

New 1D and 2D Nanoscaled Materials Based on the Tetraoxa[8]circulene Monomer

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(Received 13 August 2014; published online 29 August 2014)

New one- and two-dimensional p-conjugated materials containing a tetraoxa[8]circulene monomer are theoretically predicted on the basis of density functional theory techniques. These novel materials are predicted to demonstrate a promising hole/electron mobility properties which are typical for the ambipolar organic semiconductors. Furthermore, the growth of p-conjugation determines the strong visible light absorption of the studied systems in a great contrast to the initial lack of color of the tetraoxa[8]circulene compound. The synthesis of these new organic p-conjugated materials is an important task because of their potential practical applications in optoelectronic devices.

Keywords: Tetraoxa[8]circulene, Density functional theory, Nanotubes, Hole/electron mobility, Reorganization energy, Cyclooctatetraene core, Ambipolar semiconductors.

PACS numbers: 72.80.Le, 78.40.Me

1. INTRODUCTION

Symmetrical tetraoxa[8]circulene [1–4] are planar p-extended compounds with a circular system of condensed furan and benzene rings that has a planar cyclooctatetraene ring at the center. Some tetraoxa[8]circulenes have recently found numerous applications, for instance, for the preparation of discotic liquid crystals [3], blue organic light-emitting diodes (OLEDs) [4].

The first representative of the tetraoxa[8]circulene family was synthesized in 1968 [1] by the cyclooligomerization of α -naphthoquinone in the presence of strong mineral acids. Soon after, the simplest tetraoxa[8]circulene was also synthesized using the same method [1] from p-benzoquinone [2]. All tetraoxa[8]circulenes are thermally and chemically stable compounds and can be easily functionalized using the free CH vacancies. In this way we have predicted the possibility of their evolution to the 1D and 2D nanoscaled tetraoxa[8]circulene materials following chemical modification. A similar phenomenon was experimentally observed for the porphyrin molecules which form stable porphyrin sheets (porphyrin tetramer) with a planar cyclooctatetraene core [5, 6].

2. COMPUTATIONAL METHODS

The equilibrium structural parameters of the studied 1D and 2D compounds (see Fig. 1, 2) were optimized at the B3LYP/6-21G(d) level of the density functional theory (DFT) [7, 8] with the control of possible symmetry constraints, using the Gaussian 09 software package. With the same method the IR spectra were calculated for the 1D oligomers ($n = 1-4$) and for the simplest 2D square sheet structures containing four tetraoxa[8]circulene (TOC) units (2×2 , Fig. 1) to determine the true minimum of the total energy. All vibrational mode frequencies are real, which indicates the true minimum of the total energy finding. The electronic absorption spectra

of all the studied molecules were calculated by the time dependent (TD) DFT method [9] in gas phase using the same B3LYP functional and 3-21G basis set.

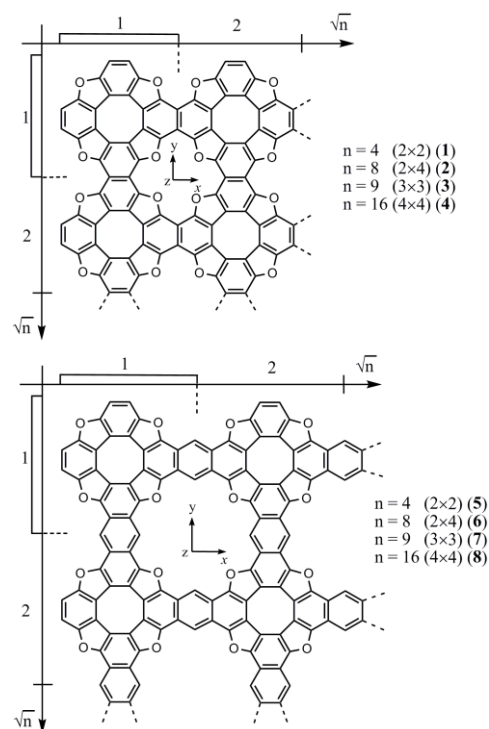


Fig. 1 – The structure of the tetraoxa[8]circulene sheets (n denotes the total numbers of tetraoxa[8]circulene units, whereas \sqrt{n} indicates the size of the corresponding compounds along xz and yz directions (except compounds 2 and 6 for which longitudinal and transversal n values are not equivalent).

All calculations were performed at the PDC supercomputers of the Royal Institute of Technology (Stockholm).

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3. RESULTS AND DISCUSSION

3.1 Structural features

All the designed compounds, including the linear 1D oligomers and 2D sheets represent completely planar nanoscaled species. The square sheets and the simplest tetraoxa[8]circulene correspond to the D_{4h} symmetry point group, whereas the linear oligomers are described D_{2h} symmetry.

The linear compounds (2×4) and other p-extended tetraoxa[8]circulene sheets are characterized by the advent of a bending opportunity. In this way, their saddle-shaped structures are formed and finally they curved into the single-wall nanotubes according to a spiralization mechanism “cochlea” model [10] (see Fig. 2, compounds **9**, **10**). The diameter and length of such nanotubes depend on the size parameters a and b of the initial sheet. Another way to modify the size of TOC-based nanotubes is the inclusion of additional benzene rings, which take place in the the naphthalene-substituted tetraoxa[8]circulene species [1–4, 11, 12].

An important observation is that the tetraoxa[8]circulene sheets **1–4** and nanotube **9**, contain the 16-crown-4 system [13, 14] (blue square in Fig. 2) which is active in respect to the metal ions extraction [13, 14] (the distance between two opposite oxygen atoms equals 4.09 Å).

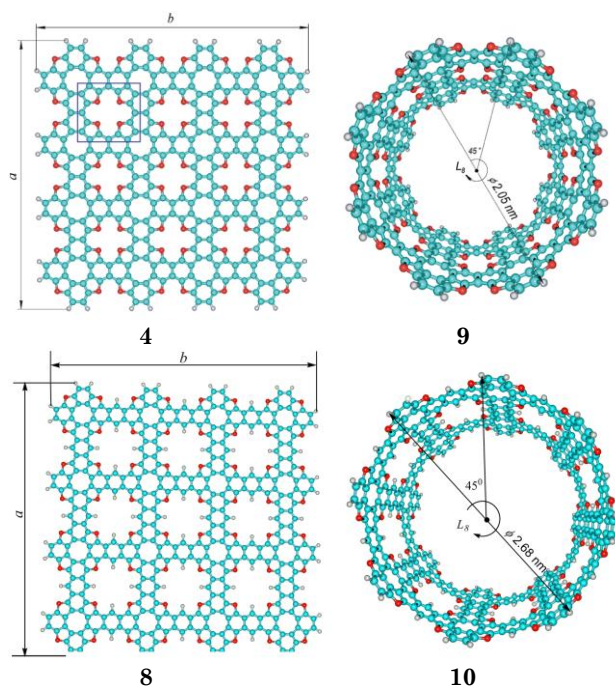


Fig. 2 – The optimized structure of the tetraoxa[8]circulene sheets **4**, **8** and corresponding nanotubes **9**, **10** all of them constructed from 16 basic TOC monomers.

3.2 Electronic absorption spectra

Experimental and calculated electronic absorption spectra of the simplest tetraoxa[8]circulene molecule were previously published and are well described [11, 12]. In particular, the absence of a visible absorption in the observed and calculated UV-vis spectra of the free TOC molecules was stressed.

Surprisingly, we have found that the tetraoxa[8]circulene sheets and nanotubes can strongly absorb light in the visible region (around 560 for compounds **1–4**, **9** and 500 nm for compounds **5–8**, **10**) in great contrast to the free TOC monomer and other p-extended tetraoxa[8]circulenes [3, 10], which demonstrate only a weak light absorption near the blue edge of the visible region (below 410 nm). Such unprecedented strong absorption by compounds **1–10** can be assigned to the formation of cyclic acene chromophores and their p-conjugation through the tetraoxa[8]circulene units. The increase in visible absorbance with the growth of the molecular surface is in good agreement with the acene chromophore dominant role.

3.3 The HOMO–LUMO gap engineering and charge carrier motilities

The HOMO–LUMO gap (HLG) of the TOC-based compounds is varied with increasing of their length from 2.69 eV for **1** compound to 2.08 eV for **4**; and from 2.74 eV for **5** to 2.51 eV for **8** (Table 1) Thus the TOC-based 2D sheets are predicted to possess a very low HLG (≈ 1.7 eV at the boundary condition) compared with most of the known 2D conjugated polymers [15].

Table 1 – The HOMO–LUMO gap values for the TOC-based nanotubes

TOC-compounds	HOMO–LUMO gap energies, eV
(1) 2×2	2.69
(2) 2×4	2.32
(3) 3×3	2.28
(4) 4×4	2.08
(5) 2×2	2.74
(6) 2×4	2.62
(7) 3×3	2.58
(8) 4×4	2.51
(9) 2×8	2.07
(10) 2×8	2.48

All p-extended TOC-based 2D frameworks **1–8**, **1D ribbons** and nanotubes **9–10** are characterized by the very small values of the electron/hole reorganization energies, calculated at the B3LYP/6-21G(d) level of theory using the algorithm described in Ref. 16, 17. In this way, the studied compounds are predicted to be good electron donors/acceptors, which is a general feature of the ambipolar semiconductors.

4. CONCLUSIONS

Nanoscaled 1D ribbons, 2D sheets and single-wall nanotubes containing directly fused tetraoxa[8]circulene monomers have been designed and described in the present work at the DFT level. The tetraoxa[8]circulene based compounds are absolutely planar compounds which exhibit bending in a prolonged ribbon and subsequently spiralling and closing into a single-wall nanotube.

The designed compounds are characterized by a strong size-dependent visible absorption because of the specific p-conjugation producing cyclic acene chromophores. All designed compounds (except the initial tetraoxa[8]circulene monomer) are predicted to be good ambipolar organic semiconductors. This prediction is supported by the very small values of the electron/hole reorganization energies.

ACKNOWLEDGEMENTS

All computations are performed with resources provided by the Swedish National Infrastructure for Computing (SNIC) at the Parallel Computer Center (PDC) through the project "Multiphysics Modeling of Molecular Materials", SNIC 020/11-23. This research was also supported by the Ministry of Education and Science of Ukraine (project number 0113U001694).

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