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Self-Assembling of n-Type Semiconductor Tri(phenanthrolino)hexaazatriphenylenes with a Large Aromatic Core

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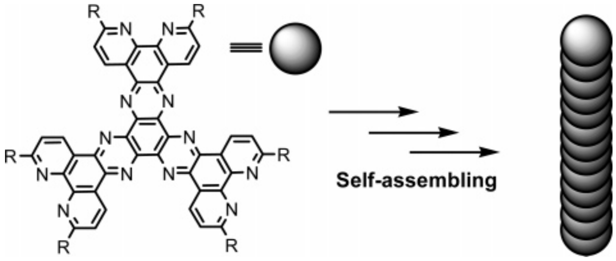
ABSTRACT



Large disk-shaped aromatic tri(phenanthrolino)hexaazatriphenylenes 5a, 5b, and 5c with six butyl, dodecyl, and 4-octylphenyl groups, respectively, were self-assembled both in solution and film state to form one-dimensional aggregates. Their n-type semiconducting nature was indicated from CV measurement, in which the first reduction potentials were evaluated at around –1.7 V (vs Fc/Fc$^+$) in dichloromethane.

n-Type semiconducting aromatic molecules have been of much interest in recent years in view of their application to electron-transporting materials in organic light-emitting diodes,[1] field-effect transistors,[2] and photovoltaics.[3] In the applications, the columnar-type π-stacked structure found in columnar liquid crystals[4] and self-assembled one-dimensional aggregates[5] is suitable for the efficient electron-transporting along the stacking direction. Such ordered supramolecular aggregates are more attractive candidates for electron-transporting materials than glassy-type amorphous aromatics with unfavorable positional and energy disorder.[6] Although large-sized self-assembling aromatics such as p-type semiconducting hexabenzocoronenes[7] are suitable as excellent carrier-transportors,[8] n-type self-assembling semiconductors are limited in small- and medium-sized aromatics.[9,10]

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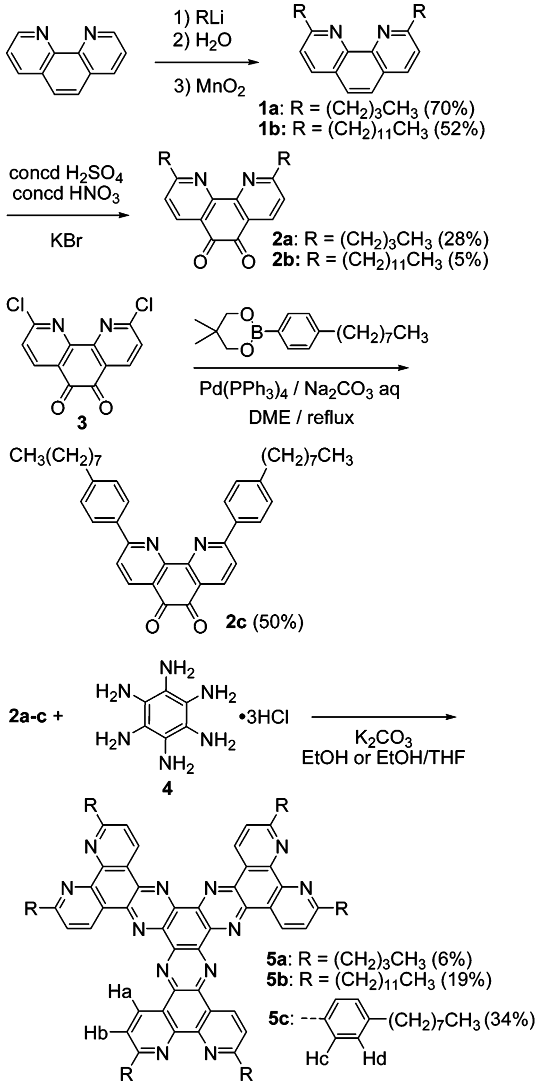
Recently, we found that n-type semiconducting hexaazatriphenylenes (HATs)[11] can be self-assembled both in solution and bulk state to form one-dimensional columnar-type aggregates.[12] This finding led us to design and prepare new n-type semiconducting large-sized aromatics based on the combination of the HAT core and other electron-deficient aromatics to improve both aggregation ability and electron affinity. A combination of the HAT core and three phenanthroline rings results in large n-type semiconductor tri(phenanthrolino)hexaazatriphenylene (TP-HAT),[13] which is composed of 13 fused six-membered rings as many as that of hexabenzocoronene.[7] Here, we report that TP-HAT derivatives provide high electron affinity as n-type semiconductor as well as strong self-assembling nature to form well-ordered one-dimensional aggregates.

TP-HATs **5a** and **5b** with six butyl and dodecyl groups, respectively, were prepared by condensation reactions of the corresponding 1,10-phenanthroline-5,6-diketones **2a** and **2b**, respectively, with hexaaminobenzene **4**[12] in refluxing ethanol in the presence of potassium carbonate (Scheme 1). In **5c** with 4-octylphenyl groups, the condensation reaction was performed in an ethanol/THF mixture system because of the poor solubility of **2c** in ethanol. The key synthetic intermediate diketones **2a** and **2b** were derived from 1,10-phenanthroline via 2,9-dialkyl derivatives **1a** and **1b**, respectively. Two alkyl groups (butyl in **1a** and dodecyl in **1b**) were introduced at the 2 and 9 positions of the phenanthroline ring by addition reaction of the corresponding alkyllithium with 1,10-phenanthroline followed by hydrolysis with water and oxidation with manganese oxide to give **1a** and **1b**.[14] The dodecyllithium reagent was prepared in situ from dodecyl iodide by treatment with *tert*-butyllithium at −65 °C, before use.[15] The 5 and 6 positions in **1a** and **1b** were oxidized by treatment with nitric acid/sulfuric acid to give **2a** and **2b**.[16] The poor isolated yields, in particular of 5% in **2b**, are attributed to the violent oxidation conditions where the alkyl chains in **1a** and **1b** were oxidized. On the other hand, another key synthetic intermediate **2c** was conveniently obtained from coupling reaction of 2,9-dichloro-1,10-phenanthroline-5,6-dione (**3**)[17] with 4-octylphenylboronate in the presence of a palladium (0) catalyst. This synthetic route has the advantage of avoiding the alkyl-chain oxidation. In **5a−c**, any mesophases could not be observed. DSC and TG measurements indicated decomposition above 350 °C.

Scheme 1. Preparation of **5a−c**



TP−HATs **5b** and **5c** can dissolve in various solvents from polar to nonpolar ones such as cyclohexane, toluene, dichloromethane, chloroform, 1,1,2,2-tetrachloroethnae, and THF. In contrast, **5a** showed poor solubility in these solvents except

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for 1,1,2,2-tetrachloroethnae at the low concentration of <0.1 mM. Thus, detailed analysis of the aggregation ability was performed mainly on **5b** and **5c**.

A direct evidence for the aggregation of **5a**−**c** is provided from MALDI-TOF mass spectrometry. In addition to the parent ions of **5a** (*m/z* 1027), **5b** (*m/z* 1699), and **5c** (*m/z* 1819), significant peaks are seen at several multiples of the parent ion up to 5135 for **5a**, 5097 for **5b**, and 7276 for **5c**, respectively, which are assemblies of five, three, and four molecules, respectively (Supporting Information).

The one-dimensional π-stacking of **5b** and **5c** molecules was corroborated by means of UV/vis and ^{1}H NMR spectroscopy. The UV/vis spectra of **5b** in 1,1,2,2-tetrachloroethane show three bands around 420, 390, and 340 nm (Figure 1a). The former two bands can be assigned to the transition from the highest ground state to the $\nu = 0$ level of the lowest excited state (0−0 transition) and to the $\nu = 1$ level (0−1 transition), respectively. Concentration- and temperature-dependent spectral change was observable in 1,1,2,2-tetrachloroethane solutions, which is attributed to dynamic exchange between monomer and aggregate species (Figure 1a and Supporting Information). The absorbance ratio (abs_{0-0}/abs_{0-1}) of the 0−0 and 0−1 transitions decreased with increasing concentration and decreasing temperature. The foregoing trend is very similar to those of π-tacked aggregates with H-type parallel stacking mode,[12b,18] which is rationalized by the molecular exciton model.[19] The H-type aggregate with wide π-face overlap is very suitable for electron-carrier transport along the π-stacked aggregate structure. Similar spectral pattern was observed in **5c**. The concentration- and temperature-dependence in **5c** was smaller than that in **5b**, indicating the superior aggregative nature of **5c** (Supporting Information).

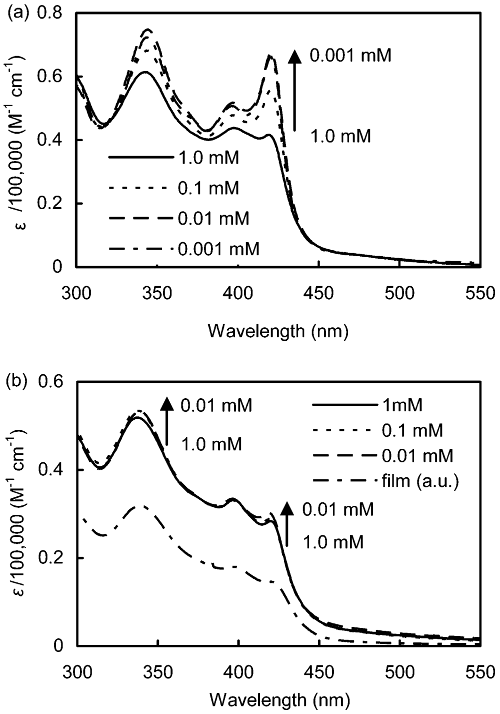

Figure 1. UV/vis spectra of **5b** at 20 °C (a) in 1,1,2,2-tetrachloroethane (0.001, 0.01, 0.1, and 1.0 mM) and (b) in cyclohexane (0.01, 0.1, and 1.0 mM) and in the spin-coating film.

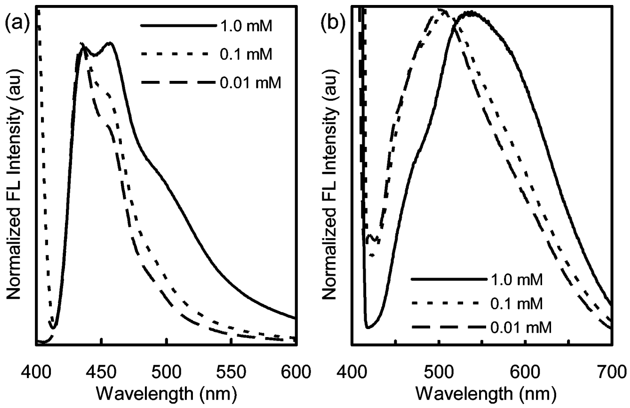

Figure 2. Fluorescence spectra of **5b** at 20 °C excited at 397 nm (a) in 1,1,2,2-tetrachloroethane (0.01, 0.1, and 1.0 mM) and (b) in cyclohexane (0.01, 0.1, and 1.0 mM).

In cyclohexane, the UV/Vis spectra of **5b** and **5c** scarcely changed depending on the concentration and temperature, indicating high stability of the aggregates in the cyclohexane solution (Figure 1b and Supporting Information). The UV/vis spectra of the spin-coating films of **5b** and **5c** are very similar to those of the cyclohexane samples (Figure 1b and Supporting Information). The results show that in the film state the **5b** and **5c** molecules are self-assembled with similar H-aggregate stacking mode created in the solution state.

In the ^{1}H NMR spectra, line-broadening effect arising from the aggregation was observed in **5a**−**c** in chloroform-d_1 and 1,1,2,2-tetrachloroethane-d_2. By addition of trifluoroacetic acid-d_1, the broad peaks became sharp according to aggregate dissociation, from which the structural assignment of **5a**−**c** is possible. At high temperature of >100 °C, the aromatic Ha and Hb proton signals on the TP-HAT ring can be sharpened to be detected in 1,1,2,2-tetrachloroethane-d_2 solutions of **5b**. In contrast, in **5c** the Ha and Hb proton signals still disappeared at >100 °C and only the Hc and Hd signals on the phenyl groups can be detected (Supporting Information).

The aggregation of **5b** and **5c** is reflected in steady-state fluorescence spectra. In 1,1,2,2-tetrachloroethane, around 500 nm excimer-like emission arising from the aggregate species of **5b** can be detected as a shoulder in addition to monomer emission around 450 nm. The population of the excimer emission increased with increasing concentration together with decreasing the monomer emission population (Figure

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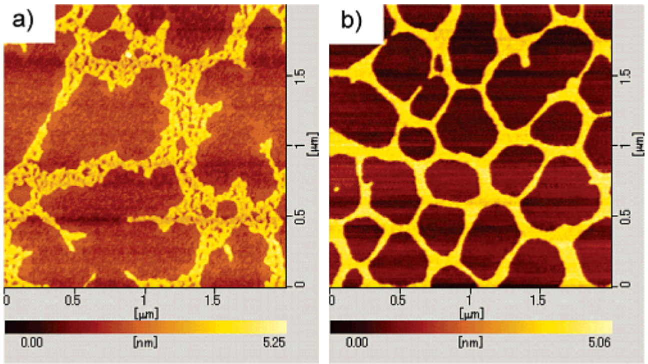

Figure 3. AFM images of (a) **5b** and (b) **5c**. The samples were prepared by drop casting from 0.01 mM cyclohexane solutions on freshly cleaved mica.

2a). The cyclohexane solutions of **5b** provide mainly weak excimer emission in all concentration regions (Figure 2b). A shift to shorter wavelengths in the emission at low concentrations is attributed to the presence of tiny amounts of monomer emission. Similar emission behavior was observed in **5c** (Supporting Information). In the film state of **5b** and **5c**, the emission is too weak to be detected, indicating the significant aggregation in the film state.

The aggregate structure of **5b** and **5c** can be visualized by atomic force microscopy (AFM) observation (Figure 3). The AFM image of **5c** on mica indicates a nanoscale honeycomb structure with height of ca. 3.0 nm, which is comparable to the molecular size of **5c** (the extended molecular size of ca. 4.2 nm, whereas the aromatic core size is ca. 2.3 nm). In **5b**, a less ordered fibrous structure with height of ca. 2.0 nm can be observed.[20]

High electron affinity as well as electrochemical stability of **5b** and **5c** are confirmed by cyclic voltammetry (Supporting Information). In **5c**, three quasireversible reduction potentials were evaluated at −1.66, −1.79, and −2.02 V (vs Fc/Fc$^+$) in dichloromethane. In **5b**, the corresponding first and second reduction potentials were not separated sufficiently. Thus, we used an averaged value of −1.70 V (vs Fc/Fc$^+$) for the first and second reduction potentials along with the third reduction potential at −1.92 V (vs Fc/Fc$^+$). The first reduction potentials in **5b** and **5c** shift more positive compared to that (−1.86 V vs Fc/Fc$^+$) of the parent HAT. The results indicate the enhancement of the electron affinity by the combination of the central HAT ring with the peripheral phenanthroline rings. No oxidation potential was observed in the cyclic voltammogram (~1.5 V), indicating the n-type semiconducting nature of TP−HATs.

In conclusion, we have demonstrated that n-type semiconducting tri(phenanthrolino)hexaazatriphenylenes with a large aromatic core can be self-assembled both in solution and film state. High electron affinity is achieved from the cooperative effects of the central hexaazatriphenylene core and the three peripheral phenanthrolino moieties. The extended aggregates of the π-stacked aromatic moieties would provide an efficient path for electron-carrier transport within the aggregate structures. We are currently in the process of electron-mobility measurement.

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Supporting Information Available: Experimental procedure and MALDI-TOF, UV−vis, fluorescence, fluorescence excitation, CV, and ^{1}H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) The observed fibrous structure would reflect the one-dimensional aggregation. Ordered fibrous structure found in **5c** would be ascribed to the additional phenyl groups, which expand the π-system to stabilze the fibrous aggregate.