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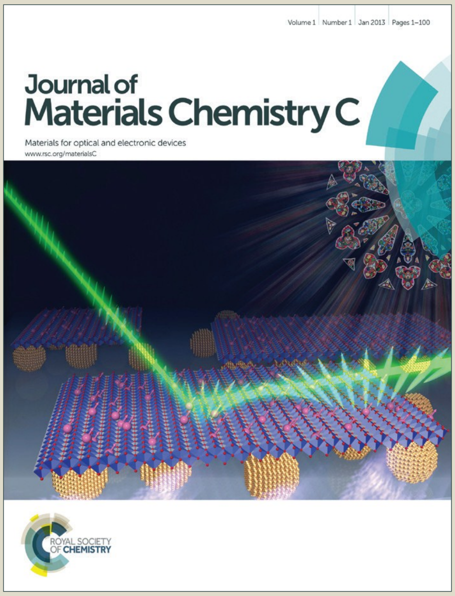

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BN-heteroacene-cored Luminogens with Dual Channel Detection for Fluoride Anion

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Very recently, polycyclic aromatic hydrocabons (PAHs) have been extremely extended by taking place of C=C units with isoelectronic B-N ones, however, BN-containing π-conjugated oligomers or polymers are still very less explored due to the lack of appropriate building blocks. Herein, on the basis of the successful synthesis of a new BN-embedded heteroacene and its brominated derivatives, a series of BN-containing oligomers have been achieved via Surzuki cross-coupling with aryl boronic esters. Their rich photophysical properties and electrochemical behaviors are essentially dependent on the main chain lengths, indicative of the fully-π-conjugated effect of such kinds of luminogens. Furthermore, these BN-containing luminogens, enable colorimetric and fluorometric dual channel detection of fluoride ion through binding to the Lewis acid boron atom of the BN moiety in high selectivity and sensitivity.

Introduction

In the past decades, significant progresses have been witnessed in polycyclic aromatic hydrocarbons (PAHs) due to their interesting physical properties and potential applications in organic electronics.[1] In order to further improve the properties, a large number of PAHs derivatives decorated with heteroatoms, such as boron (B),[2] nitrogen (N),[3] sulfur (S),[4] have been developed. Among them, BN-containing PAHs formed by the replacement of C=C unit with isoelectronic B-N fragment has been demonstrated to display obviously different electronic properties and unique self-assembly behavior by compared with their all-carbon analogues.[5] Recently, several BN-containing conjugated polymers and oligomers using BN-embedded PAHs as the key building blocks, have been reported, exhibiting some interesting physical properties, however, extending these BN-containing molecules to much larger π-conjugated systems is still a synthetic challenge. We have reported several series of BN-embedded heteroacenes with rich optoelectronic properties, and potential applications in electronic devices, such as organic light emitters (OLEDs).[6] On the basis of these previous work, currently, we are focusing on developing BN-containing polymers or oligomers with extended π-conjugated systems, and trying to find their application in a much broad scope.

The recognition and sensing of fluoride ion have aroused broad attention due to its serving as a crucial role in environmental protection medical diagnosis and forensic analysis etc. [7] In this respect, the chemosensors offer a low-cost and portable detection through the "naked-eye" observation. While, the chemosensors with luminescent properties, enable providing much more spectra information with the help of various fluorescent techniques, and thus exhibiting high selectivity and sensitivity, accessible for probing the species in a complicated system.[8] Undoubtedly, a dual-channel sensor with both colorimetric and fluorescent responses represent a much efficient probe. Typically, boron-containing luminogens have been widely known as one of the most sensitive probe for sensing fluoride ions mainly by the virtue of the luminescence response through strong or weak interactions, for example, hydrogen bonding or coordination binding interaction.[9] As well as we know, the azoborate derivatives available for detection, in particular colorimetric and fluorometric dual-channel detection for F^- are still less documented. From this viewpoint, in this paper, we present the efficiently synthesis of a new BN-embedded heteroacene and its brominated derivatives, which were then converted to a series of BN-heteroacene-cored oligomers through the Suzuki coupling with the aryl boronic esters. The photophysical properties and electrochemical behaviors of such kinds of BN-containing luminogens have been fully characterized. Furthermore, their capabilities of colorimetric and fluorometric dual role detection of fluoride ion were also systematically investigated.

Experimental

The synthetic routs of targeted molecules were depicted in **Fig 1**. At first, starting from 2,5-dibromobenzene-1,4-diamine, 2,5-dibromo-*N*1,*N*4-dihexylbenzene-1,4-diamine (**2**) with good solubility in common organic solvents was prepared. Afterwards, the key intermediate **3** was achieved by the Suzuki

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Electronic Supplementary Information (ESI) available: experimental details including synthesis, measurements and instruments. See DOI: 10.1039/x0xx00000x cross-coupling reaction of compound **2** with thiophene boronic ester. Then, it was facile to be converted to BN-dithienothiophene[a,d]anthracene (**4**) by a highly efficient cyclization of nitrogen-directed aromatic borylation, as yellow microcrystals in 78% yield after purification by column chromatography. Treatment of compound **4** with NBS resulted in a yellow mixture of mono-brominated and di-brominated intermediates **5-1** and **5-2** in a molar ratio of 1:4 (total yield: 50%) evaluated by NMR spectra analysis. However, attempt to further isolate this mixture was unsuccessful, and then directly used in the next step. After reacted with thienyl or benzyl boronic ester under Suzuki cross-coupling, the resulting crude was purified through column chromatography to offer the BN-containing oligomers **6a** (light yellow solid, yield: 10%) and **6c** (golden yellow solid; yield: 30%), or **6b** (light yellow solid; yield: 15%) and **6d** (dark yellow solid, yield: 35%), respectively (the yields calculated on the basis of the corresponding brominated intermediates **5-1** and **5-2**). All new compounds have been fully characterized by ^{1}H, ^{13}C NMR and HRMS spectroscopies, which clearly confirm the chemical structures of the as-prepared molecules.

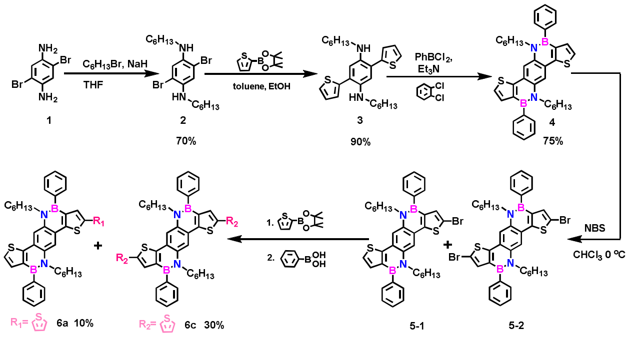

Fig 1. Synthetic Route of compound **6a-6d**

The optical properties of these BN-containing molecules were investigated by UV-vis and fluorescence spectroscopies. Their UV-vis absorption spectra feature vibronically split bands, indicative of their rigid π-conjugated structures (Fig 2). As a consequence of the terminal modification of BN-embedded heteroacene core with thienyl and phenyl moieties, the resulting oligomers show quite different absorption maxima in a sequence of **4** < **6b** < **6a** < **6d** < **6c**, in accordance with the increased tendency of the main chain lengths. The absorption maxima at λ_{max}= 444 nm for compound **6c** terminated with two thiophene moieties is red-shifted over 26 nm as compared with that of λ_{max} = 418 nm for **4** (Table 1). And the oligomers capped with thiophene ends show much red-shifted absorption maxima than those of oligomers with phenyl terminal groups due to the electron-donating property of thiophene unit. These results indicate that an extended π-conjugated systems with respect to the prolonged main chain lengths have been established in the as-prepared series of BN-containing conjugated molecules. The fluorescence spectra of these molecules show good mirror images of their corresponding UV-vis profiles with emission maxima in an order of **4** < **6b** < **6a** < **6d** < **6c** , in line with the increased sequence of their main chain length (Fig 2b). The emission maxima of these as-prepared luminogens fall in the range between λ_{max}=400 nm and 450 nm (Table 1). Notably, compound **4**, exhibits a very small Stokes shift (4 nm), indicating a tiny structural deformation between the ground and excited states associated with its fused main backbone. On the contrary, the oligomer **6a** or **6c** revealed a significantly increased Stokes shift up to 9 nm or 14 nm, respectively, due to the enhanced molecular flexibility from the rotation of the terminal thiophene groups around the C-C axles. Similar phenomenon were also observed for the oligomers **6b** and **6d**. The good fluorescence quantum yields of BN-containing molecules (**6a**-**d**) (from 0.28 to 0.43) are comparable to those of the previously reported BN-embedded heteroacenes.[10] Compound **6c** or **6d** with two terminal aryl groups has a higher fluorescence quantum yield than that of **6a** or **6b** with one terminal aryl group (Table 1), likely due to the enlarged π-conjugated system in the former case. The different fluorescence lifetimes of such kind of luminogens further manifested the influence of the slight change of the molecular backbones on their electronic behaviours (Table 1).

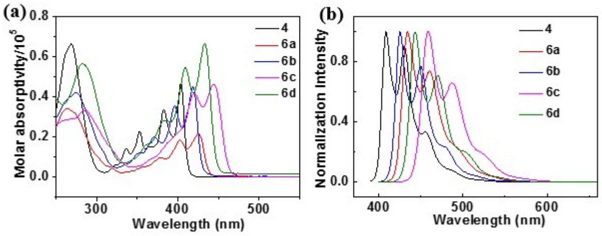

Fig 2. (a) Absorption spectra and (b) fluorescence spectra of **4**, **6a**-**6d** at 10^{-5} M in CH_2Cl_2.

Table 1. Photophysical data for **4**, **6a-d**

compd	$\lambda_{abs}{}^a$ /nm	log ε	Stokes shift/nm	λ_{em} /nm	τ/ns	$\Phi_{PL}{}^b$
4	404	4.68	4	408	2.85	36.30
6a	425	2.14	9	434	1.37	30.60
6b	418	4.49	7	425	1.54	28.47
6c	444	4.62	14	458	1.68	43.69
6d	433	6.65	10	443	1.48	37.73

[a] In CH_2Cl_2 (10^{-5} M). Only the longest λ_{max} were given. [b] Absolute value.

The electrochemical behaviours of these BN-containing conjugated molecules were subsequently investigated by cyclic voltammetry (CV) in CH_2Cl_2. In the CV profiles, these compounds exhibit irreversible oxidation processes under the measurement conditions (Fig 3). The first oxidation potentials in a sequence of **4** > **6b** > **6a** > **6d** > **6c** were observed, well in agreement with their extended π-conjugated systems. Among them, oligomer **6c** shows the lowest value of -0.59 eV of the first oxidation potential, essentially attributable to its two terminal electron-donating thiophene moieties. Accordingly, the HOMO energy levels of these compounds were evaluated from the onsets of the first oxidation potential (Table 2), and the band gap was estimated through the absorption maxima. And the lowest unoccupied molecular orbital (LUMO) energy levels were calculated according to the empirical formula: LUMO=HOMO+E_g^{opt}. A remarkable declined tendency of the band gaps in **4**> **6b** > **6a** > **6d** > **6c**, highly in accordance with the decreased main chain lengths. These results manifested that either the main chain length or the terminal group enable remarkably affecting the photophysical properties and electrochemical behaviours of such kinds of molecules. Accordingly, their electronic structures can be finely tuned via the modification of the terminal positions in the main conjugated backbones.

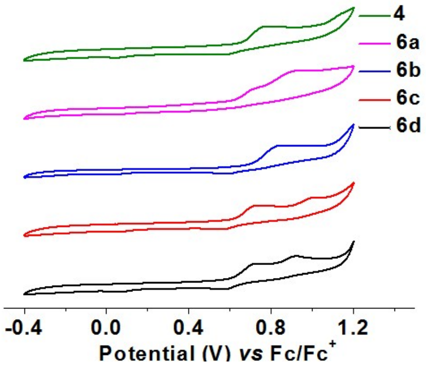

Fig 3. Cyclic voltammograms of **4**, **6a**-**6d** measured in CH_2Cl_2 (0.1 mol/L of n-Bu_4NPF_6) at a scan rate of 100 mV/s.

Table 2. Electronic structure data for **4**, **6a**-**6d**.

Compd	E_{ox1}	$HOMO^a$/eV	$LUMO^a$/eV	E_g^{opt}/eV	$HOMO^b$/eV	$LUMO^b$/eV	E_g/eV
4	-0.69	-5.49	-2.42	3.07	-5.56	-1.91	3.65
6a	-0.62	-5.42	-2.50	2.92	-5.38	-2.06	3.32
6b	-0.66	-5.46	-2.49	2.97	-5.44	-2.00	3.44
6c	-0.59	-5.39	-2.59	2.80	-5.27	-2.17	3.10
6d	-0.61	-5.41	-2.54	2.87	-5.35	-2.07	3.28

[a] HOMO=$-E_{ox1}-4.80$ eV, E_{ox1}: the first oxidation potential, evaluated from the onset; LUMO = HOMO + E_g^{opt}, E_g^{opt}: optical band gap, estimated from UV-vis absorption edge; [b] Obtained by DFT calculations.

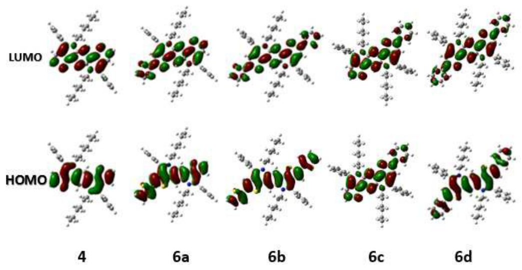

Fig 4. Wave functions for the HOMO and LUMO of **4**, **6a**-**6d**.

Furthermore, the theoretical investigation was performed through the density functional theory (DFT) calculations. The geometries of these BN-containing molecules were optimized at the B3LYP/6-31G** level, and the frontier molecular orbitals were shown in Fig 4. Evidently, both the LUMO and HOMO orbitals are delocalized over the whole main backbones, indicating the fully-π-conjugated characters of the main backbones for such kinds of luminogens. All the way, the RB3LYP/6-31G(d) calculated energy levels of HOMO, LUMO, and band gaps are also in well agreement with the experimental results.

Thanks to the existence of boron atoms in the main backbones of these luminogens, we were thus encouraged to examine their selectively sensing fluoride ions. Compound **4** was firstly testified for the detection of anions with the addition of F^-, Cl^-, Br^-, I^-, HPO_4^{2-}, HSO_4^-, $NO_2^-$and Ac^-(300 eq. relative to the molar amount of **4**) to a solution of **4** in $CHCl_3$ (1×10^{-5} M), respectively (Fig 5). Addition of tetrabutyl ammonium fluoride (TBAF), immediately resulted in a colour change of the solution from colourless to blue. While, there was no obvious colour variation as the addition of the other anions. Accordingly, the addition of F^- leads to a completely different profile of the UV-vis spectra from the original one, in which the original absorption maxima approximately disappeared, and two new broad absorption bands at λ_{max} = 575 nm and 648 nm in the low energy regions were observed, respectively. While, there was no any remarkable change for the absorption profiles as the addition of the other anions. Additionally, the solution was changed into dark colour with the addition of F^- (300 eq.) under UV light irradiation, with respect to a completely fluorescence quenching in its emission spectra. Nevertheless, the solution still releases the strong blue emission as the addition of the other anions (300 eq.), without significant changes in their emission spectra (Fig 5b).

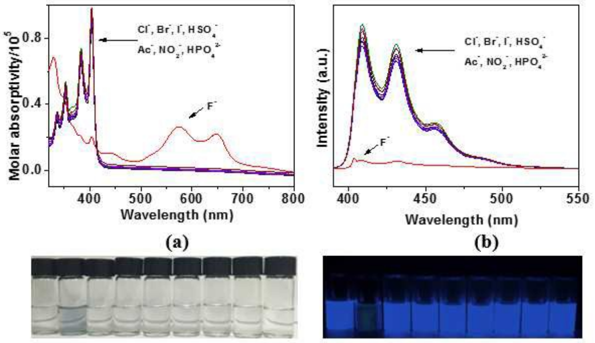

Fig 5. Compound **4** in $CHCl_3$ (1×10^{-5} M) with the addition of the different anions (300 eq.), (a) left: absorption spectra and photographs under visible light; (b) right: fluorescence spectra and photographs under UV light at 365 nm.

In order to make an insight into such colorimetric and fluorometric dual channel detection of F^- for compound **4**. Titration experiments were carried out. Upon the addition of TBAF (0-300 eq), in the absorption spectra, the intensities of the bands at 393nm and 404 nm steadily decreased, and in the meantime, two new bands at 575 and 648 nm with a clear isobestic points at 412 nm, were observed (Fig 6a). And the excessive addition of Bu$_4$NF up to 600 eq. will not change the profile of the spectra again, indicating the formation of an equilibrium between F$^-$ associated and dissociated with **4**. Meanwhile, the fluorescent emission with maxima at λ_{max}=408 nm, was gradually weakened, and nearly quenched (~98%) as the progressive addition of Bu$_4$NF up to 300 eq. (Fig 6**b**). It is worth noting that such a dual channel response to fluoride is very fast to occur, normally within 1 sec. On the basis of these phenomenon, an equilibrium arising from the F$^-$ binding to the boron atoms of the BN-heteroacene can be rationally evaluated. Also, the behaviour of F$^-$ anion seems to undergo the binding to the two boron atoms without the stepwise selectivity. Undoubtedly, such a double binding performance simultaneously occurring in the same conjugated backbone would enhance the sensitivity of the response via much strongly varying the conjugated structure of a sensor.

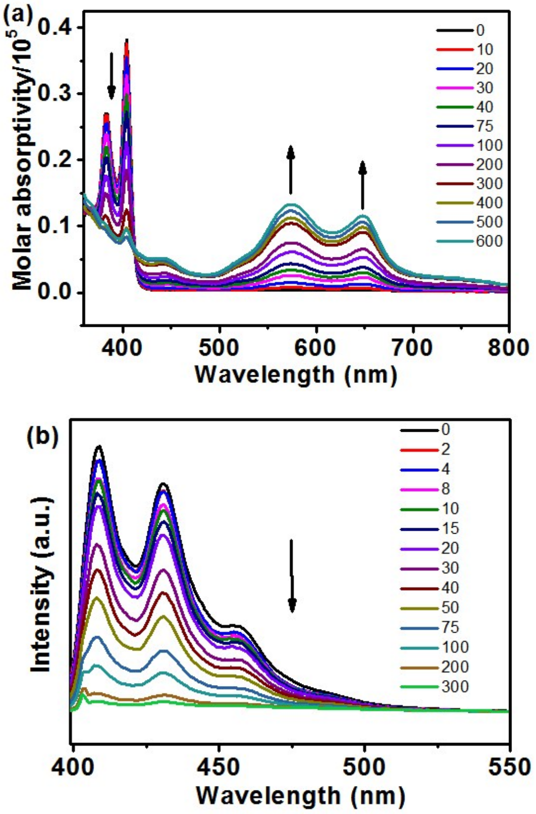

Fig 6. (a)Absorption titrations spectra of compound **4** (1×10^{-5} M in CHCl$_3$) upon addition of Bu$_4$NF (b) Fluorescence titrations spectra of compound **4** (1×10^{-5} M in CHCl$_3$) upon addition of Bu$_4$NF

The influence of the π-conjugated chain lengths for such kinds of BN-containing luminogens on their capabilities for detection of anions, were also systematically explored. As an example, we testified the detection of anions with the addition of F$^-$, Cl$^-$, Br$^-$, I$^-$, HPO$_4^{2-}$, HSO$_4^-$, NO^{2-}and Ac$^-$(200 eq.) to the solution of **6d** in CHCl$_3$ (1×10^{-5} M), respectively. As expected, upon the addition 200 eq. of Bu$_4$NF, a remarkable colour change of the solution from light yellow to dark green, was observed immediately, with respect to a new absorption maxima at 619nm generated in the low energy regions of the absorption profile (Fig. 7). It is noteworthy that the intensities of these new generated peaks will not increase again even with the addition of more than 200 eq. of Bu$_4$NF. Meanwhile, the fluorescent emission was thoroughly quenched with the addition of 200 eq. of Bu$_4$NF, as shown in either the luminescent emission of the solution or the fluorescence profiles (Fig. 8). These phenomenon manifested an established equilibrium between F$^-$, compound **6d** and F$^-$complexes **6d**. Obviously, a much less amount of TBAF was required for stimulating either colorimetric or fluorometric response in the case of compound **6d**, by compared with those of compound **4**. Such result was likely attributed to the extended π-conjugated effect as attaching phenyl units in the terminal positions of compound **4** to form compound **6d**, which will be beneficial to improving the sensitivity and selectivity through red-shifted removing the optical responses to the lower energy regions.

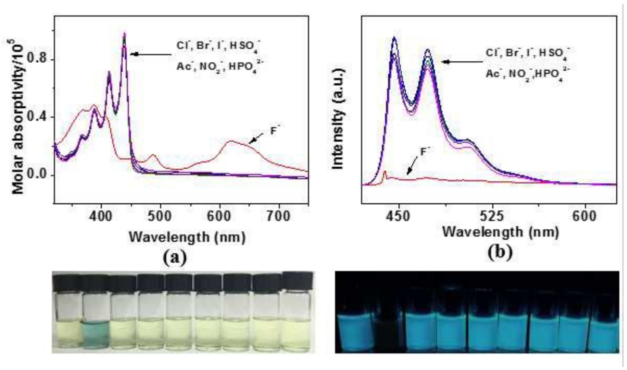

Fig 7. Compound 6d in CHCl$_3$ (1×10^{-5} M) with addition of different anions (200eq), (a) left: photographs under visible light, and right: absorption spectra (b) left: photographs under UV light at 365 nm, and right: fluorescence spectra

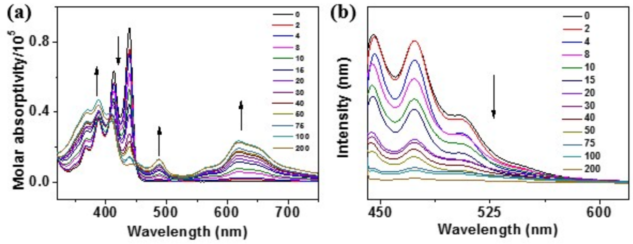

Fig 8. (a) Absorption titration spectra of compound **6d** (1×10^{-5} M in CHCl$_3$) upon addition of Bu$_4$NF. (b) Fluorescence titrations spectra of compound **6d** (1×10^{-5} M in CHCl$_3$) upon addition of Bu$_4$NF.

Conclusions

In summary, a new BN-embedded heteroacene has been readily synthesized, which can be effectively converted to one or two-fold brominated products, and thus further transformed to a series of BN-heteroacene-cored oligomers. The photophysical properties and electrochemical behaviours of such kinds of BN-containing luminogens are highly dependent on the main chain lengths, manifesting that the enlarged π-conjugated effect can be tailored through the modification in the terminal positions of BN-heteroacene. These luminogens are capable of colorimetric and fluorometric detection of F^- in high selectivity and sensitivity. In particular, such capabilities can be improved by prolonging the π-conjugated main chain lengths of the as-prepared luminogens, providing a very valuable strategy for the construction of the high-performance organic molecule sensors. The dramatic anion-specific response with colorimetric and fluorometric dual channels suggests that the as-prepared BN-containing luminogens would have potential application for sensing and imaging in environmental protect or biological medicine. On the other hand, the as-prepared brominated BN-containing heteroacenes can be used as the key building blocks for the formation of versatile oligomers/polymers with the rich electronic properties applicable in a much broad scope, such as organic solar cells and organic light-emitting diodes.

Experimental

Synthesis

All solvents and reagents employed were purchased from Sigma-Aldrich and Adamas-beta. $CHCl_3$, CH_3CN were distilled from calcium hydride. THF were distilled from Na. And all performances were carried out using standard Schlenk technique.

Instruments

^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Mercury Plus 400 (400 MHz for proton, 100 MHz for carbon) spectrometer with tetramethylsilane as the internal reference using $CDCl_3$ as solvent in all cases. Mass spectrometry was measured with an Ultra Performance Liquid Chromatography & Quadrupole-Time-of-Flight Mass Spectrometer. UV-vis spectra were recorded on a HITACHI U-4100 Spectrophotometer. Fluorescent spectra were obtained with a FluoroMax-4 spectrophotometer. Cyclic voltammetry (CV) was performed on a Chenhua 650D electrochemical analyzer in anhydrous CH_2Cl_2 containing recrystallized tetra-*n*-butyl-ammoniumhexafluorophosphate ($TBAPF_6$, 0.1 M) as supporting electrolyte at 298K. 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 Ag/AgCl reference electrode. All electrochemical measurements were carried out under an atmospheric pressure of nitrogen.

DFT calculations

All the calculations were carried out using the Gaussian 09 program package. The geometries of complexes **4, 6a-6d** were fully optimized at the B3LYP/6-31G** level. The frontier molecular orbitals were calculated for each of the compounds. In this work, all the calculations were performed in vacuum without considering the solvent.

Synthetic procedures

Synthesis of 2,5-dibromo-N1,N4-dihexylbenzene-1,4-diamine (2)

Compound 2,5-dibromobenzene-1,4-diamine (2.19 g, 8.20 mmol) and THF (60 ml) were combined in a Schlenk flask, and stirred until complete dissolution. NaH (788 mg, 19.70 mmol) was added after the mixture was cooled to 0°C for 10 minutes. Then the bromohexane (4.06 g, 24.60 mmol) was added after the mixture was cooled to 0°C for 2h. The mixture was then heated at 40°C for 12 h. After cooling to room temperature, 30 mL of H_2O was added to facilitate the workup. The mixture was extracted with ethyl acetate (100 ml, three times). Then all organic solutions were collected and dried over $MgSO_4$ and filtered. The solvent was removed to offer solid residue. Then the product was purified by chromatography on silica gel (CH_2Cl_2: PE=1:3) to give compound **2** as white solid in 70% yield (2.50 g, 5.76 mmol). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 6.80 (s, 1H), 3.72 (s, 1H), 3.05 (t, *J* = 7.0 Hz, 2H), 0.90 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm):137.9, 116.1, 110.2, 45.0, 31.7, 29.5, 26.9, 22.7, 14.2.

Synthesis of N1,N4-dihexyl-2,5-di(thiophen-2-yl)benzene-1,4-diamine (3)

Compound **2** (2.00 g, 4.61 mmol) and thiophene-2-boronic acid pinacol ester (3.90 g, 18.56 mmol) were employed in a Schlenk flask, c. After adding 90 ml toluene, 30 ml ethanol, 30 ml Cs_2CO_3 aqueous solution (2M), the mixture was degassed for 45 min. $Pd(PPh_3)_4$ (0.53 g, 0.46 mmol) was added, then the mixture was heated to 80 °C and stirred overnight. Afterwards, the resulting mixture was poured into brine and extracted by dichloromethane for several times. The combined organic phase was dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuum. The product was purified by chromatography on silica gel (CH_2Cl_2: hexane = 2:1) to give product **3** as yellow solid in 90% yield (1.83 g, 4.15 mmol). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.36 (d, *J* = 5.2 Hz, 1H), 7.23 (d, *J* = 2.6 Hz, 1H), 7.13 (dd, *J* = 4.9, 3.7 Hz, 1H), 6.78 (s, 1H), 3.07 (t, *J* = 7.1 Hz, 2H), 0.87 (t, *J* = 6.7 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$, ppm):140.2, 127.9, 126.8, 125.8, 122.3, 121.9, 116.7, 46.1, 31.6, 28.8, 26.8, 22.7, 14.1. m/z$[M+H]^+$ calcd for $C_{26}H_{37}N_2S_2$ 441.2393; HR-ESI observed 441.2384.

Synthesis of BN-dithienothiophene[a,d]anthracene (4)

To a solution of compound **3** (0.10 g, 0.23 mmol) in o-dichlorobenzene (5 mL) was added triethylamine (0.14 mg, 1.38 mmol) and phenyldichloroborane (0.11 g, 0.69 mmol). The reaction mixture was heated to 180 °C for 12 h. After cooling to the room temperature, the mixture was filtered through sand core funnel and then the residue was washed with methanol to give product **4** as yellow powder in 75% yield (0.10 g, 0.17 mmol). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.23 (s, 1H), 7.63 (dd, J = 7.9, 1.5 Hz, 2H), 7.35 (d, J = 5.0 Hz, 1H), 7.25 (d, J = 5.0 Hz, 1H), 4.29 (t, J = 7.8 Hz, 2H), 0.89 (t, J = 6.8Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, ppm):150.6, 141.3, 134.0, 133.4, 132.3, 127.9, 127.8, 123.9, 123.8, 112.7, 48.5, 31.6, 30.1, 26.9, 22.8, 14.2. m/z[M+H]$^+$ calcd for C$_{38}$H$_{43}$B$_2$N$_2$S$_2$ 613.3048; HR-ESI observed 613.3051

Synthesis of 5-1， 5-2

Compound **4** (0.50 g, 0.82 mmol) was dissolved in CHCl$_3$ (80 ml) and stirred at 0°C. Then the NBS (0.29 g, 1.64 mmol) was added in three portions. The reaction mixture was cooled at 0°C for 3h. 20 mL of H$_2$O was added to facilitate the workup. The mixture was extracted with ethyl acetate and the organic layer was dried over MgSO$_4$. The solvent was removed under reduced pressure. The crude was purified by chromatography on silica gel (CH$_2$Cl$_2$: PE=1:6) to give a mixture of **5-1**/**5-2** in a molar ratio of 1:4, as yellow solid, which was directed used in the next step due to the unsuccessful isolation.)

Synthesis of 6a and 6c

A mixture of **5-1** and **5-2** (0.20 g), formed in the last step, and thiophene-2-boronic acid pinacol ester (0.22 g, 1.04 mmol) was charged in a Schlenk flask. After adding 15 ml toluene, 5 ml ethanol, 5ml Cs$_2$CO$_3$ aqueous solution (2M), the mixture was degassed for 30min. Pd(PPh$_3$)$_4$ (0.030 g, 0.026 mmol) was added, then the mixture was heated to 80 °C and stirred overnight. The resulting mixture was poured into brine and extracted by dichloromethane for several times. The combined organic phase was dried over MgSO$_4$ and filtered. After removal offthe solvent, the crude product was purified by chromatography on silica gel (CH$_2$Cl$_2$: PE=1:10-1:6) to give **6a** in 10% yield (0.019 g, 0.027 mmol)and **6c** in 30% yield (0.063 g, 0.081 mmol), respectively.

For **6a**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.20 (s, 1H), 8.13 (s, 1H), 7.35 (d, J = 5.0 Hz, 1H), 7.26 (s, 1H), 7.24 (d, J = 5.0 Hz, 2H), 7.22 (d, J = 1.1 Hz, 1H), 7.03 (dd, J = 5.1, 3.6 Hz, 1H), 4.24 (dd, J = 15.8, 10.0 Hz, 4H), 0.90 (dt, J = 11.0, 7.0 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm):150.6, 149.5, 137.6, 136.1, 134.1, 134.0, 133.5, 132.3, 129.4, 128.0, 127.9, 127.8, 124.9, 124.6, 124.1, 123.9, 123.5, 112.7, 112.5.m/z[M+H]$^+$ calcd for C$_{42}$H$_{45}$B$_2$N$_2$S$_3$ 695.2925; HR-ESI observed 695.2948

For **6c**: ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 8.10 (s, 1H), 7.65 (dd, J = 7.9, 1.5 Hz, 2H), 7.52 (s, 1H), 7.25 (d, *J* = 5.8 Hz, 1H), 7.23 (d, *J* = 5.0 Hz, 1H), 7.03 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.26 (t, *J* = 7.9Hz, 2H), 0.91 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm):149.4, 140.9, 137.5, 136.2, 134.1, 132.2, 129.4, 128.0, 127.9, 124.9, 124.5, 123.5, 112.4, 48.4, 31.6, 29.9, 26.9, 22.8, 14.2. m/z[M+H]$^+$ calcd for C$_{46}$H$_{47}$B$_2$N$_2$S$_4$ 777.2803; HR-ESI observed 777.2797.

Synthesis of 6b and 6d

A mixture of **5-1** and **5-2** (0.20 g), formed the last step, and phenylboronic acid (0.13 g, 1.04 mmol) were charged in a Schlenk flask. After adding 15 ml toluene, 5 ml ethanol, 5 ml Cs$_2$CO$_3$ aqueous solution (2M), the resulting mixture was degassed for 30 min. Pd(PPh$_3$)$_4$ (0.030 g, 0.026 mmol) was added, then heated to 80 °C and stirred overnight. The resulting mixture was poured into brine and extracted by dichloromethane for several times. The combined organic phase was dried over MgSO$_4$, filtered. After the solvent was evaporated, the crude product was purified by chromatography on silica gel (CH$_2$Cl$_2$: petroleum ether = 1:10-1:6) to give product **6b** in 15% yield (0.028 g, 0.041 mmol) and **6d** in 35% yield (0.073 g, 0.095 mmol), respectively.

For **6b**: ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 8.22 (s, 1H), 8.20 (s, 1H), 7.42 (s, 1H), 7.36 (d, J = 2.4 Hz, 1H), 7.25 (d, J = 5.0 Hz, 1H), 4.25 (dd, J = 15.8, 10.6 Hz, 4H), 0.90 (q, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm):150.5, 149.9, 143.1, 141.3, 134.5, 134.0, 133.9, 133.4, 132.3, 132.2, 132.1, 132.0, 131.0, 128.9, 128.7, 128.6, 126.4, 124.0, 123.8, 123.6, 112.7, 112.5, 48.5, 48.4, 31.6, 31.5, 30.1, 30.0, 26.9, 22.8, 22.7, 14.2, 14.1. m/z[M+H]$^+$ calcd for C$_{44}$H$_{47}$B$_2$N$_2$S$_2$ 689.3361; HR-ESI observed 689.3348.

For **6d**: ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 8.20 (s, 1H), 7.71 – 7.62 (m, 4H), 7.55 – 7.46 (m, 3H), 7.42 (s, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 4.30 (t, *J* = 7.7Hz, 2H), 0.91 (t, *J* = 7.0 Hz, 3H).^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 149.9, 143.2, 141.9, 141.2, 134.5, 134.1, 132.3, 129.0, 127.9, 127.8, 126.5, 123.7, 112.5, 48.5,31.6,30.1,26.9, 22.8, 14.2. m/z[M+H]$^+$ calcd for C$_{50}$H$_{51}$B$_2$N$_2$S$_2$ 765.3674; HR-ESI observed 765.3647.

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