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Electron-Deficient Triphenylene and Trinaphthylene Carboximides

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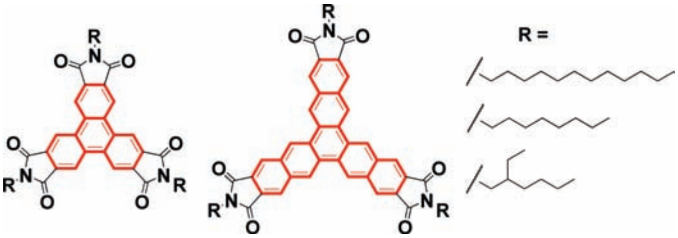
ABSTRACT



A series of triphenylene and trinaphthylene carboximides were synthesized mainly through Diels–Alder reactions between the in situ generated radialenes and *N*-alkylmaleimides. High electron affinity was obtained due to the attachment of electron-withdrawing carboximide groups. These disklike molecules can assemble into one-dimensional columnar structures in solid state and their mesophase properties were characterized by DSC, POM, and X-ray diffraction. Long-range ordered columnar phase was observed, qualifying them as potential n-type semiconductors in electronic devices.

Organic semiconductors have been widely studied from viewpoints of their fundamental optoelectronic properties and their potential applications for such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), photovoltaic cells, and sensors.[1] In the past decades, there have been many hole-transporting (p-type) semiconductors such as oligoacenes and oligothiophenes that have been prepared and used in organic electronics.[2] At the same time, electron-transporting (n-type) semiconductors are also necessary in p–n junction diodes, bipolar transistors, and complementary integrated circuits.[3] Therefore studies on n-type semiconductors have recently attracted an increasing interest. Usually, strong electron-withdrawing groups such as perfluoroalkyl chains, perfluorophenyl, and dicarboxylic imide are attached to the p-type semiconductors (e.g., oligothiophenes) to induce n-type characters.[4] Alternatively, n-type semiconductors can be also designed based on electron-

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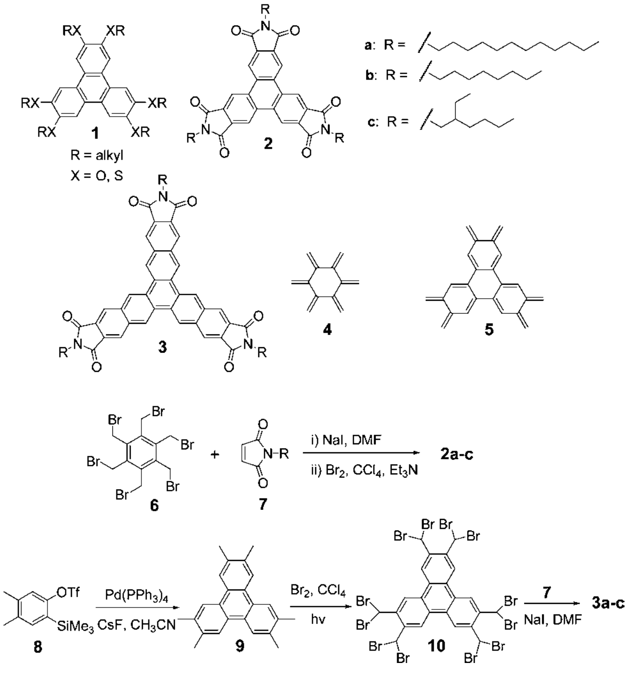
deficient heterocyclic systems.[5,6] Moreover, similar strategies have been applied to the disklike molecules, for example, n-type perylene tetracarboxylic diimide (PDI) and naphthalene tetracarboxylic diimide (NDI) have been successfully used in n-channel OFETs.[7]

Triphenylenes as a kind of discotic molecule are well-known for their remarkable self-assembling and charge transporting properties.[8] However, until today, most reports were only confined to triphenylenes **1** containing electron-donating substituents (e.g., −OR, −SR etc., Scheme 1),[9] and there are few reports to investigate the electron-deficient triphenylenes due to synthetic challenges. As analogues of triphenylene, star-shaped angularly fused oligoacenes, the so-called starphene, is another kind of interesting objective for electronic applications.[10] However, the synthesis of this type of molecule is also challenging. Herein, we report the efficient synthesis of the dicarboxylic imide-substituted triphenylenes **2** and the smallest starphene, the trinaphthylenes **3**, both of which showed desired electronic and self-assembling properties and can be used as potential n-type semiconductors in electronic devices (Scheme 1).

Scheme 1



The synthesis of dicarboxylic imide-substituted triphenylenes **2** and trinaphthylenes **3** is outlined in Scheme 1. Although the ether or thioether-substituted triphenylenes **1** can be facilely prepared by simple intermolecular oxidative cyclodehydrogenation reactions, the electron-deficient phthalimides can not undergo similar oxidative cyclotrimerization. Thus, new synthetic method has to be developed. In this paper, we successfully used Diels−Alder cycloaddition reaction of reactive radialene with maleimide for the synthesis of carboximides **2** and **3**. [6]Radialene **4,**[11] a cross-conjugated alicyclic hydrocarbon possessing six ring atoms and six exocyclic double bonds, was selected as intermediate for the synthesis of compounds **2** due to its high chemical reactivity toward dienophiles. The [6]radialene **4** was generated in situ by treatment of the hexakis(bromomethyl)benzene **6** with NaI in DMF,[11a] and this was followed by Diels−Alder cycloaddition with maleimides **7** containing different alkyl chains. The addition products were then aromatized first by reaction with bromine and followed by treatment with triethylamine to provide the desired compounds **2a−c** in 12−18% yields. The low yields of tris-cycloaddition products obtained from **6** can be attributed to the preferential formation of a linear bis-addition product with a *p*-xylylene structure and the low stability of the as-formed radialenes.[11a] Although the yields are relatively low, this is still the first practical synthesis of dicarboxylic imide-substituted triphenylenes.

A similar concept was used to synthesize the trinaphthylene carboximides **3** and the expanded radialene **5** containing six exocyclic double bonds was chosen as the intermediate structure. For that, the key synthetic intermediate hexakis(dibromomethyl)triphenylene **10** was first synthesized by bromination of hexamethyl triphenylene **9**, which was prepared by Pd-catalyzed cyclotrimerization of the benzyne

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precursor **8**.[12] The bromination was done with bromine in CCl_4 under the irradiation of light, and compound **10** was obtained as a highly insoluble solid after reaction for 5 days. The EI-mass spectrum displayed a molecular ion peak at m/z = 1259.3, confirming the formation of compound **10** (see the Supporting Information). Then the Diels−Alder cycloaddition of **10** with *N*-alkylmaleimides **7** and subsequent aromatization in the presence of NaI in DMF afforded the trinaphthylene carboximides **3** in 35−40% yields. The chemical structures of all new compounds were clearly supported by standard spectroscopic characterizations such as ^{1}H NMR, ^{13}C NMR and mass spectrometry (EI, FAB, MALDI-TOF) (see the Supporting Information).

The UV−vis absorption and photoluminescence (PL) spectra of compounds **2a**−**c** and **3a**−**c** were recorded in chloroform solution. It was found that the alkyl chains almost had no effect on the spectra and thus only the spectra for **2a** and **3a** (R = *n*-dodecyl) are shown in Figure 1. Both compounds showed well-resolved absorption and emission bands in solution, with the absorption maximum at 282 and 338 nm, and fluorescence peaks at 418 and 455 nm, for **2a** and **3a**, respectively. The significant red-shift of both absorption and emission band of **3a** in comparison with **2a** can be ascribed to the extended conjugation. In addition, both compounds displayed very similar band substructures probably because they possess very similar molecular symmetry.

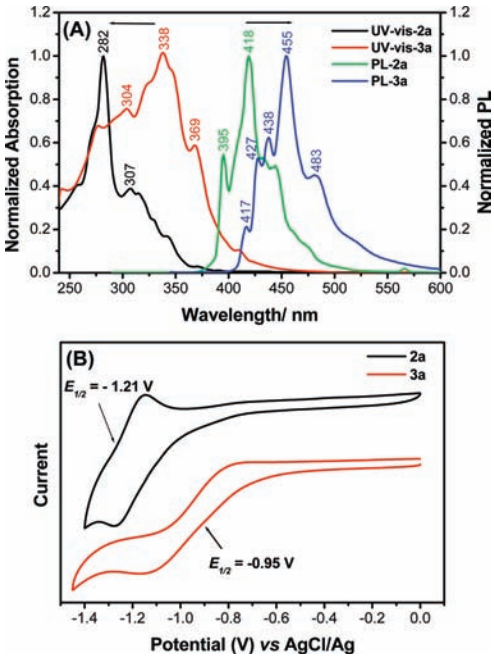

Figure 1. (A) Normalized UV−vis absorption spectra and photoluminescence spectra of compounds **2a** and **3a** in chloroform. (B) Cyclic voltammograms of compounds **2a** and **3a** in dichloromethane with 0.1 M Bu_4NPF_6 as supporting electrolyte, AgCl/Ag as reference electrode, Pt disk as working electrode, Pt wire as counter electrode, and scan rate at 100 mV/s.

The electronic properties of these carboximides were investigated by cyclic voltammetry (CV) in solutions. As shown in Figure 1B, one quasi-reversible reduction wave was observed for both **2a** and **3a**, with the $E_{1/2}$ potential at −1.21 and −0.95 V, respectively. Again, the different alkyl chains have shown less effect on the redox behavior of the respective triphenylene and trinaphthylene carboximides. No obvious redox waves were observed upon oxidation up to 1.8 V. In contrast, hexamethyltriphenylenes[12] and tris(dianisylamino)tris(hexyloxy)triphenylenes[13] showed obvious oxidation waves at 0.5−1.2 V, suggesting that after substitution of electron-withdrawing imide groups, the electron affinity of the triphenylene and trinaphthylene significantly increased. The HOMO and LUMO energy levels of compounds **2** and **3** were calculated based on the CV and UV−vis absorption data. The LUMO energy level (or electron affinity) of compound **2a** and **3a** were determined as −3.44 and −3.68 eV, respectively, indicating that both of them can serve as candidates for n-type semiconductors.[14]

For device applications, it is of importance that the discotic molecules can self-assemble into long-range ordered structures. The thermal behavior and self-assembly of compounds **2** and **3** were investigated with a combination of differential scanning calorimetry (DSC), polarizing optical microscope (POM), and wide-angle powder X-ray diffraction (XRD) (Figures S1−S11 in the Supporting Information). All compounds showed good thermal stability below 350 °C as determined by thermal gravimetric analysis (TGA). It was found that the alkyl chains and the core structures had a significant effect on the phase transition and self-assembly of these disklike molecules in the solid state. Compound **2a** with *n*-dodecyl chains became fluid upon heating and entered into an isotropic phase at 218 °C. Upon slow cooling from the isotropic phase, a mosaic texture was observed in a broad temperature range until room temperature was reached (Figure 2B), indicating an existence of a columnar liquid crystalline phase. The XRD pattern recorded at room temperature showed sharp reflections (Figure 2A), and the reflection peaks at small-angle region can be easily assigned to a two-dimensional orthorhombic unit cell with parameters a = 3.434 nm, b = 2.63 nm, and γ = 90°. The lack of reflection peaks at the wide angle region (d = 3.4−3.5 Å) which can be correlated to the intermolecular $\pi-\pi$ stacking indicated that the columnar stacking was still in a short range. On the DSC curve, there was one phase transition at 46 °C upon heating, and XRD measurement at 130 °C showed a similar pattern except that some higher order reflection peaks became broad or disappeared (see Figures S1 and S4 in the Supporting Information). These suggested that at the elevated temperature (46−218 °C), the discotic molecules entered into a columnar liquid crystalline phase with the columns in a 2D orthorhombic arrangement, and at room temperature, the molecules likely existed in a plastic crystalline phase.

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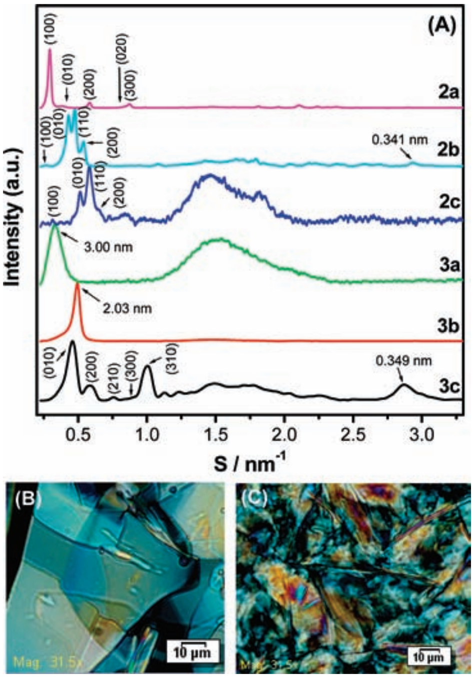

Figure 2. (A) powder XRD patterns of compounds **2a**−**c** and **3a**−**c** at room temperature. (B) POM image of compound **2a** at 215 °C. (C) POM image of compound **2b** at 190 °C.

Compound **2b** with *n*-octyl chains exhibited a similar columnar liquid crystalline phase between 158 and 228 °C with a fan-shaped texture (Figure 2c) in this phase. The XRD pattern at 190 °C only showed broad reflection; however, after cooling to room temperature, a peak at $d = 3.41$ Å which can be correlated to $\pi-\pi$ stacking of these disklike molecules was observed, indicating a long-range columnar stacking. In addition, sharp reflection peaks appeared at the small angle region and a 2D monoclinic unit cell with $a = 3.748$ nm, $b = 2.32$ nm, and $\gamma = 82°$ can be figured out to correlate the intercolumn arrangement. Compound **2c** with branched 2-ethylhexyl chains only showed one melting point upon heating. After being cooled from the clearing point, a spherical crystal appeared (Figure S11 in the Supporting Information), and the XRD at room temperature showed a similar pattern to **2b** in small angle region with a smaller 2D monoclinic lattice ($a = 3.101$ nm, $b = 1.95$ nm, and $\gamma = 85°$). The halo centered at 6.87 Å can be correlated to interactions between alkyl chains and higher order reflections.[15]

For the trinaphthylene carboximides **3a**,**b**, no phase transition was observed by DSC between −20 and +300 °C, and **3c** exhibited a melting point at 348 °C (stable below 450 °C based on TGA). POM studies disclosed that all compounds showed crystalline properties in this temperature range (Figure S11 in the Supporting Information). Compounds **3a** and **3b** showed similar XRD patterns with one reflection peak at the small angle region with a distance of 3.0 and 2.03 nm, respectively. Due to a lack of more reflection peaks, we are not able to correlate an exact 3D packing model for these molecules. However, the 2-ethylhexyl-substituted compound **3c** displayed a very different XRD pattern (Figure 2A). A strong reflection peak correlated to $\pi-\pi$ stacking distance (3.49 Å) was observed, suggesting that these disklike molecules self-assembled into a long-range ordered columnar structure. In addition, a few reflection peaks were observed in the small angle region, and a 2D orthorhombic unit call can be clearly identified with parameters $a = 3.375$ nm, $b = 2.15$ nm, and $\gamma = 90°$. This is interesting since compounds **3a** and **3b** did not exhibit such a highly ordered phase. One possible reason is that the branched alkyl chains can lock the free rotation of disks in each column, and to reach an optimized space filling, the disks may adapt a helical stacking along the column. More detailed studies by using 2D XRD will be conducted in the future to further understand this unique self-assembly.

In conclusion, a series of electron-deficient triphenylene and trinaphthylene carboximides have been successfully synthesized, and their optical properties, electronic properties, thermal properties, and self-assembly in the solid state were investigated. The observed high electron affinity and long-range columnar stacking for some of these molecules suggest that they can be used as promising n-type semiconductors in electronic devices such as field effect transistors. In addition, the synthetic method described here likely can be applied for the synthesis of higher order starphenes in the future.

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Supporting Information Available: Synthetic procedures and characterization data for all new compounds; DSC curves, powder XRD data, and POM images for compounds **2a**−**c** and **3a**−**c**.This material is available free of charge via the Internet at http://pubs.acs.org.

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