

Heterocirculenes as a new class of organic semiconductors†

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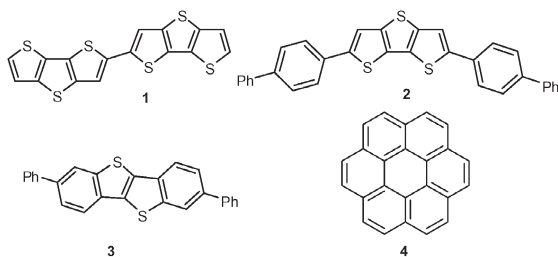
Received (in Berkeley, CA, USA) 2nd June 2008, Accepted 13th August 2008

First published as an Advance Article on the web 19th September 2008

DOI: 10.1039/b809259a

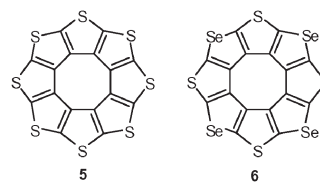
We report a fabrication of field-effect transistors using the new organic semiconductors octathio[8]circulene **5 and tetrathio-tetraseleno[8]circulene **6**. The maximum hole mobility of $9 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is, most likely, limited by one-dimensional growth of **5** and **6** in thin films.**

Organic semiconductors (OSCs) are an important class of functional materials due to their use in electronic and optoelectronic devices such as light-emitting devices (LEDs), field-effect transistors (FETs), photovoltaic cells, *etc.*¹ While the charge carrier mobilities achieved for some OSCs already rival that of amorphous silicon, the long term operational and storage stability, which is inherently linked to molecular structure, still limits the wide implementation of OFETs. Therefore, the design of new stable organic semiconducting materials is of great practical interest. Pentacene and its derivatives, as well as linear oligo- and polythiophenes have been the two most studied classes of materials in OSCs.^{2–4} However, their chemical instability, particularly towards oxygen,⁵ limits their use in practical applications. In this respect, fused oligothiophenes (such as thieno[3,2-*b*]thiophene and dithieno[3,2-*b*:2,3-*d'*]thiophene derivatives, **1–3**) are particularly interesting, as they show a combination of high charge carrier mobility with excellent stability.^{4c,6} Bis(dithienothiophene) **1** was the first OSC of this series showing good stability and a hole mobility of $0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,^{6a} and even higher mobilities of 0.4 and $2.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ have been reported more recently for compounds **2**^{6c} and **3**,^{6d} respectively.



The most common approach for increasing the mobility of OSCs is to add several benzene (thiophene) rings in a linear fashion, as exemplified by structures **1–3**. A far less explored possibility is to extend the conjugation by linking the aromatic units in a macrocycle, as in circulenes. The higher symmetry of such molecules (as compared to linear structures) is potentially more favorable for solid-state packing, although a practical advantage of this property is yet to be demonstrated. No OFETs have been reported for the parent circulene, coronene **4**, although discotic liquid crystalline derivatives of π -extended hexabenzocoronene have been employed as semiconductors in OFETs and photovoltaic cells and showed a hole mobility of up to $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁷ In the condensed state **4** and its derivatives form π -stacked columns with strong electronic coupling (and facile charge transport) along the column, but little or no electronic communication between the columns, which is responsible for pronounced one-dimensional charge transport.⁷

Introducing heteroatoms, such as S or Se, on the periphery of the circulene core, can induce intercolumnar interactions and, possibly, improve the charge-carrier mobility in such OSCs.⁸ The first all-heterocyclic octathio[8]circulene **5** (sulfur) has been recently synthesized by some of us.⁹ In the solid state and in thin films it packs in columns held together by close S...S contacts ($\sim 3.25 \text{ \AA}$),^{9,10} which could facilitate a 3D charge transport. Sulfur **5** can also be considered as a fused oligothiophene, thus establishing a structural similarity with OSCs **1–3**, as well as a planar radialene.¹¹ Here we demonstrate the applicability of **5** and its selenium analogue tetraselenotetrathio[8]circulene **6** (selenosulfur) as OSCs by fabricating thin-film transistors with these materials.



Both compounds **5** and **6** show an exceptional thermal and chemical stability in accordance with a large HOMO–LUMO gap ($> 4 \text{ eV}$) and rather low HOMO ($< -5 \text{ eV}$).⁹ Remarkably, heating either **5** or **6** in air in TGA setup shows clean sublimation at $\sim 450\text{--}500 \text{ }^\circ\text{C}$ with no sign of decomposition.

According to density functional theory (DFT) calculations at B3LYP/6-31G(d,p) level, the HOMOs are at -5.74 and -5.52 eV and LUMOs are at -0.04 and -1.03 eV , for **5** and **6**, respectively. Considering the almost total insolubility of the studied heterocirculenes, solution electrochemistry to corroborate the HOMO

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† Electronic supplementary information (ESI) available: Experimental and computational details; synthesis of **6**; AFM height histograms and 3D views; XRD and TGA data; the OFET characteristics at different deposition temperatures. See DOI: 10.1039/b809259a

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values was not possible. Thus, solid-state cyclic voltammetry was performed on vacuum sublimed films of **5** and **6** (Fig. 1). In line with DFT calculations, selenosulfur **6** is easier to oxidize than sulfur **5**. The HOMOs of **5** and **6**, derived from their oxidation potentials, are -5.7 eV ($E_{1/2} = 0.89$ V vs. Fc/Fc^+) and -5.2 eV ($E_{1/2} = 0.38$ V vs. Fc/Fc^+), respectively. \S

Thin films of heterocirculenes **5** and **6** were prepared by vacuum deposition on Si/SiO₂ substrates pre-patterned with Au circular electrodes.¹² The performance of the resulting OFETs was measured in a N₂ atmosphere (Fig. 2, Table 1).

OFETs with sulfur **5** as OSC showed a hole field effect mobility and on/off current ratio of about $9 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 10^6 , respectively. A rather high threshold voltage, ranging from -40 to -46 V was measured for these devices. This can be explained (at least partially) by the very low HOMO of **5** (-5.7 eV, see above) and the resulting hole injection barrier at the Au electrode (workfunction -5.1 eV). Selenosulfur **6** OFETs showed a lower mobility of about $1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ albeit with much lower threshold voltage of -10 V, in

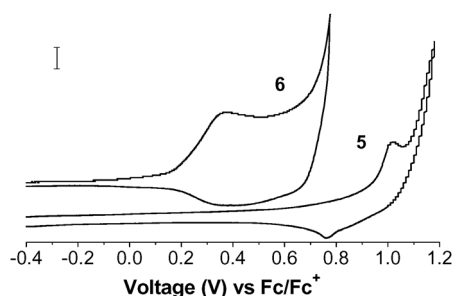


Fig. 1 Cyclic voltammetry of vacuum deposited films of **5** and **6**, recorded in Bu₄NPF₆-propylene carbonate. Vertical scale bar is 20 μA for **5** and 2 μA for **6**. Fc is ferrocene.

accordance with the higher HOMO of **6** (-5.2 eV). High device stability and on/off ratio were also observed for this OSC. Preliminary optimization efforts by changing the substrate temperature (20 – 130 °C) during deposition did not increase hole mobility (see ESI \dagger). The lower mobility of selenosulfur **6** vs. sulfur **5** is somewhat surprising. The reorganization energy for **6** (0.123 eV), as calculated at B3LYP/6-31G(d,p) level, is slightly lower than that for **5** (0.136 eV). \P Furthermore, the more polarizable selenium atoms are generally expected to provide for stronger intermolecular interactions as evidenced by increased conductivity and charge mobility, and reduced band gap in selenium-containing molecular solids and polymers, as compared to their sulfur analogues.^{6e,8,13} X-Ray diffraction (XRD) patterns for the vacuum deposited thin films of **5** and **6** show characteristic reflections at the same angles as those obtained from the single-crystal X-ray structures of these compounds (see ESI \dagger). The strongest XRD peaks for **5** and **6** are at a d -spacing of 3.52 and 3.61 Å, respectively, which correspond to the π -stacking interaction in these solids. The sharper XRD peaks of **5** (*ca.* 0.25°) vs. **6** (*ca.* 0.5°) infer somewhat better crystallinity of its films, which might partially explain the higher hole mobility. \parallel

The largest difference, however, was observed in the morphology of vacuum deposited films of **5** and **6**, as revealed by atomic force microscopy (AFM). The sulfur exhibits pronounced one-dimensional growth morphology (Fig. 3). At very low coverage (Fig. 3(a)) randomly-oriented joint needles with an average area of $12\,000 \text{ nm}^2$ and an average height of *ca.* 10 – 12 nm were observed. As the substrate coverage increases (Fig. 3(b)), the grains keep growing one-dimensionally and the needle density increases. When the growing needles coalesce, continuing this linear growth is no longer

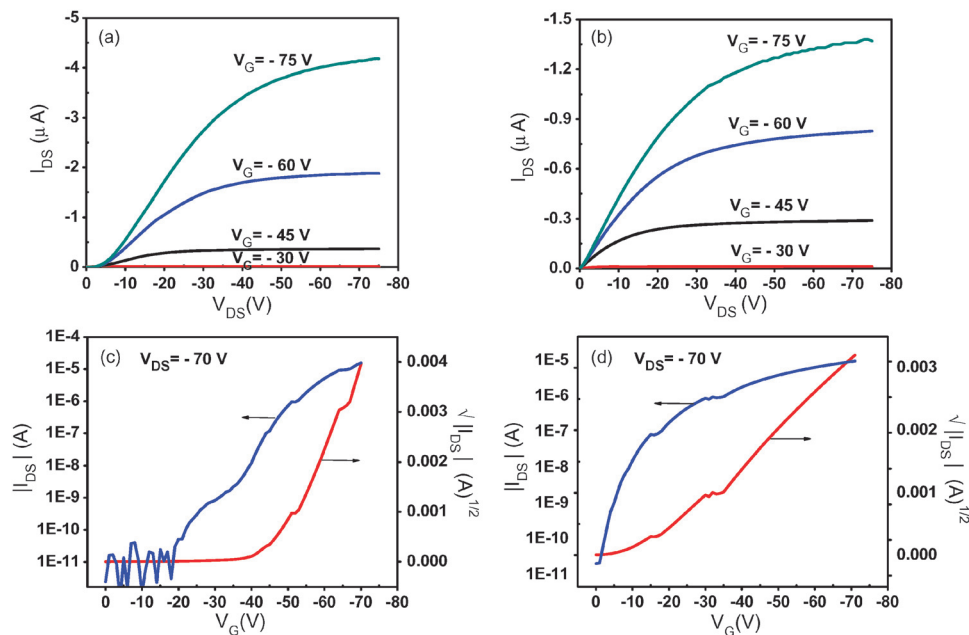


Fig. 2 (a) and (b): output characteristics of bottom-contact OFET of **5** and **6**, respectively; (c) and (d): transfer characteristics of the same devices (**5** and **6**, respectively). Deposition rate 0.2 \AA s^{-1} , nominal thickness ~ 36 nm, $W/L = 1880/6 \text{ }\mu\text{m}/\mu\text{m}$. I_{DS} is the drain/source current, and V_{DS} and V_{G} are the drain/source and the gate/source voltage, respectively.

Table 1 OFET characteristics of **5** and **6** films deposited at 25 °C

Compound	$\mu_{\text{h}}/\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	V_{T}/V	On/off
5	9×10^{-3}	-45	10^6
6	1×10^{-3}	-10	10^6

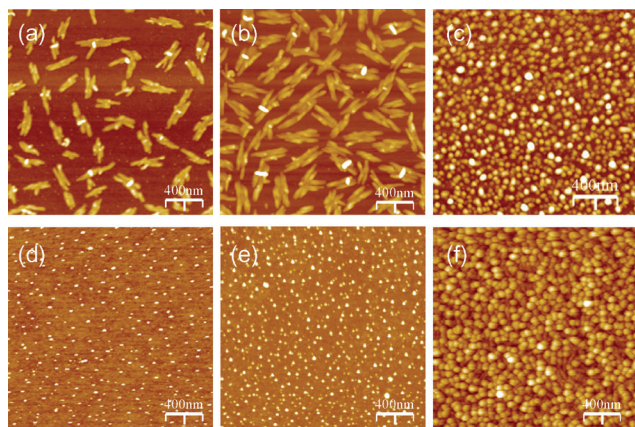


Fig. 3 AFM micrograph ($2 \mu\text{m} \times 2 \mu\text{m}$) images of thin films of **5** with deposition time of (a) 1, (b) 2 and (c) 10 min, respectively, and of **6** with deposition time of (d) 1, (e) 2 and (f) 8 min, respectively. Films grown on SiO_2/Si substrate at room temperature (deposition rate 0.2 \AA s^{-1}).

possible, and they start growing perpendicularly to the substrate (Fig. 3(c)). This growth mode hampers the formation of a continuous film, thus limiting the charge mobility.

Films of selenosulfur follow a different growth mode compared to the sulfflower. The early stages of their growth involve the nucleation of much smaller grains compared with the sulfflower, with a round shape (area $\sim 1200 \text{ nm}^2$ and 2–5 nm height, Fig. 3(d)). As the deposition time increases, the grains continue growing in the direction perpendicular to the substrate (height 6–14 nm), and their density increases (Fig. 3(e)). Thus, no substantial lateral growth of the grains is observed, resulting in a large number of grain boundaries, and negatively affecting the charge mobility. Such unfavorable growth is caused by the very low energy of molecule–surface interactions (as compared to molecule–molecule interactions), which often can be tuned by modifying the surface with organic monolayers. However, our preliminary experiments with hexamethyldisilazane-modified Si/SiO_2 surfaces showed no significant change in the growth mode.

In summary, we have demonstrated that despite a very high HOMO–LUMO gap, heterocirculenes can be used as p-type semiconductors in organic FETs. The highest hole mobility of $9 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and on-off ratio of 10^6 was achieved for octathio[8]circulene **5**. The mobility is most likely limited by the pronounced one-dimensional growth mode of circulenes in thin films which results in a very high density of grain boundaries. A better understanding and control of the film growth will be necessary for rational design of electronic devices based on heterocirculene semiconductors.

We acknowledge financial support from NSERC, FQRNT, ACS-PRF and Centre for Self-Assembled Chemical Structures. D. F. P. is thankful to DuPont Inc. for a DuPont Young Professor Award. F. R. acknowledges partial salary

support from the Canada Research Chairs program. F. C. acknowledges contract MOIF-CT 2006-40864

Notes and references

§ HOMO = $-4.8 - E_{1/2}$ (vs. Fc/Fc^+); $E_{1/2}$ defined as a midpoint between the anodic and cathodic peaks, $E_{1/2} = (E_{\text{pa}} - E_{\text{pc}})/2$.

¶ Both values are substantially lower than those of linear octathio-phenene and octaselenophene ($0.23\text{--}0.24 \text{ eV}^{14}$) although higher than that of pentacene (0.097 eV^{15}). Similar values for reorganization energies of **5** and **6** have also been recently calculated with PBE0 functional.¹⁶

|| We also mention that there is S/Se disorder and higher than stoichiometric amount of S in the circulene **6**, resulting from disproportionation in the high temperature reaction, see ESL.†

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