Synthesis and Physical Properties of Benzopyridazine-Based Conjugated Molecules

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A series of novel organic conjugated molecules (5a-5d) comprising 2,3-benzopyridiazine as electron-withdrawing core and thiophene derivatives as electron-donating arms have been synthesized successfully in good yields. The ultraviolet-visible (UV-Vis) absorption spectra and fluorescence spectra of 5a-5d revealed that the optical properties are strongly influenced by the interactions between nitrogen and sulfur atoms in the conjugated backbone, as well as the position of the alkyl chains in the thiophene rings. The experimental results and theoretical calculation data clearly indicated that the band gap and the energy levels of LUMO and HOMO could be fine-tuned by the position of alkyl chains in the thiophene rings. Thus, the structure-property correlation of this class of conjugated molecules can be well established.

Keywords benzopyridiazine, heterocycles, conjugated molecules, optoelectronic properties

Introduction

Organic conjugated molecules have been investigated intensively due to their optoelectronic properties^[1] and potential applications in many fields,^[2] such as or-ganic field effect transistors^[3,4] (OFETs), organic photovoltaics^[5] (OPVs), electrochromic devices, and organic light emitting diodes^[6] (OLEDs). One of the most critical challenges in organic electronics is to design and synthesize novel conjugated molecules, of which structures exert the key effect on photophysical properties and electronic behaviors. Typically, incorporation of substituted group or heteroatom into the conjugated backbone has been taken into account as an efficient strategy for achieving a functional system.^[7-10] Recently, nitrogen-based heterocycles, named N-heteroacenes, including pyridazine, pyrimidine and pyrazine, have received great attentions.^[11] As an example, pyridazine containing two electron-withdrawing imine nitrogen atoms represents a very promising candidate for n-type organic conjugated molecules because of its electron-deficient character.^[12] However, pyridazinebased compounds are still rarely reported, which are typically depicted in Figure 1.^[13-15] In view of extended conjugation, these compounds might suit to be explored as promising materials for organic electronics. As far as we know, fused pyridazine-cored oligothiophene derivatives have not been reported.

Donor-acceptor (D-A) conjugated molecules are highly attractive due to their excellent light harvesting



Figure 1 Chemical structures of representative diazine containing conjugated compounds.

abilities and self-assembly behaviors. Yamamoto and co-workers^[16] reported a series of conjugated polymers with D-A-D repeat unit using thiophene and pyridazine as electron-donating and electron-accepting moieties, respectively, showing strong intermolecular interaction (Figure 1). Recently, our group reported the synthesis and physical properties of a new family of *N*-hetero-acenes, comprising a tetraazaanthracene core and four thiophene derivative arms.^[17] The electrochemical characterization revealed their classical electrochemical characters. Additionally, the short S–N distances can

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be observed supporting the existence of substantial intramolecular S-N attraction in thiophene-azine derivatives. Herein, we report the design and synthesis of a series of novel organic conjugated molecules comprising 2,3-benzopyridiazine as electron-withdrawing core and thiophene derivatives as electron-donating arms, with the following considerations: (1) enabling an extended conjugated plane over the pyridazine; (2) achieving substantial intramolecular S-N interaction leading to locked conformation between donor and acceptor parts; (3) constructing a D-A-D conjugated systems. Besides, the effect of the substituted alkyl chains at different position of the thiophene ring on the properties of these molecules has been explored. Finally, optical and electrical properties of the molecules have been systematically investigated for elucidation of structure-

Scheme 1 Synthetic routes for 5a-5c

property correlation.

Results and Discussion

Synthesis and characterization

The synthetic approach to 2,3-benzodiazine-based molecules 5a-5c was shown in Scheme 1. The key intermediate 2, containing S-pyridinyl moieties as good leaving groups, was prepared by treatment of 2-mercap-topyridine with phthaloyl dichloride at 0 °C, using TEA (triethylamine) as catalyst.^[17] The pure compound 2 was obtained as pale-yellow solid by recrystallization from its dichloromethane/diethyl ether solution (yield 46%). Afterward, compound 4 was effectively achieved through the reaction of the thienyl Grignard reagents with 2 in THF. Notably, the reaction quenched by HCl



Reagents and conditions: (a) 2-mercaptopyridine, TEA, THF, 0 °C; (b) (1) Mg, THF, 35 °C; (2) THF, 0 °C; (c) N₂H₄, C₂H₅OH, r.t. or 100 °C

Scheme 2 Synthetic route for 5d



Reagents and conditions: (d) NBS, 0 $^{\circ}$ C; (e) Pd(PPh₃)₄, DMF, 100 $^{\circ}$ C

is necessary in order to avoid the rearrangement side reaction. Purified by column chromatography (CH₂Cl₂/ petroleum ether), compounds 4a - 4c were obtained with the yields of 66%, 71% and 67%, respectively. Finally, these compounds were readily converted to target molecules 5a - 5c in the yields from 67% to 95%, respectively, upon treated with hydrazine hydrate in ethanol at room temperature.

Moreover, bromination of **5a** was carried out by using *N*-bromosuccinimide (NBS) in DMF, resulting in compound **6** (Scheme 2). The cross coupling reaction between **6** and 5-hexylthiophen-2-yl-tripropylstannane in the presence of Pd(PPh₃)₄ at 100 °C, afforded compound **5d** in 80% yield after purified through column chromatography.

All compounds have been fully characterized by ¹H NMR and ¹³C NMR and high-resolution mass spectra, which are greatly in agreement with the chemical structures of these molecules. The benzopyridazine core was successfully introduced in compounds, which was estimated from ¹H NMR analyses by integrating the two aromatic signals at δ 8.5 and 7.9, which are distinctly different from the proton peaks of naphthalene ring at δ 8.2 and 7.6 in analogous compound 1,4-bis(2-thienyl)-naphthalene.^[18]

Optical properties

The UV-vis absorption spectra of molecules 5a-5dwere measured in CH₂Cl₂ (Figure 2a). The spectra of 5a, 5b and 5c exhibit one main absorption peak in near UV region (λ =300-400 nm), which are ascribed to π - π * transitions. While for 5d, besides a weaker absorption band in above region (at 317 nm), a strong absorption peak at 423 nm is observed, which is assigned to an intramolecular charge transfer (ICT) transition. 1,4-Bis(2thienyl)-naphthalene shows an absorption maximum at 327 nm,^[18] which is 18 nm blue shift by compared to its structural analogue 5a, which arises from incorporation of nitrogen atoms into the conjugated backbone of 5a to form D-A structure.

The absorption maxima are shown in a sequence of 5d > 5c > 5a > 5b. Corresponding data are summarized in Table 1. In comparison with 5a, the absorption maximum of 5b shows a blue shift of 22 nm, presumably due to a declined conjugated planarity, because of the two competition effects: on the one hand, intramolecular S-N interaction would be favorable for

locking such a molecular conformation with S atoms of the thiophene units and N atoms of the 2.3-benzopyridiazine unit in the same side; on the other hand, the steric effect from the hexyl group at the β position in each thiophene ring adjacent to the 2,3-benzopyridiazine moiety might restrict the intramolecular rotation to form the above conformation. On the contrary, an obvious red shift of 21 nm was observed for the absorption maximum of 5c, whose two hexyl chains at the α -terminal parts of the thiophene units offer electron-donating effect. Obviously, incorporating alkyl chain at the different position of the thiophene ring can exert essential effects on the optical properties of the 2,3-benzopyridiazine-based molecules. As expected, the absorption spectrum of compound 5d exhibits a noticeable red shift of 51 nm, as well as significantly enhanced absorption intensity, by compared with that of 5a, which are typically attributed to the increase in conjugated chain length.



Figure 2 Ultraviolet-visible spectra of 5a-5d in dichlorovmethane.

The fluorescence spectra of compounds 5a-5d in CH₂Cl₂ solutions were found between 350 nm and 700 nm (concentration 1.5×10^{-5} mol·L⁻¹, Figure 3). Normally, conjugated molecules comprising diazine moieties can essentially lead to weakening their fluorescence.^[11,19,20] Such phenomenon also was observed in the case of compounds 5a-5c. However, compound 5d exhibits strong fluorescence emission, which is in accordance with its intensive absorption. Obviously, enlongation of conjugated chain length via introduction of thiophene units could remarkably change the optical properties of molecules.

 Table 1
 Optoelectronic and electrochemical properties of 5a-5d

				* *				
Compd	$\lambda_{max,abs}/nm$	$\lambda_{\max,em}/nm$	E_{g}^{opta}/eV	$E_{\rm red}^{a}/{\rm V}$	LUMO ^b /eV	HOMO ^c /eV	LUMO ^d /eV	HOMO ^d /eV
5a	345	386	3.10	-2.10	-2.70	-5.80	-2.31	-5.97
5b	323	359	3.33	-1.94	-2.86	-6.19	-2.28	-5.65
5c	366	413	2.95	-2.13	-2.67	-5.62	-2.34	-5.55
5d	423	585	2.52	-1.95	-2.84	-5.36	-2.38	-5.33

^{*a*} The values of HOMO and LUMO energy levels were estimated from reduction potentials and UV-vis absorption edge (CV measured in 0.1 mol•L⁻¹ CH₂Cl₂ solution of *n*-Bu₄NPF₆ at a scan rate of 100 mV•s⁻¹); ^{*b*}LUMO= $-E_{red}$ -4.80 eV; ^{*c*}HOMO=LUMO- E_{g}^{opt} ; ^{*d*} Calculated by density functional theory.



Figure 3 Fluorescence spectra of 5a-5d in dichloromethane.

Electrochemical properties

The electrochemical behaviors of 5a-5d were studied by means of cyclic voltammetry (CV), as depicted in Figure 4. The CV profiles of 5a, 5c and 5d show a reversible one-electron reduction, but compound 5b showed irreversible reduction process. E_{red1} values of as-maded molecules are increased in an order of 5c < 5a <5d<5b. Consequently, the energy levels of the lowest unoccupied orbitals (LUMOs) are in a sequence of 5b < 5d < 5a < 5c. For compound 5c, the lowest conjugated effect might weaken the electron-donating effect of thiophene units, and strengthen the electron-withdrawing effect. Thus, compound 5c shows the highest energy level of LUMO. While for compound 5d, the positive conjugated effect can lead to lowering the LUMO energy level. The values of optical band gap (E_g) of these compounds were calculated from the absorption edges. Compound **5b** possesses the largest band gap, likely due to the lowest coplanarity as aforementioned, whereas compound 5d with the longest conjugated backbone certainly owns the narrowest band gap. The smaller band gap for compound 5c than that of 5a is assigned to the electron-donating effect of the alkyl chains at the α -terminal positions of the thiophene units. Accordingly, as shown in Table 1, compound 5d exhibits the lowest energy level of HOMO with a significant drop by 0.39 eV in comparison with that of compound 5a, probably due to the higher conjugated system in the former case. Compound 5c processes a slightly higher HOMO value (-5.62 eV) than 5a (-5.80 eV), likely attributed to the weaker electron-donating effect of the alkyl substituents. Reasonably, compound 5d with the longest conjugated backbone, shows much higher HOMO level than the other compounds. Therefore, both substituted side chain and conjugated length have pronounced influence on the electronic behaviors of the benzopyridiazine-based conjugated molecules through fine-tuning the frontier molecular orbitals (HOMO and LUMO).

Density functional theory calculations

To make insight into the energy level of the frontier



Figure 4 Cyclic voltammograms of 5a-5d in dichloromethane (scanning rate at 100 mV \cdot s⁻¹).

molecular orbitals, the geometries as well as the electronic structures of 5a-5d were calculated by using density functional theory (DFT) (B3LYP/6-31G(d) level) (Figure 5 and Table 1). A calculated dihedral angle of 0.0° between benzopyridazine and thiophene moieties for **5c** is much smaller than that of 29.3° dihedral angle for 5a, demonstrating a higher π -conjugated planarity in the former case, also in agreement with its narrower optical band gap. While, 5d possessing a larger calculated dihedral angle of 29.6° between benzopyridazine and thiophene moieties, but the smallest optical band gap of 2.52 eV, demonstrated the significant effect of the prolonged conjugated chain length on the extended π -conjugated system. It is noticed that the LUMOs for 5a, 5c and 5d primarily reside on the benzopyridazine moieties with similar electron density distributions, supporting the strong electron-withdrawing character of the benzopyridazine moiety. While the HOMOs of 5a, 5c and 5d are localized over the full conjugated backbone with higher electron density distributions on the thiophene rings.

However, for compound 5b, the LUMO and HOMO are mostly localized over the benzopyridazine and thiophene moieties, respectively, indicating the lower conjugated effect between benzopyridazine and thiophene moieties, which is geometrically supported by a larger calculated dihedral angle of 57.2° between two moieties, and in line with the declined coplanarity of the molecular backbone. Thus, the LUMO and HOMO of compound 5b are separately decided by the electron-withdrawing and electron-donating moieties. Since benzopyridazine core plays a critical role on the LUMO level for all these compound 5a-5d, their LUMO values displayed less variation. The HOMO and LUMO energy levels of 5a, 5c and 5d show similar trends to those achieved in optoelectronic characterization. Additionally, in the case of 5b, the larger deviations of the calculated values from the experimental results are likely attributed

to the opposite effects from the steric effect of alkyl chain and intramolecular interaction induced by N and S atoms as mentioned above, which make it difficult to establish an optimum conformational modeling.



Figure 5 Density-functional theory (DFT) molecular simulation results: HOMO/LUMO energy levels and their topographical representation.

Experimental

Materials

All chemical reagents and solvents were purchased from Aladdin, J&K Chemical or Sinopharm Chemical Reagent. Tetrahydrofuran (THF) was dried over sodium and freshly distilled prior to use. Triethylamine (TEA) was dried over calcium hydride. Dichloromethane (CH₂Cl₂) for Cyclic Voltammetry (CV) and Ultraviolet-visible (UV-vis) spectra studies was dried over calcium hydride. The optimum separation and purification of compounds were conducted by column chromatogram with 100–200 silica gel.

Measurement

All new compounds were characterized by ¹H, ¹³C Nuclear Magnetic Resonance (NMR), melting point measurement and mass spectrometry. ¹H NMR and ¹³C NMR spectra were recorded on a Mercury Plus 400 (400 MHz for proton) spectrometer using chloroform (CDCl₃) as solvent in all cases at ambient temperature. Melting points were measured with Jing Song X-4A Melting Point Apparatus. Mass spectrometry was measured with a BrukermicroTof-Q-II System. UV-vis absorption spectra were recorded on a HITACHI U-4100 spectrophotometer. The PL emission spectra were obtained with a FluoroMax-4 spectrophotometer. CV was performed on a Chenhua 650D electrochemical analyzer in 0.1 mol• L^{-1} *n*-Bu₄NPF₆ CH₂Cl₂ solution at 298 K. A conventional three-electrode cell was used with a platinum working electrode (surface area of 0.3 mm^2) and a platinum wire as the counter electrode. The Pt working electrode was routinely polished with a polishing alumina suspension and rinsed with acetone before use. The measured potentials were recorded with respect to an Ag/AgNO₃ (0.01 mol•L⁻¹) reference electrode. All electrochemical measurements were carried out under an atmospheric pressure of argon.

Synthesis of 1,2-di(S-(pyridine-2-yl)) benzenedithioate (2)

To a solution of 15 mL TEA in 150 mL dry THF was added 2-mercaptopyridine (10.7 g, 0.10 mol) at 0 °C under nitrogen and a solution of phthaloyl dichloride (9.1 g, 0.045 mol) in 50 mL of THF was added immediately. After the addition, the reaction was stirred for 10 min, then quenched by adding HCl (10%, 100 mL). The organic layer was extracted with CH₂Cl₂, and the combined organic layers were washed with NaOH (10%, 100 mL), NaHCO₃ (1 mol \cdot L⁻¹, 100 mL), and water and dried over MgSO₄. After recrystallization from CH₂Cl₂/ diethyl ether, the pure product 2 (13.3 g, 84%) was obtained as white crystals. ¹H NMR (400 Hz, CDCl₃) δ : 8.64 (d, J=4.4 Hz, 2H, Ph), 7.89 (dd, J=5.6, 3.2 Hz, 2H, Ph), 7.79 (d, J=1.6 Hz, 2H, Py), 7.77 (d, J=2.0 Hz, 2H, Py), 7.66 (dd, J=5.6, 3.2 Hz, 2H, Py), 7.34-7.30 (m, 2H, Py).

Synthesis of 1,2-phenylenebis(thiophene-2-yl-methanone) (4a)

Under a nitrogen atmosphere, a solution of 2-bromothiophene (2.45 g, 14.89 mmol) in 50 mL dry THF was added to Mg (0.38 g, 15.60 mmol). After the reaction mixture was stirred for 3 h, it was drop wise added to 2 (2.5 g, 7.09 mmol) in 40 mL of THF at 0 °C. Next the resulting dark brown solution was stirred at room temperature overnight and then quenched by adding HCl (10%, 100 mL). The organic layer was extracted with diethyl ether, and the combined organic layers were washed with NaOH (10%, 100 mL), NaHCO3 (1 $mol \cdot L^{-1}$, 100 mL), and water and dried over MgSO₄. Yellow solid product 4a (1.37 g, 66%) was purified by recrystallization from CH₂Cl₂/*n*-hexane. ¹H NMR (400 Hz, CDCl₃) δ: 7.73 (dd, J=5.6 3.2 Hz, 2H, Ph), 7.66 (dd, J=5.2, 1.2 Hz, 2H, Ph), 7.63 (dd, J=5.6, 3.2 Hz)2H, Th), 7.47 (dd, J=4.0, 1.2 Hz, 2H, Th), 7.06 (dd, J=4.8, 3.6 Hz, 2H, Th); ¹³C NMR (100 Hz, CDCl₃) δ : 188.52, 144.29, 139.58, 135.36, 135.19, 130.85, 129.45, 128.25; m.p. 146 °C.

Synthesis of 1,2-phenylene bis((3-hexylthiophene-2yl)methanone) (4b)

Under an nitrogen atmosphere, a solution of 3-bromo-2-hexylthiophene (5 g, 0.02 mol) in 25 mL dry THF was added to Mg (0.59 g, 0.024 mol). After the reaction mixture was stirred for 3 h, it was drop wise added to 2 (2.38 g, 6.7 mol) in 30 mL of THF at 0 °C. Next the resulting dark brown solution was stirred at room temperature overnight and then quenched by adding HCl (10%, 150 mL). The organic layer was extracted with diethyl ether, and the combined organic layers were washed with NaOH (10%), NaHCO₃ (1 $mol \cdot L^{-1}$), and water and dried over MgSO₄. Orange oil substance 4b (2.22 g, 71%) was purified by column chromatography (CH₂Cl₂/petroleum ether); ¹H NMR (400 Hz, CDCl₃) δ : 7.64 (dd, J=5.6, 3.2 Hz, 2H, Ph), 7.51 (dd, J=5.6, 3.2 Hz, 2H, Ph), 7.38 (d, J=4.8 Hz, 2H, Th-CH-3), 6.95 (d, J=5.2 Hz, 2H, Th-CH-4), 2.80

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(t, J=8.0 Hz, 4H, CH₂), 1.58–1.50 (m, 4H, CH₂), 1.30 -1.21 (m, 12H, CH₂), 0.85 (t, J=7.2 Hz, 6H, CH₃); ¹³C NMR (100 Hz, CDCl₃) δ : 189.14, 151.89, 141.40, 135.73, 131.82, 131.21, 130.33, 129.24, 31.87, 30.49, 30.27, 29.47, 22.84, 14.34.

Synthesis of 1,2-phenylenebis((5-hexylthiophene-2yl)methanone) (4c)

Under an nitrogen atmosphere, a solution of 5bromo-2-hexylthiophene (1 g, 4.05 mmol) in 5 mL dry THF was added to Mg (0.12 g, 4.85 mmol). After the reaction mixture was stirred for 3 h, it was drop wise added to 2 (0.47 g, 1.35 mmol) in 30 mL of THF at 0 $^{\circ}$ C. Next the resulting dark brown solution was stirred at room temperature overnight and then quenched by adding HCl (10%, 100 mL). The organic layer was extracted with diethyl ether, and the combined organic layers were washed with NaOH (10%), NaHCO3 (1 $mol \cdot L^{-1}$), and water and dried over MgSO₄. Orange oil substance 4c (0.42 g, 67%) was purified by column chromatography (CH₂Cl₂/petroleum ether) to provide the title compound. ¹H NMR (400 Hz, CDCl₃) δ : 7.69 (dd, J=5.6, 3.2 Hz, 2H, Ph), 7.59 (dd, J=5.6, 3.2 Hz)2H, Ph), 7.25 (d, J=4.0 Hz, 2H, Th-CH-3), 6.74 (d, J= 4.0 Hz, 2H, Th-CH-4), 2.80 (t, J=7.6 Hz, 4H, CH₂), 1.70-1.62 (m, 4H, CH₂), 1.39-1.27 (m, 12H, CH₂), 0.89 (t, J=6.8 Hz, 6H, CH₃); ¹³C NMR (100 Hz, CDCl₃) δ : 188.24, 157.56, 141.84, 139.61, 136.02, 130.60, 129.31, 125.82, 31.72, 31.53, 30.95, 28.92, 22.77, 14.30.

Synthesis of 1,4-bis(2-thienyl) benzopyridazine (5a)

A solution of hydrazine hydrate (0.47 g, 9.38 mmol) and **4a** (1.4 g, 4.7 mmol) in 125 mL ethanol was stirred overnight at room temperature. The combined organic layers were evaporated. Pale yellow solid **5a** (0.92 g, 67%) was purified by recrystallization from ethyl acetate/petroleum ether. ¹H NMR (400 Hz, CDCl₃) δ : 8.57 (dd, *J*=3.2, 6.0 Hz, 1H, Ph), 7.95 (dd, *J*=3.6, 6.4 Hz, 1H, Ph), 7.73 (d, *J*=3.6 Hz, 1H, Th), 7.61 (d, *J*=5.2 Hz, 1H, Th), 7.27–7.26 (m, 1H, Th); ¹³C NMR (100 Hz, CDCl₃) δ : 152.58, 139.25, 132.71, 129.98, 129.37, 127.90, 126.25, 125.40; HRMS-ESI *m/z*: [M+H] calcd for C₁₆H₁₀N₂S₂ 295.0364, found 295.0367; m.p. 140 °C.

Synthesis of 1,4-bis(3-hexylthiophene-2-yl) benzopyridazine (5b)

Under a nitrogen atmosphere, a solution of hydrazine hydrate (0.24 g, 4.74 mmol) and **4b** (2.07 g, 4.43 mmol) in 20 mL ethanol was stirred overnight at room temperature. After exposed to air, the reaction mixture was heated up to 80 °C and stirred for more than 24 h. The combined organic layers were dried over MgSO₄ and evaporated. Product **5b** (2.05 g, 98%) was purified by column chromatography (CH₂Cl₂/petroleum ether). ¹H NMR (400 Hz, CDCl₃) δ : 8.05 (dd, *J*=6.27, 3.32 Hz, 1H, Ph), 7.86 (dd, *J*=6.35, 3.26 Hz, 1H, Ph), 7.51 (d, *J*=5.11 Hz, 1H, Th), 7.14 (d, *J*=5.12 Hz, 1H, Th), 2.58

(t, J=8.0 Hz, 2H, CH₂), 1.55 (td, J=15.2, 7.6 Hz, 2H, CH₂), 1.18–1.09 (m, 6H, CH₂), 0.76 (t, J=7.2 Hz, 3H, CH₃); ¹³C NMR (100 Hz, CDCl₃) δ : 154.63, 143.98, 132.54, 130.92, 129.25, 127.00, 126.77, 31.69, 30.74, 29.45, 29.15 22.68, 14.25; HRMS-ESI *m*/*z*: [M+H] calcd for C₂₈H₃₄N₂S₂ 463.2242, found 463.2244.

Synthesis of 1,4-bis(5-hexylthiophene) benzopyridazine (5c)

Under a nitrogen atmosphere, a solution of hydrazine hydrate (0.057 g, 1.03 mmol) and 4c (0.4 g, 0.86 mmol) in 20 mL ethanol was stirred overnight at room temperature. After exposed to air, the reaction mixture was heated up to 80 °C and stirred for more than 24 h. The combined organic layers were dried over MgSO₄ and evaporated. Product 5c (0.38 g, 95%) was purified by column chromatography (CH₂Cl₂/petroleum ether). ¹H NMR (400 Hz, CDCl₃) δ : 8.57 (dd, J=6.4, 3.6 Hz, 1H), 7.92 (dd, J=6.4, 3.2 Hz, 1H), 7.54 (d, J=3.6 Hz, 1H), 6.93 (d, J=3.6 Hz, 1H), 2.92 (t, J=8.0 Hz, 2H, CH₂), 1.81-1.73 (m, 2H, CH₂), 1.48-1.40 (m, 2H, CH₂), 1.38 - 1.31 (m, 6H, CH₂), 0.91 (t, J = 7.2 Hz, 3H, CH₃); ¹³C NMR (100 Hz, CDCl₃) δ: 152.2, 150.47, 136.70, 132.37, 130.06, 126.26, 125.19, 31.85, 30.57, 29.10, 22.86, 14.37; HRMS-ESI m/z: [M + H] calcd for C₂₈H₃₄N₂S₂ 463.2242, found 463.2239; m.p. 63 °C.

Synthesis of 1,4-bis(5-bromothiophene-2-yl) benzopyridazine (6)

To a solution of 5a (0.50 g, 1.70 mmol) in 100 mL CHCl₃ was added NBS (0.64 g, 3.57 mmol) in 30 mL DMF over a period of 15 min at 0 °C. Under a lucifugal condition, the resulting solution was stirred for 1 d at room temperature. The reaction mixture was poured into ice and the organic layer was taken off while the water phase was extracted with CH₂Cl₂. The combined organic phase was washed with 100 mL sodium chloride solution. After the solvent was removed by rotary evaporation product 9 (0.67 g, 88%) was obtained by column chromatography (CH₂Cl₂) as a clear liquid. ¹H NMR (400 Hz, CDCl₃) δ: 8.52 (dd, *J*=3.6, 6.4 Hz, 1H), 7.98 (dd, J=4.0, 6.4 Hz, 1H), 7.49 (d, J=4.0 Hz, 1H), 7.22 (d, J=6.4 Hz, 1H); ¹³C NMR (100 Hz, CDCl₃) δ : 151.69, 140.99, 133.04, 130.29, 125.60, 125.60, 125.02, 117.42; m.p. 187 °C.

Synthesis of 1,4-bis(5'-hexy-[2,2'-bithiophene]-5-yl) benzopyridazine (5d)

Under an nitrogen atmosphere, a mixture of **9** (0.05 g, 1.11 mmol), 5-hexylthiophen-2-yl-tributylstannane (0.76 g, 1.67 mmol) and Pd(PPh₃)₄ (0.1 g) in 30 mL DMF was heated together at 100 °C with a reflux condenser. Then, the reaction mixture was stirred for 24 h. After cooling down to room temperature, the solvent was removed by rotary evaporation, and product **5d** (0.83 g, 80%) was obtained by column chromatography (CH₂Cl₂) as an orange solid. ¹H NMR (400 Hz, CDCl₃) δ : 8.59 (td, *J*=3.2, 6.4 Hz, 1H, Ph), 7.96–7.93 (m, 1H, Ph), 7.64 (t, *J*=3.8 Hz, 1H, Th), 7.23 (t, *J*=3.7 Hz, 1H,

Th), 7.15 (t, J=3.1 Hz, 1H, Th), 6.74 (t, J=2.7 Hz, 1H, Th), 2.83 (t, J=8.6 Hz, 2H, CH₂), 1.71 (t, J=0.1 Hz, 2H, CH₂), 1.35–1.32 (m, 6H, CH₂), 0.93–0.88 (m, 3H, CH₃); ¹³C NMR (100 Hz, CDCl₃) δ : 151.83, 146.75, 141.97, 137.49, 134.44, 132.63, 130.66, 126.09, 125.30, 125.11, 124.68, 123.69, 31.80, 30.47, 29.93, 29.01, 22.82, 14.33; HRMS-ESI m/z: [M + H] calcd for C₃₆H₃₈N₂S₄ 627.1997, found 627.2001; m.p. 179 °C.

Conclusions

In summary, a series of new organic conjugated molecules comprising 2,3-benzodiazine and thiophene moieties have been synthesized successfully. Our experimental and theoretical investigations revealed that both introduction of the heteroatoms in the conjugated backbone and substituted side chains at the different position of the conjugated building blocks have significant influence on the optical properties and electrochemical behaviors of these compounds via varying the geometric and electronic structures for tuning the energy levels of LUMO and HOMO. The electron-withdrawing benzopyridiazine and electron-donating thiophene moieties act as acceptor (A) and donor (D) parts in the whole conjugated system, respectively, to form a new class of D-A-D conjugated system. These fundamental results will not only provide some new candidate molecules for application in optoelectronic materials, but also helpfully understand the comprehensive effect from molecular geometric and electronic structures on electronic behavior.

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