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Band gap tunable for near-infrared absorbing chromophores with multi-triphenylamine and tris (thieno)hexaazatriphenylenes acceptors

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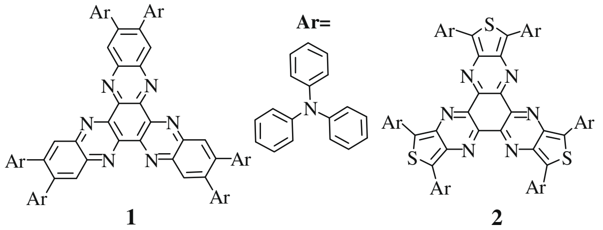
ABSTRACT

Two disk-like D–A type chromophores with multi-triphenylamine donors and hexaazatriphenylenes acceptors were synthesized and fully characterized by ^{1}H and ^{13}C NMR, elemental analysis and mass spectrometry. The effects of the hexaazatriphenylene on the optical and electrochemical properties and band gap of the chromophores were investigated. As the hexaazatriphenylene core fused with three thiophene rings, the band gaps of the compounds could be tuned from 1.65 eV to 1.15 eV. The π–π^* absorption peak and charge-transfer absorption peak of the hexaazatriphenylene compounds were red shifted from visible spectrum region (393 and 530 nm) to near-infrared spectrum region (542 and 756 nm). In addition, due to an increase in the π electronic coupling between electron donor and electron acceptor, the extinction coefficient (charge-transfer absorption) of the hexaazatriphenylene compound decreases 85% from 3.4×10^4 mol^{-1} dm^{-3} cm^{-1} to 0.5×10^4 mol^{-1} dm^{-3} cm^{-1}.

There is a continuing interest in low band gap organic materials due to their advanced electronic and electro-optic properties.[1] The main principles for constructing low band-gap polymers include tailoring the aromatic/quinoid character of a conjugated system, its rigidification into a planar conformation and the alternation of π-donor and π-acceptor fragments in the polymer chain. Furthermore, much less is known about monomeric organic compounds with a low HOMO–LUMO gap, which can be engineered by linkage of an electron donor (introducing a high-lying HOMO) and an electron acceptor (introducing a low-lying LUMO) with a spacer unit which precludes mixing of HOMO and LUMO orbitals.[2] Thus, the donor–acceptor (D–A) type of chromophores are particularly of interest to us as potential NIR chromophores because their band gap levels can be readily tuned through a variety of donors and acceptors.[3] However, compared to the vast majority of known electron donor compounds, there is only a few electron acceptor molecules have been synthesized and studied.[4]

Recently, pyrazine has been used in the design and synthesis of electron acceptor materials, owing to its electron-deficient nature.[5–8] Our research group has studied a series of pyrazine-containing acene-type conjugated molecules, and some unique structure–property relationships have been reported.[9] Among the pyrazine compounds, the hexaazatriphenylene that contains three π-deficient pyrazine nuclei at its core has been investigated as electron acceptor materials.[10] Very recently, Wang and co-workers reported the synthesis and characterization of a new series of multi-armed disk-like D–A type of NIR chromophores having a large hexaazatriphenylene heterocyclic acceptor as a core.[11] The thieno[3,4-*b*]pyrazines appear to be an ideal candidate for band gap modulation, which could lower the band gap dramatically when incorporated into a polymer backbone.[12] Furthermore, the tris (thieno)hexaazatriphenylene compounds, bearing three fused thieno[3,4-*b*]pyrazines as core, show electron-accepting ability.[13] Here, we report two tunable band gaps of chromophores for near-infrared absorbing with multi-triphenylamine donors and tris (thieno)hexaazatriphenylenes acceptors (Scheme 1).

The synthetic approach of compound **2** is outlined in Scheme 2.[14,15] Stille coupling between 2,5-dibromo-3,4-dinitrothiophene and tributyl[4-(*N*,*N*-diphenylamino)phenyl]stannane gave the intermediate **5**, which was reduced with SnCl$_2$ in the presence of HCl to afford diamine **6** in a yield of 80%. Tricondensed of the hexaketocyclohexane with precursor **6** in acetic acid gave raw



Scheme 1.

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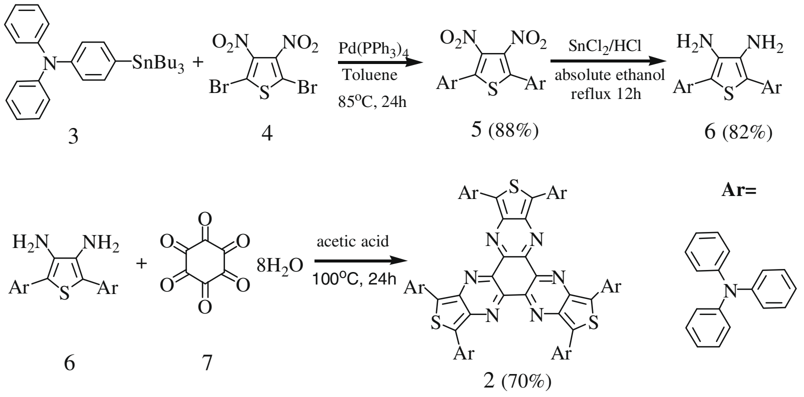

Scheme 2. Synthetic sequence of hexaazatriphenylene compound.

products. After purification by silica gel column chromatography, pure compound **2** was obtained in good yield of 70%. However, both hexaketocyclohexane and precursor **6** are air sensitive, they have to be freshly prepared. Otherwise, the yield of the condensation products drops significantly. Structures of compounds **2** and **1** were confirmed by NMR spectra, elemental analysis and mass spectra. Thermogravimetric analysis (TGA) performed under nitrogen revealed that these compounds were thermally stable with weight loss temperature beyond 400 °C.

The electrochemical properties of compounds **1** and **2** in CH_2Cl_2 were studied in a three-electrode electrochemical cell with Bu_4NClO_4 (0.1 M) electrolyte and Ag/AgCl reference electrode. The corresponding data are collected in Table 1. Figure 1 shows the cyclic voltammograms of compounds **1** and **2**. On cathodic scanning, compound **1** exhibits one reversible reduction wave at −0.70 V versus Ag/AgCl and the second quasi-reversible reduction wave at −1.06 V. Compounds **2** also exhibit two reduction waves. The first reduction wave of compound **2** is shifted by 290 mV to more positive potential compared to that of compound **1**, suggesting the enhanced electron affinity. Replaced three benzene rings in the hexaazatrinaphthylene by three electron-rich thiophene rings, compound **2** has three fused thieno[3,4-*b*]pyrazines, which is a polarized species and lowers the reduction potentials dramatically. Scanning from 0 to 1.6 V, compounds **1** and **2** show reversible multi-electron oxidation wave at 0.95 V and 0.74, respectively. Compared to compound **1,** the oxidation potential of compound **2** is shifted by 210 mV to more negative potential. It attributes to the conjugation between the aryl substituents and the hexaazatriphenylene core. The dihedral angle of 1,2-diaryl-benzene is usually larger than the dihedral angle of 1,2-diaryl-thiophene.[16,17] It is very interesting that electron-rich thiophene rings fused with hexaazatriphenylene can improve reduction potentials, and reduce oxidation potentials of the donor–acceptor type chromophores.

The lowest unoccupied molecular orbital (LUMO), the highest occupied molecular orbital (HOMO) and band gap (Eg) levels of these compounds were determined from their electrochemical data and their absorption data. The LUMO and HOMO were estimated from the onset reduction potentials and the onset oxidation potentials, respectively. The LUMO, HOMO and Eg levels of compounds **1** are −3.70, −5.35 and 1.65 eV, respectively. Fused three electron-rich thiophene rings with hexaazatrinaphthylene, the LUMO, HOMO and Eg levels of compound **2** are shifted to −3.99, −5.14 and 1.15 eV. In comparison, compound **2** has relatively lower LUMO, higher HOMO and small band gap.

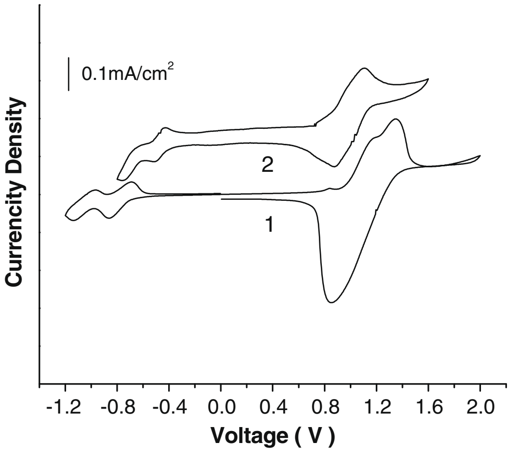

Figure 1. Cyclic voltammograms of compounds **1** and **2** were performed with a three-electrode cell in 5.0×10^{-4} mol/L dichloromethane solution with 0.1 M tetrabutylammoniumperchlorate at a scan rate of 100 mV/s. A glass carbon disk (2-mm diameter) was used as a working electrode with a Pt wire as the counter electrode and an Ag/AgCl electrode as the reference electrode.

The absorption of compound **1** and **2** was recorded in dichloromethane (Fig. 2). The absorption bands of compound **1** with peak at 393 nm are attributed to the hexaazatriphenylene core π–π* transition, while the absorption bands with peak at 530 nm are attributed to the charge-transfer absorption involving the electronic transition from the donor moieties (triphenylamine) to the

Table 1
Optical and electrochemical properties and band gap data of hexaazatriphenylene compounds

Compound	λ_{abs} (ε/10^{-4}[mol/L cm]) (nm)	(nm)	E^1_{gap} [a] (eV)	E^{ox} (V)	HOMO[b] (eV)	E^{red} (V) E^1 (V)	E^2 (V)	LUMO[c] (eV)	E^2_{gap} [d] (eV)
1	392 (3.93)	530 (3.40)	2.05	0.95	−5.35	−0.70	−1.06	−3.70	1.65
2	542 (2.40)	756 (0.50)	1.31	0.74	−5.14	−0.41	−0.65	−3.99	1.15

[a] $E^1_{gap} = 1240/\lambda^{abs}_{onset}$.
[b] HOMO = −(4.40 + E^{ox}).
[c] LUMO = −(4.40 + E^{re}).
[d] $E^2_{gap} = E^{ox} - E^{re}$.

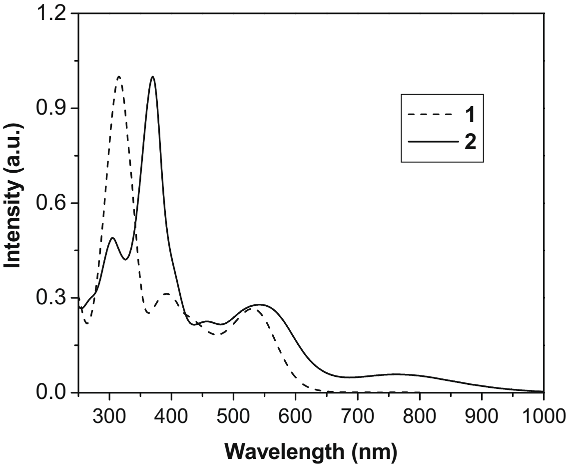

Figure 2. Absorption spectra of compounds **1** and **2** in dichloromethane solution with a concentration of 10^{-5} mol/L.

electron-deficient hexaazatriphenylene core. Compared with compound **1**, the π–π^* transition and the charge-transfer absorption of compound **2** are red shifted to 542 nm and 756 nm, respectively. The CT bands of compound **2** appear at near-infrared wavelengths (756 nm), further indicating a greater electron-accepting ability of the core of compound **2**. Replaced three benzene rings in the hexaazatrinaphthylene by three electron-rich thiophene rings, the extinction coefficient (charge-transfer absorption) of the hexaazatriphenylene compounds decreases 85% from 3.4×10^4 mol^{-1} dm^{-3} cm^{-1} to 0.5×10^4 mol^{-1} dm^{-3} cm^{-1}. This indicates that the π electronic coupling between electron donor and electron acceptor is enhanced, but charge-transfer characterization is reduced.[18]

In summary, the two chromophores with multi-triphenylamine donors and hexaazatriphenylenes acceptors have been successfully designed and synthesized. The energy band of these two chromophores has been investigated. The data indicate that the fused electron-rich thiophene is a good building block for modulate band gap of the D–A type chromophores. The disk-like D–A type compound **2** has relatively lower LUMO, higher HOMO, smaller band gap than compound **1**, corresponding to charge-transfer absorption red shifted to near-infrared spectrum band.

Acknowledgements

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15. *Compound* **2**. To a mixture of hexaketocyclohexane (0.156 g, 0.5 mmol) and the diamine **6** (1.201 g, 2 mmol) in acetic acid (60 ml) was heated at 100 °C for 24 h under nitrogen atmosphere. After the reaction mixture was cooled to room temperature, it was poured into water (100 ml) and extracted with dichloromethane (30 ml × 3). The organic layer washed with saturated aqueous sodium hydrogen carbonate solution (100 ml × 2) and brine (100 ml × 2), dried over anhydrous Na_2SO_4 and evaporated in vacuo to dryness. The residue was absorbed on silica gel and purified by column chromatography eluting with a 2:1 petroleum ether/dichloromethane mixture to yield blank solid 0.65 g (70%). ^{1}H NMR (CDCl3, 300 MHz): δ 8.40 (d, 12H, J = 8.6), 7.20 (t, 24H, J = 7.7), 7.13 (d, 12H, J = 8.7 Hz), 7.01–6.89 (m, 36H), ^{13}C NMR (CDCl3, 75 MHz): δ 197.31, 143.52, 132.91, 131.95, 131.68, 131.14, 129.73, 121.44, 118.25, 113.77. Elemental Anal. Calcd for $C_{126}H_{84}N_{12}S_3$: C, 81.26; H, 4.55; N, 9.03; S, 5.17. Found: C, 81.05; H, 4.50; N, 9.35. MALDI-TOF: calcd MW 1860.6, found 1861.8.
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