This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Tetra-hetero[8]circulenes were theoretically designed and emerged as good candidates for ambipolar organic semiconductors.

Vu Thi Thu Huong, Truong Ba Tai and Minh Tho Nguyen

In the present work, a series of new tetra-hetero[8]circulenes were theoretically designed in which heteroatoms include O, S, Se and N. Their electronic structure and characteristics of charge transport were investigated using the DFT based computational methods. Except for the compounds containing Se-atoms (3a and 3b), all remaining compounds exhibit planar and highly symmetrical structures featuring novel aromatic features: the inner eight-membered ring is anti-aromatic and the outer fused rings are aromatic. Predicted UV spectrum and reduction potential of 1a agree well with available experimental values. Following replacement of H-atoms by F-atoms, the energy levels of frontier orbitals of 1b-4b are consistently decreased as compared to those of 1a-4a. Based on the calculated properties of electrochemistry and charge transport, the molecules 1a-4a and 4b are suggested as good candidates for p-type semiconductors. More importantly, the molecules 1b-3b are revealed to be potential ambipolar organic semiconductors.

Introduction

[n]Circulenes, which consist of compounds having two concentric annulene rings, have attracted much attention as an intriguing family of aromatic polycyclic hydrocarbons. Three members of this family, including [5]circulene (corannulene), [6]circulene (coronene) and [7]circulene (pleiadannulene), have experimentally been prepared for a long time and the characteristics of their electronic structure, chemical bonding and adsorption spectra were well determined. Although earlier theoretical studies suggested that [8]circulene is unstable, this molecule was recently successfully synthesized by Wu and coworkers. Their shapes interestingly change from a bowled shape for [5]circulene to a planar structure for [6]circulene and saddled shapes for [7]- and [8]circulenes.

Recently, the family of hetero[8]circulenes appears to be even more intriguing. Replacing the outside benzene fused-rings by heterocyclic rings such as furan, thiophene... results in planar heteropolycyclic compounds with highly π-conjugated electronic structures which can eventually be used in many important applications. Octathio[8]circulene, named as sunflower, (C₁₆S₈) in which all outside fused benzene rings are replaced by eight fused thiophene rings, was for the first time synthesized in 2006, and found as a good p-type organic semiconductor by both experiment and theory. Subsequently, the electronic structure and charge transport properties of its analogues molecules such as C₁₆S₄Se₂ and C₁₆X₈ with X =O, Se, NH, CH₂, PH and PF were also extensively studied. They were suggested as either p-type or n-type organic semiconducting materials with high rate of charge hopping. More recently, Datta and his co-workers designed similar molecules, named as Si- and Ge-sulflower, in which C-atoms of C₁₆S₈ were replaced by either Si-atoms or Ge-atoms. These molecules were found to be bowled structures and exhibit a large number of metallic-like states with weak optical absorption. In a recent study, we theoretically designed a series of new hetero[8]circulenes containing borole units. These heteropolycyclics feature some intriguing aromatic characteristics at both inner and outer rings. Such interesting results stimulated us to further design of new π-conjugated materials based on the [8]circulene framework.

Tetra-hetero[8]circulenes in which only four fused benzene rings are replaced by four fused hetero-rings, have recently emerged as promising π-conjugated materials for organic electronic devices. In fact, tetraoxo[8]circulene was already found by experiment since 1960s, but its applicable properties were not properly explored. Recently, Minaev and his co-workers performed a series of theoretical and experimental studies on electronic structure, spectroscopic properties, aromaticity and bonding characteristics of tetraoxa[8]circulenes and its derivatives. Pittelkow et al. reported the preparation of a series of π-extended tetraoxa[8]circulenes and their optical and electrochemical properties. These compounds showed high thermodynamic stability and can be used as promising materials for the development of blue organic light-
emitting diodes (OLEDs). More recently, some planar
cyclooctatetraenes such as azatrioxa[8]circulenes and
diazadioxa[8]circulenes in which one and two O-atoms were
replaced by N-atoms were successfully synthesized. Their
characteristics of single-crystal X-ray structure, aromaticity,
and spectroscopy were investigated in both experiment and
theory.\(^{19}\) In other way, Minaev et al.\(^{20,21}\) reported theoretical
results on the one- and two-dimensional nano-materials
containing tetraoxa[8]circulene monomers. The authors found
that these materials can be used as ambipolar organic
semiconductors with high mobility for both hole and electron
charge carriers.

In order to further explore this intriguing class of
heteropolycyclic compounds, we herein performed theoretical
studies of structural characteristics, electronic and charge
transport properties of tetraoxo[8]circulene\(^{1a}\) and its
derivatives in two different series\(^{2a-4a}\) and\(^{1b-4b}\) using DFT-
based computational methods. The derivatives are designed by
simply replacing oxygen atoms of\(^{1a}\) with sulfur (\(^{2a}\)), selenium
(\(^{3a}\)) and NH- groups (\(^{4a}\)). Additionally, replacement of H-
atoms of compounds\(^{1a-4a}\) by fluorine results in perfluoronated
compounds\(^{1b-4b}\)* that are expected to have reduced LUMO
energy levels and can thus be used as effective n-type organic
semiconductors. Our results show that most of designed
molecules exhibit the planar structures with high degree of π-
conjugation and high rate of charge hopping.

Optimizations of the relevant geometries and calculations of
their harmonic vibrational frequencies are fully performed
using DFT. The hybrid functional B3LYP\(^{22,24}\) are used in
conjunction with the 6-31G(d,p) basis sets.\(^{25,26}\) For open-shell
systems such as cations and anions, the unrestricted formalism
(UB3LYP) is used. This popular functional was proved to be
reliable in predicting geometrical parameters and charge
transport properties of many π-conjugated systems. For each
species considered, the neutral, anionic and cationic states are
characterized. All electronic structure calculations are carried
out using the Gaussian 09\(^{27}\) suite of programs.

### 2. Charge transport properties

In order to probe the charge transport properties, the
hopping model is used.\(^{28-33}\) Accordingly, the hole and electron
carriers can be jumped between the adjacent molecules of
the organic crystals. The rate of charge hopping (\(K\)) is estimated by
using the Marcus-Hush equation (1):\(^{34}\)

\[
K = (t^2/\hbar) \exp(-\lambda/4k_B T) \sqrt{\pi/4k_B T} 
\]  

(1)

where \(t\) is the transfer integral between two adjacent
molecules, \(\lambda\) the reorganization energy, \(k_B\) Boltzmann constant
and \(T\) the temperature (298 K in our calculations). Accordingly,
a high rate of charge hopping \(K\) is obtained when the transfer
integral \(t\) between two molecules is high, and the monomers
have low reorganization energy \(\lambda\).

The transfer integral is defined by the following expression
(2):\(^{35-37}\)

\[
t = \langle \phi_i^{0,site1} | F | \phi_j^{0,site2} \rangle 
\]

(2)

where \(\phi_i^{0,site1}\) and \(\phi_j^{0,site1}\) present the HOMO (or LUMO) of
isolated molecules 1 and 2, respectively. \(F\) is the Fock operator
\((F = S.C.E.C^{-1})\) of the dimer with a density matrix from non-
interacting dimer, where \(S\) is the intermolecular overlap matrix,
\(C\) and \(\epsilon\) are the molecular orbital coefficients and energies,
respectively, from one-step diagonalization without iteration.

The transfer integral for hole \((\tau_h)\) is calculated as half of the
energy difference between the HOMO and HOMO-1 of the
dimer, while the transfer integral for electron \((\tau_e)\) is half of the
energy difference between the LUMO and LUMO+1 of the
dimer. These orbital energy levels are obtained using density
functional theory (DFT) with the PW91PW91 functional\(^{38,39}\) in
conjunction with the 6-31G(d,p) basis set. This approach has
been shown to be suitable and effective in calculations of the
transfer integrals of many organic compounds.\(^{40-48}\) We should
note that the transfer integral is functional dependent property
and their values systemically depend on the fraction of nonlocal
HF exchange incorporated in a functional. Sutton et al.\(^{48b}\)
showed that the amount of HF exchange substantially affects
the transfer integral in a linear fashion with respect to the
fraction of nonlocal HF exchange incorporated in a standard
hybrid functional.

### 2.3 Reduction and oxidation potentials in solution.

---

**Figure 1** Chemical structure of the [8]circulene and hetero[8]circulenes considered.

---

# 2. Computational Methods

## 2.1 Electronic structure calculations.

**ARTICLE**

**Journal Name**

---

2 | J. Name., 2014, 00, 1-3

This journal is © The Royal Society of Chemistry 2014
The reduction and oxidation potentials of compounds in solution are calculated by using a protocol recently developed
by Davis and Fry.\(^{49}\) Firstly, optimizations of geometries and calculations of vibrational frequencies of each compound in
the neutral, anionic and cationic charge states are performed at the
B3LYP/6-31+G(d) level. Their single point electronic energies
are obtained using a larger basis set, B3LYP/6-311+G(2df,2p). Addition of a set of diffuse functions in the
basis set is necessary to describe the structures of the ions
involved in the evaluation. The SMD/IEF-PCM solvation model\(^{50}\) in acetonitrile solvent is used to probe the solvent
effects. These methods were proven to be effective to obtain the
reduction and oxidation potentials of PHA compounds in solution.\(^{49,51}\) Davis and Fry\(^{49}\) showed that using equations 4 and
5 results in a mean absolute deviation (MAD) for the polycyclic
aromatic hydrocarbons (PAHs) of 0.023 and 0.032 mV,
respectively.

The absolute potentials at 298K are obtained using the
following equation (3):
\[
E_{\text{Abs}}^{298} = E_{\text{calc}}^{298} - 0.03766
\]
where \(E_{\text{calc}}^{298}\) is calculated from the difference in free energy
(G) at 298K between the couples neutral/cation and
anion/neutral. The value of 0.03766 accounts to small thermal
correction for a free electron at 298K.\(^{52}\)

The reduction potential is predicted in MeCN solution for
the ferrocene-ferrocenium (Fc/Fc\(^{+}\)) pair, and the standard redox
couple are calculated by using the expressions (4) and (5):
\[
\text{Reduction: } E_{1/2}^{298} = 1.056 E_{\text{Abs}}^{298} - 4.90
\]
\[
\text{Oxidation: } E_{1/2}^{298} = 0.932 E_{\text{Abs}}^{298} - 3.94
\]

3. Results and Discussion

3.1 Electronic structure and aromaticity of compounds

Geometric optimizations and calculations of harmonic
vibrational frequencies of all compounds are performed using
the hybrid functional B3LYP in conjunction with the polarized
6-31G(d,p) basis set. This method was demonstrated to provide
reliable geometries and charge transport properties of the
organic semiconductors in many previous studies.\(^{53-58}\) The
chemical structures of all compounds are shown in Figure
1, whereas their shapes are given in the electronic
Supplementary information file (ESI).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>NICS(0)</th>
<th>NICS(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>1a</td>
<td>8.4</td>
<td>-10.4</td>
</tr>
<tr>
<td>1b</td>
<td>7.1</td>
<td>-13.5</td>
</tr>
<tr>
<td>2a</td>
<td>6.7</td>
<td>-9.5</td>
</tr>
<tr>
<td>2b</td>
<td>6.8</td>
<td>-12.2</td>
</tr>
<tr>
<td>3a</td>
<td>4.1</td>
<td>-10.4</td>
</tr>
<tr>
<td>3b</td>
<td>4.3</td>
<td>-10.0</td>
</tr>
<tr>
<td>4a</td>
<td>8.0</td>
<td>-11.0</td>
</tr>
<tr>
<td>4b</td>
<td>6.7</td>
<td>-14.3</td>
</tr>
</tbody>
</table>

Figure 2 Plots of the UV spectra of all molecules 1a-4a and 1b-4b
Table 2. Oxidation and Reduction Potentials and Energy Levels of HOMO and LUMO of compounds in Acetonitrile Solution (B3LYP/6-311++G(2df,2p)

<table>
<thead>
<tr>
<th>Comp</th>
<th>E$_{1/2}^{\text{red}}$</th>
<th>E$_{1/2}^{\text{oxd}}$</th>
<th>HOMO</th>
<th>LUMO</th>
<th>Gap (eV)</th>
<th>Comp</th>
<th>E$_{1/2}^{\text{red}}$</th>
<th>E$_{1/2}^{\text{oxd}}$</th>
<th>HOMO</th>
<th>LUMO</th>
<th>Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>-2.09</td>
<td>1.47</td>
<td>-6.27</td>
<td>-2.71</td>
<td>3.55</td>
<td>1b</td>
<td>-1.83</td>
<td>1.50</td>
<td>-6.30</td>
<td>-2.97</td>
<td>3.34</td>
</tr>
<tr>
<td>2a</td>
<td>-2.20</td>
<td>1.12</td>
<td>-5.92</td>
<td>-2.60</td>
<td>3.32</td>
<td>2b</td>
<td>-1.82</td>
<td>1.44</td>
<td>-6.24</td>
<td>-2.98</td>
<td>3.26</td>
</tr>
<tr>
<td>3a</td>
<td>-2.11</td>
<td>0.87</td>
<td>-5.67</td>
<td>-2.69</td>
<td>2.98</td>
<td>3b</td>
<td>-1.82</td>
<td>1.25</td>
<td>-6.05</td>
<td>-2.98</td>
<td>3.07</td>
</tr>
<tr>
<td>4a</td>
<td>-2.58</td>
<td>0.47</td>
<td>-5.27</td>
<td>-2.22</td>
<td>3.05</td>
<td>4b</td>
<td>-2.32</td>
<td>0.90</td>
<td>-5.70</td>
<td>-2.48</td>
<td>3.22</td>
</tr>
</tbody>
</table>

Fig 3 Shapes of HOMOs and LUMOs of molecules and their energy levels in unit of eV

Computed results in Table 1 showed that the inside eight-membered rings of compounds are anti-aromatic with positive NICS values, whereas all outside rings exhibit aromaticity with negative NICS values. There is negligible difference in aromatic character of molecules with different hetero atoms. In addition, replacing H-atoms of 1a-4a by F-atoms of 1b-4a only change somewhat the aromatic feature of compounds. These aromatic features are similar to those of the sulflower C$_{18}$S$_{8}$ and its derivatives. Thus it is expected that these compounds are characterized by high π-conjugation, and thereby good ability of intramolecular charge transport.

3.2 Absorption UV spectra of compounds.

The absorption UV spectra of all compounds are predicted using the time-dependent (TD-DFT) method with the B3LYP functional in conjunction with the 6-31+G(d,p) basis set. This method was evaluated to give reliable predictions for optical spectra of organic compounds. The plots of absorption UV spectra of all compounds are displayed in Fig. 2. There is a good agreement between our theoretical predictions and the available experimental and theoretical results. Accordingly, the UV spectrum of 1a shows two local peaks with high intensity centered at 255 and 261 nm which agree well to the experimental value of 260 nm. Another local peak is located at 354 nm that is close to the experimental peaks at 358 and 376 nm. Our calculations also reveal a local peak at 416 nm which agrees well with the experimental value of 415 nm. This peak actually corresponds to a π-π* transition from HOMO to LUMO. However, this absorption has low intensity in both experimental and theoretical spectra. The low absorption intensity corresponds to a small transition moment between the ground and excited states. The transition moment is derived mainly from the integrals of the dipole moment acting on both states. In this case, it is characterized by the small overlap between the transition orbitals HOMO and LUMO. Similar observations were also found for the UV spectra of remaining compounds.
More interestingly, Figure 2 shows that the UV spectra of compounds considered tend to be red-shifted when F-atoms in 1a and 1b are replaced by S- and Se-atoms. Two high intensity peaks at 267 and 383 nm were found in the UV spectrum of 2a, whereas the 3a is characterized by two local peaks at 285 and 415 nm. Following perfluorination of compounds 1a-3a, the first local peaks in UV spectra of 1b-3b is red-shifted, while their second local peaks are blue-shifted as compared to those of 1a-3a, respectively. The UV spectra of 4a and 4b are similar to those of 2a and 2b, respectively.

### 3.3 Reduction and oxidation potentials of compounds in the solution.

The values of reduction and oxidation potentials, that are related to the energies of frontier molecular orbitals (FMO), play important role for applicability of organic semiconductors. The energy levels of HOMO (characteristic for p-type semiconductor) and LUMO (for n-type semiconductor) should be close to work functions (WF) in vacuum of electrodes in order to improve their charge transport ability. In experimental studies, some electrodes such as gold (Au) (WF ~ 5.10 eV), calcium (WF ~ 2.90 eV), and magnesium (WF ~ 3.68 eV) are commonly used. While the gold electrode is one of the best electrodes for organic electronic device, the calcium and magnesium electrodes are the preferred ones for n-type organic semiconductors due to the fact that this type of materials usually possesses a LUMO energy level of ~ 3.0-4.0 eV.

In this study, the reduction and oxidation potentials and energy levels of frontier orbitals of the molecules examined are calculated using the SMD/IEF-PCM solvation model in acetonitrile solvent (see above). All computed values are given in the Table 2, while the shapes of frontier orbitals are displayed in Fig 3.

The reduction potential of 1a is equal to -2.09 eV that is slightly higher than the highest experimental value of -2.39 eV of 1a. It can be observed that the compounds containing group VIA elements 1a-3a and 1b-3b have comparable energy levels of frontier orbitals. The LUMO and HOMO of 4a and 4b containing pyrrole units are higher. Additionally, the HOMO energy levels of the 1a-4a vary in a range of (-5.27) – (-6.27) eV, and are in the sequence of 1a < 2a < 3a < 4a. A similar trend is found for the series 1b-4b. These values are close to the work function of 5.1 eV of gold electrode, and consequently they are expected to be good candidates for p-type semiconductors.

Replacement of H-atoms in 1a-4a by F-atoms consistently decreases the energy levels of both HOMO and LUMO of 1b-4b. More importantly, the LUMOs of 1b-3b have similar energy levels and are equal to ~3.00 eV. These values are very close to that of 2.90 eV of the calcium electrode. The LUMO energy levels of 1a-3a are somewhat higher and close to 2.70 eV. Thus, the perfluorinated compounds 1b-3b can act as ambipolar organic semiconductors. 1a-3a and compounds containing pyrrole 4a and 4b have high LUMOs, and accordingly they can only be suitable for p-type organic semiconducting materials.

### 3.4 Charge transport properties of compounds

#### 3.4.1 Reorganization energy

<table>
<thead>
<tr>
<th>comp</th>
<th>$D_{\text{LUMO}}$ (Å)</th>
<th>Interaction Energy (eV)</th>
<th>Reorganization energy (eV)</th>
<th>Integral Transfer ($\tau$, meV)</th>
<th>Rate of charge hopping ($K$, $s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>B3LYP-3D</td>
<td>M06</td>
<td>hole</td>
<td>electron</td>
</tr>
<tr>
<td>1a</td>
<td>3.74</td>
<td>1.00</td>
<td>1.12</td>
<td>0.19</td>
<td>0.19</td>
</tr>
<tr>
<td>2a</td>
<td>3.85</td>
<td>1.30</td>
<td>1.40</td>
<td>0.13</td>
<td>0.24</td>
</tr>
<tr>
<td>3a</td>
<td>3.95</td>
<td>1.30</td>
<td>1.34</td>
<td>0.35</td>
<td>0.28</td>
</tr>
<tr>
<td>4a</td>
<td>3.84</td>
<td>1.04</td>
<td>1.12</td>
<td>0.17</td>
<td>0.19</td>
</tr>
<tr>
<td>1b</td>
<td>3.70</td>
<td>1.22</td>
<td>1.40</td>
<td>0.26</td>
<td>0.29</td>
</tr>
<tr>
<td>2b</td>
<td>3.62</td>
<td>1.51</td>
<td>1.68</td>
<td>0.17</td>
<td>0.28</td>
</tr>
<tr>
<td>3b</td>
<td>3.68</td>
<td>1.57</td>
<td>1.60</td>
<td>0.24</td>
<td>0.34</td>
</tr>
<tr>
<td>4b</td>
<td>3.80</td>
<td>1.36</td>
<td>1.51</td>
<td>0.25</td>
<td>0.29</td>
</tr>
<tr>
<td>C$<em>{16}$S$</em>{8}$</td>
<td>3.87</td>
<td>-</td>
<td>0.98</td>
<td>-</td>
<td>0.29</td>
</tr>
</tbody>
</table>

*aThese values obtained from reference 11.
In order to evaluate the charge transport characteristics for electron and hole of molecules, the reorganization electron energy is first considered. A molecule exhibits a high rate of charge hopping when it has low reorganization energy. The reorganization energy is defined as the sum of geometrical relaxation energies when the species goes from the neutral state geometry to charged state geometry, and vice versa (equation 6 and 7):

\[ \lambda_h = \lambda_0 + \lambda_e = [E(M) - E^0(M)] + [E(M^+) - E^0(M^+)] \]  \hspace{1cm} (6)
\[ \lambda_e = \lambda_0 + \lambda_h = [E(M) - E^0(M)] + [E(M^-) - E^0(M^-)] \]  \hspace{1cm} (7)

where \( \lambda_h \) and \( \lambda_e \) are reorganization energies for hole and electron, respectively; \( E(M^+) \) and \( E(M) \) the total energies of the cationic and anionic states with the optimized geometries of the neutral ground state, respectively; \( E(M) \) the total energy of the neutral state with the optimized geometries of the cationic species (for equation 6) and of the anionic species (for equation 7); \( E^0(M) \), \( E^0(M^+) \) and \( E^0(M^-) \) the total energies of the neutral, cationic and anionic ground state species, respectively.

In the present work, the reorganization energies for electron and hole of all compounds are calculated using the B3LYP/6-31G(d,p) method and the computed results are listed in Table 3. Except for the relatively large \( \lambda_h \) value of 3a (\( \lambda_h = 0.35 \text{ eV} \), Table 3) which is due to a large distortion of its cationic state, the reorganization energies for hole and electron of 1a-4a are quite low and vary in a range of 0.17 - 0.19 eV and 0.19 - 0.28 eV, respectively. As compared to the computed values of C\(_{16}\)(PF)\(_h\) (\( \lambda_h = 0.30 \text{ eV} \) and \( \lambda_e = 0.22 \text{ eV} \)) and perfluoropentacene (PF-PEN) (\( \lambda_h = 0.23 \text{ eV} \) and \( \lambda_e = 0.23 \text{ eV} \)) which is a typical n-type organic semiconductor, the reorganization energy for hole (\( \lambda_h \)) of 1a-4a are properly lower. Their \( \lambda_e \) values are close to those of PF-PEN and C\(_{16}\)(PF)\(_h\). Although the perfluorinated compounds 1b-4b showed the \( \lambda_h \) and \( \lambda_e \) values a bit higher than those of 1a-4a, they are also comparable to those of compounds previously reported.

3.4.2 Dimer interactions and rate of charge hopping (K)

To further probe the behaviour of charge transport, we perform calculations of the dimer interactions of molecules considered. The geometries of dimers are constructed in a translational parallel motif (Figure 4) and optimized by using the B3LYP-3D functional that contains dispersion energy (as denoted by -D) in conjunction with 6-31G(d,p) basis set.

The intermolecular interaction energy of dimers is defined by expression (8):

\[ E_{\text{int}} = 2E_{\text{monomer}} - E_{\text{dimer}} \]  \hspace{1cm} (8)

where \( E_{\text{monomer}} \) and \( E_{\text{dimer}} \) are total energies of monomer and dimer, respectively. They are computed using the functionals B3LYP-3D and M06. These approaches were previously tested as effective for evaluating the dimer interactions.\(^{12,45}\) To further consider the effect of basis sets used, we performed single point energy calculations on these optimized configurations by using functional M06 in conjunction with three different basis sets, including 6-31G(d,p), 6-311G(d,p) and 6-311+G(d,p). Our computed results pointed out that the intermolecular interaction energies of dimers tend to be increased as size of basis sets increased (Table S2, ESI). Adding polarized function only somewhat changes the interaction energies of dimers.

Our calculated results are given in Table 3 and compared with calculated properties of the previously reported C\(_{16}\)S\(_{8}\). We should note that the molecular structures of the designed compounds 1a-4a and 1b-4b are in fact similar to that of sulflower C\(_{16}\)S\(_{8}\). Thus, a comparison between C\(_{16}\)S\(_{8}\) and the molecules designed in this work appears useful to understand their charge transport characteristics.

The strong interactions between monomers in dimers of all compounds were observed. The distances between monomers (\( D_{\text{monomer}} \)) vary in a small range of 3.62 - 3.95 Å and are close to the value of 3.87 Å of C\(_{16}\)S\(_{8}\). The interaction energies between two monomers amount to 1.04 - 1.57 eV that is properly larger than the value of 0.98 eV of C\(_{16}\)S\(_{8}\). Consequently, it can be seen that integral transfers for hole of compounds are comparable to that of C\(_{16}\)S\(_{8}\), whereas their integral transfers of electron becomes much larger. Since the C\(_{16}\)S\(_{8}\) was reported as good p-type organic semiconductor, the compounds considered in this work are expected to be appropriate for both n-type and p-type semiconductors.

4. Conclusions

We theoretically designed a series of new tetra-hetero[8]circulenes based on an inner eight-membered ring. The electronic structure and characteristics of charge transport of all compounds were investigated using DFT based computational methods. Except for the compounds containing Se-atoms (3a and 3b), all remaining compounds exhibit planar and highly symmetrical structures with a novel aromatic feature: while the inner eight-membered ring is anti-aromatic, the outer fused rings are aromatic.

The predicted UV spectrum and reduction potential of 1a agree well with available experimental values. Following replacement of H-atoms by F-atoms, the energy levels of frontier orbitals of 1b-4b are consistently decreased as compared to those of 1a-4a.

Based on the properties of electrochemistry and charge transport calculated, the molecules 1a-4a and 4b can be regarded as good candidates for p-type semiconductors. More importantly, the molecules 1b-3b are revealed to exhibit characteristics suitable for ambipolar organic semiconductors.
Since the n-type and ambipolar organic semiconducting materials remain rare, we would hope that the present results will attract much attention from the experimental scientists.

At the time of finalizing this report, we interestingly found that tetrathio- and tetraselono[8]circulenes were experimentally synthesized by Wong et al.65

Acknowledgements
We are indebted to the KU Leuven Research Council (GOA) and Vlaams Supercomputer Centrum (VSC). VTTH and TBT would like to thank the FWO-Vlaanderen for Ph. D. and postdoctoral fellowships.

Notes and references
Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium.
E-mail: minh.nguyen@chem.kuleuven.be and truong.batai@chem.kuleuven.be

Electronic Supplementary Information (ESI) available: The xyz-coordinates of the optimized structures 1a-4a and 1b-4b at the neutral state. DOI: 10.1039/b000000x/

43 G. Nan and Z. Li, Organic Electronics, 2012, 13, 1229-1236