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Synthesis, Optical Properties, and Crystal Structure of 1,4-Dipropyltetracene

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We synthesized 1,4-dipropyltetracene on a 200-mg scale, the key step of which involved a Diels–Alder reaction between alkyl-substituted *o*-quinodimethane, generated in situ, and 1,4-naphthoquinone. The product was obtained as an orange solid, which was soluble in organic solvents including hexane. The optical properties of the product in solution showed no marked differences from those of other 1,4,7,10-tetraalkyltetracenes. Solid-state absorption and fluorescence spectra exhibited 20–30 nm blueshifts compared with those of 1,4,7,10-tetrapropyltetracene. X-ray analysis revealed that two propyl groups were coplanar with the tetracene ring, that there was no π overlap along the stacking direction, and that the molecules formed a herringbone structure. The peripheral alkyl chains were found to be important for controlling the molecular packing and optical properties in the solid state.

Introduction

Recently, oligoacenes, especially tetracene and pentacene, have attracted considerable interest for their excellent electronic performances as organic semiconductors in organic field-effect transistors, organic light-emitting diodes, and organic photovoltaic cells.[1] However, tetracene and pentacene are hardly soluble in organic solvents, which limits their practical application. Therefore, to achieve low-cost solution processability with high performance, soluble functionalized oligoacenes have been prepared.[2,3]

Very recently, we developed a new method for the preparation of a series of 1,4,7,10-tetraalkyltetracenes **1** (alkyl = methyl to hexyl) by using 2,5-dialkylfurans and 2,6-napthodiyne precursor.[4] The tetrasubstituted tetracenes had unique side-chain conformations and molecular arrangements in the solid state, which were found to give rise to a wide range of interesting solid-state optical properties. One of the most striking observations was that the isolated solids showed colors varying from yellow to red, which were dependent upon the alkyl side-chain length. We recognized that the alkyl side chain had the ability not only to increase solubility in organic solvents but also to control both the crystal packing and the solid-state physical properties. These results prompted us to explore further synthesis of alkyl-substituted tetracenes to clarify the relationship between the alkyl side chain and the solid-state optical properties. We believed that a reduction in the number of side alkyl chains, which creates a low-symmetry structure, would improve the solubility of the tetracene molecules and produce new molecular arrangements in the solid state.[5] We believed the latter effect would bring about new solid-state physical properties. We planned to synthesize tetracenes **2** having two alkyl side chains at the 1- and 4-positions (Figure 1). We expected that a propyl group would be the shortest side-chain length that would achieve good solubility in organic solvents. Here, we report on the synthesis, solid-state optical properties, and crystal structure of 1,4-dipropyltetracene (**2a**).

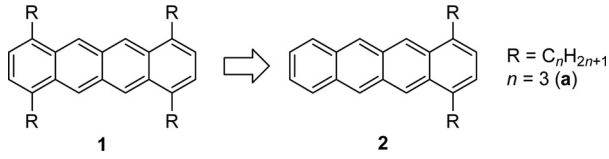

Figure 1. Chemical structures of alkyl-substituted tetracenes.

Results and Discussion

Synthesis

We developed a convenient and efficient synthetic method for 1,4-dialkyltetracenes (Scheme 1). McOmie[6a] and Kametani[6b] reported that 5,12-tetracenequinone was easily obtained by treatment of 1,2-bis(bromomethyl)benzene with 1,4-napthoquinone in the presence of NaI in DMF, which generated *o*-quinodimethane in situ and then underwent a Diels–Alder reaction. We believed that alkyl-substituted 1,2-bis(bromomethyl)benzene was a key inter-

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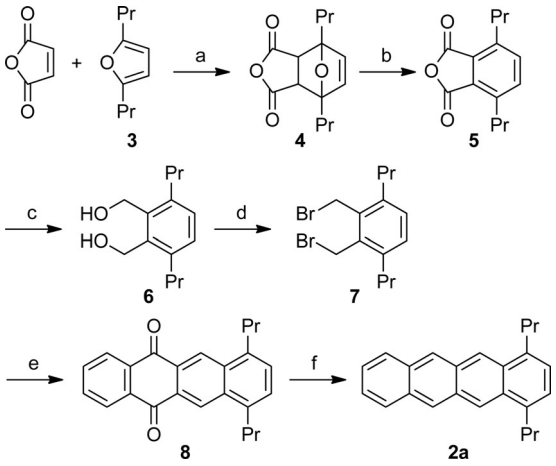
mediate, as tetracene can be easily transformed from tetracene quinone. 1,2-Bis(bromomethyl)-3,6-dimethylbenzene was prepared in four steps from a Diels–Alder reaction between 2,5-dimethylfuran and maleic anhydride by Brickwood et al.,[7] and we adopted the same protocol with the use of 2,5-dipropylfuran (**3**) in place of 2,5-dimethylfuran.



Scheme 1. Reagents and conditions: (a) Et_2O, room temp., 3 h, 76%; (b) conc. H_2SO_4, –10 to 0 °C, 30 min, 65%; (c) $LiAlH_4$, THF, reflux, 62 h, 84%; (d) PBr_3, Et_2O, room temp., 15 h, 75%; (e) 1,4-naphthoquinone, NaI, DMF, 110 °C, 19.5 h, 55%; (f) $NaBH_4$, MeOH/THF, room temp., 1 h; then 57% HI, THF, reflux, 3 h, 66%.

A Diels–Alder reaction between maleic anhydride and furan **3** produced corresponding adduct **4** in 76% yield. Because adduct **4** was apt to decompose into maleic anhydride and **3** upon standing at room temperature for several hours or when dissolved in organic solvents, **4** was dehydrated in cold, concentrated sulfuric acid to afford oily phthalic anhydride **5** as soon as possible. Phthalic anhydride **5** was reduced with $LiAlH_4$ in refluxing THF to phthalyl alcohol **6** in 84% yield after a long reaction time (more than 2 d); otherwise, a mixture of phthalide and phthalyl alcohol **6** was obtained. Phthalyl alcohol **6** was treated with PBr_3 to provide dibromide **7** in 75% yield. Because we encountered difficulties in the purification of **6** and **7** as a result of their unstable nature, we performed the above reactions without further purification. Subsequently, the generation of transient *o*-quinodimethane upon iodide-induced debromination of **7** in the presence of 1,4-napthoquinone provided stable tetracenequinone **8**, which was easily soluble in organic solvents, in 55% yield. Two consecutive procedures of hydride reduction of **8** with $NaBH_4$ in MeOH/THF and treatment of the reduction product with 57% HI in refluxing THF gave tetracene **2a** as an orange solid in 66% yield. Compound **2a** is readily soluble in common organic solvents such as THF, dichloromethane, toluene, and even hexane. Tetracene **2a** was readily prepared on a scale of several hundred milligrams and purified by column chromatography on silica gel by using hexane as an eluent. Although the solution was unstable in the presence of both light and air, compound **2a** showed high air stability in the solid state.

Absorption and Fluorescence Spectra

UV/Vis absorption and fluorescence spectra for **2a**, both in hexane and in the solid state, are shown in Figure 2. In solution, both absorption and fluorescence spectra exhibited vibrational structures (Figure 2a). Absorption peaks based on 0–0, 0–1, and 0–2 transitions were observed at 477, 447, and 421 nm, respectively. The corresponding fluorescence peaks were observed at 488, 516, and 552 nm, respectively, and exhibited a small Stokes shift of 11 nm with a fluorescence quantum yield (Φ_F) of 0.09. These wavelengths and quantum yield were similar to those for 1,4,7,10-tetraalkyltetracenes **1**. Furthermore, there was no marked difference in the spectral shape between **2a** and other tetraalkyltetracenes **1**. These facts suggest not only that molecules in dilute solution exist in a practically monodispersed state, but also that the presence of two alkyl groups at the 1- and 4-positions hardly affects the electronic structure of tetracene ring.

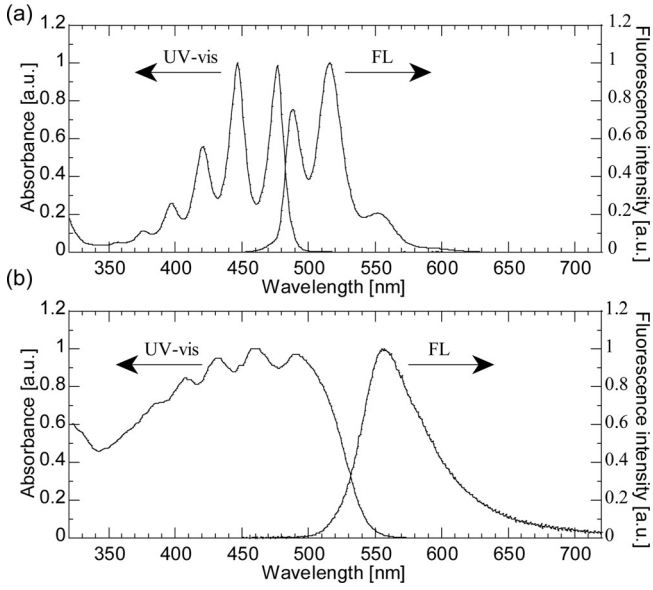


Figure 2. (a) UV/Vis absorption and fluorescence spectra of **2a** in hexane and (b) Kubelka–Munk and fluorescence spectra of **2a** in powder form.

In the solid state, the fluorescence spectrum showed one intense emission band at 557 nm with $\Phi_F = 0.23$, although the absorption (Kubelka–Munk) spectrum in a diluted KBr pellet showed a vibrational structure with peaks at 432, 460, and 491 nm (Figure 2b). The absorption edge was observed at 560 nm. The difference in photophysical properties between the solution and solid state should be ascribed to the difference in the intermolecular interactions between the tetracene rings. Also, the solid-state color of 1,4,7,10-tetrapropyltetracene (**1a**) was orange.[4] However, the absorption edge for **1a** was 580 nm, indicating a non-negligible difference in the solid-state optical properties of **2a** and **1a**. Moreover, the fluorescence emission band for **2a** in the solid state was observed at 557 nm with $\Phi_F = 0.23$, although that for **1a** was observed at 588 nm with $\Phi_F = 0.22$. In other words, both absorption and fluorescence spectra of **2a** in

the solid state exhibited blueshifts compared to those of **1a**. We expected that these subtle differences in solid-state photophysical properties were derived from different individual crystal structures.

Crystal Structure

The crystal structure of **2a** was determined (Figure 3) to observe the effect of the alkyl side chains on molecular packing. In the crystals of 1,4,7,10-tetraalkyltetracenes,[4] the following facts were observed: (1) The alkyl chains took a zigzag (all-*trans*) conformation within their zigzag plane. (2) The zigzag planes tended to be either coplanar with or perpendicular to the tetracene ring because of the torsion degrees of freedom in the alkyl chain. (3) Because of the high symmetry of **2a**, the alkyl conformations at the 1- and 7-positions (namely, a pair of diagonal components) were the same, and also those at the 4- and 10-positions (another pair of diagonal components) were the same. Moreover, for the crystal of **1a**, a pair of two propyl groups at the 1- and 7-positions took a coplanar conformation with the tetracene ring whereas another pair of two propyl groups at the 4- and 10-positions took a perpendicular conformation. In contrast, in the crystal of **2a**, the two propyl groups at the 1- and 4-positions took a coplanar conformation with the tetracene ring (Figure 3a), whose structural feature was rather similar to that of 1,4-dipropylanthracene.[5]

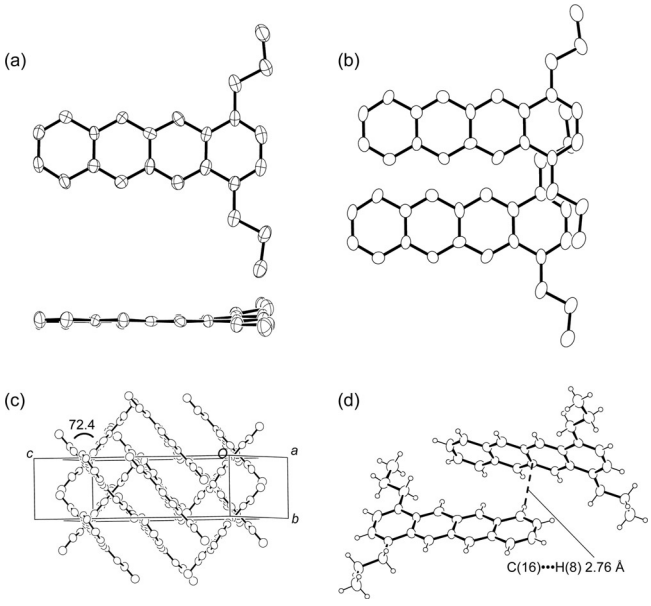


Figure 3. Crystal structure of **2a**: (a) molecular structure, showing top view (upper) and side view (lower); (b) stacking pattern of two neighboring molecules; (c) packing diagram; (d) edge-to-face interaction between nearest molecules in two adjacent columns.

The time-dependent density functional theory (TD-DFT) calculations with the B3LYP/6-31G* method with the use of the geometry obtained by X-ray analysis showed a lowest-energy absorption band at the single molecular level at 496.5 nm for **2a**, which was far from the longest absorption maximum in solution (λ_{max} = 477 nm) and it was rather close to that in the solid state (λ_{max} = 491 nm). This seemingly peculiar result suggested that the prediction of photophysical properties was very difficult at the present theoretical level and that some corrections based on intermolecular interactions, such as exciton coupling, were required to estimate the solid-state photophysical properties precisely.

Next, the stacking pattern of two neighboring molecules along the 1D stacking direction in the crystal was examined (Figure 3b). As in the case of 1,4,7,10-tetraalkyltetracenes and 1,4-dipropylanthracene, there was no π overlap between the two molecules. The tetracene rings along the column direction slipped relative to each other along the long molecular axis by 0.65 Å and along the short molecular axis by 4.48 Å. The former geometrical parameter was within the standard values for 1,4,7,10-tetraalkyltetracenes (0.10–1.49 Å) and 1,4-dipropylanthracene (1.12 Å). However, the latter parameter was larger than those for 1,4,7,10-tetraalkyltetracenes (1.32–3.76 Å) and 1,4-dipropylanthracene (3.89 Å). In addition, the interplanar distance between the adjacent tetracene planes was 3.27 Å, which was shorter than the same distances for 1,4,7,10-tetraalkyltetracenes (3.43–3.53 Å) and 1,4-dipropylanthracene (3.63 Å). Under these circumstances, different intermolecular interactions probably occurred between tetracene molecules.

When viewed down the long molecular axis, **2a** had a herringbone structure, in which the interplanar tilt angle between tetracene rings in two adjacent columns was 72.4° (Figure 3c). This molecular arrangement was dramatically different from that of **1a**, which adopted a slipped-parallel pattern without π overlap. However, the molecular packing of **2a** was similar to that of 1,4-dipropylanthracene. The difference in molecular packing arises from the nonexistence of alkyl side chains at the 7- and 10-positions in **2a**. Thus, the presence of aromatic hydrogen atoms at the 7- and 10-positions leads to an edge-to-face arrangement in the crystal because of CH–π interactions, which have been observed in numerous studies on aromatic hydrocarbons. In the crystal of **2a**, a relatively short nonbonded distance between C(16) and H(8) atoms in the two adjacent columns (2.76 Å) was observed (Figure 3d). We recognized that the alkyl side chains in the solid state not only served as a spacer but also adjusted the mutual positional relationship of the tetracene rings. Therefore, we demonstrated that the peripheral alkyl side chains on the tetracene ring played an important role in the control of the molecular packing and optical properties in the solid state.

Conclusions

In summary, we have developed an efficient method for the synthesis of 1,4-dipropyltetracene, which is readily soluble in organic solvents, including hexane, from a Diels–Alder reaction between maleic anhydride and dipropylfuran in seven steps. There was no significant difference in the optical properties of the product in solution compared to the optical properties of 1,4,7,10-tetraalkyltetracenes. The

color of 1,4-dipropyltetracene was orange, which resembled the 1,4,7,10-tetrapropyltetracenes. However, the solid-state absorption and fluorescence of 1,4-dipropyltetracene exhibited 20–30 nm blueshifts compared to those of 1,4,7,10-tetrapropyltetracene. X-ray analysis revealed that the molecular structure was planar, that there was no π overlap between the two neighboring molecules along the stacking direction, and that the molecules adopted a herringbone structure; these features were all directly ascribed to the solid-state optical properties.

Experimental Section

General: All reagents were commercially available and used without further purification. Solvents for syntheses were purified by standard methods. Column chromatography was performed on Wako silica gel C-300 (45–75 μm). Melting points were measured with a Yanaco melting point apparatus. ^{1}H and ^{13}C spectra were measured with a Bruker-Biospin DRX500 FT spectrometer. Elemental analyses were performed with a Yanaco MT-5 CHN recorder. Absorption and fluorescence spectra in solution were recorded with a Hitachi U3500 spectrophotometer and Hitachi F2500 spectrophotometer, respectively. Fluorescence yields (Φ_F) in solution were determined with 9,10-diphenylanthracene (Φ_F = 0.86)[8] in cyclohexane as the standard. Kubelka–Munk spectra were measured by using a Hitachi U3010 spectrophotometer with a Φ60 integrating sphere attachment. Fluorescence spectra in the solid state were recorded by using a Hamamatsu Photonics PMA11 calibrated optical multichannel analyzer (λ_{ex} = 325 nm), and the measurement of the absolute quantum yield (Φ_F) was performed by using a Labsphere IS-040-SF integrating sphere. TD-DFT calculations were carried out by using the B3LYP/6-31G* method with the Gaussian 03 program package.[9]

Materials: The synthesis of 2,5-dipropylfuran (**3**) was previously described.[10]

3,6-Dipropylphthalic Anhydride (5): A mixture of mortar-ground maleic anhydride (5.21 g, 53.1 mmol) and furan **3** (8.09 g, 53.1 mmol) in Et_2O (10 mL) was stirred at room temperature for 20 h. Hexane (60 mL) was added to the reaction mixture. A large part of Diels–Alder adduct **4** (6.54 g) precipitated as a white solid. The filtrate was evaporated under reduced pressure, and hexane was added to the residue to give a small part of **4** (992 mg). The combined crude product was obtained in a total yield of 57%. Because compound **4** was apt to decompose on standing at room temperature, **4** was used in the next reaction as soon as possible. To concentrated H_2SO_4 (50 mL) cooled to –10 °C was added **4** (5.74 g, 22.9 mmol) in small portions. The mixture was stirred at 0 °C for 30 min. The reaction mixture was poured onto crushed ice. The resulting product was extracted with Et_2O. The organic layer was washed with brine and dried with Na_2SO_4. After removal of solvent and drying under vacuum, **5** was obtained as an orange oil (2.28 g, 43%) and used in the next reaction without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.4 Hz, 6 H, $CH_2CH_2CH_3$), 1.67–1.72 (m, 4 H, $CH_2CH_2CH_3$), 3.04 (t, J = 7.2 Hz, 4 H, $CH_2CH_2CH_3$), 7.54 (s, 2 H, Ar-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.51, 23.55, 32.65, 127.89, 136.90, 142.51, 162.82 ppm.

1,2-Bis(hydroxymethyl)-3,6-dipropylbenzene (6): To a suspension of $LiAlH_4$ (1.44 g, 37.9 mmol) in THF (30 mL) was dropwise added a solution of **5** (1.10 g, 4.74 mmol) in THF (35 mL) at room temperature. The mixture was heated at reflux for 62 h. The mixture was cooled to room temperature and then cooled with an ice bath. To the ice-cooled mixture was cautiously added water (3 mL) and 10% H_2SO_4 (40 mL). The reaction mixture was extracted with $CHCl_3$. The combined organic layer was washed with brine and dried with Na_2SO_4. After removal of the solvents and drying under vacuum, **6** was obtained as a yellow oil (880 mg, 84%) and used in the next reaction without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.1 Hz, 6 H, $CH_2CH_2CH_3$), 1.58–1.62 (m, 4 H, $CH_2CH_2CH_3$), 2.68 (t, J = 7.7 Hz, 4 H, $CH_2CH_2CH_3$), 4.82 (s, 4 H, CH_2OH), 7.11 (s, 2 H, Ar-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.95, 25.05, 35.40, 58.43, 129.44, 137.66, 139.39 ppm.

1,2-Bis(bromomethyl)-3,6-dipropylbenzene (7): To a solution of **6** (772 mg, 3.48 mmol) in Et_2O (10 mL) was dropwise added a solution of PBr_3 (0.7 mL, 7.45 mmol) in Et_2O (10 mL) at room temperature. The mixture was stirred at room temperature for an additional 15 h. Then, the reaction mixture was poured into ice water, neutralized with aqueous $NaHCO_3$, and extracted with Et_2O. The organic layer was washed with brine and dried with Na_2SO_4. After removal of the solvent and drying under vacuum, **7** was obtained as a yellowish-white solid (990 mg, 75%) and used in the next reaction without further purification. M.p. 62–64 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.02 (t, J = 7.0 Hz, 6 H, $CH_2CH_2CH_3$), 1.66–1.70 (m, 4 H, $CH_2CH_2CH_3$), 2.68 (t, J = 7.6 Hz, 4 H, $CH_2CH_2CH_3$), 4.73 (s, 4 H, CH_2Br), 7.11 (s, 2 H, Ar-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.20, 24.03, 27.30, 34.70, 130.18, 134.51, 140.34 ppm.

7,12-Dipropyl-5,12-tetracenequinone (8): A mixture of **7** (904 mg, 2.60 mmol), 1,4-naphthoquinone (616 mg, 3.90 mmol), and NaI (1.95 g, 13.0 mmol) in DMF (8 mL) was stirred at 110 °C for 19.5 h. The reaction mixture was cooled to room temperature, then poured into 5% Na_2SO_3, and extracted with $CHCl_3$. The organic layer was washed with brine and dried with Na_2SO_4. After removal of the solvents, the residue was subjected to column chromatography ($CHCl_3$/hexane, 1:1) on silica gel to afford **8** as a yellow solid (500 mg, 56%). M.p. 155–156 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.07 (t, J = 7.2 Hz, 6 H, $CH_2CH_2CH_3$), 1.81–1.85 (m, 4 H, $CH_2CH_2CH_3$), 3.17 (t, J = 7.7 Hz, 4 H, $CH_2CH_2CH_3$), 7.45 (s, 2 H, 8-H, 9-H), 7.84 (dd, J = 3.2, 5.6 Hz, 2 H, 2-H, 3-H), 8.42 (dd, J = 3.2, 5.6 Hz, 2 H, 1-H, 4-H), 9.09 (s, 2 H, 6-H, 11-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.20, 24.29, 35.00, 126.32, 127.43, 128.73, 129.33, 134.09, 134.49, 134.63, 139.74, 183.26 ppm. $C_{24}H_{22}O_2$ (342.43): calcd. C 84.18, H 6.48; found C 84.33, H 6.77.

1,4-Dipropyltetracene (2a): To a solution of **8** (342 mg, 1.00 mmol) in MeOH (20 mL) and THF (20 mL) was added $NaBH_4$ (189 mg, 5.00 mmol) in small portions at room temperature. The mixture was stirred at room temperature for an additional hour. After neutralization with 10% AcOH, the reduction product was extracted with $CHCl_3$. The combined organic layer was washed with brine and dried with Na_2SO_4. After removal of solvents, a white solid was obtained. The solid was dissolved in THF (10 mL) and heated to reflux. Under reflux conditions, 57% HI (10 mL) was added dropwise, and then, the mixture was heated at reflux for 3.5 h. The reaction mixture was cooled to room temperature, then poured into 5% Na_2SO_3, and extracted with Et_2O. The organic layer was washed with brine and dried with Na_2SO_4. After removal of the solvents, the residue was subjected to column chromatography (hexane) on silica gel to afford **2a** as an orange solid (207 mg, 66%). M.p. 126–127 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.12 (t, J = 7.3 Hz, 6 H, $CH_2CH_2CH_3$), 1.89–1.93 (m, 4 H, $CH_2CH_2CH_3$), 3.18 (t, J = 7.7 Hz, 4 H, $CH_2CH_2CH_3$), 7.17 (s, 2 H, 2-H, 3-H), 7.54 (dd, J = 3.2, 6.6 Hz, 2 H, 8-H, 9-H), 8.01 (dd, J = 3.2, 6.6 Hz, 2 H, 7-H, 10-H), 8.69 (s, 2 H, 6-H, 11-H), 8.84 (s, 2 H, 5-H, 12-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.47, 23.38, 35.47, 123.22,

124.24, 124.98, 126.38, 128.29, 129.64, 131.02, 131.46, 136.58 ppm. $C_{24}H_{24}$ (312.45): calcd. C 92.26, H 7.74; found C 92.46, H 7.96.

X-ray Crystallography: X-ray diffraction data were collected with a Rigaku/Mercury CCD area detector diffractometer with graphite-monochromated Mo-K_α (α = 0.71070 Å) radiation, ϕ and ω scans to a maximum 2θ value of 55.0° at 223 K. The structures were solved by direct methods by using SIR92.[11] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 by using SHELXL97.[12] Hydrogen atoms were positioned geometrically and refined by using a riding model. All calculations were performed by using the teXsan program package.[13] Crystallographic data for **2a**: $0.50 \times 0.05 \times 0.02$ mm, $C_{24}H_{24}$, M = 312.45, monoclinic, space group $P2_1/n$, a = 17.69(1) Å, b = 5.538(3) Å, c = 17.87(1) Å, β = 103.220(3)°, V = 1704.3(16) Å^3, Z = 4, $D_{calcd.}$ = 1.218 g cm^{-3}, μ = 0.068 mm^{-1}, 5706 reflections measured, 2532 unique, GOF = 0.94, R = 0.065 [$I > 2\sigma(I)$], wR = 0.188 (all data). CCDC-761527 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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