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SYNTHESIS AND PROPERTIES OF *anti*/*syn*-REGIOISOMERIC MIXTURES OF ALKYL-SUBSTITUTED TETRACENES

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Abstract – We prepared *anti*/*syn*-regioisomeric mixtures of alkyl-substituted tetracenes *via* Diels-Alder reaction between asymmetric furans and 2,6-naphthodiyne synthon. The solid-state color of the mixtures changed before and after recrystallization from Et_2O, suggesting a difference in the molecular arrangements dependent on the different alkyl substituents as well as the change in the distribution of the *anti*/*syn* regioisomers after recrystallization. Slow evaporation of the recrystallized mixtures produced single crystals suitable for X-ray analysis, which revealed that the *anti* regioisomer was isolated.

INTRODUCTION

Preparation and application of organic semiconducting molecules are the subject of recent interest. Although pentacene is an important representative molecule that shows excellent hole mobilities,[1] it suffers from instability under light and air and insolubility in common organic solvents.[2] On the other hand, tetracene has a more attractive framework because it has the advantages of air stability in its solid state, solubility, and a low melting point though its mobility may be lower than that of pentacene. To develop tetracene-based semiconductors,[3] researchers have prepared many functionalized tetracenes.[4] In recent years, we have focused on alkyl-substituted tetracenes to obtain high solubilities, low melting points, and good film morphologies. Thus, we have synthesized a series of tetracenes (1,4,7,10-tetraalkyl, 1,4-dialkyl, 2,3-dialkyl, and 2,3,8,9-tetraalkyl derivatives).[5] We revealed that these compounds were not only typical semiconductors but also interesting chromophores because of the unique dependences of the solid-state color on their lengths, shapes, numbers, and substitution positions of the alkyl side chains,

despite being independent of their optical properties in solution. We found that the alkyl side chains can serve as an adjuster of the molecular arrangements to control the solid-state optical properties. Therefore, introducing a new substitution pattern may allow the development of new optical functionalities. So far, we have investigated single-component alkyl-substituted tetracenes in which all the alkyl groups are the same; however, we did not consider bimolecular mixtures composed of *anti* **1** and *syn* **2** regioisomers, in which two different types of groups were located at the 1,4,7,10-positions (Figure 1). In this study, we report the synthesis and characterization of new alkyl-substituted tetracene mixtures, 1,7- and 1,10-dihexyltetracene (**1a** and **2a**, respectively) and 1,7-dihexyl-4,10-diisopropyl- and 1,10-dihexyl-4,7-diisopropyltetracene (**1b** and **2b**, respectively).

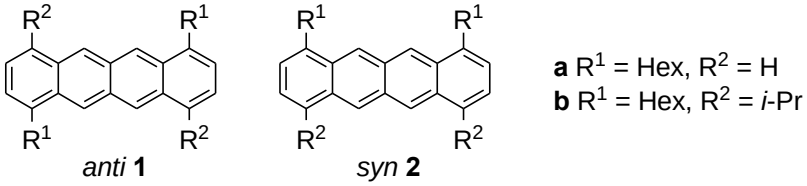
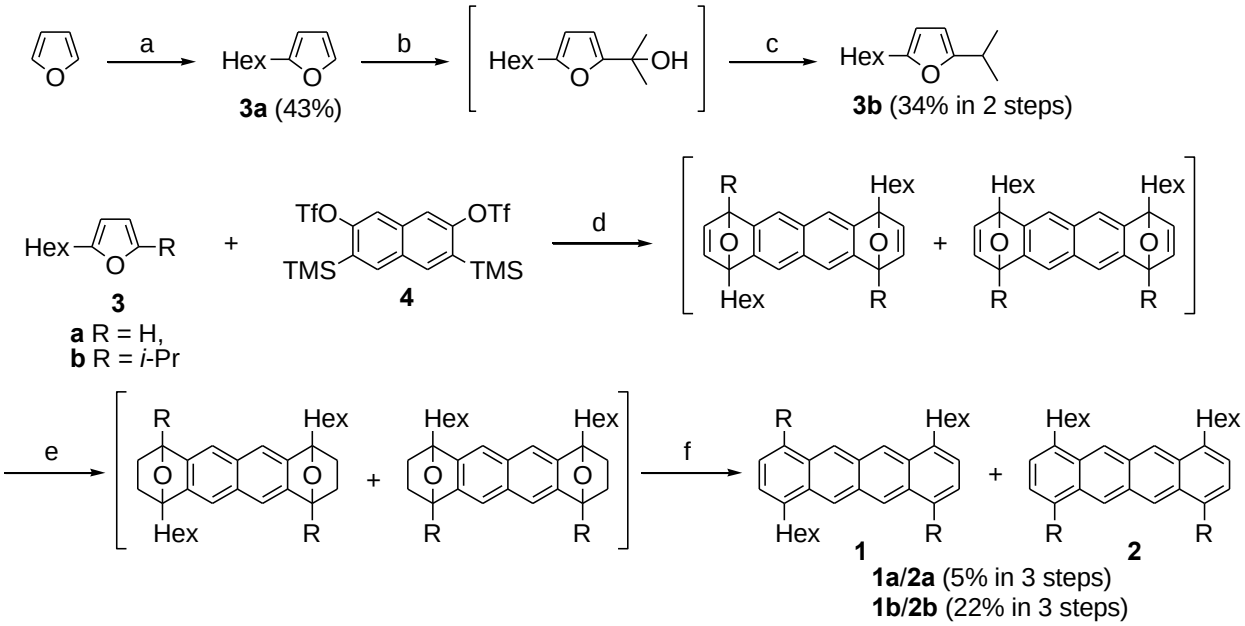


Figure 1. Chemical structures of alkyl-substituted tetracenes

RESULTS AND DISCUSSION

We prepared *anti*/*syn* mixtures of **1a**/**2a** and **1b**/**2b** *via* our recently reported procedure,[5b] by using asymmetric furans (**3a** and **3b**) and 2,6-naphthodiyne precursor **4**, as shown in Scheme 1. 2-Hexylfuran (**3a**) was prepared from a lithiation-nucleophilic substitution sequence. By using the same synthetic procedure employed for 2,5-diisopropylfuran,[5d] we synthesized 2-hexyl-5-isopropylfuran (**3b**) *via* the



Scheme 1. Reagents and conditions: (a) 1. *n*-BuLi, TMEDA, reflux; 2. HexBr, THF, rt; (b) 1. *n*-BuLi, TMEDA, reflux; 2. acetone, THF, rt; (c) H_2, Pd/C, CH_2Cl_2, rt; (d) KF, 18-crown-6, THF, rt; (e) H_2, Pd/C, EtOH, rt; (f) conc. HCl, Ac_2O, rt

reaction of lithiated **3a** and acetone followed by hydrogenolysis. Slow generation of 2,6-naphthodiyne synthon by treating **4** with excess asymmetric furans (**3a** and **3b**) in the presence of KF and 18-crown-6 in THF afforded Diels–Alder cycloadducts, which were hydrogenated, dehydrated with conc. HCl and Ac_2O, and purified *via* column chromatography to give tetracene *anti*/*syn*-regioisomeric mixtures of **1a**/**2a** and **1b**/**2b**, respectively. The tetracene mixtures were soluble in common organic solvents such as hexane and Et_2O. We could not confirm the *anti*/*syn* ratio because there were no differences in the ^1H and ^{13}C NMR signals as well as the Rf values of the *anti* **1** and *syn* **2** regioisomers.

Interestingly, after preparation, **1a**/**2a** and **1b**/**2b** were immediately isolated as an orange powder and a yellow viscous solid, respectively (Figure 2). Furthermore, recrystallization from Et_2O produced a visible change in the solid-state colors, and thus **1a**/**2a** and **1b**/**2b** were obtained as yellow and orange powders, respectively. Alkyl side chains do not absorb visible light and have little electronic effect on the tetracene ring. Therefore, the differences in the solid-state colors before and after recrystallization were most likely due to crystallochromy,[6,7] i.e., a color change caused by different intermolecular interactions based on different aggregation structures. In the step before recrystallization, we can explain the difference in color as the different molecular arrangements of tetracene rings dependent on the different substitution patterns of **1a**/**2a** and **1b**/**2b**. On the other hand, in the step after recrystallization, the result probably showed an unbalanced distribution of *anti*/*syn* regioisomers in which the more crystalline component would dominate the inherent molecular arrangements compared with the other component. This was supported by the difference in the melting points before and after recrystallization: the melting points of **1a**/**2a** and **1b**/**2b** before recrystallization were 75–77 °C and 55–57 °C, respectively; in contrast, those of **1a**/**2a** and **1b**/**2b** after recrystallization were 121–122 °C and 148–150 °C, respectively.

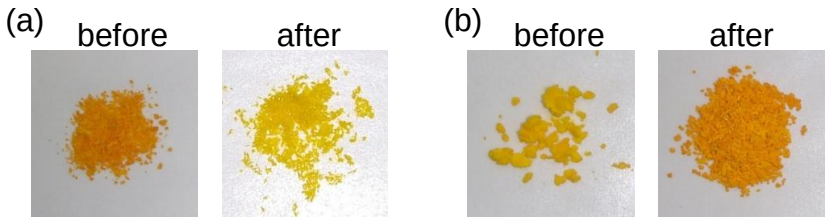


Figure 2. Photographs of *anti*/*syn* mixtures of (a) **1a**/**2a** and (b) **1b**/**2b**, showing before (left) and after (right) the recrystallization from Et_2O

We spectroscopically observed the change in the solid-state optical properties before and after recrystallization with Et_2O *via* absorption (Kubelka-Munk) and fluorescence spectra (Figure 3). The spectral profiles of **1a**/**2a** and **1b**/**2b** before and after recrystallization showed significant differences. In the absorption spectra, **1a**/**2a** and **1b**/**2b** before and after recrystallization showed structured bands. The

longest absorption maximum of **1a**/**2a** before recrystallization was 498 nm, whereas that of **1a**/**2a** after recrystallization was 483 nm (Figure 3a). In contrast, the absorption spectrum of **1b**/**2b** before recrystallization was characterized by one broad band around 500 nm, whereas that of **1b**/**2b** after recrystallization showed the longest wavelength absorption band at 489 nm with a shoulder around 520 nm (Figure 3b). The change in the absorption edges before and after recrystallization also correlated well with that of the solid-state colors. Thus, the absorption edges of **1a**/**2a** before and after recrystallization were 545 nm and 530 nm, respectively (Figure 3a), and those of **1b**/**2b** before and after recrystallization were 540 nm and 551 nm, respectively (Figure 3b). We also noted the differences in the fluorescence properties before and after recrystallization. The fluorescence quantum yields of **1b**/**2b** before and after recrystallization (0.31 and 0.27, respectively) were larger than those of **1a**/**2a** before and after recrystallization (0.04 and 0.08, respectively). We also observed a great difference in the spectral shapes between **1a**/**2a** and **1b**/**2b**. The spectrum of **1a**/**2a** before recrystallization exhibited two peaks (551 and 593 nm) and a shoulder (528 nm), and that of **1a**/**2a** after recrystallization displayed three peaks (529, 563, and 602 nm). In contrast, the spectrum of **1b**/**2b** after recrystallization illustrated one strong band at 560 nm, whereas that of **1b**/**2b** before recrystallization displayed two bands at 559 and 569 nm. All the above-mentioned results would be derived from different molecular arrangements of the tetracene moieties.

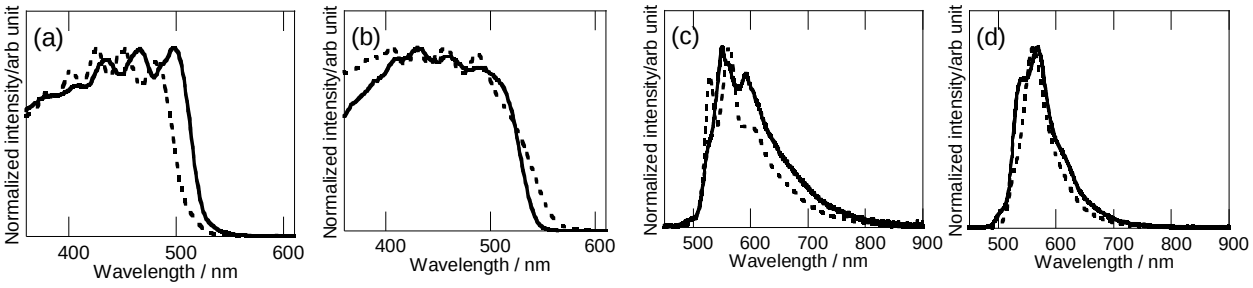


Figure 3. Kubelka-Munk spectra of (a) **1a**/**2a** and (b) **1b**/**2b** in dilute KBr pellets and fluorescence spectra of (c) **1a**/**2a** and (d) **1b**/**2b** in powder form, showing before recrystallization (solid line) and after recrystallization (dotted line)

When we performed slow evaporation of the recrystallized samples from Et_2O solutions, we succeeded in obtaining some single crystals suitable for X-ray analysis. Then, we determined their crystal structures (Figure 4).[8] The molecules proved to be *anti* regioisomers **1a** and **1b** (Figure 4a). Although we attempted recrystallization from the filtrate components under various conditions, we could not obtain any single crystals of the *syn* regioisomers. In both **1a** and **1b**, the tetracene rings were essentially planar. Their hexyl groups, except for the terminal methyl groups in **1a**, adopted zigzag conformations, and the zigzag planes were almost coplanar with the tetracene ring. The hexyl conformations in **1a** and **1b** were

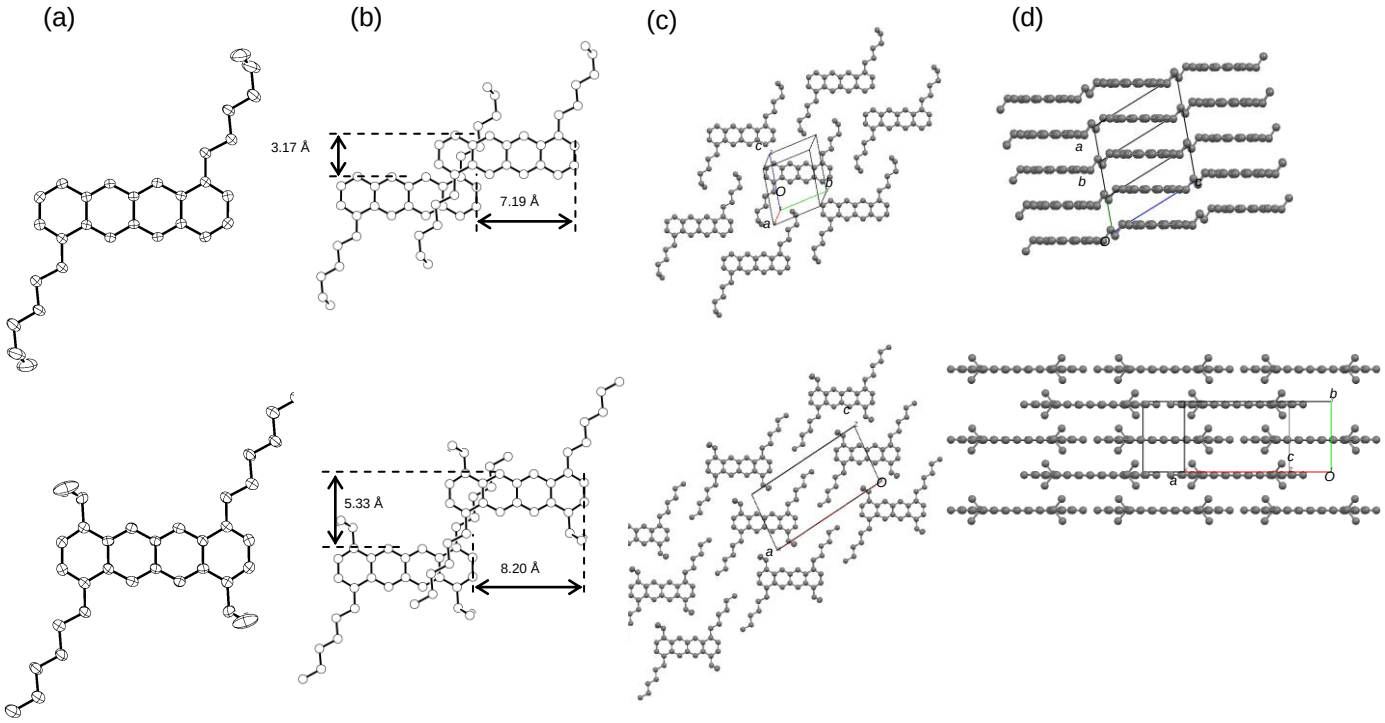


Figure 4. Crystal structures, showing (a) molecular structures, (b) stacking pairs, (c) layer structures, and (d) packing diagrams of **1a** (top) and **1b** (bottom)

completely different from those in 1,4,7,10-tetrahexyltetracene,[5b] which were perpendicular to the tetracene ring. In both **1a** and **1b**, there was no π-overlap between the two neighboring molecules along the stacking direction (Figure 4b). The mutual orientations were significantly different in **1a** and **1b**. The interplanar distances between the tetracene planes were 3.56 Å for **1a** and 3.79 Å for **1b**. The difference in the slip distance along the long molecular axis was almost 1 Å (7.19 Å for **1a** and 8.20 Å for **1b**), and the difference in the slip distance along the short molecular axis was above 2 Å (3.17 Å for **1a** and 5.33 Å for **1b**). In the packing structures, the molecules crystallized in layered structures while **1a** and **1b** appear to be stacked in a staircase-type fashion and a brickwork-type fashion, respectively (Figure 4d). Within the layer, one molecule of **1a** is surrounded by six neighboring molecules, and one molecule of **1b** is environed by eight neighboring molecules (Figure 4c). In the crystal of **1a**, the hexyl groups were arranged in a head-to-tail regularity, and we observed alternating stripes composed of alkyl and tetracene regions. These arrangements were slightly different from those in the crystal of **1b**; the existence of isopropyl groups broadened the intermolecular spacing between neighboring molecules. The differences in these molecular arrangements would probably cause the differences in the solid-state optical properties. In conclusion, we prepared *anti*/*syn*-regioisomeric mixtures of **1a**/**2a** and **1b**/**2b** to examine the effects of the alkyl substitution and the mixed molecules on the solid-state color. Interestingly, the color of **1a**/**2a** changed from orange to yellow by recrystallization from Et_2O, whereas that of **1b**/**2b** changed from

yellow to orange. The difference in the solid-state color was probably due to the different intermolecular interactions based on the different aggregation structures as well as the unbalanced distribution of the *anti*/*syn* regioisomers after recrystallization from Et_2O. X-ray analysis of single crystals prepared by slow evaporation from Et_2O revealed that *anti* **1** was isolated as single crystals.

EXPERIMENTAL

All reagents were commercially available and used without further purification. 2,6-Naphthodiyne precursor **4** was prepared according to the literature method.[5b] All reactions were performed under nitrogen atmosphere. Column chromatography was performed on a Wako C-300 silica-gel column (45–75 μm). Melting points were measured on a Yanaco melting point apparatus. ^{1}H and ^{13}C spectra were measured with a Bruker-Biospin DRX500 FT spectrometer. EI-MS spectra were measured on a Shimadzu GCMS-QP5050A. Elemental analyses were carried out on a Yanaco MT-5 CHN corder. Absorption and fluorescence spectra in solution were recorded with a HITACHI U3500 spectrophotometer and a HITACHI F2500 spectrophotometer (λ_{ex} = 365 nm), respectively. Kubelka-Munk spectra were measured using a HITACHI U3010 spectrophotometer equipped with a Φ60 integrating sphere attachment. Fluorescence spectra in the solid state were measured on a Hamamatsu Photonics PMA11 calibrated optical multichannel analyzer with a solid-state blue laser (λ_{ex} = 377 nm). Absolute quantum yields were determined with a Labsphere IS-040-SF integrating sphere.

Preparation of 2-hexylfuran (3a)

To an ice-cooled mixture of furan (2.0 mL, 27.6 mmol) and TMEDA (10 mL), 1.6 M *n*-BuLi in hexane (20 mL, 32.0 mmol) was added slowly. The mixture was refluxed for 1 h to accomplish mono-lithiation. The mixture, which changed to a brown suspension, was allowed to cool to rt and was then cooled with an ice bath. To the ice-cooled mixture, a solution of 1-bromohexane (4.8 mL, 34.4 mmol) in THF (15 mL) was added dropwise. The mixture was stirred at rt for 16 h. After quenching with water, the crude product was extracted with Et_2O, washed with brine, and dried over Na_2SO_4. After evaporation of the solvents, the residue was subjected to column chromatography (hexane) on silica gel to remove polar components. Distillation under reduced pressure (22 mmHg, > 90 °C) provided **3a** a colorless oil (1.82 g, 43%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 1.26–1.37 (m, 6H), 1.59–1.65 (m, 2H), 2.60 (t, J = 7.7 Hz, 2H), 5.95 (d, J = 3.0 Hz, 1H), 6.26 (dd, J = 1.8, 3.0 Hz, 1H), 7.27 (d, J = 1.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.96, 22.59, 27.97, 28.04, 28.90, 31.62, 104.46, 109.90, 140.50, 156.45.

Preparation of 2-hexyl-5-isopropylfuran (3b)

To an ice-cooled mixture of furan **3a** (3.00 g, 19.7 mmol) and TMEDA (6.3 mL), 1.6 M *n*-BuLi in hexane (18 mL, 28.8 mmol) was added slowly. The mixture was refluxed for 1 h. The mixture was allowed to

cool to rt and was then cooled with an ice bath. To the ice-cooled mixture, a solution of acetone (5.0 mL, 68.0 mmol) in THF (7.5 mL) was added dropwise. Then the mixture was stirred at rt for 16 h. After quenching with water, the crude alcohol was extracted with AcOEt, washed with brine, and dried over Na_2SO_4. After evaporation of the solvents, the residue was roughly purified by column chromatography ($CHCl_3$) on silica gel to give a brown oil (1.88 g). Because of its difficult purification, the product containing some impurities was used in the next reaction. A solution of the brown oil (1.88 g) in CH_2Cl_2 (50 mL) was hydrogenated over 10% Pd/C (100 mg) under atmospheric pressure at rt for 6 h. The catalyst was removed by filtration and the filtrate was concentrated under reduced pressure. Column chromatography (hexane) on silica gel afforded **3b** as a yellow oil (1.29 g, 34% from **3a**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.22 (d, J = 6.9 Hz, 6H), 1.28–1.39 (m, 6H), 1.59–1.63 (m, 2H), 2.56 (t, J = 7.6 Hz, 2H), 2.85–2.90 (m, 1H), 5.81–5.84 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.07, 21.20, 22.59, 27.79 (2C), 28.08, 28.92, 31.61, 102.74, 104.57, 154.65, 159.91.

Preparation of an *anti*/*syn* mixture of 1,7- and 1,10-dihexyltetracene (1a/2a)

KF (1.12 g, 19.3 mmol) was added to a solution of 2,6-naphthodiyne precursor **4** (2.60 g, 4.57 mmol), furan **3a** (1.54 g, 10.1 mmol), and 18-crown-6 (4.80 g, 18.2 mmol) in THF (80 mL). The mixture was stirred at room temperature for 18 h. Water was added, and the resulting mixture was extracted with $CHCl_3$. The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvents, the residue was roughly purified by column chromatography ($CHCl_3$/hexane = 1/2) to afford a bis(furan) adduct (162 mg) as a yellow oil. Because of its difficult purification, the adduct was then used in the next reaction. A solution of the adduct (162 mg) in EtOH (30 mL) was hydrogenated over 10% Pd/C (33 mg) under atmospheric pressure at rt for 4 h. The catalyst was removed by filtration, and the filtrate was concentrated under reduced pressure. To the residue was added a cold solution of conc. HCl (1 mL) and Ac_2O (5 mL) at 0 °C, and the mixture was stirred at rt for 40 min. Water was added, and the resulting mixture was extracted with $CHCl_3$. The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvents, purification by column chromatography (hexane) on silica gel afforded tetracene **1a/2a** as an orange solid (94 mg, 5% from **4**). mp 75–77 °C. Recrystallization of the orange solid from Et_2O produced a yellow solid (27 mg, 1.5% from **4**). mp 121–122 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, J = 7.1 Hz, 6H), 1.36–1.40 (m, 8H), 1.49–1.55 (m, 4H), 1.88–1.91 (m, 4H), 3.22 (t, J = 7.8 Hz, 4H), 7.21 (d, J = 6.5 Hz, 2H), 7.32 (dd, J = 6.5, 8.5 Hz, 2H), 7.88 (d, J = 8.5 Hz, 2H), 8.71 (s, 2H), 8.81 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.16, 22.73, 29.65, 30.23, 31.83, 33.37, 122.34, 124.24, 124.85, 126.86, 127.39, 129.76, 130.58, 132.06, 138.74; MS m/z 396 (M^+, 100); UV-vis (hexane) λ_{max} (log ε) = 420 (3.56), 446 (3.71), 476 nm (3.71); Fluorescence (hexane) λ_{em} = 486, 514, 551 nm (Φ = 0.18). Anal. Calcd for $C_{30}H_{36}$: C, 90.85; H, 9.15. Found: C, 90.70; H, 9.19.

Preparation of an *anti*/*syn* mixture of 1,7-dihexyl-4,10-diisopropyl- and 1,10-dihexyl-4,7-diisopropyltetracene (1b/2b)

The title compound was prepared following the same procedure as described above for **1a**/**2a** except that reagents KF (927 mg, 16.0 mmol), 2,6-naphthodiyne precursor **4** (2.20 g, 3.80 mmol), furan **5b** (1.70 g, 9.10 mmol), 18-crown-6 (3.71 g, 13.9 mmol), THF (100 mL), 10% Pd/C (200 mg), and EtOH (50 mL) were used. The title compound was obtained as a yellow viscous solid (400 mg, 22% from **4**). mp 55–57 °C. Recrystallization of the yellow solid from Et_2O produced an orange solid (350 mg, 19% from **4**). mp 148–150 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (t, J = 6.9 Hz, 6H), 1.32–1.59 (m, 24H), 1.88–1.93 (m, 4H), 3.21 (t, J = 7.8 Hz, 4H), 3.94–4.00 (m, 2H), 7.23–7.26 (m, 4H), 8.86 (s, 2H), 8.94 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.20, 22.76, 23.63, 28.68, 29.73, 30.18, 31.88, 33.35, 120.16, 122.71, 123.40, 123.98, 128.93, 130.44, 131.09, 136.57, 142.53; MS m/z 480 (M^+, 100); UV-vis (hexane) λ_{max} (log ε) = 424 (3.69), 451 (3.94), 481 nm (3.93); Fluorescence (hexane) λ_{em} = 494, 522, 558 nm (Φ = 0.11). Anal. Calcd for $C_{36}H_{48}$: C, 89.94; H, 10.06. Found: C, 89.88; H, 10.24.

X-Ray crystallographic analysis

Crystal data for **1a**: $C_{30}H_{36}$, Fw = 396.59, T = 223 K, triclinic, space group P–1, a = 7.648(4), b = 8.428(4), c = 10.406(5) Å, α = 67.430(17), β = 74.293(19), γ = 79.68(2)°, V = 594.1(5) Å^3, Z = 1, D_{calcd} = 1.108 g cm^{-3}, 4735 reflections measured, 2680 independent, 146 parameters refined, GOF = 1.091, R_1 = 0.087 [$I > 2\sigma(I)$], wR_2 = 0.303 (all data). Crystal data for **1b**: $C_{36}H_{48}$, Fw = 480.74, T = 223 K, monoclinic, space group $C2$, a = 19.570(3), b = 7.5746(11), c = 9.8068(14) Å, β = 99.493(3)°, V = 1433.8(3) Å^3, Z = 2, D_{calcd} = 1.114 g cm^{-3}, 7041 reflections measured, 3222 independent, 175 parameters refined, GOF = 0.876, R_1 = 0.087 [$I > 2\sigma(I)$], wR_2 = 0.369 (all data). Single crystals were grown from Et_2O solutions by slow evaporation. X-Ray diffraction data were collected on a Rigaku Mercury diffractometer for **1a** and a Rigaku RAXIS RAPID diffractometer for **1b** with a graphite−monochromated Mo-K$_\alpha$ (λ = 0.7107 Å) radiation. The structures were solved by direct methods using SIR2004.[9] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using SHELXL97.[10] All the H atoms were geometrically positioned and refined using a riding model. All calculations were performed using the WinGX program package.[11] Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as CCDC 805752 (**1a**) and 805751 (**1b**).

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7 There were no remarkable differences in the optical properties in solution between **1a**/**2a** and **1b**/**2b** as well as before and after recrystallization.
8. We observed that each molecule had two disordered sets of alkyl groups. For clarity, minor sites are omitted in Figure 4.
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