# ARTICLE

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Journal of Materials Chemistry

# Calix[4]arene-functionalized poly-cyclopenta[2,1-*b*;3,4*b'*]bithiophenes with good recognition ability and selectivity for small organic molecules for application in QCM-based sensors†

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Received 11th November 2003, Accepted 6th April 2004 First published as an Advance Article on the web 11th May 2004

Some  $C_{2v}$  symmetric cyclopenta[2,1-*b*;3,4-*b*']bithiophenes differently substituted at the 4 position with a calix[4]arene group were synthesized and electrochemically polymerized by anodic coupling. The polymers were characterized by cyclic voltammetry, UV-vis and FTIR spectroscopy. Quartz crystal microbalance analysis showed strong affinity and selectivity of the polymers for toluene and acetone from the gas phase. The absorption process associated with the calix unit was satisfactorily described through a Langmuir isotherm, while a very small linear contribution was given by the polythiophene backbone. The absorption capacity of these materials was found to be higher by a magnitude of three orders than those displayed by cyclopentabilihophene-based polymers devoid of the calix unit, thus supplying strong, though indirect, proof of the role played by the calix units in the absorption process.

# Introduction

Calixarenes have attracted great attention due to their ability and selectivity in hosting specifically sized ionic<sup>1</sup> and neutral molecules (benzene and substituted benzenes, acetonitrile, nitromethane, N,N-dimethylformamide)<sup>2</sup> in their cavity and it is not surprising that they have been chosen as sensing units associated with electroactive surfaces to prepare materials for sensors.<sup>3</sup> Polymer films either physically incorporating calixarenes<sup>4</sup> or covalently functionalized with calixarene units<sup>5</sup> have been widely investigated in the past and still are the subject of intense research efforts aimed at finding new materials for even more efficient on-line working sensor devices. A continuously growing number of different architectures capable of giving selective supramolecular interactions with ionic and neutral species is now available and recent literature offers clever examples of second generation calixarene functionalized polymers successfully applied in sensoristics.<sup>6</sup> The different strategies envisaged to prepare calixarene-based sensors have been exhaustively reviewed in several publications.

The oxidative electropolymerization of calixarene-functionalized five-membered heteroaromatic and bi-heteroaromatic monomers to give electroactive polymers offers some substantial advantages over the several methodologies available to prepare polymeric thin films to be used as sensing units.<sup>8</sup> In particular, it is possible to exploit, at least in theory, different techniques for producing reliable signals from the effects of the supramolecular analyte–calixarene interactions: the QCM analysis to detect the variations in weight of the film following the absorptive process and suitable electrochemical techniques to detect the changes in the electrical properties (*e.g.*: conductivity) of the poly-conjugated chain. The QCM technique is more popular than the latter since it is simple, inexpensive and gives fast, reliable and precise response to the weight increase of the films following the absorption of vapors. The microbalance apparatus can be mounted in a closed chamber where solvents were injected, according to standardized automated procedures.

The aim of the present research was to prepare highly ordered calix[4]arene-functionalized poly-bithiophenes, which could exhibit good recognition ability for specific small organic molecules selectively recognized by the cavity. Monomer **1** was first selected for this purpose (Scheme 1).

The structural design was based on the following considerations. i) Electron-rich 4H-cyclopenta[2,1-b;3,4-b']bithiophene (CPDT),<sup>9</sup> designed and successfully employed by us,<sup>10</sup> was chosen as the polymerogenic unit, since its oxidative electropolymerization occurs at rather low potentials and overoxidation defects are not introduced in the polymer. *ii*) The homotopism of the positions involved in the polymerization process (1 is  $C_{2v}$ symmetric) assures the regio- and stereo-regularity of the chain. *iii*) The 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene (3a) and its 25,27-diametrical dimethyl ether (3b) were chosen to effect the molecular recognition, since they are accessible through very simple and reliable synthetic procedures.<sup>11</sup> iv) The short linkers between CPDT and the phenolic oxygen atoms of the 1,3 distal rings of the calix moiety should guarantee the cone conformation, which is endowed with higher recognition properties than partial cone or alternate conformations.

It is known, however, that the conjugated organic polyheterocycles are more or less porous materials, capable of

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10.1039/b314345a

<sup>†</sup> Electronic supplementary information (ESI) available: <sup>1</sup>H-NMR spectra of compounds **6**, **7**, **8**, **1**, **5**, **12**; experimental procedures of the reactions of **7** with **3b** and of **9** with 1,3-dibromopropane; preparations and characterization for **4** and **5**. See http://www.rsc.org/suppdata/jm/b3/b314345g/



adsorbing volatile organic compounds, independently of the presence of functions specially tailored for this purpose. We considered it an important point of the research to devise a system to differentiate the generalized absorption effects related to the intrinsic porosity of the polymer and those produced by selective inclusion of organic molecules in the annulus of the calix units. With this view, we planned to prepare the monomer **2**, similar to **1** in its atomic composition, connectivity, symmetry and, reasonably, electrochemical oxidative potential, but devoid of the conical receptor (Scheme 1). The differences in the recognition and absorption data shown by electrodes coated with poly-**1** and poly-**2** should be mainly referable to the inclusion ability shown by the cavities of the calixarene pendants.

This paper reports: *i*) the syntheses of monomers **1**, **2** and two other  $C_{2v}$  symmetric calixarene-functionalized CPDT monomers, **4** and **5** (Scheme 2), we came across, more or less accidentally, during the development of the work and that we considered interesting in the general frame of this research; *ii*) the electropolymerization of the monomers; *iii*) the electrochemical and spectroscopic characterization of the polymers; *iv*) the evaluation of the vapor uptake ability and the selectivity of the polymers for toluene<sup>12</sup> and acetone, <sup>13</sup> which are standard strong (toluene) and weak (acetone) guest molecules.

#### **Results and discussion**

#### (1) Synthesis of the monomers

The synthesis of monomer **1** was achieved starting from CPDT: its anion in position 4 was alkylated with 1,3-dibromopropane at -70 °C to give the 4-(3-bromopropyl)cyclopenta[2,1-*b*;3,4*b*']bithiophene (6) in good yields. The same sequence was repeated on the latter to give the 4,4'-bis(3-bromopropyl)cyclopenta[2,1-b;3,4-b']bithiophene (7), which was used as a bifunctional alkylating reagent of the 5,11,17,23-tetra-*tert*butyl-25,26,27,28-tetrahydroxycalix[4]arene (**3a**). Compound **8** was isolated in satisfactory yields and then methylated at the diametrical phenolic oxygen atoms to give **1**, though in modest yields (Scheme 3).

The reaction sequence reported above is the sole method capable of affording 1, even though several other synthetic schemes have been tried. The reaction of dibromide 7 with the dianion of the calixarene diametrical dimethyl ether 3b afforded the monoalkylation product in poor yields, which, in any case, could not be cyclized to 1 even under drastic conditions.

In a further attempt to produce 1, the mono anion of the calix[4]arene dimethyl ether 3b reacted with the 4-(3-bromopropyl)cyclopenta[2,1-*b*;3,4-*b'*]bithiophene (6), described above, to give the expected alkylation product 9, together with minor quantities of the dialkylated compound 4 (Scheme 4). Both these compounds were separated by chromatography and recognized on the basis of their analytical and spectral data.

Once again, however, we were not able to convert **9** into **1** by further alkylation of the phenolic oxygen atom with 1,3dibromopropane under basic conditions, followed by basepromoted cyclization of the resulting alkylation product.

Even though 9 is a calixarene-functionalized CPDT-based system, we did not consider it a suitable monomer for the present investigation, since  $C_s$  symmetric monomers unavoidably produce stereochemically disordered polymers. We employed, instead, as a monomer  $C_{2v}$  symmetric compound 6, bearing two distal CPDT-terminated substituents, even though, in this case, the partial-cone seemed favored over the





cone conformation and extensive cross-linking during the polymerization was expected.

We also prepared substrate **5**, reasonably displaying the cone as the preferred conformation thanks to its rather rigid architecture and probably able to produce a better-organized polymer than **4**. Its synthesis was achieved by alkylation of calixarene **3a** with the dibromo derivative **11**, to give the distal diphenol **12**, which was further methylated (NaH/MeI) to afford **5**. Dibromo compound **11** was prepared by dialkylation with 1,4-dibromobutane of the 1,3-bis[4-(4*H*-cyclopenta[2,1b;3,4-b']bithiophen)yl]propane (**10**), which was synthesized in turn by stoichiometry-controlled alkylation of CPDT with 1,3dibromopropane (Scheme 5).

The synthesis of compound **2**, bearing a CPDT unit functionalized with a non-conical, quasi-isomeric, substituent of the calix, was successfully achieved through the monomethylation of known bis(5-*tert*-butyl-2-hydroxyphenyl)methane to give **13**, followed by reaction of the anion of the latter with 4,4'-bis(3bromopropyl)cyclopenta[2,1-*b*;3,4-*b'*]bithiophene (**7**) described above (Scheme 6).

The <sup>1</sup>H NMR spectra of the calixarene-functionalized CPDTs were examined in CDCl<sub>3</sub> solution at room temperature. <sup>14</sup> Two

general situations were observed: when very sharp signals were found, we could infer that the system was present in solution as a single conformational isomer, even though a clear discrimination between cone and partial cone conformers was impossible, since both display  $C_{2v}$  symmetry. This was the case for all the twin bridged CPDT systems **1**, **5**, **8**, and **12**. Broad signals indicated that the compound was present in solution as a mixture of conformational diastereoisomers in a dynamic equilibrium. Mono-functionalized CPDT monomers **4** and **9** were found to be constituted by mixtures of slowly interconverting stereoisomers.

#### (2) Electrochemical synthesis of the polymers

Monomers 1 and 5 were found to be slightly soluble in acetonitrile (*ca.*  $10^{-4}$  M), whereas higher solubility was shown by 4 and 2 (*ca.*  $10^{-3}$  and  $>10^{-2}$  M respectively). The voltammograms, performed in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> acetonitrile solution, displayed an oxidation peak at *ca.* 0.7 V (scan rate: 0.1 V s<sup>-1</sup>), quite similar for all the monomers (Table 1).

With continuous potential cycling, the redox cycle, due to the growing polymer, developed, as shown for monomer **1** in Fig. 1.





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The charge yield (ratio of the reversible charge over that for deposition, measured at the neutral state) was about 15% for 1, 30% for 4 and 5 and only 3% for the open-calix functionalized system 2. The latter observation might be attributed to a rather high solubility of the oligomers.

All the polymers displayed the CV characteristics expected for a polythiophene film with a twin redox process. A typical cyclic voltammogram is shown for poly-1 in Fig. 2.

The redox potentials  $E^{\circ}$ , taken as the average of oxidation and reduction peak potentials, are reported in Table 1 for all the polymers. The average  $E^{\circ}$  values are about 0.1 V, *i.e.* close to those shown by analogous CPDT-based polymers.<sup>15</sup>

QCM analysis indicates that the reversible oxidation process involves one electron per monomeric unit and that one

**Table 1** Oxidation peak potentials  $(E_p)$  for monomers and redox potentials  $(E^\circ)$  and maximum UV absorption  $(\lambda)$  for polymers

	1	4	5	2	CPDT
	0.70 0.10; 0.25 560	0.68 0.15; 0.30 520	0.68 0.10; 0.25 550	0.70 0.15; 0.30 520	0.65 0.10 545
<sup>a</sup> Scan ra	ate: 0.1 V s <sup>-</sup>	1			

perchlorate anion is involved in the mass exchange. The simple uptake of perchlorate to counterbalance the injected positive charge is a feature commonly encountered in polythiophenes.<sup>16</sup>



Fig. 1 Repetitive cyclic voltammetry of 1  $(10^{-4} \text{ M})$  in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> acetonitrile solution. Scan rate: 0.1 V s<sup>-1</sup>.



Fig. 2 Cyclic voltammogram of poly-1 in 0.1 M  $Bu_4NCIO_4$  acetonitrile solution. Scan rate: 0.1 V s<sup>-1</sup>. Reversible charge: 0.7 mC cm<sup>-2</sup>.

# (3) Characterization of the polymers

Undoped poly-1 and poly-2 are soluble in CHCl<sub>3</sub>, while poly-4 and poly-5 were found to be insoluble. Expected crosslinking could be responsible for these different solubility properties.

The IR spectrum of the undoped polymers, dominated by the calixarene bands, displayed a strong band at *ca.* 820 cm<sup>-1</sup> due to the inner C–H bond stretching and a weak one at 640 cm<sup>-1</sup> due to the terminal C–H bond stretching of CPDT units, in agreement with the medium DP value of the polymers (about 10).

The electronic spectral data indicated that the absorption maxima of the polymer films were located at about  $580 \pm 20$  nm, in agreement with the data shown by previously investigated CPDT-based materials.<sup>15</sup>

An analogous trend was found to be followed by the redox potentials. Poly-4 and poly-2 exhibited absorption maxima at 520 nm, while poly-1 and poly-5 showed maxima at 550–560 nm, probably as a consequence of slightly different DPs (Table 1).

The conductivity of poly-4 was found to be about  $1 \text{ S cm}^{-1}$ , while the conductivity of the other polymers could not be measured through the *in situ* technique<sup>17</sup> due to the low deposition yields.

The failure to determine reliable conductivity data for the polymers ruled out the possibility of searching for possible relationships between the vapor uptake levels in the materials and their conductivities. Thus, we resorted to the QCM technique.

#### (4) Vapor uptake monitoring by QCM

The ability of the poly-(calixarene-functionalized-CPDT)s to uptake organic vapors has been checked for thin films deposited on the QCM electrode. In order to test the adsorption ability of the plain CPDT backbone, we planned to carry out absorption measurements also on poly-CPDT itself.<sup>15</sup> As anticipated, tests were performed with a strong (toluene) and a weak (acetone) guest molecule.<sup>18</sup>

The films were produced by potential cycling, followed by a conditioning step constituted by three further CV cycles in a monomer-free electrolyte solution and final flushing of the coated electrodes with nitrogen till steady weight (about 10 minutes). The conditioning procedure was necessary to obtain reproducible results, since inaccurate storage of the films in the dry state was found to lead to a progressive decrease of their vapor uptake ability, which could decay to 50% in 24 hours.

In the cases of poly-1, poly-4 and poly-5, the mass increases regularly with the vapor additions with a very fast response time, roughly corresponding to the mixing time (*ca.* 100 s) (Fig. 3).



**Fig. 3** QCM mass increase for poly-1 following subsequent additions of toluene (0.1; 0.2; 0.3; 0.5; 0.75; 1.0; 1.5; 2.0; 2.5; 3.0  $\mu$ L). Initial mass: 9  $\mu$ g cm<sup>-2</sup>. Polymer density assumed as 1.0 g cm<sup>-3</sup>.



**Fig. 4** QCM mass increase for poly-1: plot of toluene concentration in the polymer  $(C_p)$  vs. toluene concentration in nitrogen  $(C_v)$ . Initial mass: 9 µg cm<sup>-2</sup>. Line: fitting to model  $(\chi^2 = 2 \times 10^{-7})$ .

The absorption process was found to be fully reversible, again with short response times, by flushing the cell with dry nitrogen.

The concentration of the guest toluene in the polymer *vs.* its concentration in the gas phase showed approximately Langmuir-type absorptive behavior (Fig. 4).

In fact, a significant positive slope was observed in the highconcentration side of the plots. This result may be accounted for by a twin-process Langmuir law:  $\Gamma = \beta_1 C/(1 + \beta_1 C) + \beta_2 C/(1 + \beta_2 C)$ , where  $\Gamma$  is the fraction of adsorbed molecules  $[\Delta m/\Delta m_L, i.e.$  the ratio of mass uptake  $(\Delta m)$  over the maximum allowed mass uptake  $(\Delta m_L)$ ], C is the analyte concentration in the gas phase and  $\beta$  are the adsorption constants. The equation may be simplified to:  $\Gamma = \beta_1 C/(1 + \beta_1 C) + \beta_2 C$ , given the low value of the second coordination constant  $\beta_2$  (1–4% of  $\beta_1$ ).

A very good fitting was observed and the resulting partition equilibrium constant  $\beta_1$  values are reported in Table 2 for the various polymers.

 $\Delta m_{\rm L}$  values, referred to the mass of the polymers, corresponded to a maximum absorption level of about the 10% for both solvents. Taking into account the molecular weights of

**Table 2** Partition equilibrium constants  $\beta_1$  for toluene  $\beta_1$ (Tol) and acetone  $\beta_1$ (Ac)

	1	4	5	2	CPDT
$\beta_1(\text{Tol})^a$ $\beta_1(\text{Ac})^a$	${3 \ \times \ 10^6} \ {5 \ \times \ 10^4}$	$7 \times 10^6$	$5 \times 10^{6} \\ 1 \times 10^{5}$	$\begin{array}{c} 1 \ \times \ 10^3 \\ 4 \ \times \ 10^4 \end{array}$	$5 \times 10^3$
$a \mathrm{g}^{-1} \mathrm{cm}^3$ .	<sup>b</sup> Not measured	ured.			

toluene (92), acetone (58) and the repeating unit of poly-1 (932), these data corresponded to a 1.1 : 1 analyte : calix unit molar ratio for toluene and 1.6 : 1 for acetone. This consideration suggested that, at the saturation level, one molecule of solvent is hosted in one calix annulus, in agreement with the literature data regarding toluene and acetone clathrates.<sup>12,13,18</sup>

Extra adsorption ( $\beta_2$ ), related to inclusion in the polymer matrix, is considerably more difficult and probably involves cavities located amongst the calixarene units. This suggestion is supported by results recently reported on LB films of calixarenes, for which an accumulation of liquid adsorbate within the nanopores of the matrix was found.<sup>19</sup>

We have also verified that the vapor uptake does not depend on the oxidation level of the polythiophene backbone.

The absorption constants  $\beta_1$ (Tol) shown by the calixfunctionalized polymers poly-1, poly-4 and poly-5, can be considered as extremely high. These materials display an adsorption capacity even more efficient than that shown by the highly sorbent Ni(SCN)<sub>2</sub>(4-picoline)<sub>4</sub> complex.<sup>20</sup>

Instead, poly-2 and poly-CPDT can be considered to have absorption properties comparable to those known for other polymeric materials (*e.g.* polybutadiene), which are currently used for QCM analysis of organic vapors, including toluene.<sup>21</sup>

It is interesting to note that the absorption properties for toluene of poly-1, poly-4 and poly-5 are higher by a magnitude of three orders than those exhibited by poly-2, which is devoid of the calixarene function, and by poly-CPDT (Table 2), for which much longer response times (*ca.* 20 minutes) were also observed.

These data demonstrate that the calix functions play a crucial role in determining the absorption capacity of the polymers.

It is also worth noting that poly-1, poly-4 and poly-5 are expected to have different morphology, roughness, porosity and solubility, since, as anticipated, crosslinking is certainly active in the polymerization of 4 and 5, while it is precluded in the case of 1. The absorption properties of all three polymers for toluene and acetone are, however, very similar. This observation is further proof that the calix cavity is nearly exclusively responsible for the absorption properties of these materials, since the generic vapor diffusion into a polymer matrix, related to its inherent porosity, should be strongly influenced by its morphological features.

The uptake of acetone appears, instead, quite undifferentiated amongst all the polymers, with constants falling in the range  $10^4$ – $10^5$ . The ratio of the adsorption constants for toluene over those for acetone is about 50–60, in agreement with the known different affinity of calix[4]arenes for these solvents.<sup>12,13</sup>

# Conclusions

The experiences developed in this research have demonstrated the good opportunities offered by calix[4]arene-functionalized CPDTs to design sensors for efficient and selective recognition of small organic molecules present in the gas phase. The results can be summarized as follows:

—Some calix[4]arene-functionalized cyclopentabithiophene monomers (1, 4 and 5), displaying  $C_{2v}$  symmetry, have been synthesized.

—Monomer 2, similar to 1 in its atomic composition, connectivity, symmetry and electrochemical oxidative potential, but devoid of the conical receptor, has been synthesized in order to discriminate the absorption effects related to the presence of the calix function from the generalized absorption of the vapors into the micropores of the polymer matrix.

—All the monomers have been electrochemically polymerized to give materials endowed with high constitutional and stereochemical order, thanks to the homotopism of the positions involved in the polymerization process.

—The polymers have been spectroscopically and electrochemically characterized.

—Electrodes coated with the polymers have been tested as sensors for the selective recognition of toluene and acetone present in the gas phase, since they are the standard analytes for evaluating the hosting ability of the calix moieties present in functional materials.

—The polymers could not be obtained as films thick enough to allow reliable conductivity measurements. Thus, the search for a conductivity–vapor absorption relationship was precluded.

—QCM measurements demonstrated that the absorption properties for toluene of the calixarene-functionalized polymers are extremely high, more than three orders of magnitude higher than those exhibited by poly-CPDT and poly-2, which are devoid of the calixarene function, and at least one order of magnitude higher than other calix[n]arene thin films, generally suffering for comparable analyte–surface and –bulk interactions.

—Much shorter response times (100 s) are required for the calixarene-functionalized materials than for the polymers devoid of the calixarene functions (*ca.* 20 minutes).

—In the cases of polymers bearing the calix units, the absorption process stops when one molecule of analyte per calix unit is absorbed.

—The absorption process follows the ideal behavior controlled by the Langmuir equation, with a very modest linear contribution due to the polymer matrix.

-Poly-1, poly-4 and poly-5 display very different affinities for toluene and acetone.

—The films were found not to suffer from swelling as a consequence of the absorption process into the polymer matrix.

These data demonstrate that the calix unit is the main unit responsible for the great absorption capacity and for the selectivity shown by the calix[4]arene functionalized poly-CPDTs.

# Experimental

#### Synthesis of the monomers

CPDT was prepared according to the procedure previously described by us.<sup>9</sup>

4-(3-Bromopropyl)cyclopenta[2,1-b;3,4-b']bithiophene (6). A 1.6 M BuLi solution in n-hexane (3.0 mL, 4.8 mmol) was dropped into a solution of CPDT (840 mg, 4.7 mmol) in dry THF (25 mL) at -70 °C under nitrogen. The temperature was allowed to rise to -20 °C, maintained for 20 minutes, then cooled again to -70 °C. 1,3-Dibromopropane (2 mL, 20 mmol) was added dropwise, then the cooling bath was removed and the mixture left to stand for 12 hours. MeOH (5 mL) was added and the solvent removed under reduced pressure. The residue was treated with H<sub>2</sub>O, extracted with Et<sub>2</sub>O, then, after the usual work-up, column chromatographed (silica gel/n-hexane). The title product 6 was recovered from the first fractions eluted as a pale-orange oil (720 mg, yield 51%). <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>)  $\delta$  7.19 (d, J = 2.13 Hz, 2H,  $\alpha$  thiophene), 7.05 (d, J =2.13 Hz, 2H,  $\beta$  thiophene), 3.7 (t, J = 2.67 Hz, 1H, 4'H), 3.4 (t, J = 2.35 Hz, 2H, CH<sub>2</sub>Br), 2.0 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.9 (m, 2H,  $CH_2CH_2CH_2Br$ ).

**4,4'-Bis(3-bromopropyl)cyclopenta**[**2,1-***b***;<b>3,4-***b'***]bithiophene (7).** A 1.6 M BuLi solution in *n*-hexane (1.5 mL, 2.4 mmol) was dropped into a solution of **6** (700 mg, 2.34 mmol) in dry THF (20 mL) at -70 °C under nitrogen. 1,3-Dibromopropane (2.1 ml, 20 mmol) was added dropwise, then the cooling bath was removed and the mixture left to stand for 12 hours (hexane : CH<sub>2</sub>Cl<sub>2</sub> 97 : 3). MeOH (5 mL) was added and the solvent removed under reduced pressure. The residue was

treated with water, extracted with ether, then flash chromatographed (hexane : CH<sub>2</sub>Cl<sub>2</sub> 97 : 3). The title product 7 was recovered as a pale-orange solid (710 mg, yield 73%). <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>)  $\delta$  7.21 (d, J = 4.90 Hz, 2H,  $\alpha$  thiophene), 6.96 (d, J = 4.90 Hz, 2H,  $\beta$  thiophene), 3.20 (t, J = 6.56 Hz, 4H, CH<sub>2</sub>Br), 2.10 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.40 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br).

Synthesis of 8. Dry K<sub>2</sub>CO<sub>3</sub> (0.29 g, 2.1 mmol) and 7 (0.72 g, 1.71 mmol) were added to a stirred suspension of calix[4]arene (**3a**) (1.12 g, 1.73 mmol) in dry CH<sub>3</sub>CN (50 mL). The mixture was refluxed for 20 hours, then filtered and evaporated to dryness. Column chromatography (silica gel/petroleum ether : Et<sub>2</sub>O 95 : 5) gave 8 (0.94 g, yield 60%) in a pure state as a colorless solid (dec. 320 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  9.35 (s, 2H, 2 OH), 7.19 (d, J = 4.90 Hz, 2H,  $\alpha$  thiophene), 7.15 (d, J = 4.90 Hz, 2H,  $\beta$  thiophene), 7.10 (s, 4H, H–Ar), 7.04 (s, 4H, H–Ar), 4.36 (d, J = 12.72 Hz, 4H, CH<sub>2</sub>–Ar), 3.41 (d, J = 12.72 Hz, 4H, CH<sub>2</sub>–Ar), 4.08 (broad t, 4H, 2 CH<sub>2</sub>O), 2.45 (broad m, 8H, 2 CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.21 (s, 18H, 2 *t*-Bu), 1.18 (s, 18H, 2 *t*-Bu). EI-MS *m/z* (relative intensity) 906.

Synthesis of monomer 1. A 60% NaH slurry in mineral oil (150 mg, 3.75 mmol) was added portionwise to a stirred solution of 8 (605 mg, 0.67 mmol) in THF-DMF 10 : 1(30 mL). When gas evolution stopped, (CH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub> (0.80 mL, 8.4 mmol) was added, then the mixture was refluxed for 2 hours. Solvent was removed under reduced pressure and the residue treated with a 5% NaOH solution and Et<sub>2</sub>O under stirring. The residue obtained from the organic layer, after the usual work-up, was column chromatographed (silica gel/petroleum ether : Et<sub>2</sub>O 95 : 5) to give 1 in a pure state (219 mg, yield 35%) as a colorless solid with mp > 210 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 (d, J = 5.00 Hz, 2H,  $\alpha$  thiophene), 7.20 (d, J = 5.00 Hz, 2H,  $\beta$ thiophene), 7.15 (s, 4H, H–Ar), 6.60 (s, 4H, H–Ar), 4.40 (d, J =15.00 Hz, 4H, CH<sub>2</sub>-Ar), 3.19 (d, J = 15.00 Hz, 4H, 2 CH<sub>2</sub>-Ar), 3.85 (s, 6H, 2 OCH<sub>3</sub>), 3.76 (t, J = 4.00 Hz, 4H, 2 CH<sub>2</sub>O), 2.60(m, 4H, 2 CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 2.21 (m, 4H, 2 CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.30 (s, 18H, 2 t-Bu), 1.20 (s, 18H, 2 t-Bu). EI-MS m/z (relative intensity) 934. Elemental analysis: calc for C<sub>61</sub>H<sub>74</sub>S<sub>2</sub>O<sub>4</sub>: C 78.17, H 8.06%; found C 78.08 H 7.95%.

Bis(5-tert-butyl-2-hydroxyphenyl)methane. A solution of 4-tert-butylphenol (11.91 g, 79.3 mmol) in dry Et<sub>2</sub>O (25 mL) was added dropwise to a stirred solution of EtMgBr (26 mL, 78 mmol) in dry Et<sub>2</sub>O (70 mL) under nitrogen. Most of the solvent was removed by careful heating and replaced with dry toluene (70 mL), then the mixture was progressively heated to the reflux temperature removing the residual Et<sub>2</sub>O by distillation. After a further addition of dry toluene (150 mL), paraformaldehyde (1.18 g, 39.3 mmol) was added and the mixture refluxed for 3 hours, then treated with water. After the usual work-up, the crude reaction product (12.8 g), constituted by a mixture of oligomers, was flash chromatographed (silica gel/CHCl<sub>3</sub>). The final fractions eluted gave bis(5-*tert*-butyl-2hydroxyphenyl)methane, as a colorless solid (4.84 g, yield 40%) (mp 151–154 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 (d, J = 2.44 Hz, 2H, H–Ar), 7.12 (broad s, 2H, 2 OH), 7.10 (dd,  $J_1 =$  $8.42 \text{ Hz}, J_2 = 2.43 \text{ Hz}, 2\text{H}, \text{H-Ar}), 6.75 \text{ (d}, J = 8.40 \text{ Hz}, 2\text{H},$ H-Ar), 3.95 (s, 2H, CH<sub>2</sub>), 1.30 (s, 18H, 2 t-Bu); EI-MS m/z (relative intensity) 312.

(5-*tert*-Butyl-2-hydroxyphenyl)-(5-*tert*-butyl-2-methoxyphenyl)methane (13). Sodium metal (112 mg, 4.87 mmol) was dissolved into a solution of bis(5-*tert*-butyl-2-hydroxyphenyl)methane (1.37 g, 4.38 mmol) in dry EtOH (35 mL) under nitrogen at room temperature. Iodomethane (692 mg, 4.87 mmol) was added and the solution refluxed for 2 hours at 80 °C. After removal of the solvent, H<sub>2</sub>O and Et<sub>2</sub>O were added and the pH adjusted to 5 with conc. HCl solution. After the usual work-up, the residue of the organic layer was column chromatographed (silica gel/hexane : AcOEt 9 : 1). The central fractions gave **13** as a colorless solid (860 mg, yield = 60%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.33 (d, J = 2.53 Hz, 1H, H–Ar), 7.29 (d, J = 2.51 Hz, 1H, H–Ar), 7.19 (dd,  $J_1 = 8.70$  Hz,  $J_2 = 2.53$  Hz, 1H, H–Ar), 7.11 (dd,  $J_1 = 8.42$  Hz,  $J_2 = 2.52$  Hz, 1H, H–Ar), 7.00 (s, 1H, OH), 6.81 (d, J = 8.70 Hz, 1H, H–Ar), 6.78 (d, J = 8.44 Hz, 1H, H–Ar), 3.96 (s, 3H, OCH<sub>3</sub>), 3.92 (s, 2H, CH<sub>2</sub>), 1.30 (s, 9H, 3 *t*-Bu), 1.28 (s, 9H, 3 *t*-Bu).

Synthesis of monomer 2. A solution of 13 (761 mg, 2.33 mmol) in dry DMF (30 ml) was dropped into a stirred mixture of a 60% NaH slurry in mineral oil (97 mg, 2.42 mmol) and dry DMF (30 ml) under nitrogen at room temperature. The mixture was heated at 40 °C for 20 minutes, then a solution of 7 (482 mg, 1.15 mmol) in dry DMF (50 mL) was added. After 12 hours standing at room temperature, solvent was removed under reduced pressure and the residue treated with Et<sub>2</sub>O and H<sub>2</sub>O. The residue obtained from the organic layer after the usual work-up was column chromatographed (silica gel/hexane : AcOEt 95 : 5) to give 2 as a colorless solid (789 mg, yield 75%) (mp 54-61 °C from *i*-PrOH). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.15–7.07 (m, 6H, H–Ar and  $\alpha$  thiophene), 7.01 (d, J = 2.48 Hz, 2H, H–Ar), 6.83 (d, J = 4.88 Hz, 2H,  $\beta$ thiophene), 6.75 (d, J = 8.50 Hz, 2H, H-Ar), 6.59 (d, J = 8.38 Hz, 2H, H-Ar), 3.90 (s, 4H, 2 CH2-Ar), 3.78 (s, 6H, 2  $OCH_3$ ), 3.65 (t, J = 6.26 Hz, 4H, 2 CH<sub>2</sub>O), 1.94 (m, 4H, 2 CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.29 (m, 4H, 2 CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.21 (s, 18H, 2 t-Bu), 1.18 (s, 18H, 2 t-Bu); EI-MS m/z (relative intensity) 910. Elemental analysis: calc for C<sub>59</sub> H<sub>74</sub>S<sub>2</sub>O<sub>4</sub>: C 77.76, H 8.18%; found C 77.44 H 8.07%.

#### **Electrochemical experiments**

**Chemicals and reagents.** Acetonitrile was distilled twice over  $P_2O_5$  and once over  $CaH_2$ . Tetrabutylammonium perchlorate (Bu<sub>4</sub>NClO<sub>4</sub>) was dried under vacuum at 70 °C. All other chemicals were reagent grade and used as received.

General procedures and apparatus. Experiments were performed at 25 °C under nitrogen in three electrode cells in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> acetonitrile solution. The counterelectrode was platinum; reference electrode was a silver/0.1 M silver perchlorate acetonitrile solution (0.34 V vs. SCE). The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator.

The working electrode for cyclic voltammetry was a platinum minidisc electrode (0.003 cm<sup>2</sup>). For electronic spectroscopy a  $0.8 \times 2.5$  cm<sup>2</sup> indium tin oxide (ITO) sheet (*ca.* 80% transmittance, *ca.* 20 ohm/square resistance, from Balzers, Liechtenstein) was used.

Electronic spectra were taken with a Perkin-Elmer Lambda 15 spectrometer; FTIR spectra on a Perkin Elmer FTIR 2000 spectrometer. The apparatus and procedures used in the *in-situ* conductivity experiments were previously described in detail.<sup>17</sup>

QCM measurements were performed with a platinum-coated AT-cut quartz electrode (0.2 cm<sup>2</sup>), resonating at 6 MHz, onto which the polymers were deposited as thin (*ca.* 10  $\mu$ g cm<sup>-2</sup>) films. Calibration of the quartz crystal microbalance was performed with silver deposition from a  $10^{-2}$  M solution of AgNO<sub>3</sub> in acetonitrile + 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>. The oscillator circuit was home-made and the frequency counter was a Hewlett-Packard mod.5316B. Monitoring of vapor uptake was performed with the QCM inserted in a cell taking part of a closed loop of 5 L, flushed with nitrogen by a gas pump operating at a rate of 2.5 L min<sup>-1</sup> flow. Vapor additions were performed by injecting the solvent as a liquid by means of a microsiringe.

## Acknowledgements

T. Benincori is grateful to the Dipartimento di Chimica Organica e Industriale of the Università degli Studi di Milano for hospitality. S. Rizzo thanks FIRB (Manipolazione molecolare per macchine nanometriche) for financial support. Mrs A. Randi and Mr S. Sitran of CNR are acknowledged for support in the experimental work.

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