Cite this: Phys. Chem. Chem. Phys., 2011, 13, 11965-11975

www.rsc.org/pccp

Electronic structure and absorption spectra of supramolecular complexes of a fullerene crown ether with a π -extended TTF derivative^{†‡}

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Received 25th November 2010, Accepted 5th May 2011 DOI: 10.1039/c0cp02665d

The present work is a theoretical investigation on supramolecular complexes of a fullerene crown ether (A and B isomers) with a derivative of π -extended tetrathiafulvalene (T). The geometry and the electronic structure of seven different conformers of the complex of dibenzo-18-crown-6 ether of fullero-N-methylpyrrolidine with a N-benzyl-N-(4-{[9,10-bis(1,3-dithiol-2-vlidene)-9,10dihydroanthracen-2-yl]ethynyl}benzyl)ammonium cation were determined. We calculated the complexation energies and the absorption spectra, *i.e.*, the lowest 50 excited electronic states of the complexes have been determined at the ground state optimum geometry. All calculations were carried out employing the density functional theory (DFT) and the time-dependent DFT, using the B3LYP, CAM-B3LYP, ωB97X-D, and M06-2X functionals in conjunction with the 6-31G(d,p) basis set. Various types of van der Waals interactions are observed in the complexes. Conformer complexation energies (CE) range from 2.54 to 2.14 eV in the gas phase and from 1.75 to 1.34 eV in CHCl₃ solvent at the ω B97X-D/6-31G(d,p)//M06-2X/6-31G(d,p) level of theory. There are three major features at about 390, 330, and 290 nm in the calculated absorption spectra of all the conformers. The major peaks correspond to $\mathbf{T} \rightarrow \mathbf{T}, \mathbf{T} \rightarrow \mathbf{T}/\mathbf{F}$ (electron density in both T and the fullerene F of B) and to $T \rightarrow F$ transitions, depending on the particular conformer. Other charge transfer $T \rightarrow F$ transitions are observed close to the $T \rightarrow T$ transition, indicating the possibility of photoinduced electron transfer in all these complexes.

I. Introduction

Crown ethers have stimulated considerable interest since their discovery.¹ They have interesting properties and they are particularly adaptable hosts for a large number of guests.^{2–4} During recent years the complexation of crown ethers with many guests has been investigated both experimentally and theoretically.^{2–5}

Fullerene C_{60} has been successfully used as an electron acceptor in the construction of model photosynthetic systems due to its remarkable photophysical, electrochemical and chemical properties,⁶ while π -extended tetrathiafulvalene (exTTF) derivatives have been employed as electron donors. Additionally, exTTF has proved to have exceptional properties for the stabilization of the charge-separated states generated

upon light irradiation.⁶ Recently, the formation of supramolecular complexes of different exTTF derivatives with fullerene crown ethers has been achieved by a "threading" of the exTTF containing ammonium salt through the CrE moiety, and in this manner stable 1:1 complexes between exTTF and fullerene have been achieved.^{6,7} The formation of complexes of exTTF with fullerene is associated with changes in the vis-UV spectra.^{6–8} The new absorption maxima are associated experimentally and theoretically with the formation of charge-transfer states.⁹ Similarly, other supra-molecular systems involving CrE that can mimic the photosynthetic process have potential for applications in photonic, photocatalytic, and optoelectronic devices.^{10–12}

The present work is a continuation of our previous study on the electronic and geometric structures of dibenzo-12-crown-4, dibenzo-18-crown-6, dibenzo-24-crown-8 ethers, and dibenzo-18-crown-6 ether of fullero-*N*-methylpyrrolidine and their complexes with $(CH_3)_x NH_{4-x}^+$, x = 0-4 in the gas phase and in CHCl₃ solvent.⁵ In the present work a theoretical study on the ground and excited electronic states of a supramolecular complex of dibenzo-18-crown-6 ether of fullero-*N*-methylpyrrolidine with a π -exTTF derivative is presented. One of the objectives of the present study is to determine the stability and the binding in the main conformers of the above complex by geometry optimization calculations on the ground electronic

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[†] Based on a presentation at the The Fullerene Silver Anniversary Symposium, "FSAS-2010" held in Crete, Hellas, on October 4–10, 2010.

[‡] Electronic supplementary information (ESI) available: Table S1: absolute energies of the **T**, **A**, **B**, benzene₂, C₆₀-benzene, **AT**, and **BT** systems. Coordinates of all the **AT** and **BT** optimum structures. See DOI: 10.1039/c0cp02665d

state. A further objective is the calculation of the excited electronic states and the absorption spectra of the different conformers, as well as, the determination of the effect of the different types of bonding in the minima, on their excited electronic states and their absorption spectra. The effect of solvation is also calculated. It might be noted that the study of functionalization of fullerene by attachment in a non-covalent manner *i.e.* in a manner that preserves it's characteristics, which is required in different applications as for example for the functionalization of fullerene nano-structures,¹³ is of particular interest and very important.

In what follows, in Section II we define the computational procedure, in Section III we discuss our results and in Section IV we summarize our findings.

II. Computational procedure

In our previous paper,⁵ we calculated five minima of the dibenzo-18-crown-6 ether of a fullero-*N*-methylpyrrolidine molecule. Their harmonic frequencies were calculated in order to prove that they are true minima.⁵ The two lowest minima are energetically degenerate and they differ in the direction of the crown ether, namely up (**A**) or down (**B**) with respect to fullero-*N*-methylpyrrolidine, see Fig. 1. In the present study, the supramolecular complexes of the two lowest minima **A** and **B** of the dibenzo-18-crown-6 ether of fullero-*N*-methylpyrrolidine with a π -exTTF derivative **T** *i.e.*, the *N*-benzyl-*N*-(4-{[9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl]-ethynyl}benzyl) ammonium cation, were investigated in the gas phase and in CHCl₃ solvent.

In total, 7 different low-lying in energy minima of the complex have been identified, see Fig. 1. The isomers were determined as follows: conformations that were most likely to be the energy lowest isomers were constructed. These are complexes of the minima of the crown ethers A and B with the π -exTTF derivative cation **T** at different positions, *i.e.*, the two H atoms of the N atom interact with different O atoms of the crown ether and some of the H atoms of the CH₂ or phenyl groups interact with the O atoms of the crown ether. Moreover, structures that include additional interactions between the TTF and C₆₀ and/or interactions between phenyl groups were considered. The full optimization of these structures leads to 7 different minima in the gas phase. The coordinates of all the optimized structures are included in the ESI.[‡] Single point calculations in CHCl₃ solvent were performed employing the polarizable continuum model (PCM)¹⁴ using the integral equation formalism variant.¹⁵ The PCM model is divided into a solute part lying inside a cavity, surrounded by the solvent part represented as a structureless material characterized by its macroscopic properties, i.e., dielectric constants and solvent radius. A review on PCM is given in ref. 16. This method is one of the most often used and reliable continuum solvation procedures.15-17

The calculated minima were fully optimized using the B3LYP, CAM-B3LYP, and M06-2X functionals in conjunction with the 6-31G(d,p)¹⁸ basis set in the gas phase and in CHCl₃ solvent. B3LYP is a DFT functional using Becke's three parameter gradient corrected functional¹⁹ with the gradient corrected correlation of Lee *et al.*²⁰ B3LYP is a widely used

functional and generally works well for main group chemistry. The CAM-B3LYP²¹ functional was employed, in addition to the B3LYP, for the calculations of excitation energies for all the systems of interest in the present work because TDDFT/ B3LYP calculations have been reported to underestimate the excitation energies to charge-transfer states.^{21,22} CAM-B3LYP has been developed to correct for the long-range behaviour and thus considered as more appropriate for calculation of the involvement of the charge transfer states in the absorption spectra of the complexes.²¹ M06-2X²³ is a hybrid meta exchange correlation functional, a highly nonlocal functional with double the amount of nonlocal exchange and is recommended for the study of non-covalent interactions.²⁴ The decision to employ these three functionals was based on the conclusions of our previous study on fullerene crown ether complexes employing DFT (B3LYP, M05-2X, M06-2X, MPWBIK and B2PLYP-D) in conjunction with three basis sets.⁵ Moreover, the ω B97X-D functional²⁵ was employed. This functional includes 100% long-range exact exchange, a small fraction of short-range exact exchange, a modified B97 exchange density functional for short-range interaction, and empirical dispersion corrections.²⁵

Furthermore, the applicability of the above four functionals, i.e., B3LYP, CAM-B3LYP, M06-2X, and ω B97X-D, and of the M06-HF and B97D functionals, to the present calculations was investigated by a preliminary study on geometry optimization of the benzene dimer and the fullerene-benzene system, see Fig. 2. M06-HF is a hybrid meta functional that includes 100% HF exchange and is especially suited to the description of charge-transfer electronic states.²³ B97D is a semiempirical generalized gradient approximation type functional constructed with a long-range dispersion correction.²⁶ The benzene dimer is considered as a prototype system for the evaluation of the performance of different functionals for dispersion forces between nonpolar molecules (see below for details). These test calculations are appropriate given that in all minimum energy structures there exist interactions between two phenyl groups and/or fullerene-phenyl species.

For all minima determined at all levels of theory, basis set superposition error (BSSE) corrections were made using the counterpoise procedure^{27,28} since such corrections are especially important for van der Waals (vdW) systems²⁹ which is the case of the complexes calculated here. Thus, in the calculation of all the complexation energies the BSSE has been taken into account.

For the calculation of the absorption spectra of the calculated minima, the singlet-spin excited electronic states of the separate species and of their complexes of Fig. 1 have been calculated by Time Dependent DFT $(TDDFT)^{30}$ calculations. The first step in the photoinduced charge-transfer is the absorption of radiation by the chromophore, and in the present work by **T**, and therefore it is required to calculate the excited states at least up to the absorption energies of the donor **T**. Thus, in the TDDFT calculations it was necessary to include a large number of excited states, about 50 excited states, in order to reach the **T** absorbing states because there exist many fullerene excited states at lower excitation energies. The calculations were carried out in the gas phase and in CHCl₃ solvent, so as to examine the solvent effect to the



Fig. 1 T: exTTF derivative; A and B: conformers of dibenzo-18-crown-6 ether of fullero-*N*-methylpyrrolidine viewed from two different angles; AT1–AT5 complexes of A and T; BT1–BT2 complexes of B and T. BSSE corrected energy differences from the most stable structure are shown in the gas phase (in CHCl₃ solvent) at the M06-2X/6-31G(d,p), first line, at the ω B97X-D/6-31G(d,p)//M06-2X/6-31G(d,p), second line, and at the ω B97X-D/6-31G(d,p), third line. (H atoms = white spheres, C = grey spheres, S = yellow spheres, O = red spheres and N = blue spheres).

absorption spectrum. In addition, the absorption spectra of all seven minima were calculated to examine how the different geometries of the conformers can lead to differences in the general shape of the calculated spectra and to the transitions which corresponds to the major absorption peaks.



Fig. 2 The parallel displaced minimum of the benzene dimer and C_{60} -benzene system.

All calculations were performed using the Gaussian 09 program package.³¹

III. Results and discussion

As mentioned above, we carried out some calculations on two model systems, on the benzene dimer and on the fullerenebenzene system, see Fig. 2 and Table 1. The benzene dimer is a prototype for dispersion forces between nonpolar molecules and has received much attention both from experimentalists and theorists.³²⁻³⁶ Its two minima a T-shaped one and a parallel-displaced one are energetically very close. The T-shaped structure is about 30 cm⁻¹ more stabilized than the parallel-displaced one.³⁵ Our test calculations on geometry optimization of the benzene dimer involved the parallel-displaced structure, to see how well our functionals using the 6-31G(d,p)basis set can predict the dimer. As shown in Table 1, the ω B97X-D/6-31G(d,p) method results in complexation energies without (CE_u) and with BSSE correction (CE) of 0.18 eV and 0.10 eV, respectively, practically the same with 0.11 eV at the CCSD(T)/aug-cc-pVTZ level of theory,³² and to the complete basis set limit (CBS) of the SCS-LMP2 method of 0.12 eV.³⁶ The corresponding values at the B97D/6-31G(d,p) and M06-2X/6-31G(d,p) levels of theory are smaller, *i.e.*, $CE_{\mu} =$ 0.16 and CE = 0.06 eV at the B97D/6-31G(d,p) method and

Table 1 Complexation Energies CE (eV) in the gas phase of the parallel displaced minimum of the benzene dimer and C_{60} -benzene cluster at B3LYP, CAM-B3LYP, M06-2X, M06-HF, B97D, and ω B97X-D/6-31G(d,p) levels of theory

| | CE_{u}^{a} | CE^b | CE_u^a | CE^b | |
|--------------------------|----------------------|----------------------|----------|--------------------------|--|
| Method | Benzene ₂ | Benzene ₂ | | C ₆₀ -benzene | |
| B3LYP | 0.03 | 0 | 0.01 | -0.03 | |
| CAM-B3LYP | 0.03 | -0.01 | 0.05 | -0.02 | |
| M06-2X | 0.14 | 0.06 | 0.21 | 0.12 | |
| M06-HF | 0.14 | 0.04 | 0.23 | 0.12 | |
| B97D | 0.16 | 0.07 | 0.32 | 0.22 | |
| ωB97X-D | 0.18 | 0.10 | 0.30 | 0.22 | |
| $CCSD(T)^{c}$ | | 0.110 | | | |
| $SCS-LMP2^d$ | 0.113 | 0.105 | | | |
| QSCF-DC-DFT ^e | 0.151 | 0.116 | | | |
| SAPT(DFT) ^{f,g} | | 0.119 | | | |

^{*a*} BSSE uncorrected values. ^{*b*} BSSE corrected values. ^{*c*} Ref. 32, CCSD(T)/aug-cc-pVTZ//QCISD(T)/aug-cc-pVTZ, the CBS limit is 0.115 eV. ^{*d*} Ref. 36, SCS-LMP2/aug-cc-pVTZ, the CBS limit is 0.122 eV. ^{*e*} Ref. 33, SR-PBE + LR-HF + OP + ALL/cc-pVDZ_Haug-cc-pVDZ_C. ^{*f*} Ref. 34. ^{*g*} Ref. 35.

 $CE_u = 0.14$ and CE = 0.06 eV at the M06-2X/6-31G(d,p) level of theory. In contrast, calculations employing the B3LYP and CAM-B3LYP functionals lead to minimum energy structures which have negative binding energy, once BSSE is taken into account. The calculations on the geometry optimization of the fullerene–benzene cluster (also given in Table 1) lead to similar conclusions as above regarding the applicability of the functionals. The cluster has a CE value of 0.22 eV using both the ω B97X-D and B97D functionals and 0.12 eV at the M06-2X/ 6-31G(d,p) method. As far as we know, there are no previous data regarding the binding in this system for further comparison.

We think that the ω B97X-D functional is the best choice, while the M06-2X/6-31G(d,p) method is a good choice. However, while the geometries of the benzene dimer and fullerene– benzene system were optimized with the ω B97X-D/6-31G(d,p) method, for the **AT** and **BT** minima only single point calculations

Table 2 Complexation Energies CE (eV) in the gas phase and in CHCl₃ solvent, CE_{sol} , and van der Waals bonds *R* (Å) of the **AT** and **BT** complexes at the B3LYP, CAM-B3LYP and M06-2X/6-31G(d,p) levels of theory

| Structure | $CE_u^{\ a}$ | CE^b | ${\rm CE}_{\rm sol}{}^b$ | $R_{\mathrm{H_{N^{-}}}\cdot\mathrm{O}}$ | $R_{\mathrm{H_{C}}\cdots\mathrm{O}}$ | $R_{\mathrm{ph}\cdots\mathrm{ph}}^{c}$ | $R_{\rm ph\cdots C60}$ |
|-----------|--------------|--------|--------------------------|---------------------------------------------|--------------------------------------|----------------------------------------|------------------------|
| B3LYP | | | | | | | |
| AT1 | 1.43 | 1.08 | 0.40 | $1.870, 1.942/2.460^d$ | 2.427, 2.508 | 4.219 | |
| AT2 | 1.24 | 0.87 | 0.15 | $1.999, 2.180/2.563^d$ | 2.333, 2.366, 2.440 | 4.320 | |
| BT2 | 1.27 | 0.92 | 0.20 | $2.070, 2.322/2.346^d$ | 2.462, 2.596 | | |
| CAM-B3L | YP | | | · • | | | |
| AT1 | 1.79 | 1.39 | 0.66 | $1.838, 1.880/2.434^d$ | 2.372, 2.411 | 4.042 | |
| AT2 | 1.62 | 1.20 | 0.42 | $1.928/2.597,^{d} 2.160/2.490^{d}$ | 2.309, 2.313, 2.410, 2.551 | 4.006 | |
| AT4 | 1.49 | 1.06 | 0.35 | 1.814, 1.889 | 2.767 | 4.029 | |
| BT2 | 1.63 | 1.25 | 0.48 | $2.131/2.347,^{d} 2.236/2.293^{d}$ | 2.338, 2.451 | | |
| M06-2X | | | | | | | |
| AT1 | 2.40 | 2.02 | 1.27 | $1.852, 1.823/2.415^d$ | 2.322, 2.355, 2.392 | 3.558 | |
| AT2 | 2.42 | 2.00 | 1.19 | $1.906/2.506/2.594^d$ $2.168/2.374/2.382^d$ | 2.210, 2.357, 2.369, 2.479 | 3.549 | |
| AT3 | 2.42 | 1.94 | 1.16 | $1.809/2.510^{d}, 1.863/2.222^{d}$ | 2.488, 2.537 | 3.713 | 3.288 ^e |
| AT4 | 2.27 | 1.84 | 1.09 | $1.770, 1.839/2.303^d$ | 2.407, 2.680 | 3.671 | |
| AT5 | 2.22 | 1.79 | 1.06 | $1.941, 1.880/2.423^d$ | 2.494 | 3.547 | |
| BT1 | 2.50 | 1.99 | 1.18 | $2.096, 1.942/2.285^d$ | 2.419, 2.429, 2.489, 2.523, 2.547 | 3.941 | 3.112, 3.115, 3.219 |
| BT2 | 2.36 | 1.97 | 1.19 | $2.104/2.260^d \ 2.117/2.205^d$ | 2.317, 2.423, 2.418, 2.458, 2.600 | | 3.264^{g} |
| | | | | | | | |

^{*a*} BSSE uncorrected values. ^{*b*} BSSE corrected values. ^{*c*} Distance between the two centers of the phenyl groups. ^{*d*} One H atom interacts with two or three O atoms. ^{*e*} Distance between the C_1 atom of exTTF and the nearest C atom of fullerene. ^{*f*} Distance between the center of the 4, 5 and 6 rings of exTTF and the nearest C atoms of fullerene. ^{*g*} Distance between the center of phenyl group and the middle of the nearest C–C bond distance of the fullerene, the distance between the center of phenyl group and the two nearest C atoms of the fullerene are 3.334 and 3.353 Å, see Fig. 1.

Table 3 Complexation Energies CE (eV) in the gas phase and in CHCl₃ solvent, CE_{sol} of the AT and BT complexes at the $\omega B97X\text{-}D/$ 6-31G(d,p)//M06-2X/6-31G(d,p) level of theory

| Structure | CE_{u}^{a} | CE^b | CE_{sol}^{b} |
|----------------------------|--------------------------------|-------------------|----------------|
| AT1 | -2.69 | -2.32 | -1.57 |
| AT2 | -2.55 | -2.14 | -1.34 |
| AT3 | -2.85 | -2.38 | -1.61 |
| AT4 | -2.65 | -2.23 | -1.48 |
| AT5 | -2.58 | -2.16 | -1.43 |
| BT1 | -3.04 | -2.54 | -1.75 |
| BT2 | -2.67 | -2.28 | -1.51 |
| ^a BSSE uncorrec | cted values. ^b BSSE | corrected values. | |

were carried out using their M06-2X optimized geometries. There were technical difficulties with the optimization at the ω B97X-D/6-31G(d,p) level of theory. However, the total electronic energies of the benzene dimer and fullerene–benzene systems and of the **A**, **B** and **T** species at the ω B97X-D/6-31G(d,p) level of theory are only 0.008–0.02 eV lower than the corresponding values at the ω B97X-D/6-31G(d,p)//M06-2X/6-31G(d,p) level of theory. Thus, we conclude that the complexation energies (CE) of the **AT** and **BT** minima using the single point calculations at the ω B97X-D/6-31G(d,p)//M06-2X/6-31G(d,p) level of theory will be very close to the CE values of the optimized minima at the ω B97X-D/6-31G(d,p) level of theory. Technical difficulties were also encountered with the optimization at the B97D/6-31G(d,p) level of theory. Finally, calculations were also carried out employing the commonly

and widely used B3LYP and CAM-B3LYP functionals for comparison of the results on the absorption spectra.

a. Geometry optimization and complexation energies

In the present study, 7 different minima (AT1, AT2, AT3, AT4, AT5, BT1, and BT2) have been identified for the complex of the two lowest minima A and B of the dibenzo-18-crown-6 ether of fullero-*N*-methylpyrrolidine with the T π -exTTF derivative in the gas phase and in CHCl₃ solvent, see Fig. 1. The minima of the complex are characterized with 3 symbols. The first two indicate that the minimum is a complex between A or B and T and the third the energy rank of the AT and BT structures at the M06-2X/6-31G(d,p) level of theory taking into account the BSSE correction.

All 7 minima (**AT** and **BT**, see Fig. 1) were calculated with the M06-2X functional; only three and four minima out of seven resulted from the calculations employing the B3LYP and CAM-B3LYP functionals, respectively. The remaining minima are not stable with these two functionals and further optimization leads back to the previous minima. Moreover, single point calculations at the ω B97X-D/6-31G(d,p)// M06-2X/6-31G(d,p) level of theory were carried out for all **AT** and **BT** minima. Our results with the four different types of functionals are summarized in Tables 2 and 3, where the complexation energies without (CE_u) and with BSSE correction (CE) and the vdW bond lengths of the different **AT** and **BT** conformers are given.

Table 4 Excitation energies, ΔE (eV), absorption major peaks, λ (nm), oscillator strengths, *f*-value, main excitations and their coefficients contributing to the excited state of **T**, **A**, and **B** at the B3LYP, CAM-B3LYP, and M06-2X /6-31G(d,p) levels of theory

| Struct | State | ΔE | λ | <i>f</i> -Value | Excitations |
|------------------|------------------|------------|-----|-----------------|-------------------------------------------------------------------------------------------------------------------------------------------------------|
| B3LYP | | | | | |
| Т | S_1 | 1.59 | 782 | 0.13 | $0.99 H \rightarrow L\rangle$ |
| | S_2 | 2.13 | 582 | 0.099 | $0.92 \text{H-1} \rightarrow \text{L}\rangle$ |
| | $\overline{S_3}$ | 2.22 | 559 | 0.088 | $0.93 H \rightarrow L + 1\rangle$ |
| | \mathbf{S}_7 | 2.97 | 417 | 0.23 | $0.97 H \rightarrow L + 4\rangle$ |
| | S ₁₀ | 3.22 | 386 | 0.64 | $0.91 \text{H-2} \rightarrow \text{L}\rangle$ |
| Α | S ₄₇ | 3.43 | 361 | 0.021 | $0.63 \text{H-2} \rightarrow \text{L} + 5\rangle + 0.40 \text{H-1} \rightarrow \text{L} + 5\rangle$ |
| В | S_{48} | 3.46 | 359 | 0.028 | $0.54 \text{H-2} \rightarrow \text{L} + 5\rangle + 0.45 \text{H-1} \rightarrow \text{L} + 5\rangle$ |
| CAM-B3L | YP | | | | |
| Т | S_1 | 2.90 | 428 | 0.39 | $0.87 H \rightarrow L\rangle$ |
| | S_2 | 3.46 | 359 | 0.31 | $0.82 \text{H-1} \rightarrow \text{L}\rangle$ |
| | $\overline{S_3}$ | 3.63 | 342 | 0.30 | $0.75 H \rightarrow L + 4\rangle - 0.35 H \rightarrow L + 5\rangle$ |
| | S_5 | 4.11 | 301 | 0.70 | $0.72 \text{H-2} \rightarrow \text{L}\rangle$ |
| | S ₆ | 4.15 | 299 | 0.18 | $0.51 \text{H-1} \rightarrow \text{L} + 4\rangle + 0.38 \text{H} \rightarrow \text{L} + 1\rangle$ |
| \mathbf{T}^{a} | S_1 | 2.40 | 517 | 0.37 | $0.93 H \rightarrow L\rangle$ |
| | S_2 | 3.15 | 392 | 0.52 | $0.87 \text{H-1} \rightarrow \text{L}\rangle$ |
| | $\overline{S_3}$ | 3.33 | 372 | 0.36 | $0.83 H \rightarrow L + 4\rangle$ |
| | S_5 | 3.85 | 322 | 0.80 | $0.83 \text{H-2} \rightarrow \text{L}\rangle$ |
| Α | S_{40} | 4.38 | 283 | 0.12 | $0.35 \text{H-8} \rightarrow \text{L} + 1\rangle + 0.31 \text{H-4} \rightarrow \text{L} + 3\rangle - 0.31 \text{H-3} \rightarrow \text{L} + 4\rangle$ |
| В | S_{40} | 4.38 | 283 | 0.14 | $0.42 \text{H-2} \rightarrow \text{L} + 4\rangle - 0.33 \text{H} \rightarrow \text{L} + 5\rangle - 0.29 \text{H-8} \rightarrow \text{L} + 1\rangle$ |
| M06-2X | | | | | |
| Т | S_1 | 2.69 | 460 | 0.32 | $0.92 H \rightarrow L\rangle$ |
| | S_2 | 3.29 | 376 | 0.27 | $0.87 \text{H-1} \rightarrow \text{L}\rangle$ |
| | S_3 | 3.48 | 356 | 0.25 | $0.81 H \rightarrow L + 4\rangle + 0.36 H \rightarrow L + 1\rangle$ |
| | S_8 | 4.09 | 303 | 0.34 | $0.51 \text{H-1} \rightarrow \text{L} + 4\rangle + 0.48 \text{H-2} \rightarrow \text{L}\rangle$ |
| | S_9 | 4.11 | 301 | 0.67 | $0.66 \text{H-2} \rightarrow \text{L}\rangle$ |
| Α | S ₃₉ | 4.29 | 289 | 0.13 | $0.49 \text{H-8} \rightarrow \text{L} + 1\rangle + 0.32 \text{H} \rightarrow \text{L} + 3\rangle$ |
| | S ₄₇ | 4.45 | 278 | 0.12 | $0.49 \text{H-10} \rightarrow \text{L} + 1\rangle - 0.33 \text{H-4} \rightarrow \text{L} + 5\rangle$ |
| B | S_{40} | 4.33 | 286 | 0.19 | $0.39 \text{H-8} \rightarrow \text{L} + 1\rangle + 0.34 \text{H-2} \rightarrow \text{L} + 4\rangle$ |
| | S_{46} | 4.46 | 278 | 0.079 | $0.39 \text{H-8} \rightarrow \text{L} + 1\rangle + 0.34 \text{H-3} \rightarrow \text{L} + 4\rangle$ |
| a Englanda | | | | | |

^a Emission spectrum.

In all minima, see Fig. 1, hydrogen bonds are formed between the H_N atoms, that are attached to the N atoms, and the O atoms of the crown ethers with bond distances ranging from 1.8 to 2.5 Å, see Table 2. The interactions are not always 1 to 1 and one H atom can interact with two or three O atoms. Similarly, in all minima, vdW distances between the H_C atoms of the CH₂ or phenyl groups and the O atoms of the crown ether are formed. The distances range from 2.3 to 2.6 Å. With the exception of the BT2 conformer, vdW interactions between phenyl groups are formed and the distances range from 3.5 to 3.9 Å using the M06-2X functional. Finally, interactions between C₆₀ and phenyl group are formed in **BT2**, while interactions between C_{60} and the exTTF of T are formed in BT1 and AT3 (see Fig. 1). In AT3 the interaction of C_{60} is with the 4, 6 and 7 rings of exTTF, while in **BT1** with the 3, 4 and 5 rings of the exTTF, see Fig. 1. The AT4 and AT5 conformers form different $H_{C \dots O}$ bonds. The $H_{N \dots O}$ distances

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of the calculated minima are similar with all functionals. The $R_{HC\cdots O}$ and the $R_{ph\cdots ph}$ distances are overestimated by 0.1 and 0.8 Å with B3LYP and by half of the previous values with CAM-B3LYP, *i.e.* by 0.05 and 0.5 Å, respectively, compared to the corresponding values of the M06-2X functional. Finally, the $R_{ph\cdots C60}$ distances range from 3.1 to 3.3 Å with M06-2X, while, with the B3LYP and CAM-B3LYP functionals, the interactions are not predicted (the corresponding distances are about 5.5–6 Å).

The BSSE corrected complexation energies, CE, of the calculated AT and BT complexes range from 2.54 to 2.14 eV in the gas phase, while in CHCl₃ solvent the corresponding values range from 1.75 to 1.34 eV at the ω B97X-D/6-31G(d,p)//M06-2X/6-31G(d,p) level of theory, see Table 3. BT1 is the lowest minimum, the second one is AT3 and the third one is AT1. These three minima are the most important conformers. At the M06-2X/6-31G(d,p) level of theory, BT1

Table 5 Excitation energies, $\Delta E(eV)$, absorption major peaks, $\lambda(nm)$, oscillator strengths, *f*-value, main excitations and their coefficients contributing to the excited state of **AT** and **BT** conformers at the B3LYP, CAM-B3LYP, and M06-2X /6-31G(d,p) levels of theory

| Struct | State | ΔL | <i>/</i> L | <i>j</i> -value | Excitations |
|--------|-----------------|------------|------------|-----------------|---------------------------------------------------------------------------------------------------------------------------------------------------------|
| B3LYP | | | | | |
| AT1 | S_{10} | 2.13 | 582 | 0.18 | $0.99 H \rightarrow L + 3\rangle$ |
| | S25 | 2.66 | 466 | 0.20 | $0.98 \text{H-1} \rightarrow \text{L} + 3\rangle$ |
| | S ₃₂ | 3.05 | 406 | 0.20 | $0.82 H \rightarrow L + 10\rangle + 0.43 H \rightarrow L + 9\rangle$ |
| AT2 | S ₁₁ | 2.20 | 564 | 0.18 | $0.99 H \rightarrow L + 3\rangle$ |
| | S ₂₃ | 2.72 | 455 | 0.22 | $0.98 \text{H-1} \rightarrow \text{L} + 3\rangle$ |
| | S ₂₈ | 3.02 | 411 | 0.093 | $0.67 H \rightarrow L + 7\rangle - 0.60 H \rightarrow L + 8\rangle$ |
| BT2 | S_{11} | 2.19 | 566 | 0.13 | $0.84 H \rightarrow L + 3\rangle - 0.46 H-5 \rightarrow L + 1\rangle$ |
| | S ₂₅ | 2.72 | 456 | 0.23 | $0.98 \text{H-1} \rightarrow \text{L} + 3\rangle$ |
| | S_{32} | 3.06 | 405 | 0.18 | $0.73 H \rightarrow L + 10\rangle + 0.46 H \rightarrow L + 11\rangle$ |
| CAM-B | 3LYP | | | | |
| AT1 | S_{15} | 3.22 | 385 | 0.56 | $0.86 H \rightarrow L + 3\rangle + 0.37 H \rightarrow L + 9\rangle$ |
| | S_{26} | 3.76 | 330 | 0.40 | $0.56 \text{H-1} \rightarrow \text{L} + 3\rangle - 0.51 \text{H} \rightarrow \text{L} + 9\rangle + 0.36 \text{H-1} \rightarrow \text{L} + 9\rangle$ |
| | S_{42} | 4.29 | 289 | 0.61 | $0.65 \text{H-6} \rightarrow \text{L} + 3\rangle + 0.38 \text{H-1} \rightarrow \text{L} + 9\rangle - 0.30 \text{H} \rightarrow \text{L} + 26\rangle$ |
| AT2 | S_{14} | 3.25 | 381 | 0.56 | $0.86 H \rightarrow L + 3\rangle - 0.36 H \rightarrow L + 8\rangle$ |
| | S ₂₃ | 3.78 | 328 | 0.48 | $0.64 \text{H-1} \rightarrow \text{L} + 3\rangle - 0.34 \text{H-1} \rightarrow \text{L} + 8\rangle - 0.34 \text{H} \rightarrow \text{L} + 9\rangle$ |
| | S43 | 4.31 | 288 | 0.61 | $0.65 \text{H-7} \rightarrow \text{L} + 3\rangle - 0.30 \text{H} \rightarrow \text{L} + 26\rangle$ |
| AT4 | S_{15} | 3.27 | 380 | 0.52 | $0.80 H \rightarrow L + 3\rangle - 0.35 H \rightarrow L + 9\rangle$ |
| | S ₂₄ | 3.76 | 330 | 0.15 | $0.69 H \rightarrow L + 9\rangle - 0.39 H \rightarrow L + 15\rangle$ |
| | S ₂₆ | 3.80 | 326 | 0.20 | $0.72 \text{H-1} \rightarrow \text{L} + 3\rangle - 0.40 \text{H-1} \rightarrow \text{L} + 9\rangle$ |
| | S ₄₃ | 4.31 | 288 | 0.51 | $0.64 \text{H-7} \rightarrow \text{L} + 3\rangle + 0.38 \text{H-1} \rightarrow \text{L} + 9\rangle$ |
| BT2 | S ₁₅ | 3.25 | 382 | 0.54 | $0.86 H \rightarrow L + 3\rangle + 0.38 H \rightarrow L + 9\rangle$ |
| | S25 | 3.78 | 328 | 0.52 | $0.70 \text{H-1} \rightarrow \text{L} + 3\rangle + 0.42 \text{H-1} \rightarrow \text{L} + 9\rangle + 0.36 \text{H} \rightarrow \text{L} + 9\rangle$ |
| | S44 | 4.31 | 288 | 0.38 | $0.59 \text{H-7} \rightarrow \text{L} + 3 \rangle - 0.34 \text{H-1} \rightarrow \text{L} + 9 \rangle + 0.30 \text{H} \rightarrow \text{L} + 26 \rangle$ |
| M06-2X | | | | | |
| AT1 | S ₁₅ | 3.06 | 405 | 0.47 | $0.90 H \rightarrow L + 4\rangle + 0.30 H \rightarrow L + 9\rangle$ |
| | S ₂₆ | 3.64 | 341 | 0.30 | $0.57 \text{H-1} \rightarrow \text{L} + 4\rangle - 0.55 \text{H} \rightarrow \text{L} + 9\rangle + 0.31 \text{H-1} \rightarrow \text{L} + 9\rangle$ |
| | S_{48} | 4.24 | 293 | 0.31 | $0.40 H-6 \rightarrow L + 4\rangle + 0.45 H-1 \rightarrow L + 9\rangle - 0.38 H \rightarrow L + 26\rangle - 0.36 H \rightarrow L + 21\rangle$ |
| AT2 | S ₁₆ | 3.22 | 386 | 0.53 | $0.85 H \rightarrow L + 4\rangle + 0.45 H \rightarrow L + 8\rangle$ |
| | S ₂₆ | 3.76 | 330 | 0.21 | $0.71 \text{H-1} \rightarrow \text{L} + 4\rangle + 0.47 \text{H-1} \rightarrow \text{L} + 8\rangle$ |
| | S47 | 4.28 | 289 | 0.51 | $0.37 \text{H-6} \rightarrow \text{L} + 4\rangle - 0.34 \text{H-2} \rightarrow \text{L} + 3\rangle$ |
| AT3 | S ₁₇ | 3.12 | 398 | 0.42 | $0.88 H \rightarrow L + 3\rangle - 0.28 H \rightarrow L + 8\rangle$ |
| | S ₂₇ | 3.68 | 337 | 0.13 | $0.68 \text{H-1} \rightarrow \text{L} + 3\rangle + 0.29 \text{H-1} \rightarrow \text{L} + 9\rangle$ |
| | S48 | 4.33 | 286 | 0.15 | $0.47 \text{H-2} \rightarrow \text{L} + 3\rangle + 0.42 \text{H-16} \rightarrow \text{L}\rangle$ |
| AT5 | S ₁₅ | 3.08 | 403 | 0.40 | $0.88 H \rightarrow L + 3\rangle - 0.28 H \rightarrow L + 8\rangle - 0.27 H \rightarrow L + 9\rangle$ |
| | S25 | 3.65 | 340 | 0.26 | $0.73 \text{H-1} \rightarrow \text{L} + 3\rangle - 0.35 \text{H-1} \rightarrow \text{L} + 9\rangle + 0.33 \text{H} \rightarrow \text{L} + 9\rangle$ |
| | S46 | 4.23 | 293 | 0.12 | $0.68 \text{H-6} \rightarrow \text{L}\rangle$ |
| | S ₅₀ | 4.33 | 286 | 0.16 | $0.39 \text{H-5} \rightarrow \text{L}' + 5\rangle - 0.38 \text{H-3} \rightarrow \text{L} + 5\rangle$ |
| BT1 | S_1 | 2.18 | 569 | 0.02 | $0.96 H \rightarrow L\rangle$ |
| | S19 | 3.19 | 389 | 0.35 | $0.63 H \rightarrow L + 4\rangle + 0.48 H \rightarrow L + 8\rangle + 0.44 H \rightarrow L + 6\rangle$ |
| | S29 | 3.71 | 334 | 0.22 | $0.54 \text{H-1} \rightarrow \text{L} + 4\rangle + 0.38 \text{H-1} \rightarrow \text{L} + 6\rangle + 0.47 \text{H-1} \rightarrow \text{L} + 8\rangle$ |
| | S44 | 407 | 305 | 0.065 | $0.69 H \rightarrow L + 7\rangle$ |
| | S54 | 4.28 | 290 | 0.059 | $0.31 H-1 \rightarrow L + 3\rangle$ |
| BT2 | S16 | 3.12 | 398 | 0.47 | $0.86 H \rightarrow L + 5\rangle - 0.31 H \rightarrow L + 11\rangle$ |
| | S ₂₇ | 3.68 | 337 | 0.45 | $0.69 \text{H-1} \rightarrow \text{L} + 5\rangle - 0.36 \text{H-1} \rightarrow \text{L} + 11\rangle + 0.35 \text{H} \rightarrow \text{L} + 11\rangle$ |
| | S49 | 4.22 | 291 | 0.20 | $0.39 H \rightarrow L + 26\rangle + 0.37 H \rightarrow L + 22\rangle - + 0.30 H-6 \rightarrow L + 5\rangle - 0.36 H-1 \rightarrow L + 11\rangle$ |
| | 47 | | | | |

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is the lowest energy conformer before the BSSE correction (see Table 2, column under CE_{μ}) but after the BSSE correction it lies 0.03 eV above AT1. At this level, the AT1, AT2, AT3, BT1, and BT2 conformers are nearly degenerate, *i.e.*, they lie within 0.08 eV taking into account the BSSE correction, while all seven minima are located within 0.2 eV. Using the @B97X-D functional, which includes dispersion corrections, the neardegeneracy is lifted, and the seven minima are spread over 0.4 eV. At the M06-2X/6-31G(d,p) level of theory the CE values are smaller than the corresponding values at the wB97X-D/ 6-31G(d,p)//M06-2X/6-31G(d,p) by 0.2-0.5 eV. The CE values are underestimated by about 60% with B3LYP and 45% with CAM-B3LYP in the gas phase with respect to the ω B97X-D values. In CHCl3 solvent, with all four functionals the CEsol is reduced by about 0.7 eV compared to the corresponding CE in the gas phase. The BSSE correction is calculated at about 0.4 eV for all cases and all functionals.

Finally, it might be noted that even though B3LYP is a widely used functional and generally works well and even though we concluded that the B3LYP/6-31G(d,p) methodology was our best choice in our previous study on similar complexes of dibenzo-12-crown-4, dibenzo-18-crown-6, dibenzo-24-crown-8 ethers, and dibenzo-18-crown-6 ether of fullero-*N*-methylpyrrolidine with $(CH_3)_xNH_{4-x}^+$, x = 0 - 4,⁵ for the complexes studied here, B3LYP is not the best choice. The CAM-B3LYP functional gives improved results compared to B3LYP but it remains insufficient for the calculations of all minima and it underestimates the CE values.

b. Absorption spectra

The excitation energies (ΔE), major peak (λ), oscillator strengths (*f*-value), main excitations and their coefficient contributing to the excited state of **T**, **A**, **B**, and their calculated complexes are given in Tables 4–6. The corresponding

calculated absorption spectra and the emission spectrum of T are depicted in Fig. 3. The type of the transitions of the peaks are also depicted in Fig. 3. As can be seen from Tables 4–6 and from our previous study on the absorption spectra of complexes of C₆₀ and C₅₉N with exTTF,³⁷ different functionals lead to differences in the calculated λ_{max} values (absorption maxima), while there is agreement in the general shape of the vis-UV spectra obtained with the different functionals, see Fig. 3. The CAM-B3LYP and M06-2X absorption peaks are shifted to significantly higher energies than those obtained with the B3LYP functional. However, the types of excitations corresponding to the excited states are the same in all three functionals.

T. The absorption spectrum of T has four absorption peaks. The first peak corresponds to the S1 excited state. This peak is characterized by a HOMO \rightarrow LUMO excitation, *i.e.*, from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. It is calculated at 460(428) nm by the M06-2X(CAM-B3LYP) functionals, see Table 4. The corresponding experimental peak of the salt of T with PF₆, in CD₃CN solvent is at 423 nm.⁶ The second and the third peak correspond to the S₂ and S₃ excited states and are characterized mainly by a HOMO – 1 \rightarrow LUMO and HOMO \rightarrow LUMO + 4 excitations, respectively. The fourth absorption peak is the most intense, it corresponds to a HOMO $-2 \rightarrow$ LUMO excitation and is calculated at 301 nm by both M06-2X and CAM-B3LYP functionals, see Fig. 3. It corresponds to the S₉ and S_5 excited states, respectively. It might be noted that the ordering is not the same in both functionals because some excited states are practically degenerate and the absolute order of the states changes with the two functionals. Experimentally, in CD₃CN solvent, the second, third, and fourth measured peaks of the salt of T with PF_6 are at 379, 276, and 270 nm.⁶ The emission spectrum is calculated by the CAM-B3LYP

Table 6 Excitation energies, $\Delta E(eV)$, absorption major peaks, $\lambda(nm)$, oscillator strengths, *f*-value, main excitations and their coefficients contributing to the excited state of **AT** and **BT** conformers in CHCl₃ solvent at the B3LYP, CAM-B3LYP, and M06-2X/6-31G(d,p) levels of theory

| Struct | State | ΔE | λ | <i>f</i> -value | Excitation |
|--------|-----------------|------------|-----|-----------------|------------------------------------------------------------------------------------------------------------------------------------------------|
| CAM-B3 | BLYP | | | | |
| AT1 | S ₁₅ | 3.29 | 377 | 0.71 | $0.84 H \rightarrow L + 4\rangle + 0.40 H \rightarrow L + 8\rangle$ |
| | S ₂₃ | 3.77 | 329 | 0.45 | $0.70 H \rightarrow L + 8\rangle + 0.40 H \rightarrow L + 9\rangle - 0.33 H-1 \rightarrow L + 4\rangle$ |
| | S ₃₉ | 421 | 294 | 0.29 | $0.39 H \rightarrow L + 9\rangle - 0.38 H-6 \rightarrow L + 4\rangle - 0.36 H-1 \rightarrow L + 8\rangle + 0.36 H-1 \rightarrow L + 26\rangle$ |
| | S_{45} | 4.33 | 286 | 0.28 | $0.50 \text{H-6} \rightarrow \text{L} + 4\rangle + 0.40 \text{H} \rightarrow \text{L} + 26\rangle$ |
| M06-2X | | | | | |
| AT1 | S_{15} | 3.16 | 392 | 0.67 | $0.89H \rightarrow L + 4 + 0.37 H \rightarrow L + 8 $ |
| | S_{24} | 3.66 | 339 | 0.29 | $0.77 H \rightarrow L + 8\rangle + 0.40 H \rightarrow L + 11\rangle$ |
| | S ₂₆ | 3.73 | 333 | 0.19 | $0.81 \text{H-1} \rightarrow \text{L} + 4\rangle + 0.37 \text{H-1} \rightarrow \text{L} + 8\rangle$ |
| | S_{45} | 4.33 | 286 | 0.28 | $0.50 \text{H-6} \rightarrow \text{L} + 4\rangle + 0.40 \text{H} \rightarrow \text{L} + 26\rangle$ |
| AT2 | S ₁₇ | 3.23 | 384 | 0.67 | $0.91 H \rightarrow L + 5\rangle + 0.35 H \rightarrow L + 8\rangle$ |
| | S_{24} | 3.71 | 334 | 0.22 | $0.71 H \rightarrow L + 8\rangle - 0.56 H \rightarrow L + 9\rangle$ |
| | S ₂₆ | 378 | 328 | 0.18 | $0.82 \text{H-1} \rightarrow \text{L} + 5\rangle + 0.34 \text{H-1} \rightarrow \text{L} + 8\rangle$ |
| | S_{45} | 4.33 | 286 | 0.28 | $0.50 \text{H-6} \rightarrow \text{L} + 4\rangle + 0.40 \text{H} \rightarrow \text{L} + 26\rangle$ |
| AT3 | S ₁₇ | 3.16 | 392 | 0.58 | $0.89 H \rightarrow L + 4\rangle - 0.33 H \rightarrow L + 8\rangle$ |
| | S_{25} | 3.62 | 342 | 0.15 | $0.77 H \rightarrow L + 8\rangle + 0.40 H \rightarrow L + 9\rangle$ |
| | S_{27} | 3.72 | 333 | 0.17 | $0.80 \text{H-1} \rightarrow \text{L} + 4\rangle - 0.34 \text{H-1} \rightarrow \text{L} + 8\rangle$ |
| | S_{41} | 4.05 | 306 | 0.11 | $0.48 \text{H-10} \rightarrow \text{L}\rangle + 0.48 \text{H-4} \rightarrow \text{L} + 3\rangle$ |
| BT1 | S_1 | 2.18 | 569 | 0.02 | $0.77 H \rightarrow L\rangle + 0.55 H-2 \rightarrow L\rangle$ |
| | S_{19} | 3.19 | 389 | 0.46 | $0.63 H \rightarrow L + 4\rangle + 0.41 H \rightarrow L + 5\rangle - 0.36 H \rightarrow L + 8\rangle$ |
| | S ₂₆ | 3.65 | 340 | 0.21 | $0.48 H \rightarrow L + 8 \rangle + 0.45 H \rightarrow L + 9 \rangle$ |
| | S ₃₉ | 4.03 | 308 | 0.058 | $0.51 \text{H-10} \rightarrow \text{L}\rangle + 0.44 \text{H-4} \rightarrow \text{L} + 3\rangle$ |



Fig. 3 Absorption spectrum of T, A, B and their complexes AT, BT and emission spectrum of T calculated with two functionals.

functional and the peaks are red shifted compared to those of the absorption spectrum. Moreover, the second peak becomes more intense than the first peak, see Fig. 3. Finally, the orbital level diagram and the electron density plots of the frontier orbitals of the T species are depicted in Fig. 4 and 5, respectively.

A and B. The calculated λ_{max} is at 289(286) nm for the A(B) minimum with M06-2X and at 283 nm for both minima with CAM-B3LYP. The absorption spectra of the two minima using the same functional present some small differences which diversify the two spectra. For example, the intensity of the

main peak with both functionals is higher in **B** than in **A**. It might be noted that 50 excited states were calculated with the M06-2X functional, but 40 excited states with CAM-B3LYP due to technical problems. Thus, with CAM-B3LYP we cannot observe the second peak that has been extracted with the use of M06-2X functional.

AT and BT conformers. There are three major absorption peaks in all cases. However, the absorption spectra of the conformers are similar using only either M06-2X or CAM-B3LYP functional, while the B3LYP absorption peaks are





Fig. 4 Orbital energy level diagram of **T**, **A**, **B**, **AT1**, and **BT1** species at the M06-2X/6-31G(d,p) level of theory.

shifted to significantly lower energies. Unfortunately, no experimental data exist which might be used for comparison. The three major features are at about $390(T \rightarrow T \text{ or } T \rightarrow T/F)$ for **BT1**), $330(T \rightarrow T \text{ or } T \rightarrow T/F \text{ for BT1})$, and $290(T \rightarrow T$ for AT1, AT2, AT3, AT4, BT2 or $T \rightarrow F$ for AT5, BT1) nm employing the M06-2X and the CAM-B3LYP functionals, see Table 5 and Fig. 3. Note that F stands for the fullerene of A and **B** and T/F means that the electron density is in both T and F. The first two peaks of the AT and BT conformers with the exception of the **BT1** correspond to the first two peaks of the free T species. The two peaks are blue shifted by about 30-70 nm compared to the corresponding absorption excitations of the separate T species. For the AT and BT conformers, next to the $\mathbf{T} \rightarrow \mathbf{T}$ transition, *i.e.*, within 0.1 eV and in some cases within 0.02 eV, there are charge transfer $\mathbf{T} \rightarrow \mathbf{F}$ transitions. Therefore in the studied system there is the possibility of photoinduced electron transfer and thus it may serve as a candidate for organic photovoltaics and molecular electronics applications.

The AT1 conformer presents three absorption peaks at 405, 341, and 293 nm which correspond to the S_{15} , S_{26} , and S_{48} excited states employing the M06-2X functional. The corresponding peaks using the CAM-B3LYP functional are at 385(S₁₅), 330(S₂₆), and 289(S₄₂) nm, *i.e.*, 4–20 nm underestimated, see Table 5. We observe that the absolute energy ordering of the excited states is slightly different using different functionals. This is expected because some excited states are energetically degenerate. The CAM-B3LYP functional predicts larger oscillator strengths than M06-2X not only for this conformer but also for the remaining structures. The third peak has an oscillator strength of 0.61(0.31) using the CAM-B3LYP(M06-2X) functionals. The M06-2X orbital level diagram for the T, A, and AT1 species, the electron density plots of the orbitals involved in the major absorption $T \rightarrow T$ transitions of the T species, the three major features (T \rightarrow T transitions) of AT1 and a charge transfer $T \rightarrow A$ transition of AT1 are depicted in Fig. 4 and 5. As mentioned above, the first two peaks of the AT1 conformer correspond to the first two peaks of the free T species, while the third absorption peak corresponds to S_9 excitation of T.

Fig. 5 shows the relative resemblance of the $T \rightarrow T$ transitions of the T and AT1 systems. The three peaks are blue shifted ranging from 8 to 55 nm compared to the corresponding absorption excitations of the separate T species.

The **AT2** conformer has its three peaks ($T \rightarrow T$ transitions) blue shifted compared to **AT1** at 386(S₁₆), 330(S₂₆), and 290(S₄₄) nm employing the M06-2X functional. The CAM-B3LYP peaks are at 381(S₁₄), 328(S₂₃), and 288(S₄₃) nm, practically identical to the M06-2X peaks. We observe that the



Fig. 5 M06-2X electron density plots of the frontier orbitals of the T, AT1, and BT1 species.



Fig. 6 Absorption spectrum of AT and BT conformers calculated with two functionals in CHCl₃ solvent.

absolute energy ordering of the excited states is slightly different in the **AT1** and **AT2** conformers and for the same conformer using different functionals. This is expected because some excited states are energetically degenerate, see above. The third peak of **AT2** has an oscillator strength of 0.61(0.15) using the CAM-B3LYP(M06-2X) functionals, see Table 5. We observe that with CAM-B3LYP the **AT1** and **AT2** conformers have the same oscillator strength for the third peak, while with M06-2X the **AT2** conformer has the half value.

The AT3 and AT5 conformers have been found only with the M06-2X functional, see above. They have their three peaks at 398(S₁₇), 337(S₂₇), 292(S₄₈) and 403(S₁₅), 340(S₂₅), 290(S₄₆ and S₅₀ nm, respectively. For the AT5 conformer, the S₄₆ and S₅₀ excitation corresponds to $T \rightarrow F$ and $F \rightarrow F$ transitions, see Fig. 3. The AT4 structure, using CAM-B3LYP, presents the second peak smaller than the other two peaks, in contrast to what happen to the peaks of the remaining structures.

BT1 is the lowest energy conformer with interactions between C_{60} and the exTTF of **T**. Its three major absorption peaks are at 389(S₁₉), 334(S₂₉), and a double peak around 300 nm with smaller oscillator strengths. It has an additional small peak at 569 nm, *i.e.*, $H(T) \rightarrow L(F)$ transition. As shown in Fig. 5, the first and the second major peaks correspond to $T \rightarrow T/F$ transitions, *i.e.*, the excited orbital has electron density in both **T** and **F** species. That results from the fact that C_{60} interacts with the exTTF of **T**. These transitions can be characterized as charge transfer transitions. The last two peaks are smaller than the previous and correspond to $T \rightarrow F$ transitions. Finally, this conformer presents the lowest oscillator strengths compared to the other six conformers.

BT2 has its three peaks at $398(S_{16})$, $337(S_{27})$, and $291(S_{49})$ nm employing the M06-2X functional and at $382(S_{15})$, $328(S_{25})$, and $288(S_{44})$ nm employing the CAM-B3LYP functional. All peaks correspond to $T \rightarrow T$ transitions.

In CHCl₃ solvent, the absorption spectra of the conformers (Fig. 6) are similar with those in the gas phase with peaks slightly blue shifted up to 13 nm, see Table 6. However, the oscillator strengths can differ. For example, the third absorption peak of the **AT1** structure, using the CAM-B3LYP functional, has an oscillator strength of 0.61 in the gas phase and a broad peak at 290 nm with an oscillator strength of 0.3 in CHCl₃ solvent. The peaks in solvent correspond to the same

type of transitions as in the gas phase with some exceptions. For example, the transition with the largest oscillator strength at the third major peak of the AT2, AT3, and BT1 conformers has a character $\mathbf{F} \to \mathbf{F}$ instead of $\mathbf{T} \to \mathbf{T}$ or $\mathbf{T} \to \mathbf{F}(\mathbf{BT1})$. The last two transitions also exist in CHCl₃ solvent, but their oscillator strengths are smaller than that of the $\mathbf{F} \rightarrow \mathbf{F}$ transition. It might be noted that for the BT1 species, 55 excited states were calculated in the gas phase, but 45 excited states in CHCl₃ solvent due to technical problems. Thus, the fourth peak cannot be observed in the solvent. Moreover, for the second absorption peak of the **BT1** species, the excitation with the largest oscillator strength corresponds to a $T \rightarrow T$ transition and not to $T \rightarrow T/F$ transition as happens in the gas phase. Finally, it should be noted that in the calculations with solvent we do not consider repulsion and dispersion solutesolvent interactions, which have been reported to affect the solute (hyper)polarizabilities.³⁸ We also ignored three-body effects which result from interactions between two solute molecules and a solvent molecule and could affect the interaction energies and the calculated solute electronic transition energies.³⁹ The main question of interest in the present work involves the character of the excited states and in particular the determination of the involvement of charge transfer, hence the omission of some small effects on the transition energies might be tolerated in view of the large size of the systems calculated.

IV. Conclusions

The electronic and geometric structures of different conformers of the complex of dibenzo-18-crown-6 ether of fullero-*N*methylpyrrolidine (**A** and **B** conformers) with a π -extended derivative of tetrathiafulvalene (**T**) were determined. We calculated the complexation energies and the absorption spectra, *i.e.*, about 50 excited electronic states of the complexes have been determined at the ground state optimum geometry. All calculations have been carried out employing the DFT and TDDFT methods, using the B3LYP, CAM-B3LYP, M06-2X, and ω B97X-D functionals in conjunction with the 6-31G(d,p) basis set. A summary of our main results follows.

As test calculations on the benzene dimer show the B3LYP and CAM-B3LYP functionals are not as good a choice as the M06-2X functional, while the ω B97X-D functional is the best choice for the system of interest here regarding the complexation energies (CE) and the stable structures. CAM-B3LYP gives improved results compared to B3LYP, but it does not predict all the minima and it underestimates the CE values.

The CE values of the conformers range from 2.54 to 2.14 eV in the gas phase and from 1.75 to 1.34 eV in CHCl₃ solvent at the ω B97X-D/6-31G(d,p)//M06-2X/6-31G(d,p) level of theory.

Various types of van der Waals interactions are observed in the complexes. Bonds are formed between the H atom of ammonium, of the methylene and/or the phenyl group and the O atoms of ethers. The interactions are not always 1 to 1 and in many cases one H atom interacts with two O atoms. Moreover, interactions arise between two phenyl groups or phenyl group with fullerene or exTTF with fullerene.

The absorption spectra of the conformers are similar using either M06-2X or CAM-B3LYP functional. Furthermore, the different conformers have similar spectra, even though, oscillator strengths show differences and some peaks are shifted slightly. There are three major features at about $390(T \rightarrow T \text{ or } T \rightarrow T/F)$, $330(T \rightarrow T \text{ or } T \rightarrow T/F)$, and $290(T \rightarrow T \text{ or } T \rightarrow F)$ nm. However, oscillator strengths for some peaks depend on the functional used. Moreover, other charge transfer $T \rightarrow F$ transitions are observed, next to the $T \rightarrow T$ transition. Thus, the studied complex may serve as a candidate for organic photovoltaics and molecular electronics applications.

Acknowledgements

Financial support from the EU FP7, Capacities Program, NANOHOST project (GA 201729) and the NATO grant, CBP.MD.CLG.983711 are acknowledged.

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