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Expanded π-Electron Systems, Tri(phenanthro)hexaazatriphenylenes and Tri(phenanthrolino)hexaazatriphenylenes, That Are Self-Assembled To Form One-Dimensional Aggregates

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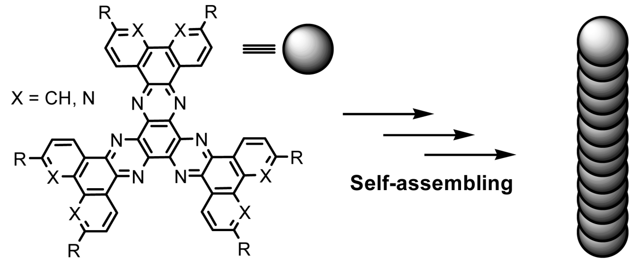

This paper reports the self-assembling and electrochemical nature of hexaazatriphenylene-based electron-deficient heteroaromatics with an expanded π-electron system. The tri(phenanthro)hexaazatriphenylenes (TPHAT-Cs) and tri(phenanthrolino)hexaazatriphenylenes (TPHAT-Ns) were prepared by condensation reactions of the corresponding phenanthrenequinones and phenanthrolinediones, respectively, with hexaaminobenzene. Their electron affinity was indicated from cyclic voltammetry measurements, in which the first reduction potentials were evaluated at around -1.7 V (vs Fc/Fc^+) in dichloromethane. In nonpolar and polar solvents and in the film state, the TPHAT-Cs and TPHAT-Ns formed one-dimensional aggregates with an H-type parallel stacking mode. In the MALDI-TOF mass spectra, significant peaks were seen at several multiples of the parent ion up to tetramer aggregates. The ^{1}H NMR spectra indicated a line-broadening effect due to the aggregation. The UV−vis and fluorescence spectra showed a concentration dependence, which is attributed to a dynamic exchange between the monomer and aggregate species. The order of the aggregative nature was estimated from the concentration dependence and the fluorescence quantum yield. By replacement of the peripheral aromatic moieties instead of the phenanthrene (TPHAT-Cs) with the phenanthroline (TPHAT-Ns), the aggregative nature was enhanced.

Introduction

Semiconducting organic compounds[1] have been very interesting in recent years in view of their application to carrier-transporting materials in organic light-emitting diodes,[2] field-effect transistors,[3] and photovoltaics.[3d,4] These semiconductors are classified into two groups: p-type semiconductors with a hole-transporting ability and n-type ones with an electron-transporting ability. The former has been extensively studied and has excellent characteristics, whereas the latter is relatively rare and has unsatisfactory performance. One of the desired performances of the organic semiconductors is a high carrier-drift mobility comparable to inorganic silicon materials. Recently, a π-stacked

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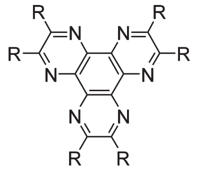
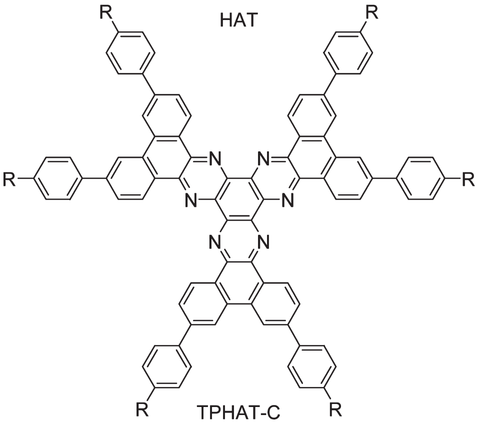
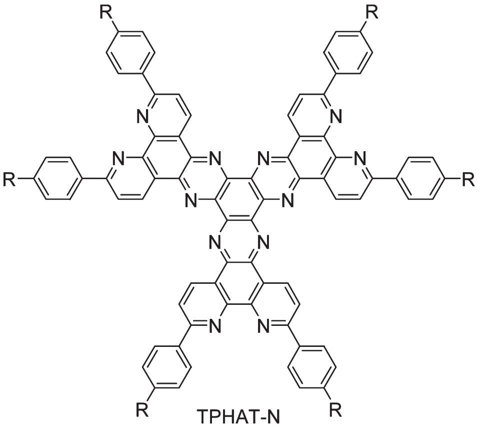
one-dimensional structure created from the self-assembly of organic semiconductors has attracted considerable attention for carrier-transport.[5,6] An efficient carrier-transport is achieved along the stacking direction. Such self-assembled aggregates with an ordered supramolecular structure are more attractive candidates as carrier-transporting materials than the glassy-type amorphous semiconductors with unfavorable positional and energy disorder.[7] A guideline for the carrier-transport was reported by Warmann and co-workers, in which the mobility empirically increases with the expanding core size of the semiconductors.[8] Large-sized semiconductors with an expanded π-electron system tend to have a positive influence on the mobility due to the increase of the self-assembling aggregative nature between the stacked molecules and due to the increase of the orbital overlap between the π-orbitals of the molecules. The p-type self-assembling semiconductor hexabenzocoronenes[9] with an expanded π-electron system are well-known as excellent carrier-transporting materials that provide a high hole-drift mobility.[10] On the other hand, the n-type self-assembling semiconductors are limited to small- and medium-sized aromatics.[11−14] Thus, the creation of a new large-sized self-assembling n-type semiconductor is one of the most important tasks in organic material science.



HAT



TPHAT-C



TPHAT-N

Recently, we have studied electron-deficient heteroaromatics in order to develop new electron-transporting semiconductors based on their high electron affinity. In these studies, we found that the n-type semiconducting hexaazatriphenylenes

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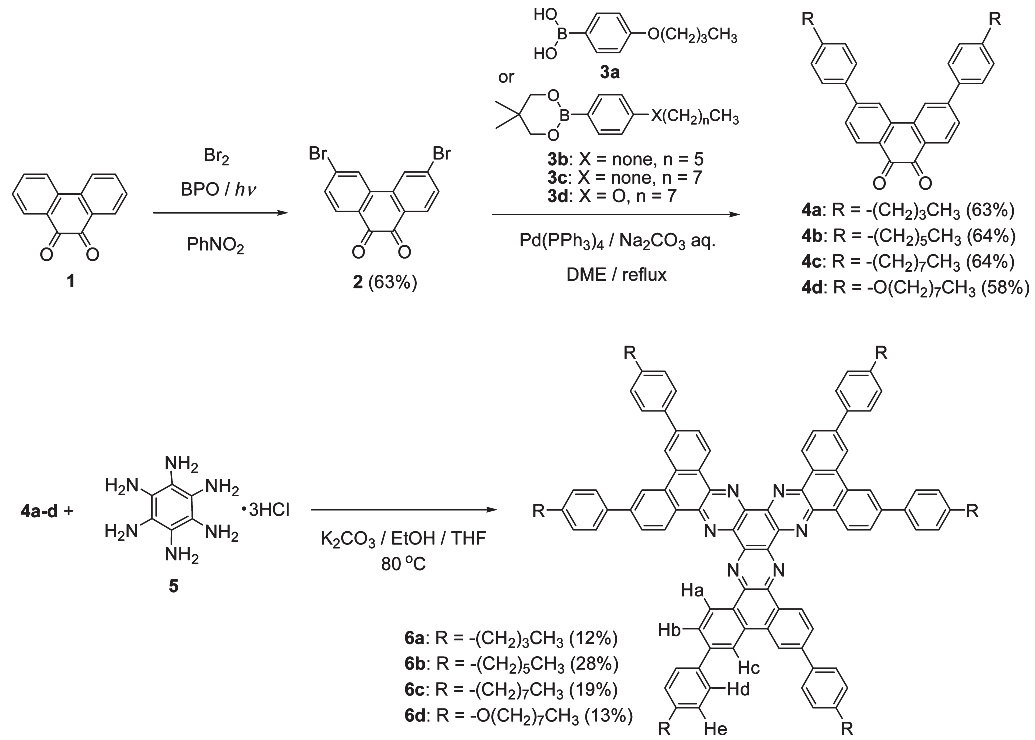
SCHEME 1. Preparation of TPHAT-Cs 6a−d



(HATs)[14,15] can be self-assembled both in solution and bulk state to form π-stacked one-dimensional aggregates.[16] The self-assembling HAT molecule is one of the new candidates as parent of a large-sized n-type semiconductor.[17] Our strategy is based on the combination of the HAT core with other aromatics to improve both its self-assembled aggregative nature and electron affinity. In this strategy, we selected the phenanthrene and phenanthroline rings as the fused aromatics, because the corresponding diketone derivatives can be obtained and reacted with hexaaminobenzene[16] to produce the desired large-sized n-type semiconductors. Combinations of the HAT core with the three phenanthrene and phenanthroline rings result in tri(phenanthro)hexaazatriphenylene (TPHAT-C) and tri(phenanthrolino)hexaazatriphenylene (TPHAT-N), respectively, which are composed of 13 fused six-membered rings similar to that of hexabenzocoronene.[9,10] In this paper, we report that the TPHAT-C and TPHAT-N derivatives provide a high electron affinity as n-type semiconductors, as well as a strong self-assembling nature to form one-dimensional aggregates.

Results and Discussion

Preparation. TPHAT-Cs **6a−d** were prepared by condensation reactions of the corresponding 3,4-disubsituted-9,10-phenanthrenequinones **4a−d** with hexaaminobenzene **5**[16] in ethanol/THF in the presence of potassium carbonate (Scheme 1). The key synthetic intermediates **4a−d** were obtained from 9,10-phenanthrenequinone (**1**) in two steps. The radical-initiated bromination of **1** gave the dibromide **2**,[18] which was converted into **4a−d** by the coupling reaction with the corresponding boronic acid **3a** and boronate esters **3b−d** in the presence of a palladium (0) catalyst.

TPHAT-Ns **14a−c** were obtained from 1,10-phenanthroline (**7**) in 7 steps (Scheme 2). 2,9-Dichloro-1,10-phenanthroline (**10**) was prepared according to a reported method[19] and

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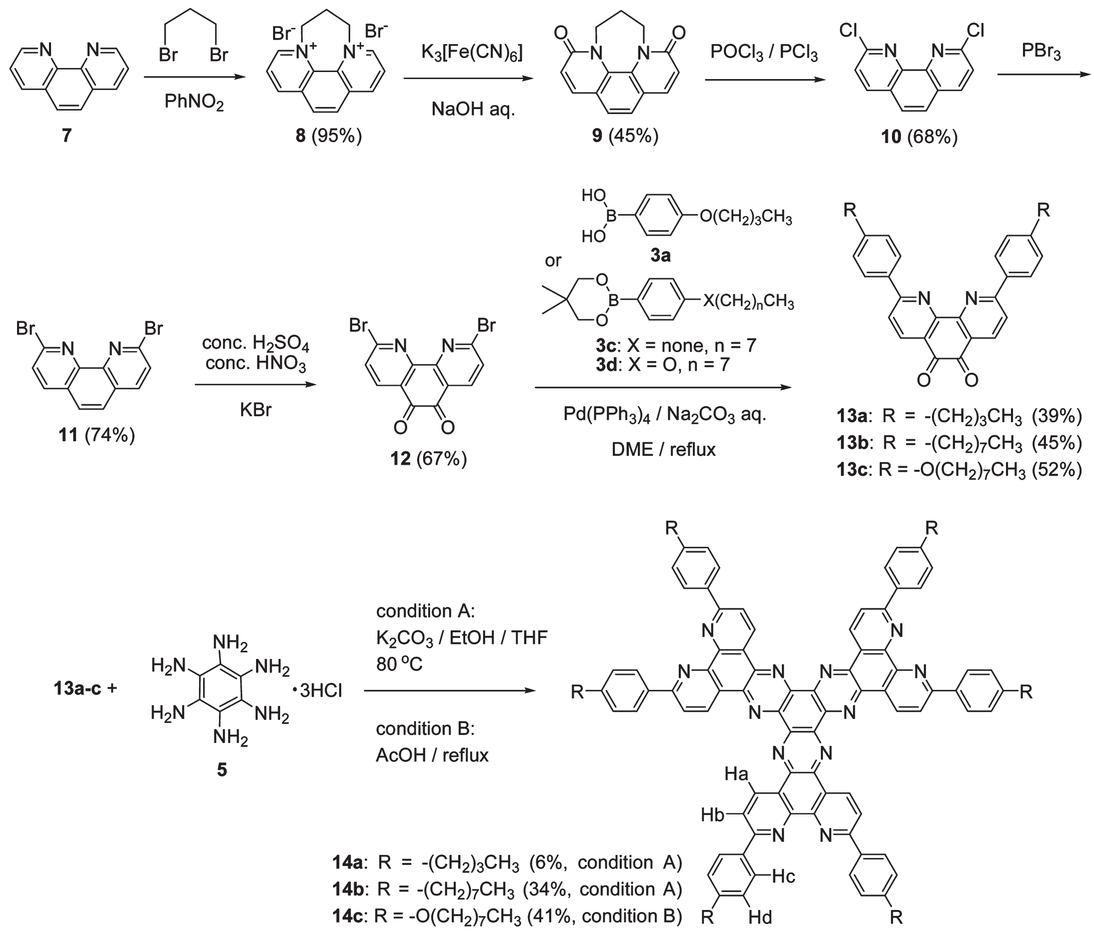
SCHEME 2. Preparation of TPHAT-Ns 14a−c



was converted into the corresponding dibromide **11** by treatment with phosphorus tribromide. The 5 and 6 positions in **11** were oxidized by the treatment with nitric acid/sulfuric acid/KBr to give **12**.[20] The coupling reactions of **12** with boronic acid **3a** and boronate esters **3c,d** gave the corresponding 2,9-disubstituted-1,10-phenanthroline-5,6-dione **13a−c** in moderate yields. Finally, the TPHAT-Ns **14a−c** were obtained by the condensation reactions of **13a−c** with hexaaminobenzene **5**.[16] In **14a** with 4-butylphenyl groups and **14b** with 4-octylphenyl groups, the preparation reaction was performed in ethanol/THF in the presence of potassium carbonate (condition A), as used in **6a−d**. Condition A was not suitable for the preparation of **14c** with 4-octyloxyphenyl groups, whereas **14c** was obtained in acetic acid at the refluxing temperature (condition B). The low isolated yield (6%) in **14a** is attributed to its poor solubility.

The TPHATs **6a−d** and **14a−c** were identified using spectroscopic methods.[21] In particular, ^{1}H NMR spectroscopy is effective for assigning the structure. In halogenated solvents, such as chloroform-d_1, dichloromethane-d_2, and 1,1,2,2-tetrachloroethane-d_2, a line-broadening effect arising from the aggregation was observed. By the addition of trifluoroacetic acid-d_1, the broad peaks in the phenanthroline-fused system **14a−c** became sharp due to aggregate dissociation. The resulting spectra provided four aromatic proton signals (Ha, Hb, Hc, and Hd shown in Scheme 2), from which the structures of **14a−c** could be assigned (Supporting Information). In contrast, the broad peaks in the phenanthrene-fused system **6a−d** still appeared even in the presence of trifluoroacetic acid-d_1. These results indicated that in **14a−c** the protonation occurs at the nitrogen atoms on the peripheral phenanthroline rings to dissociate the aggregates but not on the central HAT ring. The structural assignment in **6a−d** can be performed at high temperature. At 120 °C, the five aromatic proton signals (Ha, Hb, Hc, Hd, and He shown in Scheme 1) became sharp peaks suitable for detection in 1,1,2,2-tetrachloroethane-d_2 solutions (Supporting Information).

The TPHAT-Cs **6a−c** and TPHAT-N **14b** can dissolve in various solvents from polar to nonpolar ones, such as cyclohexane, toluene, dichloromethane, chloroform, 1,1,2,2-tetrachloroethane, and THF. Compared to **6c** bearing the octyl groups, **6d** bearing the octyloxy groups showed a poor solubility in cyclohexane. Similarly, **14c** bearing the octyloxy groups cannot dissolve in cyclohexane. For **14a**, the short alkyl chain (butyl group) significantly lowered the solubility in cyclohexane and toluene. In addition, **14a** can dissolve in 1,1,2,2-tetrachloroethane at the low concentration of < 0.1 mM. Thus, a detailed analysis of the aggregation ability was performed in the polar 1,1,2,2-tetrachloroethane for **6a−d** and **14a−c** and in the nonpolar cyclohexane for **6a−c** and **14b**.

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[21] The TPHAT-C **6c** with octyl groups shows mesophase. The details of the mesophase formation will be reported elsewhere.

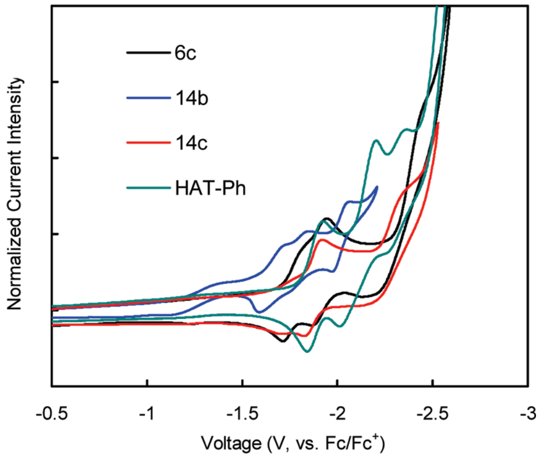

FIGURE 1. Cyclic voltammograms of **6c**, **14b**, **14c**, and HAT-Ph in dichloromethane (0.5 mM) in the presence of tetrabutylammonium hexafluoroborate (0.1 M). The current intensity for **6c** was indicated by three times to precisely compare.

TABLE 1. Half-Wave Reduction Potentials ($E_{1/2}{}^{red}$) of 6c, 14b, 14c, and HAT-Ph[a]

	$E_{1/2}{}^{red}$ (V, vs Fc/Fc$^+$)		
compound	first	second	third
6c	−1.73	−1.86	−2.25
14b	−1.66	−1.79	−2.02
14c	−1.70	−1.81	−2.21
HAT-Ph	−1.86	−2.11	−2.31

[a] Determined by cyclic voltammetry using a cell equipped with glassy carbon as the working electrode, a platinum wire as the counter electrodes, and Ag/AgNO$_3$ as the reference electrode. All electrochemical measurements were performed in a dichloromethane solution (0.5 mM) containing 0.1 M tetrabutylammonium hexafluorophosphate.

Electrochemical Properties. The high electron affinity and electrochemical stability were studied by cyclic voltammetry (Figure 1, Table 1, and Supporting Information). In **6c**, **14b**, and **14c**, three quasi-reversible reduction potentials were observed around −1.7 to −2.2 V (vs Fc/Fc$^+$). The first reduction potentials (−1.66 to −1.73 V) in **6c**, **14b**, and **14c** shift more positively compared to the reduction potential (−1.86 V) of the 2,3,6,7,10,11-hexaphenyl-1,4,5,8,9,12-hexaazatriphenylene (HAT-Ph).[16a] These results indicated an enhancement of the electron affinity by the combination of the central HAT ring with the peripheral phenanthrene/phenanthroline rings. Compared to the phenanthrene-fused **6c**, the phenanthroline-fused **14b** showed a higher electron affinity due to the electron-deficient phenanthroline ring. By replacement of the octyl group (**14b**) with the octyloxy group (**14c**), the electron affinity decreased. No oxidation potential was observed in the cyclic voltammogram (~1.5 V), indicating the n-type semiconducting nature of the TPHATs.

MALDI-TOF Mass Spectrometry. Direct evidence for the aggregation of **6a−d** and **14a−c** was obtained from the MALDI-TOF mass spectrometry, in which aggregate species can be detected up to the tetramer (Figure 2 and Supporting Information). For example, in addition to the parent ions of **6c** (*m*/*z* 1813) and **14b** (*m*/*z* 1819), significant peaks are seen at several multiples of the parent ion up to 7252 for **6c** and 7276 for **14b**, which are assemblies of four molecules (Figure 1).

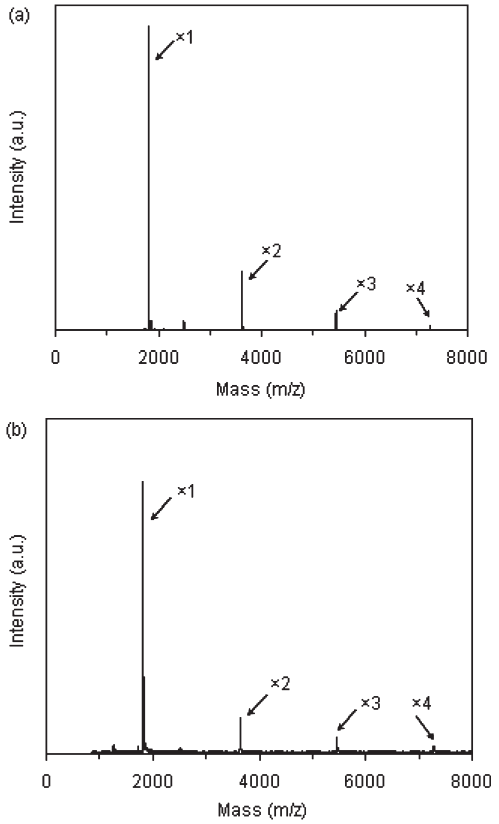

FIGURE 2. MALDI-TOF mass spectra of (a) **6c** and (b) **14b**, which indicate multiples of the parent ion up to tetramer.

UV−vis Spectroscopy. The one-dimensional π-stacking of the TPHAT molecules is indicated in the UV−vis spectra. The UV−vis spectra of **6a−d** changed depending on the concentration and temperature of the 1,1,2,2-tetrachloroethane solutions. The spectral change is attributed to a dynamic exchange between the monomer and aggregate species (Figure 3 and Supporting Information). The UV−vis spectra of **6a** in 1,1,2,2-tetrachloroethane showed three bands around 460, 440, and 370 nm (Figure 3a). 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). The absorbance ratio (abs$_{0-0}$/abs$_{0-1}$) of the 0−0 and 0−1 transitions decreased with the increase of concentration and with the decrease of temperature, leading to the facilitated aggregation. The foregoing trend is very similar to those of the π-stacked aggregates with an H-type parallel stacking mode,[16b,22] which is rationalized by the molecular exciton model.[23] The TPHAT-Cs **6a−d** provided almost the same spectral change versus the concentration to each other (Figure 3a and b, and Supporting Information). At 1.0 mM, the abs$_{0-0}$/abs$_{0-1}$ values of 0.93 for **6a**, 0.94 for **6b**, 0.95 for **6c**, and 1.00 for **6d** are almost the same, indicating the side chain groups (butyl in **6a**, hexyl in **6b**, octyl in **6c**, and octyloxy in **6d**) only slightly affect the aggregation in the TPHAT-C system.

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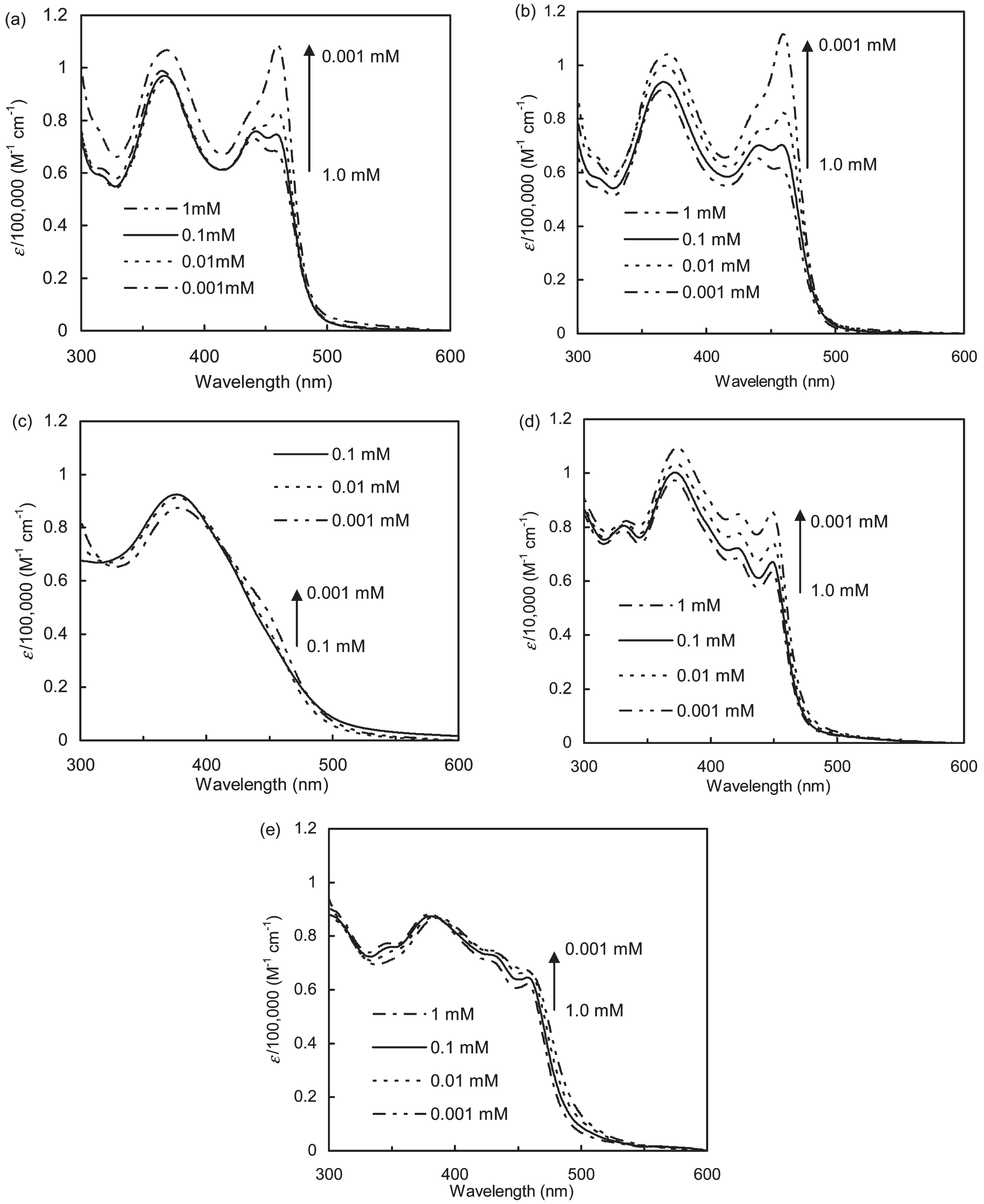

FIGURE 3. UV−vis spectra of (a) **6a**, (b) **6c**, (c) **14a**, (d) **14b**, and (e) **14c** at 20 °C in 1,1,2,2-tetrachloroethane (at 0.001, 0.01, 0.1, and 1.0 mM).

By replacement of the peripheral aromatic moieties instead of the phenanthrene (TPHAT-C system) with the phenanthroline (TPHAT-N system), the aggregative nature is significantly enhanced, and the effect of the side-chain group is clearly observed. The concentration- and temperature-dependencies in TPHAT-N **14b** bearing the octyl groups were lower than that in TPHAT-C **6c** bearing the octyl groups. At 20 °C, the $\mathrm{abs}_{0-0}/\mathrm{abs}_{0-1}$ value in **6c** significantly changed from 0.95 (1.0 mM) to 1.28 (0.001 mM), whereas the value in **14b** only slightly changed from 0.93 (1.0 mM) to 1.01 (0.001 mM) (Figure 3b and d). These results indicate the superior aggregative nature of the TPHAT-N system.

Compared to TPHAT-N **14b** bearing the alkyl chains, TPHAT-N **14c** bearing the alkoxy chains provides very slight concentration- and temperature-dependencies in the UV−vis spectra. The $\mathrm{abs}_{0-0}/\mathrm{abs}_{0-1}$ values in **14c** seldom changed with the concentration from 0.88 (1.0 mM) to 0.89 (0.001 mM) at 20 °C, indicating the high aggregation stability (Figure 3e). The enhanced aggregation in **14c** would be attributed to the expansion of the π-electron system including the oxygen atoms. Furthermore, the most significant

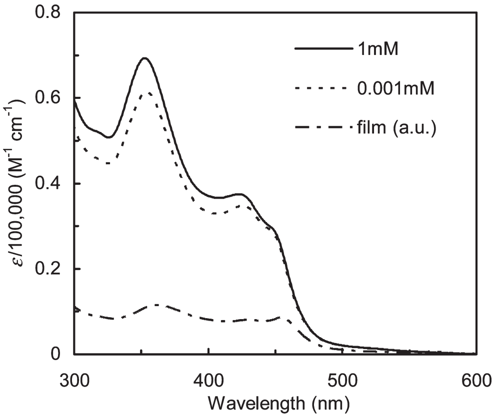

FIGURE 4. UV−vis spectra of **6a** at 20 °C in cyclohexane (at 0.001 and 1.0 mM) and in the spin-coated film.

enhancement in the aggregation was achieved in TPHAT-N **14a** bearing the short alkyl chains. The UV−vis spectra of **14a** indicated a significantly weak 0−0 transition band as a shoulder around 450 nm (Figure 3c). The reduction in the alkyl chain length from octyl (**14b**) to butyl (**14a**) significantly facilitated the aggregation. Compared to **14b** bearing the long alkyl chains, **14a** bearing the short alkyl chains seems to show less favorable solvation to increase the aggregative nature. As a summary of the foregoing results, one can conclude that the order of aggregation stability is increased as **14a** > **14c** > **14b** > **6a−d** (**6a** > **6b** > **6c** > **6d**).

In a nonpolar solvent, such as cyclohexane, the UV−vis spectra of **6a−c** and **14b** seldom changed with the concentration and temperature, indicating the high stability of the aggregates in the cyclohexane solution (Figure 4 and Supporting Information). Compared to the polar 1,1,2,2-terrachloroethane system, the TPHAT-N and TPHAT-C molecules are more tightly stacked in the nonpolar cyclohexane system.

The UV−vis spectra of the spin-coated films prepared from the cyclohexane solutions of **6a−c** and **14b** are similar to those of the solutions (Figure 4 and Supporting Information). These results showed that in the film state, the **6a−c** and **14b** molecules are self-assembled with a H-aggregate stacking mode similar to the one created in the solution state. The H-type aggregate with a wide π-face overlap is very suitable for electron-carrier transport along the π-stacked aggregate structure. The self-assembled film formation can be applied to the organic devices prepared by a wet process such as spin-coating.

Fluorescence Spectroscopy. The aggregation of the TPHATs is reflected in the fluorescence spectra. In 1,1,2,2-tetrachloroethane, a significant concentration dependence was observed due to the dynamic exchange between the monomer and aggregates species, as found in the UV−vis spectra. In the TPHAT-C **6c**, around 560 nm an excimer-like emission arising from the aggregate species can be detected in addition to the monomer emission around 490 nm. The

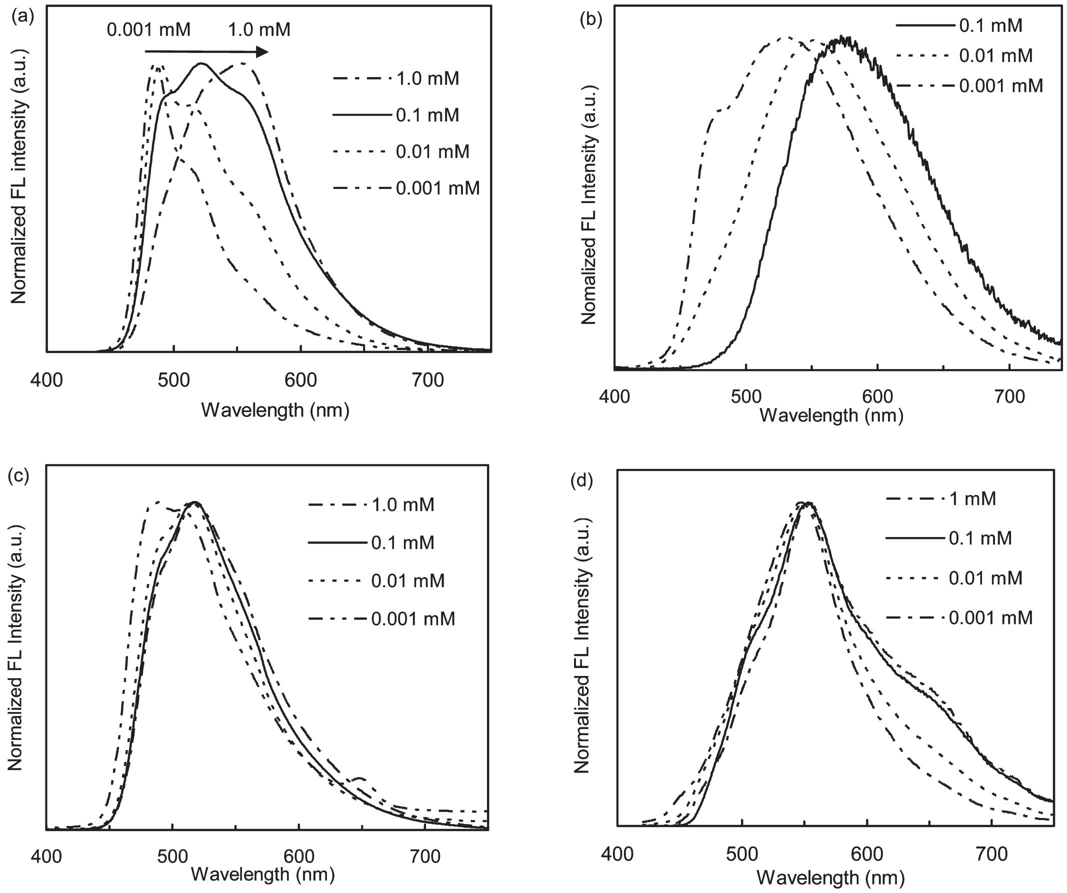

FIGURE 5. Fluorescence spectra of (a) **6c**, (b) **14a**, and (c) **14b** in 1,1,2,2-tetrachloroethane and (d) **6c** in cyclohexane at 0.001, 0.01, 0.01, and 1.0 mM (at 20 °C).

FIGURE 6. Fluorescence images of **6c** in 1,1,2,2-tetrachloroethane at 0.001, 0.01, and 0.1 mM (from left to right) under UV light (365 nm).

population of the aggregate emission increased with the increase of concentration together with the decrease of monomer emission population (Figure 5a). The aggregation dynamics can be visualized by changing the emission color from blue (0.001 mM) to green (0.1 mM) (Figure 6).[24] A similar concentration dependence was observed in TPHAT-Cs **6a**, **6b**, and **6d**. Compared to the TPHAT-Cs, the TPHAT-Ns mainly provide an aggregate emission because of their facilitated aggregation (Figures 5b and 5c). The formed aggregate emits a weak fluorescence that decreases the fluorescence quantum yield (Φ_{FL}). The Φ_{FL} values of the TPHAT-Ns are lower than those of the TPHAT-Cs: 0.30 in **6a** vs 0.07 in **14a**, 0.45 in **6c** vs 0.28 in **14b**, and 0.59 in **6d** vs 0.18 in **14c**. The order of the aggregative nature is estimated from the Φ_{FL} values (Table 2). The estimated order is **14a** > **14c** > **14b** > **6a** > **6b** > **6c** > **6d**, which is in agreement with that estimated from the UV−vis spectroscopy.

The cyclohexane solutions of **6a**−**c** and **14b** provided only weak aggregate emissions at the longer wavelength around 550−600 nm for all the concentrations. At the dilute concentration of 0.001 mM, the emission band (around 550 nm) in the cyclohexane solution of **6c** is observed at a longer wavelength than that (around 490 nm) in the 1,1,2,2-tetrachloroethane solution; nevertheless, the polarity of the cyclohexane is lower than that of 1,1,2,2-tetrachloroethane (Figure 5a and d). The bathochromic shift observed in cyclohexane would be attributed to a stabilization effect on the excited state in the aggregate.[25] The stabilization effect should be ascribed to the excimer formation in the aggregate structure or the migration of the photogenerated exciton.[26] A similar bathochromic shift was observed in **6a**, **6b**, and **14b** as described above. In the 1,1,2,2-tetrachloroethane solutions, **6a**−**c** and **14b** provide moderate Φ_{FL} values of 0.28−0.45. The Φ_{FL} values are reduced in the nonpolar cyclohexane solutions to 0.03−0.04 (Table 2). The lowering emission ability also supports the enhanced aggregation of **6a**−**c** and **14b** in the nonpolar solvent. In the film state of **6a**−**c** and **14c** prepared from cyclohexane solutions, the emission is too weak to be detected, indicating the enhanced aggregation in the film state.

TABLE 2. **Fluorescence Quantum Yields (Φ_{FL}) for 6a−d and 14a−c**[a]

	Φ_{FL}[b]	
compound	cyclohexane	1,1,2,2-tetrachloroethane
6a	0.03	0.30
6b	0.04	0.39
6c	0.04	0.45
6d		0.59
14a		0.07
14b	0.03[c]	0.28
14c		0.18

[a] Measured at 0.001 mM and excited at 420 nm. [b] Relative to fluorescein (Φ_{FL} 0.97 in ethanol, excited at 450 nm). [c] Excited at 380 nm.

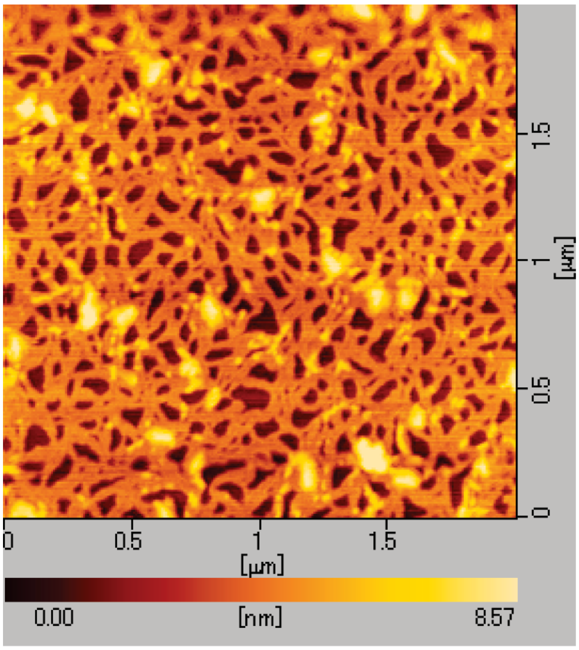

FIGURE 7. AFM image of **6a**. The sample was prepared by drop casting from a 0.01 mM cyclohexane solution on freshly cleaved mica.

AFM Observation. The π-stacked one-dimensional aggregate structure of the TPHATs can be visualized by atomic force microscopy (AFM) observations (Figure 7 and Supporting Information). The cyclohexane solutions of **6a**−**c** and **14b**, in which the TPHAT molecules are significantly self-assembled to form the one-dimensional aggregates, were casted on freshly cleaved mica. The AFM images indicate a nanoscale fibrous structure with a height of ca. 2.8−3.5 nm, which is comparable to the molecular size of the TPHATs (the extended molecular size is of ca. 3.2−4.2 nm, whereas the aromatic core size is of ca. 2.5 nm).[27] In **6a**−**c**, the height increased with the increase

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[27] The π-stacked one-dimensional aggregate is also supported by X-ray diffraction patterns of **6a**, **6b**, **6c**, and **14b** (Supporting Information). A weak reflection around 26° would be attributed to the intracolumnar π-stacking distance of ca. 0.34 nm. In contrast, a strongly sharp reflection around 2.9−3.7° (2.38 nm for **6a**, 2.69 nm for **6b**, 3.03 nm for **6c**, and 2.85 nm for**14b**) would be due to the intercolumnar packing.

of alkyl chain length: ca. 2.8−2.9 nm in **6a**, ca. 3.0−3.1 nm in **6b**, and ca. 3.4−3.5 nm in **6c**.

Conclusion

In conclusion, we have demonstrated that the electron-deficient tri(phenanthro)- and tri(phenanthrolino)hexaazatriphenylenes with an expanded π-electron system can be self-assembled to form one-dimensional aggregates. The electron affinity is enhanced by the expansion of the electron-deficient aromatic system, which is created by a combination of the central hexaazatriphenylene core with the three peripheral phenanthrene/phenanthroline rings. The extended aggregates of the π-stacked aromatic moieties would provide an efficient path for the electron-carrier transport within the one-dimensional aggregate structures. It is convinced that the present study provide new valuable information for creating as an electron-carrier transporting material in the organic devices such as an organic field effect transistor and photovoltaic cell. We are currently in the process of obtaining electron-mobility measurements.

Experimental Section

Spectroscopic Measurements. UV−vis spectra were measured in a 0.01 cm width quartz cell (1.0 mM), a 0.1 cm cell (0.1 mM), a 1.0 cm cell (0.01 mM), and a 10.0 cm cell (0.001 mM). Fluorescence spectra were measured in a 1.0 cm width quartz cell.

Preparation of Spin-Coated Films. Film samples for UV−vis and fluorescence spectroscopy were prepared by drop-casting and subsequent spin-coating (2000 rpm, 30 s) from 1.0 mM cyclohexane solutions (100 μL × 3) on quartz cell (12.5 × 12.5 × 45 mm).

Electrochemical Measurement. Cyclic voltammetry measurements were measured in deaerated dichloromethane solution (0.5 mM) containing tetrabutylammonium hexafluoroborate (0.1 M) as a supporting electrolyte at 298 K at scan rate of 10−100 mV s^{-1} (10 mV s^{-1} for **14b** and 100 mV s^{-1} for **6c**, **14c**, and HAT-Ph). The glassy carbon working electrode was polished with BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to an Ag/AgCl (saturated KCl) reference electrode.

General Procedure for Preparation of 3,6-Bis(4-butylphenyl)-9,10-phenanthrenequinone (4a). A mixture of **2** (831 mg, 2.27 mmol) and tetrakis(triphenylphosphine)palladium(0) (552 mg, 0.455 mmol) in deaerated DME (45 mL) was heated at 60 °C for 5 min under an argon atmosphere. To the mixture were added 4-butylphenylboronic acid (**3a**) (890 mg, 5.0 mmol) and deaerated aqueous 2 M sodium carbonate solution (22.5 mL) at 60 °C, and the mixture was heated at 85 °C for 18 h. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with brine and water, dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue (1.31 g) was purified by silica gel column chromatography (WAKO C300) eluting with hexane/dichloromethane (1:4, v/v) and by recrystallization from hexane/dichloromethane to give **4a** in 63% yield (677 mg, 1.43 mmol) as yellow powder: mp 211−213 °C; IR (KBr, cm^{-1}) 3023, 2955, 2927, 2856, 1671 ($\nu_{C=O}$), 1594, 1393, 1316, 1236, 1188, 926, 840, 824; ^{1}H NMR (CDCl$_3$) δ 0.96 (t, J = 7.3 Hz, 6 H), 1.41 (sept, J = 7.3 Hz, 4 H), 1.66 (quint, J = 7.3 Hz, 4 H), 2.71 (t, J = 7.3 Hz, 4 H), 7.35 (d, J = 8.3 Hz, 4 H), 7.63 (d, J = 8.3 Hz, 4 H), 7.69 (dd, J = 1.5, 8.3 Hz, 2 H), 8.26 (d, J = 1.5 Hz, 2H), 8.28 (d, J = 8.3 Hz, 2 H); ^{13}C NMR (CDCl$_3$) δ 13.9, 22.3, 33.5, 35.4, 122.4, 127.2, 128.1, 129.2, 129.7, 131.1, 136.1, 136.8, 144.3, 148.8, 180.0; FAB-MS (positive, NBA) m/z 473 [(M + 1)$^+$]. Anal. Calcd for $C_{34}H_{32}O_2$ (472.62): C, 86.40; H, 6.82. Found: C, 86.21; H, 6.81.

3,6-Bis(4-hexylphenyl)-9,10-phenanthrenequinone (4b). Yellow powder; mp 156−158 °C; IR (KBr, cm^{-1}) 3023, 2954, 2925, 2854, 1671 ($\nu_{C=O}$), 1593, 1394, 1316, 1296, 1237, 1188, 927, 842, 812; ^{1}H NMR (CDCl$_3$) δ 0.90 (t, J = 6.8 Hz, 6 H), 1.23−1.46 (m, 12 H), 1.68 (quint, J = 7.8 Hz, 4 H), 2.70 (t, J = 7.8 Hz, 4 H), 7.34 (d, J = 8.3 Hz, 4 H), 7.62 (d, J = 8.3 Hz, 4 H), 7.67 (dd, J = 1.5, 8.3 Hz, 2 H), 8.26 (d, J = 1.5 Hz, 2 H), 8.27 (d, J = 8.3 Hz, 2 H); ^{13}C NMR (CDCl$_3$) δ 14.1, 20.6, 29.0, 31.4, 31.7, 35.7, 122.4, 127.2, 128.1, 129.2, 129.7, 131.2, 136.2, 136.8, 144.3, 148.8, 180.1; FAB-MS (positive, NBA) m/z 529 [(M + 1)$^+$]. Anal. Calcd for $C_{38}H_{40}O_2$ (528.72): C, 86.32; H, 7.63. Found: C, 86.11; H, 7.59.

3,6-Bis(4-octylphenyl)-9,10-phenanthrenequinone (4c). Yellow powder: mp 157−158 °C; IR (KBr, cm^{-1}) 3023, 2956, 2925, 2853, 1671 ($\nu_{C=O}$), 1593, 1391, 1316, 1297, 1237, 1188, 927, 841, 811; ^{1}H NMR (CDCl$_3$) δ 0.90 (t, J = 6.8 Hz, 6 H), 1.23−1.42 (m, 20 H), 1.67 (quint, J = 7.8 Hz, 4 H), 2.67 (t, J = 7.8 Hz, 4 H), 7.35 (d, J = 8.3 Hz, 4 H), 7.63 (d, J = 8.3 Hz, 4 H), 7.69 (dd, J = 1.5, 8.3 Hz, 2 H), 8.26 (d, J = 1.5 Hz, 2 H), 8.28 (d, J = 8.3 Hz, 2 H); ^{13}C NMR (CDCl$_3$) δ 14.1, 22.7, 29.2, 29.3, 29.5, 31.4, 31.9, 35.7, 122.4, 127.7, 128.1, 129.3, 129.7, 131.2, 136.2, 136.8, 144.3, 148.8, 180.1; FAB-MS (positive, NBA) m/z 585 [(M + 1)$^+$]. Anal. Calcd for $C_{42}H_{48}O_2$ (584.83): C, 86.26; H, 8.27. Found: C, 85.88; H, 8.22.

3,6-Bis(4-octyloxylphenyl)-9,10-phenanthrenequinone (4d). Yellow powder; mp 110−112 °C; IR (KBr, cm^{-1}) 3069, 3054, 2954, 2922, 2851, 1659 ($\nu_{C=O}$), 1591, 1519, 1309, 1244, 1185, 824; ^{1}H NMR (CDCl$_3$) δ 0.90 (t, J = 6.8 Hz, 6 H), 1.25−1.43 (m, 16 H), 1.49 (quint, J = 6.8 Hz, 4 H), 1.83 (quint, J = 6.8 Hz, 4 H), 4.04 (t, J = 6.8 Hz, 4 H), 7.05 (d, J = 8.8 Hz, 4 H), 7.65 (dd, J = 1.5, 8.3 Hz, 2 H), 7.65 (d, J = 8.8 Hz, 4 H), 8.22 (d, J = 1.5 Hz, 2 H), 8.25 (d, J = 8.3 Hz, 2 H); ^{13}C NMR (CDCl$_3$) δ 14.1, 22.7, 26.0, 29.22, 29.24, 29.4, 31.8, 68.3, 115.2, 121.9, 127.7, 128.6, 129.4, 131.2, 131.6, 136.2, 148.4, 160.2, 180.1; FAB-MS (positive, NBA) m/z 617 [(M + 1)$^+$]. Anal. Calcd for $C_{42}H_{48}O_4$ (616.83): C, 81.78; H, 7.84. Found: C, 81.78; H, 7.82.

General Procedure for Preparation of 3,6,13,16,23,26-Hexakis(4-butylphenyl)-triphenanthro[9,10-*b*:9′,10′-*h*:9″,10″-*n*]-1,4,5,8,9,12-hexaazatriphenylene (6a). To a solution of **4a** (473 mg, 1.0 mmol) and crushed potassium carbonate (140 mg, 1.0 mmol) in dry ethanol (7.5 mL) and dry THF (15 mL) was added hexaaminobenzene trihydrochloride (**5**) (97 mg, 0.35 mmol), and the mixture was heated at the refluxing temperature for 19 h under an argon atmosphere. The reaction mixture was poured into water and extracted with chloroform. The organic layers was washed with brine and water, dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue (631 mg) was subjected to silica gel column chromatography (WAKO C300) eluting with chloroform to give crude product (285 mg). The crude product was purified by GPC eluting with chloroform to give **6a** in 12% yield (59 mg, 0.0399 mmol): viscous dark brown solid; mp >350 °C; IR (KBr, cm^{-1}) 3022, 2953, 2925, 2854, 1609, 1498, 1458, 1437, 1398, 1366, 1300, 1247, 1184, 1155, 823; ^{1}H NMR (CDCl$_2$CDCl$_2$, 120 °C) δ 1.19 (t, J = 7.3 Hz, 18 H), 1.65 (sept, J = 7.3 Hz, 12 H), 1.90 (quint, J = 7.3 Hz, 12 H), 2.88 (t, J = 7.3 Hz, 12 H), 7.37 (d, J = 6.8 Hz, 12 H), 7.66 (d, J = 6.8 Hz, 12 H), 7.83 (br-d, 6 H), 8.36 (br-s, 6 H), 9.26 (br-d, 6 H); ^{13}C NMR (CDCl$_2$CDCl$_2$, 120 °C) δ 14.1, 22.8, 33.9, 35.6, 120.5, 126.0, 127.0, 127.5, 129.0, 129.1, 131.9, 138.6, 140.6, 141.2, 141.4, 142.3; MALDI-TOF-MS (positive, dithranol) m/z 1476.90 (M$^+$, calcd for $C_{108}H_{96}N_6$, 1476.77). Anal. Calcd for $C_{108}H_{96}N_6 \cdot 0.2CHCl_3$ (1477.96): C, 86.53; H, 6.46; N, 5.60. Found: C, 86.46; H, 6.55; N, 5.72.

3,6,13,16,23,26-Hexakis(4-hexylphenyl)triphenanthro[9,10-*b*:9′,10′-*h*:9″,10″-*n*]-1,4,5,8,9,12-hexaazatriphenylene (6b). Viscous dark brown solid; mp >350 °C; IR (KBr, cm^{-1}) 3022, 2954, 2925, 2853, 1609, 1498, 1457, 1436, 1397, 1366, 1301, 1249, 1184, 1155, 817; ^{1}H NMR ($CDCl_2CDCl_2$, 120 °C) δ 1.11 (t, J = 7.3 Hz, 18 H), 1.35−1.72 (m, 36 H), 1.92 (quint, J = 7.3 Hz, 12 H), 2.86 (t, J = 7.3 Hz, 12 H), 7.35 (d, J = 7.3 Hz, 12 H), 7.62 (d, J = 7.3 Hz, 12 H), 7.77 (br-d, 6 H), 8.28 (br-s, 6 H), 9.15 (br-d, 6 H); ^{13}C NMR ($CDCl_2CDCl_2$, 120 °C) δ 14.2, 22.9, 29.5, 31.4, 32.1, 36.0, 120.5, 126.0, 127.1, 127.5, 128.9, 129.1, 132.0, 138.5, 140.8, 141.3, 141.5, 142.4; MALDI-TOF-MS (positive, dithranol) m/z 1645.08 (M^{+}, calcd for $C_{120}H_{120}N_6$, 1644.96). Anal. Calcd for $C_{120}H_{120}N_6 \cdot 0.1CHCl_3$ (1646.28): C, 86.99; H, 7.30; N, 5.07. Found: C, 87.02; H, 7.28; N, 5.09.

3,6,13,16,23,26-Hexakis(4-octylphenyl)triphenanthro[9,10-*b*:9′,10′-*h*:9′′,10′′-*n*]-1,4,5,8,9,12-hexaazatriphenylene (6c). Viscous dark brown solid; mp >350 °C; IR (KBr, cm^{-1}) 3023, 2955, 2925, 2853, 1610, 1514, 1499, 1466, 1437, 1400, 1368, 1302, 1250, 1185, 1156, 824; ^{1}H NMR ($CDCl_2CDCl_2$, 120 °C) δ 1.07 (t, J = 6.3 Hz, 18 H), 1.34−1.77 (m, 60 H), 1.90 (quint, J = 7.8 Hz, 12 H), 2.85 (t, J = 7.8 Hz, 12 H), 7.33 (br-d, 12 H), 7.59 (br-d, 12 H), 7.74 (br-d, 6 H), 8.23 (br-s, 6 H), 9.09 (br-d, 6 H); ^{13}C NMR ($CDCl_2CDCl_2$, 120 °C) δ 14.1, 22.8, 29.5, 29.8, 29.9, 31.5, 32.2, 36.0, 120.7, 126.3, 127.2, 127.6, 129.0, 129.7, 132.2, 138.5, 141.0, 141.6, 142.1, 142.5; MALDI-TOF-MS (positive, dithranol) m/z 1813.53 (M^{+}, calcd for $C_{132}H_{144}N_6$, 1813.15). Anal. Calcd for $C_{132}H_{144}N_6$ (1814.60): C, 87.37; H, 8.00; N, 4.63. Found: C, 87.15; H, 8.00; N, 4.67.

3,6,13,16,23,26-Hexakis(4-octyloxyphenyl)triphenanthro-[9,10-*b*:9′,10′-*h*:9′′,10′′-*n*]-1,4,5,8,9,12-hexaazatriphenylene (6d). Viscous dark brown solid; mp >350 °C; IR (KBr, cm^{-1}) 3036, 2952, 2925, 2854, 1606, 1514, 1499, 1472, 1367, 1246, 1179, 823; ^{1}H NMR ($CDCl_2CDCl_2$, 120 °C) δ 1.07 (t, J = 6.8 Hz, 18 H), 1.40−1.63 (m, 48 H), 1.71 (quint, J = 6.8 Hz, 12 H), 2.01 (quint, J = 6.8 Hz, 12 H), 4.17 (t, J = 6.8 Hz, 12 H), 7.08 (d, J = 8.3 Hz, 12 H), 7.63 (d, J = 8.3 Hz, 12 H), 7.77 (br-d, 6 H), 8.28 (br-s, 6 H), 9.17 (br-d, 6 H); ^{13}C NMR ($CDCl_2CDCl_2$, 120 °C) δ 14.1, 22.8, 26.5, 29.5, 29.7, 29.9, 32.1, 68.9, 115.5, 120.0, 125.9, 127.1, 128.6, 128.9, 132.0, 133.6, 141.0, 141.3, 141.4, 159.5; MALDI-TOF-MS (positive, dithranol) m/z 1909.31 (M^{+}, calcd for $C_{132}H_{144}N_6O_6$, 1909.11). Anal. Calcd for $C_{132}H_{144}N_6O_6 \cdot 0.1CHCl_3$ (1910.59): C, 82.53; H, 7.55; N, 4.37. Found: C, 82.40; H, 7.63; N, 4.32.

2,9-Dibromo-1,10-phenanthroline (11). A mixture of **10** (2.38 g, 9.55 mmol) in phosphorus tribromide (14.5 mL, 154 mmol) was heated at 170 °C for 5.5 h under an argon atmosphere. After the reaction mixture was cooled to room temperature, it was quenched by addition of cold water and neutralized with sodium hydrogencarbonate. The formed solid was collected by filtration and washed with water and methanol. The solid (2.63 g) was purified by recrystallization from chloroform to give **11** in 74% yield (2.40 g, 7.09 mmol) as white powder: mp 225−227 °C; IR (KBr, cm^{-1}) 3041, 1588, 1573, 1546, 1471, 1439, 1408, 1343, 1243, 1123, 1112, 1063, 878, 849, 786, 726, 621, 601, 573, 548; ^{1}H NMR ($CDCl_3$) δ 7.80 (d, J = 8.3 Hz, 2 H), 7.83 (s, 2 H), 8.09 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 126.5, 127.9, 128.5, 138.2, 143.1, 145.5; FAB-MS (positive, NBA) m/z 337, 339, 341 [1:2:1, (M + 1)$^{+}$]. Anal. Calcd for $C_{12}H_6Br_2N_2$ (335.89): C, 42.64; H, 1.79; N, 8.29. Found: C, 42.71; H, 1.87; N, 8.34.

2,9-Dibromo-1,10-phenanthroline-5,6-dione (12). To a mixture of **11** (2.34 g, 6.91 mmol) and KBr (8.29 g, 69.1 mmol) was added dropwise concd sulfuric acid (28 mL) along the vessel wall at 0 °C. Then concd nitric acid (14 mL) was added dropwise along the vessel wall at 0 °C. The mixture was heated at 80 °C for 3 h. After the reaction mixture was cooled to 0 °C, it was poured slowly into ice water and neutralized with saturated sodium hydrogencarbonate aqueous solution. The formed precipitate was collected by filtration and washed with water and methanol to give **12** in 67% yield (1.71 g, 4.64 mmol) as pale yellow powder. An analytical sample obtained by GPC eluting with chloroform. Mp 252−254 °C; IR (KBr, cm^{-1}) 3071, 1693 ($\nu_{C=O}$), 1601, 1561, 1436, 1356, 1296, 1234, 1122, 1108, 1076, 1012, 922, 856, 842, 745, 566; ^{1}H NMR ($CDCl_3$,) δ 7.79 (d, J = 8.3 Hz, 2 H), 8.30 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 127.1. 131.1, 138.9, 150.7, 152.2, 177.5; FAB-MS (positive, NBA) m/z 367, 369, 371 [1:2:1, (M + 1)$^{+}$]. Anal. Calcd for $C_{12}H_4Br_2N_2O_2$ (365.86): C, 39.17; H, 1.10; N, 7.61. Found: C, 38.91; H, 1.18; N, 7.43.

2,9-Bis(4-butylphenyl)-1,10-phenanthroline-5,6-dione (13a). Pale orange solid; mp 186−188 °C; IR (KBr, cm^{-1}) 3060, 3029, 2956, 2927, 2857, 1675 ($\nu_{C=O}$), 1571, 1515, 1462, 1442, 1371, 1325, 1181, 924, 829, 768; ^{1}H NMR (400 MHz) δ 0.97 (t, J = 7.3 Hz, 6 H), 1.41 (sext, J = 7.3 Hz, 4 H), 1.68 (quint, J = 7.3 Hz, 4 H), 2.74 (t, J = 7.3 Hz, 4 H), 7.42 (d, J = 8.3 Hz, 4 H), 8.00 (d, J = 8.3 Hz, 2 H), 8.31 (d, J = 8.3 Hz, 4 H), 8.53 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.3, 33.4, 35.6, 121.0, 126.5, 127.9, 129.3, 135.1, 137.9, 146.6, 153.1, 162.9, 178.9; FAB-MS (positive, NBA) m/z 475 [(M + 1)$^{+}$]. Anal. Calcd for $C_{32}H_{30}N_2O_2$ (474.23): C, 80.98; H, 6.37; N, 5.90; Found: C, 80.68; H, 6.34; N, 5.85.

2,9-Bis(4-octylphenyl)-1,10-phenanthroline-5,6-dione (13b). Yellow needles; mp 134−135 °C; IR (KBr, cm^{-1}) 3061, 3029, 2956, 2925, 2852, 1671 ($\nu_{C=O}$), 1570, 1462, 1442, 1374, 1325, 1181, 1094, 925, 829, 768; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 6.8 Hz, 6 H), 1.21−1.39 (m, 10 H), 1.69 (quint, J = 7.3 Hz, 4 H), 2.71 (t, J = 7.3 Hz, 4 H), 7.38 (d, J = 8.4 Hz, 4 H), 8.01 (d, J = 8.1 Hz, 2 H), 8.32 (d, J = 8.4 Hz, 4 H), 8.54 (d, J = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 29.25, 29.29, 29.5, 31.2, 31.9, 35.9, 120.9, 126.4, 127.9, 129.2, 135.1, 137.8, 146.6, 153.0, 162.9, 178.9; FAB-MS (positive, NBA) m/z 587 [(M + 1)$^{+}$]. Anal. Calcd for $C_{40}H_{46}N_2O_2$ (586.81): C, 81.87; H, 7.90; N, 4.77. Found: C, 81.78; H, 7.86 ; N, 4.74.

2,9-Bis(4-octyloxyphenyl)-1,10-phenanthroline-5,6-dione (13c). Pale orange solid; mp 143−144 °C; IR (KBr, cm^{-1}) 3020, 2922, 2852, 1671 ($\nu_{C=O}$), 1605, 1571, 1511, 1467, 1445, 1373, 1328, 1251, 1173, 826; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J = 6.8 Hz, 6 H), 1.27−1.42 (m, 12 H), 1.47−1.60 (m, 8 H), 1.85 (quint, J = 6.8 Hz, 4 H), 4.09 (t, J = 6.8 Hz, 4 H), 7.10 (d, J = 9.0 Hz, 4 H), 7.95 (d, J = 8.3 Hz, 2 H), 8.36 (d, J = 9.0 Hz, 4 H), 8.50 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 22.0, 29.22, 29.24, 29.4, 31.8, 68.3, 115.0, 120.2, 126.0, 129.5, 130.0, 137.7, 153.0, 161.9, 162.3, 178.8; FAB-MS (positive, NBA) m/z 619 [(M + 1)$^{+}$]. Anal. Calcd for $C_{40}H_{46}N_2O_4$ (618.35): C, 77.64; H, 7.49; N, 4.53; Found: C, 77.28; H, 7.38; N, 4.50.

3,6,13,16,23,26-Hexakis(4-butylphenyl)tri-1,10-phenanthrolino-[5,6-*b*:5′,6′-*h*:5′′,6′′-*n*]-1,4,5,8,9,12-hexaazatriphenylene (14a). Dark brown solid; mp >350 °C; IR (KBr, cm^{-1}) 3061, 3025, 2954, 2926, 2856, 1582, 1568, 1490, 1369, 1282, 1219, 1180, 1158, 1017, 829, 769; ^{1}H NMR (CD_2Cl_2:CF_3COOD, 9:1 (v/v)) δ 1.04 (t, J = 7.8 Hz, 18 H), 1.49 (sext, J = 7.8 Hz, 12 H), 1.79 (quint, J = 7.8 Hz, 12 H), 2.90 (t, J = 7.8 Hz, 12 H), 7.72 (d, J = 7.3 Hz, 12 H), 8.35 (d, J = 7.3 Hz, 12 H), 8.94 (br-d, 6 H), 10.59 (br-d, 6 H); ^{13}C NMR (CD_2Cl_2/CF_3COOD, 9:1 (v/v)) δ 14.1, 22.8, 33.7, 36.1, 126.0, 127.8, 128.6, 130.7, 131.0, 139.8, 141.0, 141.4, 144.2, 150.6, 158.7; MALDI-TOF-MS (positive, dithranol) m/z 1482.20 (M^{+}, calcd for $C_{102}H_{90}N_{12}$, 1482.74). Anal. Calcd for $C_{102}H_{90}N_{12} \cdot 0.1CHCl_3$ (1483.89): C, 82.27; H, 6.09; N, 11.28. Found: C, 82.02; H, 6.21; N, 11.08.

3,6,13,16,23,26-Hexakis(4-octylphenyl)-tri-1,10-phenanthrolino-[5,6-*b*:5′,6′-*h*:5′′,6′′-*n*]-1,4,5,8,9,12-hexaazatriphenylene (14b). Brown solid; mp >350 °C; IR (KBr, cm^{-1}) 3060, 3026, 2924, 2852, 1582, 1568, 1491, 1426, 1369, 1282, 1219, 1178, 1158, 1017, 830, 769; ^{1}H NMR (CD_2Cl_2:CF_3COOD, 9:1 (v/v)) δ 0.82 (t, J = 6.8 Hz, 18 H), 1.10−1.37 (m, 60 H), 1.70 (quint, J = 7.8 Hz, 12 H), 2.79 (t, J = 7.8 Hz, 12 H), 7.61 (d, J = 6.8 Hz, 12 H), 8.25 (d, J = 6.8 Hz, 12 H), 8.84 (br-d, 6 H), 10.50 (br-d, 6 H); ^{13}C NMR (CD_2Cl_2/CF_3COOD, 9:1 (v/v)) δ 14.2, 23.1, 29.7, 29.8, 29.9, 31.6, 32.3, 36.5, 125.9, 127.8, 128.6, 130.7, 131.1, 139.8, 141.1, 141.3, 144.2, 150.8, 158.8; MALDI-TOF-MS (positive, dithranol) m/z 1819.13 (M^{+}, calcd for $C_{126}H_{138}N_{12}$, 1819.12). Anal. Calcd for $C_{126}H_{138}N_{12}\cdot 0.1CHCl_3$ (1820.52): C, 82.65; H, 7.60; N, 9.17. Found: C, 82.39; H, 7.43; N, 9.07.

3,6,13,16,23,26-Hexakis(4-octyloxyphenyl)-tri-1,10-phenanthrolino[5,6-*b*:5′,6′-*h*:5″,6″-*n*]-1,4,5,8,9,12-hexaazatriphenylene (14c). To a solution of **13c** (118 mg, 0.20 mmol) in dearerated acetic acid (3 mL) was added hexaaminobenzene trihydrochloride (**5**) (21 mg, 0.076 mmol), and the mixture was heated at refluxing temperature for 12.5 h under an argon atmosphere. The reaction mixture was poured into water and extracted with chloroform. The organic layer was washed with 2 M sodium carbonate aqueous solution and water, dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue (98 mg) was subjected to silica gel column chromatography (WAKO C300) eluting with chloroform to give crude product (69 mg). The crude product was purified by GPC eluting with chloroform to give **14c** in 41% yield (52 mg, 0.027 mmol) as a dark brown solid: mp >350 °C; IR (KBr, cm^{-1}) 3066, 3040, 2924, 2853, 1607, 1571, 1510, 1491, 1472, 1370, 1307, 1285, 1250, 1217, 1172, 826, 772; ^1H NMR (CD_2Cl_2:CF_3COOD, 9:1 (v/v)) δ 0.95 (t, $J = 6.8$ Hz, 18 H), 1.37−1.59 (m, 60 H), 1.95 (quint, $J = 6.8$ Hz, 12 H), 4.27 (t, $J = 6.8$ Hz, 12 H), 7.40 (d, $J = 7.3$ Hz, 12 H), 8.41 (d, $J = 7.3$ Hz, 12 H), 8.88 (br-d, 6 H), 10.54 (br-d, 6 H); ^{13}C NMR (CD_2Cl_2:CF_3COOD, 9:1 (v/v)) δ 14.3, 23.1, 23.4, 29.5, 29.7, 29.8, 32.3, 69.6, 116.9, 124.6, 125.0, 126.7, 130.3, 139.4, 140.5, 140.6, 143.6, 157.7, 164.7; MALDI-TOF-MS (positive, dithranol) *m*/*z* 1915.56 (M^+, calcd for $C_{126}H_{138}N_{12}O_6$, 1915.09). Anal. Calcd for $C_{126}H_{138}N_{12}O_6\cdot 0.1CHCl_3$ (1916.52): C, 78.54; H, 7.22; N, 8.72. Found: C, 78.48; H, 7.07; N, 8.85.

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Supporting Information Available: ^1H NMR, UV−vis, fluorescence, MALDI-TOF-MS, cyclic voltammograms, AFM, X-ray diffraction, and general experimental procedures. This material is available free of charge via Internet at http://pubs.acs.org.