Synthesis of non-centrosymmetric donor–acceptor–donor hexaazatriphenylene (HAT) derivatives

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Abstract—A general synthetic strategy toward unsymmetrical hexaazatriphenylene (HAT) derivatives has been developed. The versatility of the strategy is used to synthesize a family of ambipolar donor–acceptor–donor (D–A–D) chromophores, which exhibit broad intramolecular charge transfer (ICT) bands in their solution UV–vis spectra.
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Large two-dimensional molecules with extended π-systems such as polycyclic aromatic hydrocarbons (PAHs) are the subject of increasing interest as a consequence of their technological applications.[1] Among them, nitrogen containing PAHs are of particular interest since such heteroatoms influence the electronic nature without modifying the structure. In this regard, hexaazatriphenylene (HAT) derivatives have recently attracted attention as materials for organic electronic applications because of their easy synthetic accessibility, diversity in peripheral functionality, electron deficiency, and coordination properties. Thus, these compounds can, depending on the choice of substituent, have a variety of applications, including discotic liquid-crystals,[2] *n*-type semiconducting,[3] and magnetic materials[4] or fluorescent dyes.[5] Additionally, the ligand HAT is one of the most useful multifunctional ligands because of their π-complexation ability affording not only various self-assembled frameworks but also unique electronic structures.[6] HAT and its derivatives have been studied as attractive supramolecular building blocks because these planar ligands provide a symmetrical array of three chelating sites to the metals ions, which are useful for the construction of the metal-assembled system.

Two main synthetic approaches to symmetrical HAT and its derivatives have been reported. One is the reaction of hexaaminobenzene with 1,2-diketones[7] and the other is between hexaketocyclohexane and 1,2-diaminoethylene derivatives.[8] Both routes afford a variety of symmetrical HAT derivatives but, whereas the first route affords hexaazatriphenylene with different aryl groups,[9] only the second route is relevant to synthesize HAT derivatives with electron-withdrawing groups,[10] analogous with more extensive π-systems[11] and fused systems.[12]

Whereas HATs carrying six identical substituents are well known, the synthesis of unsymmetrical HAT derivatives is still relatively unexplored. Recently, a HAT derivative with the presence of alternating donor–acceptor groups as their six peripheral substituents with NLO properties was reported because of their large molecular hyperpolarizability[13] and Fages et al. have reported the synthesis of non-symmetrical bismacrocyclic HAT derivatives by condensation of linear trisbenzil precursors with hexaaminobenzene.[14] However, the synthesis of non-centrosymmetric HAT derivatives in the HAT series is still quite rare due to the lack of practical synthetic methods.

In this Letter we report a straightforward synthesis of non-centrosymmetric HAT derivatives (Scheme 1, **3** and **4**) bearing functionalities, which pave the way for the synthesis of a variety of disubstituted HAT derivatives. 9,10-Diamino-1,4,5,8-tetraazaphenanthrene (**2**)[15] was prepared by the reaction of the very reactive hexaaminobenzene (**1**)[16] with two equivalents of glyoxal.
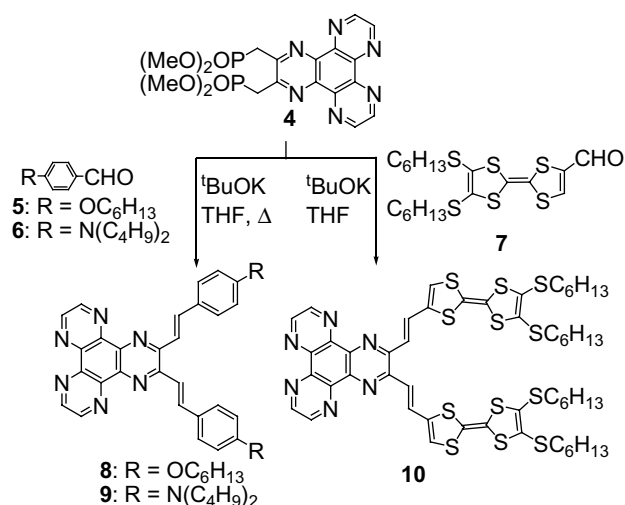
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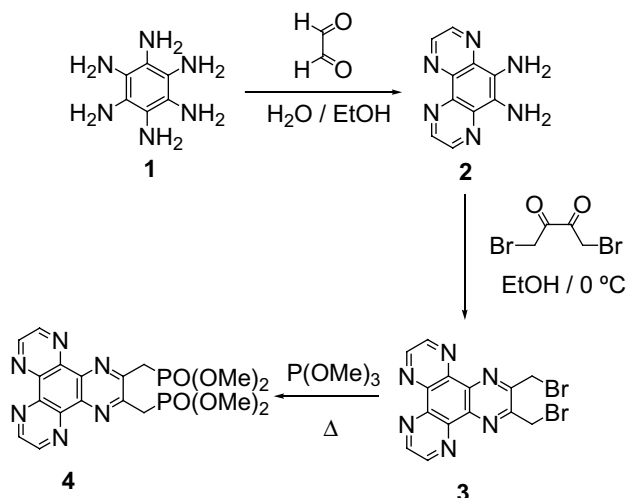
Scheme 1. Synthesis of intermediates **3** and **4**.

Further reaction of the diamino derivative **2** with 1,4-dibromo-2,3-butanedione afforded bis(bromomethyl)-hexaazatriphenylene (**3**). Finally, Arbuzov reaction of **3** with methyl phosphonate yielded hexaazatriphenylene **4** bearing two phosphonate functionalities. Both **3** and **4** are versatile building blocks, which may allow the synthesis of a variety of disubstituted HAT derivatives.

In order to explore the reactivity of bis(phosphonato methyl)hexaazatriphenylene (**4**) we have carried out Horner–Wadsworth–Emmons olefination reactions with different electron donor systems bearing aldehyde functionalities (Scheme 2, **5–7**). Thus, upon treatment of bis(phosphonato methyl)hexaazatriphenylene (**4**) with aldehydes **5–7** in refluxing dry THF, using potassium *tert*-butoxide as the base, the coresponding D–π–A–π–D systems **8–10** were obtained. The presence of alkyl chains on the peripheral donor moieties allows to obtain soluble materials, which can be appropriately characterized from the spectroscopic and electrochemical point of view.[17] High resolution ^{1}H NMR spectra reveal a trans configuration of the vinylene protons and thus confirm the stereoselectivity of the Horner–Wadsworth–Emmons reaction.

The investigation of the ambipolar character of the new systems **8–10** has been carried out by means of cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The electrochemical features of these derivatives were probed at room temperature in THF solutions using tetrabutylammonium hexafluorophosphate (TBAHPF) as the electrolyte and a platinum disk working electrode. All the potentials were measured relative to the internal standard ferrocene–ferricenium (Fc/Fc$^+$). In the negative potential regime, the characteristic three quasi-reversible waves of the hexaazatriphenylene derivatives[18] corresponding to the three consecutive reduction steps of the three pyrazine moieties of the hexaazatriphenylene were observed (Fig. 1).

It is worth mentioning that, upon introduction of the substituents in the HAT system, the first reduction potential of the HAT derivatives are less negative than in the unsubstituted HAT[19] despite the electron donor nature of the substituents. This can be explained as the result of the extension of conjugation in the substituted system, which stabilizes their LUMO. Interestingly, the less negative reduction potential within the series corresponds to the TTF derivative **10**. The non-aromatic character of TTF in the neutral state in comparison with the aromatic character of the hexyloxybenzene and dibutylaminobenzene moieties can justify the most efficient extension of the π-conjugated system in the TTF derivative and therefore the less negative reduction potential observed for **10**. Thus, the topologies and energies of the molecular orbitals have been studied by means of the DFT B3LYP/6-31G* model chemistry[20] showing that the LUMO of **8–10** is mainly localized on the HAT moiety but extends to the nearest atoms of the donor moieties across the vinylenic spacer as can be observed for the HAT–TTF$_2$ assembly **10** in Figure 2.

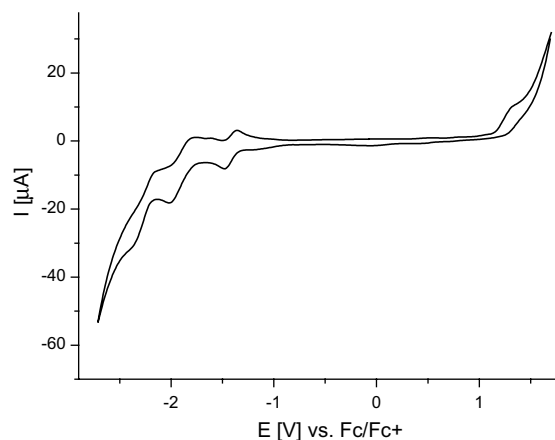**Scheme 2.** Synthesis of compounds **8**, **9**, and **10**.

Figure 1. Cyclic voltammogram of 2,3-bis-*trans*[2(4-hexyloxyphenyl-ene)-vinylene]hexaazatriphenylene (**8**) in tetrahydrofuran/tetrabutyl-ammonium hexafluorophosphate (TBAHPF) (0.1 M) at 20 °C, conc. 2×10^{-3} M, scan rate of 100 mV/s, Pt disk working electrode, Ag/Ag$^+$ reference electrode, potentials versus Fc/Fc+.
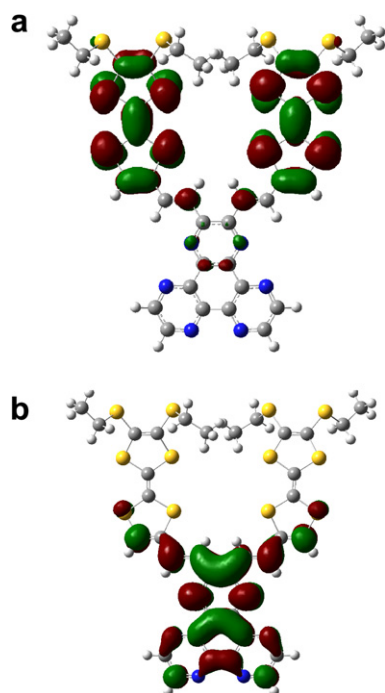
Figure 2. Molecular orbital diagrams of the (a) HOMO and (b) LUMO orbitals of the HAT–TTF$_2$ ensemble **10** (DFT B3LYP/6-31G*).

Figure 3. UV–vis absorption spectra of **8** (black solid), **9** (blue dashed), **10** (red dotted) and reference hexaazatriphenylene (green dashed-dotted) in dichloromethane.

Table 1. Redox potentials of HAT derivatives **8**–**10** determined by differential pulse voltammetry

Solvent	8	9	10
E_{red}^1 (V)	−1.40	−1.43	−1.22
E_{red}^2 (V)	−1.90	−1.92	−1.89
E_{red}^3 (V)	−2.29	−2.37	−2.50
E_{ox}^1 (V)	1.26	0.62	0.42
E_{ox}^2 (V)			0.74

Values recorded in tetrahydrofuran/tetrabutylammonium hexafluorophosphate (TBAHPF) (0.1 M) at 20 °C, concn 2×10^{-3} M, Pt disk working electrode, potentials versus Fc/Fc$^+$.

In the positive potential regime, the characteristic oxidation processes corresponding to the three different electron donor moieties were observed (Table 1).

Thus, irreversible oxidation waves were observed at 1.26 V for **8** and 0.62 V for **9** corresponding, respectively, to the oxidation of the hexyloxybenzene and dibutylaminobenzene moieties and indicating the stronger donor character of the dibutylaminobenezene moiety.[21] On the other hand, the two characteristic reversible oxidation waves of the tetrathiafulvalene moiety[22] can be observed for **10** ($E_{1/2,red}^1$: 0.45, $E_{1/2,red}^2$: 0.76). The less positive oxidation potentials observed for **10** are in agreement with the strongest donor nature of the tetrathiafulvalene moiety in comparison with the hexyloxy benzene and dibutylaminobenzene moiety. Electrochemical bandgaps of 2.51, 1.92, and 1.32 eV were determined for **8**, **9**, and **10**, respectively, based on the HOMO and LUMO energies derived from the electrochemical data
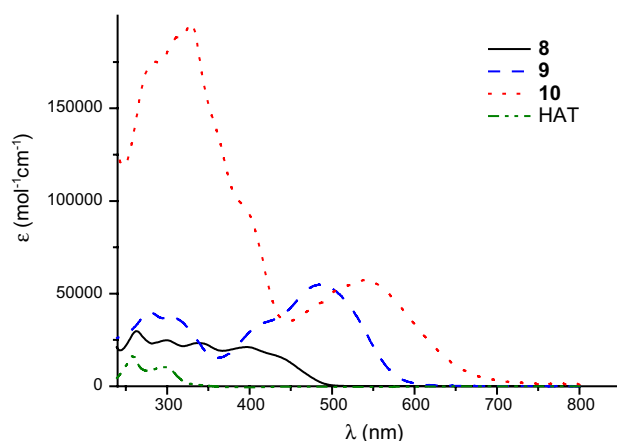
based on the assumption that the Fc/Fc$^+$ redox couple is 5.1 eV relative to vacuum.

The lowest energy absorption bands in the electronic spectra observed for compounds **8**–**10** are shown in Figure 3. Optical bandgaps of 2.53, 2.14, and 1.87 eV were determined for **8**, **9**, and **10** from the onset of the lowest energy absorption, which are in good agreement with those obtained from the electrochemical data.

The broad absorptions at low energies have a large intramolecular charge-transfer character as can be demonstrated by analyzing the electron density shift from the HOMO (localized mainly on the donor moiety) to the LUMO (localized mainly on the HAT moiety), which are the orbitals responsible for the transition (Fig. 2). Although the HOMOs of **8**–**10** are localized mainly on the donor moiety and the LUMOs mainly on the HAT system, there is a certain HOMO–LUMO overlap, which is a prerequisite to increase the probability of the charge transfer transition and suggests that these materials are good candidates to be investigated in non-linear optics.[23]

A red shift of the ICT band is observed when increasing the donor ability of the donor moiety. Thus, within the series, the tetrathiafulvalene group acts as the strongest donor, giving rise to the lowest energy ICT band for compound **10**. Also in agreement with the electrochemical data, the ICT band observed for the dibutylaminobenzene derivative **9** is red shifted in comparison with that observed for the hexyloxybenzene derivative **8**. Furthermore, all the ICT bands exhibit a solvatochromic behavior (Fig. 4).

Preliminary investigation of the emitting behavior of the new HAT derivatives shows that both **8** and **9** are strong fluorescent materials while no fluorescence was observed for **10** endowed with the strong electron donating TTF unit probably due to a more efficient intramolecular charge transfer. The emission maxima of **8** and **9** are solvent dependent. Thus, for derivative **8** the emission maximum shifts from 508 nm in cyclohexane to 513 nm in
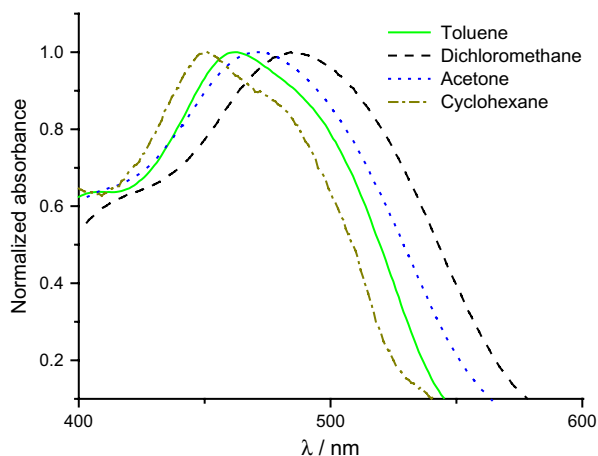
Figure 4. Solvatochromic behavior of the ICT band for **9**.

dichloromethane, which is in agreement with the previous observations of fluorescent solvatochromism in aryl-substituted hexaazatriphenylenes.[5a]

In conclusion, we have developed a synthetic route toward the preparation of the first non-centrosymmetric ambipolar hexaazatriphenylene–D$_2$ systems. Full spectroscopic and electrochemical characterization of the new D–A–D ensembles have been carried out confirming their ambipolar behavior and the presence of an intramolecular charge transfer band. Work is in progress in order to test the potential of these materials in non-linear optics.

Acknowledgments

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17. *Selected data for* **10**: ^{1}H NMR (200 MHz, CDCl$_3$). δ: 9.18 (d, 2H, J = 2 Hz), 9.16 (d, 2H, J = 2 Hz), 7.29 (d, 2H, J = 15 Hz), 6.87 (s, 2H), 6.74 (d, 2H, J = 15 Hz), 2.89 (t, 4H, J = 7 Hz), 2.82 (t, 4H, J = 7 Hz), 1.75–1.55 (m, 8H), 1.50–1.20 (m, 24H), 0.91 (t, 6H, J = 6 Hz), 0.86 (t, 6H, J = 6 Hz). ^{13}C NMR (50 MHz, CDCl$_3$) δ: 149.4, 146.7, 146.1, 142.3, 142.2, 139.7, 135.5, 130.5, 128.1, 127.8, 125.9, 123.5, 111.4, 110.4, 36.4, 36.3, 31.4, 31.3, 29.72, 29.70, 28.2, 22.55, 22.52, 14.05, 14.00. FT-IR (KBr) cm^{-1}: 3003, 2956, 2928, 1605, 1502, 1373, 942. MS (FAB, NBA) m/z: 1155 [M+H]$^+$. Elem. Anal. Calcd for C$_{52}$H$_{62}$N$_6$S$_{12}$: C, 54.03; H, 5.41; N, 7.27; S, 33.29. Found: C, 54.16; H, 5.23; N, 5.65; S, 32.98.
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