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Layered Electron Acceptors by Dimerization of Acenes End-Capped with 1,2,5-Thiadiazoles

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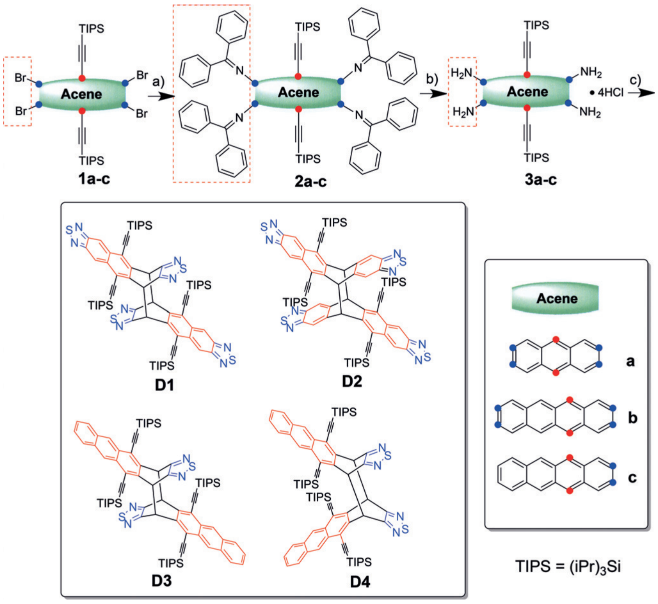
Abstract: *Layered electron acceptors **D1–4** equipped with terminal 1,2,5-thiadiazole groups have been constructed using a one-pot protocol of acene dimerization. Their molecular structures are determined using single-crystal X-ray diffraction analysis. Photophysical and electrochemical properties of these molecules present a marked dependence on conjugation length and molecular geometry. An aggregation-induced emission peak and an intramolecular excimer emission (IEE) band were observed for **D2** and **D4**, respectively. This work paves the way for the efficient synthesis of layered heteroacenes.*

Organic π-conjugated molecules have played a pivotal role in the field of organic electronics such as organic light-emitting diodes[1] and organic photovoltaic cells.[2] However, certain modes of solid-state packing for common planar organic semiconductors can pose specific problems for device performance.[3] Therefore, to suppress those packing modes, exploring nonplanar or layered organic semiconductors could be helpful. To date, 9,9′-bianthryls[4] triptycenes,[5] and spirofluorenes[6] have been commonly adopted as cores to construct nonplanar conjugated molecules. Linear acenes such as anthracene, tetracene, and pentacene were used to generate higher dimensional systems through the traditional [4π + 4π] photodimerization reaction.[7] However extended heteroacenes, especially electron acceptor molecules were hardly considered. New synthetic methods for nonplanar or layered heteroacenes are needed in order to investigate this space.

1,2,5-Thiadiazoles have proven to be strong electron acceptor moieties and their derivatives[8] have been widely applied as key building blocks for organic semiconducting materials. Herein, we synthesized the thiadiazole end-capped layered molecules **D1–4** through dimerization of heteroacenes. A one-pot reaction is employed in which formation of thiadiazole rings and dimerization are accomplished using di- and tetraamino-substituted acene precursors **3a–c** (Scheme 1). It is believed that introduction of electron-withdrawing thiadiazole rings increases the quinoid character of the conjugated system, and thus leads to dimerization without the involvement of light or oxygen.[7b,c,9] Therefore, our electron-deficient heteroacene dimerization method becomes a useful tool for preparing novel layered molecules.



Scheme 1. Synthetic route for **D1–4**: a) benzophenone imine, *rac*-BINAP, $Pd_2(dba)_3$, *t*BuONa, toluene, 110 °C, 55–65 %; b) 2.0 M HCl, THF, r.t. 90–95 %; c) TMS-Cl, PhNSO, Py, 80 °C, 57–77 % (**D1–3**) and 15 % (**D4**). Blue and red dots on acenes **a**, **b**, and **c** represent the substitution of corresponding functional groups. BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, dba = dibenzylideneacetone, TMS-Cl = trimethylsilyl chloride, PhNSO = thionylaniline, and Py = pyridine.

Di- and tetrabrominated acenes **1a–c** (Scheme 1) were obtained by standard procedures (see the Supporting Information). The synthesis of diphenylmethaneimine-substituted acenes **2a–c** were accomplished by reaction with benzophenone imine, using tris(dibenzylideneacetone)dipalladium(0) as catalyst and *rac*-BINAP as ligand. Then, amino-substituted acenes **3a–c** were obtained after hydrolysis.[10] Lastly, using N-sulfinylaniline as the cyclization reagent, **D1** and **D2** were synthesized in 57–66 % yields. Unlike the photoconversion of tetracene and pentacene derivatives which produced two isomeric dimers,[11] only the centrosymmetric **D1** and **D2** were

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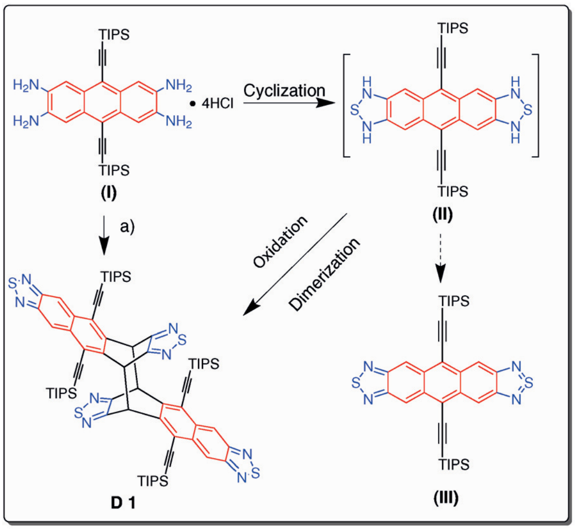

Figure 1. Proposed reaction mechanism with the anthracene case as an example. a) TMS-Cl, PhNSO, Py, 80 °C.

obtained based on **3a** and **3b**, respectively. In the case of the diamino-substituted acene **3c** as the precursor, the reaction not only produced centrosymmetric **D3** in 77 % yield, but also the planosymmetric **D4** in 15 % yield. As far as we know, this is the first report of such a one-pot reaction, which involves the cyclization reaction of di- or tetraamino-substitued acenes and dimerization of aceno[2,1,3]thiadiazole derivatives. Signals in the range of 45 to 55 ppm in the ^{13}C NMR spectra of **D1**–**4** proved the existence of saturated carbon atoms in the acene moieties. The structural details of all four compounds were confirmed by HRMS, ^{1}H NMR, ^{13}C NMR spectroscopy, and single-crystal X-ray diffraction studies.

The two-step synthesis, namely, formation of 1,2,5-thiadiazole rings and dimerization are successively completed in one pot, making this procedure convenient and efficient. Taking the anthracene case as an example (see Figure 1), we propose that, first the cyclization of amino-substituted acene (I) occurs to form the bis(dihydro-2,1,3-thiadiazole)anthracene (II), which is similar to the formation of dihydro-2,1,3-benzothiadiazole from *o*-phenylenediamine reported by Bryce.[12] Then, the unstable intermediate (II) converts directly to molecule **D1** by oxidation, whereas the originally envisaged monomer (III) could not be observed at all. This was similar to the reported case of dihydro heteroacene by Bunz and co-workers,[13] where MnO_2 was used as an oxidant. Thus the oxidative condition seems favorable to form a cycloaddition adduct.

To investigate the intermolecular interaction in the solid state of dimerized acenes **D1**–**4**, their crystals were grown by slow evaporation of tetrahydrofuran solutions. As expected based on the varying geometries of **D1**–**4**, their packing modes are quite different. The crystal structure of **D1** exhibits columnar packing, where each molecule interacts with the four nearest neighboring molecules by two types of symmetrical π–π interactions with two interplanar distances (3.55 and 3.71 Å; Figure 2).

However, with the extension of the thiadiazole termini in **D1** to benzothiadiazole in **D2**, we see two-dimensional slipped π-stacking motifs, in which the fragments of benzothiadiazole interact with naphthothiadiazole fragments of the

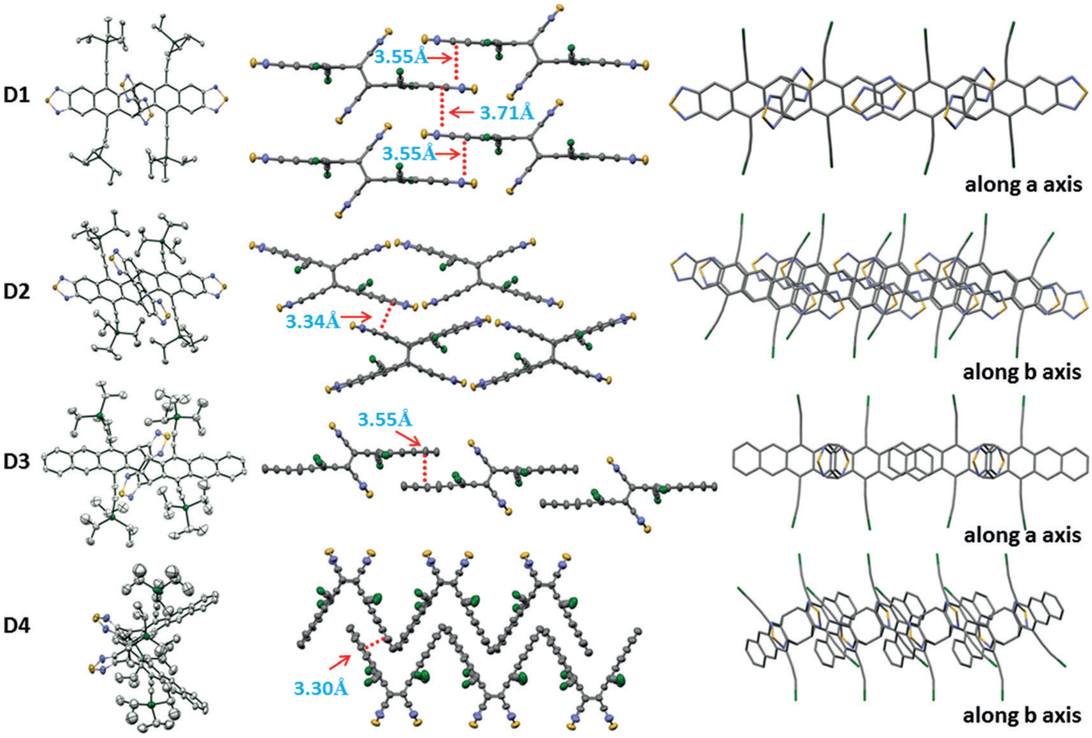

Figure 2. Structure (left), crystal packing (middle), and degree of π-face overlap (right) of four dimeric acenes (alkyl groups on Si removed for clarity).

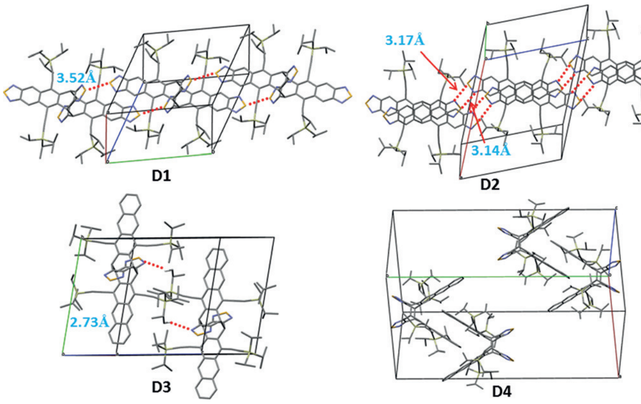

Figure 3. The involvement of heteroatoms for intermolecular interaction (red dash lines).

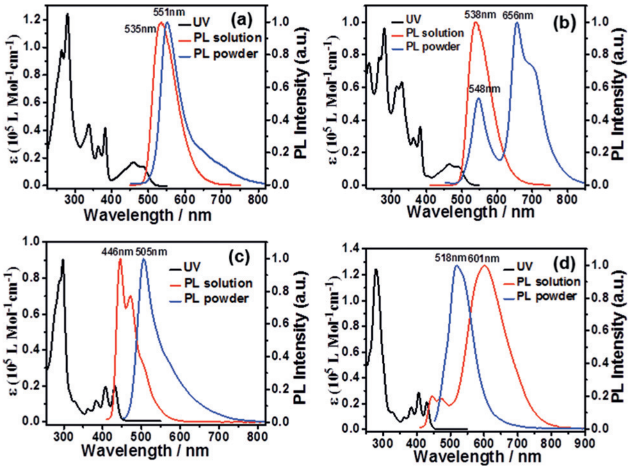

Figure 4. Absorption (black line, in CH_2Cl_2 solution) and normalized PL spectra of a) **D1** $\lambda_{Exc} = 337$ nm, b) **D2** $\lambda_{Exc} = 382$ nm, c) **D3** $\lambda_{Exc} = 380$ nm, and d) **D4** $\lambda_{Exc} = 380$ nm in CH_2Cl_2 solution (red line) and powder (blue line).

neighboring molecules. This packing mode might favor a two-dimensional isotropic charge transport in the solid.[14] **D3** forms a brick-wall-type packing motif with a π-stacking distance between the anthracene units of 3.55 Å. **D4** packs in a 2D slipped π-stacking arrangement similar to that of **D2**, with a smaller π-face separation of 3.30 Å. As far as we know, this is the first report of crystal structures of both *E* (**D3**) and *Z* (**D4**) isomers formed upon dimerization of heteroacenes.

The prominent heteroatom intermolecular interactions were also observed in their crystal packing (Figure 3). For **D1**, the distance [S⋯S (3.52 Å)] between the two sulfur atoms of two neighboring molecules is shorter than the sum of their van der Waals radii (1.85 Å). In the case of **D2**, intermolecular interactions by head-to-tail contacts of the thiadiazole moieties were observed. In comparison with **D1** and **D2**, only **D3** presents intermolecular interactions between a hydrogen atom of an isopropyl group and a nitrogen atom of the thiadiazole [N⋯H (2.73 Å)]. However, for **D4** no hydrogen bonds or intermolecular interactions between heteroatoms were observed. The crystallographic data and refinement details of the four compounds are summarized in Table S1.

Cyclic voltammograms were measured versus Fc^+/Fc in CH_2Cl_2/0.1 M Bu_4NPF_6 at a scan rate of $100\,mV\,s^{-1}$ (Figure S1, Table S2). **D1** and **D2** show reversible redox processes with half-wave reduction potentials $E_{red1/2}$ versus $Fc^+/Fc = -0.91$ V and $E_{red1/2}$ versus $Fc^+/Fc = -0.97$ V, respectively. The slightly smaller reduction potential for **D1** suggests that the thiadiazole ring has a stronger electron-withdrawing ability in comparison with benzothiadiazole. **D3** and **D4** present quite similar profiles ($E_{red1/2}$ vs. $Fc^+/Fc = -1.11$ V), which indicate no influence from intramolecular electronic interaction between face-to-face orientated aromatic rings (anthracene to anthracene, thiadiazole to thiadiazole or anthracene to thiadiazole). Furthermore, we used density functional theory (DFT) calculations to investigate the electron delocalization within two isomers (Figure S2). The frontier molecular orbitals of **D3** and **D4** were mainly delocalized over the two anthracene units.

Figure 4 depicts the UV/vis and photoluminescence (PL) spectra for **D1–4. D1** and **D2** possess similar absorption spectra, whereas their emission profiles are dramatically different. For **D1**, the peak position shifts from 535 nm in solution to 551 nm in the solid state. Similarly, **D2** displays one emission band comparable to that of **D1** in solution, yet surprisingly, an additional strong emission peak at 657 nm with a shoulder at 700 nm appears in the powder PL spectrum of **D2**. To figure out the origin of this new band, we studied the influence of aggregation effects on the fluorescence behavior by measuring the PL spectra of **D2** in THF/water mixtures with different fractions of water (fw). The new emission peak appeared from fw about 80 vol% and was relatively enhanced by further increasing the fraction of water (after normalization to 545 nm peak; Figure S3). Evidently, the new band is induced by aggregation effect.

Although the resolved vibrational features of the absorption spectra were similar for isomers **D3** and **D4** (Figure 4c and 4d), their PL spectra were very different. In comparison to 446 and 472 nm emission peaks of **D3**, **D4** shows a new strong and red-shifted band ($\lambda_{max} = 601$ nm), which does not originate from emission of the intermolecular excimer because: 1) the ratio between two emission bands of **D4** is found to be constant at varying concentration in dichloromethane solution (Figure 5a); 2) their ratio could be tuned in different solvents, as the intramolecular excimer emission is strongly dependent on the polarity of solvent (Figure 5b);[15] and 3) under the same condition, intermolecular excimer emission has not been observed for **D3**. Thus, we assign the red-shifted band to the intramolecular excimer emission (IEE)[7b,16] from the two opposite 1,4-bis((triisopropylsilyl)-ethynyl)anthracene (A-TIPS) moieties. The changes in fluorescence spectra on going from solution to solid state also differ dramatically for isomers **D3** and **D4**. For **D3**, a significant bathochromic shift from 446 to 505 nm was observed from solution to powder spectra. In contrast, the maximum emission peak of **D4** shifts hypsochromically from solution (601 nm) to powder (518 nm) spectra. We tentatively attribute the disappearance of an IEE peak in the solid-state

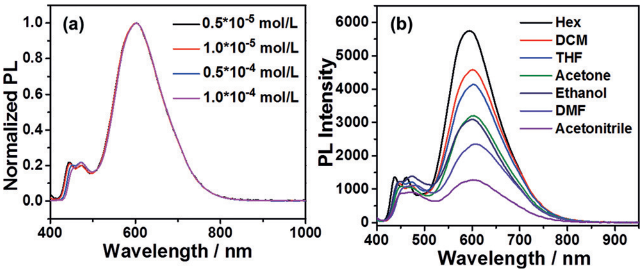

Figure 5. a) Normalized PL spectra of **D4** measured in CH_2Cl_2 solution with varying concentrations. b) PL spectra of **D4** measured in different solvents with a concentration of 1.0×10^{-5} M ($\lambda_{Exc}=380$ nm).

spectrum of **D4** to the strong intermolecular interactions of A-TIPS units which hinder the intramolecular excimer formation. It is further confirmed that the intensity of the IEE peak gradually reduced with the increasing fraction of water, whereas the A-TIPS aggregation emission peak increased correspondingly (Figure S4).

The photoluminescence quantum yields (PLQYs) of **D1** and **D2** are 0.28 ± 0.02 and 0.36 ± 0.03, respectively. The PLQY of centrosymmetric **D3** is 0.21 ± 0.02, which is five times higher than that of its isomeric planosymmetric **D4** ($\Phi=0.04\pm0.01$). That might be caused by the intramolecular self-quenching between the two opposite A-TIPS. All four materials displayed strong fluorescence signals when irradiated by UV light (365 nm) in solid state (Figure S5).

In summary, we have demonstrated herein the synthesis of layered acceptors by dimerization of thiadiazole end-capped acenes together with their crystal structures and analysis of packing motifs. Interestingly, the four compounds feature huge differences in their photophysical properties. In comparison with **D1**, **D2** with acene ring extension shows a new strong emission in the near-infrared region introduced by the aggregation effect. Compound **D3** features only A-TIPS unit emission, whereas **D4** is also characterized by intramolecular excimer fluorescence in solution. This finding provides a feasible molecular strategy to design novel molecules with aggregation or IEE effect. The photovoltaic properties and device fabrication of synthesized layered acceptors and application of the present method to other polyacene systems are currently under study in our laboratory.

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