Starburst substituted hexaazatriphenylene compounds: synthesis, photophysical and electrochemical properties

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ARTICLE INFO

ABSTRACT

Starburst-substituted hexaazatriphenylene compounds have been designed and synthesized by introducing various peripheral aryl substituents to the central heterocyclic core. The effects of various substituent groups on the photophysical and electrochemical properties of the substituted hexaazatriphenylene have been investigated. Significant red-shifts of the absorption peak (from 413 nm to 530 nm) and emission peak (from 432 nm to 700 nm) were observed when the electron-donating ability of the aryl substituents was increased, corresponding to a decrease in the band gap from 2.90 eV to 2.05 eV. Introducing bulky substituents with weak electron-donating ability enhances the fluorescence quantum yield from 23% to 87%. In contrast, incorporating aryl substituents with strong electron-donating ability decreases the fluorescence quantum yield. Also, due to the extended conjugation between the aryl substituents and the hexaazatriphenylene core, the reduction potentials of the compounds were reduced and the LUMO levels were thus increased.

Recently, there has been a growing interest in organic semiconductors due to their potential applications in electronic and optoelectronic devices. The vast majority of synthesis and structure-property relationship studies in this field has been devoted to organic semiconductors having p-type (electron donor, hole transport) properties.[1,2] N-type (electron acceptor, electron transport) organic semiconductors are rather rare compared to p-type semiconductors, and only a limited number of molecular building blocks have been synthesized, such as fluorinated compounds,[3,4] heteroaromatic ring compounds,[5,6] fullerene derivatives,[7] naphthalene and perylene diimide.[8] Recently, pyrazine has been used in the design and synthesis of N-type materials, owing to its electron-deficient nature.[9,10] Our research group has studied the synthesis and characterization of a series of pyrazine-containing acene-type conjugated molecules, and some unique structure–property relationships have been reported.[11] Among the pyrazine compounds, the hexaazatriphenylene that contains three π-deficient pyrazine nuclei at its core has been investigated as N-type materials.[12] However, the synthesis of hexaazatriphenylene compounds that are substituted with various functional groups still remains almost unexplored.[13] Considering the vast number of applications within the areas of electronics and optoelectronics,

bandgap engineering and optical/electrochemical studies of hexaazatriphenylene-based compounds are necessary.

Herein, we report the synthesis of hexaazatriphenylene compounds with peripheral aryl substituents. The corresponding optical properties (UV–vis and PL) and electrochemical properties (redox potentials and HOMO/LUMO levels) of these materials were also carefully investigated.

The synthetic approach of compounds **1a–f** is outlined in Scheme 1. The precursors **2b–f** were synthesized by the palladium-catalyzed Suzuki or Stille coupling reactions with good yield (75–85%).[14] Compounds **1a–f** were obtained by tricondensation of the hexaketocyclohexane with the aromatic diamines **2a–2f**, in acetic acid, with good yield (70–85%) and purity.[15] Unfortunately, the hexaketocyclohexane and precursors **2a–6a** are air-sensitive, therefore need to be freshly prepared. Otherwise, the yield of the condensation products will drop significantly.

To investigate the influence of aryl substituents on the optical and electrochemical properties of hexaazatriphenylene, we synthesized compound **1a** as a reference compound by the reaction of 4,5-dimethyl-o-phenylenediamine with hexaketocyclohexane in acetic acid.

The photophysical properties of the hexaazatriphenylenes **1a–f** are summarized in Table 1. The UV–vis spectrum of compound **1a** shows an absorption peak at 413 nm with a strong vibronic fine structure (Fig. 1), which is attributed to the hexaazatriphenylene core π–π* transition. By increasing the conjugation at the hexaazatriphenylene perimeter, the longest absorption bands assigned
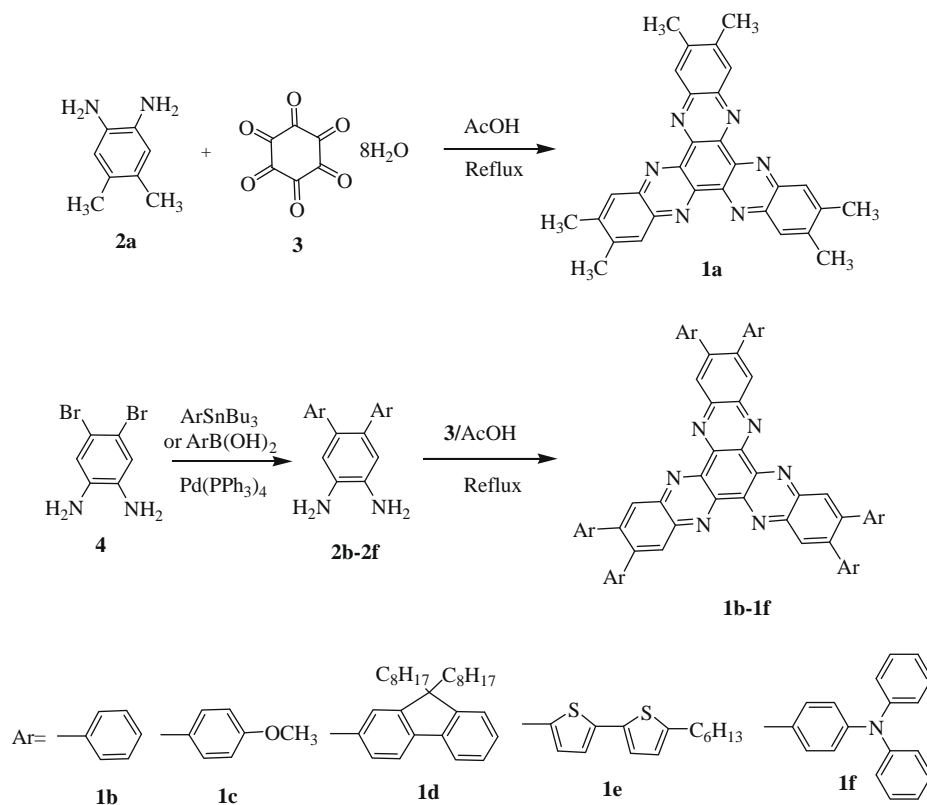
Scheme 1. Synthetic sequence of hexaazatriphenylene compounds.

Table 1
Photophysical properties of hexaazatriphenylene compounds

Compound	λ_{max}^{abs} (nm)	ε (10^4 mol^{-1} dm^{-3} cm^{-1})	λ_{max}^{fl} (nm)	φ_f (%)
1a	413	3.06	432	23[a]
1b	435	3.88	466	74[b]
1c	460	2.11	543	81[b]
1d	479	3.49	552	87[b]
1e	526	2.05	689	0.3[c]
1f	530	0.97	700	0.8[c]

[a] Fluorescence quantum yield relation to 9,10-diphenylanthracene in ethanol (95%).
[b] Fluorescence quantum yield relation to Coumarin 6 in acetonitile (63%).
[c] Fluorescence quantum yield relation to Nile red in 1,4-dioxane (68%).

to the electronic π–π^* transition undergo a bathochromic shift of the maximum absorption peak. For example, the λ_{max}^{abs} (nm) for compound **1a** is 413 nm, while for compounds **1b** (phenyl substituent), **1c** (4-methoxyphenyl substituent) and **1d** (fluorene substituent) the λ_{max}^{abs} (nm) is 435 nm, 460 nm and 479 nm, respectively. The introduction of bulky aryl substituents on the hexaazatriphenylene core produces line broadening in the absorption spectrum and less pronounced vibronic fine structure (Fig. 1). The spectral-broadening phenomena have been reported elsewhere for a twisted perylene bisimide core.[16]
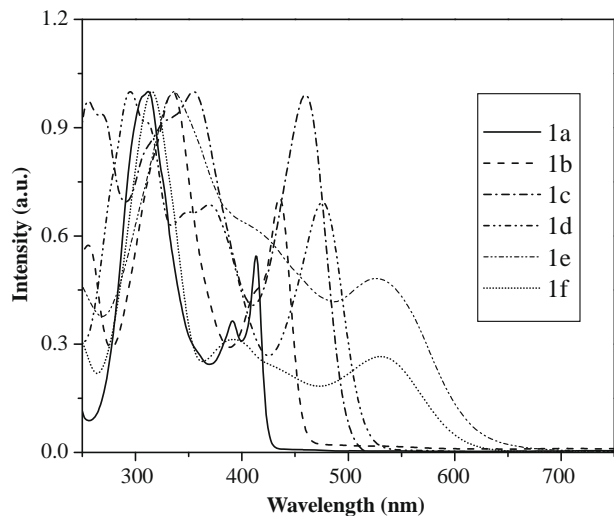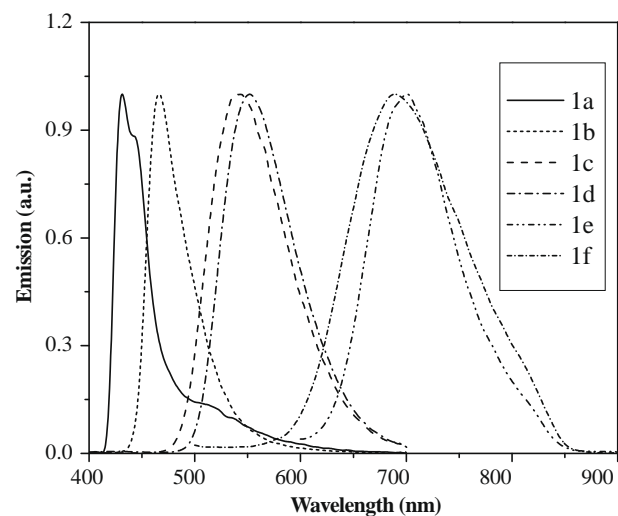

Figure 1. UV–vis absorption spectra of compound **1a–1f** in dichloromethane.

Figure 2. Photoluminescence spectra of compound **1a–1f** in dichloromethane.

Table 2
Oxidation and reduction $E_{1/2}$ potentials[a] for hexaazatriphenylene compounds

Compd	Oxidation $E_{1/2}$ (V)[a]	Reduction $E_{1/2}$ (V)[a]		LUMO/HOMO[e] (eV)	Band gap	
	1st	1st	2nd		E_g^e (eV)[c]	E_g^o (eV)[d]
1a	–	−0.96	−1.25	−3.45/−6.35[f]	–	2.90
1b	–	−0.81	−1.21	−3.62/−6.29[f]	–	2.67
1c	–	−0.82	−1.28	−3.57/−6.03[f]	–	2.48
1d	–	−0.81	−1.18	−3.60/−5.99[f]	–	2.39
1e	1.65[b]	−0.79	−1.04	−3.66/−5.66[f]	2.35	2.00
1f	0.96	−0.77	−1.06	−3.63/−5.28	1.61	2.05

[a] Potentials versus Ag/AgCl.
[b] Irreversible.
[c] Electrochemical band gap $E_g^e = E_{onset}^{ox} - E_{onset}^{re}$.
[d] Optical band gap $E_g^o = 1240/\lambda_{onset}^{abs}$.
[e] HOMO and LUMO energy were calculated with reference to ferrocene (4.8 eV) LUMO = $-(4.80 + E_{onset}^{re})$; HOMO = $-(4.80 + E_{onset}^{ox})$.
[f] HOMO = LUMO $- E_g^o$.

Compared to compounds **1a–1d**, dithiophene and triphenyl-amine-substituted hexaazatriphenylene have quite different spectral behavior (Fig. 1). The absorption spectra of compounds **1e** and **1f** show a new absorption band, with peaks located at 526 nm and 530 nm, respectively. The new absorption band is tentatively attributed to the charge-transfer absorption involving the electronic transition from the donor moieties (dithiophene or triphenylamine) to the electron-deficient hexaazatriphenylene core.[17] Furthermore, introduction of aryl substituents leads to a reduction in the HOMO–LUMO gap (from 2.90 eV to 2.05 eV, derived from the absorption spectrum).

The fluorescence emission spectra of compounds **1a–1f** in dichloromethane are presented in Figure 2. With an increase in the conjugated strength and electron-donor strength of aryl substituents, their emission wavelengths undergo red-shift. Compared to compound **1a**, which contains only peripheral methyl substituents, when the conjugation is extended by the addition of aryl substituents the emission wavelength is red-shifted from 432 nm (compound **1a**) to 700 nm (compound **1f**). The introduction of bulky conjugated substituents has a beneficial effect on the fluorescence quantum efficiencies, and fluorescence quantum yields increased from 23% (compound **1a**) to 87% (compound **1d**). However, compared with bulky conjugated substituents, aryl substituents with strong electron-donating ability have a different effect on the fluorescence quantum yield. When the electron-donating ability of these aryl substituents increased, for example, with respect to compounds **1e** and **1f**, the fluorescence quantum yields drop dramatically (Table 1). This fluorescence quenching might be due to the efficient intramolecular electron transfer between the electron donor (dithiophene and triphenylamine) and the electron acceptor (hexaazatriphenylene core).

The redox properties of these compounds were studied by cyclic voltammetry (CV), and the results are shown in Table 2. The CV scan for compound **1a** with anodic scanning from 0 to 2 V shows no peaks. On cathodic scanning, the CV scan of compound **1a** exhibits two reversible one-electron reduction waves. This indicates that the hexaazatriphenylene core has electron-accepting properties. By introducing aryl substituents to the hexaazatriphenylene core, the reduction potentials of compound **1b–d** are compared to those of compound **1a**, in which a difference of −0.15 V is observed. The increase in reduction potentials could attribute to the conjugation between the aryl substituents and the hexaazatriphenylene core. The anion radicals are more stable in the π-extended conjugation moieties.

Reduction potentials of compounds **1e** and **1f** were not further enhanced by strong electron-donor substituents on the hexaazatriphenylene core (Table 2). On anodic scanning, compound **1e** exhibits an irreversible one-electron oxidation wave at 1.65 V and compound **1f** exhibits a reversible multi-electron oxidation wave at 0.96 V.

The lowest unoccupied molecular orbital (LUMO) was estimated from the onset reduction potentials by comparison to ferrocene.[18] The highest occupied molecular orbital (HOMO) of these hexaazatriphenylene compounds was estimated from the onset oxidation potentials (compound **1f**) or from the equation (LUMO = HOMO $- E_g^o$, for compounds **1a–e**). When the electron-donating ability of these aryl substituents increased, HOMO levels of compounds **1b–f** were enhanced from −6.29 eV (compound **1b**) to −5.28 eV (compound **1f**). This indicates that the LUMOs lie on the hexaazatriphenylene core and the HOMOs lie on the aryl substituents.

In summary, starburst-substituted hexaazatriphenylene compounds have been synthesized in good yields of 70–85%. The photophysical properties of multi-aryl-substituted hexaazatriphenylene are strongly related to the electron-donating ability of these aryl substituents. Fluorescence enhancement and fluorescence quenching can be controlled by adjusting the electron-donating ability of the aryl substituents. The electrochemical properties of these compounds were investigated by cyclic voltammetry at room temperature. By incorporating aryl substituents to the peripheries of the hexaazatriphenylene core, the reduction potentials were improved due to the extended conjugation between the aryl substituents and the hexaazatriphenylene core.

Acknowledgements

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14. *General procedure for synthesis of precursor* **2b**, **2c**, **2d** *and* **2f**: To a mixture of 4,5-dibromo-*o*-phenylenediamine (2 mmol, 532 mg) and corresponding boronic acid (5 mmol) and Pd(PPh₃)₄ (0.05 mmol, 58 mg) in toluene (50 mL), 2 M K₂CO₃ solution (15 mL) was added under nitrogen atmosphere. The resulting mixture was heated at 85 °C for 24 h. The reaction mixture was poured into water and extracted with dichloromethane (20 mL × 3). The organic layer was washed with brine (50 mL), dried over Na₂SO₄ and evaporated in vacuo to dryness. The crude product was purified by column chromatography on silica gel, eluting with a 2:1 petroleum ether/ethyl acetate mixture.
Compound **2b**. White solid (yield: 83%); ¹H NMR (CDCl₃): δ 7.22–7.17 (m, 6H), 7.13 (d, J = 7.6 Hz, 4H), 6.84 (s, 2H), 3.52 (br, 4H).Compound **2c**. White solid (yield: 80%); ¹H NMR (CDCl₃) δ 7.44 (d, J = 9.0 Hz, 4H), 6.96 (s, 2H), 6.84 (d, J = 9.0 Hz, 4H), 3.43 (br, 4H).
Compound **2d**. White solid (yield: 78%); ¹H NMR (CDCl₃) δ 7.63 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H), 7.31–7.29 (m, 2H), 7.23–7.21 (m, 4H), 7.03–7.01 (m, 4H), 6.66 (s, 2H), 4.76 (br, 4H), 1.83–1.67 (m, 8H), 1.18–0.97 (m, 48H), 0.78 (t, J = 6.8 Hz, 12H).
Compound **2f**. Yellow solid (yield: 75%); ¹H NMR (CDCl₃) δ 7.39 (d, J = 7.3 Hz, 4H), 7.35–7.25 (m, 6H), 7.14–7.09 (m, 12H), 7.07 (d, J = 7.4 Hz, 4H), 7.00 (d, J = 7.2 Hz, 4H), 6.97 (s, 2H), 3.43 (br, 4H).
Compound **2e**. To a mixture of 4,5-dibromo-*o*-phenylenediamine (2 mmol, 532 mg), corresponding tributyl-stannyl (6 mmol), and Pd(PPh₃)₄ (0.05 mmol, 58 mg), toluene (60 mL) was added under nitrogen atmosphere. The resulting

mixture was heated at 85 °C for 24 h. The reaction mixture was brought to room temperature. The cooled solution was added to methanol (40 mL) to give a yellow precipitate. The crude product was purified by column chromatography on silica gel, eluting with a 2:1 petroleum ether/ethyl acetate mixture. Yellow solid (yield: 86%); ¹H NMR (CDCl₃): δ 7.04 (m, 6H), 6.85 (s, 2H), 6.71 (d, J = 7.3 Hz, 2H), 3.43 (br, 4H), 2.81 (t, J = 7.6 Hz, 4H), 1.73 (t, J = 7.4 Hz, 4H), 1.42–1.33 (m, 12H), 0.91(t, J = 6.5 Hz, 6H).
15. *General procedure for the cyclization of hexaazatriphenylene*: A mixture of hexaketocyclohexane(1 mmol) and the corresponding diamine (4 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 was washed with saturated aqueous sodium hydrogen carbonate solution (100 mL × 2) and brine (100 mL × 2), dried over anhydrous Na₂SO₄ 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.
Compound **1a**. Yellow solid (yield: 85%), ¹H NMR (DMSO-d₆): δ 8.13 (s, 6H), 3.34 (s, 18H). Elemental Anal. Calcd for C₃₀H₂₄N₆: C, 76.90; H, 5.16; N, 17.94. Found: C, 76.81; H, 5.01; N, 18.33. MALDI-TOF: calcd: 468.2, found: 469.0.
Compound **1b**. Yellow solid (yield: 82%), ¹H NMR (CDCl₃): δ 8.81 (s, 6H), 7.63 (s, 30H). ¹³C NMR (CDCl₃): δ 145.96, 143.89, 142.93, 139.85, 131.50, 129.98, 128.25, 127.75 Elemental Anal. Calcd for C₆₀H₃₆N₆: C, 85.69; H, 4.31; N, 9.99. Found: C, 85.43; H, 4.41; N, 10.15. MALDI-TOF: calcd: 840.3, found: 840.5.
Compound **1c**. Yellow solid (yield: 78%), ¹H NMR (CDCl₃): δ 9.07 (s, 6H), 7.30 (d, J = 8.7 Hz, 12H), 6.90 (d, J = 8.8 Hz, 12H). ¹³C NMR (CDCl₃): δ 159.31, 145.50, 143.61, 142.83, 132.43, 131.19, 131.03, 113.80, 55.27 Elemental Anal. Calcd for C₆₆H₄₈N₆O₆: C, 77.63; H, 4.74; N, 8.23. Found: C, 77.38; H, 4.68; N, 8.41. MALDI-TOF: calcd: 1020.4, found: 1020.9.
Compound **1d**. Orange solid (yield: 74%), ¹H NMR (CDCl₃): δ 8.93 (s, 6H), 7.69, 7.64 (m, 12H), 7.50 (s, 6H), 7.43 (d, J = 7.8 Hz, 6H), 7.35 7.34 (m, 18H), 1.96 (t, J = 7.7 Hz, 24H), 1.25, 1.07 (m, 48H), 0.87 (t, J = 6.7 Hz, 18H). ¹³C NMR (CDCl₃): δ 150.97, 146.43, 143.95, 142.99, 140.97, 140.60, 138.82, 131.77, 128.99, 127.34, 126.82, 124.45, 122.81, 120.00, 119.51, 55.22, 40.59, 31.89, 30.09, 29.45, 29.31, 23.96, 22.66, 14.10. Elemental Anal. Calcd for C₁₉₈H₂₅₂N₆: C, 87.55; H, 9.35; N, 3.09. Found: C, 87.29; H, 9.03; N, 3.29. MALDI-TOF: calcd: 2174.0, found: 2175.1.
Compound **1e**. Black solid (yield: 70%), ¹H NMR (CDCl₃): δ 8.79 (s, 6H), 7.05, 7.04 (m, 18H), 6.71 (d, J = 6.4 Hz, 6H), 2.84 (t, J = 7.5 Hz, 12H), 1.751.65 (m, 12H), 1.43, 1.34 (m, 36H), 0.93 (t, J = 6.3 Hz, 18H). ¹³C NMR (CDCl₃): δ 146.17, 143.95, 142.89, 140.45, 138.58, 138.20, 134.32, 131.45, 129.73, 124.98, 124.05, 123.50, 31.61, 31.23, 30.26, 28.79, 22.61, 14.10. Elemental Anal. Calcd for C₁₀₈H₁₀₈N₆S₁₂: C, 69.19; H, 5.81; N, 4.48; S, 20.52. Found: C, 69.32; H, 5.73; N, 4.63. MALDI-TOF: calcd: 1872.5, found: 1874.1.
Compound **1f**. Red solid (yield: 72%), ¹H NMR (CDCl₃): δ 8.74 (s, 6H), 7.327.22 (m, 36H) 7.18 (d, J = 6.9 Hz, 24H), 7.09 (t, J = 7.8 Hz, 24H). ¹³C NMR (CDCl₃): δ 147.50, 145.65, 143.66, 142.94, 133.56, 130.85, 130.60, 129.40, 124.89, 123.33, 122.32 Elemental Anal. Calcd for C₁₃₂H₉₀N₁₂: C, 85.97; H, 4.92; N, 9.11. Found: C, 85.72; H, 5.13; N, 9.32. MALDI-TOF: calcd: 1844.2, found: 1845.0.
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