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Tetraalkoxyphenanthrene-Fused Thiadiazoloquinoxalines: Synthesis, Electronic, Optical, and Electrochemical Properties, and Self-Assembly

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Abstract: π -Extended thiadiazoloquinoxaline (TQ) derivatives **1a,b–3a,b**, in which a tetraalkoxyphenanthrene moiety is annulated with the TQ core and benzene rings are incorporated via the ethynylene spacer, were synthesized. They display absorption bands reaching into 750 nm

and possess the electron-affinity comparable to [60]fullerene. The CF₃- and OMe-substituents on the benzene rings have moderate effects on modulation of the HOMO and LUMO levels. Tetraalkoxyphenanthrene-fused TQs **1a,b–3a,b** aggregate in the solid state and assemble in solution through π - π stacking interactions. The self-assembly of **1a,b–3a,b** into 1D superstructures was confirmed, and the difference in the alkoxy groups and the solvents for self-assembly proved to change their morphology. Comparison of the properties of **1a** and those of reference compounds **4** and **5** clarified the effects of both the fusion of the phenanthrene moiety and the introduction of ethynylene spacers on the properties.

Keywords: thiadiazoloquinoxaline $\cdot \pi - \pi$ interactions \cdot self-assembly \cdot alkyne \cdot phenanthrene

Introduction

The field of π -conjugated materials has recently gained significant importance because of their potential utility in future-generation electronic devices such as organic photovoltaics (OPVs), organic light-emitting diodes (OLEDs), and organic field-effect transistors (OFETs).¹ In the molecular design, it is important to control both the electronic structure and the solid-state structure of π -conjugated molecules appropriately to achieve optimal function of the above mentioned devices.² As a consequence, polycyclic aromatic hydrocarbons (PAHs) were extensively studied over the years,³ because they tend to show intriguing photophysical and electrochemical properties (*e.g.* strong fluorescence and multistep redox behavior) and form a dense molecular packing due to their planar and rigid π -frameworks. Among PAHs, oligoacenes with linearly annulated benzene units, in particular, pentacene and its derivatives have constituted important class of π -electron-rich materials.⁴ Although acenes are inherently susceptible to oxidative degradation,⁵ the incorporation

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of an alkynyl group efficiently enhances the oxidation stability,⁶ which enables them to be prominent examples of p-type semiconducting materials for high performance devices. The replacement of benzene rings with heteroaromatic rings in the acene framework is known to drastically change electronic properties. Azaacenes, which contain electron-deficient heteroaromatics such as pyridine or pyrazine rings, possess electron-accepting ability and thus have attracted considerable attention as promising candidates for n-type semiconducting materials.⁷

[1,2,5]Thiadiazolo[3,4-g]quinoxaline (TQ) is classified as an azaacene molecule with an o-quinoid structure.⁸ TQ possesses an outstanding electron-accepting ability due to the presence of electron-deficient thiadiazole and pyrazine rings,⁹ and has become one of the most important building blocks for the construction of π -functional materials.¹⁰ For instance, the embedding of electron-donating units at the 4- and 9-positions of TQ unit has been recognized as the useful approach to create compounds with low energy gap since the pioneering work by Yamashita and co-workers.^{9a} Very recently, Salleo, Andersson, and co-workers have synthesized alternating TQ-thiophene polymers with the extremely low energy gap of *ca*. 0.7 eV that is among the lowest value reported to date and disclosed that these polymers can function as active materials in OFETs and electrochromic devices.^{10f} Baumgarten and co-workers also reported analogous TQ-based semiconducting polymers, in which the TQ unit is connected to the thiophene unit via an ethynylene π -spacer, and demonstrated that the incorporation of the π -spacer allows for high planarity of the polymer backbone and thereby provokes the strong solid-state packing.^{10d}

The self-association behavior through effective π - π stacking interaction of π -conjugated molecules is one of the key factors for achieving their morphological organization and structural order at mesoscopic length scale by self-assembly.¹¹ In this context, extension of the conjugated framework by fusing aromatic systems into the TQ scaffold would be a rational design strategy to not

only modulate electronic structures but also bring about self-association properties in solution originating from an enlarged π -surface, because π - π stacking interaction is strongly associated with the size of the conjugated aromatic surface. Some TQ derivatives with extended fused π -systems have been synthesized by several research groups so far;¹² for instance, TQ derivatives incorporating triisopropylsilylethynyl groups were reported by Baumgarten and co-workers.^{12g} However, the elucidation of structure–property relationships of TQs with extended fused π -systems still remains as an important issue to give the guideline for the molecular design of TQ-based π -functional materials.^{12b} In addition, there is no report on self-association in TQs to the best of our knowledge, although the formation of 1D superstructures of TQs was demonstrated by Lee and co-workers.^{12c} It is considered that the lack of the self-association property of TQs in solution is mainly attributable to attached bulky substituents, which prevent the π -surfaces of the polycyclic molecules from approaching each other to guarantee the solubility.

Here, we present the synthesis of π -extended TQ derivatives **1a,b–3a,b** and their electronic, optical, and electrochemical properties and self-assembling behavior (Chart 1). Compounds **1a,b–3a,b** possess both large π -surface and high planarity due to the fusion of a tetraalkoxyphenanthrene moiety with the TQ scaffold and the introduction of ethynylene spacers between the TQ moiety and the benzene rings.¹³ We envisaged that tetraalkoxyphenanthrene-fused TQs **1a,b–3a,b** not only show self-association behavior in solution through π - π stacking interactions but also form self-assembled 1D superstructures by the interplay of π - π stacking interactions and van der Waals interactions stemming from the attached alkoxy chains.¹⁴ The effects of the substituents on the benzene rings (*i.e.* H-, CF₃-, and OMe-substituents) and the phenanthrene moiety (*i.e.* linear decyloxy and branched 2-ethylhexyloxy groups) on the overall properties of **1a,b–3a,b** are disclosed. We also focused our attention on elucidation of the effects of the phenanthrene moiety

 and the introduction of ethynylene spacers on the properties of the resulting molecules from the viewpoint of the structure–property relationships, and thus the comparison of the properties of **1a** with those of reference compounds **4** and **5** is reported.

Chart 1. π-Extended Thiadiazoloquinoxalines 1a,b–3a,b and Reference Compounds 4 and 5



Results and Discussion

Synthesis. The synthetic route of π -extended TQs **1a**,**b**–**3a**,**b** is outlined in Scheme 1. First, we investigated the condensation of 2,3,6,7-tetrakis(decyloxy)-9,10-dihydrophenanthrene-9,10-dione, **6a**.¹⁵ which obtained by oxidative cyclization of benzil with was 4,7-dibromo-2,1,3-benzothiadiazole-5,6-diamine $(7)^{16}$ in acetic acid under reflux to synthesize TQ 9a as a key intermediate (Table S1 in the Supporting Information), but the desired 9a was obtained in only 3% yield; the starting materials were recovered in ca. 90% even after 3 days. We then examined the alternative synthetic route of 9a. The condensation of 6a with diamine 7 in acetic acid gave 8a (Scheme 1). Then, the intramolecular oxidative cyclization of 8a by the treatment

with vanadium (V) oxitrifluoride was carried out in CH₂Cl₂ at room temperature, and gratifyingly we obtained 9a in 66% yield in two steps. In a similar manner, 9b was obtained in 46% yield in two steps from $6b^{17}$ via 8b. Such intramolecular cyclization was thought to be challenging because the electron-accepting TQ moiety would increase the oxidation potential which makes the oxidative cyclization hard to occur to some extent. The Pd-catalyzed Sonogashira coupling reaction between **9a,b** and the corresponding ethynylbenzene derivatives gave **1a,b–3a,b** in 3–38% yields; the consideration of the reaction conditions (e.g. Pd catalyst, reaction temperature, and reaction solvent) did not improve the product yields in our hands. The particularly low yield of 2a is attributed to the severely low solubility, which leads to the substantial loss of material. During the completion of the present work, Baumgarten and co-workers reported the efficient synthetic route of ethynylated TQ derivatives.^{12g,18} Whereas 1a-3a having linear decyloxy groups are soluble in only chlorinated solvents, 1b-3b having branched 2-ethylhexyloxy groups are readily soluble in various solvents such as acetone, toluene, and THF. The synthesis of 4 and 5 is shown in Schemes S1 and S2, respectively, in the Supporting Information.¹⁹





^{*a*} Reagents and conditions: (i) 4,7-dibromo-2,1,3-benzothiadiazole-5,6-diamine (7), AcOH, 80 °C; (ii) vanadium (V) oxitrifluoride, CH₂Cl₂, RT; (iii) ethynylbenzene, [Pd(PPh₃)₄], CuI, RT; (iv) 1-ethynyl-4-(trifluoromethyl)benzene, [Pd(PPh₃)₄], CuI, RT (for **2a**) or 0 °C (for **2b**), (v) 1-ethynyl-4-methoxybenzene, [Pd(PPh₃)₄], CuI, RT (for **3a**) or 0 °C (for **3b**).

Electronic and Optical Properties. In the electronic absorption spectra in CHCl₃ (Figure 1), 1a–3a displayed broad absorption bands reaching into 750 nm. Compounds 1b–3b showed almost the same spectra of the corresponding 1a–3a (Figure S5 in the Supporting Information).^{20,21} The longest absorption maximum (λ_{max}^{abs}) of 1a is red-shifted relative to those of 4 and 5 by 84 nm and 54 nm, respectively (654 nm (1a), 570 nm (4), 600 nm (5)), clearly indicating that combination of the fusion of the phenanthrene moiety with the TQ core and the introduction of ethynylene spacers between the TQ core and the benzene rings effectively extend π -conjugation in 1a. Considering that the λ_{max}^{abs} and the absorption onset (λ_{onset}) of 5 are red-shifted compared to the corresponding values of 4, the phenanthrene moiety may have a larger effect on the extension of π -conjugation in 1a than the ethynylene spacers. Whereas the λ_{max}^{abs} value of 2a is almost the same as that of 1a, the λ_{max}^{abs} value of 3a is apparently red-shifted relative to that of 1a (660 nm (2a), 684 nm (3a)).



Figure 1. Electronic absorption spectra of 1a–3a, 4, and 5 in CHCl₃ at RT.

We conducted density functional theory (DFT) calculations of 1'-5', where the decyloxy or 2-ethylhexyloxy groups in 1-5 were replaced with the methoxy groups, at the PBE0/6-31G(d) level to obtain further insight into the electronic properties.²² The optimized structure of 1' is highly planar, and thus the TQ moiety and the benzene rings attached to the TQ moiety via the ethynylene

spacer lie in the same plane (Figure S1).²³ The planarity of **4**' and **5**' is apparently lower than **1**'. Thus, in **4**' the dihedral angle between the dimethoxybenzene ring and the TQ moiety is 34° , and in **5**' the angle between the benzene ring and the TQ moiety is 46° (Figure S1); there exist steric repulsions between the two dimethoxybenzene rings in **4**' and between the benzene rings and the TQ moiety in **5**'. This finding indicates that the efficient extension of π -conjugation in **1** relative to **4** and **5** observed in the electronic absorption spectra is attributed to the high planarity together with the large conjugated framework in **1**.

Figure 2 shows the HOMOs and LUMOs of 1'-5'.²⁴ The HOMO of 1' is delocalized over the π -conjugated framework, whereas its LUMO is relatively localized in the TQ and ethynylene moieties. The HOMO of 4' has almost no contribution from the dimethoxybenzene rings. This manifests that the fusion of the phenanthrene moiety results in the effective π -conjugation in 1 compared to 4. The ethynylene spacers are found to enable both the HOMO and LUMO to be delocalized and thus extend π -conjugation in 1 relative to 5.

3.39 e\

2 95 6

2.94 eV

_2 89 e\/



50

51 52 53

54 55 56

57 58

59 60 and

5

is

not

clear

quinoxalinophenanthrophenazine derivatives.²⁶

at

present,

-5.23 eV

–5.32 eV

quantum yield (Φ_f) is 0.12.²⁵ This result suggests that the fluorescence quenching in 1–3 and 5 is

attributable to the phenanthrene moiety. Although the reason for the nonfluorescent nature of 1-3

similar fluorescence quenching is

9

in

observed

Electrochemical Properties. We first performed cyclic voltammetry (CV) experiments on **1**–**5** in *o*-dichlorobenzene (0.1 mol L^{-1} *n*Bu₄NPF₆, standard Fc⁺/Fc) to investigate their electrochemical properties (Figure S7). Compounds **1**–**5** showed two TQ-centered 1e⁻ reduction steps. The first and second reduction processes of the TQ derivatives are reversible or quasi-reversible in general; the second reduction process of **3a** is exceptionally irreversible. This illustrates that electrochemically generated anionic species of the present TQs are essentially stable. Whereas **5** showed one reversible 1e⁻ oxidation step, **1**–**4** displayed irreversible oxidation steps, indicating that the cationic species of **1**–**4** are unstable, and their instability comes from the ethynylene spacers.

We further conducted differential pulse voltammetry (DPV) measurements on 1–5 to determine their redox potentials, ionization potentials (IP), and electron affinity (EA) (Figure S8); DPV affords better sensitivity than CV and results in sharper peak onsets due to the sharper current response. As summarized in Table 1, the first reduction potential (E_{red}) of 1a is positively shifted as compared to those of 4 and 5 (-1.13 V (1a), -1.21 V (4), -1.34 V (5)), and the difference of the first E_{red} values of 1a and 5 is larger than that of 1a and 4. This result demonstrates that both the phenanthrene moiety and the ethynylene spacers effectively increase the electron-accepting ability, and the latter has the more marked effect than the former. The oxidation potential (E_{ox}) of 1a is negatively shifted relative to that of 4 and almost the same as that of 5 (0.63 V (1a), 0.75 V (4), 0.61 V (5)), indicating that the phenanthrene moiety exclusively increases the donor ability. The electrochemical HOMO–LUMO gap (ΔE_{redox}) of 1a is smaller than those of 4 and 5 (1.76 V (1a), 1.96 V (4), 1.95 V (5)), which is consistent with the finding that the λ_{max}^{abs} value of 1a is red-shifted relative to those of 4 and 5.

1 2 3 4 5 6 7 8 9 10	Τa) 1a- ΗC (Δ)
11 12 13 14 15	1:
16 17 18 19	2:
20 21 22 23	3:
23 24 25 26	4
27 28 29 30	5
31 32 33 34	C
35 36	a h
37	0.2
38 39	PB
40	me
41 42	pot
43	the
44 45	cor
45 46	Info
47	
48 49	

Table 1. Oxidation and Reduction Potentials, Ionization Potentials (IP), and Electron Affinity (EA) of la–3a, 4, and 5 by DPV in *o*-Dichlorobenzene (0.1 mol L⁻¹ *n*Bu₄NPF₆)^{*a*}, Theoretically Calculated HOMO and LUMO Levels,^{*b*} and Electrochemical (ΔE_{redox}),^{*c*} Theoretical (ΔE_{calcd}),^{*d*} and Optical Gaps ΔE_{opt})^{*e*}

	$E_{\rm ox}/{ m V}$	$E_{\rm red}/{\rm V}$	HOMO/eV ^b	LUMO/eV ^b	$\Delta E_{\rm redox}/{ m V}$	$\Delta E_{\text{calcd}}/\text{eV}$	$\Delta E_{\rm opt}/{\rm eV}$
	(IP/eV)	(EA/eV)					
1a	0.63	-1.13, -1.58	-5.21	-3.11	1.76	2.10	1.89
	(-5.86)	(-4.10)					
2a	0.72	-1.08, -1.50	-5.50	-3.39	1.80	2.11	1.87
	(-5.95)	(-4.15)					
3 a	0.48	-1.15, -1.62	-4.96	-2.95	1.63	2.01	1.81
	(-5.71)	(-4.08)					
4	0.75	-1.21, -1.72	-5.23	-2.94	1.96	2.29	2.17
	(-5.98)	(-4.02)					
5	0.61	-1.34, -1.89	-5.32	-2.89	1.95	2.43	2.06
	(-5.84)	(-3.89)					
C ₆₀		-1.08, -1.48	-6.33	-3.30			
		(-4.15)					

^{*a*} All potentials are given versus the Fc⁺/Fc couple used as external standard. Pulse width of 0.1 s in a period of 0.2 s. IP and EA were determined using a work-function value of -5.23 eV for Fc⁺/Fc. ^{*b*} Calculated by the PBE0/6-31G(d) level for **1**'-**5**', where the decyloxy or 2-ethylhexyloxy groups in **1**-**5** were replaced with the methoxy groups. ^{*c*} Electrochemical gap, ΔE_{redox} , is defined as the potential difference between the first oxidation potential and the first reduction potential. ^{*d*} Theoretical gap, ΔE_{calcd} , is defined as the energy difference between the HOMO and the LUMO calculated by the DFT method. ^{*e*} Optical gap, ΔE_{opt} , is defined as the energy corresponding to the longest λ_{max}^{abs} . The data for **1b**-**3b** are summarized in Table S14 in the Supporting Information.

When compared to **1a**, both the E_{ox} and E_{red} values of **2a** are positively shifted, and the values of **3a** are negatively shifted (Table 1), and thus the electron-accepting CF₃- and electron-donating OMe-substituents on the benzene rings were found to alter the redox potentials. The positive shift of the E_{ox} values from **1a** to **2a** is roughly similar to that of the first E_{red} values, while the negative shift of the E_{ox} values from **1a** to **3a** is more pronounced than that of the first E_{red} values. As a

consequence, the ΔE_{redox} value of **2a** becomes almost the same as that of **1a**, and the ΔE_{redox} value of **3a** becomes moderately smaller than that of **1a** (1.80 V (**2a**), 1.63 V (**3a**)).²⁷ These phenomena might be explained by the FMO plots of **2**' and **3**'. The CF₃-substituents in **2**' have almost no contribution to both the HOMO and LUMO (Figure 2b), and hence the CF₃-substituents are likely to stabilize the HOMO and LUMO to almost the same degree by the inductive effect. Although the OMe-substituents in **3**' have also almost no contribution to the LUMO as is the case with **2**', the noticeable contribution to the HOMO is observed (Figure 2c), and thus the OMe-substituents are considered to markedly destabilize the HOMO relative to the LUMO by the resonance effect.

A good correlation exists between the optical HOMO–LUMO gaps (ΔE_{opt}) estimated from the electronic absorption spectra and the ΔE_{redox} values in **1–5**. Noticeably, the electron affinity of **1–3** are comparable to that (–4.15 eV) of [60]fullerene (C₆₀), which is the benchmark of n-type organic semiconductor materials.²⁸

Aggregation Properties in the Solid State. We first investigated aggregation properties of 1–3 in the solid state by MALDI-TOF mass spectrometry. Besides the molecular ion peaks of 1–3, the peaks ascribed to their aggregated species were detected (Figures 3 and S9). For example, as shown in Figure 3, the peaks for 1a were seen at m/z 2326 and 3489, which correspond to the assemblies of two and three molecules, respectively, in addition to the parent ion (m/z 1163). This apparently illustrates the aggregation tendency of 1–3 in the solid state.





Figure 3. MALDI-TOF-MS spectrum of 1a (dithranol, positive).

Next, the electronic absorption spectra of the drop-casted films of **1–3** were measured (Figures 4 and S10). The λ_{\max}^{abs} values of **1–3** in the solid state are red-shifted compared with those in CHCl₃ solution by *ca*. 30–70 nm (Table S15), strongly supporting marked structural organization in the film by intermolecular π – π stacking interactions. The absorption bands in the region of 400–600 nm of **1a–3a** are broader than those of the corresponding **1b–3b**, suggesting that the aggregative nature of **1a–3a** is stronger than **1b–3b**, respectively, and thus the linear alkoxy chains in the former enable the neighboring molecules to come closer resulting in the stronger π – π stacking interactions than the branched alkoxy chains in the latter (*vide infra*).



Figure 4. Electronic absorption spectra of 3a in CHCl₃ (dashed line) and the drop-casted film (solid line) at RT.

Self-Association Properties in Solution. We measured ¹H NMR spectra of present TQs except for **2a** in CDCl₃ at various concentrations to investigate their self-association properties; the extremely low solubility of **2a** hampered the spectral measurements at a high concentration. The ¹H NMR signals of **1a,b**, **2b**, **3a,b**, and **5** in CDCl₃ were concentration dependent, and the aromatic signals shifted upfield upon increasing the concentration (Figures 5 and S11–S16); the upfiled shifts of the phenanthrene protons are particularly remarkable.^{29,30} Such shifts illustrate that they associate by π - π stacking interactions in CDCl₃, and thereby the aromatic protons are placed in the shielding regions produced by the neighboring aromatic rings. On the other hand, the aromatic signals of **4** were independent on concentration, indicating that there is almost no self-association occurring. The lack of self-association property of **4** should be attributed to its smaller π -plane than **1–3** and **5** and/or lower planarity than **1–3**.



Figure 5. ¹H NMR spectra of **1a** in CDCl₃ in various concentrations at RT. The small amount of impurity included in CDCl₃ is labeled with asterisk.

The diffusion constants (*D*) of **1a** proved to be almost independent on concentration by DOSY NMR experiments (Table S16), suggesting that a monomer–dimer equilibrium predominantly exists in a CHCl₃ solution of **1a**.³¹ Therefore, we determined association constants (K_{dim}) of **1a**,**b**, **2b**, **3a**,**b**, and **5** on the basis of a monomer–dimer model by nonlinear least-squares fitting of their

concentration-dependent ¹H NMR chemical shifts (Table 2).³² The K_{dim} value of **1a** is significantly higher than that of **5** (111 ± 2 mol⁻¹ L (**1a**), 15 ± 2 mol⁻¹ L (**5**)), clearly indicating that the ethynylene spacers enhance the planarity of the π -conjugated framework and thereby increase the self-association ability efficiently (*vide supra*). The lower K_{dim} value (11 ± 3 mol⁻¹ L) of **1b** than **1a** should derive from the sterically bulky 2-ethylhexyloxy groups in **1b**. Although the difference of the K_{dim} values among **1b**–**3b** seems insignificant, the higher self-association ability of **2b** than **1b** and **3b** is supported by the pronounced upfield shifts of the aromatic protons of **2b** as compared to **1b** and **3b** in the region of 0.006–3 mmol L⁻¹ (Figures S12, S13, and S15). This observation implicates that the CF₃-substituents have the electronic and/or steric effects on enhancement of π – π stacking interactions.³³

	$K_{\rm dim}/{ m L}~{ m mol}^{-1}$		$K_{\rm dim}/{ m L}~{ m mol}^{-1}$
1 a	$111~\pm~2$	1b	11 ± 3
2a	N.D. ^a	2b	38 ± 1
3a	138 ± 4	3 b	22 ± 4
4	$N.D.^b$	5	15 ± 2

Table 2. Self-Association Constants (K_{dim}) in CDCl₃ at RT Determined by ¹H NMR Spectroscopy

^a Not determined due to insolubility. ^b Almost no self-association.

We measured the electronic absorption spectra of **1a**,**b**, **2b**, and **3a**,**b** in CHCl₃ at various concentrations.³⁴ In the absorption spectra of **1a** and **3a**, upon increasing the concentration the ε values around 720–770 nm increased and those around 650–700 nm decreased with a quasi-isosbestic point (Figures 6 and S17). The concentration region (*ca*. 0.05–2 mmol L⁻¹) in which the absorption spectral changes of **1a** and **3a** arise is almost consistent with that in which the pronounced chemical shift changes for their aromatic protons occur in the ¹H NMR spectra described

above. Thus, it is reasonable to assume that the observed absorption spectral changes of **1a** and **3a** originate in their self-association behavior. Unlike **1a** and **3a**, the absorption spectra of **1b–3b** proved to be almost independent on the applied concentration. These results are in accordance with the finding that the K_{dim} values of **1a** and **3a** are higher than those of **1b–3b** as demonstrated by the ¹H NMR spectral measurements.³⁵



Figure 6. Electronic absorption spectra of 1a in CHCl₃ in various concentrations at RT.

To obtain insight into the structure of the self-assembled dimers of 1–3 in solution, we performed the DFT calculations for 1'–3'. Because 1'–3' have the dipole moments of 1.64 D, 2.20 D, and 0.41 D, respectively, from the thiadiazole ring to the pyrazine ring (PBE0/6-31G(d)), they are expected to form the dimers in an antiparallel manner, where the dipole moment should be canceled out. The optimization of the self-assembled dimers of 1'–3' based on this assumption gave the plausible structures, in which the TQ moiety is located above the phenanthrene moiety of the adjacent molecule in an offset arrangement (Figures 7 and S3).^{36,37} These optimized structures suggest that the shielding effect for the phenanthrene protons is more pronounced than that for the benzene protons and thus reasonably explain the fact that the phenanthrene protons show the greater upfield shifts than the benzene protons in the ¹H NMR spectra with increasing the concentration.



Figure 7. (a) Top and (b) side view of the plausible structure of self-assembled dimer of **1**' optimized at the PBE0/6-31G(d) level.

Moreover, we compared the HOMO–LUMO gaps of the self-assembled dimers of 1'-3' with those of the corresponding monomers by the DFT calculations (PBE0/6-31G(d)) to investigate the change in the electronic structures upon formation of the dimeric structures (Table S3). The

estimated HOMO–LUMO gaps of the dimers of 1'-3' are smaller than those of the corresponding monomers by 0.06–0.10 eV, which is consistent with the finding that the absorption onset of 1-3 in the electronic absorption spectra are red-shifted with increasing the concentration.³⁸ Overall, the experimental and theoretical results strongly support the formation of the dimers in an antiparallel manner upon self-association in solution.

Formation of Self-Assembled Structures. Because 1–3 show assembling properties in both the solid state and the solution, we expected the fabrication of micro- and nanometer-sized superstructures of 1–3 through self-assembly by phase transfer method with a mixed solvent system, in which the molecules in solution experience solubility change during a slow diffusion of a poor solvent into the solution, thus initiating the formation of self-assembled clusters.³⁹ To CHCl₃ solutions of 1a–3a, MeOH was slowly added.⁴⁰ The resulting mixtures were allowed to stand at 0 °C, and purple fibrous materials formed (Figure S19). To investigate the morphology of the materials obtained, we carried out SEM experiments, which confirmed the construction of well-defined structures from 1a–3a with high aspect ratio (Figure 8).⁴¹ Compounds 1a and 3a formed long 1D nanobelts with the length up to 100 μ m and the thicknesses of 100–500 nm (Figure 8a,c). Meanwhile, 2a provided more flexible nanofibers with narrower widths of about 30–80 nm (Figure 8b).



Figure 8. SEM images of self-assembled clusters of (a) 1a, (b) 2a, and (c) 3a obtained from CHCl₃/MeOH solvent system.

We also attempted to fabricate self-assembled structures of **1b–3b** in CHCl₃/MeOH solvent system, but higher solubility of **1b–3b** than **1a–3a** hampered the formation of precipitates. On the basis of the finding that the solubility of **1b–3b** in CH₂Cl₂ is somewhat lower than that in CHCl₃, we applied CH₂Cl₂/MeOH solvent system for **1b–3b**, which afforded the purple, fibrous materials.⁴² The SEM measurements confirmed the significant morphological difference, *i.e.* shape, size, and appearance, in the self-assembled clusters between **1a–3a** and **1b–3b**, respectively. Compounds **1b** and **3b** produced mictometer-sized 1D whiskers with a rough surface (Figure 9a,c), and the widths of

these clusters were non-uniform. Compound **2b** exhibited flexible globular morphology, which were entangled into complicated networks, with average widths of around 250 nm (Figure 9b). The difference of the alkoxy chains is considered to affect the degree and balance of intermolecular noncovalent interactions, namely π - π stacking interactions between the π -conjugated frameworks and van der Waals interactions between the alkoxy chains, as the driving force for self-assembly of **1a,b-3a,b**. Therefore, it is likely that the structural difference of the alkoxy chains in the phenanthrene moiety between **1a-3a** and **1b-3b** is responsible for the observed morphological difference, although the effect of the chlorinated solvents used on the morphology cannot be excluded at all. The result that the morphology of the clusters of **2a,b** markedly differed from that of **1a,b** and **3a,b** may stem from large hydrophobicity of the CF₃-substituents in **2a,b**.





Figure 9. SEM images of self-assembled clusters of (a) **1b**, (b) **2b**, and (c) **3b** obtained from CH₂Cl₂/MeOH solvent system.

Solvent is an important factor for molecular self-assembly in the solution-based process. We performed the fabrication of self-assembled clusters for **1b–3b** by replacement of the good solvent from CH₂Cl₂ to acetone; compounds **1a–3a** are almost insoluble in acetone.⁴³ The morphology of the self-assemblies of **1b–3b** formed in acetone/MeOH proved to be different from that formed in CH₂Cl₂/MeOH (Figure 10), and the morphological change was especially pronounced in **2b**. Thus, **1b–3b** formed 1D nanowhiskers, whose surfaces are markedly smooth, with widths of 250–350 nm. The observed morphological change depending on the solvents used may be associated with the facts

that acetone is a hydrophilic solvent, while CH₂Cl₂ is a hydrophobic one and/or the solubility of **1b–3b** in acetone is lower than that in CH₂Cl₂.⁴⁴



Figure 10. SEM images of self-assembled clusters of (a) 1b, (b) 2b, and (c) 3b obtained from acetone/MeOH solvent system.

The powder X-ray diffraction (PXRD) patterns of the self-assembled clusters of **1b–3b** obtained from CH₂Cl₂/MeOH and acetone/MeOH were recorded to examine the effect of the solvents for self-assembly on the molecular arrangements in the superstructures (Figure 11).⁴⁵ There are two

distinct 2θ regions where the characteristic reflection peaks are observable; one is the smaller angle region ($2\theta = ca. 4-7^{\circ}$) and the other is the larger angle region ($2\theta = ca. 23-30^{\circ}$). For the latter larger- 2θ region, the corresponding *d*-spacing values are ranging from 3.0 to 3.8 Å. Considering that the distance between a pair of π -conjugated frameworks in Figure 7 is estimable to be 3.4 Å, such larger- 2θ region surely contains the peak reflecting the $\pi-\pi$ stacking periodicity.⁴⁶ There are multiple peaks in this larger- 2θ region, but the strong peaks similarly locate around $2\theta = ca. 26^{\circ}$ for all the clusters of **1b–3b**, independent of used solvents.⁴⁷ A desirable agreement between the calculated *d*-spacing value and the estimated $\pi-\pi$ stacking distance supports our structural assignment discussed above. Thus, the commonality of the peaks at $2\theta = ca. 26^{\circ}$ corresponding to $\pi-\pi$ stacking periodicity for **1b–3b** indicates that the interaction between the π -conjugated frameworks is the key for the self-assembly of TQs prepared in this study.

The other smaller-2 θ reflections of the clusters of **1b**-**3b** also give us the valuable information for the effects of substituents attached to the benzene rings on the packing and stacking arrangement of the clusters because the peak appearances are characteristic in **1b**-**3b**. The strong peaks around 2θ = ca, 5° are observable for all the self-assembled clusters of **1b**-**3b**, independent of the used solvents. However, the peak shape is quite different, *i.e.*, the single peak for **1b**, the two peaks for **2b**, and the other lower-2 θ peaks are accompanied for **3b**. Among these peak features, the single peak for **1b** is basically understandable because it contains no substituent on the benzene rings. The corresponding *d*-spacing is 18 Å, which is attributable to the lateral dimension of the smallest unit of the cluster, namely, the self-assembled dimer as shown in Figure 7. The split peaks in **2b** and **3b** are likely to be due to the substituent effect. As expected from Figure 7, the substituents on the benzene rings in **2b** and **3b** should overlap with the 2-ethylhexyloxy groups on the phenanthrene moiety. The CF₃ group in **2b** is bulky and hydrophobic, and hence it is considered that the

repulsion between the CF₃ and 2-ethylhexyloxy groups occurs and partly separates the packing distance between a lateral pair of the clusters, giving the slight peak shift into the lower-2 θ side; a combination of original peak position and partial peak shift is ascribed to the characteristic peak split in **2b**. In the case of **3b**, the similar alkyl families of the OMe and 2-ethylhexyloxy groups are easily conjugated, which restricts the periodicity of lateral arrangement of the clusters, resulting in the remarkable intensity decrease of $2\theta = ca$. 5° peak. In turn, the strong peak newly appears around the further lower 2θ of *ca*. 4°, corresponding to *d*-spacing value of 22 Å. Perhaps, the OMe groups displace the parallel stacking of the cluster frameworks, and the resulting slip-off separates the lateral arrangement of the frameworks. The remarkable intensity decrease of the peaks at $2\theta = ca$. 5° is coincident with such slip-off arrangement model.

The solvents used remarkably affect the broadness of the above mentioned reflection peaks. The clusters of **1b**–**3b** obtained from CH₂Cl₂/MeOH gave moderately sharp peaks. The diffraction patterns of the clusters of **1b** and **2b** obtained from acetone/MeOH presented significantly broader peaks than those of **1b** and **2b** obtained from CH₂Cl₂/MeOH, respectively. This apparently indicates that the crystallinity of assembled **1b** and **2b** decreases upon changing a good solvent from CH₂Cl₂ to acetone. It is noticeable that unlike in cases of **1b** and **2b**, the cluster of **3b** obtained from CH₂Cl₂/MeOH in spite of the drastically different morphology depending on the solvents used. Thus, the cluster of **3b** possesses both uniform morphology and moderate crystallinity, although the reason for this finding is not clear at present. Overall, it is considered that the substituents on the benzene rings in **1b–3b** dominate the packing and stacking arrangement of the clusters in Å level. In contrast, the solvents for self-assembly play important roles in control over the crystallinity and morphology of their clusters in the nanometer scale.⁴⁸



Figure 11. PXRD patterns of superstructures of (a) **1b**, (b) **2b**, and (c) **3b** obtained from CH₂Cl₂/MeOH solvent system (black lines) or an acetone/MeOH solvent system (gray lines).

Conclusion

We have designed and synthesized π -extended thiadiazoloquinoxaline (TQ) derivatives **1a,b–3a,b**, in which the tetraalkoxyphenanthrene moiety is fused with the TQ core and the benzene rings are introduced via the ethynylene spacer, by oxidative transannular cyclization and Sonogashira coupling with ethynylarenes as key steps, and demonstrated their intriguing electronic, optical, and electrochemical properties and self-assembling behavior. The compounds in this work would be of interest as π -functional materials owing to their appealing properties, such as the light absorption up to 750 nm, the strong electron-accepting ability comparable to [60]fullerene, and the aggregation and self-association properties through π - π stacking interactions. By investigating the properties of **1a** and the reference compounds **4** and **5**, it can be concluded that the combination of the fusion of the phenanthrene moiety and the introduction of ethynylene spacers effectively extends π -conjugation and enhances the acceptor potency and the self-association ability. The substituents on the benzene rings proved to modulate the electronic properties moderately. Compounds **1a,b-3a,b** produced nano- and microscopic 1D self-assembled clusters with high aspect ratios, and the difference in the alkoxy groups on the TQ moiety and the solvents for self-assembly was found to influence the morphology of the clusters. We believe that the present study will provide a valuable guideline for the creation of TQ-based materials in organic electronics.

Experimental Section

Preparation of 4,7-dibromo-2,1,3-benzothiadiazole-5,6-diamine (7). To a solution of 4,7-dibromo-5,6-dinitro-2,1,3-benzothiadiazole (**10**) (1.00 g, 2.60 mmol) in acetic acid (15 mL) was added in small portions iron powder (1.76 g, 31.5 mmol) at 100 °C. After the mixture was stirred at 100 °C for 1.5 h, EtOH (4.0 mL) was added to the mixture. After the resulting mixture was heated for another 1.5 h, the precipitate was collected by filtration and washed with MeOH. The residue was extracted by Soxhlet's extractor with EtOAc for 3 days, and the extract was concentrated under reduced pressure to afford **7** (0.42 g, 1.30 mmol, 50%) as brown needles; the original procedure for purification was modified to obtain an analytically pure sample. The ¹H NMR data are in agreement with those previously reported.¹⁶ ¹H NMR (300 MHz, DMSO-*d*₆): δ 6.39 (4H, s).

Preparation of 9a. A mixture of **6a** (260 mg, 0.31 mmol) and **7** (100 mg, 0.31 mmol) in acetic acid (30 mL) was heated at 80 °C for 22 h. After addition of water (30 mL), the mixture was extracted with CH_2Cl_2 (15 mL × 3). The combined organic phase was washed with water (20 mL × 5), dried over anhydrous MgSO₄, and concentrated under reduced pressure. The residue was subjected to column chromatography (SiO₂; toluene/hexane 3:1) to afford crude **8a** as red solids containing inseparable impurities. To a solution of crude **8a** (0.31 g) in CH₂Cl₂ (20 mL) was added vanadium (V) oxytrifluoride (0.15 g, 1.21 mmol) in two portions in a period of 2 h at room temperature under an argon atmosphere. After the mixture. The organic phase was separated, and the aqueous phase

was extracted with CHCl₃ (50 mL × 4). The combined organic phase was washed with water (10 mL × 2), dried over anhydrous MgSO₄, and concentrated under reduced pressure. The residue was subjected to column chromatography (SiO₂; CH₂Cl₂/hexane 1:2), and the collected material was washed with hexane (20 mL) to afford **9a** (0.23 g, 0.21 mmol, 66% in two steps) as brown solids. An analytically pure sample was obtained by recycling GPC eluting with CHCl₃. M.p. 212–214 °C; ¹H NMR (500 MHz, CDCl₃, 40 °C): δ 7.84 (2H, s), 7.06 (2H, s), 4.12 (4H, t, *J* = 6.5 Hz), 4.00 (4H, t, *J* = 6.3 Hz), 1.97–1.88 (8H, m), 1.63–1.57 (8H, m), 1.52–1.35 (48H, m), 0.93 (6H, t, *J* = 7.0 Hz), 0.92 (6H, t, *J* = 7.0 Hz); ¹³C NMR (125 MHz, CDCl₃, 40 °C): δ 152.8, 151.3, 149.0, 144.1, 137.7, 127.4, 122.0, 112.6, 109.1, 106.1, 69.4, 68.6, 32.20, 32.18, 30.06, 30.00, 29.97, 29.91, 29.8, 29.65, 29.63, 26.55, 26.52, 22.9, 14.2 (25 signals out of 30 expected); UV–vis (CHCl₃): λ_{max}^{abs} (ε) 260 (38600), 282 (40000), 310 (50500), 476 (27200), 607 nm (sh, 2300); MALDI-TOF-MS (Dith, positive): *m/z* 1121.7 [(M + H)⁺]; anal. calcd for C₆₀H₈₈Br₂N₄O₄S: C, 64.27; H, 7.91; N, 5.00%, found: C, 64.09; H, 8.00; N, 4.96%.

Preparation of 9b. A mixture of **6b** (0.78 g, 1.08 mmol) and **7** (0.35 g, 1.08 mmol) in acetic acid (20 mL) was heated at 80 °C for 21 h. After addition of water (50 mL), the mixture was extracted with CH_2Cl_2 (20 mL × 3). The combined organic phase was washed with water (20 mL × 5), dried over anhydrous MgSO₄, and concentrated under reduced pressure. The residue was subjected to column chromatography (SiO₂; CH₂Cl₂/hexane 1:2) to afford crude **8b** as red solids containing inseparable impurities. To a solution of crude **8b** (0.84 g) in CH₂Cl₂ (20 mL) was added vanadium (V) oxytrifluoride (0.40 g, 3.23 mmol) in two portions in a period of 2 h at room temperature under an argon atmosphere. After the mixture was further stirred at room temperature for 5 h, aqueous citric acid (10%, 100 mL) was added to the mixture. The organic phase was separated, and the

aqueous phase was extracted with CHCl₃ (30 mL × 3). The combined organic phase was washed with water (20 mL × 2), dried over anhydrous MgSO₄, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂; CH₂Cl₂/hexane 1:3) and recrystallization from acetone/MeOH to afford **9b** (0.50 g, 0.50 mmol, 46% in two steps) as brown solids. An analytically pure sample was obtained by recycling GPC eluting with CHCl₃. M.p. 206–207 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.36 (2H, s), 7.42 (2H, s), 4.17 (4H, d, *J* = 5.6 Hz), 4.13 (4H, d, *J* = 5.6 Hz), 1.94–1.91 (4H, m), 1.71–1.39 (32H, m), 1.08 (6H, t, *J* = 7.6 Hz), 1.06 (6H, t, *J* = 7.6 Hz), 0.98 (6H, t, *J* = 7.0 Hz), 0.97 (6H, t, *J* = 7.0 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 153.6, 151.4, 149.5, 144.9, 138.1, 127.9, 122.2, 112.8, 109.4, 106.0, 71.7, 71.3, 39.8, 39.4, 30.93, 30.88, 29.42, 29.39, 24.2, 23.39, 23.30, 14.38, 14.33, 11.6, 11.5 (25 signals out of 26 expected); UV–vis (CHCl₃): λ_{max}^{abs} (ε) 261 (40100), 282 (42100), 311 (52700), 480 (28800), 607 nm (sh, 2200); MALDI-TOF-MS (Dith, positive): *m*/*z* 1008.2 (M⁺); anal. calcd for Cs₂H₇₂Br₂N₄O₄S: C, 61.90; H, 7.19; N, 5.55%, found: C, 61.83; H, 7.02; N, 5.48%.

Preparation of 1a. A suspension of **9a** (108 mg, 96.6 μ mol) in THF/Et₃N (8:1, 90 mL) was bubbled with argon with stirring for 30 min and **9a** was dissolved by heating at *ca.* 50–60 °C. The resulting solution was allowed to cool to room temperature, and ethynylbenzene (30 mg, 0.30 mmol), CuI (3 mg, 15 μ mol), and [Pd(PPh₃)4] (18 mg, 15 μ mol) were added to the solution. The resulting mixture was stirred at room temperature for 19 h under an argon atmosphere. CH₂Cl₂ (45 mL) was added to the mixture. The resulting mixture was filtered through a bed of silica gel, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂; toluene) to afford **1a** (17 mg, 15 μ mol, 15%) as purple solids. An analytically pure sample was obtained by recycling GPC eluting with CHCl₃. M.p. 201 °C (decomp.); ¹H NMR (600 MHz,

CDCl₃): δ 8.81 (2H, s), 7.87–7.86 (4H, m), 7.58 (2H, s), 7.45–7.44 (6H, m), 4.26 (4H, t, *J* = 5.4 Hz), 4.25 (4H, t, *J* = 5.1 Hz), 1.99–1.95 (4H, m), 1.92–1.87 (4H, m), 1.60–1.29 (56H, m), 0.90 (6H, t, *J* = 6.9 Hz), 0.89 (6H, t, *J* = 6.9 Hz); ¹³C NMR (150 MHz, CDCl₃, 50 °C): δ 153.8, 153.0, 149.5, 144.2, 141.4, 132.3, 128.9, 128.5, 127.8, 124.1, 123.4, 113.1, 109.5, 106.8, 105.2, 86.5, 69.7, 68.8, 32.2, 29.97, 29.94, 29.91, 29.89, 29.84, 29.75, 29.63, 29.61, 26.54, 26.45, 22.9, 14.2 (31 signals out of 36 expected); UV–vis (CHCl₃): λ_{max}^{abs} (ε) 265 (40700), 313 (52500), 323 (52500), 499 (21600), 646 (7100), 654 nm (7800); MALDI-TOF-MS (Dith, positive): *m/z* 1162.9 (M⁺); HR-FAB-MS (NBA, positive): *m/z* calcd for C₇₆H₉₈N4O4S⁺ 1162.7309, found 1162.7316 (M⁺).

Preparation of 1b. A solution of **9b** (100 mg, 99.1 μmol) in THF/Et₃N (8:1, 30 mL) was bubbled with argon with stirring for 30 min. Ethynylbenzene (40 mg, 0.40 mmol), CuI (4 mg, 20 μmol), and [Pd(PPh₃)₄] (23 mg, 20 μmol) were added to the solution at 0 °C. The resulting mixture was stirred at room temperature for 9 h under an argon atmosphere. CH₂Cl₂ (20 mL) was added to the mixture. The resulting mixture was filtered through a bed of silica gel, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂; EtOAc/hexane 1:19) and recrystallization from acetone/MeOH to afford **1b** (15 mg, 15 μmol, 15%) as purple solids. An analytically pure sample was obtained by recycling GPC eluting with CHCl₃. M.p. 155–156 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.84 (2H, s), 7.87–7.86 (4H, m), 7.61 (2H, s), 7.46–7.44 (6H, m), 4.18 (4H, d, *J* = 6.0 Hz), 4.16 (4H, d, *J* = 5.4 Hz), 1.93–1.89 (2H, m), 1.81–1.77 (2H, m), 1.66–1.30 (32H, m), 1.03 (6H, t, *J* = 7.5 Hz), 0.94 (12H, t, *J* = 7.2 Hz), 0.89 (6H, t, *J* = 6.9 Hz); ¹³C NMR (150 MHz, CDCl₃): δ 153.8, 153.5, 149.9, 144.7, 141.4, 132.2, 129.1, 128.6, 128.1, 123.7, 123.2, 113.1, 109.3, 106.3, 105.4, 86.0, 71.8, 70.9, 40.1, 39.8, 30.90, 30.83, 30.81, 29.44, 29.39, 24.18, 24.13, 23.28, 23.22, 14.3, 11.6 (31 signals out of 32 expected); UV–vis (CHCl₃): λ μmol³b.

(55800), 505 (23300), 653 nm (7100); MALDI-TOF-MS (Dith, positive): m/z 1050.7 (M⁺); HR-FAB-MS (NBA, positive): m/z calcd for C₆₈H₈₂N₄O₄S⁺ 1050.6057, found 1050.6055 (M⁺).

Preparation of 2a. A suspension of 9a (120 mg, 107 µmol) in THF/Et₃N (8:1, 120 mL) was bubbled with argon with stirring for 30 min and **9a** was dissolved by heating at *ca*. 50–60 °C. The resulting solution allowed cool temperature, and was to to room 1-ethynyl-4-(trifluoromethyl)benzene (57 mg, 0.33 mmol), CuI (3 mg, 15 µmol), and [Pd(PPh₃)₄] (18 mg, 15 µmol) were added to the solution. The resulting mixture was stirred at room temperature for 23 h under an argon atmosphere. CHCl₃ (60 mL) was added to the mixture. The resulting mixture was filtered through a bed of silica gel, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂; toluene) and reprecipitation from CH₂Cl₂/MeOH to afford **2a** (5 mg, 3 µmol, 3%) as purple solids. M.p. 203 °C (decomp.); ¹H NMR (300 MHz, CDCl₃, 50 °C): δ 8.63 (2H, s), 7.91 (4H, d, J = 8.1 Hz), 7.69 (4H, d, J = 8.1 Hz), 7.50 (2H, s), 4.23 (4H, t, J = 6.5 Hz), 4.17 (4H, t, J = 6.5 Hz), 2.01-1.83 (8H, m), 1.65-1.27 (56H, m),0.93–0.87 (12H, m); ¹³C NMR: Not available due to low solubility; UV–vis (CHCl₃): λ_{max}^{abs} (ε) 255 (38400), 312 (48500), 506 (22000), 628 (5700), 660 nm (sh, 5700); MALDI-TOF-MS (Dith, positive): *m/z* 1298.7 (M⁺); HR-FAB-MS (NBA, positive): *m/z* calcd for C₇₈H₉₆F₆N₄O₄S⁺ 1298.7056, found 1298.7055 (M⁺); anal. calcd for C₇₈H₉₆F₆N₄O₄S: C, 72.08; H, 7.45; N, 4.31%, found: C, 71.76; H, 7.31; N, 4.18%.

Preparation of 2b. A solution of **9b** (200 mg, 0.20 mmol) in THF/Et₃N (8:1, 50 mL) was bubbled with argon with stirring for 30 min. 1-Ethynyl-4-(trifluoromethyl)benzene (135 mg, 0.79 mmol), CuI (8 mg, 40 μ mol), and [Pd(PPh₃)₄] (46 mg, 40 μ mol) were added to the solution at 0 °C. The resulting mixture was stirred at 0 °C for 6 h under an argon atmosphere. CH₂Cl₂ (20 mL) was

added to the mixture. The resulting mixture was filtered through a bed of silica gel, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂; EtOAc/hexane 1:40) and recrystallization from acetone/MeOH to afford **2b** (42 mg, 35 µmol, 18%) as purple solids. An analytically pure sample was obtained by recycling GPC eluting with CHCl₃. M.p. 134–136 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.75 (2H, s), 7.95 (4H, d, *J* = 8.1 Hz), 7.71 (4H, d, *J* = 8.1 Hz), 7.58 (2H, s), 4.17 (4H, d, *J* = 5.7 Hz), 4.10 (4H, d, *J* = 4.8 Hz), 1.93–1.88 (2H, m), 1.80–1.76 (2H, m), 1.64–1.32 (32H, m), 1.03 (6H, t, *J* = 7.4 Hz), 0.97–0.89 (18H, m); ¹³C NMR (150 MHz, CDCl₃): δ 153.8, 153.7, 149.9, 145.0, 141.6, 132.3, 128.3, 127.3, 125.6, 125.6, 122.9, 112.8, 109.4, 106.2, 103.5, 87.9, 71.8, 71.0, 40.0, 39.7, 30.9, 30.8, 29.9, 29.37, 29.31, 24.15, 24.05, 23.3, 23.2, 14.30, 14.23, 11.6, 11.4; UV–vis (CHCl₃): λ_{max}^{abs} (ε) 255 (47200), 312 (60300), 506 (29000), 628 (6300), 660 nm (sh, 6500); MALDI-TOF-MS (Dith, positive): *m*/*z* 1186.7 (M⁺); HR-FAB-MS (NBA, positive): *m*/*z* calcd for C₇₀H₈₀F₆N₄O₄S⁺ 1186.5804, found 1186.5801 (M⁺).

Preparation of 3a. A suspension of **9a** (54 mg, 48 µmol) in THF/Et₃N (8:1, 40 mL) was bubbled with argon with stirring for 30 min and **9a** was dissolved by heating at *ca.* 50–60 °C. The resulting solution was allowed to cool to room temperature, and 1-ethynyl-4-methoxybenzene (16 mg, 0.12 mmol), CuI (1 mg, 6 µmol), and [Pd(PPh₃)₄] (7 mg, 6 µmol) were added to the solution. The resulting mixture was stirred at room temperature for 11 h under an argon atmosphere. CH₂Cl₂ (20 mL) was added to the mixture. The resulting mixture was filtered through a bed of silica gel, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂; toluene) to afford **3a** (17 mg, 14 µmol, 29%) as purple solids. An analytically pure sample was obtained by recycling GPC eluting with CHCl₃. M.p. 207 °C (decomp.); ¹H NMR (400 MHz, CDCl₃): δ 8.63 (2H, s), 7.76 (4H, dd, *J* = 2.0 & 8.8 Hz), 7.48 (2H, s),

6.94 (4H, dd, J = 2.0 & 8.8 Hz), 4.22 (4H, t, J = 5.6 Hz), 4.21 (4H, t, J = 5.8 Hz), 3.89 (6H, s), 1.97–1.90 (8H, m), 1.59–1.29 (56H, m), 0.92–0.88 (12H, m); ¹³C NMR (75 MHz, CDCl₃, 50 °C): δ 160.4, 153.6, 152.7, 149.3, 143.9, 141.1, 133.8, 127.6, 123.4, 116.4, 114.3, 112.9, 109.3, 106.6, 105.4, 85.8, 69.6, 68.7, 55.4, 32.2, 30.0, 29.9, 29.8, 29.6, 26.6, 26.5, 22.9, 14.2 (28 signals out of 37 expected); UV–vis (CHCl₃): λ_{max}^{abs} (ε) 266 (52700), 325 (61700), 449 (14200), 504 (21000), 650 (12100), 684 nm (13000); MALDI-TOF-MS (Dith, positive): m/z 1222.6 (M⁺); HR-FAB-MS (NBA, positive): m/z calcd for C₇₈H₁₀₂N₄O₆S⁺ 1222.7520, found 1222.7521 (M⁺).

Preparation of 3b. A solution of 9b (51 mg, 49 µmol) in THF/Et₃N (8:1, 30 mL) was bubbled with argon with stirring for 30 min. 1-Ethynyl-4-methoxybenzene (53 mg, 0.40 mmol), CuI (2 mg, 10 μ mol), and [Pd(PPh_3)_4] (12 mg, 10 μ mol) were added to the solution at 0 °C. The resulting mixture was stirred at 0 °C for 2 h under an argon atmosphere. CH₂Cl₂ (20 mL) was added to the mixture. The resulting mixture was filtered through a bed of silica gel, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂; EtOAc/hexane 1:3) and recrystallization from acetone/MeOH to afford **3b** (21 mg, 18 µmol, 38%) as purple solids. An analytically pure sample was obtained by recycling GPC eluting with CHCl₃. M.p. 139–141 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.79 (2H, s), 7.80 (4H, dd, J = 2.0 & 9.0 Hz), 7.59 (2H, s), 6.96 (4H, dd, J = 2.0 & 9.0 Hz, 4.17 (4H, d, J = 5.6 Hz), 4.16 (4H, d, J = 4.4 Hz), 3.89 (6H, s), 1.92–1.88 (2H, m), 1.82–1.79 (2H, m), 1.68–1.32 (32H, m), 1.04 (6H, t, *J* = 7.4 Hz), 0.96 (6H, t, *J* = 7.4 Hz), 0.94 (6H, t, J = 7.2 Hz), 0.89 (6H, t, J = 7.0 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 160.3, 153.6, 153.3, 149.7, 144.3, 141.2, 133.8, 127.9, 123.2, 115.9, 114.2, 112.9, 109.1, 106.1, 105.7, 85.4, 71.7, 70.9, 55.4, 40.1, 39.7, 30.88, 30.78, 29.43, 29.37, 24.1, 23.29, 23.25, 14.3, 11.65, 11.57 (31 signals out of 33 expected); UV-vis (CHCl₃): λ_{max}^{abs} (ε) 266 (52700), 325 (61700), 449 (14200), 504 (21100), 650 (12100), 684

nm (13000); MALDI-TOF-MS (Dith, positive): *m/z* 1110.9 (M⁺); HR-FAB-MS (NBA, positive): *m/z* calcd for C₇₀H₈₆N₄O₆S⁺ 1110.6268, found 1110.6263 (M⁺).

Preparation of 4: A mixture of 6a (26 mg, 31 µmol) and 7 (10 mg, 31 µmol) in acetic acid (10 mL) was heated at 80 °C for 22 h. After addition of water (30 mL), the mixture was extracted with CH₂Cl₂ (15 mL \times 3). The combined organic phase was washed with water (20 mL \times 5), dried over anhydrous MgSO₄, and concentrated under reduced pressure. The residue was subjected to column chromatography (SiO₂; toluene/hexane 3:1) to afford crude 8a as red solids containing inseparable impurities. A solution of crude 8a (30 mg) in THF/Et₃N (2:1, 30 mL) was bubbled with an argon with stirring for 30 min. Ethynylbenzene (13 mg, 0.12 mmol), CuI (1 mg, 6 µmol), and [Pd(PPh₃)₄] (7 mg, 6 µmol) were added to the mixture under an argon atmosphere. After the mixture was stirred at room temperature for 30 min, CH₂Cl₂ (15 mL) was added to the mixture. The resulting mixture was filtered through a bed of silica gel, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂; toluene) to afford 4 (9 mg, 8 µmol, 25% in two steps) as purple solids. An analytically pure sample was obtained by recycling GPC and reprecipitation from CH₂Cl₂/MeOH. M.p. 120–122 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.82–7.79 (4H, m), 7.58 (2H, d, J = 2.2 Hz), 7.43–7.42 (6H, m), 7.29 (2H, dd, J = 2.2 & 8.4 Hz), 6.82 (2H, d, J = 8.4 Hz, 4.04 (4H, t, J = 6.6 Hz), 3.95 (4H, t, J = 6.6 Hz), 1.89–1.81 (4H, m), 1.80–1.73 (4H, m), 1.52-1.27 (56H, m), 0.89 (6H, t, J = 7.2 Hz), 0.88 (6H, t, J = 7.0 Hz); ¹³C NMR (150 MHz, CDCl₃): δ 154.7, 154.1, 151.3, 149.0, 141.0, 132.3, 131.1, 129.3, 128.6, 124.1, 123.4, 115.3, 113.4, 112.5, 105.6, 85.3, 69.37, 69.27, 32.10, 32.08, 29.86, 29.80, 29.77, 29.61, 29.56, 29.53, 29.40, 29.36, 26.24, 26.20, 22.9, 14.3 (32 signals out of 36 expected); UV-vis (CHCl₃): λ_{max}^{abs} (ε) 313 (42900), 528 (17100), 570 nm (sh, 12800); MALDI-TOF-MS (Dith, positive): m/z 1164.8 (M⁺); HR-FAB-MS

(NBA, positive): *m*/*z* calcd for C₇₆H₁₀₀N₄O₄S⁺ 1164.7465, found 1164.7469 (M⁺).

Preparation of 5: To a solution of 5,6-dinitro-4,7-diphenyl-2,1,3-benzothiadiazole (11)⁴⁹ (120 mg, 0.32 mmol) in acetic acid (30 mL) was added iron powder (214 mg, 3.8 mmol) and the resulting suspension was heated at 80 °C for 3 h. After addition of water (50 mL), the resulting mixture was extracted with EtOAc (30 mL \times 3). The combined organic phase was washed with water (20 mL \times 3), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to afford crude 4,7-diphenyl-2,1,3-benzothiadiazole-5,6-diamine (12) as orange solids. A mixture of crude 12 (100 mg) and 2,3,6,7-tetrakis(decyloxy)-9,10-dihydrophenanthrene-9,10-dione (262 mg, 0.31 mmol) in acetic acid (60 mL) was heated at 80 °C for 14 h. After addition of water (50 mL), the mixture was extracted with CH₂Cl₂ (30 mL \times 3). The combined organic phase was washed with water (20 mL \times 5), dried over anhydrous MgSO₄, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂; toluene/hexane 5:1) to afford 5 (119 mg, 0.11 mmol, 34% in two steps) as dark green solids. An analytically pure sample was obtained by recycling GPC. M.p. 192–194 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.42 (2H, s), 8.15 (4H, dd, J = 1.2 & 7.8 Hz), 7.65 (4H, dd, J = 7.5 & 7.8 Hz), 7.56 (2H, dd, J = 1.2 & 7.5 Hz), 7.53 (2H, s), 4.21 (4H, t, J = 6.6 Hz), 4.10 (4H, t, J = 6.9 Hz), 1.96–1.91 (8H, m), 1.58–1.53 (8H, m), 1.47–1.28 (48H, m), 0.90 (6H, t, J = 6.9 Hz), 0.89 (6H, t, J = 6.9 Hz); ¹³C NMR (75 MHz, CDCl₃, 40 °C): δ 152.7, 152.5, 149.7, 143.6, 137.4, 135.9, 133.5, 129.1, 128.1, 127.5, 124.0, 109.9, 107.2, 70.0, 68.9, 32.1, 29.95, 29.86, 29.80, 29.75, 29.70, 29.60, 29.55, 26.3, 22.9, 14.2 (26 signals out of 34 expected); UV-vis (CHCl₃): λ_{max}^{abs} (ɛ) 258 (49700), 308 (56400), 460 (25200), 480 (sh, 23900), 600 nm (sh, 4000). MALDI-TOF-MS (Dith, positive): m/z 1114.6 (M⁺); HR-FAB-MS (NBA, positive): m/z calcd for C₇₂H₉₈N₄O₄S⁺ 1114.7309, found 1114.7302 (M⁺).

Supporting Information

General experimental methods, photophysical data, electrochemical data, theoretical data, MALDI-TOF-MS spectra, concentration-dependent ¹H NMR and UV–vis spectra, and GPC profiles and ¹H and ¹³C NMR spectra of new compounds (PDF)

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The authors declare no competing financial interest.

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- (19) Thermogravimetric analyses of 1–5 suggested that they would gradually decompose at over 300 °C under a nitrogen atmosphere (Table S12); however, 1a–3a decompose at *ca.* 200 °C under air.
- (20) The concentration of CHCl₃ solution for 1a,b-3a,b was $10^{-5} 10^{-6}$ mol L⁻¹. No deviation from the Lambert–Beer law was observed, indicating that the self-association of 1a,b-3a,b is negligible within the studied concentration range.
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- (23) Just like 1', the optimized structures of 2' and 3' are also planar.
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- (25) The fluorescence lifetime (τ_f) of **4** is determined to be 2.35 ns by the time-correlated single-photon counting method; the emission decay profile was numerically fitted by single exponential kinetics. The radiative (k_r) and nonradiative (k_{nr}) values were calculated to be 5.1 $\times 10^7 \text{ s}^{-1}$ and $37 \times 10^7 \text{ s}^{-1}$, respectively.
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- (28) Although the preliminary mobility tests on the spin-coated films of **1a**,**b** were tried by means of an FET method with a bottom contact configuration, neither n- nor p-type channel characteristic was observed unfortunately.
- (29) The DFT calculations for 1'-3' at the GIAO/PCM/WP04/6-31G(d)//PBE0/6-31G(d) level,

where solvation was taken into account by using the scrf = (solvent = chloroform) keyword, revealed that the singlet peaks in the high- and low-field regions are identified with the proton signals at the 4,5- and 1,8-positions of the phenanthrene moiety, respectively (Figure S2).

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- (34) We were not able to measure the absorption spectra of 2a at various concentrations due to its low solubility.
- (35) We also measured the absorption spectra of 1b-3b in acetone at various concentrations to investigate the effect of solvent polarity on the self-association. The spectral changes of 1b-3b in acetone are greater than those in CHCl₃ (Figure S18), implying that the solvophobic effect facilitates the self-association ability of 1b-3b in acetone relative to that in CHCl₃; however, we did not determine the association constants of 1b-3b in acetone.
- (36) The optimized structures of the self-assembled dimers for 1'-3' resemble each other.
- (37) The plausible stacked structures are very similar to the crystal packing structures of π -extended TQ derivatives synthesized by Baumgarten and co-workers [Ref. 12g].
- (38) We note that the distribution of the HOMOs and LUMOs of the dimers is different from that in the monomers (Figure S4), which is indicative of the orbital interactions in the self-assembled

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- (41) We prepared the self-assemblies of 1a, 2a, and 3a from CHCl₃/hexane solvent system. The SEM measurements showed that the morphology of the assemblies were almost independent of poor solvents (Figure S20); however, the widths of the nanofibers from 2a obtained by CHCl₃/hexane solvent system are *ca*. 20–30 nm, which are narrower than those obtained by CHCl₃/MeOH solvent system.
- (42) The precipitate of **1b–3b** formed by addition of 70–80 vol.% of MeOH to the corresponding CH₂Cl₂ solution (*ca.* 1 mg mL⁻¹).
- (43) The precipitate of **1b–3b** formed by addition of 40–50 vol.% of MeOH to the corresponding acetone solution (*ca.* 1 mg mL⁻¹).
- (44) For the morphological control by the solvents used, see: Nakanishi, T. *Chem. Commun.* 2010, 46, 3425.
- (45) The PXRD measurements for the clusters of **1a–3a** could not be conducted due to the insufficient amount of materials.
- (46) (a) Schmidt-Mende, L.; Fechtenkötter, A. F.; Müllen, K.; Moons, E.; Friend, R. H.; Mackenzie, J. D. Science 2001, 293, 1119. (b) Xiao, S.; Tang, J.; Beetz, T.; Guo, X.; Tremblay, N.; Siegrist, T.; Zhu, Y.; Steigerwald, M.; Nuckolls, C. J. Am. Chem. Soc. 2006, 128, 10700.
- (47) The assembled 1b, 2b, and 3b obtained from CH₂Cl₂/MeOH exhibited defined peaks at 23.5, 25.0, 26.2, and 27.3° (*d* spacing 3.8, 3.6, 3.4, and 3.3 Å), 23.7, 26.0, and 28.7° (*d* spacing 3.7, 26.0, and 28.7°).

3.4 and 3.1 Å), and 23.0 and 26.0° (*d* spacing 3.8 and 3.4 Å), respectively.

- (48) Baumgarten and co-workers have recently reported that the pseudo dimers formed by ethynylated TQs assemble in a brick wall packing style with slight vertical offset [Ref. 12g]. On the basis of this finding, the present TQs may also assemble in a similar packing style in their self-assembling clusters.
- (49) Kato, S.-i.; Furuya, T.; Nitani, M.; Hasebe, N.; Ie, Y.; Aso, Y.; Yoshihara, T.; Tobita, S.;
 Nakamura, Y. *Chem. Eur. J.* 2015, *21*, 3115.