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Low Bandgap Coplanar Conjugated Molecules Featuring Dynamic Intramolecular Lewis Acid-Base Coordination

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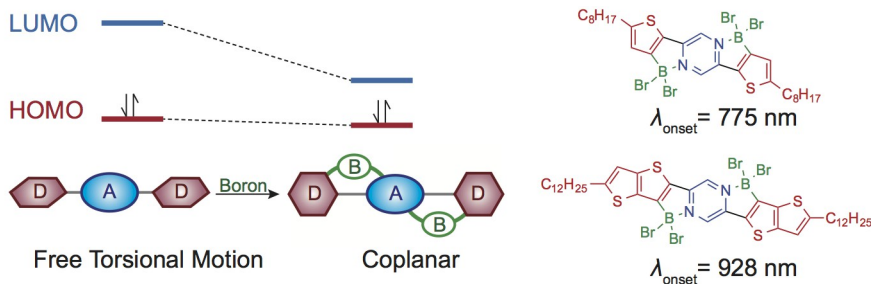
ABSTRACT: Intramolecular Boron-Nitrogen coordination was employed to extend the π-conjugation and to lower the LUMO level of donor-acceptor-donor conjugated molecules. Adopting a rigid and coplanar conformation, these molecules possessed narrowed bandgaps and near-infrared absorption. The dynamic nature of B—N coordination made it possible to manipulate the electronic structures and optical characters by using Lewis basic competing solvents.

Low bandgap materials are pivotally important in applications associated with photovoltaic devices and near-infrared (NIR) absorbing materials.[1] Among them, π-conjugated organic materials are particularly captivating on account of their composition of earth-abundant elementals, high photo-absorptivity through direct bandgaps, and facile yet controllable solution processibility.[2] Two practical strategies were often involved in the design and synthesis of low bandgap π-conjugated organic compounds: (1) Incorporation of conjugated electron donating and accepting units in an alternating manner[3] and (2) extension of the coherent π-electron delocalization.[4]

The first strategy relies on the recombination of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of the alternating electron donating and accepting units to afford a higher HOMO and a lower LUMO, hence a narrowed bandgap.[5] In order to achieve an extremely low bandgap, an electron rich donor unit is often employed. This approach, however, could lead to a high lying HOMO of the resulting product, which can be easily oxidized and suffer from stability issues in ambient environment.[4b] In this context, a strategy that deepens the LUMO level while maintains the HOMO level is of significance for the goal of stable low bandgap organic materials. Additionally, lower LUMO energy could lead to *n*-type materials with high electron affinities, which are less accessible compared to widely investigated *p*-type organic materials.[6]

In the context of the second strategy, namely, extension of π-electron delocalization, conjugated polymers are preferable compared to small molecules because of their longer possible conjugation.[7] The effective coherent conjugation length of conventional single-strand conjugated polymers, however, is severely limited by the torsional motion in between the aromatic units.[8] A coplanar π-system with restricted torsional disorder, in contrast, is expected to enjoy a much longer coherent conjugation along the backbone.[4c,9] Thus, locking the entire π-system into a coplanar conformation through a second strand of bonds emerged as an important method towards materials with lower bandgaps.[10]

Yamaguchi *et al.* demonstrated[11] in 2006 the use of non-covalent B—N coordination formed between a boryl-thienyl unit and an adjacent thiazole unit, which led to a partially coplanar molecule and a lower bandgap. Since then, several examples of B—N bond promoted, step ladder-type conjugated small molecules, oligomers and polymers have been reported.[6a,12] It is still a challenge, however, to achieve coplanarity of an entirely π-conjugated molecule with more than two aromatic units through B—N bonds. Recently, acceptor-donor-acceptor conjugated ladder molecules featuring B—N bridging bonds were synthesized.[12c] The analogous donor-acceptor-donor coplanar molecule, however, has not been achieved yet because of significant deactivation effect of the nitrogen centers in the central acceptor unit. Herein, we report a feasible new strategy of using B—N coordination to achieve simultaneously (1) coplanarity through the entire π-backbones and (2) low lying LUMO levels in small donor-acceptor-donor molecules.

The target model compounds **2** and **4** were designed in a way that the formation of B—N bonds not only fixes torsional conformation of the entire π-conjugated system, but also imposes stronger electron-withdrawing characteristics on the central electron-poor units. Combination of these two effects would lower LUMO energy levels and bandgaps significantly. On one hand, electron-donating thiophene or thienothiophene units were installed as the terminals of **2** and **4**, respectively. On the other hand, a pyrazine unit was selected as the central electron-accepting unit because it can donate two pairs of electron into two opposite directions in a central symmetric manner. Because these two nitrogen atoms are on the *para-* positions to one another, the mutual deactivation effect on their Lewis basicity was relatively weak. Eventually, highly symmetrical C_{2h} compounds with fused aromatic rings can be constructed.
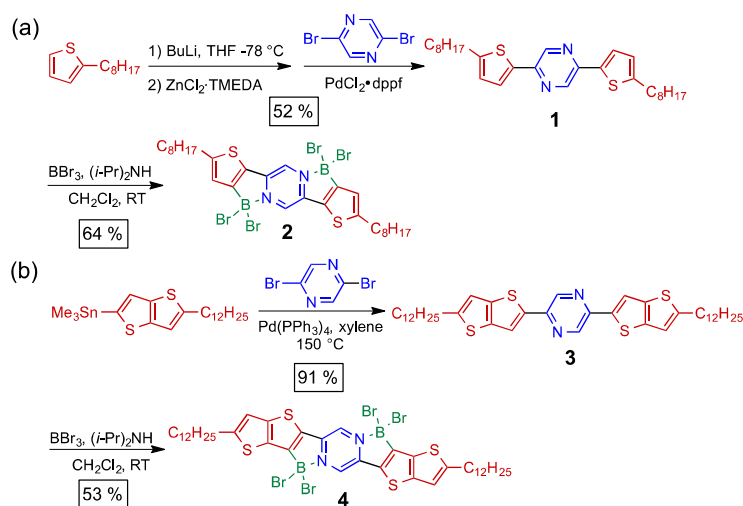
Scheme 1. Synthesis of B—N bridged donor-acceptor-donor ladder-type molecules **2** and **4**.

The two-step synthesis of **2** started with Negishi coupling between 2-octylthiophene and dibromopyrazine, which afforded the linear conjugated molecule **1**. The second step involved *N*-directed electrophilic aromatic substitution of the electron-rich thiophene with BBr_3.[12a,12c] Owing to its strong Lewis acidity, BBr_3 was firstly coordinated with the nitrogen atoms on pyrazine. This process made the C4 position of the thiophene unit spatially favorable for the subsequent electrophilic aromatic substitution. In the presence of diisopropylamine, one-pot formation of two B—N coordination bonds and two C—B covalent bonds was accomplished to constitute two stable 5-membered rings in the product **2**. These rings fused the two thiophene units and the central pyrazine unit together and confined the conformation of the entire π-system into a coplanar geometry. A similar strategy was adopted to synthesize thienothiophene-derived analogue **4**, which possessed a further extended conjugation backbone with seven fused rings. By treating the precursor **3** with pure BBr_3 as a stronger borylation reagent in the presence of an excess amount of diisopropylamine, **4** was formed and isolated in 53% yield. In either cases, the electron rich nature of thiophene or thienothiophene promoted the electrophilic

substitution reaction, in which two C—B covalent bonds and two B—N coordination bonds formed in one-pot. ^{11}B NMR corroborated the chemical environment and the sp^3 hybridized nature of the boron center[13]: The lone pair donated from the nitrogen center shielded the boron nuclei, leading to a significant ==downfield== chemical shift on the spectra (Compound **2**: −4.26 ppm; Compound **4**: −4.12 ppm).
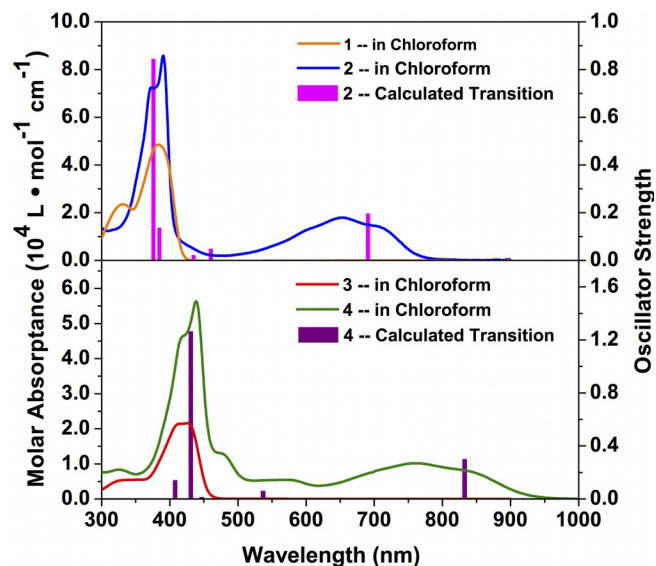

Figure 1. Solution phase UV-vis-NIR spectra and calculated oscillator strength [B3LYP/6-311G(d,p)] of **2** (top) and **4** (bottom), in comparison to their precursor **1** and **3**.

Compared to their precursors **1** and **3,** the absorption spectra of **2** and **4** in CHCl₃ were dramatically red-shifted to the NIR region (**Figure 1)**, corresponding to low optical bandgaps of 1.59 eV and 1.34 eV, respectively. **4** demonstrated an even lower bandgap on account of the extended conjugation and the more electron-rich nature of thienothiophene. Time-dependent density function theory (TD-DFT) was employed to simulate the energy transition and oscillator strength of both **2** and **4** (**Figure 1**). These calculated transitions matched well with the experimental spectra. Such a good agreement can be attributed to the limited conformational variation in these rigid molecules, thanks to the strong bridging intramolecular B—N bonds. The low energy absorption bands at 700 nm of **2** and that at 820 nm of **4** were attributed to the transition from HOMO to LUMO. Besides, the transitions from HOMO to LUMO+1 mainly contributed to the absorption below 450 nm with high intensities. The noticeable vibrational progressions presented in the spectra of **2** and **4** in chloroform, even for the low energy HOMO—LUMO bands, further corroborated their rigid conformation in solution.[14]
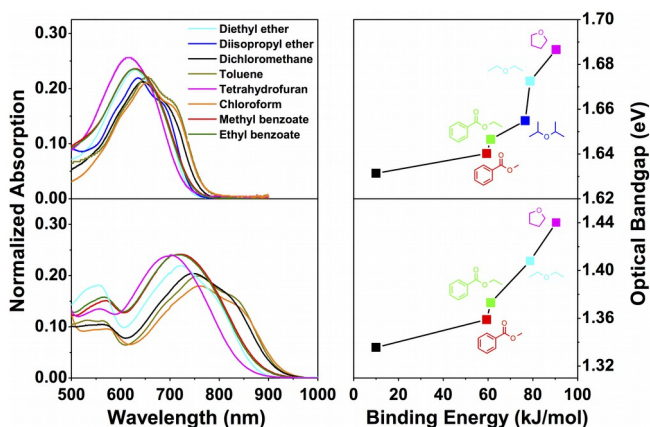
Figure 2. Charge transfer absorption of **2** (**a**) & **4** (**b**) in a variety of organic solvents and the correlation between optical bandgaps of **2** (**c**) and **4** (**d**) with the Lewis basicities of organic solvents (binding energy with BF$_3$).

It is expected that the intrinsically dynamic B—N coordination should be controllable in the presence of certain external stimulus. For example, the addition of Lewis base should weaken this bond by competing in binding with the boron center so that the thermodynamic equilibrium would be driven to a less planar conformation. As a result, the electronic structure and optical property of these compounds can be controlled actively: In a Lewis basic solvent, the B—N bond should be more labile and the molecular conformation should be less rigid, translating into a blue shifted absorption spectrum, and *vice versa*.

In this context, UV-vis-NIR spectra of **2** and **4** were examined in various solvents with different Lewis basicity but similar dielectric constants (from 3.8 to 9.2). In general, the low energy absorption peaks were blue-shifted in Lewis basic solvents (**Figure 2a, b**). The optical HOMO—LUMO bandgaps measured in these solvents were plotted against a parameter that indicated the solvent Lewis basicity, namely, binding affinity between the solvent and BF$_3$.[15] It was clearly shown that the bandgap increased monotonously (**Figure 2c, d**) as the Lewis basicity increased, because the intramolecular B—N coordinations were weakened. To exclude the solvation effects such as dipole interaction[16] and the electronic polarization[17], the optical bandgaps were also plotted against dielectric constants of these solvents (**Figure S6**) and showed no significant correlation. Thus, the employment of Lewis basic solvents realized a rational control over optical bandgaps of these dynamic B—N bridged molecules in NIR region through competitive coordination interactions.
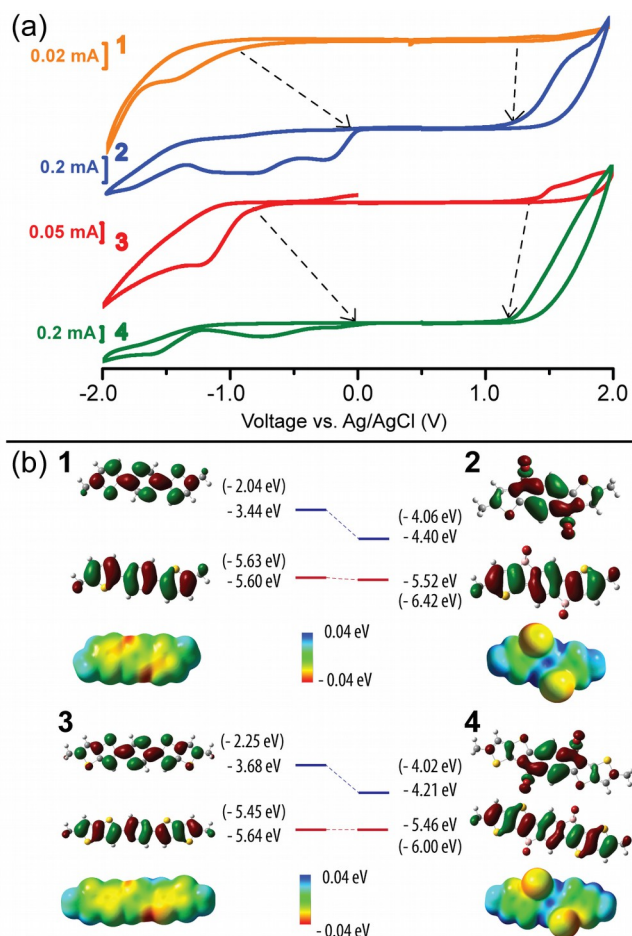
Figure 3. (a) Cyclic voltammetry of **1~4** (green), 0.10 M *n*-Bu$_4$NPF$_6$ in CH$_3$CN; (The comparison of reduction onsets and oxidation onsets for **2**, **4** and their precursors were shown in dotted lines.) (b) HOMO, LUMO energy levels [experimental data & calculated values (in parenthesis)], calculated molecular orbitals and electrostatic potential map for **1~4**.

Frontier orbital energy levels of molecules **1~4** were investigated by using a combination of experimental and theoretical techniques. Cyclic voltammetry traces (**Figure 3a)** of both **2** and **4** in solution showed irreversible reduction peaks around 0.0 V versus Ag/AgCl reference electrode, which was about 1 V lower than their precursors **1** and **3**, respectively. The oxidation onsets for **1~4** were all similar around 1.2 V versus Ag/AgCl. These values suggested that the B—N bond formation lowered the LUMO level but not the HOMO level, as expected. These experimental data was further corroborated by DFT calculation (**Figure 3b)**. Compared to **1** & **3**, both **2** & **4** exhibited a dramatically decreased LUMO levels lower than −4.0 eV, in contrast to the almost unchanged HOMO levels, agreeing well with the values from the electrochemical experiments. The coordination between boron and nitrogen significantly lowered LUMO energy levels for **2** & **4**, while no significant impact was observed on the HOMO. As mentioned above, it represents an ideal situation to reach a low bandgap without increasing the HOMO level for stability conGroup A will present their research work update next week.cern.
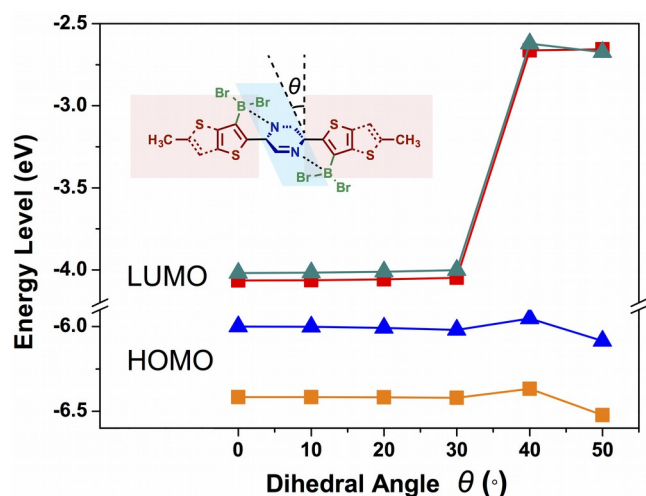
Figure 4. Calculated energy levels of **2** (□) & **4** (△) at different dihedral angles.

To understand how the dynamic nature of B—N bond and conformational change impact the electronic structure of **2** and **4**, HOMO & LUMO energy levels were calculated for different molecular conformations by changing the dihedral angles (θ) between the pyrazine unit and the electron rich unit. As the dihedral angle increased from 0° to 30°, LUMO energy levels of **2** and **4** slightly increased, leading to wider bangaps (**Figure 4**, **Table S1 & S2**). This can be attributed to the weakened coordination and the twisted structures. The most abrupt change of the electronic structures took place when the dihedral angle increased from 30° to 40°: The calculated bandgap increased from 2.37 eV to 3.71 eV for **2** and from 2.02 eV to 3.33 eV for **4**, owing to the drastic change of LUMO energy levels (**Figure 4**). These data suggested that the B—N coordination bond would undergo definitive dissociation when the dihedral angle between the donor and acceptor units was increased to over 40°. In this context, the Lewis basic solvent induced blue shift of spectra was primarily an electronic effect rather than a result of conformational change.

It has been commonly observed[18] that the strong withdrawing resonance effect of a tri-coordinated boron functional group can induce an enhanced charge transfer effect, leading to a red-shifted optical absorption. In our cases, however, a new charge transfer band was observed after the coordination event. Meanwhile, when B—N coordination bond was disrupted, the difference on the calculated bandgaps for **2** & **4** and their precursors was much smaller (**Table S1 & S2**). To further understand the mechanism, the electrostatic potential maps for **1~4** were depicted after geometry optimization. As show in **Figure 3b**, thiophene or thienothiophene units demonstrated an increased electrostatic potential after the formation of B—N bonds, suggesting an electron density decrease.[19] The upfield shift of the proton resonance signals for thiophene or thienothiophene on ^{1}H NMR spectrum could serve as an indirect evidence. Additionally, the positive electrostatic potential on pyrazine also increased dramatically after

the coordination event, because pyrazine became partially positively charged and more electron-deficient. According to the DFT calculation, while the HOMO energy levels were still delocalized upon the whole molecule, LUMO energy levels of **2** and **4** were more localized on pyrazine compared to their non-boron precursors **1** & **3**. This observation suggested that LUMO energy levels of **2** & **4** were mainly contributed by the π* orbital of the positively charged pyrazine. This comprehensive electron withdrawing effect and the coordination behavior explained the deep LUMO levels and the unchanged HOMO levels of **2** & **4**.

In conclusion, an integrated strategy to low-bandgap coplanar organic materials was developed on the basis of intramolecular Lewis acid-base coordination. Feasible synthesis of the model compounds was achieved through a *N*-directed borylation reaction on donor-acceptor-donor precursors. Low-lying LUMO of the small molecule led to a bandgap as low as 1.3 eV. More interestingly, on account of the dynamic nature of the Lewis acid-base coordination, the corresponding bandgaps of the resulting systems can be actively modulated by using external competing reagents, such as Lewis basic solvents. With deep LUMO and coplanar conformation achieved simultaneously, this work sets a promising model for the future design and development of low bandgap *n*-type materials using a similar principle.

Acknowledgement

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