Microscopic details of the sensing ability of 15-crown-5-ether functionalized poly(bithiophene)

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ABSTRACT

Host-guest interactions between alkali ions (Li^+, Na^+ and K^+) and a functionalized poly(bithiophene) with a 15-crown-5-ether covalently linked to two adjacent thiophene rings have been analyzed using theoretical methods. Results indicate that the considerable conformational flexibility of the polymer backbone is reduced when the cation accommodates in the cavity of the macrocycle. The enthalphic and entropic contributions to the binding have been estimated using quantum mechanical calculations and molecular dynamics trajectories, respectively. The enthalpic term becomes more favorable when the size of the cation decreases, while the entropy calculated for the "free state → bound state" process decreases when the size of the cation increases. On the other hand, calculated atomic-centered charges reflect that the π-conjugated system of the conducting polymer undergoes a partial oxidation upon the binding process. Moreover, the accommodation of the alkali cation in the macrocycle produces an increase of both the ionization potential and the lowest $\pi-\pi^*$ transition energy of the polymer.

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1. Introduction

Crown ether functionalized polythiophenes (PThs) have been widely acclaimed as one of the most prominent families of chemical sensors [1,2]. Their success lay in the strength of the binding between the cationic species and the ether oxygen atoms, which strongly depends on the chemical nature of the former, combined with the remarkable transport properties, electrical conductivity and rate of energy migration characteristic of PTh-based conducting polymers [3]. Moreover, selectivity towards a specific metal cation can be easily achieved varying the size of the ether macrocycle. Thus, while the macrocyclic crown ether moiety confers the necessary selectivity in the receptor site, the PTh polyconjugated backbone provides the measurable optical and electronic responses desirable in chemical sensors [4,5].

Since Sone and co-workers [6] prepared in 1989 the first crown ether functionalized thiophenes several modifications to improve the sensory performance of such devices have been carried out.
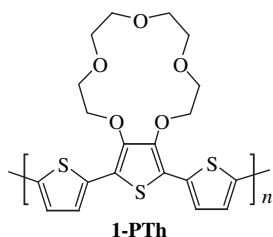
Although the very first attempts did not show a great improvement in terms of selectivity [7–9], crown ethers functionalized PThs displaying a satisfactory sensory response towards alkali cations were synthesized in 1993 by the groups of Swager [10] and Bäuerle [4,5]. Specifically, the crown ether macrocycle was attached directly to the PTh backbone through 3–3′ linkages [10] and through a flexible oxa-alkyl chain affixed in the β position of the thiophene rings [4,5], respectively. Further research in this field was focused in the variation of both the ether macrocycle size as well as the way of linking the crown ether to the PTh chain. Regarding to the latter, it should be remarked that the most common strategies are the variation of the oxa-alkyl length [11,12], the use of a vinilyc linkage [13] and the covalent linking of the ether crown in the thiophene β-positions [12,14–16]. Interestingly, the two later approaches allowed the optimization of the signal transduction by maximizing the electronic interaction between the interaction sites and the π-conjugated chain. More recently, Roncali and co-workers reported a series of macrocyclic oxyethylene-bridged oligo- and polythiophenes in which the oxyethylene groups were attached to the internal β-position of the terminal thiophene units through sulfide linkages. Such molecules showed conformational transitions in presence of Ba^{2+}, Sr^{2+} and Pb^{2+} [17–19].

Recently, we investigated *in silico* the effects of crown ethers attached to the 3 and 3′ positions of the same thiophene unit

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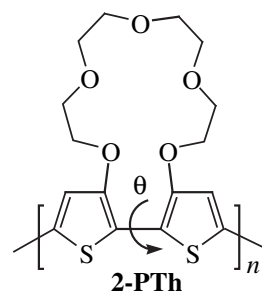
Scheme 1. Molecular structure of polythiophene functionalized with 15-crown-5-ether attached to the 3 and 3′ positions of the same thiophene ring.

(abbreviated 1-PTh; Scheme 1) on the structural and electronic properties of the PTh backbone [20] as well as their affinity for alkali ions [21]. Quantum mechanics (QM) calculations led to conclude that the size of the ether crown does not affect neither the effective conjugation of the PTh backbone nor its conformational preferences. In spite of QM calculations evidenced that the attractive character of the binding energy between neutral conducting polymers and alkali ions increases as the size of the ion decreases, Molecular Dynamics (MD) simulations explained the experimental selectivity towards Na^+ with respect to Li^+ in basis of the entropic contribution.

Among the aforementioned PThs derivatives, that functionalized with a 15-crown-5-ether attached to the 3 and 3′ positions of adjacent thiophene rings (abbreviated 2-PTh; Scheme 2), where 15 is the total number of non-hydrogen atoms contained in the cyclic polyether and 5 is the number of ether oxygen atoms, shows an excellent selectivity towards Na^+ with respect to the Li^+ and K^+ alkali cations [10,22]. It should be noted that in 2-PTh the macrocycle is attached to a bithiophene repeating unit, which represents a significant difference with respect to 1-PTh, *i.e.* formally 2-PTh is a poly(bithiophene) (PbTh) derivative. Although the sensory mechanism of this detector is expected to be ruled by a conformational shift in the crown ether when the cation is complexed, no microscopic information about these mechanistic aspects has been reported yet. The main objectives of this work can be summarized as follows: (i) examine the effect of the crown ether on the internal rotation of the bithiophene unit of 2-PTh and the changes induced by the binding of the alkali-metals (Li^+, Na^+, and K^+); (ii) determine the binding energies of complexes formed by 2-PTh and alkali-metal ions; (iii) ascertain the influence of the binding in the electronic properties of conducting material, *i.e.* the electron transfer, the charge distribution, the ionization potential (IP) and the lowest $\pi-\pi^*$ transition energy (ε_g). It should be emphasized that no previous molecular study about the sensing abilities of a restrained polythiophene derivative, *i.e.* a system with the macrocycle simultaneously attached to two repeating units, has been previously reported. Therefore, microscopic details provided by both QM calculations and MD simulations are expected to be particularly useful to ascertain the advantages of this kind of molecular architecture with respect to the simplest one, *i.e.* that in which each macrocycle is linked to a single repeating unit.

2. Methods

Both QM calculations and MD simulations were performed considering a model molecule of 2-PTh with $n = 1$ (see Scheme 2). All QM calculations were performed using the Gaussian 03 computer program [23]. Geometry optimizations were carried out in the gas phase using the B3LYP method [24,25] combined with the 6-31+(d,p) basis set [26]. The energy profile associated to the rotation of the inter-ring dihedral angle θ (Scheme 2), $E = E(\theta)$, was computed in absence and presence of alkali-metals using the flexible rotor approximation, *i.e.* each point of the path was

Scheme 2. Molecular structure of poly(bithiophene) functionalized with the crown-ether attached to the 3 and 3′ positions of adjacent thiophene rings.

obtained from geometry optimization of the whole molecule at a fixed value of θ, the inter-ring dihedral angle S-C-C-S being scanned in steps of 30°. Minimum-energy conformations were derived from complete geometry optimizations. All the calculations of complexes involving alkali-metals were performed using the unrestricted formalism of the B3LYP functional, *i.e.* UB3LYP. Binding energies were calculated as the difference between the total energy of the optimized complex and the energies of the isolated monomers, the basis set superposition error being corrected by applying the counterpoise method [27].

All classical calculations were performed using the NAMD program [28]. The preliminary exploration of the potential energy hypersurfaces of the planar and twist conformations of the crown ether in 2-PTh was performed using a procedure based on consecutive series of heating-cooling MD cycles, following the principles of classic simulated annealing strategy [29,30]. For each conformation, a randomly generated arrangement was brought to 900 K, and that temperature was kept for 50 ns, coordinates and velocities being stored every 100 ps. These 500 structures were cooled down to 298 K at a rate of 6 K per 25 ps, and subsequently, their conformational energies were minimized applying 3×10^3 steps of conjugated gradient.

Force-field parameters for 2-PTh, with the exception of electrostatic ones, were taken from the AMBER99 libraries [31,32]. The molecular electrostatic potential (MEP) was computed at the (U)HF/6-31G(d) level for 2-PTh. Partial charges were obtained by fitting the rigorously defined quantum mechanical molecular electrostatic potential to the coulombic electrostatic potential [33]. The solvent structure was described by using the dichloromethane all-atom model of the AMBER libraries [34].

Each 2-PTh···M^+ (with $M^+ = Li^+$, Na^+, and K^+) complex was placed in the center of an orthorhombic simulation box filled with 578 dichloromethane solvent molecules, which was previously equilibrated under NPT conditions (temperature 298 K and 1 atm of pressure). Initially, the conformation of the 2-PTh was kept frozen at that provided for the corresponding complex by QM calculations. Systems were relaxed to the experimental density value by performing new NPT-MD simulations with the solute frozen (Belly conditions). Before running MD trajectories, each simulation box was equilibrated as a whole system, that is, solute plus solvent molecules, by using the following strategy. First, 3×10^3 steps of energy minimization were performed to relax conformational and structural tensions. After this, different consecutive rounds of short MD runs were performed: 0.2 or 0.4 ns of NVT-MD (thermal relaxation, NVT: constant composition, volume and temperature) followed by 1 ns of isobaric relaxation (NPT-MD). Both temperature and pressure were controlled by the weak coupling method, the Berendsen thermo-barostat [35], using a time constant for the heat bath coupling and a pressure relaxation time of 1 ps. All the NPT-MD production simulations were 10 ns long, the numerical integration step being 1 fs. Coordinates were stored every 1000 steps (2 ps intervals) for subsequent analysis.

In all the simulations, the bond lengths and angles of the thiophene rings were kept fixed to the values provided by quantum mechanical calculations, whereas the 15-crown-5-ether macrocycles and the solvent molecules were not restrained. Periodic boundary conditions were applied by using the nearest image convention, the nonbonded pair list being updated every 20 MD steps. Atom-pair distance spherical-cut-offs were applied to all nonbonding interactions at 14 Å. To avoid discontinuities in both the Lennard-Jones and the electrostatic potentials, a switch function was applied to allow a continuum decay of energy when atom pair distances are larger than 12 Å.

3. Results and discussion

3.1. Effect of the crown ether on the conformation of poly (bithiophene): comparison with other functionalized polythiophene derivatives

Polymer backbone conformation plays a crucial role on the properties of PTh derivatives since deviation of the inter-ring dihedral angles from planarity has always strong impact on the π-electronic structure and, consequently, on the electrical and optical properties. In the first stage of this investigation, MD simulations were used to generate representative arrangements of both the planar and twisted conformations of the crown ether in 2-PTh. Specifically, the preliminary exploration of the potential energy hypersurfaces of such two conformations was performed applying the conventional simulated annealing strategy [29,30], as is explained in the Methods section. In order to locate the most stable arrangement of each conformation, the 10 structures of lower energy for each set were fully optimized at the B3LYP/6-31 + G(d,p) level. The most stable arrangement of each conformation was used as starting point to compute the $E = E(\theta; planar)$ and $E = E(\theta; twisted)$ profiles on a model system formed by a single bithiophene repeating unit ($n = 1$ in Scheme 2). The final potential energy curve $E = E(\theta)$, which is displayed in Fig. 1, was constructed by mixing the $E = E(\theta; planar)$ and $E = E(\theta; twisted)$ profiles. Thus, for each value of θ the energy of the structures calculated for the planar and twisted profiles were compared and the most stable one was selected for its incorporation in $E = E(\theta)$.

Interestingly, the lowest energy minimum was found at $\theta = 62.2°$, which corresponds to a conventional syn-gauche$^+$ conformation. This result is very similar to that found in a previously reported sensor based on complex calix[4]arene macrocycles attached to adjacent thiophene rings either through QM and MM calculations [36,37] or through X-ray crystallography and NMR spectroscopy [38].
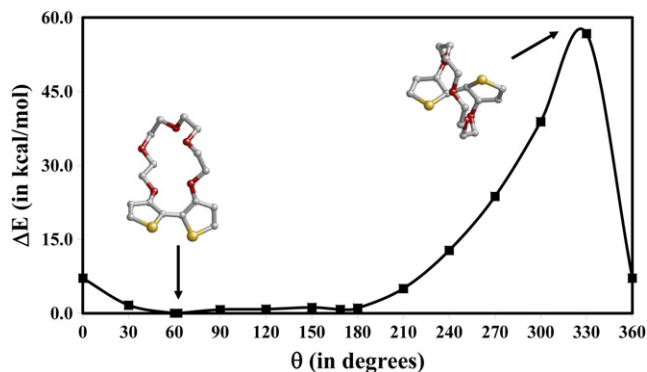
Furthermore, 2-PTh shows a local minimum at $\theta = 168.7°$ (anti conformation), which is 0.8 kcal mol^{-1} less stable than the global one. This value is very close to the inter-ring dihedral angle found for the lowest energy structure of 1-PTh ($\theta = -168.9°$) [21].

The energy profile shows that the accessible conformations of 2-PTh are those comprised between the syn-gauche$^+$ and anti ones, i. e. the energy relative to the global minimum is lower than 1.7 kcal mol^{-1} for values of θ comprised between 30° and 180°. Thus, the inter-ring conformational flexibility is higher for this crown ether functionalized PbTh than for the aforementioned calix[4]arene based sensor, even though in both cases the macrocycles were attached to the bithiophene repeating unit. Thus, in the calix[4]arene derivative the accessible conformations were restricted to those comprised between the syn-gauche$^+$ ($\theta = 30°$) and gauche–gauche$^+$ ($\theta = 120°$) [36]. This must be attributed to the fact that the conformational flexibility of the 15-crown-5-ether is significantly higher than that of the calix[4]arene, in which the only flexible dihedral angles are those associated to the methylene bridging groups, i.e. the methylene groups allow the rotation of the rigid phenolic rings. On the other hand, the energy penalty associated to conformations outside the aforementioned θ range is very high in 2-PTh. More precisely the rotation of θ provokes geometric strain that is alleviated by deforming not only bond angles but also some bond lengths, like the inter-thiophene C^α–$C^{\alpha'}$ linkage [36].

The potential energy curve $E = E(\theta)$ allows explain the different ionochromic responses of the 15-crown-5 and calix[4]arene PbTh derivatives, even though both materials are highly selective sensors towards Na$^+$ with respect to Li$^+$ and K$^+$. Thus, the rotational freedom is more restricted in the calix[4]arene derivative than in 2-PTh, i.e. the planar anti is energetically unfavored and favored, respectively, which agrees with the fact that the shift in the UV–vis absorption spectrum upon Na$^+$ exposure is smaller in the former sensor ($\Delta\lambda_{max} = 32$ nm) [38] than in the latter one ($\Delta\lambda_{max} = 91$ nm) [10].

On the other hand, the conformational flexibility of 2-PTh is severely limited with respect to that of 1-PTh because in the macrocycle of the former is linked to different thiophene rings. On the other hand, the highest energy barrier calculated at the B3LYP/6-31G(d) level for different analogues of 1-PTh, which differs in the size of the macrocycle, i.e. 9-crown-3-ether, 12-crown-4-ether and 15-crown-5-ether functionalized PThs, was comprised between 6.0 and 7.0 kcal mol^{-1} [20]. This barrier was also predicted to be 6.0 kcal mol^{-1} for poly(3,4-ethylenedioxythiophene) [39]. Moreover, in all these compounds the global minimum was found at $\theta \approx 180°$. These results and those displayed in Fig. 1 indicate that the influence of the crown ether conformation on the polymer backbone is significantly lower when the macrocycle is attached to a single thiophene ring than to a bithiophene repeating unit.

3.2. Changes induced by the binding of alkali-metals in the conformation of the crown ether functionalized poly(bithiophene)

Fig. 2 shows the potential energy curves $E = E(\theta)$ of complexes formed by a model system of 2-PTh ($n = 1$ in Scheme 2) and an alkali-metal ion M$^+$ (M = Li, Na and K). For each value of θ the initial structure of 2-PTh was taken from the $E = E(\theta)$ curve obtained for the non-complexed system (Fig. 1), whereas M$^+$ was located close to the geometric center of the 15-crown-5-ether receptor. The global minimum obtained for 2-PTh$\cdots$Li$^+$ and 2-PTh$\cdots$K$^+$ complexes, i.e. $\theta = 48.5°$ (syn-gauche$^+$) and $\theta = 87.4°$ (gauche–gauche$^+$), respectively, are displaced with respect that found for non-complexed 2-PTh. In opposition, the standard syn-gauche$^+$ conformation, $\theta = 60.1°$, was kept as the global minimum for the 2-PTh$\cdots$Na$^+$ complex. This fact suggests that the 15-crown-5-ether cavity owns the suitable size to host the Na$^+$, whereas a re-arrangement of the receptor is necessary to accommodate Li$^+$ and K$^+$.
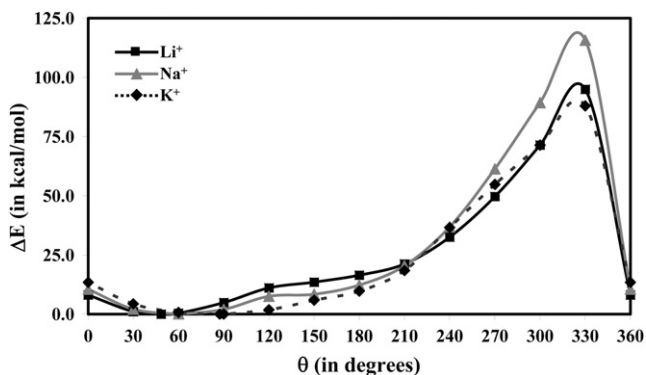

Fig. 1. Potential energy curve for the internal rotation of 2-PTh ($n = 1$ in Scheme 2) as a function of the inter-ring dihedral angle (θ) at the B3LYP/6-31 + G(d,p) level of theory. Energies are relative to the global minimum.

Fig. 2. Potential energy curve for the internal rotation of 2-PTh···M$^+$ ($n = 1$ in Scheme 2) complexes with M$^+$ = Li$^+$, Na$^+$, K$^+$ as a function of the inter-ring dihedral angle (θ) at the B3LYP/6-31 + G(d,p) level of theory. Energies are relative to the global minimum.

The variation in the value of θ induced by M$^+$ is less pronounced in 2-PTh···M$^+$ than in 1-PTh···M$^+$, the inter-ring dihedral angle of 1-PTh underwent variations of around 30°–45° upon complexation with an alkali cation [21]. On the other hand, the accommodation of the alkali cation in the receptor produces a drastic reduction of the accessible conformations to the 2-PTh backbone. Thus, θ is restricted to the *syn-gauche*$^+$ conformation for Li$^+$ and Na$^+$ and to both the *syn-gauche*$^+$ and *gauche–gauche*$^+$ for K$^+$. In all the cases the *anti* conformation ($\theta = 180.0°$) is energetically disfavored with respect to the global minimum, the energy penalty being 16.5, 12.3 and 9.7 kcal mol^{-1} for Li$^+$, Na$^+$ and K$^+$, respectively.

The global minimum found for each of the three 2-PTh···M$^+$ complexes is depicted in Fig. 3. Inspection of the O···M$^+$ distances allows to conclude that in all the cases the cation is placed in the geometric center of the cavity. Thus, alkali cations are penta-coordinated with the five oxygen atoms of the crown ether. Comparison with the results previously obtained for 1-PTh···M$^+$ complexes [21] indicates that the attachment of the receptor to a bithiophene rather than to a single thiophene unit improves the coordination pattern.

3.3. Binding energies and entropies of complexes formed by crown ether functionalized poly(bithiophene) and alkali-metals

The binding energies ($E_{b,CP}$) of the complexes calculated applying the CP method [27] are −101.8, −78.6 and −54.5 kcal/mol for complexes involving Li$^+$, Na$^+$ and K$^+$, respectively. The strength of the binding decreases with the radius of the ion, which is consistent with results previously obtained for 1-PTh···M$^+$ complexes [21]. The order of affinity predicted by the $E_{b,CP}$ values, Li$^+$ > Na$^+$ > K$^+$, does not agree with the experimental observations (Na$^+$ > Li$^+$ > K$^+$) [10]. This deficiency should be attributed to the fact that QM calculations only provide information about the enthalpic component of the binding, whereas a significant entropic contribution is expected in those complexes in which size of the alkali cation is not appropriated to fit perfectly within the cavity of the crown ether macrocycle.

In order to ascertain the influence of the entropy on the affinity of 2-PTh towards Li$^+$, Na$^+$ and K$^+$, 10 ns of NPT (constant composition, pressure and temperature) Molecular Dynamics (MD) simulations were performed in dichloromethane solution. Fig. 4 shows the temporal evolution of the distance from the alkali ion to the geometric center of the macrocycle (D). The Na$^+$ accommodates in the center of the crown ether cavity after 1 ns, keeping this position throughout the rest of the trajectory. On the other hand, the K$^+$ approaches the crown ether in 0.9 ns remaining close to the
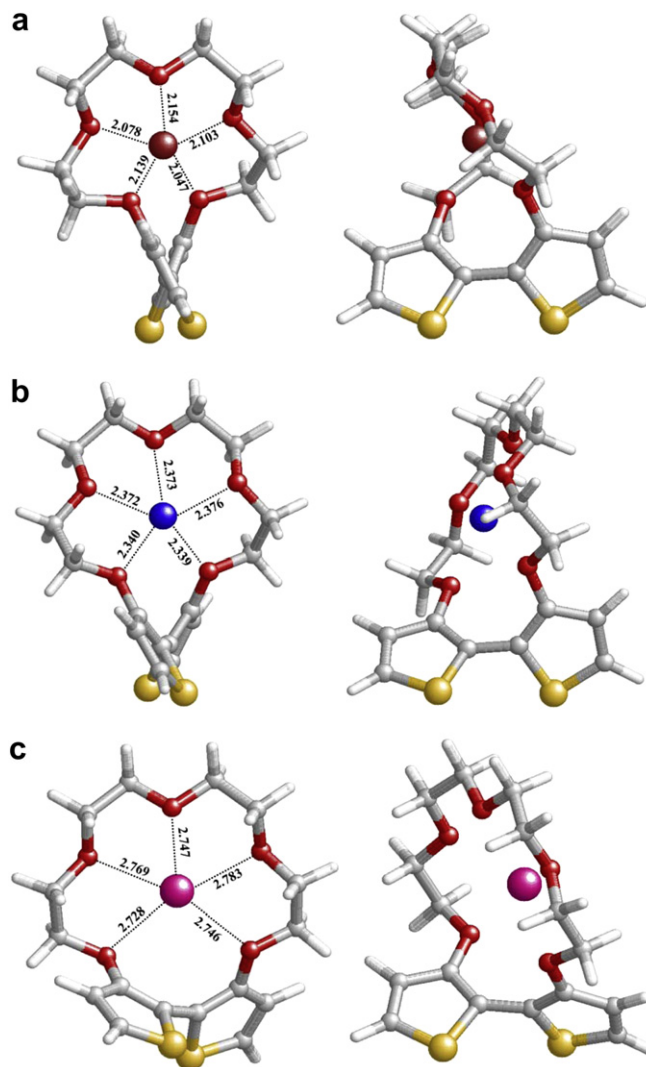

Fig. 3. Two projections of the minimum-energy structures obtained for 2-PTh···M$^+$ ($n = 1$ in Scheme 2) complexes with M$^+$ = Li$^+$ (a), Na$^+$ (b), and K$^+$ (c). The O···M$^+$ distances [Å] are displayed in all cases.

center of the receptor during almost the whole trajectory, *i.e.* it moves out once at 2.0 ns for a very short time and in the last ps of the trajectory. Regarding to the Li$^+$, its position with respect to the geometric center of the crown ether undergoes large fluctuations throughout the whole trajectory. The averaged D value is 3.96 ± 0.71, 1.50 ± 0.35 and 3.45 ± 0.31 Å for Li$^+$, Na$^+$ and K$^+$, respectively.

MD results evidence that the affinity of 2-PTh towards Li$^+$ is considerably affected by the entropy, whereas the affinity towards Na$^+$ and K$^+$ is mainly ruled by the enthalpy. The relative entropy (ΔS) was estimated using the method originally developed by Schlitter [40] and later improved by van Gunsteren and co-workers [41]. The entropies of the free state were determined by using MD trajectories (4 ns) in which the ions remained relatively distant from the receptor, *i.e.* no complex was formed. The ΔS values calculated for the formation of the 2-PTh···M$^+$ complexes (free state → bound state) are 5.64, 2.75 and 1.22 cal K^{-1} mol^{-1} for Li$^+$, Na$^+$ and K$^+$ respectively. These values should be attributed to the relationship between the size of the alkali cation and the thermal breathing of the macrocycle. The small size of Li$^+$ allows large fluctuations of the cavity, while the conformational flexibility of the crown ether is reduced by Na$^+$ and K$^+$. The entropic component
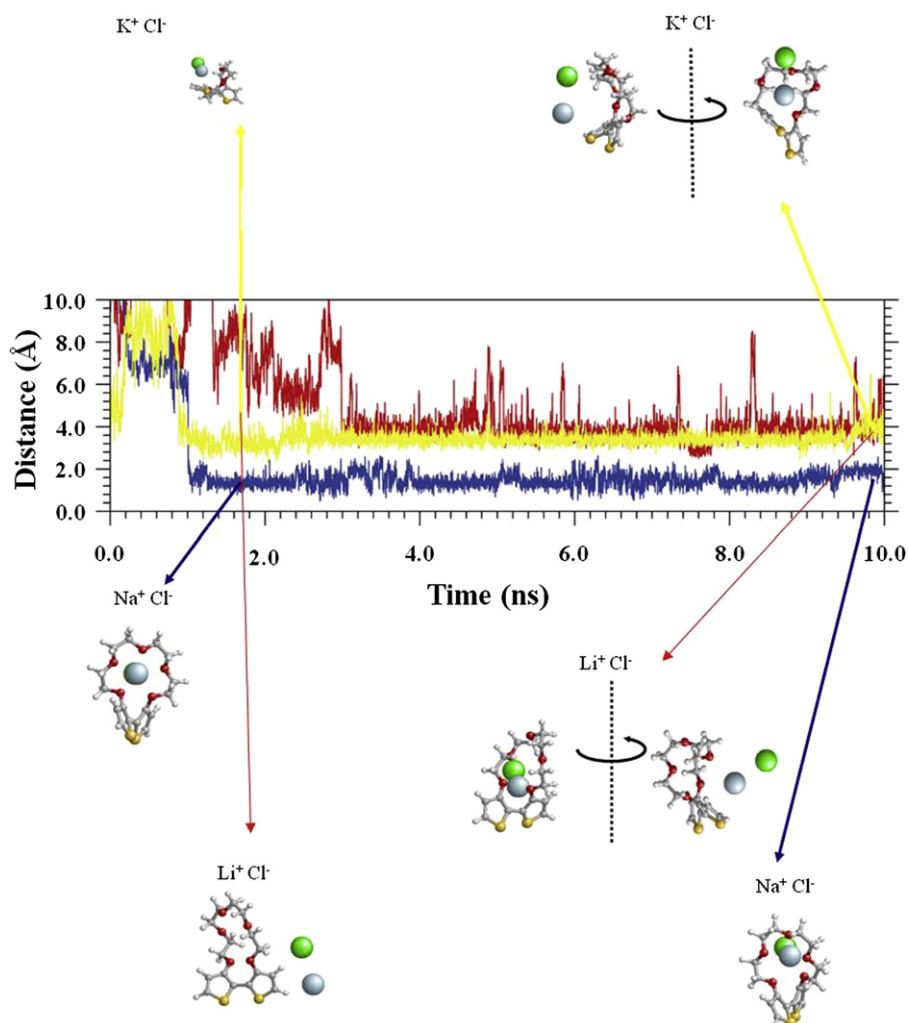
Fig. 4. Evolution of the distance from the alkali cation to the geometric center of the 15-crown-5-ether macrocycle (*D*) derived from NPT-MD simulations in dichloromethane solution of 2-PTh···M$^+$ (*n* = 1 in Scheme 2) complexes with M$^+$ = Li$^+$ (red line), Na$^+$ (blue line) and K$^+$ (yellow line). The insets show selected snapshots for each 2-PTh···M$^+$ complex: M$^+$ and Cl$^-$ are represented as grey and green balls, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

reduces the high affinity of 2-PTh towards Li$^+$ predicted by QM calculations, in which the enthalpic was the only term considered.

3.4. Effect of the binding on the electronic properties of the functionalized poly(bithiophene)

Atom-centered electrostatic charges were derived from the quantum mechanical electrostatic potentials calculated for the geometries optimized at the B3LYP/6-31 + G(d,p) level. The charges on the alkali cation (Q_M) and the thiophene rings (Q_{Thp}), which were estimated as the sum of the corresponding atom-centered charges, are summarized in Table 1. In all cases the cation produces a partial oxidation of the π-conjugated system, as reflects the enhancement of the positive charge hosted in the thiophene rings. The charge transfer induced by M$^+$ decreases in the order Li$^+$ > K$^+$ > Na$^+$, which represents a significant difference with respect to the 1-PTh···M$^+$ complexes [21]. More specifically, a significant enhancement of the charge transfer was detected for the K$^+$ when the macrocycle is attached to a bithiophene repeating unit.

In order to get a deeper insight into the influence of the complexation on the electronic properties, the ionization potentials (IP) as well as the lowest π−π* transition energies (ε_g) calculated for the minimum-energy structures of the uncomplexed 2-PTh as

well as for the three 2-PTh···M$^+$ complexes are included in Table 1. The evaluation of ε_g was performed using the time-dependent density functional theory (TD-DFT) [42], electronic excitations being evaluated at the B3LYP/6-31 + G(d,p) level using the previously optimized geometries. On the other hand, the IP of each system was estimated using the Koopmans' theorem (KT) [43]. As can be seen, in all cases complexation of 2-PTh leads to increase the IP value, such increment ranging from 3.27 (Na$^+$) to 3.50 eV (K$^+$). This behavior is in complete agreement with the aforementioned partial oxidation underwent by the thiophene rings when complexed with alkali cations. On the other hand, the increase in the ε_g

Table 1
Charge on each thiophene ring[a] (Q_{Thp}; in e.u), electrostatic charge on the alkali cation (Q_M; in e.u.), ionization potential (IP; in eV) and lowest π−π* transition energy (ε_g; in eV) obtained for the investigated systems at the B3LYP/6-31 + G(d,p) level.

System	$Q_{Thp,1}$	$Q_{Thp,2}$	Q_M	IP	ε_g
2-PTh	—	—	—	5.37	4.01
2-PTh ···Li$^+$	0.277	0.227	0.618	8.70	4.24
2-PTh ···Na$^+$	0.233	0.248	0.694	8.64	4.35
2-PTh ···K$^+$	0.295	0.373	0.691	8.87	4.46

[a] The charge on the π-conjugated system was obtained by summing the electrostatic atom-centered charges.

upon complexation is less pronounced, *i.e.* the increment ranges from 0.23 to 0.45 eV, but proportional to the cation size.

4. Conclusions

This work reports a comprehensive study about the structural and electronic properties of 2-PTh, a crown ether functionalized poly (bithiophene) in which each macrocycle is covalently linked to a bithiophene repeating unit. The calculated potential energy curve $E = E(\theta)$ indicates that, in spite of the restrictions imposed by the macrocycle, the polymer backbone presents a significant degree of conformational flexibility. However, such flexibility is significantly reduced when an alkali cation is accommodated in the cavity of the macrocycle. Furthermore, with the exception of Na^+, whose size is appropriated to fit in the cavity of the receptor, the accommodation of a cation in the receptor provokes a significant conformational change.

Although in the three 2-PTh$\cdots M^+$ complexes the alkali cation occupies the geometric center of the macrocycle and is penta-coordinated with the ether oxygen atoms, the weight of the enthalpic and entropic contributions to the binding is different in each case. Thus, QM calculations predict that the order followed by the enthalpic contribution is $Li^+ > Na^+ > K^+$. However, MD trajectories on both complexed and uncomplexed systems indicated that the entropic contribution reduces the affinity of 2-PTh towards Li^+.

On the other hand, the alkali cation produces a partial oxidation of 2-PTh, as evidenced the accumulation of positive charge on the thiophene rings. The charge transfer induced by the K^+ has been found to be high in comparison with that reported for other receptors. The binding of M^+ alters both the IP and the ε_g, the increment found for the former being particularly remarkable. The increase of these electronic properties is consistent with the partial oxidation of the π-aromatic system.

Acknowledgements

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