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**Ruling chains:** A set of *n*-type conjugated molecules containing a tetraazaanthracene core and different alkyl-chain arms is presented. In binary solvent mixtures, self-assembly into 2D sheet-like nanostructures takes place (see picture). By using different alkyl chains, morphology can be sensibly modified. The weak interactions arising from the heteroatoms in the conjugated backbones play a key role in the formation and stabilization of the layered structures.



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Two-Dimensional Nanostructures by the Assembly of*n*-Type Tetraazaanthracene-Based Conjugated Molecules DOI: 10.1002/cphc.201300444

## Two-Dimensional Nanostructures by the Assembly of *n*-Type Tetraazaanthracene-Based Conjugated Molecules

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On the basis of our previous communication concerning a new family of thiophene-armed tetraazaanthracene molecules, we present a further intensive investigation on this class of compounds substituted with different alkyl chains and their self-assembled two-dimensional (2D) nanostructures. These tetraazaanthracene molecules with different alkyl chains were prepared in good yields using the synthetic strategy we developed. In addition to the expected typical *n*-type character, one compound exhibited aggregation behavior upon electrochemical reduction. Moreover, all molecules in the neutral state showed a strong tendency to aggregate in a binary solvent, as confirmed by optical spectral measurements. To investigate such self-assembly behavior, a phase-transfer method with a dichloromethane/methanol (2:3) binary solvent system was used to prepare the nanostructures. By means of atomic force microscopy, transmission electron microscopy, and X-ray diffraction, we found that the morphology of assembled 2D sheetlike structures could be adjusted by varying the alkyl chain. The weak interactions arising from the heteroatoms (N and S) in the conjugated backbones play a key role in the formation and stabilization of layered structures.

### 1. Introduction

In the last few years, two-dimensional (2D) materials have attracted immense attention<sup>[1]</sup> because of their prominent features such as high surface area, and structural flexibility, along with potential applications in energy storage and conversion, electronics, catalysis, and sensing.<sup>[2]</sup> Self-assembly of small molecules has provided an appealing strategy for the bottom-up construction of free-standing 2D nanosheets.<sup>[3]</sup> Typically, these long-range ordered nanostructures are stabilized by various non-covalent intermolecular forces, such as hydrogen bonds,<sup>[5]</sup>  $\pi$ - $\pi$ ,<sup>[4]</sup> ionic,<sup>[6]</sup> and charge-transfer interactions.<sup>[7]</sup> Regarding the use of aromatic building blocks in self-assembly, the conjugated backbone cannot only provide  $\pi$ - $\pi$  interactions to stabilize the self-organized nanostructures, but also offers anisotropic channels for the transportation of charge carriers.<sup>[8]</sup>

Admittedly, *n*-type organic semiconductors show potential applicability in organic thin-film field-effect transistors (OTFTs)<sup>[9]</sup> and organic solar cells (OSCs).<sup>[10]</sup> However, the self-assembly of *n*-type conjugated molecules has been less explored.<sup>[11]</sup> There-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cphc.201300444. fore, it is highly desirable to develop n-type organic semiconductors that can self-assemble into 2D nanostructures.

Recently, we developed an efficient synthesis of an H-shaped 2,3,7,8-tetraazaanthracene with four thiophene arms,<sup>[12]</sup> for which an electrochemical study revealed a typical *n*-type character.<sup>[12]</sup> The embedded heteroatoms (N and S) in the conjugated backbone imparted not only donor–acceptor (D–A) charge-transfer features, but also different intermolecular non-covalent forces, such as N···S, S···S, and hydrogen bonds, which have an important impact on their solid-state packing. In addition, the substituted alkyl chains at the periphery of the conjugated backbone can improve their solubility and influence the molecular packing by means of cooperative van der Waals interactions.<sup>[13]</sup>

Inspired by these findings, we designed and synthesized a series of H-shaped molecules comprising a 2,3,7,8-tetraazaanthracene core and thiophene arms substituted with different alkyl chains (Figure 1). Their unique self-assembled 2D nanostructures, obtained by a phase-transfer method, were the focus of attention. All the compounds have been fully characterized by <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) and high-resolution mass spectra (HRMS-ESI), showing full consistency.



Figure 1. Chemical structures of 1-4.

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Scheme 1. Synthesis of target molecules 1-4.

### 2. Results and Discussion

Alkyl-modified  $\pi$ -conjunction compounds 1–4 (Scheme 1) were synthesized from the key starting compound pyromellitoyl chloride (5). In accord with our previously reported method,<sup>[12]</sup> 5 was prepared from 1,2,4,5-benzenetetracarboxylic anhydride and phosphorus pentachloride at 190°C. Unfortunately, it was not possible to obtain compound 7 directly by reaction of thienyl Grignard reagents with 5. Therefore, the S-pyridinyl moiety was adopted as an appropriate leaving group to substitute the chloride group, by treating 5 with 2-mercaptopyridine as the reactant, and triethylamine (TEA) as the catalyst at  $0^{\circ}C$ for 30 min. To avoid rearrangement, the reaction was worked up by quick addition of dilute hydrochloric acid. The resulting solid was recrystallized in dichloromethane/diethyl ether, to yield compound 6 (Scheme 1) as pale-yellow crystals. Afterwards, freshly prepared 2-thienylmagnesium bromide was added to the suspension of 6 in tetrahydrofuran (THF) at 0°C, affording 7a-d in yields from 31-34%. Finally, 7a-d were treated with excess hydrazine hydrate, to build up the target compounds 1-4 in good yields.

As typical examples of the prepared compounds, the electrochemical behavior of 1 and 2 was studied by cyclic voltammetry (CV, Figure 2). The CV of 2 shows successive reversible cathodic peaks, indicative of *n*-type character. Notably, a slight splitting into an intense redox peak at -1.12 V and a shoulder redox peak at around -0.91 V can be observed, in contrast with the reduction redox process of 1, displaying only one well-resolved peak at -0.89 V with a hexyl substituted group.<sup>[11]</sup> Such phenomenon is likely due to the aggregation



Figure 2. Cyclic voltammograms of a) 1<sup>[12]</sup> and b) 2 in dichloromethane (scan rate:  $100 \text{ mV s}^{-1}$ ).

Aggregate morphology was investigated by scanning electron microscopy (SEM). The declined solubility of formed aggregates can lead to the formation of a suspension, which can help preserving the integrity of the nanostructures, protecting

behavior of 2 in the reduced state.<sup>[14]</sup> Encouraged by such an unexpected result, attempts to understand the effect of the alkyl chain on the self-assembly behavior of 1-4 were carried out.

The optical properties of compound 2 were investigated in a series of binary solvent mixtures (dichloromethane/methanol) to elucidate the self-assembly process. Upon addition of methanol (< 50% volume fractions) to the dichloromethane solution of 2, the intensity of the main absorption bands in the UV/Vis spectra is only slightly increased (Figure 3a). However, on in-



Figure 3. a) UV/Vis absorption and b) fluorescence emission spectra  $(10^{-5} M)$ showing variations in intensity for a dichloromethane/methanol mixture with different methanol fractions.

creasing the methanol content up to 50%, the intensity of the main absorption maxima initially declines, and then becomes broad with a leveling-off of long-wavelength tails at higher methanol contents, which are typical characteristics of the formation of nanometric aggregates.<sup>[15]</sup> In contrast, a dramatic change in fluorescence is observed when methanol is added to the dichloromethane solution of 2 (Figure 3b). Gradually increasing the volume fraction of methanol from 0 to 30% significantly enhances emission intensity, along with a redshift in the emission band from 568 to 581 nm. The enhancement by effect of the methanol fraction (up to 30%) leads to a significant increase in emission intensity (Figure 3b, ∇), probably due to a solvent effect. The emission is progressively guenched upon further increase of the methanol fraction (40%, Figure 3 b,  $\diamond$ ). This result suggests that the aggregation of **2** was formed in a binary solvent system with dichloromethane/methanol > 3:2.[16]

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**Figure 5.** a) AFM images of 2D aggregates formed by **2**. b) Representation of a possible ordered arrangement for the assembly of **2**, illustrating that the thickness is approximately equivalent to ten mono-layers.

them from deformation, as they are being transferred to a solid substrate.<sup>[6a]</sup> We conducted the assembly of 1-4 from a binary solvent system in an optimized 2:3 ratio of dichloromethane/ methanol. Typically, 2, 12, 24, and 48 h were required for 1-4 to form pronounced aggregates, respectively. As shown in Figure 4a, b, remarkable 2D sheetlike nanostructures are found for 1 and 2. The sheets of 1 show equilateral rhombus-shaped structures with a size of 10-30 µm. Self-assembly of 2 leads to similar nanosheets with size



Figure 6. SEM images of aggregates from the suspensions of a) 3 and b) 4 (The samples were prepared by dropcasting of the suspensions in dichloromethane/methanol onto the silicon substrate).

in the range of  $1-2 \,\mu$ m. Transmission electron microscopy (TEM) images confirm the nanosheet morphologies for **1** and **2**. As shown in Figure 4c, **1** comprises a 2D nanosheet with an equilateral length and width of 20–30  $\mu$ m, with multiple-layer stacking. Notably, the size of 2D aggregates formed from **2** is more dispersive, with the same length and width of 1  $\mu$ m (Figure 4d). The well-dispersed 2D nanosheet of **2** was further investigated by atomic force microscopy (AFM, Figure 5a), from which a thickness of ~29.3 nm was measured.

Interestingly, pending arms of long octadecyl ( $C_{18}$ ) chains (Figure 6a) lead to disk-like nanosheets with a diameter of ~600 nm (**3**), which stand in contrast to those of **1** and **2**. Note that the edges of the 2D structures become darker on going from **1** to **3**, which is probably attributable to the different rates of the self-assembly processes. Furthermore, we found that **4**, substituted with branched  $C_{6-2}$  alkyl chains, leads to the rod-like assembled structures with a length from 200  $\mu$ m to 2 mm (Figure 6b). Tailoring the decorated alkyl chains for compounds **1–4** is seemingly an efficient way to control the self-assembly behavior in a binary co-solvent system.

To elucidate the structural influence of the supramolecular arrangement and macroscopic morphology, powder X-ray diffraction (XRD) was employed to analyze the aggregation behavior of 1-4. The diffraction pattern of 1 exhibits intense, sharp peaks, indicating the high crystallinity of the assembled 2D nanosheets. Accordingly, the peaks at  $2\theta = 4.2$ , 8.4, and  $16.9^{\circ}$  in Figure 7a can be indexed as (100), (200), and (300) reflections, respectively, and are associated with a lamellar packing.<sup>[17]</sup> Compounds 2 and 3 also reveal three well-resolved diffraction peaks in the range 2-10°, with the formation of a lamellar structure (Figure 7 b, c). The reflection peaks of 1-3 at  $2\theta = 20 - 21^{\circ}$  are known to originate from the ordered packing of alkyl chains. The strong peak at a small angle in 1 dwarfs the peaks at  $2\theta = 20-21^{\circ}$ , a magnification of the region (Figure 7a) provides a better view. In addition, the reflection peaks at  $2\theta = 23-25^{\circ}$  can be attributed to the  $\pi-\pi$  stacking of aromatic segments.<sup>[17c]</sup> Notably, with the increase in alkyl-chain length from 1 to 3, the intensity of the peaks at 20-21° becomes stronger, suggesting enhanced interaction of the alkyl chains. In contrast to 1-3, the XRD pattern of 4 have a lower

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Figure 7. X-ray diffraction patterns of 1–4 plotted against the angle  $2\theta$  (298 K).

intensity, along with less defined and broader peak shapes, and deprived of the typical reflections related to lamellar features (Figure 7 d). In the small-angle region, sharp and clear reflections at  $2\theta$  values of 4.2, 3.0, and  $2.3^{\circ}$  for **1–3**, respectively, are noted. As a consequence, the calculated XRD *d* spacings of the (100) reflection value are 2.04, 2.94, and 3.87 nm, respectively, on the basis of Bragg's law. These results suggest that the compounds with longer alkyl chains have a larger interlayer spacing in the aggregates.<sup>[6a]</sup>

Considering the thickness of the 2D nanostructures in **2** is ~29.3 nm and the calculated XRD *d* spacing of the (100) reflection value is 2.94 nm, a proposed molecular arrangement for **2** is shown in Figure 5 b. The schematic representation indicates that the 2D nanosheets of **2** are expected to consist of ten layers. Note that the  $\Delta d$  value between **1** and **2** (0.90 nm) is similar to that between **2** and **3** (0.93 nm). These values are likely to derive from the double length of the hexyl chain moieties, and are in line with values from earlier reports.<sup>[18]</sup> Hence, the lamellar *d* spacing within the assemblies increases linearly with the carbon number of the alkyl chains (Figure 8), from which we can deduce the molecular arrangements in the assemblies of **1**–**3** should be the same.<sup>[19]</sup> Importantly, the lamel-



**Figure 8.** The linear relationship between the lamellar *d* spacing and the carbon number of the alkyl chain reveals the same molecular arrangements for compounds **1–3**.

lar *d* spacing calculated from wide-angle X-ray diffraction (2.04 nm) of **1** is exactly equal to the value derived from X-ray single-crystal analysis,<sup>[12]</sup> implying the same molecular arrangement in both, the 2D assemblies and the crystals. Based on the structural analysis and the strong support for a long-range ordered assembly, a mechanism is proposed to explain the formation of 2D nanostructures. As depicted in Figure 9, we can



Figure 9. Packing diagram and illustration of the 2D nanostructures formation for 1.

simulate the process of 2D formation on the basis of crystal structure analysis of 1.<sup>[12]</sup> The analysis showed that four thiophene arms extend out of the rigid tetraazaanthracene plane through free rotation around the C-C bonds.<sup>[12]</sup> Such a nonplanar molecular conformation would allow multi-intermolecular interactions, including S-S interactions (0.385 nm), hydrogen bonding of N…H (0.292 nm), and C…H– $\pi$  (0.340 nm) and  $\pi$ - $\pi$  interactions (0.333, 0.378 nm) (Figure S1 in the Supporting Information), to create a synergistic effect for molecular self-assembly along two axial directions, ultimately giving rise to a single-layer nanosheet (route A). Subsequently, each single sheet of assembled structures can undergo lamellar packing by van der Waals interactions, resulting in a crystal structure similar to those herein presented. The weak interaction from the hydrogen bonding between nitrogen and hydrogen atoms in neighboring molecules (0.292 nm) may also contribute to the stability of the arrays, facilitating nanostructure formation for 1-4. This is confirmed by Fourier transform infrared (FT-IR) spectroscopy (Figure 10), in which the typical peaks located at 3446, 3434, 3445, and 3443 cm<sup>-1</sup> for **1–4**, respectively, can be ascribed to the N-H bond.<sup>[20]</sup> These weak interactions depend solely on the relative location of each molecule, and serve as the driving force for the simultaneous growth of the microsheets along two axial directions, thus leading to the formation of a rhomboid pattern with little differences in width and length, rather than a ribbon-like or rectangular pattern.

### 3. Conclusion

In summary, a series of *n*-type thiophene-armed tetraazaanthracene molecules with different peripheral alkyl chains were

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Figure 10. FT-IR spectra of 1–4. The peaks at 3446, 3434, 3445, and 3443 cm<sup>-1</sup> can be ascribed to the vibrational modes of the N–H bond.

prepared. The electron-rich heteroatoms (N and S) in the molecular backbone play an important role in creating multiple weak intermolecular interactions, inducing the formation of layered structures in the solid-state packing. The self-assemblies of these molecules in a binary solvent system of dichloromethane/methanol reveal remarkable 2D nanosheet morphologies, which can be tuned by the modification of the peripheral alkyl chains. This work offers a new approach to the creation of uniform 2D organic nanomaterials, which may have potential applications in organic electronics.

### **Experimental Section**

### **General Method**

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Mercury Plus 400 (Varian, USA, 400 MHz for proton) spectrometer with tetramethylsilane as the internal reference using  $\mathsf{CDCI}_{\scriptscriptstyle 3}$  as the solvent in all cases. Mass spectra were recorded on a Bruker microTOF-Q-II system. All yields given refer to isolated yields. UV/Vis spectra were recorded on a HITACHI U-4100 spectrophotometer. The fluorescence spectroscopy emission spectra were obtained with a Fluoro-Max-4 spectrophotometer. CV was performed on an Chenhua 650D electrochemical analyzer in distilled dichloromethane containing recrystallized tetra-n-butyl-ammonium hexafluorophosphate (TBAPF6, 0.1 M) as the supporting electrolyte at 298 K. XRD measurements were carried out on a D/max-2200/PC (Rigaku Corp., Japan) using Cu (40 kV, 30 mA) radiation. SEM measurements were performed on an FEI Sirion-200 field emission scanning electron microscope. The samples were prepared by dropcasting the suspensions onto silicon wafers. TEM characterizations were carried out on a JEM-2100 (JEOL Ltd., Japan) with an accelerating voltage of 200 kV. The samples were prepared by drop-casting the suspensions onto copper grids covered with carbon film. AFM studies were carried out on a Multimode Nanoscope (ID Ltd., USA) operated in tapping mode at room temperature. The samples were prepared by drop-casting the suspensions onto silicon wafers. X-ray crystallography was performed using a CAD4 DIFFAC-TIS 586 diffractometer.

#### Materials

All reagents were obtained from commercial suppliers such as Aladdin and J&K Chemical. All solvents were supplied by Sinopharm Chemical Reagent and used as received unless otherwise noted. All air-sensitive reactions were carried out under a nitrogen atmosphere and performed using Schlenk techniques. THF was used freshly distilled from a suspension heated at reflux under nitrogen in the presence of sodium and benzophenone. Triethylamine (TEA) was heated to reflux with calcium carbide prior to use. Dichloromethane for fluorescence spectroscopy and UV/Vis spectra studies were distilled from calcium hydride.

#### Synthesis of Precursors (5-7)

1,2,4,5-Benzenetetracarbonyl tetrachloride (5), 1,2,4,5-tetra(S-(pyridine-2'-yl))benzenetetrathioate (6), and 1,2,4,5-tetra(5'-hexyl-thieno-2'-yl)benzene (7 a) were synthesized following published procedures as described in our previous paper.<sup>[12]</sup>

## Synthesis of 1,2,4,5-Tetra(5'-Dodecyl-Thieno-2'-yl)Benzene (7 b)

A solution of 2-bromo-5-dodecylthiophene (3.7 g, 11.18 mmol) in THF (15 mL) was added drop wise to a mixture of iodine-activated magnesium (0.29 g, 12.31 mmol) in THF (5 mL), and the mixture was refluxed for 4 h at 50 °C under a nitrogen atmosphere to form the Grignard reagent. Afterwards, the cold reagent was slowly added to a flask containing 6 (1.0 g, 1.62 mmol) in dry THF (50 mL) at 0°C, and stirred overnight. Then, the reaction was quenched with 10% HCl (100 mL), and extracted with ether. The combined organic fractions were washed with 1 M NaOH and water until reaching neutral pH, then dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. After purification by recrystallization from dichloromethane/diethyl ether, the product was obtained as a white solid (0.63 g, 33.1%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 7.98$  (s, 1 H), 7.36 (d,  ${}^{3}J_{H-H} = 4.0$  Hz, 2 H), 6.79 (d,  ${}^{3}J_{H-H} = 4.0$  Hz, 2H), 2.82 (t, <sup>3</sup>J<sub>H-H</sub>=7.6 Hz, 4H), 1.71-1.65 (m, 4H), 1.63-1.57 (m, 36 H), 0.90–0.86 ppm (m, 6 H);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta =$ 186.61, 158.68, 141.05, 140.92, 136.53, 129.71, 126.17, 32.15, 31.57, 31.03, 29.89, 22.93, 14.37 ppm; m.p. 166-168 °C.

# Synthesis of 1,2,4,5-Tetra(5'-Octodecyl-Thieno-2'-yl)Benzene (7 c)

A solution of 2-bromo-5-octodecylthiophene (3.0 g, 7.20 mmol) in THF (10 mL) was slowly added to a mixture of iodine-activated magnesium (0.21 g, 8.64 mmol) in THF (5 mL), to form the Grignard reagent in 4 h. Afterwards, the cold reagent was slowly added to a flask containing 6 (0.64 g, 1.01 mmol) in dry THF (50 mL) at 0°C, and stirred overnight. Then, the reaction was guenched with 10% HCl (100 mL), and extracted with dichloromethane. The combined organic fractions were washed with 1 M NaOH and water until neutral pH was measured, then dried over Na2SO4, and the solvent was removed under reduced pressure. After purification by recrystallization from dichloromethane/diethyl ether, the product was obtained as a white solid (0.65 g, 39.3 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta\!=\!7.98$  (s, 1 H), 7.36 (d,  ${}^3J_{\rm H\!-\!H}\!=\!4.0$  Hz, 2 H), 6.79 (d,  ${}^3J_{\rm H\!-\!H}\!=\!4.0$  Hz, 2H), 2.82 (t, <sup>3</sup>J<sub>HH</sub>=7.6 Hz, 4H), 1.71-1.67 (m, 4H), 1.65-1.20 (m, 60 H), 0.90–0.86 ppm (m, 6 H);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta =$ 186.59, 158.66, 141.03, 140.91, 136.51, 129.69, 126.15, 32.16, 31.58, 31.03, 29.94, 22.94, 14.37 ppm; m.p. 149-151 °C.

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### Synthesis of 1,2,4,5-Tetra(5'-(2"-Ethylhexyl)-Thieno-2'-yl)-Benzene (7d)

А solution 2-bromo-5-(2-ethylhexyl)thiophene of (0.65 a. 2.36 mmol) in THF (3 mL) was slowly added to a mixture of iodineactivated magnesium (63 mg, 2.83 mmol) in THF (2 mL), to form the Grignard reagent in 4 h. Afterwards, the cold reagent was slowly added to a flask containing 6 (211 mg, 0.337 mmol) in dry THF (50 mL) at 0 °C, and stirred overnight. Then, the reaction was guenched with 10% HCl (100 mL), and extracted with ether. The combined organic fractions were washed with 1 M NaOH and water until reaching neutral pH, then dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. After purification by column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether as the eluent, the product was obtained as a pale yellow solid (110 mg, 34.1%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.00 (s, 1 H), 7.35 (d, <sup>3</sup>J<sub>H-H</sub> = 4.0 Hz, 2 H), 6.77 (d,  ${}^{3}J_{H-H} = 4.0$  Hz, 2 H), 2.76 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 4 H), 1.60-1.57 (m, 6H), 1.34-1.28 (m, 12H), 0.89-0.86 ppm (m, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = 186.54$ , 157.40, 148.18, 141.05, 136.42, 129.71, 127.10, 41.67, 34.99, 32.57, 29.01, 25.69, 23.16, 14.32, 10.97 ppm; m.p. 99-101 °C.

### Synthesis of 1,4,6,9-Tetra(5-Hexyl-Thien-2-yl)-2,3,7,8-Tetraazaanthracene (1)

1,4,6,9-Tetra(5-hexyl-thien-2-yl)-2,3,7,8-tetraazaanthracene was synthesized following published procedures as described in our previous paper.<sup>[12]</sup>

#### Synthesis of 1,4,6,9-Tetra(5-Dodecyl-Thien-2-yl)-2,3,7,8-Tetraazaanthracene (2)

A suspension of hydrazine hydrate (0.17 g, 3.36 mmol) and **7b** (0.5 g, 0.42 mmol) in ethanol (50 mL) was stirred for 2 days at room temperature. After removing the solvent under reduced pressure, the product was obtained as a yellow solid (0.45 g, 90.5%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.85 (s, 1H, Ph), 7.71(d, <sup>3</sup>J<sub>H-H</sub>=3.7 Hz, 2H, Th-H-3), 6.97 (d, <sup>3</sup>J<sub>H-H</sub>=3.7, 2H, Th-*CH*-4), 2.89 (d, <sup>3</sup>J<sub>H-H</sub>=6.8 Hz, 4H, *CH*<sub>2</sub>), 1.75–1.69 (m, 4H, *CH*<sub>2</sub>), 1.77–1.27 (m, 36H, *CH*<sub>2</sub>), 0.90–0.85 ppm (m, 6H, *CH*<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 152.32, 151.00, 136.07, 130.68, 126.40, 125.70, 32.16, 31.92, 30.69, 29.93, 29.85, 29.69, 29.60, 29.49, 22.93, 14.37 ppm; HRMS-ESI: *m/z* calculated for C<sub>74</sub>H<sub>110</sub>N<sub>4</sub>S<sub>4</sub> [*M*+Na] 1205.7511, found, 1205.7529; m. p. 153–155 °C.

### Synthesis of 1,4,6,9-Tetra(5-Octodecyl-Thien-2-yl)-2,3,7,8 Tetraazaanthracene (3)

A suspension of hydrazine hydrate (0.052 g, 1.05 mmol) and **7** c (0.2 g, 0.13 mmol) in ethanol (50 mL) was stirred for 2 days at room temperature. After removing the solvent under reduced pressure, the product was obtained as a yellow solid (0.17 g, 86.3%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.84 (s, 1 H, Ph), 7.71 (d, <sup>3</sup>J<sub>H-H</sub> = 3.8 Hz, 2 H, Th-H-3), 6.99 (d, <sup>3</sup>J<sub>H-H</sub> = 3.8, 2 H, Th-CH-4), 2.95 (t, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, 4 H, CH<sub>2</sub>), 1.84–1.80 (m, 4 H, CH<sub>2</sub>), 1.64–1.25 (m, 60 H, CH<sub>2</sub>), 0.89–0.85 ppm (m, 4 H, CH<sub>3</sub>); <sup>13</sup>C NMR spectra could not be well resolved due to the poor solubility of **3** in common organic solvents. HRMS-ESI: *m/z* calculated for C<sub>98</sub>H<sub>158</sub>N<sub>4</sub>S<sub>4</sub> [*M*+H] 1520.1448; found, 1520.1515; m.p. 124–126 °C.

### Synthesis of 1,4,6,9-Tetra(5-(2-Ethylhexyl)-Thien-2-yl)-2,3,7,8-Tetrazaanthracene (4)

A suspension of hydrazine hydrate (35.8 mg, 0.715 mmol) and **7d** (85.8 mg, 0.089 mmol) in ethanol (30 mL) was stirred for 2 days at room temperature. The solvent was removed under reduced pressure. After purification by column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether, the product was obtained as a red solid (68 mg, 80.3%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.84 (s, 1H, Ph), 7.71 (d, <sup>3</sup>J<sub>H</sub> = 3.8 Hz, 2H, Th-*H*-3), 6.99 (d, <sup>3</sup>J<sub>H-H</sub> = 3.8, 2H, Th-CH-4), 2.89 (d, <sup>3</sup>J<sub>H</sub> = 6.7 Hz, 4H, CH<sub>2</sub>), 1.75–1.69 (m, 6H, CH<sub>2</sub>), 1.44–1.32 (m, 12H, CH<sub>2</sub>), 0.89–0.85 ppm (m, 12H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 152.24, 150.60, 136.41, 130.57, 126.68, 126.31, 125.69, 41.75,34.58, 32.71, 29.14, 25.86, 23.26, 14.37, 11.09 ppm; HRMS-ESI: *m/z* calculated for C<sub>58</sub>H<sub>78</sub>N<sub>4</sub>S<sub>4</sub> [*M*+H] 958.5188, found, 959.5200; m.p. 143–145 °C.

# Preparation of the Self-assembly Systems by Phase Transfer (PT) Method

Methanol can increase the polarity of a solvent system and induce better phase separation for amphiphilic molecules,<sup>[6a,21]</sup> so we used a PT method with a dichloromethane/methanol binary solvent system to investigate the self-assembly of **1–4**.

### Self-Assembly of 1-4

Compound 1: A homogeneous solution of **1** was prepared in  $CH_2Cl_2$  (4 mL, ~1 mM) at room temperature in a clean 20 mL sample vial. Methanol (6 mL, poor solvent) was slowly added to the solution so that two phases could be maintained. The biphasic mixture was left undisturbed to induce assembly, which finally resulted in a yellow suspension. The procedure for **2–4** was the same, using instead ~0.5 mM concentrations of each corresponding compound.

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**Keywords:** nanostructures • noncovalent interactions • selfassembly • tetraazaanthracene • two-dimensional structures

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