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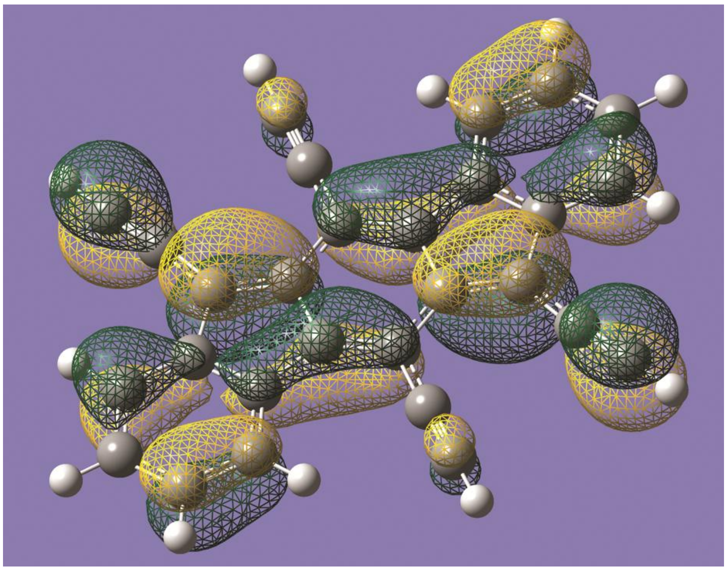

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COMMUNICATION

Angular-shaped naphthodifurans, naphtho[1,2-*b*;5,6-*b*′]- and naphtho[2,1-*b*;6,5-*b*′]-difuran: are they isoelectronic with chrysene?†‡

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Although angular-shaped naphthodifurans, naphtho[1,2-*b*;5,6-*b*′]- and naphtho[2,1-*b*;6,5-*b*′]-difuran, are formally isoelectronic with chrysene as their thiophene counterparts, naphtho[1,2-*b*;5,6-*b*′]- and naphtho[2,1-*b*;6,5-*b*′]-dithiophene, the HOMO energy level of naphthodifurans is much higher than those of naphthodithiophenes and chrysene. The difference in electronic structure in the ground state can be explained by distinct electronic perturbation from the outermost aromatic rings.

Acenedithiophenes (AcDTs), such as benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT)[1] and anthra[2,3-*b*:6,7(7,6)-*b*′]dithiophene (ADT),[2] are prototypical heteroacenes and have been widely utilized as important π-cores for the development of not only molecular organic semiconductors but also polymer semiconductors for organic field-effect transistors (OFETs)[3,4] and organic photovoltaics (OPVs).[5,6] Among the AcDT family including larger AcDTs, such as tetracenodithiophenes (TDTs) and pentacenodithiophenes (PDTs),[7] naphthodithiophenes (NDTs) had been long missing members owing to the lack of practical methods for their syntheses. Recently, we have successfully established efficient and selective syntheses of four isomeric naphthodithiophenes (NDT*n*, *n* = 1–4, Fig. 1)[8,9] and reported their properties. Despite the structural similarity, their electronic structures are significantly different and depend largely on the molecular shapes; the linear-shaped NDT1 and NDT2 are naphthacene-like with high-lying HOMO energy levels ($E_{\mathrm{HOMO}} \sim -5.3$ eV), whereas the angular-shaped NDT3 and NDT4 are chrysene-like with deep E_{HOMO} of ~ -5.8 eV.[9] Not just the difference in the electronic features of the NDT*n*s at the molecular level, the molecular- and polymer- semiconductors consisting of the NDT*n* cores showed diverse device characteristics depending on the NDT isomers. Among the molecular semiconductors, *e.g.*, diphenyl derivatives (DPh-NDT*ns*), the linear-shaped NDT1 gave the best mobility of up to 1.5 cm^2 V^{-1} s^{-1},[9] whereas in the polymer semiconductors, *i.e.*, PNDT*n*-BTs, the angular-shaped NDT3 gave the highest mobility of up to 0.8 cm^2 V^{-1} s^{-1}.[10] These results on NDT*n* isomers indicate that the core electronic structure is one of the key properties in the development of heteroacenes and their application to organic semiconducting materials.

We have also recently reported the linear-shaped naphtho[2,3-*b*;5,6-*b*′]difuran (NDF1) and found that its electronic structure is much influenced by the poor aromaticity of furan rings compared to that of the thiophene, resulting in a relatively low-lying HOMO energy level ($E_{\mathrm{HOMO}} \sim -5.5$ eV) compared to those of NDT1.[11] This result poses an interesting viewpoint: the aromaticity of constituent chalcogenophene rings influences the whole electronic structure of the fused aromatic ring system, which then prompts us to elucidate the electronic structure of angular-shaped naphthodifurans, naphtho[1,2-*b*;5,6-*b*′]difuran (NDF3)[12] and naphtho[2,1-*b*;6,5-*b*′]difuran (NDF4).[13] In the present contribution, we discuss the electronic structures of NDF3 and NDF4 in comparison with corresponding NDT3/NDT4 and also the linear-shaped NDF1 and NDT1.

The reported synthesis of NDF3 involves a polyphosphoric acid-mediated cyclization reaction of 1,5-bis(ω-dimethyloxylethyloxo)naphthalene,[14] often resulting in a blackish tar containing NDF3. To obtain pure NDF3, therefore, a tedious purification step is usually required. For this reason, we have

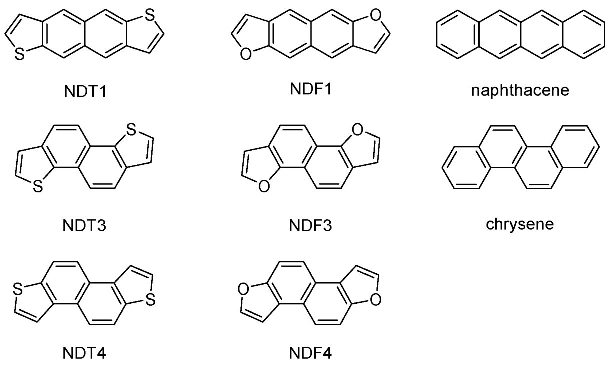

Fig. 1 Molecular structures of naphthodithiophenes (NDT*ns*), naphthodifurans (NDF*ns*), and related hydrocarbons.[8]

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‡ Electronic supplementary information (ESI) available: Synthetic details of NDF3 and NDF4, cyclic voltammogram of NDF1/NDT1 and 2,6-dimethoxynaphthalene, energy diagrams of NDT1/3/4 and NDF1/3/4 based on the DFT-MO calculations. See DOI: 10.1039/c2cc31546g

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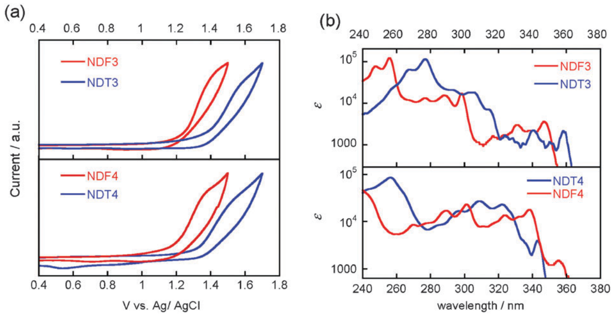

Fig. 2 Cyclic voltammograms (a) and absorption spectra (in dichloromethane) (b) of NDF3/NDT3 and NDF4/NDT4.

developed an improved synthesis of NDF3 from 2,6-dibromo-1,5-naphthalenediol *via* a base-mediated cyclization reaction of 1,5-diacetoxy-2,6-bis[(trimethylsilyl)ethynyl]naphthalene.[15] Analogously, NDF4 was also synthesized from 1,5-dibromo-2,6-naphthalenediol (see ESI‡).[14]

Cyclic voltammograms of NDF3/NDT3 and NDF4/NDT4 are depicted in Fig. 2(a). Similar to NDT3 and NDT4, the oxidation waves of NDF3 and NDF4 are irreversible, but the oxidation of NDFs occurs at a lower potential than that of NDTs by *ca.* 0.2 V, which is in sharp contrast to those of the linear-shaped naphtho[2,3-*b*;6,7-*b*′]dichalcogenophenes (NDF1/NDT1), where the furan analogue (NDF1) shows much higher oxidation potential ($+1.11$ V) than the thiophene analogue (NDT1, $+0.96$ V) (Fig. S2, ESI‡).[9b,11] The HOMO energy levels expected from the oxidation onsets are -5.6 eV for NDF3, -5.8 eV for NDT3, -5.6 eV for NDF4, and -5.7 eV for NDT4. Absorption spectra depicted in Fig. 2(b), on the other hand, indicate that the HOMO–LUMO energy gaps estimated from the absorption edge are not quite different for all the systems (3.4–3.6 eV).

Depicted in Fig. 3 is a schematic representation of HOMO and LUMO energy levels of NDT1/NDT3/NDT4 (blue lines) and NDF1/NDF3/NDT4 (red lines). From linear NDT1 to angular NDT3/4, the HOMO energy level shifts downwards and the LUMO level is almost constant, resulting in a larger HOMO–LUMO gap for NDT3/4 than that of NDT1. In contrast, for the NDF series, the HOMO energy levels are not changed so much. As a result, the HOMO energy levels of NDF3/NDF4 are higher than that of NDT3/NDT4 by *ca.* 0.2 eV, whereas HOMO–LUMO gaps estimated from the absorption edges are almost constant, resulting in high-lying LUMO energy levels for NDF3/NDF4 than for NDT3/NDT4 (Fig. 3).[16]

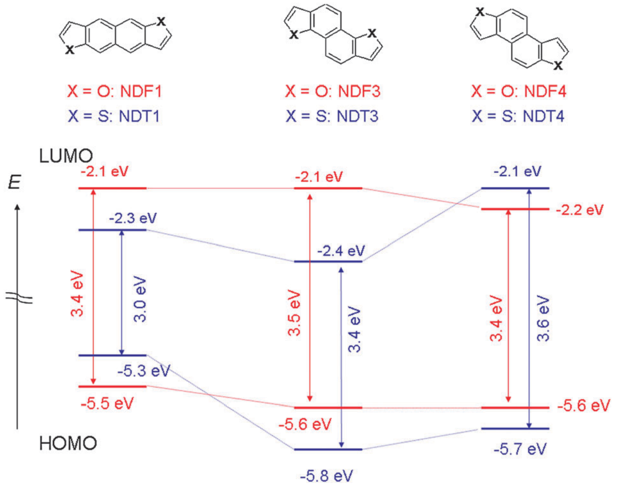

Fig. 3 Schematic representation of the frontier orbitals energy levels of NDF1/NDT1, NDF3/NDT3 and NDF4/NDT4. The HOMO energy levels (E_{HOMO}) and HOMO–LUMO energy gaps (ΔE) were estimated from oxidation onset in cyclic voltammograms and absorption edges in the UV-vis absorption spectra. The LUMO energy levels (E_{LUMO}) were calculated from: $E_{\mathrm{LUMO}} = E_{\mathrm{HOMO}} + \Delta E$.

It is somewhat surprising that the tendency of HOMO energy levels for the NDF- and NDT-series is quite different. To explain these results, we consider that the overall electronic structures of acenedichalcogenophenes should be affected by the aromaticity of outermost chalcogenophene rings. The ground state structure of NDF3/NDT3 and NDF4/NDT4 can be expressed by two canonical resonance structures, a chrysene-like or a substituted naphthalene-like structure (Fig. 4). We speculate that the chrysene-like structure is dominant over the substituted naphthalene-like structure for NDT3/NDT4 owing to higher aromaticity of thiophene than furan. This is in good agreement with the HOMO energy level of chrysene (5.9 eV below the vacuum level) determined by an identical method.[9] On the other hand, the lower aromaticity of furan rings makes NDF3/NDF4 (even NDF1) a substituted naphthalene-like structure, which could make the fused position of furan rings less influential on their ground state electronic structures. This consideration is consistent with the fact that NDF1 and NDF3/NDF4 have similar HOMO energy levels (-5.5 to -5.6 eV). Furthermore, cyclic voltammograms of 1,5-dimethoxynaphthalene and 2,6-dimethoxynaphthalene were measured (Fig. S1, ESI‡) as model compounds for "substituted naphthalenes" with oxygen functionalities, and their HOMO energy level was estimated to be within -5.5 to -5.6 eV, which qualitatively supports this speculation.

To get further insight into the electronic structure of the angular-shaped naphthodichalcogenophenes, we calculate nucleus-independent chemical sifts (NICSs) for the central naphthalene part in chrysene, NDF3/NDF4, and NDT3/NDT4.[17] The NICS for the central naphthalene in chrysene was calculated to be -7.7 ppm, which is much larger than that of naphthalene (-10.0 ppm), clearly indicating that the aromatic nature of the central naphthalene part in chrysene is quite reduced, and the aromatic stabilization is indeed

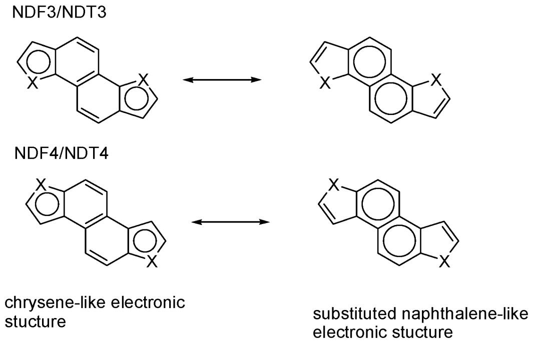

Fig. 4 Two resonance structures of NDF3/NDT3 and NDF4/NDT4.

localized in the outermost benzene rings. In sharp contrast, the NICS for the naphthalene part in NDF3/NDF4 (−10.5 and −10.4 ppm, respectively) is very close to that of naphthalene, strongly implying the localized aromatic nature on the naphthalene part in the NDF3 structure. In the case of NDT3/NDT4, the NICS was calculated to be −9.3 ppm, which is in between the two extremes, chrysene and naphthalene. The value, however, is slightly larger than that of naphthalene, indicating that reduced aromaticity in the naphthalene part in NDT3/NDT4 is most likely.

In summary, we experimentally demonstrated that the electronic structures of the angular-shaped NDFs are significantly different from those of their corresponding NDTs, and the origin of the difference can be boiled down to the distinct aromaticity between furan and thiophene that strongly affects the overall electronic structure of naphthodichalcogenophenes. As a result, the angular-shaped NDFs should not be isoelectronic with chrysene and are totally different π-electronic systems from the thiophene counterparts. Although the angular-shaped NDF3/NDF4 has not so far been exploited as the building units for optoelectronic materials,[18] their characteristic features including relatively high-lying HOMO energy levels make it an interesting ingredient for the development of new functional π-materials.

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