly correspond with the splitting pattern expected for proximally disubstituted derivatives.

The complexation ability of **4a**–**4c** towards selected anions (benzoate, $H_2PO_4^-$, $HSO_4^-$) was measured by standard $^1$H NMR titration experiments in DMSO-$d_6$. Albeit dimerization or oligomerization of ureido-substituted calixarenes was described in the literature, no self-assembly behaviour was observed under experimental conditions and only monomeric species were taken into the calculations of the complexation constants [9]. All anions were used as tetrabutylammonium salts to avoid possible inclusion of cationic species into the cavity of calix[4]arene.

The complexation proceeds under fast exchange conditions, hence, the addition of the corresponding anion resulted in a large down-field shift of an amidic signal. For instance, the singlet of the –NH– group moved from 9.82 ppm to 11.42 ppm upon the addition of 8 eqs. of benzoate anions. Large complexation induced chemical shifts ($\Delta$ClS $\approx$ 1.6 ppm) suggest that the binding of $BzO^-$ proceeds *via* hydrogen bonding with amidic –NH– functions (Fig. 1). It is obvious from Table 1 that the complexation abilities of **4b** and **4c** towards benzoate anion are comparable and only about three times higher than that of monoamide **4a**. On the other hand, there is a considerable difference in case of $H_2PO_4^-$ anion. While receptors **4a** and **4c** gave almost similar results ($K \approx 45$ $M^{-1}$), proximally disubstituted receptor **4b** exhibited a forty times larger complexation constant ($K = 1800$ $M^{-1}$). It indicates the crucial role of the substitution pattern for the complexation ability [5a]. As $H_2PO_4^-$ represents a tetrahedrally shaped anion, $HSO_4^-$ anion with the same 3D structure was measured for comparison. Interestingly, none of novel receptors **4a**–**4c** showed any measurable interaction.

The TTF unit is frequently used not only for its interesting electrochemical behaviour [11], but it is also a suitable chromophore [12]. Hence, the presence of this structural motif allowed us




**Scheme 1.** Reagents and conditions: (i) $NaNO_3$/TFA-AcOH, room temp., 4.5 h, **2a** (25%), **2b** (19%), **2c** (21%); (ii) $SnCl{\cdot}2H_2O$/EtOH, reflux, 12 h, **3a** (82%), **3b** (75%), **3c** (97%); (iii) **7**/$Et_3N$/THF, room temp., overnight, **4a** (75%), **4b** (64%), **4c** (73%).

to carry out a complementary UV/vis titration experiment with **4b** (Fig. 2). The binding of $H_2PO_4^-$ anion resulted in a well-defined isosbestic point at 472 nm suggesting the 1:1 binding stoichiometry. The obtained set of absorption spectra was analysed by the nonlinear least-squares method assuming the formation of a 1:1 complex. The result ($K = 1800 \pm 100\ M^{-1}$) is fully comparable with that obtained by the $^1H$ NMR titration experiments for receptor **4b**. Because DMSO is a highly competitive solvent, to reveal the complexation ability of **4b** under less competitive conditions we carried out the UV/vis titrations in MeCN. Indeed, a much higher complexation constant was obtained ($K = 8000 \pm 1000\ M^{-1}$).

The differences between proximal **4b** and distal **4c** receptors can be also documented by the oxidation behaviour of the attached TTF units. Their one-electron oxidation to corresponding radical-cations was studied in deoxygenated MeCN upon the addition of $NOSbF_6$ as an oxidation agent. While the original UV/vis spectra of monoamide **4a** and diamides **4b**, **4c** derivatives are almost identical characterized by broad bands around 315 and 415 nm, the oxidation invoked dramatic changes (Fig. 3A). The spectrum of **4a** bearing one TTF unit was converted to a new one with absorption bands at 430 and about 580 nm. Proximal **4b** behaved similarly to give new absorption bands at 429 and 580 nm. These absorption bands indicate the formation of monomeric $TTF^{+\bullet}$ radical-cation because $TTF^{+\bullet}$ has the absorption bands at 435 and 525 nm [13]. The spectral conversion of **4c** was examined by the gradual addition of $NOSbF_6$ (Fig. 3B). The addition of 0.25 eq. of $NOSbF_6$ (*per* TTF unit) led to a development of absorption bands at 393 and 430 nm. The appearance of new absorption at 755 nm is accelerated by the addition of next 0.25 eq. of $NOSbF_6$ *per* TTF group (Fig. 3B). Using the literature data [13] the absorption band around 750 nm can be assigned to radical-cation π-dimer $(TTF^{+\bullet})_2$. Unfortunately, higher excess of oxidizing agent led to a fast decomposition of all receptors and did not allow us to evaluate the behaviour of our compounds at higher oxidation states of TTF. The appearance of $(TTF^{+\bullet})_2$ is evidently due to the spatial arrangement of two TTF units in **4c** because the oxidation experiments carried out with proximal derivative **4b** did not show any formation of dimer $(TTF^{+\bullet})_2$, but only of the monomeric radical-cation $TTF^{+\bullet}$. This fact can be explained by the pinched cone conformation [1] of the receptors known to bring closer the substituents of the opposite phenol units.

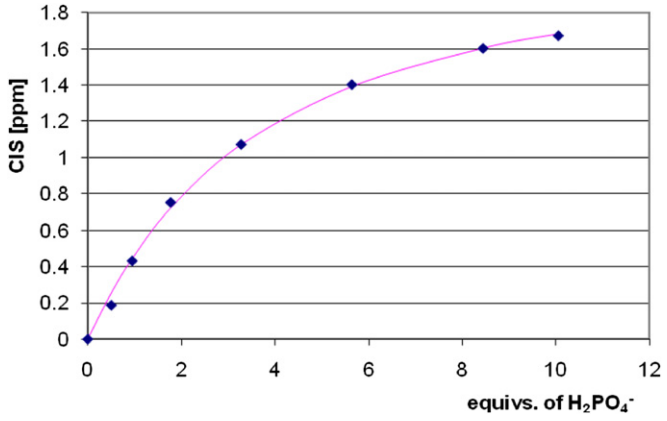



**Fig. 1.** $^1H$ NMR titration curve of **4c** with $BzO^-$ anion (300 MHz, 298 K, DMSO-$d_6$).

**Table 1**
Complexation constants $K$ [$M^{-1}$] in DMSO-$d_6$ at 298 K supposing the 1:1 stoichiometry.

| Anion[a] | 4a | 4b | 4c |
|---|---|---|---|
| $H_2PO_4^-$ | 47 ± 3 | 1800 ± 100 | 43 ± 8 |
| $BzO^-$ | 20 ± 2 | 61 ± 9 | 74 ± 6 |
| $HSO_4^-$ | n[b] | n[b] | n[b] |

[a] Anions were used as tetrabutylammonium salts.
[b] No complexation observed.

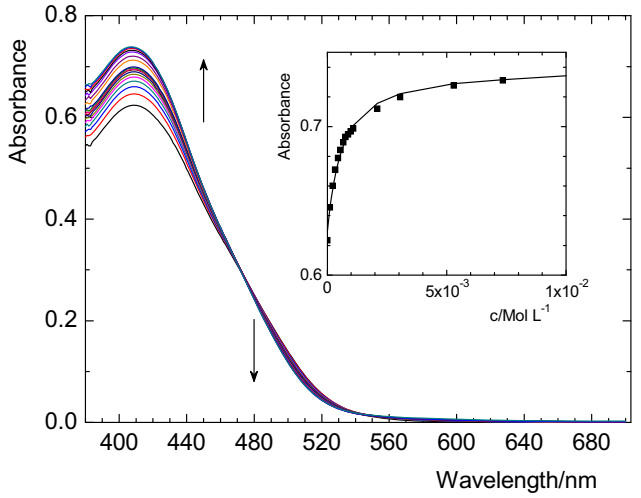



**Fig. 2.** UV/vis titration of **4b** ($1.12 \times 10^{-4}$ M) with $H_2PO_4^-$ in DMSO; arrows show changes due to increasing concentration of $H_2PO_4^-$ up to $1.67 \times 10^{-2}$ M. Inset: Binding isotherm recorded at 410 nm. The solid line is a global least-squares fit to the experimental data.

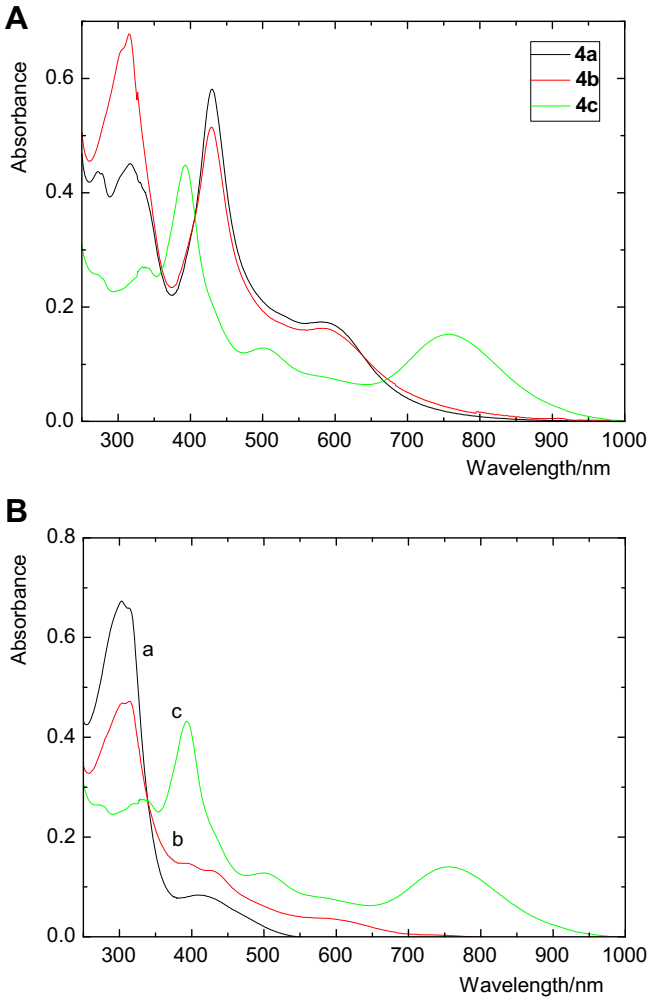



**Fig. 3.** A) UV/vis spectra of compounds **4a**–**4c** after oxidation by 0.5 eq. of $NOSbF_6$ *per* TTF unit in MeCN at 298 K; B) UV/vis spectra of **4c** (a) upon addition of $NOSbF_6$: 0.25 (b) and 0.5 (c) eq. of $NOSbF_6$ *per* TTF unit in MeCN at 298 K.

In conclusion, the introduction of the TTF units onto the upper rim of calix[4]arene immobilised in the *cone* conformation led to new receptors for anions acting *via* hydrogen bonding of the amidic functions. Interestingly, proximally disubstituted derivative exhibits stronger complexation of $H_2PO_4^-$ if compared with the diametrically substituted analogue. It indicates the crucial role of a substitution pattern in the receptor design. Different behaviour of both regioisomers was also documented by one-electron oxidation of these receptors.

## Acknowledgements

This research was supported by the Czech Science Foundation (No. 203/09/0691) and by the Grant Agency of the Academy of Sciences of the Czech Republic (No. IAAX08240901). The authors also thank the Ministry of Education, Youth and Sports of the Czech Republic (MSM 6046137301) for financial support.

## Appendix. Supplementary information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.dyepig.2011.06.001.

## References

[1] For books on calixarenes see: (a) Gutsche CD. Calixarenes: an introduction. 2nd ed. Cambridge: The Royal Society of Chemistry, Thomas Graham House; 2008;
(b) Vicens J, Harrowfield J, Backlouti L, editors. Calixarenes in the nanoworld. Dordrecht: Springer; 2007;
(c) Asfari Z, Böhmer V, Harrowfield J, Vicens J, editors. Calixarenes 2001. Dordrecht: Kluwer Academic Publishers; 2001;
(d) Mandolini L, Ungaro R. Calixarenes in action. London: Imperial College Press; 2000;
(e) Gutsche CD. In: Stoddart JF, editor. Calixarenes revisited: monographs in supramolecular chemistry, vol. 6. Cambridge: The Royal Society of Chemistry; 1998.

[2] For recent books and reviews on anion recognition see: (a) Sessler JL, Gale PA, Cho WS. Anion receptor chemistry. Cambridge: The Royal Society of Chemistry; 2006;
(b) Schmidtchen FP. Chem Soc Rev 2010;39:3916–35;
(c) Gale PA. Coord Chem Rev 2006;250:3219–44;
(d) Gale PA, Garcia-Garrido SE, Garric J. Chem Soc Rev 2008;37:151–90;
(e) Schottel BL, Chifotides HT, Dunbar KR. Chem Soc Rev 2008;37:68–83;
(f) Vilar R, editor. Recognition of anions. Structure and bonding, vol. 129. Berlin: Springer; 2008.

[3] For review on calixarene-based anion receptors see: (a) Matthews SE, Beer PD. In: Calixarenes; 2001. p. 421–39 (see Ref. [1c]). (b) Lhoták P. Top Curr Chem 2005;255:65–96;
(c) Matthews SE, Beer PD. Supramol Chem 2005;17:411–35.

[4] For some recent examples of urea-substituted calixarene-bases receptors see: (a) Schazmann B, Alhashimy N, Diamond D. J Am Chem Soc 2006;128:8607–14;
(b) Babu JN, Bhalla V, Kumar M, Mahajan RK, Puri RK. Tetrahedron Lett 2008;49:2772–5;
Quinlan E, Matthews SE, Gunnlaugsson T. J Org Chem 2007;72:7497–503;
Schazmann B, Diamond D. New J Chem 2007;31:587–92.

[5] (a) Lang K, Curinová P, Dudic M, Prosková P, Stibor I, Stastny V, et al. Tetrahedron Lett 2005;46:4469–72;
(b) Lhoták P, Svoboda J, Stibor I. Tetrahedron 2006;62:1253–7;
(c) Stibor I, Budka J, Michlová V, Tkadlecová M, Pojarová M, Curinová P, et al. New J Chem 2008;32:1597–607;
(d) Kroupa J, Stibor I, Pojarová M, Tkadlecová M, Lhoták P. Tetrahedron 2005;64:10075–9;
(e) Curinová P, Stibor I, Budka J, Sykora J, Lang K, Lhoták P. New J Chem 2009;33:612–9.

[6] For examples of calixarene-TTF conjugates see: (a) Lee MH, Cao QY, Kim SK, Sessler JL, Kim JS. J Org Chem 2011;76:870–4;
(b) Zhao BT, Blesa MJ, Mercier N, LeDerf F, Salle M. New J Chem 2005;29:1164–7;
(c) Blesa MJ, Zhao BT, Allain M, LeDerf F, Salle M. Chem Eur J 2006;12:1906–14;
(d) Lyskawa J, Canevet D, Allain M, Salle M. Tetrahedron Lett 2010;51:5868–72;
(e) Zhao BT, Zhou Z, Yan ZN, Belhadj E, LeDerf F, Salle M. Tetrahedron Lett 2010;51:5815–8.

[7] Casnati A, Fochi M, Minari P, Pochini A, Reggiani M, Ungaro R. Gazz Chim Ital 1996;126:99–106.

[8] Kelderman E, Derhaeg L, Heesink GJT, Veroom W, Engbersen JFJ, Van Hulst NF, et al. Angew Chem Int Ed Engl 1992;31:1075–7.
[9] Ref [5a] describes dimerization of distally disubstituted ureidocalix[4]arenes. This phenomenon can be observed only in HB-noncompetitive solvents ($CDCl_3$, $CD_2Cl_2$) and the corresponding dimerization constants are very small ($K_D < 100\ M^{-1}$). Similar dimerization can be also found in: Scheerder J, Vreekamp RH, Engbersen JFJ, Verboom W, van Duynhoven JPM, Reinhoudt DN J Org Chem 1996;61:3476–81.
[10] Garin J, Orduna J, Uriel S, Moore AJ, Bryce MR, Wegener S, et al. Synthesis 1994;5:489–93.
[11] (a) Canevet D, Salle M, Zhang G, Zhang D, Zhu D. Chem Commun; 2009:2245–69;
(b) Park JS, Karnas E, Ohkudo K, Chen P, Kadish KM, Fukuzumi S, et al. Science 2010;329:1324–7.
[12] Park JS, LeDerf F, Bejger CM, Lynch VM, Sessler JL, Nielsen KA, et al. Chem Eur J 2010;16:848–54.
[13] (a) Lyskawa J, Salle M, Balandier JY, LeDerf F, Levillain E, Allain M, et al. Chem Commun; 2006:2233–5;
(b) Yoshizawa M, Kumazawa K, Fujita M. J Am Chem Soc 2005;127:13456–7;
(c) Ziganshina AY, Ko YH, Jeon WS, Kim K. Chem Commun; 2004:806–7.