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Synthesis and Properties of Rhomboidal Macrocyclic Subunits of Graphdiyne-Like Nanoribbons

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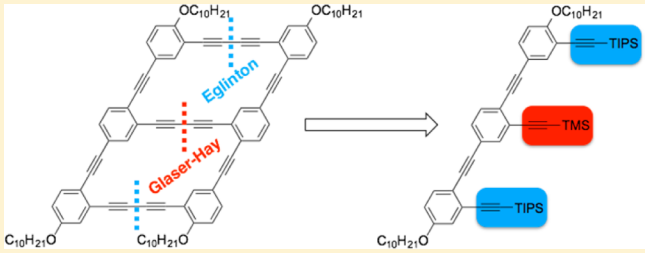
Supporting Information

ABSTRACT: Rhomboidal macrocyclic subunits of graphdiyne-like nanoribbon (GDNR) bearing both alkyne and diyne units, allowing for multichannel π-conjugation, were synthesized using an oxidative Glaser-type ring closing reaction. These subunits, called the "meshes" of the nanoribbon, possess phenyl groups with decyloxy solubilizing chains on each corner. The yields of the ring closing reaction highly depend on the metal (Cu or Pd) catalyst used for the macrocyclization step. Increasing the width of the meshes from one macrocycle to two fused macrocycles resulted in a decrease of the bandgap by 0.23 eV as shown by optical spectroscopy. The optimized geometries of the meshes alongside their HOMO and LUMO orbitals were calculated using DFT calculations at the B3LYP/6-31+G** level of theory. The results showed a nearly planar conformation for both meshes with HOMO and LUMO orbitals entirely delocalized over the molecules.



INTRODUCTION

Carbon allotropes have been the subject of intense research in the past 25 years owing to their astonishing electronic and optical properties.[1] Depending on their size and shape, these materials can be semiconducting or conducting, making them potentially useful for a wide range of applications.[2] For many reasons including ease of synthesis and thermodynamic stability, carbon allotropes containing exclusively sp^2-hybridized carbon atoms such as fullerenes, carbon nanotubes, and graphene have been the most studied by far. Much less efforts have been devoted to the synthesis and characterization of sp-hybridized allotropes such as 1D polyynes[3−5] and 2D graphynes and graphdiynes.[6,7] Yet, many theoretical reports suggest that alkyne-based 2D materials could exhibit similar, or even better, charge mobility than other allotropes.[7] Also, Narita et al. suggested that graphdiyne might be a promising material for compound intercalation and insertion since the pores are larger than those of graphene because of the butadiyne spacing unit.[8] Furthermore, theoretical studies showed that 1D graphdiyne nanoribbons might have electronic properties similar to those of graphene nanoribbons, as their band gap varies as a function of their width.[9−11]

The main reason for the lack of attention toward the sp-carbon-based allotropes among the scientific community is the difficulty of preparing them using either a top-down or a bottom-up approach. In fact, the intrinsic instability and relatively high reactivity of the C−C triple bond (two π orbitals) preclude the use of thermal process to prepare them. Thus, an efficient method for the synthesis of 2D graphyne has never been reported while 2D graphdiyne has been obtained from hexaethynylbenzene via homocoupling reaction on copper surface.[12] Although interesting to probe the physical properties of graphdiyne, this technique provides very small amounts of undefined materials, which limits its usefulness for several applications.

As first synthetic efforts toward the bottom-up preparation of well-defined graphyne and graphdiyne materials, some research groups reported the preparation of small graphyne and graphdiyne substructures, mostly macrocyclic compounds, to study their physical properties.[13−20] The synthesis of small substructures also allowed the assessment of synthetic feasibility for the preparation of bigger fragments and, eventually, two-dimensional graphyne and graphdiyne. However, the high number of synthetic steps required to obtain rather small fragments seemed to discourage further investigations toward this aim, although experimental and theoretical evidence suggests that efforts invested in the pursuit of this goal might be worthwhile.

One logical strategy to further explore the synthetic feasibility of graphyne and graphdiyne-like materials is to prepare 1D nanoribbons rather than 2D sheets. In fact, 1D nanoribbons can be obtained from polymeric precursors as soluble materials that can be studied using standard characterization techniques. Solution-phase synthesis of graphene nanoribbons of different width and edge configuration has been successfully achieved recently following the polymeric precursor strategy.[21−26]

Herein we report the bottom-up solution synthesis of model compounds of graphdiyne-type nanoribbon using a Glaser-type ring-closure reaction. These models compounds, hereafter called

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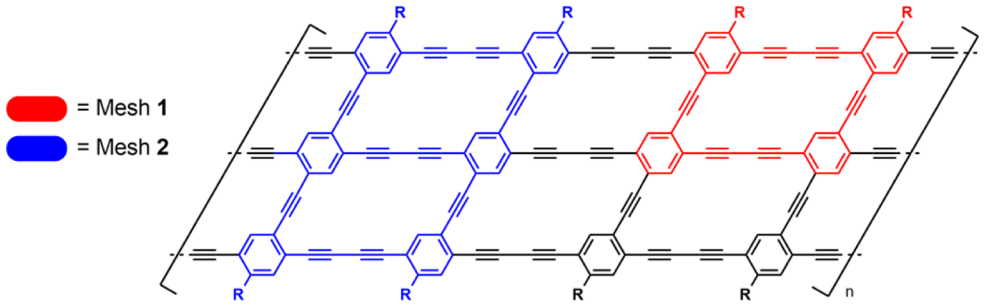
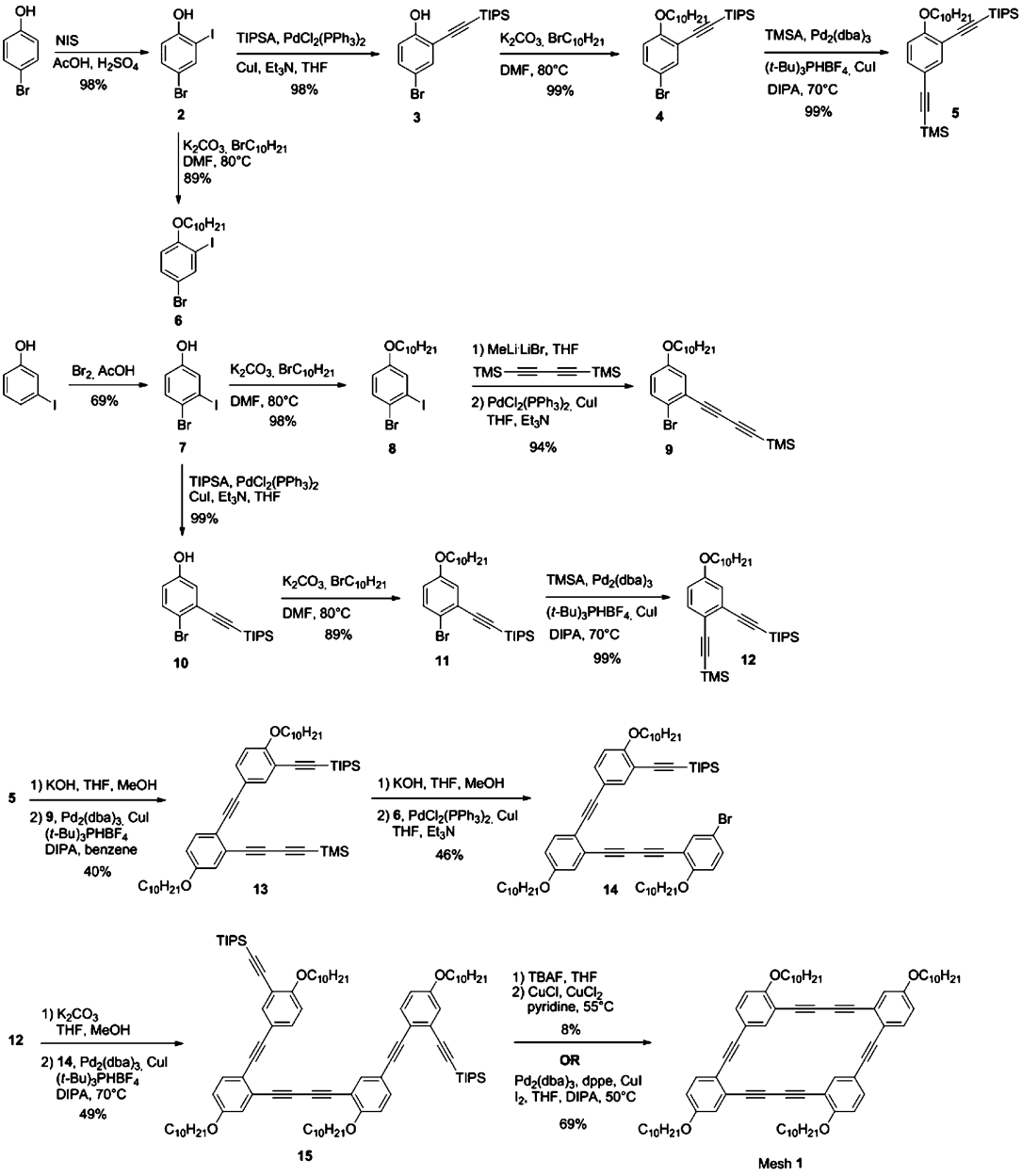


Figure 1. Model compounds mesh **1** and mesh **2** are indicated in red and blue, respectively, designed on the basis of a graphdiyne-like nanoribbon.

Scheme 1. Synthesis of Model Compound Mesh 1



the "meshes" of the nanoribbon shown in Figure 1, were synthesized and studied using optical spectroscopy to evaluate to what extent the bandgap of the nanoribbons can be modulated through the variation of its diameter. DFT calculations were also performed to corroborate the experimental data.

The requirements for the synthesis of shape-persistent phenylacetylene macrocycles have to be considered in the design of the meshes.[27] Highly diluted conditions have to be used to avoid intermolecular cross-linking while regioselective ring-closure reactions are necessary to avoid faulty linkage that would

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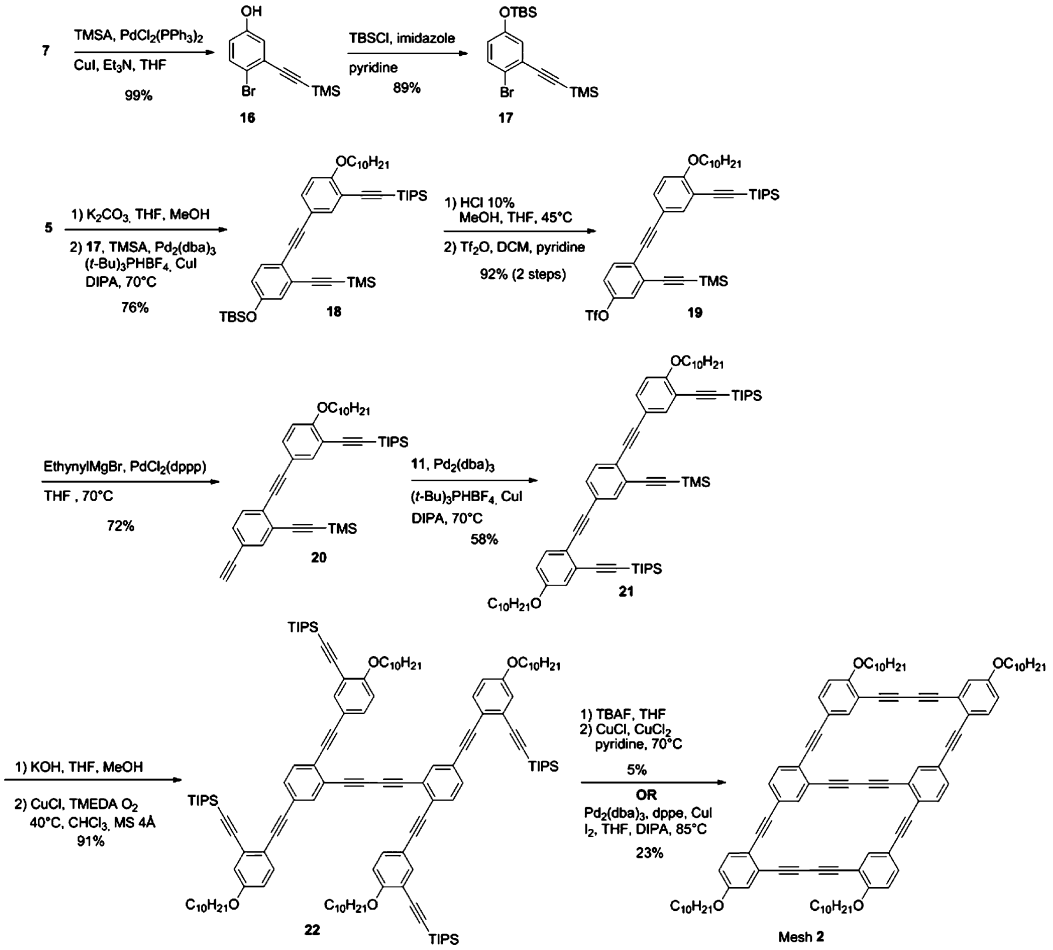
Scheme 2. Synthesis of Model Compound Mesh 2



impact the structural integrity of the macrocycle and, consequently, its properties.

Taking into account all these requirements for a successful synthesis, we designed a nanoribbon (Figure 1) that contains structural similarities to both graphyne and graphdiyne. In fact, alkyne linkers were used for the preparation of the precursors while diyne units were introduced at the very end of the synthesis by alkyne oxidative homocouplings. The major motivation behind the use of both structural features is the ease of synthesis of alkyne-based precursors, as the introduction of diyne moieties all over the structure of the macrocycles would have involved a significantly more tedious synthesis, lower intermediate stability, and lower yields overall.

Because mesh **1** is an asymmetric shape-persistent macrocycle, we used a strategy involving the intramolecular ring closure of a four-membered phenylacetylene oligomer in a pseudo-dilute solution.[28,29] Under optimized conditions, this strategy generally affords macrocycles in moderate to high yields, depending on the reactivity of the terminal alkyne involved and the strain in the macrocycle.[30] To the best of our knowledge, a four-membered macrocycle with phenyl groups on each corner with alternating alkyne and diyne units has never been reported.

RESULTS AND DISCUSSION

Synthesis. The synthesis of mesh **1**, which is the simplest repeating unit of the nanoribbon (Figure 1), is depicted in Scheme 1. Starting from 4-bromophenol, an iodination reaction using *N*-iodosuccinimide (NIS) under acidic conditions was conducted to obtain compound **2** in good yield.[31] Then a standard Castro–Stephen–Sonogashira reaction with triisopropylsilylacetylene (TIPSA) was performed to provide compound **3** in excellent yield. After a Williamson etherification with 1-bromodecane was conducted to increase the solubility of mesh **1**, a second Castro–Stephen–Sonogashira cross-coupling with trimethylsilylacetylene (TMSA) was achieved to afford compound **5**. It is worth mentioning that particular conditions for the later Castro–Stephen–Sonogashira cross-coupling had to be developed as the standard procedure using $PdCl_2(PPh_3)_2$ and Cu(I) failed to afford the desired compound. In addition to the known lower reactivity of the C–Br bond toward palladium oxidative addition, the presence of an electron-donating alkoxy group in the para position may also explain the need for particular conditions.[32] The reaction conditions on this highly deactivated bond toward Sonogashira coupling were inspired by Fu, Buchwald, and co-workers.[33]

Compound **5** was selectively deprotected in alkaline conditions and immediately coupled to compound **9**, obtained in three steps from compound **7**,[34] to provide compound **13**. The third phenyl was added by selectively deprotecting the alkyne bearing the TMS group and coupling it to compound **6** to afford compound **14**. Finally, the oligomeric precursor was obtained by removing the TMS protecting group on **12** followed by a Castro–Stephen–Sonogashira cross-coupling on compound **14** to obtain the open mesh **15**.

After the removal of the TIPS protecting groups with TBAF (compound **15′**), mesh **1** was synthesized under pseudo-dilute

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conditions using Eglinton conditions. Mesh **1** was obtained in a low 8% yield, mainly due to the formation of longer oligomers during the course of the cyclization reaction. This low yield prompted us to optimize this reaction and try other homocoupling methods. On the basis of previous work by Haley et al.,[35] we decided to test a Pd-catalyzed alkyne dimerization that, for some ring closure reactions, gave a yield much better than that for the Cu-catalyzed reaction. The yield discrepancy between the two reactions could be attributed to the difference in the geometry of the metal−acetylide intermediate. In fact, it was suggested that the Cu-catalyzed reaction proceeds through a Cu(I) acetylide arranged in a pseudo-trans configuration while the Pd-catalyzed intermediate is organized in a cis complex, although this mechanism is still under debate. For the ring closure of compound **15**, this change had a beneficial effect as the yield was increased to 69%.

Using a similar iterative strategy, we undertook the synthesis of mesh **2** (Scheme 2). Even though this molecule is bigger than mesh **1**, its synthesis is much less tedious since it is symmetrical. Thus, its long sides containing three phenyl rings can be dimerized through oxidative Glaser homocoupling to form the precursor of mesh **2**.

After a Castro−Stephen−Sonogashira cross-coupling between compound **7** and TMSA, the hydroxyl group was protected with a *tert*-butyldimethylsilyl (TBS) group in order to avoid side reactions in subsequent couplings. Then the resulting compound **17** was cross-coupled with the selectively deprotected compound **5** to give compound **18**. Triflate moiety was introduced (compound **19**) after removal of the TBS and a Kumada cross-coupling provided compound **20** with a terminal alkyne in 72% yield. It is worth noting that a standard Castro−Stephen−Sonogashira cross-coupling using TMSA failed to provide the desired compound. Optimization of the reaction parameters such as the catalyst, ligand, solvent, and temperature all failed to deliver compound **20** in acceptable yield. In addition to the known low reactivity of triflate toward oxidative addition in Pd-catalyzed reaction,[36] the presence of an electron-donating unit (alkoxy) in para position makes the triflate highly unactivated toward palladium oxidative addition, and therefore no reactivity was observed for the Castro−Stephen−Sonogashira reaction. Thus, a Kumada cross-coupling using several equivalents of ethynylmagnesium bromide and $PdCl_2$(dppp) was the only way to obtain compound **20** in good yield. This compound was then coupled to compound **11** in moderate yield to give the half-mesh bearing a TMS-protected alkyne in its center. Chemioselective deprotection of this alkyne using alkaline conditions followed by a Glaser−Hay oxidative dimerization yielded the open mesh **22**. Finally, deprotection of the four alkynes using TBAF (compound **22′**) followed by Eglinton ring closure produced mesh **2** in a low 5% yield (two steps). This low yield can be attributed in part to the relatively low solubility of mesh **2** that makes the purification steps difficult. We also performed the ring closure with the Pd−alkyne dimerization, which increased the yield to 23%.

Optical Properties. To establish the relationship between the width of graphdiyne-like nanoribbons and their electronic properties, UV−visible spectra of meshes **1** and **2** were recorded in dilute solution, and the results are summarized in Table 1. Unfortunately, we were unable to obtain good quality films of meshes **1** and **2**. The absorption spectra in chloroform solution are shown in Figure 2. Surprisingly, the λ_{max} value (355 nm) of mesh **2** is almost identical compared to that measured for mesh **1** (λ_{max} = 357 nm). However, the optical bandgap of mesh **2** (2.90 eV) measured at the onset of the absorption band (428 nm) is significantly lower than for mesh **1** (3.13 eV, onset = 396 nm) as a result of a more extended conjugation.

Table 1. Summary of the Optical Properties of Meshes 1 and 2 and Their Precursors in Chloroform Solution

compound	λ_{max} (nm)	λ_{emi} (nm)	ϕ_F	Stokes Shift (nm)	E_g (eV)
15′	299	412	–	113	–
mesh **1**	357	413	0.21	56	3.13
22′	340	420	–	80	–
mesh **2**	355	425	0.43	70	2.90

Useful information about these π-conjugated systems can also be found by comparing the absorption and fluorescence spectra of meshes **1** and **2** with their precursors (**15′** and **22′**, respectively). On one hand, no shift in the absorption spectrum was observed from compound **15′** to mesh **1**, which was expected as the new linkage created upon ring closure is in meta position relative to the conjugation axis. On the other hand, the appearance of more defined vibronic structures in absorption spectra of meshes **1** and **2** along with the relatively small Stokes shift (113 and 80 nm, respectively) is another proof of a more rigid π-conjugated system. Interestingly, mesh **2** is twice as fluorescent (ϕ_F = 43%) as mesh **1** (ϕ_F = 21%) in solution.

DFT Calculations. The geometries of meshes **1** and **2** were optimized at the B3LYP/6-31+G** level of theory (see Supporting Information). The undistorted butadiyne units show no sign of geometric strain while the ideal angles of ca. 120° between the phenyl and the ortho-substituted alkyne and the planarity of the system suggest a stable macrocyclic conformation. The frontier orbitals were extracted from the optimized geometries and are shown in Figure S1, Supporting Information. For both meshes **1** and **2**, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are delocalized over the entire molecule, with an increased contribution from the phenyl group for the HOMO. Furthermore, the calculated values for the HOMO−LUMO bandgap (3.29 and 2.95 eV for meshes **1** and **2**, respectively) are in good agreement with the experimentally determined values.

Extending the model compound to a two-mesh section results in an important change in the shapes of the modeled frontier orbitals. In fact, most of the electronic density is localized at the inner part of the molecule (Figure S2, Supporting Information). However, contribution from the *p*-phenylbutadiynylene edges cannot be overlooked, as the HOMO-1 was found to be only 0.29 eV lower than the HOMO, with the HOMO-2, HOMO-3, and HOMO-4 also being very close in energy (see Supporting Information). For the extended mesh, a bandgap of 2.52 eV was calculated (see Supporting Information) which is 0.45 eV lower than that for mesh 2. Thus, one can hypothesize that the width of the nanoribbon will be an important electronic influential parameter, underlining the importance of controlling the width of the nanoribbon.

Nucleus-independent chemical shifts (NICS)[37,38] is a convenient computational method from which the effects of a magnetic field on the ring current can be quantified, thus providing information about the delocalization of π electrons in a conjugated system.[39] Therefore, NICS scans have been performed at the PBE0/6-31+G** level of theory from 0 to 5 Å of the ring center for both meshes **1** and **2** (see Supporting Information). Interestingly, a slightly positive NICS (1) value of 0.8163 and 1.0487 was found for meshes **1** and **2**, respectively, suggesting a small degree of antiaromaticity in both compounds. These results are in disagreement with the intrinsic design of the

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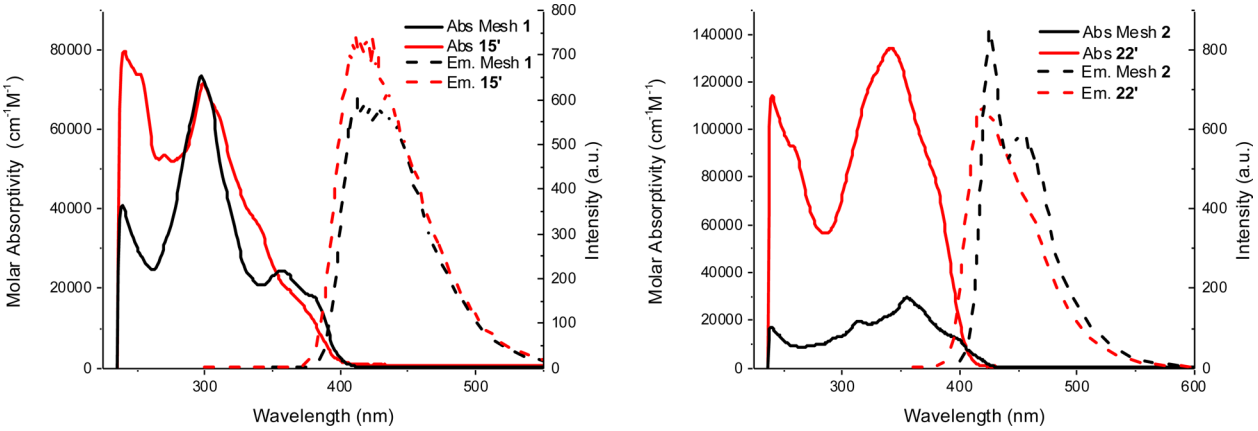

Figure 2. Absorption (solid lines) and emission (dashed lines) spectra of meshes **1** and **2** in $CHCl_3$.

meshes that should disrupt aromatic conjugation due to the interconnection in meta. Also, from the electron count, one finds that the macrocyclic entities of the meshes should be nonaromatic. These affirmations are supported experimentally by taking into account the minimal downfield shift of the internal protons that is observed upon macrocyclization of the compounds ($\Delta\delta$ = 0.09 and 0.28/0.32 ppm for meshes **1** and **2**, respectively), in line with a nonaromatic system. To verify the contribution of aromaticity to the NICS values, planar models in which the monoyne functionalities were excised were subjected to the same type of NICS scan. Interestingly, a practically identical value was obtained for the open (without monoyne) and closed form (see Supporting Information), confirming that the electronic delocalization is not induced by paratropic ring current effects but rather by electronic delocalization over the longitudinal axis of the meshes.

CONCLUSIONS

Two soluble macrocyclic subunits of graphdiyne-like nanoribbon containing alkyne and diyne moieties were synthesized. Spectroscopic characterization and DFT calculations revealed that the electronic properties of graphdiyne-like nanoribbons can be modulated through the variation of their diameter. Also, we found that the HOMO and LUMO orbitals are delocalized over the entire molecules, providing efficient π-conjugation in the longitudinal axis (nanoribbon axis). With this study, we now have all in hand to successfully conduct the synthesis and characterization of the analogous graphdiyne-like nanoribbons from polymeric precursors.

EXPERIMENTAL SECTION

NMR spectra were recorded at 400 or 500 MHz. Signals are reported as m (multiplet), s (singlet), d (doublet), t (triplet), and dd (doublet of doublet), and coupling constants are reported in hertz (Hz). The chemical shifts are reported in ppm (δ) relative to residual solvent peak or TMS. High resolution mass spectra were recorded with a time-of-flight spectrometer in flow infusion analysis. Ions were generated by a Kr UV lamp in an APPI source with toluene/anisole mixture as dopant when required. Spectra ranging from 100 to 3200 m/z were recorded with typical resolution of 5000 to 15 000 and typical precision of ±1 ppm or less. The mass analyzer was calibrated with standard solutions provided by the manufacturer and covering the spectral range described above.

4-Bromo-2-((triisopropylsilyl)ethynyl)phenol (3). To a solution of compound **2** (4.80 g, 16.1 mmol) in degassed THF (80 mL) and Et_3N (20 mL) were added $PdCl_2(PPh_3)_2$ (0.451 g, 0.642 mmol) and CuI (0.184 g, 0.964 mmol). Then TIPSA (4.32 mL, 19.3 mmol) was added, and the reaction was stirred overnight. The solution was diluted in Et_2O, extracted three times with saturated aqueous NH_4Cl, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes to hexanes/ethyl acetate 97:3) to afford compound **3** as light yellow oil (5.57 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 2.4 Hz, 1H), 7.33 (dd, J = 8.8, 2.4 Hz, 1H), 6.84 (d, J = 8.8 Hz, 1H), 5.80 (s, 1H), 1.14 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 133.7, 133.3, 116.2, 111.8 (2C), 100.3, 99.4, 18.6, 11.2. HRMS (APPI$^+$): m/z calcd for $C_{17}H_{26}BrOSi$: 353.0931; found: 353.0936 $[M + H]^+$.

((5-Bromo-2-(decyloxy)phenyl)ethynyl)triisopropylsilane (4). To a solution of compound **3** (5.60 g, 15.8 mmol) in DMF (48 mL) were added K_2CO_3 (8.87 g, 64.2 mmol) and 1-bromodecane (4.96 mL, 23.9 mmol). The reaction was stirred at 80 °C overnight. Upon cooling, the solution was diluted with CH_2Cl_2, extracted three times with water, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes to hexanes/ethyl acetate 97:3) to afford compound **4** as a colorless oil (7.81 g, 99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 2.5 Hz, 1H), 7.33 (dd, J = 8.8, 2.5 Hz, 1H), 6.71 (d, J = 8.9 Hz, 1H), 3.96 (t, J = 6.3 Hz, 2H), 1.83−1.76 (m, 2H), 1.53−1.44 (m, 2H), 1.36−1.23 (m, 12H), 1.14 (s, 21H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 135.9, 132.2, 115.1, 113.0, 111.7, 101.7, 96.1, 68.7, 32.0, 29.7, 29.6, 29.5, 29.4, 26.3, 22.8, 18.7, 14.2, 11.4. HRMS (APPI$^+$): m/z calcd for $C_{27}H_{46}BrOSi$: 493.2496; found: 493.2498 $[M + H]^+$.

Compound 5. To a solution of compound **4** (7.80 g, 15.8 mmol) in degassed DIPA (79 mL) in a high pressure tube were added $Pd_2(dba)_3$ (0.289 g, 0.316 mmol), CuI (0.120 g, 0.632 mmol), and $(t\text{-Bu})_3PHBF_4$ (0.367 g, 1.26 mmol). Then TMSA (4.47 mL, 31.6 mmol) was added, and the tube was sealed. The solution was stirred at 70 °C overnight. Upon cooling, the mixture was diluted in CH_2Cl_2, extracted three times with saturated aqueous NH_4Cl, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes to hexanes/CH_2Cl_2 4:1) to afford compound **5** as a yellow oil (7.98 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 2.1 Hz, 1H), 7.34 (dd, J = 8.6, 2.1 Hz, 1H), 6.74 (d, J = 8.6 Hz, 1H), 3.97 (t, J = 6.3 Hz, 2H), 1.78 (dd, J = 8.9, 6.4 Hz, 2H), 1.52−1.43 (m, 2H), 1.36−1.22 (m, 12H), 1.13 (s, 21H), 0.88 (t, J = 6.8 Hz, 3H), 0.23 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 137.3, 133.3, 114.8, 113.2, 111.3, 104.4, 102.1, 95.2, 92.7, 68.6, 31.9, 29.6, 29.5, 29.3 (2C), 26.2, 22.7, 18.7, 14.1, 11.3, 0.0. HRMS (APPI$^+$): m/z calcd for $C_{32}H_{55}OSi_2$: 511.3786; found: 511.3801 $[M + H]^+$.

4-Bromo-1-(decyloxy)-2-iodobenzene (6). To a solution of compound **2** (5.00 g, 16.7 mmol) in DMF (51 mL) were added K_2CO_3 (9.36 g, 67.7 mmol) and 1-bromodecane (5.24 mL, 25.3 mmol), and the solution was stirred at 80 °C overnight. Upon cooling, the solution was diluted in CH_2Cl_2, extracted three times with water, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes) to afford compound **6** as a white solid (6.56 g, 89%), mp = 30−32 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 2.4 Hz, 1H), 7.38 (dd, J = 8.7, 2.4 Hz,

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1H), 6.66 (d, J = 8.7 Hz, 2H), 3.97 (t, J = 6.4 Hz, 3H), 1.86−1.77 (m, 2H), 1.55−1.44 (m, 2H), 1.40−1.23 (m, 12H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 141.1, 132.0, 113.1, 113.0, 87.4, 69.6, 31.9, 29.5 (2C), 29.3 (2C), 29.0, 26.0, 22.7, 14.1. HRMS (APPI$^+$): m/z calcd for $C_{16}H_{24}BrIO$: 438.0050; found: 438.0055 $[M^*]^+$.

1-Bromo-4-(decyloxy)-2-iodobenzene (8). To a solution of compound **7** (5.00 g, 16.7 mmol) in DMF (51 mL) were added K_2CO_3 (9.36 g, 67.7 mmol) and 1-bromodecane (5.24 mL, 25.3 mmol). The reaction was stirred at 80 °C overnight. Upon cooling, the solution was diluted with CH_2Cl_2, extracted three times with water, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes) to afford compound **8** as a light yellow oil (7.18 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.8 Hz, 1H), 7.38 (d, J = 2.9 Hz, 1H), 6.75 (dd, J = 8.8, 2.9 Hz, 1H), 3.89 (t, J = 6.5 Hz, 2H), 1.79−1.71 (m, 2H), 1.47−1.38 (m, 2H), 1.36−1.23 (m, 12H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 132.5, 126.0, 119.9, 116.3, 101.2, 68.5, 32.0, 29.7, 29.5, 29.4, 29.2, 26.1, 22.8, 14.3. HRMS (APPI$^+$): m/z calcd for $C_{16}H_{24}BrIO$: 438.0050; found: 438.0067 $[M^*]^+$.

((2-Bromo-5-(decyloxy)phenyl)buta-1,3-diynyl)-trimethylsilane (9). To a solution of 1,4-bis(trimethylsilyl)buta-1,3-diyne (5.31 g, 27.3 mmol) in dry THF (101 mL) in a flame-dried flask was added a solution of MeLi/LiBr complex 1.5 M in Et_2O (18.2 mL, 27.3 mmol) dropwise at room temperature. The mixture was stirred 3 h and quenched with saturated aqueous NH_4Cl. The solution was diluted in pentane, extracted three times with water, and dried over sodium sulfate. The solution was concentrated without drying and heating. To a solution of compound **8** (4.00 g, 9.11 mmol) in THF (91 mL) and Et_3N (10 mL) was added a pentane solution of the monoprotected alkyne. The mixture was degassed 30 min, and $PdCl_2(PPh_3)_2$ (0.320 g, 0.455 mmol) and CuI (0.087 g, 0.455 mmol) were added. The reaction was stirred overnight. The mixture was diluted in CH_2Cl_2, extracted three times with saturated aqueous NH_4Cl, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes to hexanes/CH_2Cl_2 23:2) to afford compound **9** as a dark orange oil (3.70 g, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 8.9 Hz, 1H), 7.02 (d, J = 3.0 Hz, 1H), 6.78 (dd, J = 8.9, 3.0 Hz, 1H), 3.90 (t, J = 6.6 Hz, 2H), 1.80−1.72 (m, 2H), 1.47−1.38 (m, 2H), 1.38−1.23 (m, 12H), 0.89 (t, J = 6.9 Hz, 3H), 0.25 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 133.1, 124.2, 119.6, 118.2, 116.6, 92.4, 87.5, 77.9, 74.8, 68.5, 31.9, 29.6, 29.3 (2C), 29.0, 25.9, 22.7, 14.1, −0.4. HRMS (APPI$^+$): m/z calcd for $C_{23}H_{33}BrOSi$: 432.1479; found: 432.1499 $[M^*]^+$.

4-Bromo-3-((triisopropylsilyl)ethynyl)phenol (10). To a solution of compound **7** (3.38 g, 11.3 mmol) in degassed THF (56 mL) and Et_3N (14 mL) were added $PdCl_2(PPh_3)_2$ (0.317 g, 0.452 mmol) and CuI (0.129 g, 0.678 mmol). Then TIPSA was added (3.8 mL, 16.9 mmol), and the reaction was stirred overnight. The solution was diluted with CH_2Cl_2, extracted three times with saturated aqueous NH_4Cl, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes to hexanes/CH_2Cl_2 17:3) to afford compound **10** as a light yellow oil (3.99 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.7 Hz, 1H), 6.99 (d, J = 3.0 Hz, 1H), 6.67 (dd, J = 8.7, 3.0 Hz, 1H), 4.82 (s, 1H), 1.14 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 133.2, 126.3, 120.4, 117.3, 116.5, 104.4, 96.3, 18.6, 11.3. HRMS (APPI$^+$): m/z calcd for $C_{17}H_{26}BrOSi$: 353.0931; found: 353.0921 $[M + H]^+$.

((2-Bromo-5-(decyloxy)phenyl)ethynyl)triisopropylsilane (11). To a solution of compound **10** (4.90g, 13.9 mmol) in DMF (42 mL) were added K_2CO_3 (7.77 g, 56.2 mmol) and 1-bromodecane (4.35 mL, 21.0 mmol). The solution was stirred at 80 °C overnight. Upon cooling, the solution was diluted in CH_2Cl_2, extracted three times with water, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes to hexanes/ethyl acetate 49:1) to afford compound **11** as a light yellow oil (6.11 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.9 Hz, 1H), 7.02 (d, J = 3.0 Hz, 1H), 6.72 (dd, J = 8.9, 3.0 Hz, 1H), 3.91 (t, J = 6.5 Hz, 2H), 1.80−1.72 (m, 2H), 1.48−1.39 (m, 2H), 1.37−1.23 (m, 12H), 1.15 (s, 21H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 132.9, 126.1, 119.2, 116.7, 116.2, 104.9, 95.7, 68.3, 31.9, 29.6 (2C), 29.4 (2C), 29.2, 26.0, 22.7, 18.7, 14.1, 11.3. HRMS (APPI$^+$): m/z calcd for $C_{27}H_{46}BrOSi$: 493.2496; found: 493.2510 $[M + H]^+$.

Compound 12. To a solution of compound **11** (3.15 g, 6.38 mmol) in degassed DIPA (32 mL) in a high-pressure tube were added $Pd_2(dba)_3$ (0.117 g, 0.128 mmol), CuI (0.049 g, 0.255 mmol), and (t-Bu)$_3$PHBF$_4$ (0.148 g, 0.510 mmol). Then TMSA (1.80 mL, 12.8 mmol) was added, and the tube was sealed. The solution was stirred at 70 °C overnight. Upon cooling, the mixture was diluted in CH_2Cl_2, extracted three times with saturated aqueous NH_4Cl, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes to hexanes/CH_2Cl_2 17:3) to afford compound **12** as a yellow oil (3.23 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.6 Hz, 1H), 6.95 (d, J = 2.4 Hz, 1H), 6.77 (dd, J = 8.7, 2.7 Hz, 1H), 3.93 (t, J = 6.5 Hz, 2H), 1.80−1.71 (m, 2H), 1.48−1.39 (m, 2H), 1.38−1.23 (m, 12H), 1.15 (s, 21H), 0.88 (t, J = 6.8 Hz, 3H), 0.23 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 134.2, 127.0, 118.1, 117.8, 115.1, 105.2, 103.5, 96.1, 94.5, 68.1, 31.9, 29.5 (2C), 29.3 (2C), 29.1, 26.0, 22.7, 18.8, 14.1, 11.3, 0.0. HRMS (APPI$^+$): m/z calcd for $C_{32}H_{55}OSi_2$: 511.3786; found: 511.3814 $[M + H]^+$.

Compound 13. To a solution of compound **5** (1.46 g, 2.85 mmol) in THF/methanol 1:1 (29 mL) were added KOH (0.646 g, 11.4 mmol) and 3 drops of water. The reaction was stirred until the TLC showed a complete reaction. The solution was diluted in benzene, extracted three times with water, and dried over sodium sulfate. The solvent was removed in vacuo and transferred to a flask charged with compound **9** (1.03 g, 2.38 mmol). The substrates were dissolved in DIPA (48 mL) and benzene (20 mL) and degassed for 30 min. $Pd_2(dba)_3$ (0.044 g, 0.048 mmol), CuI (0.018 g, 0.095 mmol), and (t-Bu)$_3$PHBF$_4$ (0.055 g, 0.190 mmol) were added. The reaction mixture was stirred overnight. Upon cooling with an ice/water bath, the mixture was carefully quenched with saturated aqueous NH_4Cl. The solution was diluted in CH_2Cl_2, extracted three times with saturated aqueous NH_4Cl, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes to hexanes/CH_2Cl_2 17:3) to afford compound **13** as a dark orange solid (0.759 g, 40%), mp = 76−78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 2.2 Hz, 1H), 7.48 (dd, J = 8.6, 2.1 Hz, 1H), 7.40 (d, J = 8.7 Hz, 1H), 7.00 (d, J = 2.6 Hz, 1H), 6.87 (dd, J = 8.7, 2.6 Hz, 1H), 6.80 (d, J = 8.8 Hz, 1H), 4.00 (t, J = 6.2 Hz, 2H), 3.91 (t, J = 6.5 Hz, 2H), 1.87−1.73 (m, 4H), 1.56−1.49 (m, 2H), 1.48−1.41 (m, 2H), 1.39−1.25 (m, 24H), 1.19 (s, 21H), 0.97−0.88 (m, 6H), 0.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 158.4, 136.5, 133.4, 133.0, 124.8, 119.6, 117.9, 116.6, 115.1, 113.3, 111.4, 102.3, 95.0, 91.8, 91.6, 88.1, 86.6, 77.7, 75.5, 68.6, 68.3, 32.0 (2C), 29.7 (2C), 29.6, 29.5, 29.4, 29.2, 26.3, 26.0, 22.8, 18.8, 18.7, 14.2, 11.4, −0.3. HRMS (APPI$^+$): m/z calcd for $C_{52}H_{79}O_2Si_2$: 791.5613; found: 791.5616 $[M + H]^+$.

Compound 14. To a solution of compound **13** (1.14 g, 1.44 mmol) in THF/methanol 3:2 (16 mL) were added K_2CO_3 (0.664 g, 4.80 mmol) and 3 drops of water. The reaction was stirred until the TLC showed a complete reaction. The solution was diluted in benzene, extracted three times with water, and dried over sodium sulfate. The solvent was removed in vacuo and transferred to a flask charged with compound **6** (0.527 g, 1.20 mmol). The substrates were dissolved in THF (12 mL) and Et_3N (1.34 mL) and degassed for 30 min. $PdCl_2(PPh_3)_2$ (0.042 g, 0.060 mmol) and CuI (0.011 g, 0.060 mmol) were added. The reaction mixture was stirred overnight. The solution was diluted in $CHCl_3$, extracted three times with saturated aqueous NH_4Cl, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes to hexanes/CH_2Cl_2 17:3) to afford compound **14** as an orange solid (0.564 g, 46%), mp = 64−65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 2.0 Hz, 1H), 7.59 (d, J = 2.5 Hz, 1H), 7.52 (dd, J = 8.6, 1.9 Hz, 1H), 7.42 (d, J = 8.6 Hz, 1H), 7.38 (dd, J = 8.9, 2.5 Hz, 1H), 7.04 (d, J = 2.4 Hz, 1H), 6.88 (dd, J = 8.7, 2.5 Hz, 1H), 6.81 (d, J = 8.7 Hz, 1H), 6.73 (d, J = 8.9 Hz, 1H), 4.03−3.92 (m, 6H), 1.87−1.74 (m, 6H), 1.57−1.41 (m, 6H), 1.41−1.23 (m, 36H), 1.16 (s, 21H), 0.95−0.85 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 160.2, 158.4, 136.7, 136.3, 133.4, 133.3, 132.9, 125.3, 119.5, 117.7, 116.5, 115.2, 113.7, 113.6, 113.3, 111.9, 111.5, 102.3, 95.1, 92.0, 86.8, 81.4, 78.9, 77.8, 77.6, 69.2, 68.6, 68.3, 32.0 (2C), 29.7 (3C), 29.6, 29.5, 29.4 (2C), 29.2,

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29.0, 26.3, 26.1, 26.0, 22.8, 18.7, 14.2 (2C), 11.4. HRMS (APPI$^+$): m/z calcd for $C_{65}H_{94}BrO_3Si$: 1031.6148; found: 1031.6178 $[M + H]^+$.

Compound 15. To a solution of compound **12** (0.338 g, 0.662 mmol) in THF/methanol 5:3 (8 mL) were added KOH (0.148 g, 2.65 mmol) and 3 drops of water. The reaction was stirred until the TLC showed a complete reaction. The solution was diluted in benzene, extracted three times with water, and dried over sodium sulfate. The solvent was removed in vacuo and transferred to a flask charged with compound **14** (0.341 g, 0.331 mmol). The substrates were dissolved in DIPA (11 mL) and benzene (5 mL) and degassed for 30 min. $Pd_2(dba)_3$ (0.006 g, 0.007 mmol), CuI (0.003 g, 0.013 mmol), and $(t\text{-Bu})_3PHBF_4$ (0.008 g, 0.026 mmol) were added. The reaction mixture was stirred at 70 °C for 72 h. Upon cooling, the mixture was diluted in $CHCl_3$, extracted three times with saturated NH_4Cl, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes to hexanes/$CHCl_3$ 3:2) to afford compound **15** as a yellow solid (0.452 g, 49%), mp = 46−48 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 10.8, 2.1 Hz, 2H), 7.51 (dd, J = 8.6, 2.2 Hz, 1H), 7.44 (dd, J = 8.6, 2.1 Hz, 1H), 7.40 (dd, J = 8.7, 3.4 Hz, 2H), 7.02 (dd, J = 15.5, 2.6 Hz, 2H), 6.87 (dd, J = 8.7, 2.7 Hz, 1H), 6.83 (dd, J = 8.7, 2.6 Hz, 2H), 6.79 (d, J = 8.7 Hz, 1H), 4.05 (t, J = 6.7 Hz, 2H), 3.96 (t, J = 6.5 Hz, 6H), 1.87−1.69 (m, 8H), 1.51−1.40 (m, 8H), 1.38−1.22 (m, 48H), 1.12 (s, 21H), 1.11 (s, 21H), 0.92−0.82 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 160.2, 158.5, 158.4, 137.6, 136.7, 133.7, 133.4, 133.2, 132.9, 126.9, 125.5, 119.4, 118.0 (2C), 117.6, 116.5, 115.9, 115.3, 115.1, 113.2, 111.8, 111.7, 111.5, 105.3, 102.3, 95.0, 94.8, 91.9, 90.4, 87.5, 86.7, 83.0, 80.7, 77.9, 77.8, 69.1, 68.6, 68.3, 68.2, 31.9, 29.6 (4C), 29.4, 29.3, 29.2, 29.1, 29.0, 26.2, 26.0 (2C), 25.9, 22.7, 18.7 (2C), 14.1, 11.3 (2C). HRMS (APPI$^+$): m/z calcd for $C_{94}H_{139}O_4Si_2$: 1388.0206; found: 1388.0199 $[M + H]^+$.

Compound 15′. To a solution of compound **15** (0.452 g, 0.326 mmol) in degassed THF (33 mL) was added tetrabutylammonium fluoride (1.30 mL, 1.30 mmol). The reaction was stirred for 2 h. The solution was diluted in $CHCl_3$, extracted three times with brine, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes/$CHCl_3$ 7:3 to 3:7) to afford the corresponding unprotected alkyne as a white powder (0.336 g, 96%), mp = 77−79 °C, which was further subjected to a copper or palladium homocoupling. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, J = 4.7, 2.1 Hz, 2H), 7.53 (dd, J = 8.6, 2.1 Hz, 1H), 7.49 (dd, J = 8.6, 2.1 Hz, 1H), 7.44−7.39 (m, 2H), 7.04 (dd, J = 4.2, 2.7 Hz, 2H), 6.90−6.83 (m, 4H), 4.08−4.01 (m, 4H), 3.96 (t, J = 6.6 Hz, 4H), 1.88−1.73 (m, 8H), 1.52−1.41 (m, 8H), 1.40−1.19 (m, 48H), 0.93−0.83 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9, 160.0, 158.6, 158.4, 137.4 (2C), 133.9, 133.5, 133.0, 132.6, 125.7, 125.6, 119.5, 118.4, 117.8, 117.4, 116.5, 116.0, 115.6, 115.4, 112.0, 111.9 (2C), 111.8, 91.9, 90.8, 87.2, 87.1, 82.2, 81.5, 81.0, 80.9, 79.3, 78.6, 78.0 (2C), 69.1, 68.9, 68.3 (2C), 31.9, 29.6 (4C), 29.4, 29.3, 29.1, 29.0, 28.9, 26.0, 25.9 (2C), 22.7, 14.1 (2C). HRMS (APPI$^+$): m/z calcd for $C_{76}H_{99}O4$:1075.7538; found: 1075.7541 $[M + H]^+$. UV/vis ($CHCl_3$) λ_{max} (ε) 297 (74 057), 356 (24 336), 381 (18 066) nm. Fluorescence ($CHCl_3$) λ_{max} 412 nm.

Mesh 1. Conditions A. To a solution of unprotected alkyne (0.093 g, 0.087 mmol) in degassed pyridine (44 mL) were added CuCl (0.608 g, 6.15 mmol) and $CuCl_2$ (0.128 g, 0.952 mmol). The reaction mixture was stirred at 55 °C for 13 h. Pyridine was removed in vacuo. The crude product was diluted in $CHCl_3$, extracted three times with saturated aqueous NH_4Cl, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes/$CHCl_3$ 4:1 to 1:1), precipitated in DCM at −78 °C, and filtered to afford mesh **1** as a white powder (0.007 g, 8%).

Conditions B. To a solution open to air of $Pd_2(dba)_3$ (0.004 g, 0.005 mmol), diphenylphosphinoethane (0.004 g, 0.009 mmol), CuI (0.003 g, 0.014 mmol), and I_2 (0.012 g, 0.046 mmol) in THF (93 mL) and DIPA (93 mL) was added over a period of 24 h a solution of unprotected alkyne (0.100 g, 0.093 mmol) in THF (47 mL). The reaction mixture was stirred at 50 °C during the addition and 2 h after the addition was completed. Upon cooling, the solvents were removed in vacuo. The crude product was diluted in $CHCl_3$, extracted three times with saturated aqueous NH_4Cl, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was recrystallized from $CHCl_3$ to afford mesh **1** as a white powder (0.088 g, 69%), decomposition = 135−140 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C) δ 7.80 (s, 2H), 7.45 (d, J = 7.2 Hz, 2H), 7.40 (d, J = 8.6 Hz, 2H), 7.06 (s, 2H), 6.90−6.84 (m, 4H), 4.10 (t, J = 6.6 Hz, 4H), 3.98 (t, J = 6.5 Hz, 4H), 1.92−1.85 (m, 4H), 1.84−1.75 (m, 4H), 1.58−1.51 (m, 4H), 1.45−1.25 (m, 52H), 0.93−0.85 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$, 50 °C) δ 161.1, 158.5, 137.8, 133.2, 132.2, 126.0, 119.6, 117.5, 116.4, 115.9, 112.4, 112.1, 91.8, 87.3, 80.4, 78.4, 78.0, 77.9, 69.3, 68.4, 31.8, 29.5 (3C), 29.3 (2C), 29.2, 29.1, 29.0, 25.9 (2C), 22.6, 13.9 (2C). HRMS (APPI$^+$): m/z calcd for $C_{76}H_{97}O_4$: 1073.7381; found: 1073.7382 $[M + H]^+$. UV/vis ($CHCl_3$) λ_{max} (ε) 240 (79 661), 298 (71 447) nm. Fluorescence ($CHCl_3$) λ_{max} 413 nm.

4-Bromo-3-((trimethylsilyl)ethynyl)phenol (16). To a solution of compound **7** (3.00 g, 10.0 mmol) in degassed THF (50 mL) and Et_3N (6 mL) were added $PdCl_2(PPh_3)_2$ (0.282 g, 0.401 mmol) and CuI (0.115 g, 0.602 mmol). Then TMSA was added (2.13 mL, 15.1 mmol), and the reaction was stirred overnight. The solution was diluted with CH_2Cl_2, extracted three times with saturated aqueous NH_4Cl, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes to hexanes/CH_2Cl_2 2:3) to afford compound **16** as a brown oil (2.70 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.7 Hz, 1H), 6.97 (d, J = 3.0 Hz, 1H), 6.66 (dd, J = 8.7, 3.0 Hz, 1H), 5.76 (s, 1H), 0.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 133.2, 125.9, 120.1, 117.5, 116.5, 102.7, 99.8, −0.2. HRMS (APPI$^+$): m/z calcd for $C_{11}H_{13}BrOSi$: 267.9914; found: 267.9926 $[M^*]^+$.

(4-Bromo-3-((trimethylsilyl)ethynyl)phenoxy) (*tert*-butyl)-dimethylsilane (17). To a solution of compound **16** (2.14 g, 7.94 mmol) in DMF (19 mL) were added imidazole (1.60 g, 23.5 mmol) and TBSCl (1.65 g, 11.0 mmol). The solution was stirred overnight. The solution was diluted in ethyl acetate, extracted three times with water, washed with brine, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes) to afford compound **17** as an orange solid (2.70 g, 89%), mp = 33−35 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.7 Hz, 1H), 6.96 (d, J = 2.9 Hz, 1H), 6.66 (dd, J = 8.7, 2.9 Hz, 1H), 0.97 (s, 9H), 0.27 (s, 9H), 0.18 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 133.0, 125.8, 124.9, 122.2, 117.3, 102.9, 99.3, 25.6, 18.1, −0.2, −4.5. HRMS (APPI$^+$): m/z calcd for $C_{17}H_{27}BrOSi2$:382.0784; found: 382.0770 $[M^*]^+$.

Compound 18. To a solution of compound **5** (3.59 g, 7.02 mmol) in THF/methanol 1:1 (35 mL) were added K_2CO_3 (1.46 g, 10.5 mmol) and 3 drops of water. The reaction was stirred until the TLC showed a complete reaction. The solution was diluted in benzene, extracted three times with water, and dried over sodium sulfate. The solvent was removed in vacuo and transferred to a flask charged with compound **17** (2.69 g, 7.02 mmol). The substrates were dissolved in DIPA (70 mL) and degassed for 30 min. $Pd_2(dba)_3$ (0.129 g, 0.140 mmol), CuI (0.053 g, 0.281 mmol), and $(t\text{-Bu})_3PHBF_4$ (0.163 g, 0.562 mmol) were added. The reaction mixture was stirred at 70 °C for 48 h. Upon cooling, the solution was diluted in CH_2Cl_2, extracted three times with saturated aqueous NH_4Cl, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes to hexanes/CH_2Cl_2 17:3) to afford compound **18** as a yellow solid (3.95 g, 76%), mp = 78−80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 2.1 Hz, 1H), 7.40 (dd, J = 8.6, 2.2 Hz, 1H), 7.34 (d, J = 8.5 Hz, 1H), 6.95 (d, J = 2.5 Hz, 1H), 6.79 (d, J = 8.7 Hz, 1H), 6.76 (dd, J = 8.5, 2.5 Hz, 1H), 4.00 (t, J = 6.2 Hz, 2H), 1.84−1.76 (m, 2H), 1.53−1.45 (m, 2H), 1.37−1.23 (m, 12H), 1.13 (s, 21H), 0.98 (s, 9H), 0.88 (t, J = 6.8 Hz, 3H), 0.27 (s, 9H), 0.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 155.1, 136.9, 132.8, 132.7, 126.7, 123.5, 120.8, 119.4, 115.3, 113.3, 111.4, 103.3, 102.2, 98.3, 95.1, 91.4, 87.0, 68.6, 31.9, 29.6, 29.5, 29.3, 26.2, 25.6, 22.7, 18.7, 18.2, 14.1, 11.3, 0.0, −4.4. HRMS (APPI$^+$): m/z calcd for $C_{46}H_{73}O_2Si_3$: 741.4913; found: 741.4940 $[M + H]^+$.

Compound 19. To a solution of compound **18** (3.95 g, 5.32 mmol) in THF (24 mL) and MeOH (12 mL) was added an aqueous solution of HCl 10% (6 mL). The reaction was stirred at 45 °C overnight. Upon cooling, the mixture was diluted in CH_2Cl_2, extracted three times with

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water, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes/ethyl acetate 1:1) to afford the corresponding alcohol as a light brown oil (3.32 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 2.1 Hz, 1H), 7.40 (dd, J = 8.6, 2.2 Hz, 1H), 7.36 (d, J = 8.5 Hz, 1H), 6.95 (dd, J = 2.7, 0.4 Hz, 1H), 6.81−6.75 (m, 2H), 4.92 (s, 1H), 4.00 (t, J = 6.3 Hz, 2H), 1.85−1.76 (m, 2H), 1.54−1.45 (m, 2H), 1.37−1.22 (m, 12H), 1.13 (s, 21H), 0.88 (t, J = 6.8 Hz, 3H), 0.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 154.8, 136.9, 133.0, 132.7, 126.8, 119.0, 118.7, 116.1, 115.2, 113.3, 111.5, 103.0, 102.1, 98.8, 95.1, 91.3, 86.8, 68.6, 31.9, 29.6, 29.5, 29.3, 26.2, 22.7, 18.7, 14.1, 11.3, 0.0. HRMS (APPI$^+$): m/z calcd for $C_{40}H_{59}O_2Si_2$: 627.4048; found: 627.4035 $[M + H]^+$.

To a solution of the previous alcohol (2.60 g, 4.14 mmol) in degassed CH_2Cl_2 (41 mL) in a flame-dried flask was added catalytic amount of pyridine (0.67 mL). The solution was cooled with an ice/water bath, and trifluoromethanesulfonic anhydride 1.0 M in CH_2Cl_2 (4.97 mL, 4.97 mmol) was added dropwise. The solution was stirred at room temperature for 2 h. The solution was quenched with saturated aqueous NH_4Cl, diluted in CH_2Cl_2, extracted three times with water, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes to hexanes/CH_2Cl_2 17:3) to afford compound **19** as a light yellow solid (2.92 g, 93%), mp = 67−69 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 2.1 Hz, 1H), 7.53 (dd, J = 8.7, 0.3 Hz, 1H), 7.44 (dd, J = 8.6, 2.2 Hz, 1H), 7.40 (d, J = 2.6 Hz, 1H), 7.19 (dd, J = 8.7, 2.6 Hz, 1H), 6.82 (d, J = 8.7 Hz, 1H), 4.01 (t, J = 6.2 Hz, 2H), 1.87−1.77 (m, 2H), 1.56−1.47 (m, 2H), 1.38−1.24 (m, 12H), 1.16 (s, 21H), 0.89 (t, J = 6.8 Hz, 3H), 0.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 147.9, 137.2, 133.1, 133.0, 127.6, 126.9, 124.7, 121.2, 118,7 (q, J = 322.2 Hz), 114.2, 113.5, 111.5, 101.9, 101.4 (2C), 95.5, 94.9, 85.5, 68.7, 31.9, 29.6 (2C), 29.5, 29.4, 29.3, 26.2, 22.7, 18.7, 14.1, 11.3, −0.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ −72.7. HRMS (APPI$^+$): m/z calcd for $C_{41}H_{57}F_3O_4SSi_2$: 758.3463; found: 758.3474 $[M^*]^+$.

Compound 20. To a solution of compound **19** (2.92 g, 3.84 mmol) in degassed THF (39 mL) in a flame-dried high-pressure tube was added $PdCl_2$(dppp) (0.454 g, 0.769 mmol). Then a 0.45 μm filtered solution of ethynylmagnesium bromide 0.5 M in THF (30.8 mL, 15.4 mmol) was added to the solution, and the tube was sealed. The reaction was stirred at 70 °C overnight. Upon cooling, the solution was quenched with water and diluted in CH_2Cl_2. The pH of the aqueous layer was lowered to 7 with an aqueous solution of HCl 10%. The organic layer was extracted three times and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes to hexanes/CH_2Cl_2 22:3) to afford compound **20** as a yellow solid (1.76 g, 72%), mp = 68−70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 2.1 Hz, 1H), 7.62 (d, J = 1.4 Hz, 1H), 7.45−7.43 (m, 1H), 7.43−7.41 (m, 1H), 7.38 (d, J = 1.7 Hz, 1H), 6.81 (d, J = 8.7 Hz, 1H), 4.01 (t, J = 6.3 Hz, 2H), 3.15 (s, 1H), 1.86−1.77 (m, 2H), 1.55−1.45 (m, 2H), 1.38−1.24 (m, 12H), 1.14 (s, 21H), 0.88 (t, J = 6.8 Hz, 3H), 0.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 137.2, 135.7, 133.0, 131.6, 131.3, 126.5, 125.6, 121.4, 114.6, 113.4, 111.5, 102.4, 101.9, 99.4, 95.4, 94.9, 86.8, 82.5, 79.1, 68.7, 31.9, 29.6, 29.5, 29.4, 29.3, 26.2, 22.7, 18.7, 14.1, 11.3, −0.0. HRMS (APPI$^+$): m/z calcd for $C_{42}H_{59}OSi_2$: 635.4099; found: 635.4130 $[M + H]^+$.

Compound 21. To a solution of compound **20** (1.76 g, 2.77 mmol) and compound **12** (1.64 g, 3.33 mmol) in degassed DIPA (56 mL) were added $Pd_2(dba)_3$ (0.051 g, 0.055 mmol), CuI (0.021 g, 0.111 mmol), and (t-Bu)$_3$PHBF$_4$ (0.064 g, 0.222 mmol). The reaction mixture was stirred for 24 h at 70 °C. Upon cooling, the solution was diluted in CH_2Cl_2, extracted three times with saturated aqueous NH_4Cl, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes to hexanes/CH_2Cl_2 17:3) to afford compound **21** as a yellow solid (1.67 g, 58%). mp = 86−88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, J = 1.6, 0.6 Hz, 1H), 7.66 (d, J = 2.2 Hz, 1H), 7.46−7.44 (m, 1H), 7.43−7.42 (m, 2H), 7.40−7.39 (m, 1H), 7.02 (d, J = 2.6 Hz, 1H), 6.86−6.80 (m, 2H), 4.04−3.94 (m, 4H), 1.85−1.74 (m, 4H), 1.55−1.41 (m, 4H), 1.39−1.24 (m, 24H), 1.18−1.12 (m, 42H), 0.89 (t, J = 6.8 Hz, 6H), 0.30 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 158.8, 137.2, 135.4, 133.4, 133.0, 131.2, 130.9, 127.2, 125.5, 125.3, 123.1, 118.1, 117.6, 115.3, 114.8, 113.4, 111.5, 105.1, 102.7, 102.0, 98.8, 95.3, 95.0, 94.5, 90.5, 87.2, 68.7, 68.2, 31.9, 29.6 (3C), 29.5, 29.4, 29.3, 26.2, 26.0, 22.7, 18.7 (2C), 14.1, 11.4, 11.3, 0.0. HRMS (APPI$^+$): m/z calcd for $C_{69}H_{103}O_2Si_3$: 1047.7260; found: 1047.7281 $[M + H]^+$.

Compound 22. To a solution of compound **21** (0.544 g, 0.519 mmol) in THF/methanol 4:1 (16 mL) were added KOH (0.123 g, 2.20 mmol) and 3 drops of water. The reaction was stirred until the TLC showed a complete reaction. The solution was diluted in $CHCl_3$ extracted three times with water and dried over sodium sulfate. The solution was filtered through a short silica gel plug. The solvent was removed in vacuo, and the residue was transferred to a flask charged with CuCl (0.005 g, 0.052 mmol), TMEDA (0.02 mL, 0.156 mmol), and molecular sieves 4 Å in $CHCl_3$ degassed with air during 1 h. The reaction was stirred at 40 °C for 24 h. An additional catalytic charge of CuCl and TMEDA was added, and the reaction was stirred at 40 °C for another 24 h. Upon cooling, the solution was diluted in $CHCl_3$, extracted three times with saturated aqueous NH_4Cl, washed with water and brine, and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes/$CHCl_3$ 9:1 to 3:2) to afford compound **22** as a yellow solid (0.462 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.70 (m, 2H), 7.62 (d, J = 2.1 Hz, 2H), 7.49−7.46 (m, 2H), 7.46 (s, 2H), 7.45 (d, J = 1.5 Hz, 2H), 7.42 (d, J = 8.7 Hz, 2H), 7.01 (d, J = 2.8 Hz, 2H), 6.84 (dd, J = 8.6, 2.7 Hz, 2H), 6.68 (d, J = 8.9 Hz, 2H), 3.97 (t, J = 6.5 Hz, 4H), 3.90 (t, J = 6.2 Hz, 4H), 1.83−1.68 (m, 8H), 1.49−1.40 (m, 8H), 1.40−1.21 (m, 48H), 1.13 (s, 42H), 1.10 (s, 42H), 0.91−0.85 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 158.9, 136.9, 135.8, 133.7, 133.4, 131.6, 131.4, 127.3, 126.5, 124.2, 123.2, 118.1, 117.4, 115.3, 114.3, 113.3, 111.6, 105.1, 102.1, 95.6, 95.2 (2C), 90.9, 90.3, 86.8, 80.7, 77.9, 68.6, 68.2, 31.9, 29.7, 29.6 (2C), 29.4, 29.3, 29.2, 26.2, 26.0, 22.7, 18.7 (2C), 14.1, 11.4, 11.3. HRMS (APPI$^+$): m/z calcd for $C_{132}H_{186}O_4Si_4$: 1947.3423; found: 1947.3455 $[M^*]^+$.

Compound 22′. To a solution of compound **22** (0.159 g, 0.082 mmol) in degassed THF (10 mL) was added a solution of tetrabutylammonium fluoride 1 M in THF (0.65 mL, 0.653 mmol). The reaction was stirred for about 30 min or until the product had completely precipitated. Methanol was added to the mixture and filtered. The residue was collected in $CHCl_3$, and the solvent was removed in vacuo to afford the corresponding unprotected alkyne as a light yellow solid (0.108 g, 99%), decomposition = 115−120 °C, which was further subjected to a copper or palladium homocoupling. ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C) δ 7.77 (s, 2H), 7.69 (s, 2H), 7.50 (s, 2H), 7.48 (s, 4H), 7.45 (d, J = 8.7 Hz, 2H), 7.06 (s, 2H), 6.90 (dd, J = 8.6, 2.4 Hz, 2H), 6.76 (d, J = 8.6 Hz, 2H), 4.03−3.96 (m, 8H), 3.37 (s, 2H), 3.22 (s, 2H), 1.85−1.76 (m, 8H), 1.51−1.42 (m, 8H), 1.42−1.24 (m, 48H), 0.94−0.85 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$, 50 °C) δ 160.5, 159.1, 137.5, 135.4, 133.8, 133.2, 131.7, 131.2, 126.9, 126.1, 124.6, 123.2, 118.1, 117.9, 116.1, 114.8, 112.3, 112.1, 95.6, 90.7, 90.6, 87.1, 82.0, 81.5, 81.1 (2C), 79.2, 78.2, 69.0, 68.4, 31.8 (2C), 29.5 (2C), 29.3 (2C), 29.2 (2C), 29.1, 29.0, 25.9 (2C), 22.6, 13.9. HRMS (APPI$^+$): m/z calcd for $C_{96}H_{106}O_4$: 1322.8086; found: 1322.8080 $[M^*]^+$. UV/vis ($CHCl_3$) λ_{max} (ε) 240 (114 429), 340 (134 603) nm. Fluorescence ($CHCl_3$) λ_{max} 420 nm.

Mesh 2. Conditions A. The residue (0.462 g, 0.237 mmol) was dissolved in pyridine (100 mL) and degassed for 30 min. The solution was stirred at 70 °C until the product was completely soluble. CuCl (1.67 g, 16.8 mmol) and $CuCl_2$ (0.35 g, 2.61 mmol) were added, and the reaction was stirred at 70 °C for 24 h. Upon cooling, the solvent was removed in vacuo. An aqueous solution of HCl 10% was added to the residue, and the mixture was filtered. The crude product was purified by silica gel column chromatography (hexanes/$CHCl_3$ 1:1 to 1:4), precipitated in CH_2Cl_2 at −78 °C, and filtered to afford mesh **2** as a yellow-green powder (0.014 g, 5%).

Conditions B. To a solution open to air of $Pd_2(dba)_3$ (0.004 g, 0.004 mmol), diphenylphosphinoethane (0.004 g, 0.010 mmol), CuI (0.005 g, 0.026 mmol), and I_2 (0.010 g, 0.039 mmol) in THF (38 mL) and DIPA (38 mL) was added the unprotected alkyne (0.050 g, 0.038 mmol). The reaction mixture was stirred at 85 °C for 48 h. Upon cooling, the solvents were removed in vacuo. The crude product was precipitated in cold

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methanol and filtered. The residue was recrystallized from $CHCl_3$ at −35 °C and purified by another recrystallization from DCM at −75 °C to afford mesh **2** as a yellow-green powder (0.012 g, 23%), decomposition = 155−160 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C) δ 8.05 (s, 2H), 8.01 (d, J = 2.3 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 7.45 (s, 4H), 7.42 (dd, J = 8.9, 1.9 Hz, 2H), 7.24 (d, J = 2.4 Hz, 2H), 6.92 (dd, J = 8.8, 2.7 Hz, 2H), 6.84 (d, J = 8.9 Hz, 2H), 4.09 (t, J = 6.6 Hz, 4H), 4.04 (t, J = 6.6 Hz, 4H), 1.88−1.79 (m, 8H), 1.45−1.26 (m, 56H), 0.91 (t, J = 6.8 Hz, 12H). HRMS (APPI$^+$): m/z calcd for $C_{96}H_{103}O_4$: 1319.7851; found: 1319.7842 $[M + H]^+$. UV/vis ($CHCl_3$) λ_{max} (ε) 240 (16 761), 314 (20 387), 354 (29 727) nm. Fluorescence ($CHCl_3$) λ_{max} 425, 455 nm.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01752.

Computational details and ^{1}H, ^{13}C, and ^{19}F NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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