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Synthesis of Substituted Trinaphthylenes

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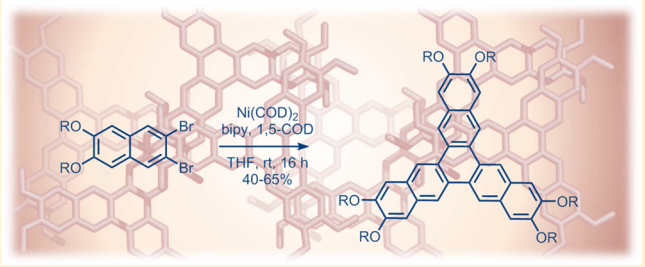
Supporting Information

ABSTRACT: A short synthesis of six trinaphthylenes is reported. The cyclotrinaphthylenes carry six alkoxy groups, and derivatives featuring OHex, OBu, OiPr, OPr, OEt, and OMe substituents can be obtained by an ordinary $Ni(COD)_2$-promoted, Yamamoto-type coupling reaction. Cyclotrimerization yields range from 38% to 65%. Dependent upon their structure, the cyclotrinaphthylenes assume different packing patterns, according to single-crystal X-ray structure determination. The crystal structures of such trinaphthylenes were hitherto undescribed.



INTRODUCTION

Here we describe a dramatically shortened synthesis of soluble, processable hexakisalkoxytrinaphthylenes (**4**), using a common $Ni(COD)_2$-based cyclotrimerization reaction at ambient temperature. Large aromatic compounds are in the crosshairs of materials science. They are powerful charge transport materials, excellent emitters in organic light-emitting diodes (OLEDs), and superb donor materials in organic photovoltaic devices.[1] However, there is also a more transcendent aspect to arene and acene chemistry, viz., the fundamental questions both for new structures and for the abbreviated preparations of known materials, which would allow their facile access in larger quantities and perhaps in fewer steps. We have analyzed a particular substance class, the hexakisalkoxytrinaphthylenes, for an overhaul of their synthesis. These materials and their smaller derivatives, the triphenylenes,[2] are attractive as liquid crystals[3] and also as potential charge transport materials,[4] as shown by Müllen et al. for their smaller congeners.[5]

The current synthesis of compounds such as **4** starts from the dibromide **1**, which, in a four-step synthetic sequence, is transformed into the direct precursor of **4**, the silane **3**. Compound **3** is then cyclotrimerized using $(Ph_3P)_4Pd$ in acetonitrile. While this clever sequence, reported by Maly et al.,[6,7] made the alkoxytrinaphthylenes accessible for the first time, the synthesis of the precursors **2** and **3** is cumbersome; it requires cryogenic (−100 °C) temperatures that are not conveniently available, in addition to using BuLi as a reagent in two of the steps. While the cyclotrimerization has a yield of around 45%, the overall yield, starting from 2,3-dihydroxynaphthalene, is, over five steps, only around 10%.

Wu et al.[8] also reported a series of highly interesting electron-accepting trinaphthylenes, which they built up by a clever application of different hexaradialenes, the precursors of which they obtained exactly the same way Maly et al.[7] prepared their trinaphthylenes. The hexaradialenes were then reacted with a substituted maleic imide to give the desired naphthylenes. The underlying Pd-catalyzed trimerization route used both by Maly and by Wu was mentioned by Galow et al.,[9] who employed this method originally developed by Guitian et al.[10] Guitan et al. claimed that a formed aryne would cyclotrimerize using a Pd catalyst. These are the developments that led to our quest to furnish a more facile approach toward the overall class of the enlarged triphenylenes.

RESULTS AND DISCUSSION

After we were able to demonstrate that substituted 2,3-dibromo-TIPSA-pentacenes (TIPSA = (triisopropylsilyl)-acetylene) smoothly trimerize at room temperature into tris(pentacenylene)s, using $Ni(COD)_2$ in the presence of bipyridine, we set out to explore this method for the synthesis of the already known cyclotrinaphthylenes.[11] Scheme 1 shows the synthesis of Maly,[6] in which the common precursor **1** is first transformed into a hydroxy bromide, **2**,[6] and further elaborated into **3**. Pd-catalyzed cyclotrimerization yielded **4**. In our case we reasoned that the direct cyclization of the dibromides **1a−f** should be possible. Scheme 1 demonstrates that **1a−f** indeed cyclize under conditions we have developed, using $Ni(COD)_2$ in the presence of additional bipyridine in THF at room temperature (16 h), to give **4a−f** in 38−65% yield after chromatography and crystallization. If the yields are determined from 2,3-dihydroxynaphthalene, they range from 20% to 36%. This shortens the access and gives the cyclotrinaphthylenes in much higher overall yield and under more convenient conditions, developed by us.

The formed trinaphthylenes **4a−f** are crystalline, yellow to colorless solids, which do not form particularly good films on glass. However, crystallization of the six compounds was possible and was perfomed either by slow evaporation of a dichloromethane solution or by overlaying this solution with

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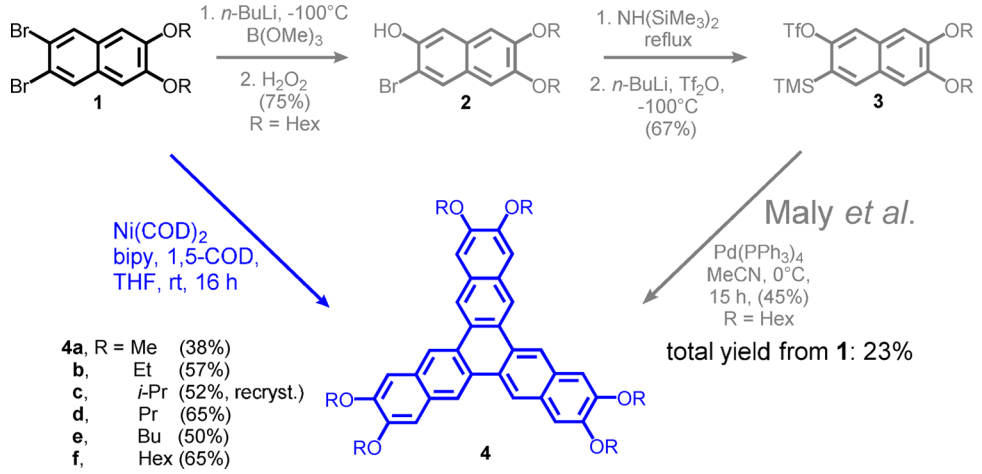
J. Org. Chem. 2016, 81, 193−196

Scheme 1. Synthesis of Trinaphthylenes 4a–f Using a Straightforward Method Developed Here[a]



[a]Compounds **1a,f** and **4f** are literature known.[6,7]

methanol. The unit cells of **4a–e** include dichloromethane molecules. As expected, the X-ray crystal structures vary with the substituent size.

The trinaphthylene derivatives **4a** and **4b** (small alkyl chains) show similar packing patterns (Figure 1). One can see planes

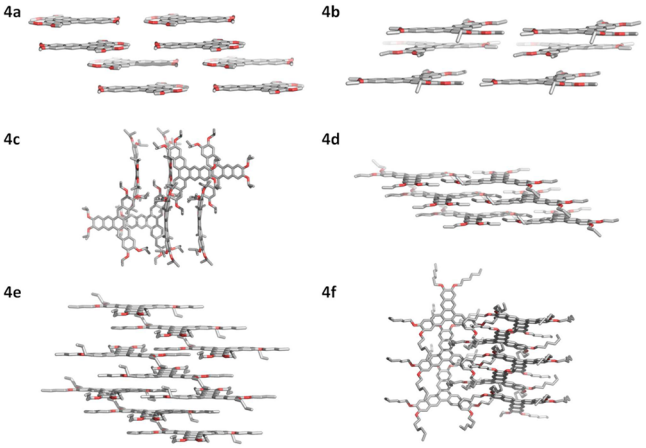


Figure 1. Crystal packing of trinaphthylene derivatives **4**: methyloxy (**4a**), ethyloxy (**4b**), isopropyloxy (**4c**), propyloxy (**4d**), butyloxy (**4e**), and hexyloxy (**4f**).[7]

with a distance of 3.5 Å for **4a**. In the case of structure **4b**, the distance between two layers alternates between 3.6 and 3.8 Å. All molecules in the same layer have the same orientation, while the orientation of the molecules in the layer beneath and above is rotated by 180°. The trinaphthylene core of **4a** is almost planar, and the molecules of **4b** show a slight intramolecular deformation of 7°. The distortion was measured by construction of an average plane for each "naphthylene arm" and by determining the angle between these planes. The solid-state packing of **4c** is different. The crystal structure shows an independent one-dimensional stacklike periodicity with a distance of 8.2 Å between the trinaphthylenes. The molecules in neighboring parallel "stacks" are tilted with respect to each other by an angle of 65°, and there is no $\pi-\pi$ interaction. The molecule undergoes an extreme distortion showing an angle of 20°. Replacing isopropyloxy (**4c**) by *n*-propyloxy (**4d**) substituents results in a brick wall motif, separated by alkyl solvent areas without any $\pi-\pi$ overlap. The two-dimensional stacking causes a slight deformation (2.5°) of the molecular geometry. The structure of **4e** is similar to that of **4d**, except for additional solvent molecules incorporated into the brick wall of **4e**. The longest chain we used in this synthesis is *n*-hexyloxy (**4f**).[7] The structure of **4f** does not contain solvent molecules, but the bulky substituents support a one-dimensional stacked motif, where the molecules (in the parallel stacks) are tilted toward each other by an angle of 73°. The main difference from structure **4c** is that there are $\pi-\pi$ interactions within the stacks over a distance of 3.5 Å. The intramolecular twist is about 7°. Concerning their use in electric devices, the structures **4d** and **4e** are the most promising, due to the $\pi-\pi$ interactions and the parallel orientation of the molecules. Though the device performance cannot be derived from the crystal structure itself, the construction of devices and measuring are planned. To our knowledge, these are the first X-ray crystal structures of such trinaphthylenes, and it is surprising to see how the alkoxy units really dominate and modulate the packing behavior of these attractive materials from herringbone to stackwise packing.

The cyclotrinaphthylenes **4** are easily oxidized (Figure 2). Reversible oxidation occurs at 0.45 V vs Fc. The absorption and emission spectra of three representatives are shown in Figure 3. They are largely independent of the structure of the alkoxy groups and feature a weak absorption maximum at around 395 nm and a structured emission at 407 nm. The low intensity of

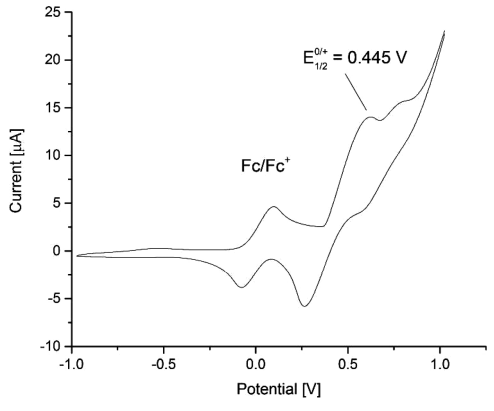


Figure 2. Cyclic voltammogram of **4c** vs ferrocene.

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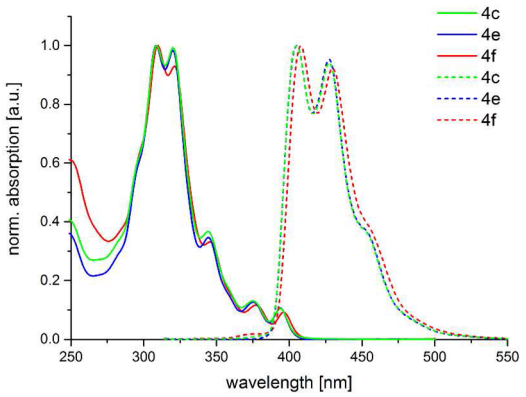

Figure 3. Absorption and emission spectra of representative derivatives of **4**.

the absorption band is due to the D_{3d} symmetry, in which the frontier molecular orbitals are degenerate, and therefore, the HOMO−LUMO transition is symmetry forbidden.

CONCLUSIONS

In conclusion, we have prepared the cyclotrinaphthylenes **4a−f** in reasonable to good yields in a streamlined synthetic approach, using an effective Yamamoto coupling protocol. Single-crystal structures of all six representatives **4a−f** were obtained. We find that the packing of the targets is strongly determined by the alkoxy substituents, more so than by the core. Some of the derivatives give stacked geometries in the solid state, while others form more of a herringbone-type arrangement. The observed packing is not easily predictable, as isopropyloxy and hexyloxy groups give herringbone-type packing, while the other derivatives prefer a more columnar packing, in which the disklike cores stack on top of each other. In the future, we will explore the synthesis of larger triacenylenes by this new and powerful method, and we will optimize their film-forming and processing properties to make them useful for organic electronics applications.

EXPERIMENTAL SECTION

General Procedure 1 (GP1): Formation of 2,3-Dibromo-6,7-dialkoxynaphthalenes 1a−f. In a heatgun-dried Schlenk flask, 6,7-dibromonaphthalene-2,3-diol and a haloalkane were dissolved in dry THF. The mixture was stirred for 20 h at ambient temperature, and the resulting solid was isolated and purified.

2,3-Dibromo-6,7-dimethoxynaphthalene (1a). 6,7-Dibromonaphthalene-2,3-diol (250 mg, 786 μmol) was reacted according to GP1 with iodomethane. A pale yellow solid was isolated after the crude product was dissolved in ethyl acetate and after washing with water (239 mg, 691 μmol, 88%). Mp: 148−152 °C. ^{1}H NMR (300.51 MHz, $CDCl_3$): δ = 7.93 (s, 2 H), 6.95 (s, 2 H), 3.97 (s, 6 H), ^{13}C{H} NMR ($CDCl_3$, 300.51 MHz): δ = 150.6 (2 C), 130.6 (2 C), 129.3 (2 C), 119.7 (2 C), 105.2 (2 C), 56.1 (2 C). MS (HR-MALDI$^+$) (m/z): calcd for $C_{12}H_{10}{}^{81}Br_2O_2{}^+$ 347.9001, found 347.9010; calcd for $C_{12}H_{10}{}^{79}Br^{81}BrO_2{}^+$ 345.9027, found 345.9051; calcd for $C_{12}H_{10}{}^{79}Br_2O_2{}^+$ 343.9048, found 343.9052.

2,3-Dibromo-6,7-diethoxynaphthalene (1b). 6,7-Dibromonaphthalene-2,3-diol (800 mg, 2.52 mmol) was reacted according to GP1 with bromoethane. A colorless solid was isolated after column chromatography (silica gel; petroleum ether/EtOAc, 2/1; 837 mg, 2.24 mmol, 89%). Mp: 133 °C. ^{1}H NMR ($CDCl_3$ 400.33 MHz): δ = 7.93 (s, 2 H), 6,97 (s, 2 H), 4.18 (q, J = 7.0 Hz, 4 H), 1.53 (t, J = 7.0 Hz, 6 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.7 MHz): δ = 150.3 (2 C), 130.6 (2 C), 129.4 (2 C), 119.5 (2 C), 106.4 (2 C), 64.6 (2 C), 14.7 (2 C). MS (HR-EI$^+$) (m/z): calcd for $C_{14}H_{14}{}^{81}Br_2O_2{}^+$ 405.9314, found 405.9309; $C_{14}H_{14}{}^{79}Br^{81}BrO_2{}^+$ 403.9335, found 403.9328; calcd $C_{14}H_{14}{}^{79}Br_2O_2{}^+$ 371.9355, found 371.9347.

2,3-Dibromo-6,7-diisopropoxynaphthalene (1c). 6,7-Dibromonaphthalene-2,3-diol (268 mg, 841 μmol) was reacted according to GP1 with 2-bromopropane. A pale yellow solid was isolated after column chromatography (silica gel; petroleum ether/EtOAc, 1/1; 302 mg, 751 μmol, 89%). Mp: 108 °C. ^{1}H NMR ($CDCl_3$ 300 MHz): δ = 7.92 (s, 2 H), 7.03 (s, 2 H), 4.60 (sept, J = 6.1 Hz, 1 H), 1.41 (d, J = 6.1 Hz, 6 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.7 MHz): δ = 150.3 (2 C), 130.5 (2 C), 129.5 (2 C), 119.5 (2 C), 110.2 (2 C), 72.0 (2 C), 22.1 (4 C). MS (HR-EI$^+$) (m/z): calcd for $C_{16}H_{18}{}^{81}Br_2O_2{}^+$ 403.9633, found 403.9619; calcd for $C_{16}H_{18}{}^{79}Br^{81}BrO_2{}^+$ 401.9653, found 401.9626; calcd for $C_{16}H_{18}{}^{79}Br_2O_2{}^+$ 399.9667, found 399.9663.

2,3-Dibromo-6,7-dipropoxynaphthalene (1d). 6,7-Dibromonaphthalene-2,3-diol (800 mg, 2.52 mmol) was reacted according to GP1 with 1-bromopropane. A colorless solid was isolated after column chromatography (silica gel; petroleum ether/EtOAc, 3/1; 970 mg, 2.41 mmol, 96%). Mp: 139 °C. ^{1}H NMR ($CDCl_3$ 400.33 MHz): δ = 7.92 (s, 2 H), 6.97 (s, 2 H), 4.05 (t, J = 5.4 Hz, 4 H), 1.92 (sext, 4 H), 1.09 (t, J = 7.4 Hz, 6 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.7 MHz): δ = 150.7 (2 C), 130.5 (2 C), 129.4 (2 C), 119.4 (2 C), 105.6 (2 C), 70.5 (2 C), 22.6 (2 C), 10.6 (2 C). MS (HR-EI$^+$) (m/z): calcd for $C_{16}H_{18}{}^{81}Br_2O_2{}^+$ 403.9627, found 403.9615; calcd for $C_{16}H_{18}{}^{79}Br^{81}BrO_2{}^+$ 401.9648, found 401.9632; calcd for $C_{16}H_{18}{}^{79}Br_2O_2{}^+$ 399.9668, found 399.9651.

2,3-Dibromo-6,7-dibutoxynaphthalene (1e). 6,7-Dibromonaphthalene-2,3-diol (977 mg, 3.10 mmol) was reacted according to GP1 with 1-bromobutane. A pale yellow solid was isolated after column chromatography (silica gel; petroleum ether/EtOAc, 15/1; 520 mg, 1.21 mmol, 39%). Mp: 87 °C. ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ = 7.88 (s, 2 H), 6.92 (s, 2 H), 4,06 (t, J = 6.5 Hz, 4H), 1.90−1.84 (m, 4 H), 1.58−1.51 (m, 4 H), 1.01 (t, J = 7.5 Hz, 6 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ = 150.5 (2 C), 130.4 (2 C), 129.2 (2 C), 119.3 (2 C), 106.2 (2 C), 68.6 (2 C), 31.1 (2 C), 19.4 (2 C), 14.0 (2 C). MS (HR-EI$^+$) (m/z): calcd for $C_{18}H_{22}{}^{81}Br_2O_2{}^+$ 431.9946, found 431.9962; calcd for $C_{18}H_{22}{}^{79}Br^{81}BrO_2{}^+$ 429.9966, found 429.9954; calcd for $C_{18}H_{22}{}^{79}Br_2O_2{}^+$ 427.9987, found 428.0009.

2,3-Dibromo-6,7-bis(hexyloxy)naphthalene (1f). The substituted naphthalene derivate (250 mg, 786 μmol) was reacted according to GP1 with 1-bromohexane. A pale yellow solid was isolated after column chromatography (silica gel; petroleum ether/EtOAc, 2/1; 248 mg, 510 μmol, 65%). ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ = 7.92 (s, 2 H), 6.96 (s, 2 H), 4.08 (t, J = 6.53 Hz, 4 H), 1.86−1.92 (m, 4 H), 1.48−1.55 (m, 4 H), 1.32−1.40 (m, 8 H), 0.92 (t, J = 7.5 Hz, 6 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ = 150.6 (2 C), 130.5 (2 C), 129.3 (2 C), 119.4 (2 C), 106.3 (2 C), 69.0 (2 C), 31.7 (2 C), 29.1 (2 C), 25.9 (2 C), 22.8 (2 C), 14.2 (2 C). Other data can be found in the literature.[6]

General Procedure 2 (GP2): Formation of 2,3,8,9,14,15-Hexaalkoxytrinaphthylenes 4a−f. In a heatgun-dried Schlenk flask, 1,5-cyclooctadiene (COD; 2.00 equiv) and 2,2'-bipyridine (1.25 equiv) were dissolved in dry THF under glovebox conditions. Then Ni(1,5-COD)$_2$ (1.25 equiv) was added to give a purple solution. The dibromonaphthalene was dissolved in dry THF and added dropwise over 20 min. The mixture was stirred for 16 h at ambient temperature. Then the mixture was filtered through a silica plug and eluted with dichloromethane before the solvent was removed under reduced pressure. Purification by either flash column chromatography or recrystallization furnished the substituted trinaphthylene.

2,3,8,9,14,15-Hexamethoxytrinaphthylene (4a). The naphthalene derivate **1a** (255 mg, 593 μmol) was reacted according to GP2. A colorless crystalline solid was isolated after recrystallization from dichloromethane (61 mg, 109 μmol, 38%). Mp: >300 °C dec. ^{1}H NMR (CD_2Cl_2, 400.33 MHz): δ = 8.92 (s, 6 H), 7.34 (s, 6 H), 4.06 (s, 18 H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.7 MHz): δ = 150.9 (6 C), 129.3 (6 C), 127.8 (6 C), 120.7 (6 C), 106.4 (6 C), 56.2 (6 C). IR: ν = 2929, 2853, 2827, 1789, 1463, 1423, 1248, 1220, 1147, 1007, 874, 472. MS (HR-MALDI$^+$) (m/z): calcd for $C_{36}H_{30}O_6{}^+$ 558.2042, found 558.2035; calcd for $C_{72}H_{61}O_{12}{}^+$ [2M + H$^+$] 1117.4158, found 1117.4138.

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J. Org. Chem. 2016, 81, 193−196

2,3,8,9,14,15-Hexaethoxytrinaphthylene (4b). The naphthalene derivate **1b** (350 mg, 936 μmol) was reacted according to GP2. A colorless crystalline solid was isolated after column chromatography (silica gel; petroleum ether to petroleum ether/EtOAc, 2/1; 113 mg, 175 μmol, 57%). Mp: >300 °C. dec. ^{1}H NMR ($CDCl_3$, 600.24 MHz): δ = 8.69 (s, 6 H), 7.22 (s, 6 H), 4.27 (q, J = 6.9 Hz, 12 H), 1.60 (t, J = 6.9 Hz,18 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150.9 MHz): δ = 149.6 (6 C), 128.7 (6 C), 127.4 (6 C), 120.2 (6 C), 107.2 (6 C), 64.4 (6 C), 14.9 (6 C). IR: ν = 2972, 2925, 1627, 1492, 1466, 1246, 1207, 1153, 1037, 872. MS (HR-MALDI$^+$) (m/z): calcd for $C_{42}H_{42}O_6^+$ 642.2981, found 642.2970; calcd for $C_{84}H_{85}O_{12}^+$ [2M + H$^+$] 1285.6036, found 1285.5998.

2,3,8,9,14,15-Hexaisopropoxytrinaphthylene (4c). The naphthalene derivate **1c** (350 mg, 870 μmol) was reacted according to GP2. A colorless crystalline solid was isolated after column chromatography (silica gel; petroleum ether to petroleum ether/EtOAc, 3/1; 109 mg, 157 μmol, 52%). Mp: >275 °C, dec. ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ = 8.72 (s, 6 H), 7.38 (s, 6 H) 4.73 (quint, J = 5.5 Hz, 6 H), 1.52 (d, J = 5.5 Hz, 36 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz): δ = 149.6 (6 C), 129.1 (6 C), 127.5 (6 C), 120.3 (6 C), 111.5 (6 C), 71.9 (6 C), 22.3 (12 C). IR: ν = 2975, 2931, 1473, 1239, 1207, 1101, 930, 876, 536, 479. MS (HR-MALDI$^+$) (m/z): calcd for $C_{48}H_{54}O_6^+$ 726.3920, found 726.3915.

2,3,8,9,14,15-Hexapropoxytrinaphthylene (4d). The naphthalene derivate **1d** (350 mg, 870 μmol) was reacted according to GP2. A colorless solid was isolated after column chromatography (silica gel; petroleum ether to petroleum ether/EtOAc, 3/1; 136 mg, 218 μmol, 65%). Mp: 238−240 °C. ^{1}H NMR ($CDCl_3$ 400.33 MHz): δ = 8.75 (s, 6 H), 7.26 (s, 6 H), 4.16 (t, J = 6.5 Hz, 12 H), 2.04−1.95 (m, 12 H), 1.15 (t, J = 7.4 Hz, 18 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.7 MHz): δ = 150.1 (6 C), 128.9 (6 C), 127.5 (6 C), 120.3 (6 C), 107.6 (6 C), 70.5 (6 C), 22.7 (6 C), 10.7 (6 C). IR: ν = 2961, 2930, 2876, 1465, 1247, 1208, 1148, 876, 528, 471. MS (HR-MALDI$^+$) (m/z): calcd for $C_{48}H_{54}O_6^+$ 726.3920, found 726.3929; calcld for $C_{96}H_{108}O_{12}^+$ [2M] 1453.7874, found 1453.7947.

2,3,8,9,14,15-Hexabutoxytrinaphthylene (4e). The naphthalene derivate **1e** (203 mg, 740 μmol) was reacted according to GP2. A colorless crystalline solid was isolated after column chromatography (petroleum ether to petroleum ether/EtOAc, 3/1; 63 mg, 51.9 μmol, 50%). Mp: 219−221 °C. ^{1}HNMR ($CDCl_3$, 400.33 MHz): δ = 8.80 (s, 6 H), 7.28 (s, 6 H), 4.20 (t, J = 6.5 Hz, 12 H), 1.99−1.92 (m, 12 H), 1.66−1.57 (m, 12 H), 1.06 (t, J = 7.4 Hz, 18 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.7 MHz): δ = 150.2 (6 C), 128.9 (6 C), 127.6 (6 C), 120.3 (6 C), 107.6 (6 C), 68.8 (6 C), 31.4 (6 C), 19.5 (6 C), 14.1 (6 C). IR: ν = 2955, 2868, 1489, 1460, 1436, 1246, 1209, 1147, 881, 731, 699. MS (HR-MALDI$^+$) (m/z): calcd for $C_{54}H_{68}O_6^+$ 812.5016, found 812.4986.

2,3,8,9,14,15-Hexakis(hexyloxy)trinaphthylene (4f). The naphthalene derivate **1f** (350 mg, 720 μmol) was reacted according to GP2. A colorless crystalline solid was isolated after column chromatography (petroleum ether to petroleum ether/EtOAc, 15/1; 151 mg, 166 μmol, 65%). ^{1}H NMR ($CDCl_3$ 500.13 MHz): δ = 8.76 (s, 6 H), 7.24 (s, 6 H), 4.18 (t, J = 6.7 Hz, 12 H), 1.99−1.93 (m, 12 H), 1.61−1.55 (m, 12 H), 1.45−1.38 (m, 24 H), 0.96 (t, J = 7.0 Hz, 18 H). IR: ν = 2924, 2856, 1491, 1465, 1248, 1210, 1157, 1018, 878, 471. MS (HR-MALDI$^+$) (m/z): calcd for $C_{66}H_{91}O_6^+$, [M + H]$^+$, 979.6810, found 979.6810. Other data can be found in the literature.[7]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02481.

X-ray crystallographic data and ^{1}H and ^{13}C NMR spectra of all new compounds (PDF)

X-ray crystallographic data for **4a−f** in CIF format (ZIP)

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Notes

The authors declare no competing financial interest.

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