EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201201752

Oligo(naphthylene–ethynylene) Molecular Rods

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Keywords: Self-assembly / Surface chirality / Surface analysis / Conformation analysis / Cross-coupling / Nanostructures

Molecular rods designed for surface chirality studies have been synthesized in high yields. The molecules are composed of oligo(naphthylene–ethynylene) skeletons and functionalized at their two termini with carboxylic acids and hydrophobic groups. The molecular skeletons were constructed by means of palladium-catalyzed Sonogashira reactions between naphthyl halides and acetylenes. The triazene functionality was used as a protected iodine precursor to allow linear extension of the molecular rods during the syntheses. The carboxylic acid groups in the target molecules were protected as esters during the synthesis to keep the large aromatic molecules soluble during their syntheses. These rigid oligomers were designed to form lamella-like structures when adsorbed on a surface, through which multiple distinguishable surface conformations should be obtainable. Preliminary scanning tunneling microscopy imaging confirmed these properties.

Introduction

Self-assembly of molecules when adsorbed on surfaces has attracted considerable attention during the last decade,[1–3] and scanning tunneling microscopy (STM) has proven an invaluable tool for the characterization of molecular structures confined in two dimensions on a surface.[4] A widely used strategy to create highly ordered assemblies is to utilize planar aromatic compounds designed to interact through noncovalent interactions. Particular interest has been devoted to chiral surface assemblies and to how chirality is transferred from the molecular to the supramolecular level.[5,6] Many achiral molecules become chiral upon surface adsorption as a result of the reduction in symmetry.[7] For prochiral molecules, opposite surface enantiomers are created, depending upon the face of the molecule that adjoins the surface.[8]

Chirality can also result from the molecular conformation. However, the importance of conformational degrees of freedom for assembly of chiral structures has received only limited attention.[9,10] In previous work we studied prochiral molecular rods formed from oligo(phenylene ethynylene)s terminated by two *tert*-butyl-salicylaldehyde moieties.[11,12] For these compounds the two opposite surface enantiomers formed patterns with opposite organizational chirality. The resolution into homochiral domains involved chiral switching of the absorbed molecules, which underwent thermally induced rotations of their terminal salicylaldehyde groups. This dynamic switching process allows molecules to adjust to the chirality of the lattice island into which they are integrating. In this manner, information on conformation and chirality is passed from the lattice to new molecules diffusing into the lattice.

Here we set out to extend this principle of passing information between molecules in self-assembled structures, allowing for more systematic investigation. For this purpose we synthesized a new class of molecules designed for their ability *i*) to achieve multiple discrete surface conformations, and *ii*) to form lattices of predictable geometry in which information is easily passed from one molecule to another. The designed compounds, **1**, **2**, and **3** (Figure 1) each contain a number of naphthylene units that in the gas/solvated state have freedom to rotate around the ethynylene-naphthylene backbone.

If these compounds are adsorbed on a surface with their backbone and naphthyl moieties parallel to the surface plane, each naphthyl moiety can assume one of two discrete orientations pointing either right or left relative to the backbone. This two-level situation is analogous to binary digits as used in information technology. The compounds thus represent either three bits (compounds **1** and **2**) or five bits (compound **3**). The total number of discrete conformation states is $2^3 = 8$ for compounds **1** and **2** and $2^5 = 32$ for compound **3**; examples are shown in Figure 2 (a). All of

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201201752.

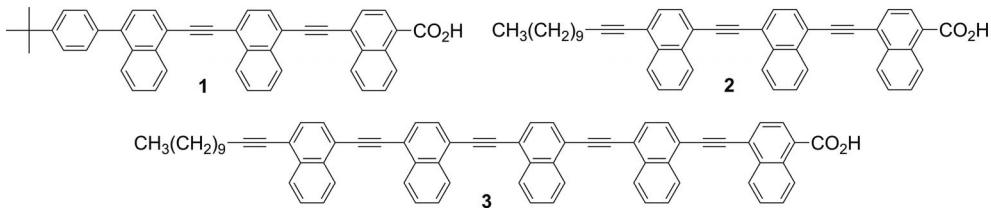


Figure 1. Structure of oligo(naphthylene–ethynylene) molecular rods including two three-bit (**1** and **2**) compounds and one five-bit (**3**) compound.

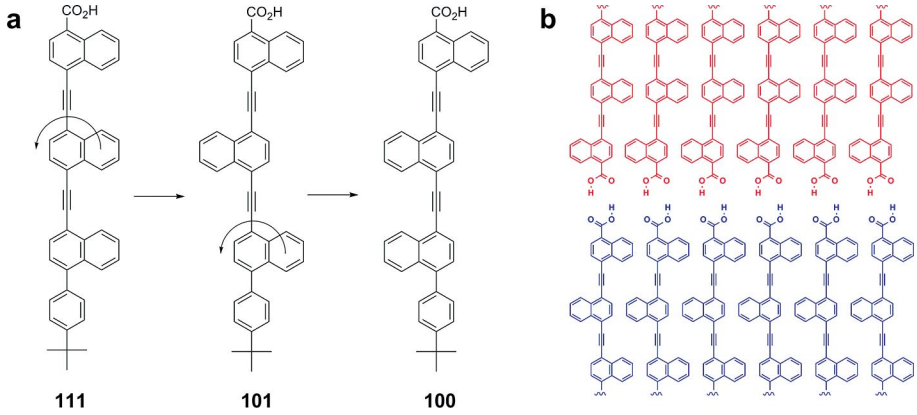


Figure 2. a) Switching of three-bit molecule **1**. The three-bit binary numbers correspond to the orientations of the three naphthyl groups in the adsorbed molecules (0 = left, 1 = right) counting from the carboxylic acid terminus. b) Desired lamellar-type molecular alignment in two homochiral lines.

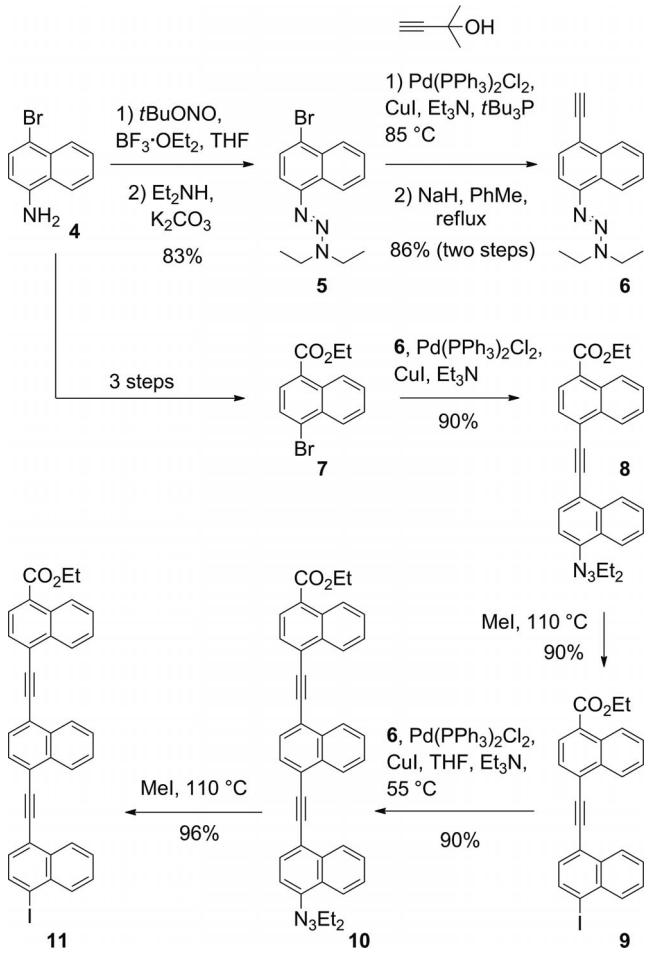
these conformational states are chiral and can be grouped into enantiomeric pairs. On the basis of our previous observation that *tert*-butylsalicylaldehyde groups in adsorbed compounds can rotate, we anticipated that it might be possible for the adsorbed molecules to switch between the conformational states, as illustrated in Figure 2 (a). Furthermore, the molecules were designed to favor assembly into a lamellae-type lattice as shown in Figure 2 (b). The bit compounds were therefore each equipped with a terminal carboxylic acid group, because previous STM studies have shown that it is favorable for two carboxylic acid groups to interact through two hydrogen bonds and align the substituents in a linear fashion.[13] At the other terminal position of each bit compound we attached a nonpolar group such as a *tert*-butylaryl group or a dodecynyl group to favor van der Waals interactions between these groups.[14] Most importantly, this type of lamellar lattice provides optimal closest packing of the oligo(naphthylene–ethynylene) backbone of compounds with the *same* surface conformation (i.e., the best conditions for transfer of information from one molecule to its neighbor through intermolecular interactions). The capability to switch conformation/chirality by undergoing conformational changes should enable the molecules to accommodate to the chirality of the surrounding template and thereby create homochiral surface domains.[8,9,15,16]

Results and Discussion

The synthesis of symmetrical rods based on the oligo(naphthylene–ethynylene) model was reported by Benniston and Harriman.[17,18] Their strategy involved the use of standard Sonogashira cross-coupling reactions and trialkylsilyl protecting groups for the alkynes. Although the yields of the procedure were convincing, purification was reported to be extremely difficult and to involve numerous chromatographic separations. As an alternative we applied an iterative reaction sequence consisting of Sonogashira cross-coupling followed by conversion of a triazene into an aryl iodide.[19] This strategy permits the synthesis of unsymmetrical rods based on the oligo(naphthalene–ethynylene) pattern and involves easy chromatographic purification.

We found the commercially available 4-bromonaphthalen-1-amine (**4**, Scheme 1) to be a suitable starting material. The presence of an aryl bromide unit enables Sonogashira cross-coupling, whereas the amine can be transformed into a diazonium salt that can subsequently be converted into a variety of useful functional groups. Compound **4** was hence transformed into a diazonium salt, which upon treatment with diethylamine formed triazene **5** in very good yield (Scheme 1). Subsequently, **5** was treated with 2-methylbut-3-yn-2-ol in a Sonogashira cross-coupling reaction. Substitution of the widely used ligand Ph_3P with the more electron-rich phosphane tBu$_3$P resulted in an increased yield, probably by accelerating the rate-determining oxidative addition of the aryl halide.[20] The cross-coupled product could be deprotected with sodium hydride in toluene at reflux to yield **6** (86% over two steps).

In addition, the diazonium salt of **4** was converted into ethyl ester **7** by a sequence of literature procedures (see the Supporting Information). The presence of an ester serves to increase the solubilities of the synthesized compounds and,

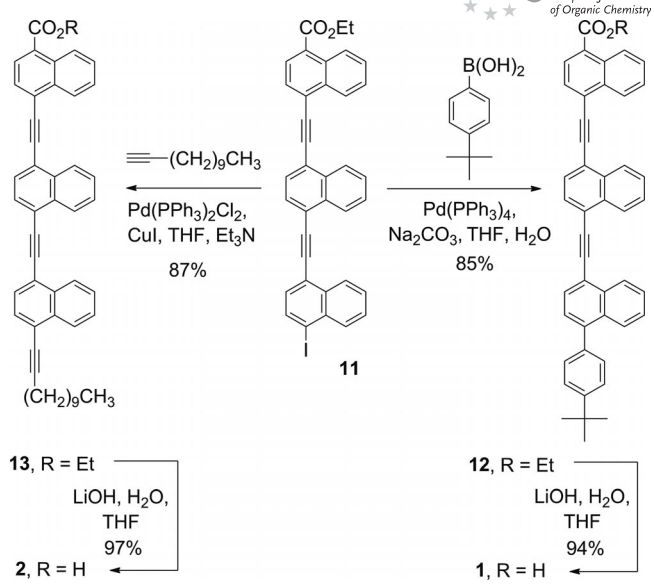


Scheme 1.

furthermore, prevents the acid-labile triazenes from being degraded by the carboxylic acid.

With the two modules **6** and **7** to hand, the next step was to perform a Sonogashira cross-coupling reaction to obtain **8** in 90% yield. Aryltriazenes act as aryl iodide precursor groups that are stable under the conditions applied in the palladium-catalyzed coupling reactions, as well as in the basic acetylene deprotection step. On treatment of aryltriazene **8** with MeI, the aryl iodide **9** was obtained in excellent yield, thus making the aryltriazene a perfect precursor for the aryl iodide.[21]

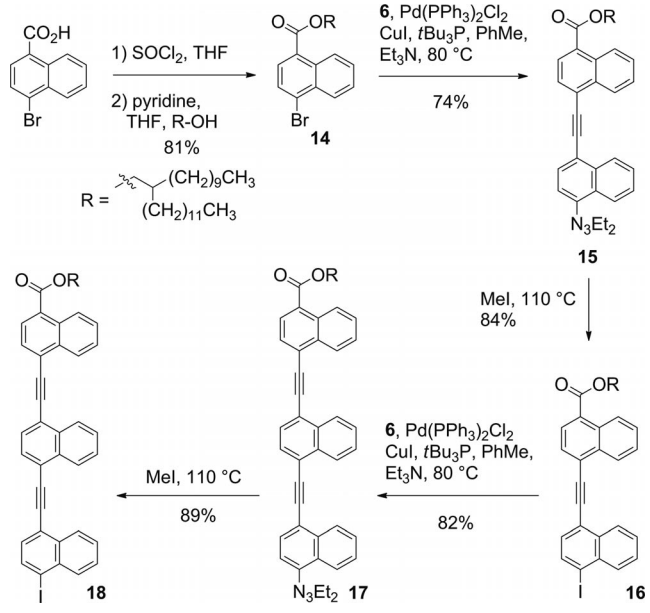
The aryl iodide moiety present in **9** permitted incorporation of the third naphthylene module by coupling it to **6** to yield **10**, which was then converted to aryl iodide **11**. Further modules of **6** could in principle be incorporated to elongate the rod beyond the trimer. This was not pursued, due to low solubility of the trinaphthyl molecules. Compound **11** was terminated with a 4-*tert*-butylphenyl moiety by Suzuki cross-coupling to afford **12** in 85% yield (Scheme 2). The *tert*-butyl group can easily be distinguished in STM studies, thus enabling identification of the arrangements of individual molecules on the surface.[22] Finally, the ester was cleaved under basic conditions to give the product **1** in 94% yield. The product was characterized by ^{1}H NMR spectroscopy, HRMS, and STM as described below.



Scheme 2.

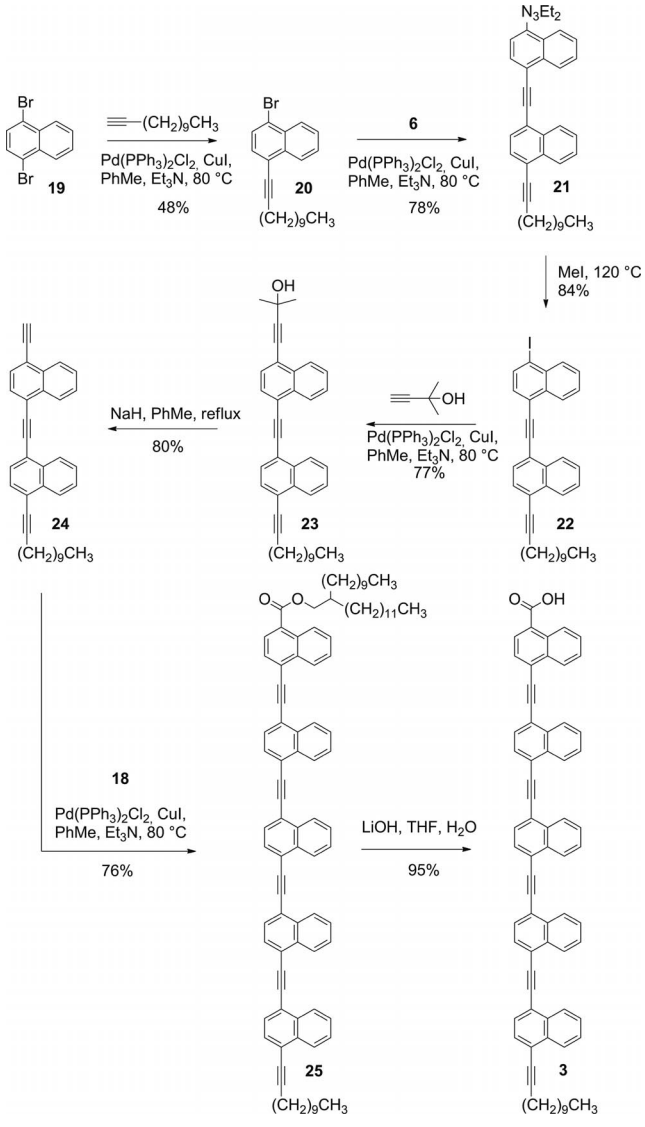
In the same vein, **11** was coupled to dodecyne to yield **13**, followed by ester hydrolysis to give **2**.

In order to synthesize a pentanaphthyl analogue, a convergent synthetic approach was applied. 4-Bromo-1-naphthoic acid was converted into the acyl chloride and treated with 2-decyltetradecan-1-ol to yield **14** (Scheme 3). The large ester moiety was introduced into **14** to provide sufficient solubility for adducts produced in subsequent reactions. The tris(naphthylene–ethynylene) compound was synthesized in a manner similar to that described in Scheme 1, except that toluene was employed as a nonpolar solvent in the cross-coupling reactions in order to improve the conditions for the hydrophobic reactants (reaction sequence **14** to **18**, Scheme 3).



Scheme 3.

The lower part of the pentanaphthyl compound was synthesized from 1,4-dibromonaphthalene (**19**, Scheme 4), which was coupled to dodecyne to afford the monosubstituted product **20** in a moderate yield, due to competing formation of the disubstituted product. Compound **6** could be utilized to obtain the dinaphthyl species **21**, which could subsequently be turned into the aryl iodide **22**. Interestingly, this reaction required a higher temperature than the equivalent steps above, presumably due to the change in the aryl substituent. To install the required ethynylene link between the tri- and dinaphthyl derivatives, **22** was treated with 2-methylbut-3-yn-2-ol to give **23**, which was then deprotected to yield **24**. The two parts **18** and **24** could be brought together in a high-yielding Sonogashira cross-coupling to provide the pentanaphthyl compound **25**. The solubility of **25** far exceeded the solubility of **12**, as a consequence of the long aliphatic chains.



Scheme 4.

Finally, the ester was hydrolyzed to yield the desired carboxylic acid **3**. In contrast with **25**, this compound proved to be practically insoluble in organic solvents, including DMSO, which made characterization by NMR spectroscopy impossible. The compound was therefore characterized by HRMS and elemental analysis. Compounds **15**, **16**, **17**, **18**, and **25** were further characterized by measuring the excitation and emission spectra. As expected, we observed increased values of λ_{max} for increasing length of the conjugated rods, in agreement with previously published results (see the Supporting Information).[17]

To verify the molecular structures and to establish the feasibility of transferring the molecules to solid surfaces, we performed preliminary STM experiments. To test deposition from the liquid phase we used compound **2**, with an aliphatic side chain (dissolved in DMF, <1 mM). As shown in the STM image (Figure 3, b), obtained under ambient conditions, well-ordered lamella structures are formed on deposition of **2** on HOPG (Highly Ordered Pyrolytic Graphite) preheated to 50 °C. The aliphatic side chain and carboxylic acid of **2** apparently do favor the alignment of the molecular backbones into close-packed rows (bright regions) qualitatively resembling the designed lamella struc-

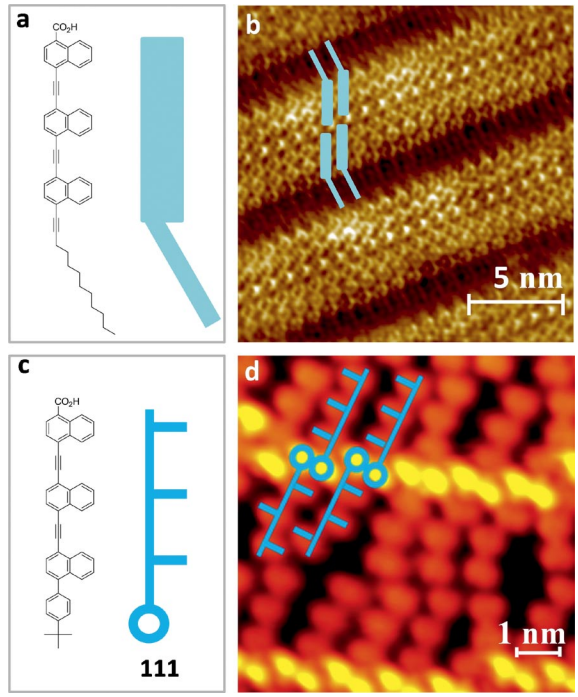


Figure 3. a) Molecular structure and simplified model of **2**. The wider rod represents the molecular backbone of three naphthylene units regardless of different conformations, and the narrow rod corresponds to the alkane chain. b) STM image of **2** on HOPG. The superimposed blue models each represent one molecule. The yellow regions correspond to the (naphthylene–ethynylene) skeleton whereas the darker bands indicate the interdigitating alkyl chains. Imaging parameters: I = 0.02 nA, U_{tip} = 0.5 V. c) Molecular structure and simplified model of **1**. The blue model represents one of the eight possible conformers. d) UHV STM image of **1** on Au(111). As visualized by the models it is possible to distinguish the individual molecular conformations. The *tert*-butyl units are imaged as very bright protrusions and the three connected lighter protrusions represent the naphthylene units. Image size: 80 Å × 80 Å, tunneling parameters: I = –0.390 nA, V = –0.940 V.

ture (Figure 2, b). The resolution is, however, not sufficient to distinguish the individual molecular conformations. Attempts to image compounds **1** and **3** by STM under ambient conditions were unsuccessful.

Higher resolution can be obtained under UHV (Ultra High Vacuum) STM. Thermal deposition of **1** by sublimation from a heated glass crucible onto a Au(111) single crystal seems very promising. A resulting lamellae type arrangement is shown in the STM image in Figure 3 (d). The bright yellow protrusions are attributable to the *tert*-butyl groups, in accordance with our previous studies,[9,11,12] and the orange protrusions clearly show the three naphthyl groups on the molecular backbone. The carboxylic acid moieties are not directly observed in the STM images. The molecules have, however, a strong preference for aligning in head-to-head arrangements in both ambient and UHV STM. According to previous reports, carboxylic acid moieties of molecules absorbed on surfaces can interact strongly through hydrogen bonding,[23] and we therefore believe that the head-to-head interactions observed in the STM images in Figure 3 are also guided by the carboxylic acid groups. In addition, we believe that the hydrophobic interactions of the *tert*-butyl groups in **1** and of the alkyl chain in **2** also play a crucial role in the formation of the molecular patterns. Most importantly, the conformational states of the adsorbed molecules can clearly be distinguished, as indicated by the superimposed schematic models. Unfortunately, our preliminary UHV STM experiments with **2** and **3** were unsuccessful; this was probably due to fragmentation of the compounds during the sublimation process, because fragments of the molecules were observed by UHV STM. In future studies we will address the stability issues, either by optimizing the sublimation procedures or by synthesizing more stable analogues. Furthermore, we will more closely analyze the results obtained with compound **2** to understand fully the associated dynamics and chirality of these lamella-like self-assembled structures.

Conclusions

In conclusion, we have designed and synthesized three molecular rod molecules with potential to achieve multiple discrete conformations at a surface for studies in the field of surface chirality and interactions between molecules. The syntheses were conducted by use of carbon-carbon cross-coupling reactions and triazyl/iodide conversions as the key steps. Preliminary scanning tunneling microscopy studies of two of the investigated oligomers show the formation of close-packed double-row lamella domains. Further studies will address the distribution/selection of conformational states and the transfer of conformation information in these and similar structures. The STM investigations were to some extent hampered by low resolution of the STM under ambient conditions and by stability issues affecting **2** and **3** during the sublimation process required for UHV STM imaging. In future work we will aim to solve these issues and in turn also to introduce homochiral substituents at the individual switching moieties in order to program the molecules to adopt specific preferred conformations at the surface.[11,12] This would enable the "writing" of bit-type information by the homochiral molecules in lattices of non-chiral molecules by co-deposition.

Experimental Section

General: All chemicals were used as received from appropriate suppliers without further purification unless otherwise noted. HPLC grade solvents were used without further drying unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) analysis performed on silica gel 60 F_{254} TLC plates. Spots were visualized with UV light (254 nm). Flash column chromatography was carried out with silica gel 60 (230–400 mesh). NMR spectroscopy was recorded with a 400 spectrometer at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR), calibrated to the residual solvent peak. The following abbreviations are used for NMR spectroscopy data: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet. Melting points are uncorrected. All compounds synthesized were determined to be >95% pure by ^{1}H NMR spectroscopy. HRMS was conducted with electrospray ionization.

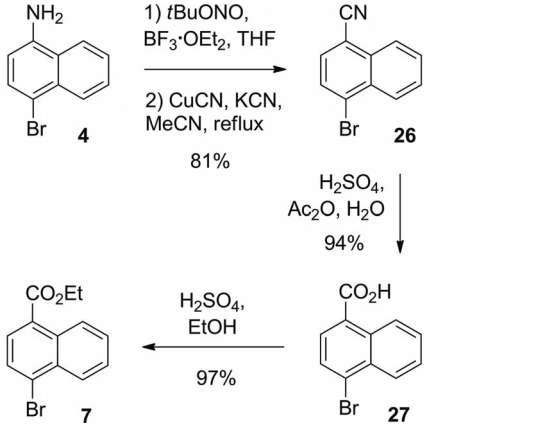
Caution: Specially designed glassware was used for the sealed tube experiments (see photograph in the Supporting Information). Reaction mixtures must be allowed to cool before the tubes are opened.

1-(4-Bromonaphthalen-1-yl)-3,3-diethyltriaz-1-ene (5): 4-Bromonaphthalen-1-amine (2.0 g, 9.0 mmol) in THF (25 mL) was added at –15 °C to an oven-dried vessel containing $BF_3{\cdot}OEt_2$ (2.26 mL, 18.0 mmol), followed by *t*BuONO (2.14 mL, 18.0 mmol). After the mixture has been stirred at –15 °C for 1 h, the temperature was raised to 0 °C over a period of 30 min. Diethylamine (7.4 mL, 72 mmol) and potassium carbonate (8.3 g, 60 mmol) were added sequentially. The reaction mixture was stirred at 0 °C for 2 h, after which it was poured into water (50 mL) and the aqueous layer was extracted with ethyl acetate (3× 25 mL). The combined organic phases were washed with brine and dried with $MgSO_4$, and the solvent was evaporated in vacuo. Purification by flash chromatography (CH_2Cl_2) yielded the product as a red syrup (2.28 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (d, J = 8.3 Hz, 1 H), 8.33 (d, J = 8.1 Hz, 1 H), 7.85 (d, J = 8.1 Hz, 1 H), 7.69 (t, J = 7.6 Hz, 1 H), 7.64 (t, J = 7.6 Hz, 1 H), 7.46 (d, J = 8.1 Hz, 1 H), 3.86 (q, J = 7.2 Hz, 4 H), 1.37 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.7, 132.6, 130.9, 130.3, 127.4, 127.1, 126.1, 124.5, 118.8, 112.2, 48.9, 42.0, 13.7, 10.3 ppm. HRMS: calcd. for $C_{14}H_{16}BrN_3Na$ $[M + Na]^+$ 328.0425; found 328.0432.

3,3-Diethyl-1-(4-ethynylnaphthalen-1-yl)triaz-1-ene (6): Compound **5** (419 mg, 1.37 mmol), bis(triphenylphosphane)palladium(II) dichloride (46 mg, 0.07 mmol), and copper(I) iodide (12 mg, 0.07 mmol) were placed in a flame-dried Schlenk flask. After three successive vacuum/argon cycles, 2-methylbut-3-yn-2-ol (0.67 mL, 6.8 mmol) and triethylamine (15 mL) were introduced, both by syringe. The reaction mixture was stirred at 85 °C overnight. It was then poured into water (25 mL), and the aqueous layer was extracted with ethyl acetate (3× 15 mL). The combined organic phases were dried with $MgSO_4$, and the solvent was evaporated in vacuo. Purification by flash chromatography (ethyl acetate/pentane 1:4, v/v) yielded the protected cross-coupled product as a yellow syrup. Deprotection was performed by dissolving the acetylene compound in toluene (20 mL); sodium hydride (80 mg, 60% min-

eral oil suspension, 2.0 mmol) was then added, and the mixture was heated at reflux overnight. The reaction mixture was then poured into water (15 mL) and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried with $MgSO_4$, and the solvent was evaporated in vacuo. Purification by flash chromatography (ethyl acetate/pentane 1:7, v/v) yielded the product as a yellow syrup (297 mg, 86%, two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, J = 8.4 Hz, 1 H), 8.41 (d, J = 8.1 Hz, 1 H), 7.78 (d, J = 7.9 Hz, 1 H), 7.64 (t, J = 7.5 Hz, 1 H), 7.58 (t, J = 7.5 Hz, 1 H), 7.51 (d, J = 7.9 Hz, 1 H), 3.88 (q, J = 7.1 Hz, 4 H), 3.53 (s, 1 H), 1.36 (t, J = 7.1 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.5, 134.7, 132.0, 129.3, 127.0, 126.0, 125.9, 124.4, 116.1, 111.0, 82.9, 81.7, 49.4, 41.2, 14.2, 11.3 ppm. HRMS: calcd. for $C_{16}H_{18}N_3$ [M + H]$^+$ 252.1501; found 252.1501.

Compound **7** was synthesized by modified literature procedures as shown below:



4-Bromo-1-naphthonitrile (26):[24] BF_3·OEt_2 (2.5 mL, 19.5 mmol) was placed in a three-necked round-bottomed flask fitted with an addition funnel, a septum, and a reflux condenser,. The temperature was lowered to –15 °C. A solution of 4-bromonaphthalen-1-amine (**4**, 3.0 g, 13.5 mmol) in DME (13 mL) was added dropwise, followed by the addition of a solution of *t*BuONO (2.1 mL, 17.7 mmol) in DME (20 mL) over a period of 15 min. After the mixture had been stirred at –15 °C for 1 h, the temperature was raised to 5 °C over a period of 20 min. Pentane (50 mL) was added, and the suspended compound was collected by filtration under suction and washed with pentane (50 mL at 0 °C and 50 mL at room temperature). The green-brown solid was suspended in MeCN (40 mL) and added at room temperature to a solution of KCN (2.78 g, 42.6 mmol) and CuCN (1.27 g, 14.2 mmol) in MeCN (25 mL) and water (8 mL). The mixture was heated at reflux for 2 h and was then allowed to cool to room temperature. The aqueous layer was extracted with ethyl acetate (3 × 50 mL), the combined organic phases were dried with $MgSO_4$, and the solvent was evaporated in vacuo. Purification by flash chromatography (CH_2Cl_2) yielded the product as red crystals (2.53 g, 81%), m.p. 100–102 °C (lit. 100 °C).[25] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, J = 7.7 Hz, 1 H), 8.11 (d, J = 7.3 Hz, 1 H), 7.73 (d, J = 7.7 Hz, 1 H), 7.64 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.1, 132.5, 131.8, 129.6, 129.4, 129.1, 128.1, 125.8, 117.5, 110.2, 110.0 ppm. HRMS: calcd. for $C_{11}H_6NBrNa$ [M + Na]$^+$ 253.9581; found 253.9582.

4-Bromo-1-naphthoic Acid (27):[26] Naphthonitrile **26** (2.26 g, 9.74 mmol) was dissolved in glacial acetic acid (10 mL), concentrated sulfuric acid (8 mL), and water (4 mL). The resulting mixture was heated at reflux for 20 h and was then allowed to cool to room temperature and poured into ice/water. Upon stirring, a precipitate formed; it was collected by filtration, washed with water until clear, and dried in vacuo to yield the product as a beige solid (2.30 g, 94%), m.p. 218–220 °C (lit. 215–218 °C).[27] ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 13.40 (s, 1 H), 8.90 (m, 1 H), 8.24 (m, 1 H), 8.01 (d, J = 7.6 Hz, 1 H), 7.99 (d, J = 7.6 Hz, 1 H), 7.74 (m, 2 H) ppm. ^{13}C NMR (100 MHz, DMSO): δ = 168.5, 132.2, 131.8, 130.5, 129.8, 128.9, 128.6, 128.5, 127.5, 127.4, 126.7 ppm. HRMS: calcd. for $C_{11}H_7O_2BrNa$ [M + Na]$^+$ 272.9527; found 272.9541.

Ethyl 4-Bromo-1-naphthoate (7):[28] 4-Bromo-1-naphthoic acid (**27**, 1.93 g, 7.72 mmol) was added to ethanol (50 mL) and concentrated H_2SO_4 (0.1 mL), after which the resulting slurry was heated to reflux for 20 h. The reaction mixture was allowed to cool to room temperature, and water (20 mL) was added. The milky white water/ethanol suspension was extracted with methyl *tert*-butyl ether (3 × 15 mL), the combined organic extracts were washed with saturated brine (15 mL) and dried with $MgSO_4$, and the solvent was evaporated in vacuo. The crude oil was purified by flash chromatography (ethyl acetate/pentane 1:4, v/v) to yield the product as yellow crystals (2.08 g, 97%), m.p. 40–42 °C (lit. 43.5 °C).[28] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.95 (d, J = 9.9 Hz, 1 H), 8.31 (d, J = 9.9 Hz, 1 H), 7.97 (d, J = 7.9 Hz, 1 H), 7.80 (d, J = 7.9 Hz, 1 H), 7.63 (m, 2 H), 4.47 (q, J = 7.1 Hz, 2 H), 1.46 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 132.6, 132.4, 130.2, 129.1, 128.8, 128.6, 127.9, 127.8, 127.6, 126.5, 61.5, 14.6 ppm. HRMS: calcd. for $C_{13}H_{11}O_2BrNa$ [M + Na]$^+$ 300.9840; found 300.9837.

Ethyl Ester 8: Compounds **7** (36 mg, 0.13 mmol) and **6** (37 mg, 0.15 mmol), bis(triphenylphosphane)palladium(II) dichloride (9 mg, 0.01 mmol), and copper(I) iodide (3 mg, 0.01 mmol) were placed in a flame-dried Schlenk flask. After three successive vacuum/argon cycles, triethylamine (15 mL) was introduced by syringe. The reaction mixture was stirred at room temperature overnight. It was then poured into water (25 mL), and the aqueous layer was extracted with ethyl acetate (3 × 15 mL). The combined organic phases were washed with brine and dried with $MgSO_4$, and the solvent was evaporated in vacuo. Purification by flash chromatography (ethyl acetate/pentane 1:5, v/v) yielded the product as a red syrup (52 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.01 (m, 1 H), 8.71 (m, 2 H), 8.54 (d, J = 8.3 Hz, 1 H), 8.21 (d, J = 7.6 Hz, 1 H), 7.89 (d, J = 7.9 Hz, 1 H), 7.88 (d, J = 7.6 Hz, 1 H), 7.76–7.51 (m, 5 H), 4.51 (q, J = 7.1 Hz, 2 H), 3.92 (q, J = 7.1 Hz, 4 H), 1.50 (t, J = 7.1 Hz, 3 H), 1.39 (t, J = 7.1 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 147.7, 134.5, 133.8, 131.9, 131.6, 129.7, 129.5, 129.0, 128.3, 127.3, 127.2, 127.2, 127.2, 126.9, 126.4, 126.2, 126.0, 124.6, 116.8, 111.2, 96.6, 92.1, 61.5, 49.4, 42.1,14.7, 14.6, 11.5 ppm. HRMS: calcd. for $C_{29}H_{27}N_3O_2Na$ [M + Na]$^+$ 472.2001; found 472.2023.

Ethyl Ester 9: Compound **8** (50 mg, 0.11 mmol) and methyl iodide (5 mL) were placed in a sealed tube. The solution was degassed and the tube was sealed. After heating at 110 °C overnight, the starting triazene had been completely consumed. During this time, diethyldimethylammonium iodide precipitated from the solution. The reaction mixture was poured into pentane (10 mL), filtered, and concentrated. Purification by flash chromatography (ethyl acetate/pentane 1:10, v/v) yielded the product as an orange powder (48 mg, 90%), m.p. 113–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.99 (m, 1 H), 8.60 (m, 1 H), 8.49 (m, 1 H), 8.26–8.05 (m, 3 H), 7.88 (m, 1 H), 7.68 (m, 4 H), 7.57 (m, 1 H), 4.51 (q, J = 7.5 Hz, 2 H), 1.49 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 137.2, 134.4, 133.8, 133.7, 133.0, 131.5, 131.5, 129.5, 128.6, 128.5,

128.5, 128.4, 128.1, 127.4, 127.1, 126.9, 126.5, 125.9, 121.9, 101.6, 94.4, 93.5, 61.6, 14.7 ppm. HRMS: calcd. for $C_{25}H_{17}IO_2Na$ [M + Na]$^+$ 499.0171; found 499.0181.

Ethyl Ester 10: Compounds **9** (153 mg, 0.32 mmol) and **6** (89 mg, 0.35 mmol), bis(triphenylphosphane)palladium(II) dichloride (23 mg, 0.033 mmol), and copper(I) iodide (5 mg, 0.03 mmol) were placed in a flame-dried Schlenk flask. After three successive vacuum/argon cycles, THF (6 mL) and triethylamine (6 mL) were introduced, both by syringe. The reaction mixture was stirred at 55 °C overnight. It was then poured into water (25 mL), and the aqueous layer was extracted with ethyl acetate (3 × 15 mL). The combined organic phases were washed with brine and dried with $MgSO_4$, after which the solvent was evaporated in vacuo. Purification by flash chromatography (CH_2Cl_2/pentane 1:3, v/v) yielded the product as a red syrup (173 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.02 (m, 1 H), 8.74 (d, J = 8.4 Hz, 1 H), 8.68 (m, 2 H), 8.59 (m, 2 H), 8.20 (d, J = 7.6 Hz, 1 H), 7.91 (m, 4 H), 7.72 (m, 5 H), 7.59 (m, 2 H), 4.52 (q, J = 7.1 Hz, 2 H), 3.92 (q, J = 7.1 Hz, 4 H), 1.50 (t, J = 7.1 Hz, 3 H), 1.39 (t, J = 7.1 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 147.5, 134.4, 133.8, 133.4, 133.3, 131.8, 131.5, 130.6, 129.9, 129.6, 129.6, 129.4, 128.4, 127.9, 127.8, 127.7, 127.4, 127.3, 127.8, 127.0, 126.8, 126.5, 126.2, 126.2, 126.0, 124.6, 123.1, 120.9, 117.1, 111.3, 96.1, 95.4, 93.8, 92.4, 61.5, 49.4, 42.1,14.7, 14.6, 11.5 ppm. HRMS: calcd. for $C_{41}H_{33}N_3O_2Na$ [M + Na]$^+$ 622.2470; found 622.2470.

Ethyl Ester 11: Compound **10** (152 mg, 0.24 mmol) and methyl iodide (5 mL) were placed in a sealed tube. The solution was degassed and the tube was sealed. After heating at 110 °C overnight, the starting triazene had been completely consumed. During this time, diethyldimethylammonium iodide precipitated from solution. The reaction mixture was poured into pentane (10 mL), filtered, and concentrated. Purification by flash chromatography (CH_2Cl_2/pentane 1:5, v/v) yielded the product as a yellow powder (146 mg, 96%), m.p. 158–160 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.11–8.89 (m, 1 H), 8.77–8.42 (m, 4 H), 8.26–8.06 (m, 3 H), 7.89 (m, 3 H), 7.83–7.60 (m, 6 H), 7.55 (d, J = 7.6 Hz, 1 H), 4.51 (q, J = 7.1 Hz, 2 H), 1.50 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 137.2, 134.4, 133.8, 133.7, 133.3, 133.2, 133.0, 131.5, 131.3, 130.5, 130.2, 129.6, 129.5, 129.5, 128.6, 128.5, 128.4, 128.1, 128.0, 127.8, 127.8, 127.4, 127.1, 126.9, 126.9, 126.6, 126.0, 122.2, 121.7, 101.2, 95.1, 94.2, 94.0, 93.9, 61.5, 14.8 ppm. HRMS: calcd. for $C_{37}H_{23}IO_2Na$ [M + Na]$^+$ 649.0640; found 649.0637.

Ethyl Ester 12: Compound **11** (55 mg, 0.088 mmol), 4-(*tert*-butyl)-phenylboronic acid (31 mg, 0.17 mmol), and tetrakis(triphenylphosphane)palladium(0) (5 mg, 0.004 mmol) were placed in a flame-dried Schlenk flask. After three successive vacuum/nitrogen cycles, THF (7 mL) and Na_2CO_3 (2 M, 0.1 mL) were introduced, both by syringe. The reaction mixture was stirred at 65 °C overnight. It was then poured into water (10 mL), and the aqueous layer was extracted with diethyl ether (3 × 15 mL). The combined organic phases were washed with brine and dried with $MgSO_4$, and the solvent was evaporated in vacuo. Purification by flash chromatography (CH_2Cl_2/pentane 1:3, v/v) yielded the product as a yellow powder (47 mg, 85%), m.p. 192–194 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.08–8.99 (m, 1 H), 8.74–8.58 (m, 3 H), 8.22 (d, J = 7.6 Hz, 1 H), 8.08 (d, J = 8.4 Hz, 1 H), 7.94 (m, 4 H), 7.80–7.63 (m, 5 H), 7.63–7.45 (m, 5 H), 7.39 (m, 2 H), 4.53 (q, J = 7.1 Hz, 2 H), 1.51 (t, J = 7.1 Hz, 3 H), 1.45 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 150.7, 141.9, 137.5, 135.5, 135.5, 135.4, 133.9, 133.8, 133.4, 131.9, 131.5, 130.6, 130.5, 130.5, 130.1, 130.0, 129.5, 129.4, 128.4, 128.1, 127.9, 127.8, 127.8, 127.1, 127.1, 127.0, 126.9, 126.8, 126.6, 126.1, 125.5, 122.7, 121.3, 120.3, 95.3, 95.2, 94.0, 92.8, 61.5, 34.9, 31.7, 14.7 ppm. HRMS: calcd. for $C_{47}H_{36}O_2Na$ [M + Na]$^+$ 655.2613; found 655.2617.

Acid 1: LiOH (20 mg, 0.83 mmol), dissolved in water (2 mL), was added to a solution of **12** (40 mg, 0.063 mmol) in THF (5 mL). The reaction mixture was heated at reflux overnight. Upon acidification (conc. HCl), a precipitate formed; this was collected by filtration, washed with water (5 mL) and THF (5 mL), and dried in vacuo to yield the product as a yellow powder (36 mg, 94%), m.p. 290–292 °C. ^{1}H NMR (400 MHz, DMSO): δ = 8.96 (d, J = 8.5 Hz, 1 H), 8.71–8.54 (m, 4 H), 8.17 (m, 6 H), 7.91 (m, 6 H), 7.56 (m, 5 H), 1.37 (s, 9 H) ppm. HRMS: calcd. for $C_{45}H_{32}O_2Na$ [M + Na]$^+$ 627.2300; found 627.2304. No ^{13}C NMR spectrum could be obtained, due to low solubility.

Ethyl Ester 13: Compound **11** (100 mg, 0.16 mmol), dodec-1-yne (133 mg, 0.80 mmol), bis(triphenylphosphane)palladium(II) dichloride (11 mg, 0.016 mmol), and copper(I) iodide (3 mg, 0.016 mmol) were placed in a flame-dried Schlenk flask. After three successive vacuum/argon cycles, THF (10 mL) and triethylamine (1 mL) were introduced, both by syringe. The reaction mixture was stirred at 55 °C overnight. It was then poured into water (25 mL), and the aqueous layer was extracted with ethyl acetate (3 × 15 mL). The combined organic phases were washed with brine and dried with $MgSO_4$, after which the solvent was evaporated in vacuo. Purification by flash chromatography (CH_2Cl_2/pentane 1:3, v/v) yielded the product as a red syrup (92 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.04–8.98 (m, 1 H), 8.70–8.54 (m, 4 H), 8.43 (d, J = 8.0 Hz, 1 H), 8.20 (d, J = 7.6 Hz, 1 H), 7.96–7.85 (m, 3 H), 7.82 (d, J = 7.5 Hz, 1 H), 7.78–7.62 (m, 7 H), 4.51 (q, J = 7.1 Hz, 2 H), 2.61 (t, J = 7.1 Hz, 2 H), 1.71 (quint, J = 7.1 Hz, 2 H), 1.55 (quint, J = 7.1 Hz, 2 H), 1.50 (t, J = 7.1 Hz, 3 H), 1.45–1.23 (m, 12 H), 0.90 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 133.5, 133.4, 133.1, 133.1, 133.0, 131.3, 130.3, 130.1, 129.9, 129.4, 129.2, 129.2, 128.1, 127.8, 127.6, 127.5, 127.3, 127.1, 127.0, 126.9, 126.8, 126.7, 126.6, 126.5, 126.3, 125.8, 123.1, 122.2, 121.2, 120.4, 97.9, 94.9, 94.6, 93.8, 93.5, 78.7, 61.3, 31.9, 29.6, 29.6, 29.4, 29.2, 29.1, 28.9, 22.7, 19.9, 14.4, 14.1 ppm. HRMS: calcd. for $C_{49}H_{44}O_2Na$ [M + Na]$^+$ 687.3239; found 687.3238.

Acid 2: LiOH (20 mg, 0.83 mmol), dissolved in water (1 mL), was added to a solution of **13** (40 mg, 0.060 mmol) in THF (5 mL). The reaction mixture was heated at reflux overnight. Upon acidification (conc. HCl), a precipitate formed; it was collected by filtration, washed with water (5 mL) and THF (5 mL), and dried in vacuo to yield the product as a yellow powder (37 mg, 97%), m.p. 236–238 °C. ^{1}H NMR (400 MHz, DMSO): δ = 8.96 (d, J = 8.4 Hz, 1 H), 8.70–8.54 (m, 4 H), 8.34 (d, J = 8.1 Hz, 1 H), 8.18 (d, J = 7.5 Hz, 1 H), 8.15–8.05 (m, 2 H), 7.98 (d, J = 7.5 Hz, 1 H), 7.95–7.63 (m, 8 H), 2.61 (quint, J = 6.9 Hz, 2 H), 1.65 (quint, J = 6.9 Hz, 2 H), 1.49 (quint, J = 6.9 Hz, 2 H), 1.35–1.15 (m, 12 H), 0.82 (t, J = 6.9 Hz, 3 H) ppm. HRMS: calcd. for $C_{47}H_{40}O_2Na$ [M + Na]$^+$ 658.2848; found 658.2853. No ^{13}C NMR spectrum could be obtained, due to low solubility.

2-Decyltetradecyl 4′-Bromo-1′-naphthoate (14): 4-Bromo-1-naphthoic acid (**27**, 1.00 g, 3.94 mmol) was heated at reflux in $SOCl_2$ (15 mL) in a round-bottomed flask for 15 min, followed by removal of excess $SOCl_2$ in vacuo. The acid chloride was then dissolved in THF (30 mL), 2-decyltetradecan-1-ol (1.16 g, 3.28 mmol), and pyridine (0.2 mL). The solution was heated at reflux at 70 °C overnight. The reaction mixture was then poured into water (50 mL), and the aqueous layer was extracted with diethyl ether (3 × 30 mL). The combined organic phases were washed with brine and dried with $MgSO_4$, after which the solvent was evaporated in vacuo. Purification by flash chromatography (diethyl ether/pentane 2:98, v/v)

yielded the product as a light yellow oil (1.56 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.97 (m, 1 H), 8.34 (m, 1 H), 7.99 (d, J = 7.9 Hz, 1 H), 7.83 (d, J = 7.9 Hz, 1 H), 7.71–7.57 (m, 2 H), 4.33 (d, J = 5.7 Hz, 2 H), 1.84 (sept, J = 6.0 Hz, 1 H), 1.52–1.18 (m, 40 H), 0.89 (t, J = 6.7 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 132.5, 132.2, 129.9, 128.9, 128.6, 128.4, 127.7, 127.6, 127.5, 126.3, 68.1, 37.5, 31.9, 31.5, 30.0, 29.7, 29.6, 29.4, 26.8, 22.7, 14.1 ppm. HRMS: calcd. for $C_{35}H_{55}BrO_2Na$ $[M + Na]^+$ 609.3283; found 609.3277.

Tetradecyl Ester 15: Compounds **14** (1.00 g, 1.70 mmol) and **6** (428 mg, 1.70 mmol), bis(triphenylphosphane)palladium(II) dichloride (119 mg, 0.17 mmol), and copper(I) iodide (32 mg, 0.17 mmol) were placed in a flame-dried Schlenk flask. After three successive vacuum/argon cycles, toluene (35 mL), triethylamine (5 mL), and tri-*tert*-butylphosphane (0.34 mL, 1 M, 0.34 mmol) were introduced, by syringe in each case. The reaction mixture was stirred at 80 °C overnight. It was then poured into water (50 mL), and the aqueous layer was extracted with diethyl ether (3 × 25 mL). The combined organic phases were washed with brine and dried with $MgSO_4$, and the solvent was evaporated in vacuo. Purification by flash chromatography (CH_2Cl_2/pentane 1:3, v/v) yielded the product as a yellow syrup (954 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.08–8.99 (m, 1 H), 8.75–8.69 (m, 2 H), 8.55 (d, J = 7.8 Hz, 1 H), 8.20 (d, J = 7.6 Hz, 1 H), 7.90 (d, J = 7.9 Hz, 2 H), 7.75–7.54 (m, 5 H), 4.36 (d, J = 5.7 Hz, 2 H), 3.93 (q, J = 7.0 Hz, 4 H), 1.87 (sept, J = 6.0 Hz, 1 H), 1.51–1.23 (m, 46 H), 0.89 (t, J = 6.9 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 147.4, 134.2, 133.6, 131.6, 131.4, 129.6, 129.4, 129.3, 128.8, 128.0, 127.2, 127.2, 127.0, 126.7, 126.3, 125.9, 125.7, 124.3, 116.6, 111.0, 96.4, 91.9, 68.0, 49.4, 42.1, 37.5, 31.9, 31.5, 30.0, 29.7, 29.7, 29.6, 29.4, 26.8, 22.7, 14.7, 14.1, 11.5 ppm. HRMS: calcd. for $C_{51}H_{71}N_3O_2Na$ $[M + Na]^+$ 780.5444; found 780.5440.

2-Decyltetradecyl Ester 16: Compound **15** (572 mg, 0.76 mmol) and methyl iodide (7 mL) were placed in a sealed tube. The solution was degassed, and the tube was sealed. After heating at 110 °C overnight, the starting triazene had been completely consumed. During this time, diethyldimethylammonium iodide precipitated from the solution. The reaction mixture was poured into pentane (20 mL), filtered, and concentrated onto silica. Purification by flash chromatography (CH_2Cl_2/pentane 1:9, v/v) yielded the product as a yellow oil (498 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.01–8.98 (m, 1 H), 8.64–8.59 (m, 1 H), 8.53–8.47 (m, 1 H), 8.20–8.12 (m, 3 H), 7.89 (d, J = 7.6 Hz, 1 H), 7.74–7.62 (m, 4 H), 7.58 (d, J = 7.6 Hz, 1 H), 4.35 (d, J = 5.7 Hz, 2 H), 1.85 (sept, J = 6.0 Hz, 1 H), 1.52–1.17 (m, 40 H), 0.87 (t, J = 6.8 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 137.0, 134.2, 133.6, 133.5, 132.8, 131.3, 131.2, 129.2, 129.2, 128.4, 128.1, 128.0, 127.9, 127.1, 126.9, 126.6, 126.4, 125.7, 121.7, 101.3, 94.2, 93.3, 68.1, 37.5, 31.9, 31.5, 30.0, 29.7, 29.4, 26.8, 22.7, 14.1 ppm. HRMS: calcd. for $C_{47}H_{61}INa$ $[M + Na]^+$ 807.3614; found 807.3615.

2-Decyltetradecyl Ester 17: Compounds **16** (396 mg, 0.50 mmol) and **6** (190 mg, 0.76 mmol), bis(triphenylphosphane)palladium(II) dichloride (35 mg, 0.05 mmol), and copper(I) iodide (9 mg, 0.05 mmol) were placed in a flame-dried Schlenk flask. After three successive vacuum/argon cycles, toluene (20 mL), triethylamine (4 mL), and tri-*tert*-butylphosphane (0.10 mL, 1 M, 0.10 mmol) were introduced, by syringe in each case. The reaction mixture was stirred at 80 °C overnight. It was then poured into water (50 mL), and the aqueous layer was extracted with diethyl ether (3 × 25 mL). The combined organic phases were washed with brine and dried with $MgSO_4$, and the solvent was evaporated in vacuo. Purification by flash chromatography (CH_2Cl_2/pentane 1:2, v/v) yielded the product as a yellow syrup (381 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.06–9.03 (m, 1 H), 8.78–8.56 (m, 5 H), 8.21 (d, J = 7.8 Hz, 1 H), 7.92 (t, J = 7.6 Hz, 4 H), 7.78–7.58 (m, 7 H), 4.37 (d, J = 5.7 Hz, 2 H), 3.93 (q, J = 7.0 Hz, 4 H), 1.88 (sept, J = 6.0 Hz, 1 H), 1.51–1.23 (m, 46 H), 0.89 (t, J = 6.9 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 147.3, 134.2, 133.6, 133.2, 133.1, 131.5, 131.4, 130.4, 129.6, 129.4, 129.2, 129.2, 128.1, 127.9, 127.5, 127.4, 127.1, 127.0, 126.9, 126.8, 126.6, 126.4, 126.0, 126.0, 125.7, 124.3, 122.9, 120.7, 116.9, 111.1, 95.9, 95.2, 93.6, 92.2, 68.1, 49.4, 42.1, 37.5, 32.0, 31.5, 30.0, 29.7, 29.7, 29.6, 29.4, 26.8, 22.7, 14.7, 14.1, 11.5 ppm. HRMS: calcd. for $C_{63}H_{77}N_3O_2Na$ $[M + Na]^+$ 930.5913; found 930.5916.

2-Decyltetradecyl Ester 18: Compound **17** (164 mg, 0.18 mmol) and methyl iodide (7 mL) were placed in a sealed tube. The solution was degassed, and the tube was sealed. After heating at 110 °C overnight, the starting triazene had been completely consumed. During this time, diethyldimethylammonium iodide precipitated from the solution. The reaction mixture was poured into pentane (20 mL), filtered, and concentrated onto silica. Purification by flash chromatography (CH_2Cl_2/pentane 1:5, v/v) yielded the product as a red powder (150 mg, 89%), m.p. 90–92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.02–8.98 (m, 1 H), 9.67–8.63 (m, 1 H), 9.61–8.56 (m, 2 H), 9.51 (d, J = 9.2 Hz, 1 H), 8.22–8.10 (m, 3 H), 7.93–8.87 (m, 3 H), 7.75–8.63 (m, 6 H), 7.56 (d, J = 7.6 Hz, 1 H), 4.35 (d, J = 5.6 Hz, 2 H), 1.85 (sept, J = 6.0 Hz, 1 H), 1.52–1.17 (m, 40 H), 0.87 (t, J = 7.0 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 137.0, 134.2, 133.6, 133.5, 133.1, 133.1, 132.8, 132.1, 132.0, 131.9, 131.3, 131.1, 130.2, 130.0, 129.3, 129.2, 128.5, 128.4, 128.3, 128.0, 127.8, 127.6, 127.1, 126.9, 126.7, 126.4, 125.8, 121.9, 121.5, 101.0, 94.9, 93.9, 93.8, 93.6, 68.1, 37.5, 31.9, 31.5, 30.0, 29.7, 29.4, 26.8, 22.7, 14.1 ppm. HRMS: calcd. for $C_{59}H_{67}IO_2Na$ $[M + Na]^+$ 957.4083; found 957.4083.

1-Bromo-4-(dodec-1-yn-1-yl)naphthalene (20): 1,4-Dibromonaphthalene (2.00 g, 6.99 mmol), dodec-1-yne (1.28 g, 7.69 mmol), bis(triphenylphosphane)palladium(II) dichloride (245 mg, 0.35 mmol), and copper(I) iodide (66 mg, 0.35 mmol) were placed in a flame-dried Schlenk flask. After three successive vacuum/argon cycles, toluene (40 mL) and triethylamine (10 mL) were introduced, both by syringe. The reaction mixture was stirred at 80 °C overnight. It was then poured into water (50 mL), and the aqueous layer was extracted with diethyl ether (3 × 25 mL). The combined organic phases were washed with brine and dried with $MgSO_4$, after which the crude product was concentrated onto silica. Purification by flash chromatography (pentane) yielded the product as a pale yellow oil (1.25 g, 48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (m, 1 H), 8.24 (m, 1 H), 7.71 (d, J = 7.7 Hz, 1 H), 7.65–8.58 (m, 2 H), 7.45 (d, J = 7.7 Hz, 1 H), 2.56 (t, J = 7.1 Hz, 2 H), 1.71 (quint, J = 7.1 Hz, 2 H), 1.53 (quint, J = 7.1 Hz, 2 H), 1.40–1.12 (m, 12 H), 0.89 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.6, 131.7, 130.0, 129.4, 127.6, 127.4, 127.2, 126.9, 122.5, 122.0, 96.8, 78.0, 31.9, 29.7, 29.6, 29.4, 29.2, 29.1, 28.8, 22.7, 19.8, 14.1 ppm. HRMS: calcd. for $C_{22}H_{27}BrNa$ $[M + Na]^+$ 393.1194; found 393.1196.

Alkyne 21: Compounds **20** (300 mg, 0.81 mmol) and **6** (227 mg, 0.90 mmol), bis(triphenylphosphane)palladium(II) dichloride (57 mg, 0.08 mmol), and copper(I) iodide (15 mg, 0.08 mmol) were placed in a flame-dried Schlenk flask. After three successive vacuum/argon cycles, toluene (20 mL), triethylamine (10 mL), and tri-*tert*-butylphosphane (0.16 mL, 1 M, 0.16 mmol) were introduced, by syringe in each case. The reaction mixture was stirred at 80 °C overnight. It was then poured into water (40 mL), and the aqueous layer was extracted with diethyl ether (3 × 25 mL). The combined

organic phases were washed with brine and dried with $MgSO_4$, after which the crude product was concentrated in vacuo. Purification by flash chromatography (CH_2Cl_2/pentane 1:4, v/v) yielded the product as a yellow oil (342 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (d, J = 8.5 Hz, 1 H), 8.60 (d, J = 7.9 Hz, 1 H), 8.54 (d, J = 8.3 Hz, 1 H), 8.41 (d, J = 7.7 Hz, 1 H), 7.86 (d, J = 7.9 Hz, 1 H), 7.80 (d, J = 7.5 Hz, 1 H), 7.74–7.51 (m, 6 H), 3.92 (q, J = 7.0 Hz, 4 H), 2.60 (t, J = 7.1 Hz, 2 H), 1.73 (quint, J = 7.1 Hz, 2 H), 1.55 (quint, J = 7.1 Hz, 2 H), 1.47–1.09 (m, 18 H), 0.89 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.1, 134.2, 133.5, 133.0, 131.3, 129.7, 129.6, 129.4, 129.3, 127.0, 126.9, 126.8, 126.7, 126.0, 125.7, 124.2, 122.2, 121.2, 117.2, 111.0, 97.4, 94.7, 92.2, 78.8, 49.4, 42.1, 31.9, 29.6, 29.5, 29.3, 29.2, 29.1, 28.9, 22.7, 19.9, 14.7, 14.1, 11.5 ppm. HRMS: calcd. for $C_{38}H_{43}N_3Na$ [M + Na]$^+$ 564.3355; found 564.3357.

Alkyne 22: Compound **21** (175 mg, 0.32 mmol) and methyl iodide (5 mL) were placed in a sealed tube. The solution was degassed, and the tube was sealed. After heating at 125 °C overnight, the starting triazene had been completely consumed. During this time, diethyldimethylammonium iodide precipitated from solution. The reaction mixture was poured into pentane (15 mL), filtered, and concentrated onto silica. Purification by flash chromatography (CH_2Cl_2/pentane 1:6, v/v) yielded the product as a yellow oil (153 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (m, 2 H), 8.40 (d, J = 9.0 Hz, 1 H), 8.20–8.09 (m, 2 H), 7.80 (d, J = 7.5 Hz, 1 H), 7.73–7.59 (m, 5 H), 7.55 (d, J = 7.7 Hz, 1 H), 2.59 (t, J = 7.1 Hz, 2 H), 1.73 (quint, J = 7.1 Hz, 2 H), 1.55 (quint, J = 7.1 Hz, 2 H), 1.44–1.15 (m, 12 H), 0.88 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.0, 134.2, 133.6, 133.4, 133.0, 132.7, 131.0, 130.0, 129.4, 128.3, 127.7, 127.2, 127.0, 127.0, 126.9, 126.4, 123.0, 122.2, 120.3, 100.7, 97.8, 93.8, 92.8, 78.7, 31.9, 29.7, 29.6, 29.3, 29.2, 29.1, 28.8, 22.7, 19.9, 14.1 ppm. HRMS: calcd. for $C_{34}H_{33}INa$ [M + Na]$^+$ 591.1525; found 591.1529.

Protected Alkyne 23: Compound **22** (30 mg, 0.053 mmol), bis(triphenylphosphane)palladium(II) dichloride (7 mg, 0.01 mmol), and copper(I) iodide (2 mg, 0.01 mmol) were placed in a flame-dried Schlenk flask. After three successive vacuum/argon cycles, 2-methylbut-3-yn-2-ol (0.055 mL, 0.058 mmol), toluene (15 mL), and triethylamine (2 mL) were introduced, by syringe in each case. The reaction mixture was stirred at 80 °C overnight. It was then poured into water (25 mL), and the aqueous layer was extracted with ethyl acetate (3 × 15 mL). The combined organic phases were washed with brine and dried with $MgSO_4$, and the solvent was evaporated in vacuo. Purification by flash chromatography (CH_2Cl_2) yielded the product as a yellow syrup (21 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59–8.50 (m, 2 H), 8.40 (d, J = 8.0 Hz, 1 H), 8.33 (d, J = 8.0 Hz, 1 H), 7.80 (d, J = 8.0 Hz, 1 H), 7.79 (d, J = 8.0 Hz, 1 H), 7.70–7.58 (m, 6 H), 2.59 (t, J = 7.1 Hz, 2 H), 2.18 (s, 1 H), 1.75 (s, 6 H), 1.71 (quint, J = 7.1 Hz, 2 H), 1.53 (quint, J = 7.1 Hz, 2 H), 1.40–1.20 (m, 12 H), 0.88 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.4, 133.1, 133.0, 132.9, 130.0, 129.8, 129.8, 129.4, 127.3, 127.3, 127.2, 127.0, 126.8, 126.6, 126.5, 126.5, 122.9, 121.6, 121.1, 120.4, 100.5, 97.8, 94.1, 93.4, 80.2, 78.7, 66.0, 31.9, 31.6, 29.6, 29.6, 29.3, 29.2, 29.1, 28.8, 22.7, 19.9, 14.1 ppm. HRMS: calcd. for $C_{39}H_{40}ONa$ [M + Na]$^+$ 547.2977; found 547.2978.

Deprotected Alkyne 24: Sodium hydride (5 mg, 60% mineral oil suspension, 0.13 mmol) was added to a solution of **23** (14 mg, 0.027 mmol) in toluene (1 mL), and the mixture was stirred at 80 °C for 2 h. The solvent was removed in vacuo, and the crude product was loaded directly onto a silica column and eluted with CH_2Cl_2. The product was obtained as a yellow oil (10 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63–8.49 (m, 2 H), 8.40 (m, 1 H), 7.83 (d, J = 8.0 Hz, 1 H), 7.81 (d, J = 7.5 Hz, 1 H), 7.76 (d, J = 7.5 Hz, 1 H), 7.72–7.61 (m, 6 H), 3.60 (s, 1 H), 2.61 (t, J = 7.1 Hz, 2 H), 1.74 (quint, J = 7.2 Hz, 2 H), 1.54 (quint, J = 7.1 Hz, 2 H), 1.44–1.19 (m, 12 H), 0.89 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.4, 133.4, 133.0, 132.9, 130.6, 130.1, 129.7, 129.4, 127.5, 127.4, 127.3, 127.3, 126.9, 126.6, 126.5, 126.5, 123.0, 122.2, 120.5, 120.4, 97.9, 94.3, 93.3, 83.6, 81.6, 78.7, 31.9, 29.6, 29.5, 29.4, 29.2, 29.1, 28.9, 22.7, 19.9, 14.1 ppm. HRMS: calcd. for $C_{36}H_{34}Na$ [M + Na]$^+$ 489.2558; found 489.2530.

2-Decyltetradecyl Ester 25: Compounds **18** (47 mg, 0.050 mmol) and **24** (25 mg, 0.055 mmol), bis(triphenylphosphane)palladium(II) dichloride (7 mg, 0.01 mmol), and copper(I) iodide (2 mg, 0.01 mmol) were placed in a flame-dried Schlenk flask. After three successive vacuum/argon cycles, toluene (5 mL), and triethylamine (2 mL) were introduced, both by syringe. The reaction mixture was stirred at 40 °C overnight. It was then poured into water (10 mL), and the aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined organic phases were washed with brine and dried with $MgSO_4$, and the crude product was concentrated in vacuo. Purification by flash chromatography (CH_2Cl_2) yielded the product as a red solid (49 mg, 76%), m.p. 248 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.03–8.97 (m, 1 H), 8.69–8.55 (m, 7 H), 8.42 (d, J = 8.0 Hz, 1 H), 8.19 (d, J = 7.6 Hz, 1 H), 7.97–7.89 (m, 7 H), 7.87–7.82 (m, 2 H), 7.79–7.50 (m, 11 H), 4.35 (d, J = 5.6 Hz, 2 H), 2.61 (t, J = 7.1 Hz, 2 H), 1.85 (sept, J = 6.0 Hz, 1 H), 1.74 (quint, J = 7.2 Hz, 2 H), 1.52–1.10 (m, 54 H), 0.88 (m, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 134.3, 134.2, 134.1, 133.4, 133.2, 132.5, 132.4, 132.1, 130.3, 129.3, 129.1, 129.1, 128.9, 128.8, 128.3, 128.3, 128.2, 127.1, 126.9, 126.8, 126.7, 126.6, 126.5, 126.5, 126.4, 126.3, 126.1, 125.9, 125.7, 125.5, 125.5, 125.4, 124.9, 123.3, 122.2, 114.4, 67.1, 52.4, 38.4, 36.5, 36.1, 31.7, 30.9, 30.5, 29.0, 28.7, 28.6, 28.6, 28.3, 27.8, 27.0, 26.1, 25.8, 21.7, 18.9, 18.7, 13.1 ppm. HRMS: calcd. for $C_{95}H_{100}O_2Na$ [M + Na]$^+$ 1296.7655; found 1296.7642.

Acid 3: LiOH (5 mg, 0.21 mmol), dissolved in water (0.5 mL), was added to a solution of **25** (24 mg, 0.024 mmol) in THF (2 mL). The reaction mixture was heated in a vial at 55 °C overnight. Upon acidification (conc. HCl), a precipitate formed; it was collected by filtration. The collected precipitate was washed with water (5 mL) and THF (5 mL) and dried in vacuo to yield the product as a red powder (17 mg, 95%), m.p. 194 °C (decomp.). HRMS: calcd. for $C_{71}H_{52}O_2Na$ [M + Na]$^+$ 959.3865; found 959.3858. $C_{71}H_{52}O_2$: calcd. C 90.99, H 5.59; found C 90.92, H 5.61. ^{1}H NMR and ^{13}C NMR spectra could not be obtained, due to low solubility.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra, photograph of glassware, UV/Vis and fluorescence spectra.

Acknowledgments

The authors acknowledge financial support from the Danish National Research Foundation for support to the Centre for DNA Nanotechnology (CDNA) and the Sino-Danish Center for Molecular Nanostructures on Surfaces.

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Received: December 27, 2012
Published Online: March 19, 2013

