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Conjugated Oligoyne-Bridged [60]Fullerene Molecular Dumbbells: Syntheses and Thermal and Morphological Properties

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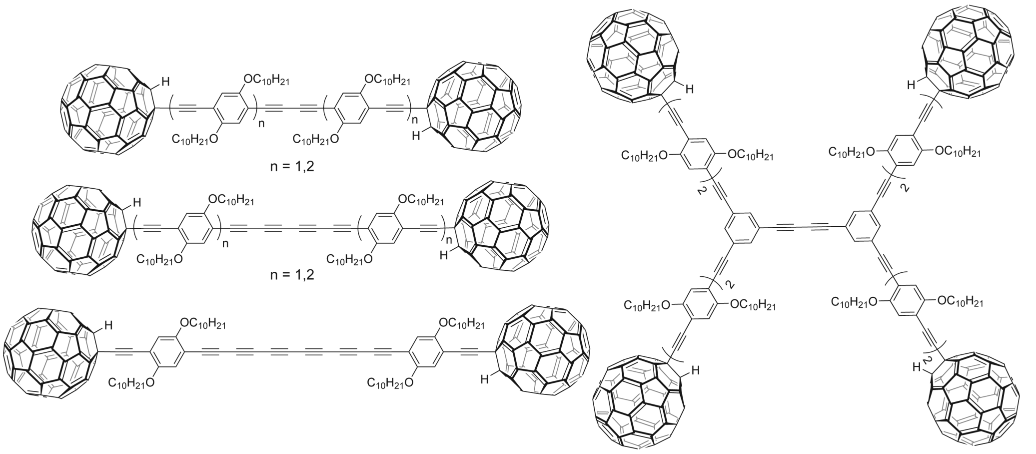

A series of linear and star-shaped π-conjugated oligomer hybrids (**2**−**5**) composed of an oligoyne core, ranging from 1,3-butadiyne to 1,3,5,7,9,11-dodecahexayne, and fullerenyl end-capping groups has been synthesized and studied. The molecular structures of these fullerene−oligoyne hybrids were assembled through three key reactions: Pd-catalyzed cross-coupling, Cu-catalyzed oxidative homocoupling, and an in situ alkynylation reaction on [60]fullerene. The properties of these compounds were investigated by UV−vis spectroscopy, differential scanning calorimetry (DSC), and atomic force microscopy (AFM) with the purpose of understanding the thermal reactivity arising from the oligoyne moieties as well as the morphological properties on surface. Our study shows that these fullerene−oligoyne hybrids tend to aggregate in different morphologies, including nanospheres, nanoflakes, and continuous thin films, while the morphological properties appear to be subject to the influence of molecular factors such as oligomer chain length, solubilizing alkylphenyl groups, and the thermal reactivity of the oligoyne unit. The correlation between molecular property and interfacial aggregation behavior evinced by these fullerene−oligoyne hybrids suggests a viable approach to exert bottom-up control over the structures and properties of fullerene based nanomaterials.

Introduction

Carbon-based nanomaterials are envisioned to play an important role in next generation electronic and optoelectronic technologies.[1] Over the past two decades, the discovery and characterization of a number of appealing carbon allotropes, such as buckminster [60]fullerene, carbon nanotubes (CNTs), and carbynes (i.e., one-dimensional sp carbon polymers), have not only promoted extensive studies on the fundamental properties of nanostructured carbons at various levels but also provided material scientists with the brick and mortar to fabricate new advanced molecular devices with enhanced performance and function.[1−9] In recent years, there has been a growing interest in [60]fullerene (C_{60}) containing composite materials[10,11] because C_{60} and its

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(1) *Carbon Nanomaterials*; Gogotsi, Y., Ed.; CRC Press: Boca Raton, FL, 2006.

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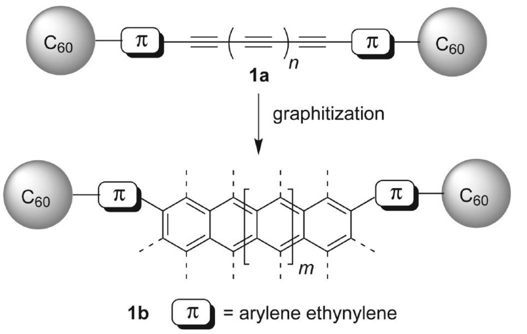
derivatives are the most commonly employed molecular building components in the formation of bulk heterojunctions (BHJs) with conducting polymers, which leads the way to the quest for high-performance polymer solar cells.[12−14] Efficiency of the BHJ solar cell has been steadily improved in the recent literature, boding well for a potential solution to the challenge of cost-effectively harnessing solar energy.[12,15−19] However, continued and synergistic efforts to optimize both the materials and the device structure are still needed before this technology becomes commercially viable.

It has been demonstrated that the nanomorphology of the solid thin film in a BHJ solar cell plays a vital role in dictating the device performance.[12,20−22] In the ideal case, acceptors (C_{60} derivatives) and donors (conjugated polymers) should form a bicontinuous, microphase separate network to ensure efficient exciton diffusion. The morphological properties of C_{60}−polymer blends are related to numerous factors, ranging from molecular properties (e.g., the structure and solubility/miscibility of C_{60} derivatives and polymers[20,23]) to postproduction treatment methods (e.g., electrical treatment[24] and thermal annealing[25,26]). To better understand these complicated issues as well as to establish structure−property relationship for guiding rational design and fine-tuning, the synthesis and characterization of new C_{60}-containing molecular systems are crucial and indispensable.

SCHEME 1. Graphitization of Bisfullerene−Oligoyne Dumbbells 1a via Alkyne Cross-Linking Reactions



In this paper, we report our recent investigations on a series of conjugated oligoyne-bridged multifullerene molecular ensembles. Particular emphasis has been placed on dumbbell-shaped bisfullerene−oligoyne hybrids like motif **1a** illustrated in Scheme 1. Various dumbbell-shaped C_{60}−oligomer−C_{60} molecular architectures have drawn considerable attention in the fields of photoinduced energy/electron transfer, organic photovoltaics, organic nonlinear optics, and molecular machinery.[27−32] In the literature, arylene-based conjugated oligomers such as oligo(phenylene ethynylene)s,[31,33,34] oligo(phenylene vinylene)s,[30,35] and oligothiophenes[27,36] have been conveniently employed as the π-bridges to assemble C_{60}−π−C_{60} dumbbells, owing to their rich electronic and photonic characteristics as well as satisfactory compatibility with diverse synthetic and processing conditions. Fullerene dumbbells bearing conjugated oligoyne π−bridges,[37−41] however, have been scarcely exploited in device fabrications, primarily due to the conspicuous synthetic challenge and chemical instability of the oligoyne species.[7,8] Conjugated oligoynes are the substructure of an appealing carbon allotrope, namely carbyne.[42−44] Aside from the fundamentally

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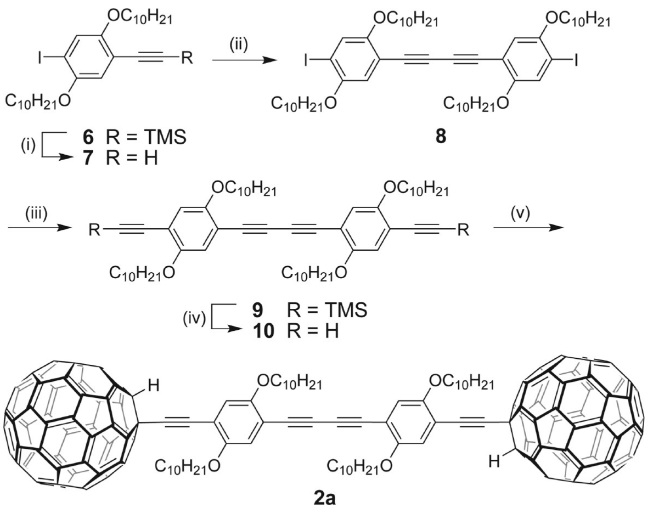
intriguing aspect,[45−48] conjugated oligoynes also exhibit unique physical and chemical properties that are very useful for the preparation of certain carbon-based functional polymer materials and molecular devices.[5,49−57] In the context of material synthesis, conjugated oligoynes can be used as the precursors to various carbon materials. For example, highly ordered conjugated polyenyne networks can be obtained from topochemically controlled polymerization of oligoynes.[45,58−61] In addition, oligoynes have also been reported to form graphite,[56] multiwall carbon nanotubes,[55,62] onion- and diamond-like nanostructures,[63,64] and porous carbon materials[65] through various carbonization pathways such as thermal decomposition.

Fullerene−oligoyne hybrids were first explored by Diederich[39−41] and Komatsu[38] in 1996 as a new class of molecular carbon allotropes. In 1999, the Hirsch group reported a butadiyne-linked lipofullerene that underwent diacetylene cross-linking reaction to form nanospheres in solution under controlled conditions.[66] Taking advantage of the solid-state reactivity of oligoynes, Nierengarten and co-workers in a recent study prepared a fullerene derivative attached with polymerizable butadiyne moieties. Upon annealing at 100 °C, the fullerene compound cross-linked in the matrix of poly(phenylene vinylene)s to stabilize initially formed phases in BHJ solar cells, which resulted in improved device performance.[67] This thermally induced cross-linking strategy opened a new avenue for optimization of C_{60}-based solar cell devices.

SCHEME 2. Synthesis of C_{60}−Butadiyne−C_{60} Dumbbell 2a[a]



[a]Reagents and conditions: (i) K_2CO_3, CH_3OH, THF, 99%; (ii) CuCl/TMEDA, air, acetone, 75%; (iii) TMSA, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, 81%; (iv) K_2CO_3, CH_3OH, THF, 96%; (v) C_{60}, LHMDS, THF then TFA, 25%.

Our group has recently investigated the thermally induced polymerization of a 1,3,5,7-octatetrayne centered $C_{60}-\pi-C_{60}$ molecular dumbbell.[37] To our great interest, the compound was found to polymerize on the surface at 160 °C to form uniform and highly ordered arrays of nanospheres. With this success, we continued to investigate a series of analogous $C_{60}-\pi-C_{60}$ dumbbells **1a** (see Scheme 1). In these compounds, the structures of oligoyne and arylene π-linkage groups were systematically varied by conjugation length in order to facilitate the study of structure−property relationships. In addition to this, the incorporation of oligoyne central units was also envisaged to serve a springboard toward nanostructured carbon networks with fullerenyl pendants; for example, fullerene−oligoyne **1a** was anticipated to yield highly cross-linked polymers such as **1b** via a thermally induced graphitization[56] pathway proposed in Scheme 1. Exploration in this direction should benefit the development of novel fullerene-based carbon materials. In the following content, we present the synthetic routes to various fullerene−oligoyne hybrids, in which Sonogashira coupling, Hay coupling, and an in situ C_{60} alkynylation reaction were employed as the key steps. With these compounds in hand, the interfacial self-aggregation behavior and correlation with molecular and experimental parameters were examined through combined analyses using UV−vis spectroscopy, differential scanning calorimetry (DSC), and atomic force microscopy (AFM).

Results and Discussion

Synthesis of C_{60}−Butadiyne−C_{60} dumbbells. The synthesis of butadiyne-bridged $C_{60}-\pi-C_{60}$ molecular dumbbell **2a** is outlined in Scheme 2. It began with desilylation of compound **6**[31] with K_2CO_3, which gave terminal alkyne **7** in 99% yield. Hay coupling[68] of **7** generated phenylbutadiynylene **8** in a yield of 75%. Compound **8** was cross-coupled with trimethylsilylacetylene (TMSA) under the catalysis of Pd/Cu

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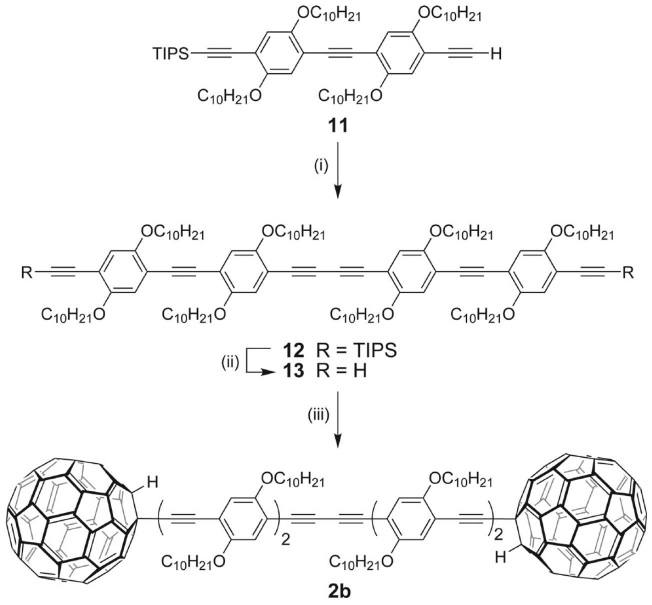
SCHEME 3. Synthesis of Long C_{60}−Butadiyne−C_{60} Dumbbell 2b[a]



[a]Reagents and conditions: (i) CuCl/TMEDA, air, acetone, 43%; (ii) TBAF, THF, 81%; (iii) C_{60}, LHMDS, THF then TFA, 32%.

to yield oligomer **9**, which was subsequently converted into terminal diyne **10** via protiodesilylation. Compound **10** was subjected to an in situ alkynylation[31,34] with C_{60} using LHMDS as base, followed by quenching with trifluoroacetic acid (TFA), affording the first target C_{60}−butadiyne−C_{60} dumbbell **2a** in 25% yield.

In a similar manner, a longer C_{60}−butadiyne−C_{60} dumbbell **2b** was prepared through the synthetic route shown in Scheme 3. The synthesis began with a monotriisopropylsilyl (TIPS)-protected phenylacetylene dimer **11**.[31] Oxidative homocoupling of **11** in the presence of Cu(I) catalyst gave phenylbutadiynylene oligomer **12** in 43% yield. Removal of the TIPS groups in **12** with tetrabutylammonium fluoride (TBAF) gave oligomer **13**, which was then converted into bisfullerenyl dumbbell **2b** via the in situ alkynylation protocol described above.

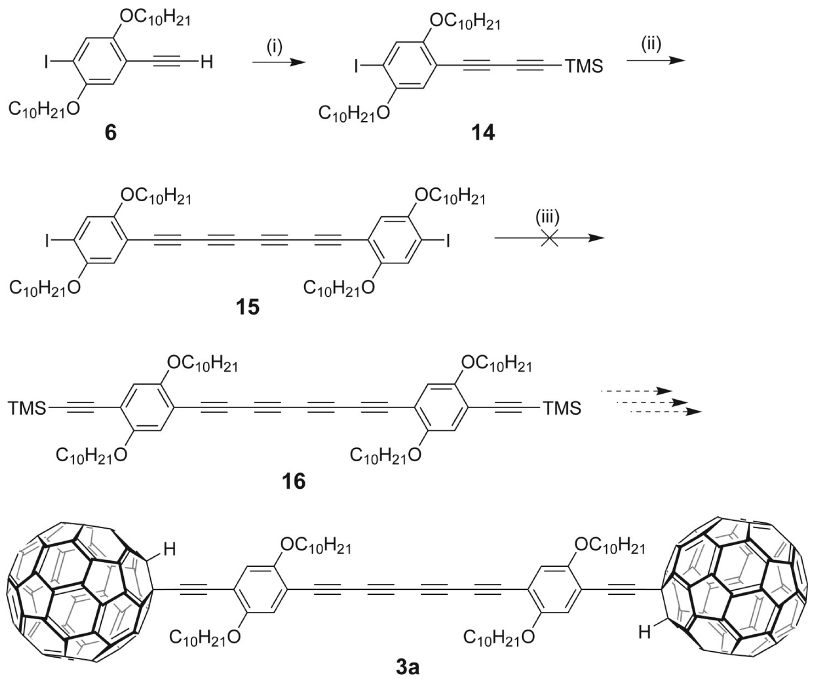
Synthesis of C_{60}−Octatetrayne−C_{60} dumbbells. With the success in the preparation of butadiynylene-bridged bisfullerene dumbbells, the synthesis of their 1,3,5,7-octatetrayne-bridged homologues was then undertaken. Our initial attempt was made on C_{60}−octatetrayne−C_{60} dumbbell **3a**, using the synthetic route shown in Scheme 4, wherein TMS-protected phenyloctatetrayne **16** was planned as a key intermediate. To make compound **16**, phenylbutadiyne **14** was first prepared via a mixed Hay coupling between phenylacetylene **6** and excess TMSA. In this reaction, compound **14** was easily separated from another major product, bis(trimethylsilyl)butadiyne, through flash column chromatography in a satisfactory yield of 68%. Desilylation of **14** followed by another Hay coupling afforded bis(iodophenyl) end-caped octatetrayne **15**. With compound **15** in hand, the desired intermediate **16** was supposed to be readily accessible via a Sonogashira coupling with TMSA. However, the coupling reaction executed under typical Sonogashira conditions (i.e., $Pd(PPh_3)_2Cl_2$/CuI and Et_3N in THF) resulted in an intractable mixture rather than the desired product. This unexpected difficulty hence forced us to seek an alternative route to prepare suitable phenyloctatetrayne precursor.

As shown in Scheme 5, phenylbutadiyne **14** was cross coupled with triisopropylsilylacetylene (TIPSA) to give compound **17**. Selective removal of the TMS group in **17** with K_2CO_3, followed by a Hay coupling, afforded TIPS end-capped phenyloctatetrayne **19**. Oligomer **19** was desilylated with TBAF to give compound **20**, which was immediately subjected to an in situ alkynylation with C_{60}, furnishing the target C_{60}−tetrayne−C_{60} dumbbell **3a** in 31% yield.

Following a similar strategy, a longer octatetrayne-bridged bisfullerenyl dumbbell **3b** was prepared. The detailed synthetic steps are outlined in Scheme 6. Mono-TIPS-protected phenylacetylene dimer **11** was first elongated by one more acetylenic unit through a mixed Hay coupling with excess TMSA, affording phenylacetylene oligomer **21**. Compound **21** was selectively desilylated with K_2CO_3 to give terminal diyne **22**, which underwent an oxidative homocoupling to form octatetrayne centered phenylacetylene oligomer **23**. Removal of the TIPS groups in **23** with TBAF, followed by an in situ alkynylation with C_{60}, gave bisfullerene dumbbell **3b** in a satisfactory yield of 33%.

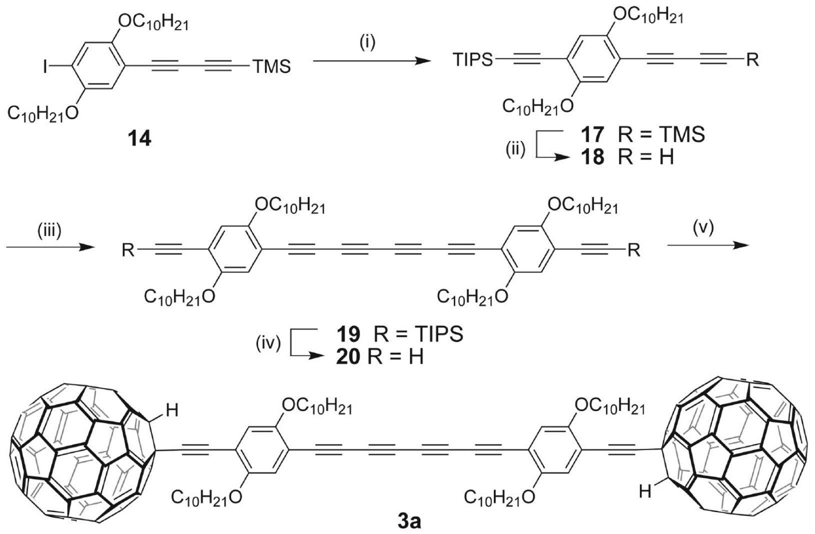
Synthesis of C_{60}−Dodecahexayne−C_{60} Dumbbell. At this point, all the synthesized butadiyne- and octatetrayne-bridged bisfullerene dumbbells showed good chemical stability at room temperature due to the presence of bulky fullerenyl end-capping groups. Indeed, these compounds could be stored at room termperature under N_2 for more than 2 months without significant decomposition. After longer term storage, however, the fullerene−oligoyne adducts gradually formed insoluble black substances likely as a result of cross-linking reactions in the solid state. The effort to construct longer oligoyne-bridged dumbbells ensued, although the increasing instability of higher oligoynes was recognized as a potential risk beforehand. Outlined in Scheme 7 is the synthesis of a C_{60}−dodecahexayne−C_{60} dumbbell **4**. First, desilylation of compound **17**, followed by Hay coupling with excess TMSA, gave phenylhexatriyne precursor **25**. Compound **25** was subjected to another iteration of desilylation and Hay coupling to yield TIPS end-capped phenyldodecahexayne **27**. Hexayne **27** was isolated through flash column chromatography as a brownish wax with moderate chemical stability. Treating **27** with TBAF led to terminal alkyne intermediate **28**, which showed very poor chemical stability. For this reason, compound **28** was immediately reacted with C_{60} following the in situ alkynylation protocol. After quenching with TFA, C_{60}−dodecahexayne−C_{60} dumbbell **4** was obtained in an overall yield of 5% based on the consumption of precursor **27**. Like its hexayne precursors, compound **4** was unstable, which allowed only a fleeting lifetime for ^{1}H NMR spectroscopic characterization. It is also worth noting that terminal alkyne intermediates involved in this synthetic route, including **18**, **26**, and **28**, are also quite unstable. Therefore, once acquired they were immediately carried on to the subsequent synthetic steps without further purification. In particular, phenyldodecahexayne **28** was found to retain moderate stability only in dilute solution. Once the solvent was evaporated off, compound **28** decomposed instantaneously into insoluble black solids. (Although conjugated oligoynes, particularly higher oligoynes, have been reported to be explosive in nature, we

SCHEME 4. Attempted Synthesis of C_{60}–Octatetrayne–C_{60} Dumbbell 3a[a]



[a]Reagents and conditions: (i) TMSA, CuCl/TMEDA, air, acetone, 68%; (ii) (a) K_2CO_3, CH_3OH, THF, (b) CuCl/TMEDA, air, acetone, 53%; (iii) TMSA, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF.

SCHEME 5. Synthesis of C_{60}–Octatetrayne–C_{60} Dumbbell 3a[a]



[a]Reagents and conditions: (i) TIPSA, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, 86%; (ii) K_2CO_3, CH_3OH, THF; (iii) CuCl/TMEDA, air, acetone, 53% over two steps; (iv) TBAF, THF, 77%; (v) C_{60}, LHMDS, THF then TFA, 31%.

have so far not experienced any explosions in handling the aforementioned oligoyne species. Nevertheless, caution still must be exercised in handling these unstable oligoyne-derived compounds.)

Synthesis of Star-Shaped Oligoyne-Centered Tetrafullerene Adducts. Apart from the linear C_{60}–oligoyne–C_{60} dumbbells, a series of star-shaped oligoyne cored tetrafullerene adducts (see Figure 1) was also pursued in our synthesis.

The effort toward the synthesis of compound **29a** is described in Scheme 8. Starting from methyl 3,5-diiodobenzoate (**30**), benzaldehyde **32** was obtained through two steps of typical functional group interconversions. Compound **32** was then converted into terminal alkyne **34** via a Corey–Fuchs reaction.[69] Hay coupling of **34** led to phenyldiyne **35** as a pale white solid with limited stability. Compound **35** was immediately subjected to a Sonogashira coupling reaction with terminal alkyne **36** to yield star-shaped phenylacetylene oligomer **37**. Treatment of oligomer **37** with TBAF in THF removed the TIPS end groups, affording compound **38** which is the key precursor to target

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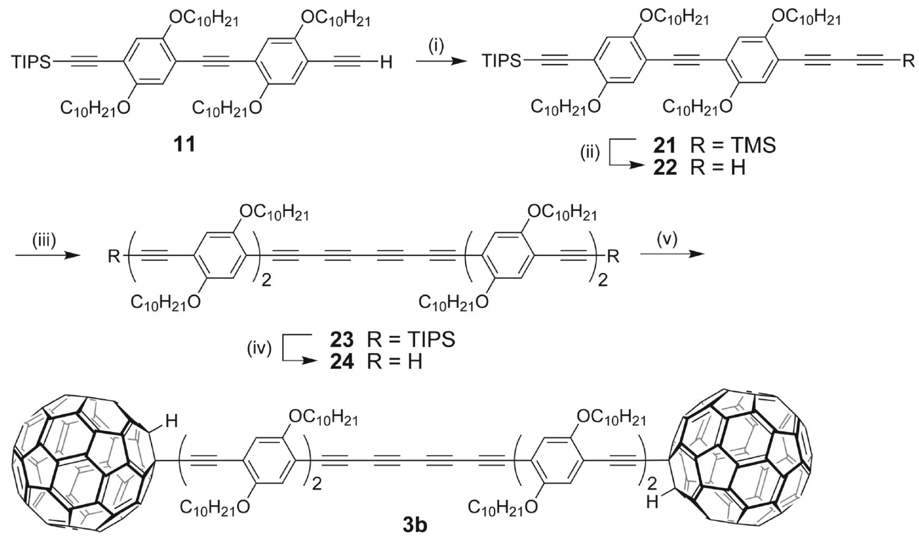
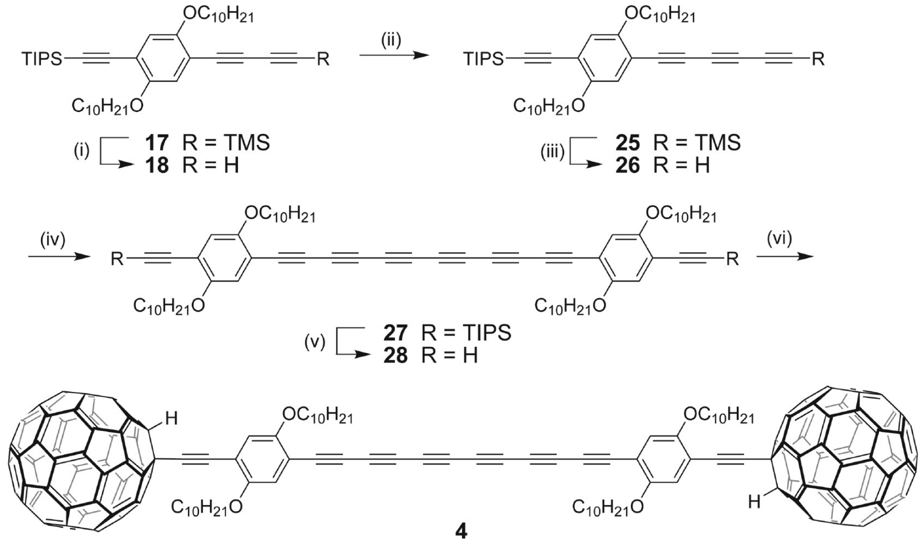
(69) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, *36*, 3769–3772.

SCHEME 6. **Synthesis of Long C_{60}−Octatetrayne−C_{60} Dumbbell 3b**[a]



[a]Reagents and conditions: (i) TMSA, CuCl/TMEDA, air, acetone, 79%; (ii) K_2CO_3, CH_3OH, THF; (iii) CuCl/TMEDA, air, acetone, 85% over two steps; (iv) TBAF, THF, 84%; (v) C_{60}, LHMDS, THF then TFA, 33%.

SCHEME 7. **Synthesis of C_{60}−Dodecahexayne−C_{60} Dumbbell 4**[a]



[a]Reagents and conditions: (i) K_2CO_3, CH_3OH, THF; (ii) TMSA, CuCl/TMEDA, air, acetone, 90% over two steps; (iii) K_2CO_3, CH_3OH, THF; (iv) CuCl/TMEDA, air, acetone, 39% over two steps; (v) TBAF, THF; (vi) C_{60}, LHMDS, THF then TFA, 5% over two steps.

tetrafullerene adduct **29a**. However, the in situ alkynylation reaction between C_{60} and **38** in the presence of LHMDS resulted in some insoluble substances, the molecular structures of which could not be clearly identified.

In parallel with the above synthetic effort for **29a**, an octatetrayne-centered star-shaped tetrafullerene adduct **29b** was also targeted. As shown in Scheme 9, terminal alkyne **34** was first deprotonated with a strong base, LDA, and then silylated with TMSCl to give compound **39**. From compound **39**, phenylacetylene oligomer **40** was readily prepared in 89% yield via a Sonogashira coupling reaction with **36**. Compound **40** was desilylated with K_2CO_3 to form terminal alkyne **41**, which was subjected to a Hay coupling with excess TMSA to produce oligomer **42**. Selective desilylation of **42** followed by another Hay coupling afforded octatetrayne-cored phenylacetylene oligomer **44** in a very good yield. Compound **44** was desilylated with TBAF to afford terminal alkyne **45**. To our dismay, the synthesis of **29b** also reached a dead end at this point, as precursor **45** was not able to produce the desired tetrafullerene adduct via the in situ alkynylation reaction.

Speculating that the low solubility of tetrafullerene products **29a**,**b** could be the main reason for the failed in situ alkynylation reactions, we continued to pursue another group of star-shaped tetrafullerene adducts (**5a** and **5b**), which contain more solubilizing bis(decyloxy)-substituted phenylene units. As illustrated in Scheme 10, a Sonogashira coupling reaction between phenylbutadiyne **35** and phenylacetylene

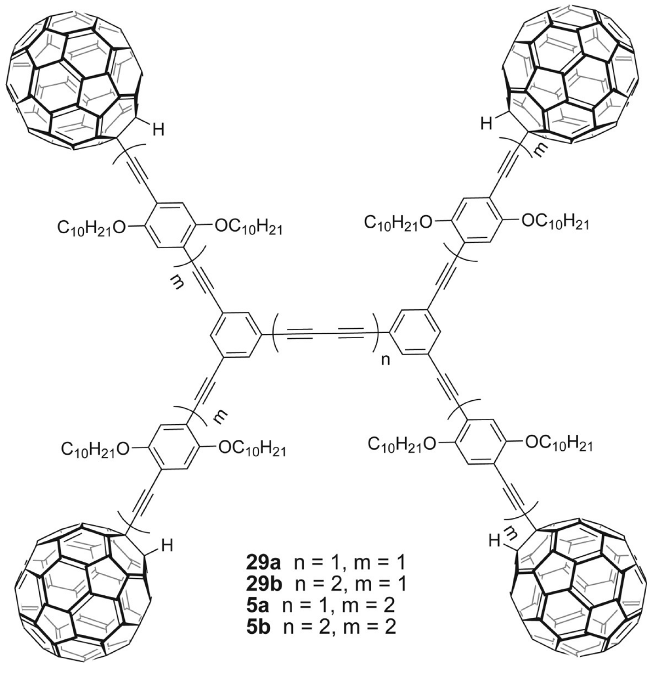


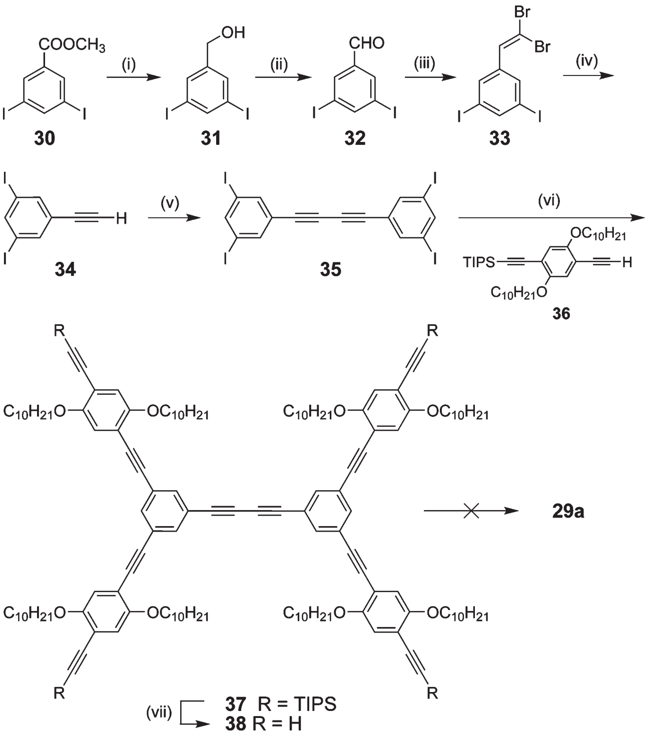
FIGURE 1. Star-shaped tetrafullerene–oligoyne adducts.

dimer **11** gave TIPS-protected phenylacetylene oligomer **46** in a yield of 86%. Removal of the TIPS groups in **46** with TBAF afforded terminal alkyne **47**, which was subsequently converted into tetrafullerene adduct **5a** via the in situ alkynylation reaction with C_{60}. Although the yield of the alkynylation reaction was around 20%, it is still a satisfactory result considering the fact that *four* fullerenyl groups were incorporated in a single synthetic step.

In a similar manner, octatetrayne-centered tetrafullerene adduct **5b** was anticipated to be readily prepared from oligomer precursor **52** as shown in Scheme 11. The synthesis of TIPS protected star-shaped phenylacetylene oligomer **52** was implemented following the same iterative strategy as used in the synthesis of oligomers **45** and **47**. When oligomer **52** was subjected to a typical desilylation with TBAF, however, a new problem emerged: the resulting terminal alkyne **53** was too unstable to be isolated as a neat product. In fact, compound **53** was found to decompose so rapidly into a dark colored substance, presumably through cross-linking or polymerization of the tetrayne moieties, that no opportunity could be seized to carry it into subsequent in situ alkynylation reaction. In this case, it was the instability of precursor **53** that thwarted the acquisition of tetrafullerene adduct **5b**, albeit compound **5b** was envisaged to be a stable and soluble product.

Thermal Properties. Conjugated oligoynes such as diacetylenes, triynes, and tetraynes, show the propensity to polymerize in the solid state or in concentrated solutions upon activation by heat, irradiation (e.g., UV–vis, γ-ray), or mechanical forces (e.g., pressure).[45] The polymerization may take place through a diversity of mechanisms. The most intriguing one is the topochemically controlled polymerization, through which highly ordered poly(enyne) networks can be obtained.[58−61] Scheme 12 illustrates the possible topochemical polymerization pathways for octatetraynes, which lead to polyacetylene (PA), polydiacetylene (PDA), and polytriacetylene (PTA) frameworks, respectively.

SCHEME 8. Attempted Synthesis of Star-Shaped Tetrafullerene Adduct 29a[a]

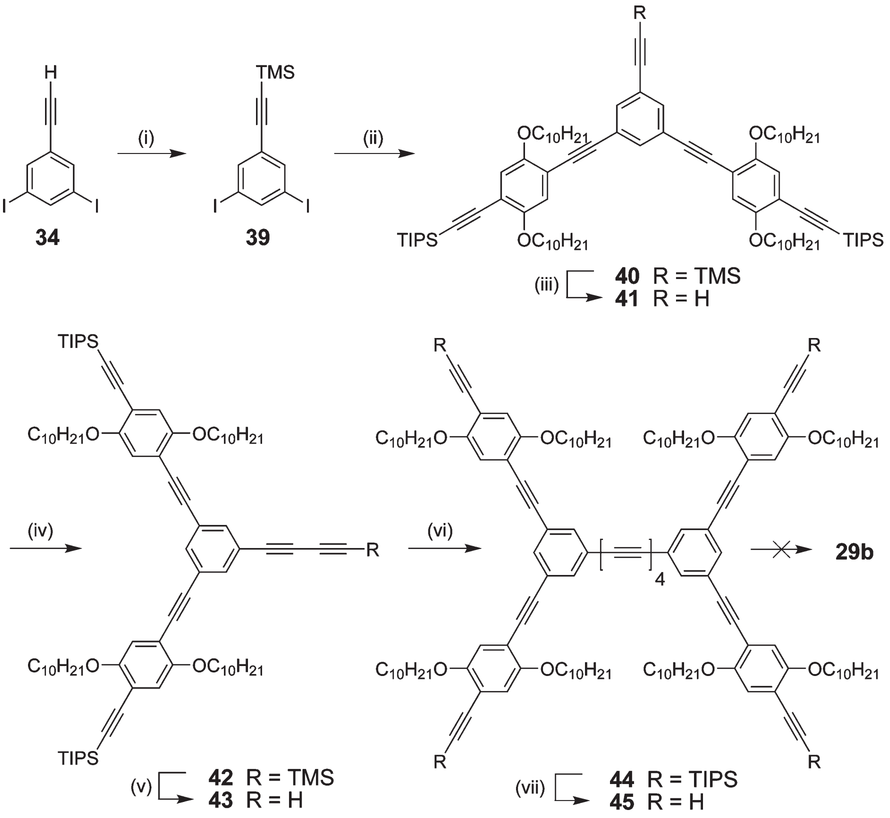


[a]Reagents and conditions: (i) DIBAL, CH_2Cl_2, 95%; (ii) PCC, CH_2Cl_2, 95%; (iii) CBr_4, PPh_3, CH_2Cl_2, 93%; (iv) LDA, THF, 87%; (v) CuCl/TMEDA, air, acetone, 65%; (vi) $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, 76%; (vii) K_2CO_3, CH_3OH, THF, 73%.

For topochemical polymerization to occur, the oligoyne monomers must be organized with particular geometries in the solid state to ensure minimal atomic and molecular motion during the transformation.[5,45,58−61] The specific demand for packing considerably limits the access to highly ordered carbon nanostructures via topochemical polymerization of sterically hindered oligoynes. In view of the bulkiness of end groups (i.e., bis(decyloxyl)phenyl and fullerenyl) present in the oligoyne derivatives herein synthesized, the possibility of inducing their topochemical polymerization is ruled out. On the other hand, for oliogynes with random solid-state structures, mixed polymerization or cross-linking reactions usually prevail at elevated temperatures resulting in interesting carbonized materials, such as carbon nanospheres,[50,51,66] carbon nanotubes,[55,62] graphite fibers, and ribbons.[56] To shed light on the thermal properties and reactivities, differential scanning calorimetric (DSC) analysis was performed on C_{60}–oligoyne–C_{60} dumbbells (**2** and **3**) and corresponding phenyloligoyne precursors (**9** and **19**) under N_2 atmosphere.

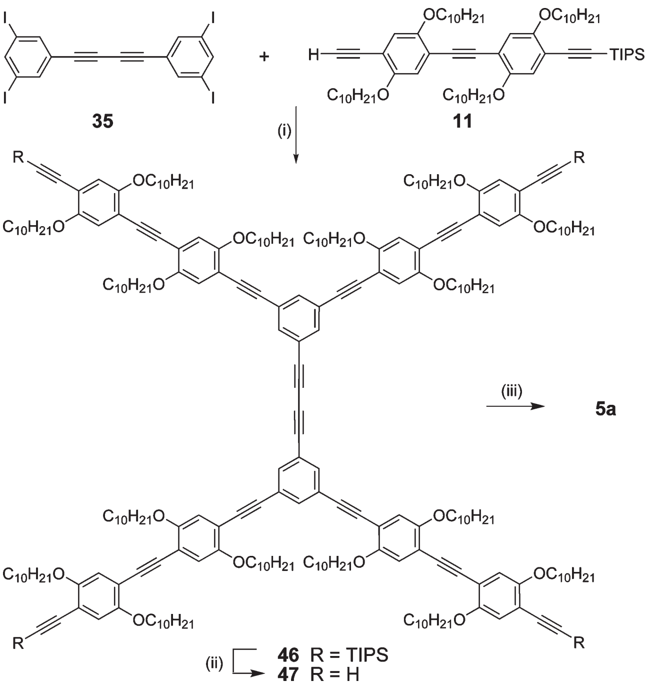
Figure 2A shows the DSC results of short C_{60}–diyne–C_{60} dumbbell **2a**. The thermogram features a broad exothermic peak with moderate intensity centered at 145 °C and a noticeable hump (exothermic) around 198 °C. Compared to the DSC profile of diyne precursor **9** (see Figure S-100, Supporting Information), the first exothermic peak can be ascribed to a low-degree, random cross-linking of diyne moieties, and the bisfullerene–diyne dumbbell **2a** appears to be more thermally robust than diyne precursor **9** in the

SCHEME 9. **Attempted Synthesis of Star-Shaped Tetrafullerene Adduct 29b**[a]



[a]Reagents and conditions: (i) LDA, THF then TMSCl, 81%; (ii) **36**, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, 89%; (iii) K_2CO_3, CH_3OH, THF, 100%; (iv) TMSA, CuCl/TMEDA, air, acetone, 89%; (v) K_2CO_3, CH_3OH, THF, 81%; (vi) CuCl/TMEDA, air, acetone, 86%; (vii) TBAF, THF.

SCHEME 10. **Synthesis of Star-Shaped Butadiyne-Cored Tetrafullerene Adduct 5a**[a]



[a]Reagents and conditions: (i) $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, 86%; (ii) TBAF, THF, 100%; (iii) LHMDS, C_{60}, THF then TFA, 20%.

temperature range of ca. 100−270 °C, owing to the presence of bulky C_{60} end-capping groups which considerably hinders the thermal reactivity of the diyne moieties. At temperatures higher than 270 °C, the DSC trace drifts abruptly to the endothermic direction, which is likely due to the decomposition of the phenylacetylene components.[70]

The DSC profile of short C_{60}−tetrayne−C_{60} dumbbell **3a** (Figure 2B) shows only one relatively broad exothermic peak ranging from 156 to 240 °C with a maximum at 212 °C. The broad peak width suggests that the tetrayne moiety in **3a** undergoes polymerization in a random, rather than the regioselective (topochemical) manner. Unlike that of diyne dumbbell **2a**, the DSC thermogram of tetrayne dumbbell **3a** remains nearly flat from 240 to 350 °C, manifesting good thermal stability for the polymerized product in this temperature range. Moreover, the enthalpy for the exothermic process (ΔH) is determined to be 77.6 kJ · mol^{-1}. Since this value is considerably smaller than that of tetrayne precursor **19** (317.7 kJ · mol^{-1}), it can be inferred that the degree of polymerization involved is kind of low.

The DSC trace of long C_{60}−diyne−C_{60} dumbbell **2b** (Figure 2C) shows a weak exothermic peak at 141 °C along with a barely noticeable hump at 196 °C. The features herein are clear indicative of appreciable thermal robustness and very low solid-state reactivity of **2b** in comparison to the

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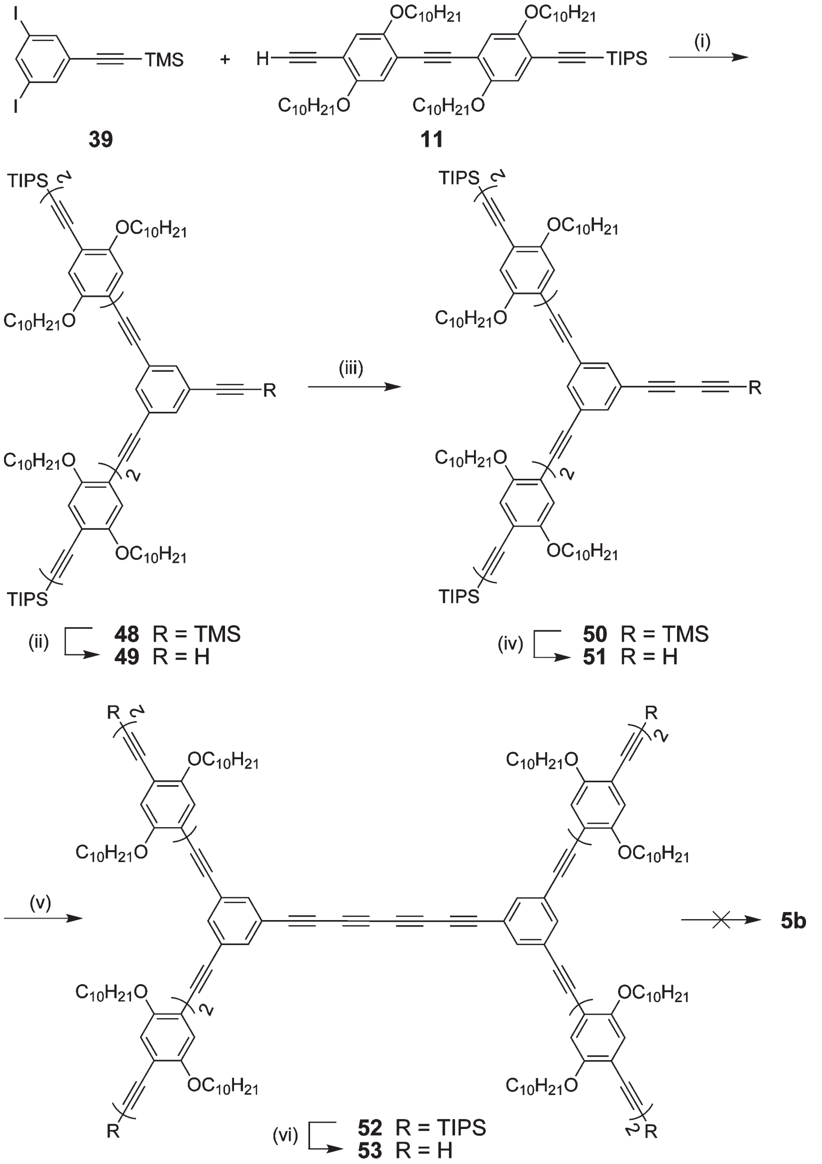
[70] Karim, S. M. A.; Nomura, R.; Masuda, T. *Polym. Bull.* **1999**, *43*, 305–310.

SCHEME 11. Attempted Synthesis of Star-Shaped Octatetrayne-Cored Tetrafullerene Adduct 5b[a]



[a]Reagents and conditions: (i) $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, 94%; (ii) K_2CO_3, CH_3OH, THF, 83%; (iii) TMSA, CuCl/TMEDA, air, acetone, 84%; (iv) K_2CO_3, CH_3OH, THF, 91%; (v) CuCl/TMEDA, air, acetone, 83%; (vi) TBAF, THF, 0%.

other fullerene−oligoyne species. The DSC thermogram of long C_{60}−tetrayne−C_{60} dumbbell **3b** (Figure 2D) shows a strong, broad exotherm peaking at 140 °C, together with a weak exothermic hump at 198 °C. The features are tied to tetrayne polymerization or cross-linking in the solid state, and the temperature range in which the thermal reactions take place are much lower than that for short C_{60}−tetrayne−C_{60} dumbbell **3a**. The increased thermal reactivity is likely due to the longer distance between the bulky fullerenyl groups and central tetrayne unit in **3b**, which in turn reduces the steric hindrance. In addition to the exothermic features, a pronounced baseline drift to the endothermic direction is observed at temperature higher than 270 °C, likely due to the degradation of the phenylacetylene moieties.

To investigate the structural changes of the oligoyne units in response to thermal annealing, UV−vis spectroscopic analysis was performed on the C_{60}−oligoyne−C_{60} adducts. In our experiments, each compound was measured by UV−vis spectroscopy under three different circumstances, (1) in solution (toluene), (2) in solid thin film at room temperature, and (3) in solid thin film after heating at 160 °C for ca. 1 h. The heating of thin films was intended to induce solid-state polymerization reactions. The heating temperature was chosen at 160 °C for a 2-fold reason: first, it was a common temperature at which most of the oligoyne−C_{60} adducts show exothermic processes in their DSC data (see Figure 2). Second, both the fullerene and phenylene units are known to be stable at this temperature so that only oligoyne thermal polymerization can be induced for investigation.

In line with the results of DSC analysis, the UV−vis absorption profiles of diyne-centered fullerene adducts **2a**, **2b**, and **5a** did not show significant changes before and after thermal annealing, indicating relative thermal stability of the

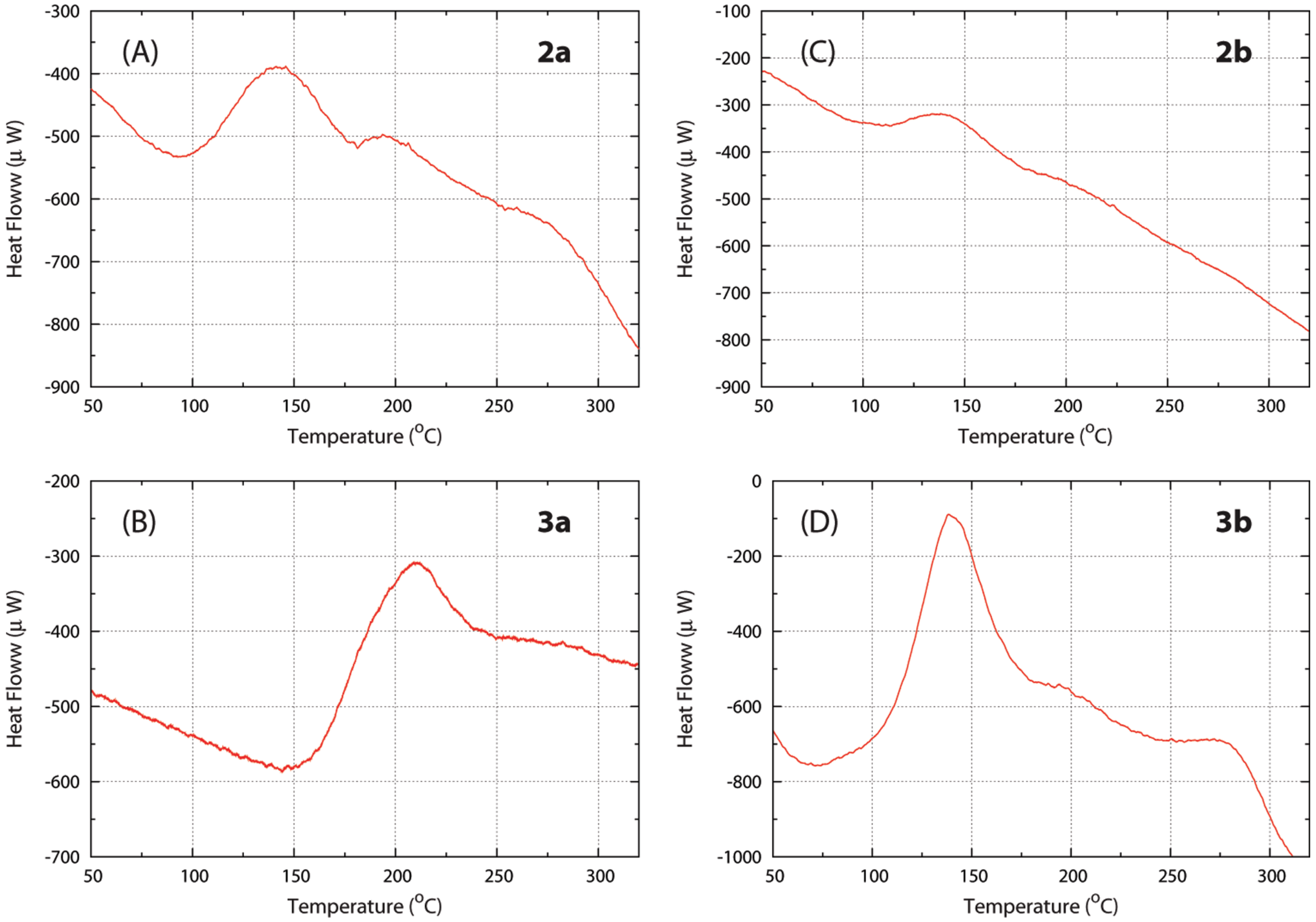
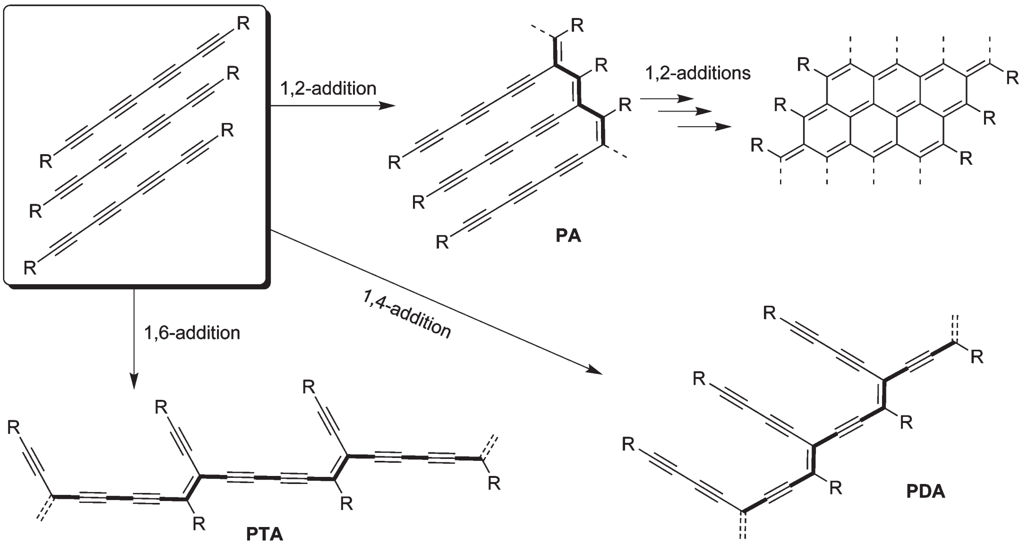


FIGURE 2. DSC profiles for (A) short C_{60}−diyne−C_{60} **2a**, (B) short C_{60}−tetrayne−C_{60} **3a**, (C) long C_{60}−diyne−C_{60} **2b**, and (D) long C_{60}−tetrayne−C_{60} **3b**. Scan rate: 5 °C/min.

SCHEME 12. Structures of Carbon Polymers Resulting from Different Probabilities of Topochemical Polymerization of Octatetraynes



diyne moieties at 160 °C (see Figure S-101, Supporting Information).

For tetrayne-centered bisfullerene dumbbells **3a** and **3b**, pronounced thermal reactivity of tetrayne moieties at 160 °C was detected by UV−vis analysis. As shown in Figure 3A, the UV−vis spectrum of short C_{60}−tetrayne−C_{60} dumbbell **3a** measured in solution shows three distinctive absorption bands in the region of 380−460 nm, which are characteristic of the vibronic modes of a conjugated tetrayne. In the spectrum of its solid thin film, the same set of vibronic bands

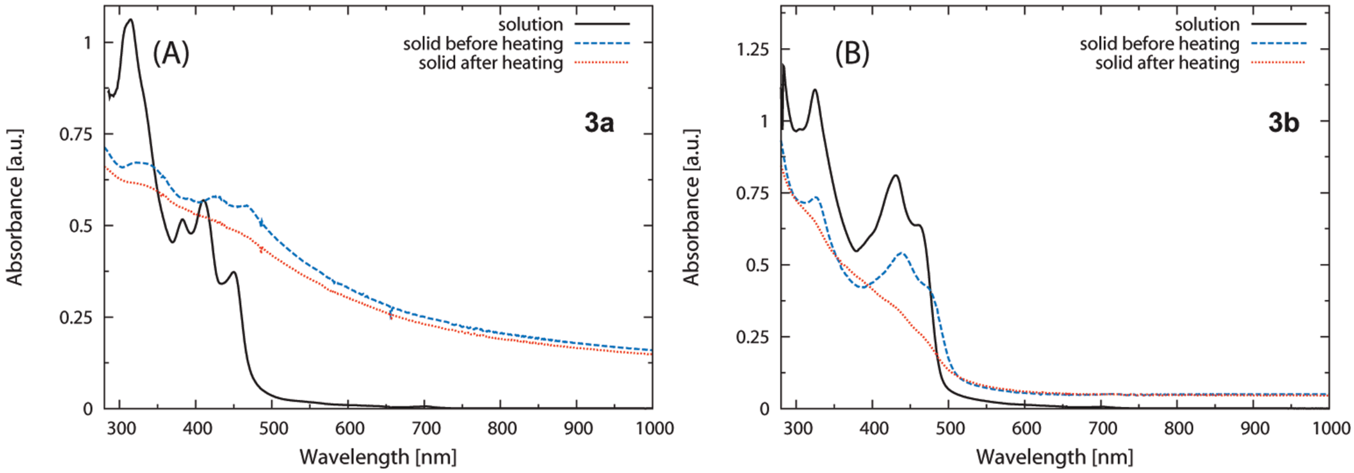


FIGURE 3. UV−vis spectra of tetrayne-centered bisfullerene dumbbells **3a** and **3b** measured in solution, solid film, and solid film after heating at 160 °C for ca. 1 h.

is still discernible, but appears to be substantially broadened in shape, likely resulting from aggregation effects. After heating the film at 160 °C for 1 h, markedly different UV−vis absorption features can be observed: the three characteristic tetrayne bands disappear completely, while the high-energy bands (below 350 nm) and the fullerene absorption tail (beyond ca. 550 nm) are hardly changed. The UV−vis results in association with its DSC data corroborate the occurrence of thermally induced solid-state polymerization of the tetrayne moieties in the thin film of **3a** upon thermal annealing.

To gain a deeper insight into the thermal reactivity of tetrayne dumbbell **3a**, IR spectroscopic analysis was undertaken on its solid samples before and after heating at 160 °C for 1 h. From the IR data given in Figure 4, it is observed that the vibrational frequency at ca. 2100 cm^{-1} characteristics of $C\equiv C$ bond stretching completely vanished after thermal annealing. The disappearance of the $C\equiv C$ band indicates that the thermal reactions involve acetylenic units and the resulting polymers contain highly symmetrical $C\equiv C$ structures and/or fused aromatic rings as proposed in Scheme 1.[56] In the meantime, the heated thin film gives rise to a new vibrational band at 1728 cm^{-1}, which is typical of $C{=}O$ stretching. Given the fact that the heating of the solid samples was conducted in an open air environment, it is very likely that oxygen participated in the solid-state reaction to form carbonyl groups at the terminal sites of the polymer networks. To further investigate the crystalline properties of the polymers resulting formed thermal annealing, X-ray powder diffraction (XRD) analysis was also undertaken. However, the results do not manifest any crystalline features.

In Figure 3B, the UV−vis spectrum of long C$_{60}$−tetrayne−C$_{60}$ dumbbell **3b** measured in solution shows two discernible vibronic bands of tetrayne in the region of 390 to 480 nm. The solid thin film gives rise to a spectral envelope silimar to that obtained in the solution phase, indicating relatively weak $\pi-\pi$ aggregation as a result of increased bulky solubilizing bis(decyloxy)phenylacetylene subunits in comparison to its short analogue **3a**. After heating the solid film of **3b** at 160 °C for 1 h, the UV−vis absorption bands corresponding to the tetrayne moiety are completely lost, which offers another piece of evidence for solid-state polymerization of the tetrayne units in **3b** in addition to the DSC results.

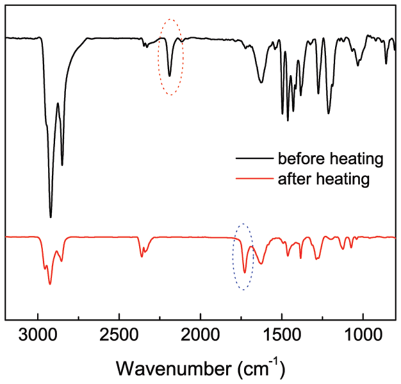


FIGURE 4. IR spectra for short C$_{60}$−tetrayne−C$_{60}$ dumbbell **3a** before and after heating at 160 °C for 1 h.

Morphological Properties. As mentioned in the Introduction, the nanomorphology of fullerene-based materials has become a topic of growing interest, owing to its importance for the optimization of fullerene−polymer BHJ solar cells. In our study, the morphological properties of oligoyne-cored fullerene adducts on surface were studied by atomic force microscopic (AFM) analysis. In the experiments, samples of oligoyne−C$_{60}$ adducts were first prepared in dilute solutions (ca. 10^{-6}−10^{-7} M in toluene). The solutions were spin-cast on freshly cleaved mica surfaces at a spin rate of 2,000 rpm. Surface morphologies of the resulting thin films were examined by AFM (operated in the noncontact mode) both before and after thermal annealing at 160 °C for 1 h. The acquired AFM images are detailed in the Supporting Information.

Short diyne dumbbell **2a** is found to agglomerate into spherical nanoclusters on the mica surface before heating, and the distribution of the nanospheres of **2a** is in a relatively narrow range of ca. 10−20 nm. After the sample is heated at 160 °C for 1 h, there are no noticeable morphological changes observed for the nanospheres (Figure S-102, Supporting Information).

Long diyne dumbbell **2b** aggregates on mica forming a pattern of cross-linked “worms”. The vertical heights of

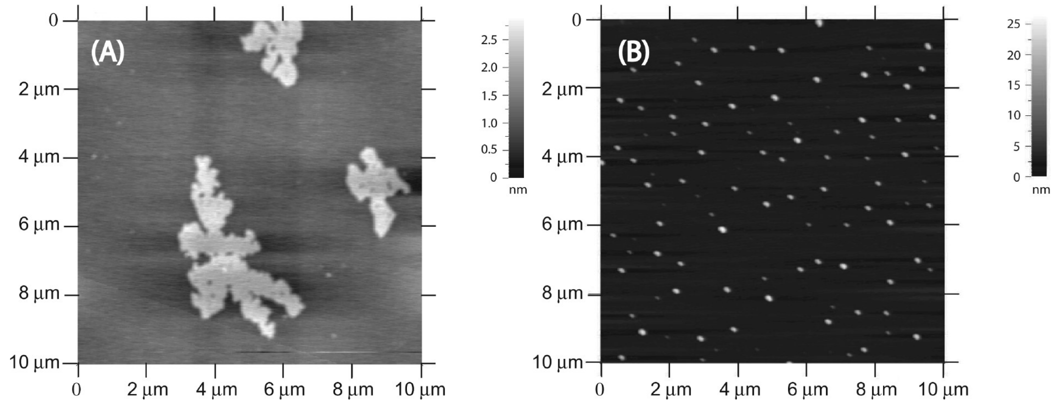


FIGURE 5. Surface morphology of short C_{60}−tetrayne−C_{60} dumbbell **3a** on mica measured by AFM: (A) before heating; (B) after heating at 160 °C for ca. 1 h.

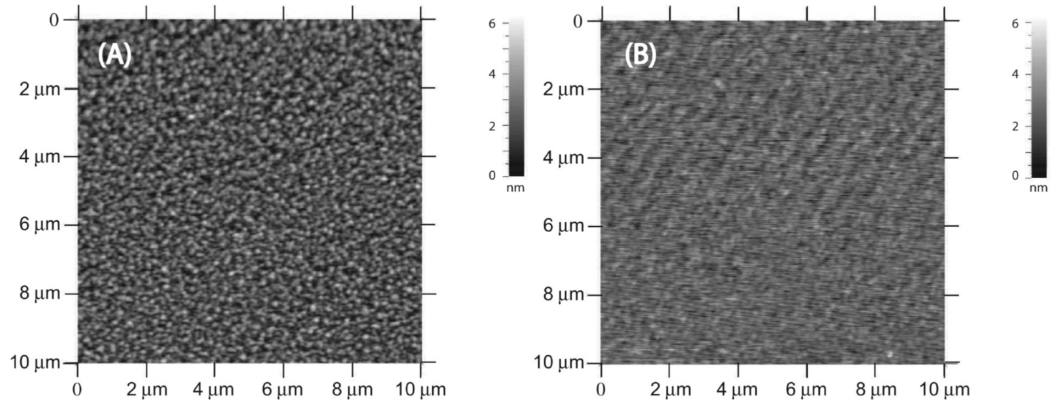


FIGURE 6. Surface morphology of long C_{60}−tetrayne−C_{60} dumbbell **3b** on mica measured by AFM: (A) before heating; (B) after heating at 160 °C for ca. 1 h.

these "worms" are rather uniform, ranging from ca. 4 to 6 nm (Figure S-103, Supporting Information). Like the short diyne dumbbell, these unique nanostructures show no significant changes in morphology after heating, which is consistent with the relatively high thermal stability of diyne species as revealed by previous DSC and UV−vis analyses.

The most remarkable morphological transformation corresponding to solid-state polymerization is found in the case of short C_{60}−tetrayne−C_{60} dumbbell **3a**. As shown in Figure 5, compound **3a** forms discrete "flake-like islands" on the surface with vertical heights around 1−2 nm. The thickness of these aggregates fits well the depth of nanostructures composed of single or double molecular layer of compound **3a**, given that the diameter of C_{60} is approximately 1 nm. After heating at 160 °C for ca. 1 h, the random "flakes" were transformed into an ordered array of spherical nanoparticles on the surface, with rather narrowly distributed vertical diameters. Cross-section analysis shows that the average vertical diameter of these nanospheres is around 20 nm. The transformation from random aggregates of **3a** into ordered, uniform nanospheres by means of thermal annealing can be related to the solid-state polymerization of the tetrayne moiety in **3a** as revealed by DSC, UV−vis, and IR analyses.

Long C_{60}−tetrayne−C_{60} dumbbell **3b** displays better film forming properties than its short homologue **3a**. As can be seen from Figure 6A, the surface morphology for aggregates of **3b** appears as a random, continuous thin film with a roughness of ca. 2−4 nm. After heating at 160 °C for ca. 1 h, the thin film became smoother and the roughness was measured to be less than 1 nm on average (see Figure 6B). In contrast to the case of **3a**, there are no discrete nanostructures observed from the AFM image of thermally annealed tetrayne **3b**. It therefore transpires that the additional two alkyloxy-substituted phenylacetylene subunits have greatly altered the surface aggregation behavior of dumbbell-shaped bisfullerene adducts.

Star-shaped tetrafullerene−diyne adduct **5a** forms a mixture of spherical, semispherical, and short "worm-like" nanoaggregates on the surface of mica (Figure S-104, Supporting Information). The height distribution of these nanostructures is narrow and measured to be about 1 nm, which corresponds well to single molecular layered aggregates. After thermal annealing at 160 °C for ca. 1 h, the morphological features are virtually unchanged. This result attests to the good thermal stability of **5a** at 160 °C as indicated by its UV−vis and DSC analyses.

Conclusions

We have demonstrated in this paper the synthesis of a series of dumbbell-shaped linear bisfullerene−end-capped conjugated oligoynes as well as a star-shaped tetrafullerene−oligoyne. The employment of butadiyne and octatetrayne central bridges resulted in stable fullerene−oligoyne adducts at ambient temperatures, whereas the stability of adducts involving higher oligoynes decreased sharply. The stability and reactivity of the oligoyne units in the solid state at elevated temperatures were examined by UV−vis, FT-IR, and DSC techniques. Morphological changes of these compounds in association with thermally induced polymerization were monitored by AFM imaging. The conjugated diyne moieties of corresponding fullerene−oligoyne adducts showed relative thermal stability at temperatures below ca. 250 °C, although evidence for low-degree diyne cross-linking was obtained from DSC and UV−vis analyses. Thermal annealing therefore had rather insignificant effects on the nanomorphologies of the interfacial aggregates of fullerene−diyne adducts. Fullerene-tetrayne adducts, in contrast, were found to be more thermally labile. The increased thermal reactivity of the tetrayne unit exerted drastic influence on the morphological features of the fullerene−tetrayne aggregates. The most noteworthy result comes from the thermal annealing of short fullerene−tetrayne dumbbell **3a**, where thermally induced tetrayne polymerization in the solid state transformed amorphous flake-like aggregates into uniform, highly ordered arrays of nanospheres. On the basis of the combined thermal, spectroscopic, and morphological analyses, a general correlation between surface aggregation behavior and molecular structure can be established for the fullerene−oligoyne hybrid compounds. The more fullerene components present in molecular composition, the much stronger tendency the molecules would display to aggregate into discrete spherical nanostructures on surface. On the other hand, the incorporation of more solubilizing alkyl groups renders reduced ability to form discrete nanoaggregates but facilitates the formation of continuous thin films. Finally, it is believed that better understanding of the fundamental solid-state properties should form the key stepping stone for finding practical uses of these new fullerene−oligoyne adducts in molecular device applications.

Experimental Section

General Methods. All chemicals were purchased from commercial sources and used as received. All reactions were performed in standard, oven-dried glassware under a N_2 atmosphere unless otherwise noted. THF was distilled from sodium/benzophenone. Et_3N and toluene were distilled from LiH. Catalysts $Pd(PPh_3)_4$ and $Pd(PPh_3)_2Cl_2$ were prepared from $PdCl_2$ according to standard procedures. Hay catalyst (CuCl/TMEDA in acetone) was prepared according to the procedure reported in the literature.[71] Thin-layer chromatography (TLC) was carried out with silica gel 60 F254 covered on plastic sheets and visualized by UV light or $KMnO_4$ stain, and flash column chromatographic separation was performed over silica gel.

Compound 2a. To an oven-dried round-bottomed flask equipped with a magnetic stirrer were added compound **10** (50 mg, 0.057 mmol), C_{60} (205 mg, 0.286 mmol), and dry THF (240 mL). The mixture was sonicated at 0 °C for 5 h to form a brownish suspension. Lithium hexamethyldisilazide (LHMDS) (0.29 mL, 1 M, 0.29 mmol) was added dropwise at rt under N_2 protection. The mixture was further stirred at rt for 1 h, and then trifluoroacetic acid (TFA) (0.1 mL) was added to the suspension to quench the reaction. Removal of the solvent in vacuo followed by silica flash column chromatography (hexanes/toluene, 3:1) afforded compound **2a** (32 mg, 0.014 mmol, 25%) as a brown solid: IR (KBr) 2921, 2852, 2200, 2087, 1654, 1602, 1496, 1464 cm^{-1}; ^{1}H NMR ($CDCl_3/CS_2$, 500 MHz) δ 7.22 (s, 2H), 7.15 (s, 2H), 7.08 (s, 2H), 4.13 (t, J = 6.1 Hz, 4H), 4.10 (t, J = 5.2 Hz, 4H), 1.96−1.89 (m, 8H), 1.68−1.62 (m, 4H), 1.60−1.54 (m, 4H), 1.40−1.20 (m, 48H), 0.88 (t, J = 6.5 Hz, 6H), 0.83 (t, J = 7.3 Hz, 6H); ^{13}C NMR ($CDCl_3/CS_2$, 125 MHz) δ 155.2, 154.4, 151.6, 151.4, 147.8, 147.5, 146.8, 146.61, 146.60, 146.4, 146.0, 145.9, 145.7, 145.64, 145.57, 144.9, 144.7, 143.4, 142.82, 142.79, 142.33, 142.26, 142.21, 142.1, 141.9, 141.8, 140.6, 140.5, 136.3, 135.4, 117.6, 117.1, 114.2, 113.5, 98.4, 80.5, 80.1, 79.9, 69.9, 69.6, 62.1, 55.7, 32.3, 30.4, 30.2, 30.1, 30.0 (br), 29.8 (br), 29.6 (br), 29.4, 29.1, 26.8, 26.4, 23.1, 14.51, 14.47; HRMS (MALDI-TOF) calcd for $C_{180}H_{90}O_4$, 2314.6839, found 2315.5138 [M + H]$^+$.

Compound 2b. Compound **2b** (32 mg, 0.010 mmol, 32%) was obtained as a brownish solid via the same in situ alkynylation protocol as described in the synthesis of **2a**, using compound **13** (53 mg, 0.031 mmol), C_{60} (112 mg, 0.156 mmol), LHMDS (0.16 mL, 1 M, 0.16 mmol), and dry THF (150 mL): IR (KBr) 2920, 2851, 2199, 2139, 2090, 1653, 1603, 1495, 1464, 1424 cm^{-1}; ^{1}H NMR ($CDCl_3/CS_2$, 500 MHz) δ 7.29 (s, 2H), 7.18 (s, 2H), 7.13 (s, 2H), 7.04 (s, 2H), 7.03 (s, 2H), 4.15 (m, 8H), 4.04 (m, 8H), 1.96−1.85 (m, 16H), 1.70−1.50 (m, 16H), 1.40−1.20 (m, 96H), 0.92−0.82 (m, 24H); ^{13}C NMR ($CDCl_3/CS_2$, 125 MHz) δ 155.3, 154.8, 153.9, 153.6, 151.9, 151.8, 147.9, 147.7, 147.0, 146.7, 146.5, 146.1, 146.0, 145.9, 145.75, 145.67, 145.0, 144.8, 143.5, 143.3, 142.90, 142.87, 142.4, 142.35, 142.29, 142.2, 141.98, 141.91, 140.7, 140.6, 136.4, 135.5, 118.2, 117.6, 117.4, 117.2, 115.6, 115.2, 113.3, 113.0, 97.9, 92.3, 92.0, 80.5, 79.9, 79.7, 70.1, 70.0, 69.8, 62.2, 55.8, 32.2, 30.2, 30.1, 30.01, 29.96, 29.89, 29.85, 29.7, 29.63, 29.57, 29.4, 26.8, 26.3, 26.2, 22.9, 14.4; HRMS (MALDI-TOF) calcd for $C_{236}H_{178}O_8$, 3139.3522, found 3139.2679 [M]$^+$.

Compound 3a. Compound **3a** (32 mg, 0.016 mmol, 31%) was obtained as a brownish solid via the same in situ alkynylation protocol as described in the synthesis of **2a**, using compound **20** (48 mg, 0.052 mmol), C_{60} (189 mg, 0.263 mmol), LHMDS (0.27 mL, 1 M, 0.27 mmol), and dry THF (240 mL): IR (KBr) 2920, 2850, 2190, 2115, 1628 cm^{-1}; ^{1}H NMR ($CDCl_3/CS_2$, 500 MHz) δ 7.19 (s, 2H), 7.12 (s, 2H), 7.04 (s, 2H), 4.10 (t, J = 6.5 Hz, 4H), 4.08 (t, J = 7.1 Hz, 4H), 1.90−1.84 (m, 8H), 1.64 (m, 4H), 1.54 (m, 4H), 1.46−1.15 (m, 48H), 0.90 (t, J = 6.2 Hz, 6H), 0.83 (t, J = 6.0 Hz, 6H); ^{13}C NMR ($CDCl_3/CS_2$, 125 MHz) δ 156.7, 154.7, 151.9, 151.7, 148.2, 147.9, 147.1, 147.0, 146.9, 146.8, 146.3, 146.20, 146.16, 146.03, 145.99, 145.90, 145.2, 145.0, 143.8, 143.2, 143.1, 142.7, 142.6, 142.5, 142.4, 142.22, 142.16, 140.93, 140.89, 136.6, 135.7, 118.2, 117.3, 115.7, 112.3, 99.3, 80.6, 80.5, 75.4, 70.3, 70.0, 69.6, 65.4, 62.4, 56.0, 32.6 (br), 30.5, 30.3 (br), 30.1 (br), 26.7 (br), 23.4 (br), 14.8 (br); HRMS (MALDI-TOF) calcd for $C_{180}H_{90}O_4$, 2362.6839, found 2362.8538 [M]$^+$.

Compound 3b. Compound **3b** (36 mg, 0.011 mmol, 33%) was obtained as a brownish solid via the same in situ alkynylation protocol as described in the synthesis of **2a**, using compound **24** (58 mg, 0.033 mmol), C_{60} (130 mg, 0.181 mmol), LHMDS (0.18 mL, 1 M, 0.18 mmol), and dry THF (150 mL): IR (KBr) 2922, 2852, 2192, 2117, 2077, 1653, 1603, 1541, 1506, 1496 cm^{-1}; ^{1}H NMR ($CDCl_3/CS_2$, 500 MHz) δ 7.29 (s, 2H), 7.19 (s, 2H), 7.13 (s, 2H), 7.03 (s, 2H), 7.01 (s, 2H), 4.17−4.01 (m, 16H), 1.97−1.82 (m, 16H), 1.70−1.49 (m, 16H), 1.40−1.20 (m, 96H), 0.95−0.82 (m, 24H); ^{13}C NMR ($CDCl_3/CS_2$, 125 MHz) δ 156.7, 155.0, 154.1, 153.7, 152.0, 151.9, 148.1, 147.9, 147.2, 146.9, 146.7, 146.3, 146.0, 145.9, 145.2, 145.0, 143.7, 143.5, 143.10, 143.08, 142.63, 142.55, 142.50, 142.4, 142.2, 141.88, 141.81, 140.9, 140.8, 136.6, 135.7, 118.6, 117.7, 117.4, 116.9, 115.2, 113.7, 111.5, 98.2, 93.2, 92.0, 80.7, 80.0, 75.4, 70.3, 70.2, 70.1, 70.0, 69.3, 65.2, 62.4, 56.0, 32.4, 30.4, 30.3, 30.15, 30.09, 30.04, 29.9, 29.8, 29.7, 29.6, 27.0, 26.5, 26.4, 23.2, 23.1 14.59, 14.56; HRMS (MALDI-TOF) calcd for $C_{240}H_{178}O_8$ 3187.3522, found 3187.8099 [M]$^+$.

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[71] Zhao, Y.; MacDonald, R.; Tykwinski, R. R. *J. Org. Chem.* **2002**, *67*, 2805–2812.

Compound 4. Compound **4** (6.00 mg, 0.0025 mmol, 5%) was obtained as a brownish unstable solid via the same in situ alkynylation protocol as described in the synthesis of **2a**, using compound **28** (50 mg, 0.052 mmol), C_{60} (185 mg, 0.257 mmol), LHMDS (0.26 mL, 1 M, 0.26 mmol), and dry THF (180 mL): ^{1}H NMR ($CDCl_3/CS_2$, 500 MHz) δ 7.16 (s, 2H), 7.10 (s, 2H), 7.01 (s, 2H), 4.09−4.05 (m, 8H), 1.93−1.84 (m, 8H,), 1.65−1.60 (m, 4H), 1.54−1.50 (m, 4H), 1.29−1.19 (m, 48H), 0.90−0.81 (m, 12H); HRMS (MALDI-TOF) calcd for $C_{188}H_{90}O_4$ 2410.6992, found 2410.6839 $[M]^+$.

Compound 5a. Compound **5a** (11 mg, 0.0017 mmol, 20%) was obtained as a brownish solid via the same in situ alkynylation protocol as described in the synthesis of **2a**, using compound **47** (30 mg, 0.0083 mmol), C_{60} (60 mg, 0.083 mmol), LHMDS (0.10 mL, 1 M, 0.10 mmol), and dry THF (120 mL): IR (KBr) 2922, 2851, 2211, 2150, 1632, 1576, 1504, 1464 cm^{-1}; ^{1}H NMR ($CDCl_3/CS_2$, 500 MHz) δ 7.73 (s, 2H), 7.68 (s, 4H), 7.30 (s, 4H), 7.20 (s, 4H), 7.16 (s, 4H), 7.09 (s, 4H), 7.06 (s, 4H), 4.17−4.01 (m, 32H), 1.93−1.87 (m, 32H), 1.70−1.54 (m, 32H), 1.42−1.20 (m, 192H), 0.91−0.81 (m, 48H); ^{13}C NMR ($CDCl_3/CS_2$, 125 MHz) δ 155.0, 154.3, 154.1, 154.0, 152.1, 152.0, 148.2, 147.9, 147.2, 146.9, 146.8, 146.3, 146.23, 146.17, 146.0, 145.9, 145.2, 145.0, 143.7, 143.14, 143.11, 142.7, 142.6, 142.53, 142.44, 142.22, 142.15, 140.9, 140.8, 136.6, 135.7, 135.1, 125.1, 122.9, 117.9, 117.7, 117.6, 117.4, 115.6, 115.4, 113.9, 113.5, 98.1, 93.4, 92.4, 92.2, 88.4, 80.9, 70.3, 70.2, 70.1, 70.0, 62.5, 56.0, 32.5, 30.5, 30.4, 30.3, 30.2, 30.1, 30.0, 27.1, 26.8, 26.6, 23.3, 14.7; HRMS (MALDI-TOF) calcd for $C_{488}H_{362}O_{16}$ 6476.7513, found 6476.2834 $[M]^+$.

1,4-Bis(decyloxy)-2-ethynyl-5-iodobenzene (7). To a solution of compound **6** (472 mg, 0.771 mmol) in 1:1 MeOH/THF (20 mL) was added K_2CO_3 (50 mg, 0.36 mmol). After being stirred at rt for 2 h, the reaction solvent was evaporated in vacuo. To the residue were added hexanes and aq HCl (1 M). The organic layer was isolated, washed with brine, and dried over $MgSO_4$. Filtration to remove $MgSO_4$ followed by evaporation under vacuum afforded deprotected terminal alkyne **7** (412 mg, 0.762 mmol, 99%): mp 50−51 °C; IR (KBr) 3289, 2955, 2921, 2850, 2107, 1588, 1495, 1467 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29 (s, 1H), 6.87 (s, 1H), 3.96 (t, J = 6.4 Hz, 2H), 3.93 (t, J = 6.4 Hz, 2H), 3.29 (s, 1H), 1.81−1.78 (m, 4H), 1.54−1.44 (m, 4H), 1.36−1.25 (m, 24 H), 0.90−0.87 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.3, 152.2, 124.3, 117.2, 112.7, 88.8, 82.2, 80.1, 70.6, 70.4, 32.3, 30.0, 29.8, 29.58, 29.57, 26.6, 26.5, 26.3, 23.1, 14.5; MS (APCI) calcd for $C_{28}H_{45}IO_2$ 540.3, found 541.3 $[M + H]^+$.

1,4-Bis(2,5-bis(decyloxy)-4-iodophenyl)buta-1,3-diyne (8). Compound **7** (215 mg, 0.387 mmol) was dissolved in acetone (10 mL), and then Hay catalyst (5 mL) was added. The mixture was stirred at rt under exposure to air for 36 h. When TLC analysis showed no starting material present, acetone was evaporated in vacuo, and $CHCl_3$ (10 mL) was added. The resulting content was washed with aq HCl (1 M), satd $NaHCO_3$, and brine sequentially. The organic layer was dried over $MgSO_4$ and evaporated in vacuo to give the crude product. The crude product was purified by silica flash column chromatography (hexanes/CH_2Cl_2, 85:15) to yield compound **8** (160 mg, 0.146 mmol, 75%) as a pale yellow solid: mp 104−105 °C; IR (KBr) 2918, 2847, 2149, 1494 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29 (s, 2H), 6.87 (s, 2H), 3.96 (t, J = 6.0 Hz, 4H), 3.93 (t, J = 6.8 Hz, 4H), 1.83−1.77 (m, 8H), 1.50−1.44 (m, 8H), 1.36−1.25 (m, 48 H), 0.88 (t, J = 6.5 Hz, 6H), 0.86 (t, J = 6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.0, 152.2, 124.4, 117.0, 112.7, 89.6, 79.2, 79.0, 70.54, 70.50, 32.3, 30.01, 29.99, 29.7, 29.5, 26.5, 26.3, 23.1, 14.5; HRMS (MALDI-TOF) calcd for $C_{56}H_{88}I_2O_4$ 1078.4772, found 1078.4464 $[M]^+$.

1,4-Bis(2,5-bis(decyloxy)-4-((trimethylsilyl)ethynyl)phenyl)buta-1,3diyne (9). Compound **8** (481 mg, 0.446 mmol), trimethylsilylacetylene (0.32 mL, 1.37 mmol), $PdCl_2(PPh_3)_2$ (31 mg, 0.044 mmol), CuI (17 mg, 0.091 mmol), and Et_3N (15 mL) were added to THF (15 mL). The solution was bubbled with N_2 at rt for 5 min and then stirred at rt under N_2 protection for 4 h. After the reaction was complete as checked by TLC analysis, the solvent was removed by rotary evaporation. To the residue obtained was added $CHCl_3$. The mixture was filtered through a $MgSO_4$ pad. It was then sequentially washed with aq HCl (10%) and brine. The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The crude product was then purified by silica flash column chromatography (hexanes/CH_2Cl_2, 10:1) to yield compound **9** (367 mg, 0.360 mmol, 81%) as a yellow solid: mp 119−120 °C; IR (KBr) 2923, 2901, 2869, 2850, 2157, 1499, 1469 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.92 (s, 2H), 6.91 (s, 2H), 3.97 (t, J = 7.2 Hz, 4H), 3.94 (t, J = 6.5 Hz, 4H), 1.82−1.77 (m, 8H), 1.51−1.45 (m, 8H), 1.34−1.28 (m, 48 H), 0.88 (t, J = 7.1 Hz, 6H), 0.86 (t, J = 7.1 Hz, 6H), 0.26 (s, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.3, 154.4, 118.0, 117.7, 115.2, 113.2, 101.4, 101.3, 79.8, 79.7, 70.1, 69.9, 32.3, 30.0, 29.9, 29.8, 29.6, 29.4, 26.4, 26.3, 23.1, 14.5, 0.4; HRMS (MALDI-TOF) calcd for $C_{66}H_{106}O_4Si_2$ 1018.7630, found 1019.1772 $[M]^+$.

1,4-Bis(2,5-bis(decyloxy)-4-ethynylphenyl)buta-1,3-diyne (10). To a solution of compound **9** (367 mg, 0.360 mmol) in 1:1 MeOH/THF (20 mL) was added K_2CO_3 (50 mg, 0.036 mmol). After being stirred at rt for 1 h, the reaction solvent was removed by rotary evaporation. The residue was dissolved in $CHCl_3$ and sequentially washed with aq HCl (10%) and brine. The organic layer was dried over $MgSO_4$. Filtration to remove $MgSO_4$ followed by evaporation under vacuum afforded **10** as a yellow solid (302 mg, 0.345 mmol, 96%): mp 110−111 °C; IR (KBr) 3283, 2923, 2850, 2140, 2105, 1500, 1469 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.96 (s, 2H), 6.95 (s, 2H), 3.971 (t, J = 6.4 Hz, 4H), 3.965 (t, J = 7.1 Hz, 4H), 3.35 (s, 2H), 1.84−1.77 (m, 8H), 1.50−1.41 (m, 8H), 1.36−1.25 (m, 48 H), 0.88 (t, J = 7.1 Hz, 6H), 0.86 (t, J = 6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.2, 154.4, 118.3, 118.1, 114.2, 113.6, 83.3, 80.3, 79.6, 70.2, 70.1, 32.3, 30.01, 29.99, 29.89, 29.5, 26.3, 23.1, 14.5; HRMS (MALDI-TOF) calcd for $C_{60}H_{90}O_4$ 874.6839, found 875.6830 $[M + H]^+$.

1,4-Bis(4-((2,5-bis(decyloxy)-4-((triisopropylsilyl)ethynyl)-phenyl)ethynyl)-2,5-bis(decyloxy)phenyl)buta-1,3-diyne (12). To a solution of **11** (226 mg, 0.224 mmol) in acetone (30 mL) was added Hay catalyst (5 mL). The mixture was stirred at rt under exposure to air overnight. The reaction solvent was evaporated in vacuo. To the residue was added $CHCl_3$. The resulting content was washed with aq HCl (1 M), satd $NaHCO_3$, and brine sequentially. The organic layer was dried over $MgSO_4$ and evaporated in vacuo to give the crude product, which was further purified by silica flash column chromatography (hexanes/CH_2Cl_2, 3:1) to give compound **12** (96 mg, 0.048 mmol, 43%) as a yellow solid: mp 72−73 °C; IR (KBr) 2924, 2852, 2146, 1622, 1497, 1470 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.99 (s, 4H), 6.94 (s, 4H),4.03−3.94 (m, 16H), 1.86−1.77 (m, 16H), 1.50 (m, 16H), 1.36−1.25 (m, 96 H), 1.15 (s, 42H), 0.89−0.85 (m, 24H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.8, 154.2, 153.8, 118.4, 118.3, 117.5, 117.0, 115.9, 114.64, 114.61, 113.0, 103.4, 97.0, 92.7, 91.6, 80.0, 79.8, 70.3, 70.2, 69.7, 32.3, 30.09, 30.05, 30.00, 29.93, 29.88, 29.8, 29.7, 29.6, 26.6, 26.4, 23.1, 19.1, 14.5, 11.8; HRMS (MALDI-TOF) calcd for $C_{134}H_{218}O_8Si_2$ 2011.6190, found 2012.2954 $[M + H]^+$.

1,4-Bis(4-((2,5-bis(decyloxy)-4-ethynylphenyl)ethynyl)-2,5-bis-(decyloxy)phenyl)buta-1,3-diyne (13). To a solution of compound **12** (303 mg, 0.154 mmol) in THF (20 mL) was added TBAF (0.1 mL, 1 M, 0.1 mmol). The mixture was stirred at rt for 12 h. The reaction solvent was evaporated in vacuo. To the residue was added $CHCl_3$. The resulting content was washed with aq HCl (1 M), satd $NaHCO_3$, and brine sequentially. The organic layer was dried over $MgSO_4$ and evaporated in vacuo to give the crude product, which was further purified by silica flash column chromatography (hexanes/CH_2Cl_2, 7:3) to yield compound **13**

(211 mg, 0.124 mmol, 81%) as a yellow solid: mp 93−94 °C; IR (KBr) 3315, 2925, 2850, 2195, 2136, 2106, 1639, 1618, 1497, 1469 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.02 (s, 6H), 7.01 (s, 2H), 4.06−3.99 (m, 16H), 3.38 (s, 2H), 1.89−1.80 (m, 16H), 1.54−1.46 (m, 16H), 1.40−1.26 (m, 96H), 0.93−0.89 (m, 24H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.4, 154.6, 153.8, 118.4, 118.3, 117.51, 117.46, 115.8, 115.3, 113.2, 113.1, 92.3, 91.8, 82.8, 80.5, 80.0, 79.8, 70.2, 70.0, 32.3, 30.11, 30.05, 30.03, 30.00, 29.9, 29.73, 29.71, 29.64, 29.62, 26.4, 23.1, 14.5; HRMS (MALDI-TOF) calcd for $C_{116}H_{178}O_8$ 1699.3522, found 1699.4987 $[M]^+$.

((2,5-Bis(decyloxy)-4-iodophenyl)buta-1,3-diynyl)trimethylsilane (14). To a flask containing compound **6** (849 mg, 1.57 mmol), trimethylsilylacetylene (0.70 mL, 4.9 mmol), and acetone (20 mL) was added Hay catalyst (2 mL). The mixture was stirred at rt under exposure to air for 2 h. When TLC analysis showed no starting material present, hexanes (40 mL) was added. The resulting content was washed with aq HCl (1 M), satd $NaHCO_3$, and brine sequentially. The organic layer was dried over $MgSO_4$ and evaporated in vacuo to give a dark yellow solid. The crude product was purified by silica flash column chromatography (hexanes/CH_2Cl_2, 5:1) to yield compound **14** (675 mg, 1.06 mmol, 68%) as a yellow solid: mp 41−42 °C; IR (neat) 2922, 2851, 2208, 2104, 1496 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31 (s, 1H), 6.87 (s, 1H), 3.98 (t, J = 7.1 Hz, 2H), 3.94 (t, J = 6.5 Hz, 2H), 1.82 (m, 4H), 1.50 (m, 4H), 1.40−1.22 (m, 24 H), 0.92 (t, J = 5.9 Hz, 6H), 0.26 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.3, 152.1, 124.4, 117.3, 112.1, 92.0, 89.8, 88.4, 79.0, 73.5, 70.50, 70.47, 32.3, 30.0, 29.7, 29.5, 26.5, 26.3, 23.1, 14.5, 0.1; MS (APCI) Calcd for $C_{33}H_{53}IO_2Si$ 636.7, found 636.3 $[M]^+$.

1,8-Bis(2,5-bis(decyloxy)-4-iodophenyl)octa-1,3,5,7-tetrayne (15). To a solution of compound **14** (277 mg, 0.401 mmol) in 1:1 MeOH/THF (8 mL) was added K_2CO_3 (20 mg, 0.14 mmol). After being stirred at rt for 2 h, the reaction mixture was quenched with water (10 mL) and then extracted with hexanes (30 mL). The organic layer was isolated, washed with brine, and dried over $MgSO_4$. Filtration to remove $MgSO_4$ followed by concentration under vacuum afforded a dark solid, which was immediately transferred into a flask containing acetone (6 mL) and Hay catalyst (2 mL). The mixture was stirred at rt under exposure to air overnight and then was briefly worked up to afford the crude product, which was further purified by silica flash column chromatography (hexanes/CH_2Cl_2, 9:1) to give compound **15** (132 mg, 0.107 mmol, 53%) as a yellow solid: mp 70−71 °C; IR (neat) 2916, 2849, 2198, 1494 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27 (s, 2H), 6.82 (s, 2H), 3.93 (t, J = 6.3 Hz, 4H), 3.90 (t, J = 6.3 Hz, 4H), 1.81−1.75 (m, 8H), 1.51−1.43 (m, 8H), 1.35−1.29 (m, 48 H), 0.89−0.87 (m, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.1, 152.2, 124.2, 117.1, 111.1, 91.1, 79.3, 74.9, 70.5, 70.4, 68.8, 64.8, 32.40, 32.37, 30.06, 30.02, 29.83, 29.78, 29.76, 29.6, 29.5, 26.5, 26.4, 23.18, 23.15, 14.69, 14.58; HRMS (MALDI-TOF) calcd for $C_{60}H_{88}I_2O_4$ 1126.4772, found 1126.1290 $[M]^+$.

((2,5-Bis(decyloxy)-4-((triisopropylsilyl)ethynyl)phenyl)buta-1,3-diynyl)trimethylsilane (17). Compound **14** (675 mg, 1.06 mmol), triisopropylsilylacetyelene (0.28 mL, 1.2 mmol), $PdCl_2(PPh_3)_2$ (37 mg, 0.053 mmol), CuI (30 mg, 0.16 mmol), and Et_3N (3 mL) were added to THF (20 mL). The solution was bubbled with N_2 at rt for 5 min and then stirred at 45 °C under N_2 protection overnight. After the reaction was complete as checked by TLC analysis, the solvent was removed by rotary evaporation. To the residue were added $CHCl_3$ and aq HCl (1 M). The organic layer was isolated, washed with brine, and dried over $MgSO_4$. Filtration to remove $MgSO_4$ followed by evaporation under vacuum afforded the crude product which was then purified by silica flash column chromatography (hexanes/CH_2Cl_2 10:1) to yield compound **17** (630 mg, 0.911 mmol, 86%) as a pale yellowish wax: IR (neat) 2924, 2857, 2201, 2151, 2100, 1497 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.90 (s, 1H), 6.89 (s, 1H), 3.97 (t, J = 7.1 Hz, 2H), 3.92 (t, J = 5.8 Hz, 2H), 1.82−1.72 (m, 4H), 1.50−1.42 (m, 4H), 1.40−1.24 (m, 24 H), 1.14 (s, 21H), 0.89 (t, J = 7.1 Hz, 6H), 0.23 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.5, 154.5, 118.1, 117.8, 115.7, 112.4, 103.1, 97.9, 92.2, 88.5, 79.4, 73.9, 70.3, 69.7, 32.3, 32.2, 30.3, 30.1, 30.0, 29.81, 29.78, 29.6, 29.0, 26.6,26.4, 26.2, 23.1, 19.4, 19.2, 19.0, 18.9, 18.6, 14.5, 11.8, 0.1; HRMS (MALDI-TOF) calcd for $C_{44}H_{74}O_2Si_2$ 690.5227, found 691.2629 $[M + H]^+$.

1,8-Bis(2,5-bis(decyloxy)-4-((triisopropylsilyl)ethynyl)phenyl)-octa-1,3,5,7-tetrayne (19). To a solution of compound **17** (277 mg, 0.401 mmol) in 1:1 MeOH/THF (8 mL) was added K_2CO_3 (20 mg, 0.14 mmol). After being stirred at rt for 2 h, the reaction mixture was quenched with water (10 mL) and then extracted with hexanes (30 mL). The organic layer was isolated, washed with brine, and dried over $MgSO_4$. Filtration to remove $MgSO_4$ followed by concentration under vacuum afforded a dark solid, which was immediately transferred into a flask containing acetone (6 mL) and Hay catalyst (2 mL). The mixture was stirred at rt under exposure to air overnight and then was briefly worked up to afford the crude product. Silica flash column chromatography (hexanes/CH_2Cl_2, 9:1) gave compound **19** (132 mg, 0.107 mmol, 53%) as a brownish solid: mp 58−59 °C; IR (neat) 2921, 2852, 2193, 2150, 1498 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.89 (s, 4H), 3.97 (t, J = 6.6 Hz, 4H), 3.91 (t, J = 6.6 Hz, 4H), 1.83−1.74 (m, 8H), 1.51−1.44 (m, 8H), 1.40−1.24 (m, 48 H), 1.14 (s, 42H), 0.89 (m, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.4, 154.5, 117.9, 117.7, 116.6, 111.4, 103.1, 98.7, 79.7, 75.3, 70.2, 69.7, 69.1, 65.0, 32.4, 32.3, 30.4, 30.0, 29.9, 29.8, 29.6, 29.0, 26.4, 26.2, 23.2, 23.1, 19.4, 19.2, 19.1, 19.0, 18.9, 18.7, 14.5, 11.8; HRMS (MALDI-TOF) calcd for $C_{82}H_{130}O_4Si_2$ 1234.9508, found 1235.1084 $[M]^+$.

1,8-Bis(2,5-bis(decyloxy)-4-ethynylphenyl)octa-1,3,5,7-tetrayne (20). To a solution of compound **19** (190 mg, 0.154 mmol) in THF (4 mL) was added TBAF (0.09 mL, 1 M, 0.09 mmol). The mixture was stirred at rt for 10 min. The solvent was removed by rotary evaporation. To the residue were added $CHCl_3$ and aq HCl (1 M). The organic layer was isolated, washed with brine, and dried over $MgSO_4$. Filtration to remove $MgSO_4$ followed by evaporation under vacuum afforded the crude product, which was further purified by silica flash column chromatography (hexanes/CH_2Cl_2, 1:9) to yield compound **20** (110 mg, 0.119 mmol, 77%) as a brownish waxy solid: IR (KBr) 3314, 3293, 2916, 2850, 2195, 1604, 1530 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.94 (s, 2H), 6.93 (s, 2H), 3.96 (t, J = 6.4 Hz, 8H), 3.38 (s, 2H), 1.82−1.76 (m, 8H), 1.50−1.42 (m, 8H), 1.40−1.22 (m, 48H), 0.88 (m, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.4, 154.3, 118.3, 118.1, 115.2, 112.0, 83.9, 80.1, 79.8, 74.9, 70.2, 70.1, 69.1, 64.9, 32.35, 32.33, 30.0, 29.79, 29.75, 29.6, 29.5, 29.3, 29.1, 26.44, 26.29, 23.0, 22.9, 14.56, 14.53; HRMS (MALDI-TOF) calcd for $C_{64}H_{90}O_4$ 922.6839, found 922.7046 $[M]^+$.

((4-((2,5-Bis(decyloxy)-4-((triisopropylsilyl)ethynyl)phenyl)-ethynyl)-2,5-bis(decyloxy)phenyl)buta-1,3-diynyl)trimethylsilane (21). To a solution of **11** (590 mg, 0.586 mmol) and trimethylsilylacetylene (1.02 mL, 3.52 mmol) in acetone (20 mL) was added Hay catalyst (5 mL). The mixture was stirred at rt under exposure to air overnight. The reaction solvent was evaporated in vacuo. To the residue was added $CHCl_3$. The resulting content was washed with aq HCl (1 M), satd $NaHCO_3$, and brine sequentially. The organic layer was dried over $MgSO_4$ and evaporated in vacuo to give the crude product. Silica flash column chromatography (hexanes/CH_2Cl_2, 4:1) gave compound **21** (513 mg, 0.465 mmol, 79%) as a yellow solid: mp 70−71 °C; IR (KBr) 2923, 2852, 2196, 2150, 2100, 1622, 1497, 1468, 1389 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.96 (s, 1H), 6.93 (s, 3H), 4.02−3.93 (m, 8H), 1.83−1.77 (m, 8H), 1.50−1.47 (m, 8H), 1.34−1.24 (m, 48 H), 1.15 (s, 21H), 0.90−0.86 (m, 12H), 0.23 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.7, 154.8, 153.8, 153.7, 118.5, 118.4, 117.4, 116.9, 116.1, 114.7, 112.3, 103.5, 97.0, 92.8, 92.1, 91.5, 88.6, 79.6, 73.9, 70.3, 70.1, 69.6, 32.4, 30.1, 29.98, 29.89, 29.8, 29.7, 29.6, 26.7, 26.4, 23.1, 19.1, 14.5, 11.8, 0.1; MS (APCI) calcd for $C_{72}H_{118}O_4Si_2$ 1102.9, found 1103.7 $[M + H]^+$.

1,8-Bis(4-((2,5-bis(decyloxy)-4-((triisopropylsilyl)ethynyl)-phenyl)ethynyl)-2,5-bis(decyloxy)phenyl)octa-1,3,5,7-tetrayne (23). To a solution of compound **21** (513 mg, 0.465 mmol) in 1:1 MeOH/THF (30 mL) was added K_2CO_3 (100 mg, 0.72 mmol). After being stirred at rt for 2 h, the reaction solvent was evaporated in vacuo. To the residue were added $CHCl_3$ and then aq HCl (1 M). The organic layer was isolated, washed with brine, and dried over $MgSO_4$. Filtration to remove $MgSO_4$ followed by concentration under vacuum afforded a dark solid, which was immediately transferred into a flask containing acetone (20 mL) and Hay catalyst (5 mL). The mixture was stirred at rt under exposure to air for 12 h. The reaction solvent was evaporated in vacuo. To the residue was added $CHCl_3$. The resulting content was washed with aq HCl (1 M), satd $NaHCO_3$, and brine sequentially. The organic layer was dried over $MgSO_4$ and evaporated in vacuo to give the crude product. Silica flash column chromatography (hexanes/CH_2Cl_2, 4:1) gave compound **23** (405 mg, 0.196 mmol, 85%) as a brownish solid: mp 71−72 °C; IR (KBr) 2923, 2853, 2194, 2149, 1623, 1499, 1468, 1423, 1388 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 6.98 (s, 2H), 6.97 (s, 2H), 6.95 (s, 4H), 4.04−3.94 (m, 16H), 1.85−1.81 (m, 16H), 1.51−1.48 (m, 16H), 1.37−1.25 (m, 96 H), 1.16 (s, 42H), 0.92−0.87 (m, 24H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.7, 154.8, 153.8, 153.7, 118.5, 118.3, 117.2, 117.0, 116.9, 114.8, 114.5, 111.3, 103.4, 97.1, 93.4, 91.4, 79.9, 75.4, 70.3, 70.14, 70.08, 69.7, 69.2, 65.1, 32.4, 32.3, 30.1, 29.88 (br), 29.83, 29.81, 29.75, 29.71, 29.68, 29.66, 29.6 (br), 29.5, 29.3, 26.7, 26.44, 26.38, 23.13, 23.09, 19.2, 14.53, 14.49, 11.8; HRMS (MALDI-TOF) calcd for $C_{138}H_{218}O_8Si_2$ 2059.6190, found 2060.3330 $[M + H]^+$.

1,8-Bis(4-((2,5-bis(decyloxy)-4-ethynylphenyl)ethynyl)-2,5-bis-(decyloxy)phenyl)octa-1,3,5,7-tetrayne (24). To a solution of compound **23** (405 mg, 0.196 mmol) in THF (25 mL) was added TBAF (0.1 mL, 1 M, 0.1 mmol). The mixture was stirred at rt for 3 h. The reaction solvent was evaporated in vacuo. To the residue was added $CHCl_3$. The resulting content was washed with aq HCl (1 M), satd $NaHCO_3$, and brine sequentially. The organic layer was dried over $MgSO_4$ and evaporated in vacuo to give the crude product, which was further purified by silica flash column chromatography (hexanes/CH_2Cl_2, 3:1) to yield compound **24** (287 mg, 0.164 mmol, 84%) as a brownish solid: mp 92−93 °C; IR (KBr) 3314, 2924, 2851, 2194, 2106, 1627, 1499, 1468, 1422, 1386 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 6.973 (s, 2H), 6.969 (s, 2H), 6.961 (s, 4H), 4.01−3.96 (m, 16H), 3.34 (s, 2H), 1.85−1.78 (m, 16H), 1.52−1.44 (m, 16H), 1.36−1.24 (m, 96H), 0.90−0.86 (m, 24H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.63, 154.58, 153.8, 153.7, 118.5, 118.4, 117.5, 117.3, 116.9, 115.1, 113.4, 111.4, 93.0, 91.6, 82.9, 80.4, 79.9, 75.3, 70.2, 70.1, 70.0, 69.2, 65.1, 33.3, 30.09, 30.05, 29.99, 29.8, 29.7, 29.6, 29.5, 29.4, 26.4, 23.1, 14.5; HRMS (MALDI-TOF) calcd for $C_{120}H_{178}O_8$ 1747.3622, found 1748.8991 $[M + H]^+$.

((2,5-Bis(decyloxy)-4-((triisopropylsilyl)ethynyl)phenyl)hexa-1,3,5-triynyl)trimethylsilane (25). To a solution of compound **17** (1.00 g, 1.45 mmol) in 1:1 MeOH/THF (60 mL) was added K_2CO_3 (500 mg, 3.62 mmol). After being stirred at rt for 2 h, the reaction solvent was evaporated in vacuo. To the residue were added hexanes and aq HCl (1 M). The organic layer was isolated, washed with brine, and dried over $MgSO_4$. Filtration to remove $MgSO_4$ followed by evaporation under vacuum afforded the deprotected terminal alkyne, which was immediately transferred into a flask containing trimethylsilylacetylene (15 mL, 0.11 mol), acetone (90 mL), and Hay catalyst (10 mL). The mixture was stirred at rt under exposure to air for 6 h. When TLC analysis showed no starting material present, the reaction solvent was evaporated in vacuo. To the residue was added $CHCl_3$. The resulting mixture was washed with aq HCl (1 M), satd $NaHCO_3$, and brine sequentially. The organic layer was dried over $MgSO_4$ and evaporated in vacuo to give a brown wax. The crude product was purified by silica flash column chromatography (hexanes/CH_2Cl_2, 95:5) to yield compound **25** (930 mg, 1.30 mmol, 90% based on the consumption of **17**) as a brown wax: IR (KBr) 2924, 2854, 2170, 2152, 2077, 1450, 1469 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 6.88 (s, 2H), 3.96 (t, J = 6.6 Hz, 2H), 3.90 (t, J = 6.6 Hz, 2H), 1.78−1.75 (m, 4H), 1.47−1.45 (m, 4H), 1.29−1.27 (m, 24 H),1.13 (s, 21H), 0.90−0.87 (m, 6H), 0.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.0, 154.3, 117.7, 117.5, 116.2, 111.4, 102.8, 98.2, 89.7, 88.5, 79.3, 73.9, 70.0, 69.5, 68.3, 62.0, 32.14, 32.13, 29.84, 29.81, 29.7, 29.60, 29.58, 29.55, 29.4, 26.4, 26.2, 22.94, 22.91, 18.9, 14.36, 14.33, 11.6, 0.27; HRMS (MALDI-TOF) calcd for $C_{46}H_{74}O_2Si_2$ 714.5227, found 715.4420 $[M + H]^+$.

1,12-Bis(2,5-bis(decyloxy)-4-((triisopropylsilyl)ethynyl)phenyl)-dodeca-1,3,5,7,9,11-hexayne (27). To a solution of compound **25** (930 mg, 1.30 mmol) in 1:1 MeOH/THF (40 mL) was added K_2CO_3 (200 mg, 1.40 mmol). After being stirred at rt for 1.5 h, the reaction solvent was evaporated in vacuo. To the residue were added $CHCl_3$ and then aq HCl (1 M). The organic layer was isolated, washed with brine, and dried over $MgSO_4$. Filtration to remove $MgSO_4$ followed by concentration under vacuum afforded a dark solid, which was immediately transferred into a flask containing acetone (80 mL) and Hay catalyst (10 mL). The mixture was stirred at rt under exposure to air for 2 h. The reaction solvent was evaporated in vacuo. To the residue was added $CHCl_3$. The resulting mixture was washed with aq HCl (1 M), satd $NaHCO_3$, and brine sequentially. The organic layer was dried over $MgSO_4$ and evaporated in vacuo to give the crude product. The crude product was further purified by silica flash column chromatography (hexanes/CH_2Cl_2, 95:5) to give compound **27** (325 mg, 0.253 mmol, 39%) as a brownish wax: IR (KBr) 2925, 2859, 2153, 2046, 1499, 1466, 1416 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 6.89 (s, 2H),6.88 (s, 2H), 3.97 (t, J = 6.4 Hz, 4H), 3.92 (t, J = 6.4 Hz, 4H), 1.78−1.77 (m, 8H), 1.47−1.45 (m, 8H), 1.33−1.27 (m, 48 H), 1.13 (s, 42H), 0.91−0.87 (m, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.9, 154.5, 117.9, 117.8, 117.1, 110.8, 102.9, 99.1, 79.5, 74.9, 70.2, 69.7, 69.1, 65.8, 64.5, 63.4, 32.5, 32.3, 30.0, 29.97, 29.87, 29.79, 29.75, 29.5, 26.5, 26.4, 23.13, 23.09, 19.2, 19.0, 14.54, 14.53, 11.8; HRMS (MALDI-TOF) calcd for $C_{82}H_{130}O_4Si_2$ 1282.9508, found 1284.1663 $[M +H]^+$.

(3,5-Diiodophenyl)methanol (31). To a solution of compound **30** (1.00 g, 2.58 mmol) in dry CH_2Cl_2 (20 mL) was added DIBAL (8.67 mL, 1 M in THF, 8.67 mmol) at 0 °C in two portions during a period of 4 h. The reaction was treated with aq HCl (1 M) slowly at 0 °C and then extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by silica flash column chromatography (hexanes/CH_2Cl_2, 4:1) to give **31** (880 mg, 2.45 mmol, 95%) as a white solid: mp 147−148 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.98 (s, 1H), 7.69 (s, 2H), 4.62 (d, J = 6.6 Hz, 2H), 1.76 (t, J = 5.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 94.3, 94.1, 91.8, 81.7, 73.8; GC−MS (EI) calcd for $C_7H_6I_2O$ 360, found 360 (100%) $[M]^+$. The characterizations are consistent with the literature data.[72]

3,5-Diiodobenzaldehyde (32). To a stirred solution of PCC (1.37 g, 6.34 mmol) in CH_2Cl_2 (20 mL) was added a solution of **31** (1.14 g, 3.17 mmol) in CH_2Cl_2 (10 mL). The reaction was stirred at rt for 2 h. The solvent was removed under vacuum, giving the crude product of **32**, which was then purified by silica flash column chromatography (hexanes/EtOAc, 80:20) to give compound **32** (1.08 g, 3.02 mmol, 95%) as a white solid: mp 133−134 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.83 (s,1H), 8.29

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(t, J = 1.3 Hz, 1H), 8.14 (d, J = 1.3 Hz, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 189.5, 151.0, 139.4, 138.2, 95.7; GC−MS (EI) calcd for $C_7H_4I_2O$, 358, found 358 (100%) [M]$^+$, 329 (12%) [M − CHO]$^+$. The characterizations are consistent with the literature data.[73]

1-(2,2-Dibromovinyl)-3,5-diiodobenzene (33). To a flask filled with dry CH_2Cl_2 (30 mL) were added CBr_4 (0.94 g, 2.8 mmol) and PPh_3 (1.49 g, 5.69 mmol). The mixture was stirred at rt for 5 min to produce a red solution. Then a solution of compound **32** (0.68 g, 1.9 mmol) in CH_2Cl_2 (15 mL) was added dropwise. The reaction was stirred overnight. The solvent was removed by rotary evaporation. The crude product was then purified by silica flash column chromatography (hexanes/CH_2Cl_2, 95:5), affording compound **33** (0.91 g, 1.77 mmol, 93%) as a white solid: mp 58−59 °C; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.99 (s, 1H), 7.78 (s, 2H), 7.27 (s, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 144.9, 138.7, 136.3, 133.8, 94.9, 93.1; MS (APCI) calcd for $C_8H_4{}^{79}Br^{81}BrI_2$, 513.7, found 513.8 [M]$^+$.

1-Ethynyl-3,5-diiodobenzene (34). LDA (2.5 mL, 1.8 M in THF, 4.43 mmol) was slowly added to a solution of **33** (910 mg, 1.77 mmol) in THF (15 mL) at −78 °C. After being stirred at this temperature for 1 h, the reaction was quenched by addition of satd aq NH_4Cl solution (10 mL). The mixture was diluted with hexanes (100 mL), and the organic phase was then washed with brine, dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified by silica flash column chromatography (hexanes), affording compound **34** (544 mg, 1.54 mmol, 87%) as a white solid: mp 128−129 °C; ^{1}H NMR (CDCl$_3$, 500 MHz,) δ 8.03 (s, 1H), 7.78 (s, 2H), 3.17 (s, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 145.7, 140.1, 125.8, 94.3, 80.5, 80.0; GC−MS calcd for $C_8H_4I_2$ 354, found 354 (100%) [M]$^+$, 227 (23%) [M − I]$^+$. The characterizations are consistent with the literature data.[74]

1,4-Bis(3,5-diiodophenyl)buta-1,3-diyne (35). To a solution of **34** (70 mg, 0.20 mmol) in acetone/CH_2Cl_2 (20 mL, 1:1) was added Hay catalyst (2 mL). The mixture was stirred at rt under exposure to air for 48 h. The solvent was removed by rotary evaporation. To the residue was added aq HCl (1 M, 20 mL). The mixture was extracted with a large volume of $CHCl_3$. The organic solution was washed with brine and dried over $MgSO_4$. Then $CHCl_3$ was removed under vacuum to give the crude compound, which was further purified by recrystallization from $CHCl_3$ to give pure **35** (46 mg, 0.065 mmol, 65%) as a white solid: mp > 200 °C dec; IR (KBr) 3075, 3027, 2911, 2198, 1760, 1735, 1618, 1566, 1523, 1399 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.78 (t, J = 1.1 Hz, 2H), 7.50 (d, J = 1.1 Hz, 4H); a meaningful ^{13}C NMR spectrum was not obtained due to low solubility; MS (APCI) calcd for $C_{16}H_6I_4$ 705.7, found 705.7 [M]$^+$.

1,4-Bis(3,5-bis((2,5-bis(decyloxy)-4-((triisopropylsilyl)ethynyl)-phenyl)ethynyl)phenyl)buta-1,3-diyne (37). Compound **35** (44 mg, 0.063 mmol), compound **36** (150 mg, 0.252 mmol), $PdCl_2(PPh_3)_2$ (8.9 mg, 0.013 mmol), and CuI (4.8 mg, 0.0063 mmol) were added to Et_3N (10 mL). The solution was bubbled with N_2 at rt for 5 min and then stirred at rt under N_2 protection for 12 h. After the reaction was complete as checked by TLC analysis, the solvent was removed by rotary evaporation. To the residue obtained was added $CHCl_3$. The mixture was filtered through a $MgSO_4$ pad and then was sequentially washed with aq HCl (10%) and brine. The organic layer was dried over $MgSO_4$, concentrated under vacuum, and purified by silica flash column chromatography (hexanes/CH_2Cl_2, 8:2) to yield compound **37** (123 mg, 0.0478 mmol, 76%) as a yellow solid: mp 87−88 °C; IR (KBr) 2924, 2859, 2211, 2150, 1633, 1578, 1501, 1467, 1421, 1386 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.67 (s, 2H), 7.62 (d, J = 1.3 Hz, 4H), 6.95 (s, 4H), 6.94 (s, 4H), 4.02(t, J = 6.5 Hz, 8H), 3.97 (t, J = 6.5 Hz, 8H), 1.87−1.76 (m, 16H), 1.57−1.47 (m, 16H), 1.31−1.21 (m, 96 H), 1.53 (s, 84H), 0.89 (t, J = 6.8 Hz, 12H), 0.85 (t, J = 7.0 Hz, 12H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 154.5, 153.8, 135.1, 134.9, 124.8, 122.6, 118.0, 116.7, 114.8, 113.6, 103.1, 97.0, 92.8, 87.9, 80.6, 74.9, 70.0, 69.5, 32.16, 32.13, 29.9, 29.85, 29.83, 29.7, 29.69, 29.62, 29.6, 26.4, 26.38, 22.9, 18.9, 14.3, 11.6; HRMS (MALDI-TOF) calcd for $C_{172}H_{266}O_8Si_4$ 2571.9485, found 2573.5731 [M + H]$^+$.

1,4-Bis(3,5-bis((2,5-bis(decyloxy)-4-ethynylphenyl)ethynyl)-phenyl)buta-1,3-diyne (38). To a solution of compound **37** (123 mg, 0.0478 mmol) in THF (6 mL) was added TBAF (0.05 mL, 1 M, 0.05 mmol). The mixture was stirred at rt for 30 min, and the solvent was removed by rotary evaporation. To the residue were added $CHCl_3$ and aq HCl (1 M). The organic layer was isolated and washed with brine and dried over $MgSO_4$. Filtration to remove $MgSO_4$ followed by evaporation under vacuum afforded the crude product, which was further purified by silica flash column chromatography (hexanes/CH_2Cl_2, 7:3) to yield compound **38** (68 mg, 0.035 mmol, 73%) as a brownish wax: IR (KBr) 3283, 2923, 2852, 2210, 2104, 1604, 1578, 1533, 1501, 1469, 1420, 1389 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.68 (s, 2H), 7.63 (d, J = 1.5 Hz, 4H), 6.99 (s, 4H), 6.98 (s, 4H), 4.01 (t, J = 6.1 Hz, 16H), 3.36 (s, 4H), 1.87−1.80 (m, 16H), 1.57−1.46 (m, 16H), 1.42−1.21 (m, 96 H), 0.89 (t, J = 7.2 Hz, 12H), 0.85 (t, J = 6.6 Hz, 12H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 154.3, 153.9, 135.1, 130.0, 124.7, 122.6, 118.0, 117.2, 114.1, 113.4, 93.0, 87.6, 82.7, 80.5, 80.1, 74.9, 69.9, 32.1, 29.9, 29.79, 29.77, 29.66, 29.57, 29.55, 29.53, 29.4, 26.3, 26.1, 22.9, 14.3; HRMS (MALDI-TOF) calcd for $C_{136}H_{186}O_8$ 1947.4148, found 1947.1021 [M]$^+$.

((3,5-Diiodophenyl)ethynyl)trimethylsilane (39). To a solution of compound **34** (120 mg, 0.234 mmol) in THF (8 mL) was added LDA (0.39 mL, 1.8 M in THF, 0.70 mmol) dropwise at −78 °C. The reaction was maintained at −78 °C and stirred for 1 h. To the formed red solution was added TMSCl (0.12 mL, 0.94 mmol) dropwise and the mixture was stirred for 1.5 h. To the light yellow solution was added aq HCl (1 M, 5 mL) at −78 °C. The reaction was then warmed to rt and extracted with CH_2Cl_2. The organic phase was washed with brine, dried over $MgSO_4$, concentrated under vacuum, and purified by silica flash column chromatography (hexanes/CH_2Cl_2, 1:9) to give compound **39** (80 mg, 0.19 mmol, 81%) as a colorless oil: ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.02 (t, J = 1.3 Hz, 1H), 7.79 (d, J = 1.1 Hz, 2H), 0.27 (s, 9H); GC−MS (EI) calcd for $C_{11}H_{12}ISi$ 426, found 426 (40%) [M]$^+$, 411 (100%) [M − CH$_3$]$^+$. The characterizations are consistent with the literature data.[75]

(4,4′-(5-((Trimethylsilyl)ethynyl)-1,3-phenylene)bis(ethyne-2,1-diyl)bis(2,5-bis(decyloxy)-4,1-phenylene))bis(ethyne-2,1-diyl)bis-(triisopropylsilane) (40). Compound **39** (54 mg, 0.13 mmol), compound **36** (150 mg, 0.252 mmol), $PdCl_2(PPh_3)_2$ (9 mg, 0.01 mmol), and CuI (8 mg, 0.03 mmol) were added to Et_3N (5 mL). The solution was bubbled with N_2 at rt for 5 min and then stirred at rt under N_2 protection for 12 h. After the reaction was complete as checked by TLC analysis, the solvent was removed by rotary evaporation. To the residue obtained was added $CHCl_3$. The mixture was filtered through a $MgSO_4$ pad and then was sequentially washed with aq HCl (10%) and brine. The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified by silica flash column chromatography (hexanes/CH_2Cl_2, 85:15) to yield compound **40** (158 mg, 0.116 mmol, 89%) as a yellow wax: IR (KBr) 2925, 2862, 2152, 1579, 1500, 1467, 1422, 1386 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.61 (s, 1H), 7.57 (d, J = 1.5 Hz, 2H),

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6.95 (s, 2H), 6.93 (s, 2H), 4.02 (t, J = 6.7 Hz, 4H), 3.96 (t, J = 6.2 Hz, 4H), 1.87−1.76 (m, 8H), 1.57−1.46 (m, 8H), 1.42−1.22 (m, 48 H), 1.16 (s, 42H), 0.89 (t, J = 7.0 Hz, 6H), 0.86 (t, J = 7.3 Hz, 6H), 0.26 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.8, 154.0, 134.7, 134.4, 124.6, 124.3, 118.3, 116.9, 114.9, 114.0, 103.8, 103.4, 97.1, 95.9, 93.8, 87.6, 70.3, 69.7, 32.3, 30.1, 30.0, 29.94, 29.91, 29.81, 29.80, 29.77, 29.6, 26.6, 26.5, 23.1, 19.1, 19.0, 14.5, 11.8, 0.3; HRMS (MALDI-TOF) calcd for $C_{89}H_{142}O_4Si_3$ 1359.0216, found 1359.2765 $[M]^+$.

(4,4′-(5-Ethynyl-1,3-phenylene)bis(ethyne-2,1-diyl)bis(2,5-bis(decyloxy)-4,1-phenylene))bis(ethyne-2,1-diyl)bis(triisopropylsilane) (41). To a solution of compound **40** (158 mg, 0.116 mmol) in MeOH/THF (20 mL, 1:1) was added K_2CO_3 (50 mg, 0.36 mmol). The mixture was stirred at rt for 2 h, and then the solvent was removed by rotary evaporation. The residue was diluted in CH_2Cl_2 and sequentially washed with aq HCl (10%) and brine. The organic layer was dried over $MgSO_4$, concentrated under vacuum, and purified by silica flash column chromatography (hexanes/CH_2Cl_2, 9:1) to yield compound **41** (150 mg, 0.116 mmol, 100%) as a yellow wax: IR (KBr) 3312, 2925, 2862, 2212, 2151, 1603, 1581, 1499, 1467, 1422, 1385 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.65 (s, 1H), 7.59 (d, J = 1.4 Hz, 2H), 6.95 (s, 2H), 6.94 (s, 2H), 4.02 (t, J = 6.1 Hz, 4H), 3.97 (t, J = 6.0 Hz, 4H), 3.10 (s, 1H), 1.86−1.78 (m, 8H), 1.56−1.48 (m, 8H), 1.42−1.22 (m, 48H), 1.16 (s, 42H), 0.90 (t, J = 6.8 Hz, 6H), 0.86 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.7, 154.0, 134.85, 134.84, 124.7, 123.3, 118.2, 116.9, 115.0, 113.9, 103.4, 97.2, 93.2, 87.8, 82.5, 78.6, 70.2, 69.7, 32.3, 30.12, 30.07, 30.04, 29.96, 29.92, 29.83, 29.80, 29.78, 26.63, 26.60, 23.1, 19.2, 14.5, 11.8; HRMS (MALDI-TOF) calcd for $C_{86}H_{134}O_4Si_2$ 1286.9821, found 1286.9424 $[M]^+$.

(4,4′-(5-((Trimethylsilyl)buta-1,3-diynyl)-1,3-phenylene)bis(ethyne-2,1-diyl)bis(2,5-bis(decyloxy)-4,1-phenylene))bis(ethyne-2,1-diyl)bis(triisopropylsilane) (42). To a flask containing acetone (8 mL) were added **41** (161 mg, 0.116 mmol), trimethylsilylacetylene (0.164 mL, 1.16 mmol), and Hay catalyst (2 mL). The mixture was stirred at rt under exposure to air for 40 h. When TLC analysis showed no starting material present, acetone was evaporated in vacuo. $CHCl_3$ (30 mL) was added, and the resulting content was washed with aq HCl (1 M), satd $NaHCO_3$, and brine sequentially. The organic layer was dried over $MgSO_4$, evaporated under vacuum, and purified by silica flash column chromatography (hexanes/CH_2Cl_2, 4:1) to yield compound **42** (143 mg, 0.103 mmol, 89%) as a yellow wax: IR (KBr) 2925, 2861, 2211, 2151, 2102, 1620, 1579, 1499, 1467, 1421, 1385 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.65 (s, 1H), 7.56 (d, J = 1.3 Hz, 2H), 6.95 (s, 2H), 6.93 (s, 2H), 4.02 (t, J = 6.4 Hz, 4H), 3.97 (t, J = 6.4 Hz, 4H), 1.87−1.78 (m, 8H), 1.57−1.46 (m, 8H), 1.41−1.25 (m, 48 H), 1.16 (s, 42H), 0.90 (t, J = 7.0 Hz, 6H), 0.87 (t, J = 7.0 Hz, 6H), 0.25 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.7, 154.0, 135.3, 135.2, 124.9, 122.6, 118.2, 116.9, 115.0, 113.8, 103.3, 97.2, 93.0, 91.8, 88.1, 88.0, 75.5, 75.4, 70.2, 69.7, 32.3, 30.12, 30.07, 30.00, 29.94, 29.87, 29.80, 29.76, 26.61, 26.57, 23.1, 19.1, 19.0, 14.5, 11.8, 0.0; HRMS (MALDI-TOF) calcd for $C_{91}H_{142}O_4Si_3$ 1383.0216, found 1384.0779 $[M + H]^+$.

(4,4′-(5-(Buta-1,3-diynyl)-1,3-phenylene)bis(ethyne-2,1-diyl)bis(2,5-bis(decyloxy)-4,1-phenylene))bis(ethyne-2,1-diyl)bis(triisopropylsilane) (43). To a solution of compound **42** (143 mg, 0.103 mmol) in MeOH/THF (8 mL, 1:1) was added K_2CO_3 (50 mg, 0.36 mmol). The mixture was stirred at rt for 2 h, and then the solvent was removed by rotary evaporation. The residue was diluted in CH_2Cl_2 and sequentially washed with aq HCl (10%) and brine. The organic layer was dried over $MgSO_4$, concentrated under vacuum, and purified by silica flash column chromatography (hexanes/CH_2Cl_2, 85:15) to yield compound **43** (110 mg, 0.0838 mmol, 81%) as a yellow wax: IR (KBr) 3312, 2925, 2861, 2214, 2151, 1617, 1578, 1499, 1467, 1422, 1385 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.67 (s, 1H), 7.60 (d, J = 1.4 Hz, 2H), 6.95 (s, 2H), 6.93 (s, 2H), 4.02 (t, J = 6.6 Hz, 4H), 3.97 (t, J = 6.6 Hz, 4H), 2.50 (s, 1H), 1.87−1.77 (m, 8H), 1.57−1.46 (m, 8H), 1.42−1.23 (m, 48H), 1.16 (s, 42H), 0.90 (t, J = 7.1 Hz, 6H), 0.86 (t, J = 7.1 Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.5, 153.8, 135.2, 135.1, 124.8, 122.0, 117.9, 116.6, 114.9, 113.5, 103.1, 97.0, 92.7, 88.0, 74.6, 73.8, 72.0, 70.0, 69.5, 68.2, 32.1, 29.92, 29.86, 29.82, 29.73, 29.69, 29.62, 29.59, 29.56, 26.40, 26.38, 22.9, 18.9, 14.3, 11.6; HRMS (MALDI-TOF) calcd for $C_{88}H_{133}O_4Si_2$ 1309.9742, found 1311.6287 $[M + H]^+$.

1,8-Bis(3,5-bis((2,5-bis(decyloxy)-4-((triisopropylsilyl)ethynyl)phenyl)ethynyl)phenyl)octa-1,3,5,7-tetrayne (44). To a round-bottom flask containing acetone (8 mL) were added compound **43** (110 mg, 0.0838 mmol) and Hay catalyst (5 mL). The mixture was stirred at rt under exposure to air for 20 h. When TLC analysis showed no starting material present, acetone was evaporated in vacuo. To the residue was added $CHCl_3$, and the resulting content was washed with aq HCl (1 M), satd $NaHCO_3$, and brine sequentially. The organic layer was dried over $MgSO_4$, concentrated under vacuum, and purified by silica flash column chromatography (hexanes/CH_2Cl_2, 85:15) to yield compound **44** (94 mg, 0.036 mmol, 86%) as a pale yellow solid: mp 89−90 °C; IR (KBr) 2924, 2856, 2208, 2150, 1577, 1500, 1467, 1421, 1408, 1387 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.68 (s, 2H), 7.61 (d, J = 1.5 Hz, 4H), 6.95 (s, 4H), 6.93 (s, 4H), 4.02 (t, hJ = 6.7 Hz, 8H), 3.97 (t, J = 6.7 Hz, 8H), 1.88−1.78 (m, 16H), 1.59−1.47 (m, 16H), 1.44−1.26 (m, 96H), 1.16 (s, 84H), 0.90 (t, J = 7.0 Hz, 12H), 0.88 (t, J = 7.0 Hz, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.5, 153.9, 135.6, 135.4, 124.9, 121.5, 117.9, 116.6, 114.9, 113.4, 103.1, 97.1, 92.6, 88.2, 76.3, 75.4, 70.0, 69.5, 67.8, 63.8, 32.2, 32.1, 30.0, 29.9, 29.74, 29.71, 29.6, 26.4, 22.94, 22.93, 18.9, 18.8, 14.4, 14.3, 11.6; HRMS (MALDI-TOF) calcd for $C_{176}H_{266}O_8Si_4$ 2619.9485, found 2620.6651 $[M + H]^+$.

1,4-Bis(3,5-bis((4-((2,5-bis(decyloxy)-4-((triisopropylsilyl)ethynyl)phenyl)ethynyl)-2,5-bis(decyloxy)phenyl)ethynyl)phenyl)buta-1,3-diyne (46). Compound **35** (30 mg, 0.043 mmol), compound **11** (173 mg, 0.172 mmol), $PdCl_2(PPh_3)_2$ (6.0 mg, 0.0086 mmol), and CuI (3.3 mg, 0.017 mmol) were added to Et_3N (10 mL). The solution was bubbled with N_2 at rt for 5 min and then stirred at rt under N_2 protection for 12 h. After the reaction was complete as checked by TLC analysis, the solvent was removed by rotary evaporation. To the obtained residue was added $CHCl_3$. The mixture was filtered through a $MgSO_4$ pad and then was sequentially washed with aq HCl (10%) and brine. The organic layer was dried over $MgSO_4$, concentrated under vacuum, and purified by silica flash column chromatography (hexanes/CH_2Cl_2, 7:3) to yield compound **46** (156 mg, 0.0369 mmol, 86%) as a yellow wax: IR (KBr) 2924, 2855, 2213, 2149, 1624, 1579, 1507, 1467, 1425, 1385 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.68 (s, 2H), 7.63 (d, J = 6.4 Hz, 4H), 7.02 (s, 4H), 7.00 (s, 4H), 6.96 (s, 4H), 6.94 (s, 4H), 4.07−4.02 (m, 24H), 3.97 (t, J = 6.4 Hz, 8H), 1.88−1.77 (m, 32H), 1.59−1.46 (m, 32H), 1.39−1.25 (m, 192H), 1.15 (s, 84H), 0.91−0.84 (m, 48H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.8, 154.2, 153.9, 153.7, 135.3, 135.1, 125.0, 122.8, 118.3, 117.6, 117.4, 116.9, 115.3, 114.7, 114.5, 113.6, 103.4, 97.0, 93.2, 92.3, 91.6, 88.1, 80.7, 75.1, 70.3, 70.2, 70.0, 69.6, 32.4, 30.2, 30.12, 30.08, 29.99, 29.91, 29.81, 29.76, 26.7, 26.6, 26.4, 23.2, 19.2, 14.6, 11.8; HRMS (MALDI-TOF) calcd for $C_{283}H_{440}O_{16}Si_4$ 4221.2850, found 4221.5151 $[M]^+$.

1,4-Bis(3,5-bis((4-((2,5-bis(decyloxy)-4-ethynylphenyl)ethynyl)-2,5-bis(decyloxy)phenyl)ethynyl)phenyl)buta-1,3-diyne (47). To a solution of compound **46** (156 mg, 0.0369 mmol) in THF (6 mL) was added TBAF (0.1 mL, 1 M, 0.1 mmol). The mixture was stirred at rt for 30 min, and then the solvent was removed by rotary evaporation. To the residue were added $CHCl_3$ and aq HCl (1 M). The organic layer was isolated, washed with brine, and dried over $MgSO_4$. Filtration to remove $MgSO_4$ followed by evaporation under vacuum and silica flash column chromatography (hexanes/CH_2Cl_2, 7:3) afforded compound **47** (133 mg, 0.0369 mmol, 100%) as a brownish solid: mp 61−62 °C; IR

(KBr) 3315, 3296, 2924, 2853, 2209, 2105, 1602, 1577, 1506, 1468, 1426, 1387 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.68 (s, 2H), 7.63 (s, 4H), 7.02 (s, 4H), 7.003 (s, 4H), 6.998 (s, 4H), 6.98 (s, 4H), 4.06−3.99 (m, 32H), 3.35 (s, 4H), 1.88−1.79 (m, 32H), 1.58−1.41 (m, 32H), 1.38−1.23 (m, 192 H), 0.90−0.83 (m, 48H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 154.4, 154.1, 153.7, 153.6, 135.1, 134.9, 124.8, 122.6, 118.3, 117.5, 117.34, 117.27, 115.14, 115.06, 113.6, 112.9, 93.0, 91.7, 91.6, 87.9,82.5, 80.6, 80.3, 74.9, 70.0, 69.8, 32.1, 30.0, 29.90, 29.85, 29.81, 29.80, 29.7, 29.59, 29.56, 29.4, 26.4, 26.2, 22.9, 14.3; HRMS (MALDI-TOF) calcd for $C_{248}H_{362}O_{16}$ 3596.7513, found 3597.7497 [M + H]$^+$.

Compound 48. Compound **39** (70 mg, 0.16 mmol), compound **11** (329 mg, 0.326 mmol), PdCl$_2$(PPh$_3$)$_2$ (11.4 mg, 0.0163 mmol), and CuI (6.2 mg, 0.033 mmol) were added to Et$_3$N (6 mL). The solution was bubbled with N$_2$ at rt for 5 min and then stirred at rt for 8 h. After the reaction was complete as checked by TLC analysis, the solvent was removed by rotary evaporation. The residue was diluted in CHCl$_3$, and the mixture was filtered through a MgSO$_4$ pad. The solution obtained was sequentially washed with aq HCl (10%) and brine. The organic layer was dried over MgSO$_4$, concentrated under vacuum, and purified by silica flash column chromatography (hexanes/CH$_2$Cl$_2$, 4:1) to yield compound **48** (330 mg, 0.151 mmol, 94%) as a yellow solid: mp 42−43 °C; IR (KBr) 2925, 2855, 2210, 2148, 1624, 1579, 1508, 1469, 1426, 1386 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.62 (s, 1H), 7.58 (d, J = 1.6, 2H), 7.02 (s, 2H), 6.99 (s, 2H), 6.96 (s, 2H), 6.95 (s, 2H), 4.04−4.01 (m, 12H), 3.96 (t, J = 6.5 Hz, 4H), 1.87−1.76 (m, 16H), 1.53−1.48 (m, 16H), 1.37−1.24 (m, 96 H), 1.16 (s, 42H), 0.90−0.83 (m, 24H), 0.27 (s, 9H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 154.5, 153.9, 153.6, 153.5, 134.6, 134.2, 124.3, 124.0, 118.1, 117.4, 117.3, 116.7, 114.9, 114.5, 114.2, 113.6, 103.6, 103.2, 96.7, 95.7, 93.3, 92.0, 91.4, 87.4, 70.0, 69.9, 69.8, 69.4, 32.1, 29.90, 29.86, 29.76, 29.7, 29.69, 29.6, 29.59, 29.4, 26.4, 26.3, 26.2, 22.9, 18.9, 14.3, 11.6, 0.1; HRMS (MALDI-TOF) calcd for $C_{145}H_{230}O_8Si_3$ 2183.6899, found 2183.0253 [M]$^+$.

Compound 49. To a solution of compound **48** (336 mg, 0.154 mmol) in MeOH/THF (6 mL, 1:1) was added K$_2$CO$_3$ (50 mg, 0.36 mmol). The mixture was stirred at rt for 2 h, and then the solvent was removed by rotary evaporation. The residue was diluted in CH$_2$Cl$_2$ and sequentially washed with aq HCl (10%) and brine. The organic layer was dried over MgSO$_4$, concentrated under vacuum, and purified by silica flash column chromatography (hexanes/CH$_2$Cl$_2$, 7:3) to yield compound **49** (268 mg, 0.127 mmol, 83%) as a yellow solid: mp 65−66 °C; IR (KBr) 3262, 2955, 2924, 2855, 2209, 2149, 1670, 1626, 1580, 1508, 1467, 1426, 1385 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.66 (s, 1H), 7.60 (d, J = 0.9 Hz, 2H), 7.03 (s, 2H), 7.00 (s, 2H), 6.96 (s, 2H), 6.95 (s, 2H), 4.06−4.02 (m, 12H), 3.96 (t, J = 6.6 Hz, 4H), 3.11 (s, 1H), 1.89−1.77 (m, 16H), 1.57−1.48 (m, 16H), 1.42−1.26 (m, 96H), 1.16 (s, 42H), 0.92−0.85 (m, 24H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 154.8, 154.2, 153.9, 153.7, 134.9, 134.8, 124.7, 123.2, 118.3, 117.5, 117.4, 116.9, 115.2, 114.7, 114.5, 113.7, 103.4, 96.9, 93.4, 92.2, 91.6, 87.8, 82.5, 78.6, 70.2, 70.1, 70.0, 69.6, 32.3, 30.14, 30.08, 29.9, 29.8, 29.7, 26.7, 26.6, 26.4, 23.1, 19.2, 14.5, 11.8; HRMS (MALDI-TOF) calcd for $C_{142}H_{222}O_8Si_2$ 2111.6503, found 2112.6151 [M + H]$^+$.

Compound 50. To a flask containing acetone (10 mL) were added compound **49** (268 mg, 0.127 mmol), trimethylsilylacetylene (0.179 mL, 1.27 mmol), and Hay catalyst (5 mL). The mixture was stirred at rt under exposure to air for 45 h. When TLC analysis showed no starting material present, acetone was evaporated under vacuum, and to the residue was added CHCl$_3$ (30 mL). The resulting mixture was washed with aq HCl (1 M), satd NaHCO$_3$, and brine sequentially. The organic layer was dried over MgSO$_4$, concentrated under vacuum, and purified by silica flash column chromatography (hexanes/CH$_2$Cl$_2$, 7:3) to yield compound **50** (235 mg, 0.106 mmol, 84%) as a yellow solid: mp 57−58 °C; IR (KBr) 2958, 2924, 2854, 2209, 2150, 2101, 1624, 1579, 1557, 1539, 1507, 1467, 1427, 1386 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.66 (s, 1H), 7.58 (d, J = 1.4 Hz, 2H), 7.03 (s, 2H), 7.00 (s, 2H), 6.96 (s, 2H), 6.95 (s, 2H), 4.06−4.02 (m, 12H), 3.96 (t, J = 6.0 Hz, 4H), 1.88−1.80 (m, 16H), 1.55−1.50 (m, 16H), 1.41−1.26 (m, 96H), 1.16 (s, 42H), 0.92−0.86 (m, 24H), 0.26 (s, 9H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 154.8, 154.3, 153.9, 153.7, 135.24, 135.19, 124.9, 122.7, 118.4, 117.6, 117.5, 116.9, 115.4, 114.8, 114.6, 113.7, 103.5, 96.9, 93.2, 92.3, 91.8, 91.6, 88.1, 88.0, 75.5, 75.4, 70.3, 70.2, 70.0, 69.7, 32.3, 30.13, 30.07, 29.98, 29.9, 29.8, 26.7, 26.6, 26.4, 23.1, 19.1, 14.5, 11.8, 0.0; HRMS (MALDI-TOF) calcd for $C_{147}H_{230}O_8Si_3$ 2207.6899, found 2207.8487 [M]$^+$.

Compound 51. To a solution of compound **50** (230 mg, 0.104 mmol) in MeOH/THF (20 mL, 1:1) was added K$_2$CO$_3$ (50 mg, 0.36 mmol). The mixture was stirred at rt for 1 h, and then the solvent was removed by rotary evaporation. The residue was diluted in CHCl$_3$ and then sequentially washed with aq HCl (10%) and brine. The organic layer was dried over MgSO$_4$, concentrated under vacuum, and purified by silica flash column chromatography (hexanes/CH$_2$Cl$_2$, 7:3) to yield compound **51** (201 mg, 0.094 mmol, 91%) as a yellow solid: mp 57−58 °C; IR (KBr) 3314, 2924, 2855, 2212, 2149, 1670, 1636, 1578, 1560, 1542, 1508, 1468, 1426, 1386 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.71 (s, 1H), 7.63 (d, J = 1.5 Hz, 2H), 7.06 (s, 2H), 7.03 (s, 2H), 6.99 (s, 2H), 6.98 (s, 2H), 4.08−4.02 (m, 12H), 3.98 (t, J = 6.7 Hz, 4H), 2.50 (s, 1H), 1.90−1.80 (m, 16H), 1.58−1.50 (m, 16H), 1.42−1.25 (m, 96H), 1.19 (s, 42H), 0.92−0.87 (m, 24H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 154.8, 154.3, 153.9, 153.7, 135.4, 135.3, 125.0, 122.3, 118.4, 117.6, 117.5, 116.9, 115.5, 114.8, 114.6, 113.6, 103.5, 96.9, 93.1, 92.3, 91.6, 88.2, 74.8, 74.0, 72.3, 70.3, 70.2, 70.0, 69.7, 68.3, 32.4, 30.16, 30.12, 30.08, 30.05, 29.98, 29.95, 29.92, 29.8, 26.67, 26.63, 26.4, 23.1, 19.2, 14.5, 11.8; HRMS (MALDI-TOF) calcd for $C_{144}H_{222}O_8Si_2$ 2135.6503, found 2135.6761 [M]$^+$.

Compound 52. To a flask containing acetone/CH$_2$Cl$_2$ (10 mL, 1:1) were added compound **51** (200 mg, 0.0940 mmol) and Hay catalyst (5 mL). The mixture was stirred at rt under exposure to air for 2 h. When TLC analysis showed no starting material present, acetone was evaporated in vacuo. CHCl$_3$ (30 mL) was added. The resulting content was washed with aq HCl (1 M), satd NaHCO$_3$, and brine sequentially. The organic layer was dried over MgSO$_4$, concentrated under vacuum, and purified by silica flash column chromatography (hexanes/CH$_2$Cl$_2$, 7:3) to yield compound **52** (166 mg, 0.0389 mmol, 83%) as a yellow wax: IR (KBr) 2923, 2854, 2207, 2149, 1578, 1507, 1467, 1426, 1388 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.69 (s,2H), 7.62 (d, J = 1.5 Hz, 4H), 7.02 (s, 4H), 6.99 (s, 4H), 6.96 (s, 4H), 6.95 (s, 4H), 4.06−4.01 (m, 24H), 3.96 (t, J = 6.7 Hz, 8H), 1.88−1.76 (m, 32H), 1.55−1.48 (m, 32H), 1.37−1.25 (m, 192H), 1.16 (s, 84H), 0.90−0.85 (m, 48H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 154.8, 154.3, 153.9, 153.7, 135.6, 125.2, 121.7, 118.4, 117.6, 117.5, 117.0, 115.5, 114.7, 114.6, 113.5, 103.5, 97.0, 93.0, 92.3, 91.6, 88.4, 75.6, 70.3, 70.2, 70.0, 69.7, 68.0, 64.0, 32.3, 30.2, 30.11, 30.06, 29.9, 29.8,29.7, 26.6, 26.4, 23.1, 19.1, 14.6, 14.5, 11.8; HRMS (MALDI-TOF) calcd for $C_{288}H_{442}O_{16}Si_4$ 4269.2850, found 4269.2584 [M]$^+$.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectroscopic characterization data of all new compounds. DSC data of compounds **9** and **19**. UV−vis absorption and AFM analyses of compounds **2a**, **2b**, and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.