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Complexes of C60 With Cyclic Oligoisothianaphthenes. A Theoretical Study

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Complexes of C60 with cyclic and linear oligoisothianaphthenes containing 8 and 12 repeating units have been modeled at M05-2X/6-311G**//M05-2X/6-31G* level of theory. Basis set superposition error (BSSE) corrected binding energies of neutral donor-acceptor complexes vary from 6 to 14 kcal/mol depending on the complex arquitecture and donor type. The inclusion complexes formed by C60 and cyclooligoisothianaphthenes containing 8 repeating units were found to be the most stable ones due close matching between host and guest molecules. Only weak charge transfer from oligoisothianaphthene to C60 fragment (< 0.04 electron) is detected in the ground state while almost complete electron transfer from oligoisothianaphthenes fragments to C60 has been found in the excited state. One electron oxidation or reduction in most of the cases slightly increases binding energies of the complexes with positive charge being totally concentrated at oligoisothianaphthenes fragment while in anion radicals the negative charge is located entirely at C60 moiety. © 2011 Wiley Periodicals, Inc.

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Introduction

The actual trend in research and development of novel photovoltaic materials is intended to discover a credible cost/efficiency compromise to make feasible their use as power sources. The polymer-based organic photovoltaic devices have introduced the possibility of developing cheap and easy techniques to generate energy from light.[1] In 1986, Tang[1b] accomplished a 1% power conversion efficiency with an organic photovoltaic cell based on low molecular weight organic thin-film, and since then great advances have been made resulting in a numerous strategies to improve the performance of solar cells based on polymers.[2] Solar cells based on conjugated polymers alone have been promising candidates for use in low-cost electronics and photovoltaic devices;[3] however, their quantum efficiency was low. Nonetheless, mixing electron-donor-type polymers with suitable electron acceptors[4] resulted in highly efficient materials due to effective breaking apart of excitons into free charge carriers.

Among electron-donor-type polymers, polythiophenes (**PThs**) probably are the most important materials for photovoltaic devices due to their excellent performance and power conversion efficiencies.[5] It has recently been demonstrated[6] that 2D-macrocyclic oligothiophenes are able to form complexes with C60. C60-fullerenes are adsorbed in a monolayer of cyclot[12]hiophene and self-assemble in a second layer whose crystallinity is governed by the formation of 1:1 π-donor– π-acceptor (**D–A**) complexes.

Two different types of complexes were detected; type **A**, where C60 is located in the internal cavity of a macrocycle and type **B**, where C60 is placed at the rim of macrocycle. Experimental data suggested that complex of **B** type is the most stable for cyclooligothiophene containing 12 repeating units and this fact has been confirmed by calculations.[7]

On the other hand, nothing is known about the complexes of cyclooligoisothianaphthenes with C60. As seen from Figure 1 chemical structures of polyisothianaphthene (**PITN**) is closely related to that of **PTh**. Similar to **PTh**, **PITN** is a donor polymer and should be able to form complexes with C60. What is more important, **PITN** is a low band gap polymer (1 vs. 2.1 eV in **PTh**)[8] and, therefore, is a promising material for photovoltaic applications. Therefore,

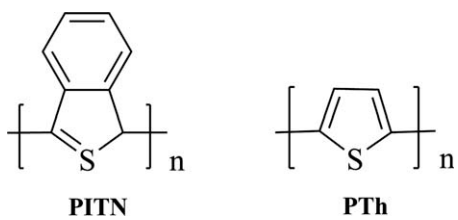

Figure 1. Chemical structures of **PITN** and **PTh**.

the goal of this contribution is to study the nature and electronic properties of complexes between C60 and cyclo oligoisothianaphthenes, using quantum chemistry tools.

Computational details

The modeling of charge transfer (CT) complexes, where dispersion interactions have an important contribution to the total binding energy, is a challenging task requiring methods taking into account dynamic correlation. It has been shown earlier[9] that MPWB1K functional performs well for π-π stacking interaction in complexes of cyclic oligoisothianaphthenes. In this work, however, we applied M05-2X functional combined with 6-31G* basis set for geometry optimizations followed by a

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single point energy calculations using larger 6-311G** basis set. Restricted and unrestricted formalisms were used for closed shell (neutral) and open shell systems (cation- and anion-radicals), respectively. No counter ions were considered for charged molecules.

M05-2X functional belongs to forth rung of Jacob's ladder[10] incorporating electron spin density, density gradient, kinetic energy density, and Hartree-Fock (HF) exchange. This particular functional incorporates 56% of HF exchange. Calculations were carried out using Gaussian 09[11]suit of programs. Basis set superposition errors (BSSE) have been estimated for all complexes using counterpoise correction method implemented in Gaussian 09 code. In its original form, density functional theory (DFT) is only applicable to ground-states. The Runge-Gross theorem[12] extends the theory into the time-domain, called time-dependent DFT (TD-DFT), thus allowing the treatment of electronically excited states. Currently, TD-DFT is the most widely applied tool for modeling electronic spectra.[13]

M05-2X overperforms MPWB1K functional for π-π stacking energies;[10] moreover, M05-2X model reproduces within 0.1 eV the lowest unoccupied molecular orbital (LUMO) energy of C60 measured in acetonitrile (3.7 and 3.8 eV (exp)).[14] Therefore, M05-2X functional provides reliable description of the systems under investigation.

Cyclooligoisothianaphthenes containing 8 and 12 repeating units as a donor component for the complex formation are shown in Figure 2. They denoted as **Cn** where **n** is the number of repeating units in oligoisothianaphthenes. Their complexes with C60 are marked as **CnA** or **CnB**, depending on the complex type (Fig. 3) Linear oligoisothianaphthenes are denoted as **Ln** and complexes between C60 and a linear oligoisothianaphthenes are indicated as **LCn**, Cation and anion radicals are referred to as + and −, respectively.

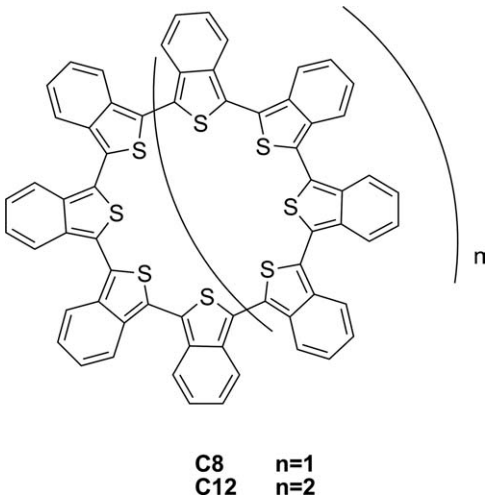

Figure 2. Cyclooligoisothianaphthenes host molecules.

It has been demonstrated that the ground state structure of **PITN** is open shell singlet.[15] Therefore, the stability of the electronic states of all oligoisothianaphthenes has been tested first using "stable" keyword to ensure that the lowest electronic state is found. It was found out that all oligoisothianaphthenes have closed shell singlet ground state.

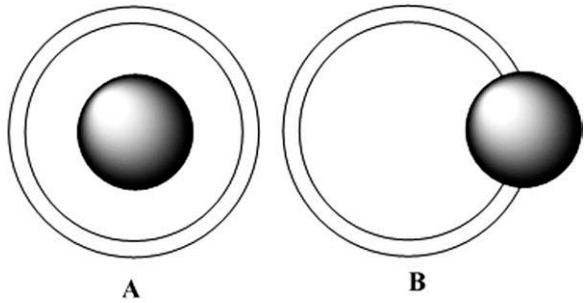

Figure 3. Mutual orientation of C60 and oligoisothianaphthenes in C60-cyclooligoisothianaphthenes complexes.

Results and Discussion

Geometry of c60-cyclooligoisothianaphthenes complexes

Figure 4 depicts the geometries of optimized complexes. For both macrocycles **C8** and **C12** were detectedcomplexes of **A** and **B** type. As seen from Figure 4, the formation of complex **C8A** results in a drastic change in the macrocycle conformation. Thus, **C8** adopts a conic conformation (Fig. 4) in complex **C8A** to maximize the overlap between π orbitals of C60 and the corresponding orbitals of cyclooligoisothianaphthene macrocycle.

On the other hand, the complexation does not affect significantly the conformation of macrocycles in other complexes. The closest distances between the macrocycle and C60 molecule in complexes were found to be of 3.27 Å for **C8A**, 2.76 Å for **C8B**, 3.62 Å for **C12A** and 2.73 Å for **C12B**, respectively. Cyclooligoisothianaphthenes and C60 are also able to form complexes by the interaction of π cloud of the macrocycle rim and the π system of C60 (**B**). Actually, this type of complexes is the most stable, according to experimental data,[6] for some of the complexes between C60 and cyclooligothiophenes.

Binding energies

Table 1 shows calculated binding energies of studied complexes. As seen from the table, the BSSE represents very important correction to the binding energy Thus, for **C8A**, the counterpoise correction represents almost half of the binding energy since geometry of this complex favors large BSSE. For the complexes formed by linear oligoisothianaphthenes or **B**-type complexex BSSE is less important and their relative stabilities are similar for BSSE corrected and uncorrected energies.

As seen from Table 1, the most stable complexes are **C8A** and **C12A** due to close matching between macromolecular cavity adopting conic shape and C60. The stability of "inclusion" complexes decreases from **C8** to **C12** due to increasing mismatch between the size of the molecular cavity and C60. The complexes of **A** type were found to be more stable than **B** type complexes for all macrocycle sizes. There have been found a correlation between binding energies and electron donating properties of oligoisothianaphthene molecules for **B** type complexes and those formed by linear oligomers. Thus, the

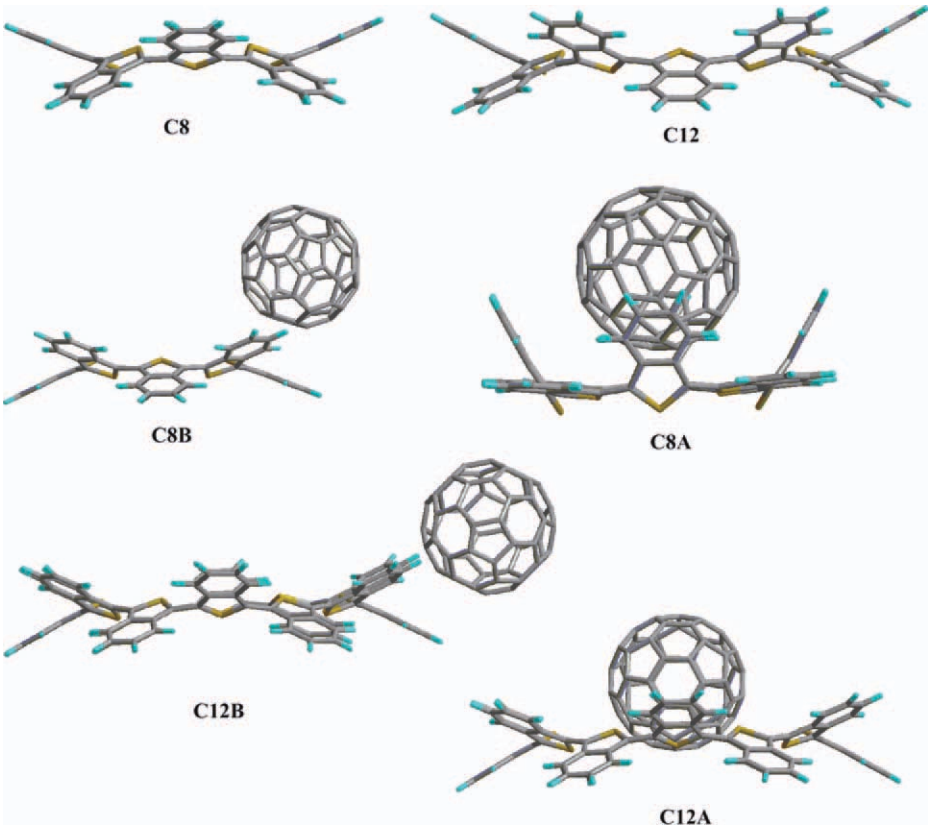

Figure 4. M05-2X/6-31G(d) optimized geometry of cyclooligoisothianaphthenes and their complexes. C60-cyclooligoisothianaphthenes complexes are denoted as **CnX** where **n** is the number of isothianaphthene units in cycloisothianaphthene fragment, and **X** is the type of complex according to Figure 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ionization potential of donor molecules increases in the order **L12**, **L8**, **C8**, and **C12** (Table 3). The binding energies of the CT complexes decrease in the same direction when **A** type of complexes are excluded.

Excited states properties

Table 2 shows S0→S1 excitation energies for cyclic oligoisothianaphthenes, their linear analogues and the corresponding complexes with C60. The energy of S0→S1 transitions in cyclooligothiophene-C60 complexes varies from 1.61 eV for **C8A** to 2.14 eV **LC8** (Table 2), depending on TD-DFT scheme used for calculations. However, both models are consistent with each other; TD-M05-2X and TD-CAM-B3LYP predict similar trends in transition energies. Thus, both methods predict the lowest transition energy for **C8A** and the highest for **LC8**. In general, S0→S1 energies of C60 – oligoisothianaphthene complexes are of 0.5 eV lower compared with similar complexes C60 with oligothiophenes[7] and, therefore they are more suitable for photovoltaic applications.

The comparison of TD-M05-2X and TD-CAM-B3LYP models for calculation of excitation energies shows that for the donor fragments both functional deliver very similar results. Calculated S0→S1 energy for CT complexes, however, is of 0.16–0.27 eV higher for CAM-B3LYP model, especially designed for the treatment of CT excited states[16] demonstrating that TD-M05-2X model produces reasonably results for CT excited states too due to high fraction of HF exchange. For **A** type "inclusion" complexes the most important contribution for S0→S1 transition is HOMO→LUMO excitation while for **B** type complexes or those of C60 with linear oligoisothianaphthene there are a number of excitations involved into S0→S1 transition. To visualize better the nature of the electron

Table 1. M05-2X/6-311G**//M05-2X/6-31G* counterpoise corrected (E_1) and uncorrected (E_2) binding energies in kcal/mol. Charges on C60 fragment in S0 (q_g) and S1 (q_{ex}) states in neutral and charged complexes. Charge difference on C60 fragment in S1 and S0 states (Δq).

Complex	E_1	E_2	q_{ex}[a]	q_g[b]	Δq
C8A	13.79	21.08	−0.76	−0.03	0.73
C8B	7.53	10.62	−0.06	−0.03	0.03
			−0.99[c]		0.96[c]
C12A	9.23	13.40	−0.78	−0.04	0.74
C12B	5.77	7.94	−0.92	−0.03	0.89
LC8	9.15	12.63	−0.89	−0.03	0.86
LC12	9.30	12.76	−0.92	−0.03	0.89
C8A+	14.72	22.56	–	–	–
C8A−	11.17	19.20	–	–	–
C8B+	8.29	11.32		–	–
C8B−	8.52	11.47	–	–	–
LC8+	8.49	12.16	–	–	–
LC8−	9.39	13.12	–	–	–
C12A+	11.49	15.82	–	–	–
C12A−	10.1	15.3	–	–	–
C12B+	8.09	10.10	–	–	–
C12B−	8.83	11.20	–	–	–
LC12+	8.95	12.78	–	–	–
LC12−	9.80	13.52	–	–	–

[a] Calculated at TD-CAM-B3LYP/6-311G**//M05-2X/6-31G* level.
[b] Calculated at CAM-B3LYP/6-311G**//M05-2X/6-31G* level.
[c] Mulliken charges calculated for S2 state.

Table 2. S0→S1 transition energies (E_g, eV) in cyclooligothiophenes and 'C60-cyclooligothiophene complexes estimated at TD-M05-2X/6-311G**//M05-2X/6-31G* and TD-CAM-B3LYP/6-311G**//M05-2X/6-31G* level of theory.

Molecule	E_g[a]	E_g[b]
C8A	1.61	1.82
C8B	1.70	1.86
	1.71[c]	1.94[c]
C12A	1.76	2.02
C12B	1.80	2.07
LC8	1.92	2.14
LC12	1.91	2.13
C8	1.90	1.89
C12	2.16	2.13
L8	2.39	2.36
L12	2.24	2.20

[a] M05-2X. [b] CAM-B3LYP. S0→S2 transition.

Table 3. Vertical (v) and adiabatic (a) ionization potentials (IP) and electron affinity (EA), relaxation energies (λ_+, λ_-) estimated at M05-2X/6-311**//M05-2X/6-31G* level of theory in eV.

Molecule	IP_v	IP_a	λ_+[a]	EA_v	EA_a	λ_-[b]
C8A	5.91	5.69	0.22	2.50	2.59	0.09
C8B	5.88	5.72	0.16	2.60	2.71	0.11
C12A	5.95	5.52	0.43	2.65	2.99	0.34
C12B	5.94	5.77	0.20	2.72	2.81	0.09
LC8	6.17	5.65	0.52	2.62	2.69	0.07
LC12	6.14	5.56	0.58	2.65	2.70	0.05
C60	–	–		2.60	2.66	0.06
C8	5.89	5.76	0.13	–	–	–
C12	5.96	5.87	0.09	–	–	–
L8	6.19	5.64	0.55	–	–	–
L12	6.10	5.57	0.53	–	–	–

[a] $\lambda_+ = IP_v$-IP_a. [b] $\lambda_- = EA_a$-EA_v.

excitations in CT complexes, natural transition orbitals were used.[17] Figure 5 depicts the dominant natural transition orbital pairs for S0→S1 transitions in selected CT complexes. In all cases except for **C8B**, the electron transfer from donor fragment to acceptor one (C60) occurs. It is noteworthy that in the case of **B**, type complex, where C60 interacts with macrocycle rim the electron transfer occurs mostly from the macrocycle part closed to C60 (Fig. 5). In the case of **C8B**, S0→S1 transition does not result in the electron transfer from cyclooligoisothianaphthene moiety to C60. To monitor the change of the electron density on excitation the Mulliken charges in S0 and S1 state were also calculated.

As seen (Table 1) the CT in the ground state of the complexes is minimal not exceeding 0.05 electron for all complexes**.** In all complexes except for **C8B** strong electron transfer exists from donor to acceptor unit in S1 state. For **C8B** complex electron transfer is observed in S2 state (Fig. 6). Complexes of **A** type show weaker CT in the excited state compared with **B** type or linear complexes due to better overlapping between orbitals of the donor and the acceptor fragments. The CT in the ground state of **LC8** and **LC12** complexes are similar to those of **B** type due to the similarity in the interaction pattern between donor and acceptor moieties.

Cation and anion radicals

Table 1 presents binding energies of charged CT complexes. Electron detachment and electron attachment change the binding energies of CT complexes. Both reduction and oxidation slightly increases the binding in all complexes except for **C8A** and **LC8** where the reduction decreases binding energies The change in binding energies, however, is only moderate. In the case of oxidation, positive charge is localized at donor fragment while in case of the reduction the negative charge is located at acceptor fragment (Fig. 7).

Both oxidation and reduction decrease donor–acceptor interaction in CT complexes. However, the origin of interactions in CT complexes is not entirely donor–acceptor, there is a significant contribution from dispersion interactions as well.

Strength of dispersion interactions is related to the polarizability of the involved species. Table 4 lists calculated isotropic polarizabilities of neutral and charged species involved in CT complex formation. As seen, cation radicals of oligoisothianaphthenes (both cyclic and linear) possess much higher polarizabilities compared with neutral species. On the other hand, polarizability of C60 increases only slightly on one electron reduction. Therefore, oxidation leads to an increase of dispersion interactions in CT complexes sometimes overcompensating a decrease in donor–acceptor interactions. This effect is less notorious on the reduction due to only moderate increase of the polarizability of C60 anion compared with neutral C60 and could be a reason for a decrease in binding energy in **C8A-**, comparing with neutral complex. As seen from Figure 7 the charge distribution is not symmetrical in cation radicals which is related with large relaxation energies (λ) of cation radicals (Table 3) leading to the localization of a polaron cation.[18] The reduction of CT complexes changes very little the geometry of donor and acceptor component in CT complexes which is reflected in low λ_- (Table 3) for anion radicals. The negative charge in anion radicals is mostly located in C60 fragment and its rigid structure impedes the deformation. On the other hand, there is notorious geometrical changes of cyclooligoisothianaphthene component in cation radicals where aromatic structure is transformed to quinoid one in the area of localization of polaron cation. Thus, the inter ring bond lengths shorten from 1.45 in neutral complexes to 1.41 Å in the area of localization of polaron cations in cation radicals.

A comparison between λ's of the complexes formed by cyclyoligothiophenes and cyclooligoisothianaphthene with C60 demonstrated that for the most stable **C8A** type if complexes λ_+ is smaller for cyclooligoisothianaphthene (0.22 vs. 0.29 eV.) while λ_- is smaller for cyclyoligothiophene (0.09 vs. 0.06 eV).[7] In all other cases the relaxation energies are higher for cyclooligoisothianaphthene complexes. This is due to larger geometrical changes occurring on electron detachment or electron attachment for oligoisothianaphthenes compared with cyclyoligothiophenes. Since smaller relaxation energies correspond to higher charge mobility[19] C8A compnex probably the best potential candidate for photovoltaic applications.

Conclusions

All studied macrocycles are able to form two types of CT complexes. **A** and **B** and their binding energies depend on the

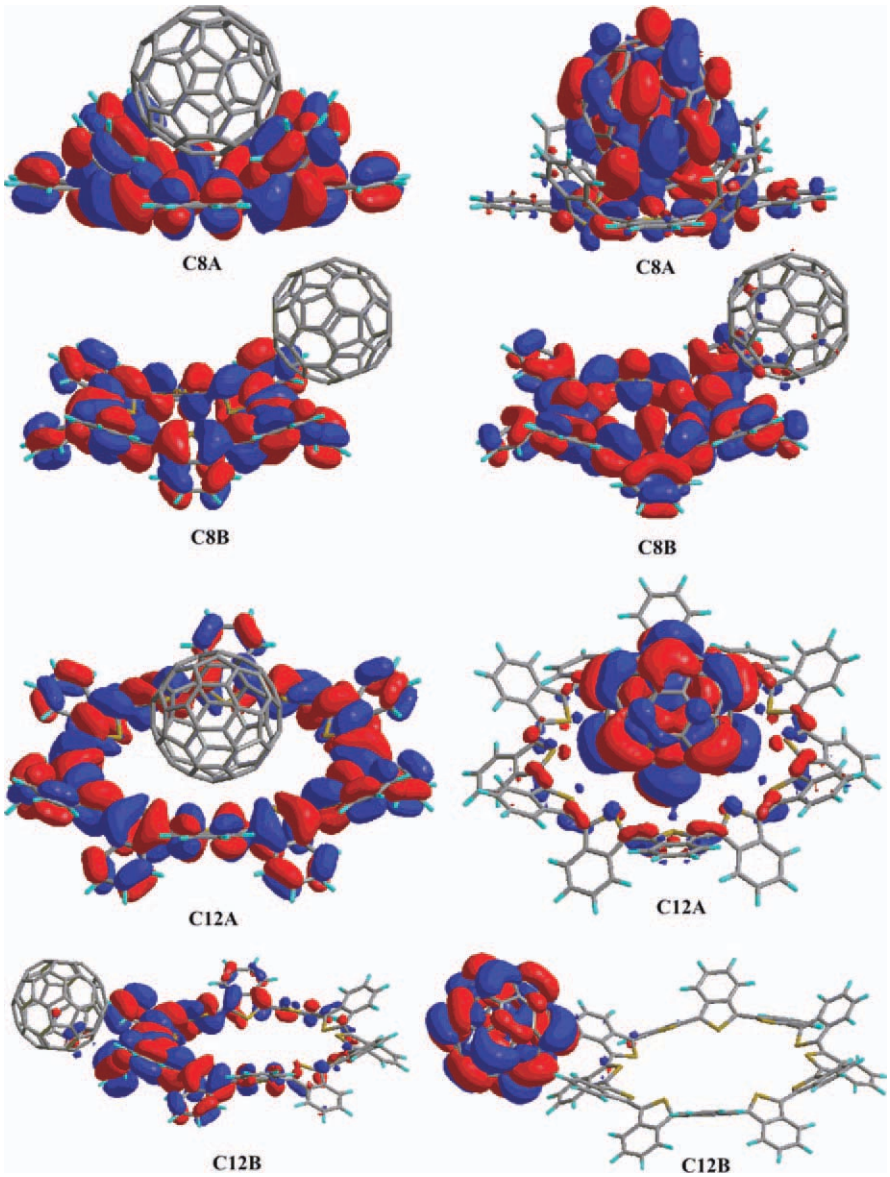

Figure 5. The dominant natural transition orbital pairs for S0→S1 transitions in selected CT complexes calculated at CAM-B3LYP/6-311G**//M05-2X/6-31G* level. The 'hole' is on the left, the 'particle' on the right. The associated eigenvalues are 0.957, 0.818, 0.914, and 0.984, for **C8A**, **C8B**, **C12A**, and **C12B**, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

architecture of the donor component. **A** type 'inclusion' complexes were found to be the most stable ones. BSSE represents an important fraction of the binding energies and should be taken into account for binding energy estimation. The highest binding energy is predicted for **C8A** complex. All complexes show little CT in the ground state. However, there is almost

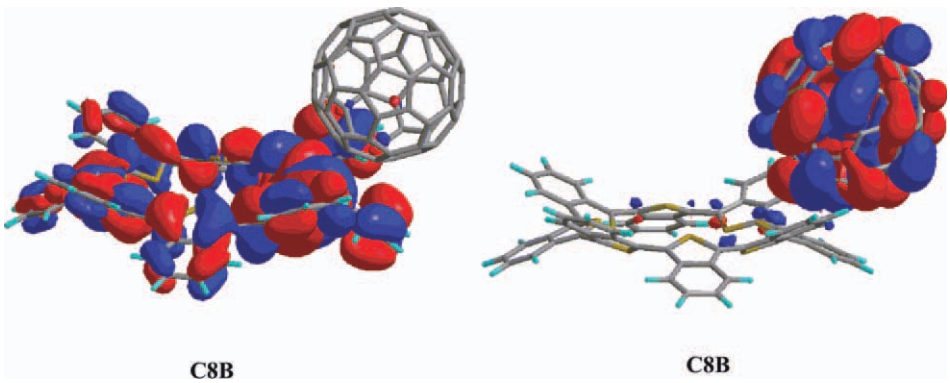

Figure 6. The dominant natural transition orbital pairs for S0→S2 transition in **C8B** complex calculated at CAM-B3LYP/6-311G**//M05-2X/6-31G* level. The 'hole' is on the left, the 'particle' on the right. The associated eigenvalue is 0.990. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

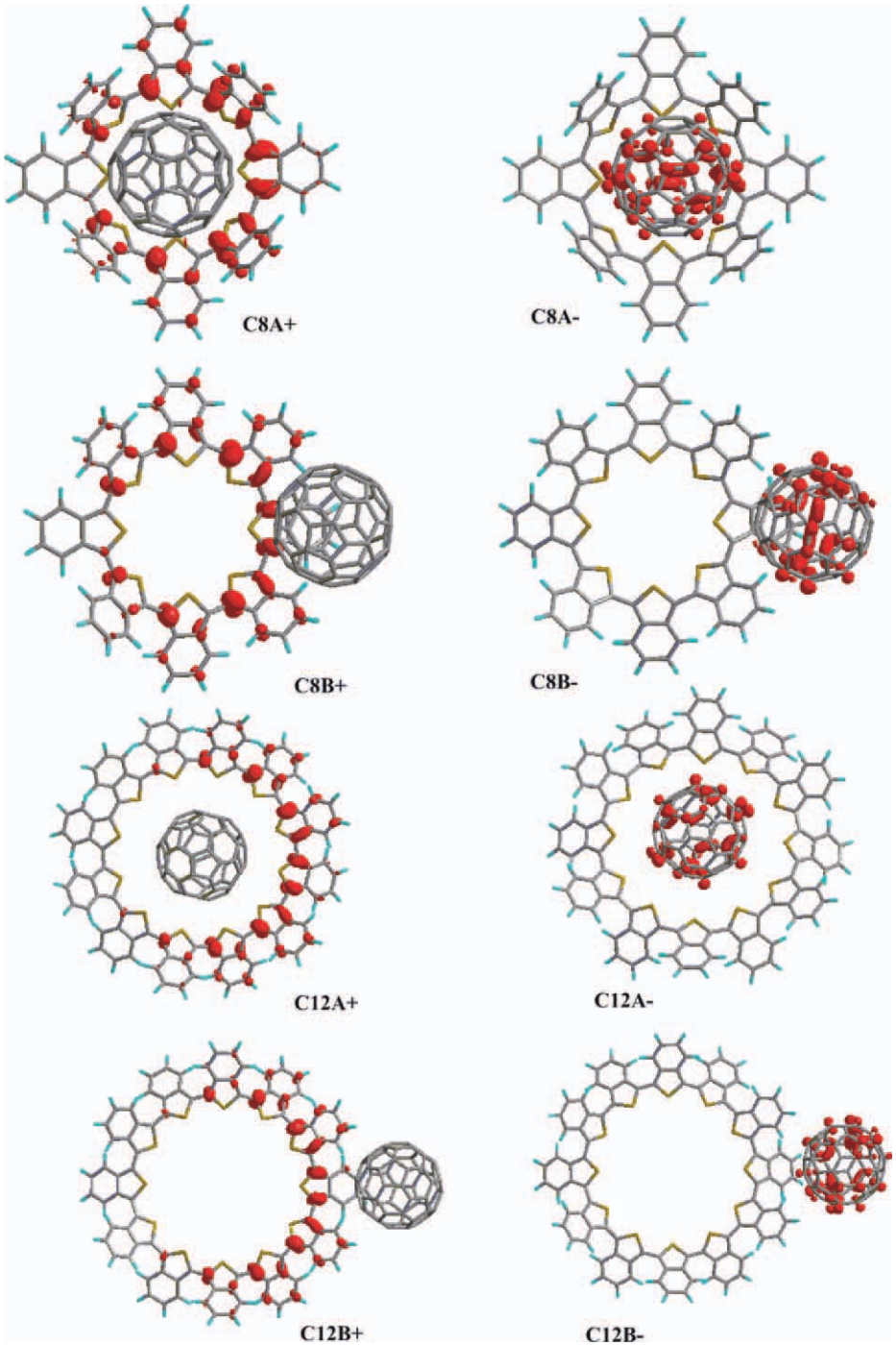

Figure 7. Spin density distribution in cation and anion radicals of selected complexes estimated at M05-2X/6-31G* level. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 4. Isotropic static polarizabilities of oligoisothianaphthenes and C60 estimated at M05-2X/6-311G**//M05-2X/6-31* level in au^3

Molecule	Neutral	Cation	Anion
L8	1123.9	2962.2	–
L12	1810.9	8318.5	–
C8	1140.1	2228.4	–
C12	1779.1	18696.9	–
C60	484.7	–	530.7

complete electron transfer to C60 fragment in all complexes in the excited state. S0→S1 energies of C60—oligoisothianaphthene complexes are lower compared with similar complexes C60 with oligothiophenes and, therefore they are more suitable for photovoltaic applications. One electron oxidation or reduction of the complexes leads to the localization of positive or negative charge at oligoisothianaphthene or C60 fragment, respectively. Relaxation energies were found to be significantly higher for cation radicals than for anion radicals due to greatest flexibility of donor component compared with [60]fullerene.

Keywords: DFT · C60 · PITN · charge transfer · excited state

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