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Evidence of Enhanced Conjugation in *ortho*-Arylene Ethynylenes with Transition Metal Coordination

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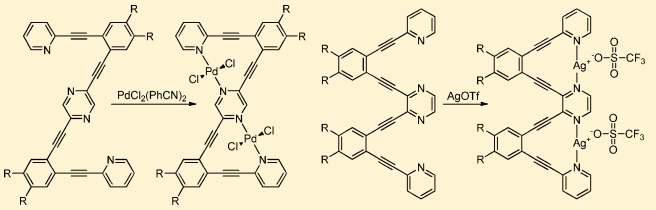
Supporting Information

ABSTRACT: The effective conjugation of *ortho* and *ortho-alt-para*-arylene ethynylenes, with appropriately positioned pyridine and pyrazine heterocycles, increases upon binding to Ag(I) and Pd(II) cations. Significant bathochromic shifts in the electronic spectra, witnessed upon introduction of these metal bridges, are consistent with enhanced electron delocalization in the unsaturated backbone. Control studies suggest that this electronic behavior is attributable exclusively (in the case of Ag(I)) or partially (in the case of Pd(II)) to conformational restrictions of the conjugated backbones.



p-Arylene ethynylenes, such as *p*-phenylene ethynylene, are common targets for chemists as they exhibit interesting optical,[1] conducting,[2] and chemosensing/biosensing properties[3−5] that can be used in a variety of technological applications.[6] *Ortho* and *meta* variants, on the other hand, receive much less attention in this field as they lack the attractive electronic properties of *para* systems. Beyond fundamental differences between delocalization pathways,[7] conjugation deficiencies are a result of thermodynamically favorable helix formation in *ortho* and *meta* arylene ethynylenes.[8−11] Upon helix formation, the π system becomes twisted, precluding efficient electron delocalization in the unsaturated backbone. *Para* systems, on the other hand, can achieve efficient orbital overlap via free rotation of the conjugated backbone. Moreover, the electronics of *para*-arylene ethynylenes can be optimized via synthetic manipulation so that free rotation is restricted, locking the molecule in a coplanar conformation.[12]

Enforced coplanarity in *p*-arylene ethynylene systems can be achieved through a number of strategies, including hydrogen bonding,[12,13] transition metal coordination,[14−16] and steric hindrance.[17] Enforcing planarity in these structures enhances electronic conjugation, making these molecules exciting targets for technological development.[18] Similar strategies have been exploited for stabilizing helices in *meta* oligomers.[19,20] Little effort, however, has been put into enforcing planarity in *ortho* and *meta* structures for the purposes of enhancing electronic properties.

As an entry point into this field, our focus was to establish a general strategy for enforcing planarity in *ortho*-type arylene ethynylenes (i.e., *ortho* and *ortho-alt-para* systems) (Figure 1). To this end, we identified 1,2-bis(2′-pyridinylethynyl)benzene (Figure 2) as a structural element that contains an *ortho* orientation and can be conformationally restricted via transition metal coordination. This well-studied ligand binds to a number of different metal cations, including Ag(I) and Pd(II),[21−24] and can be used in metal sensing[25] or as a ligand in the Heck reaction.[26] For our purposes, the transition metal cation serves as a bridge, restricting rotation within the macrocyclic structure.

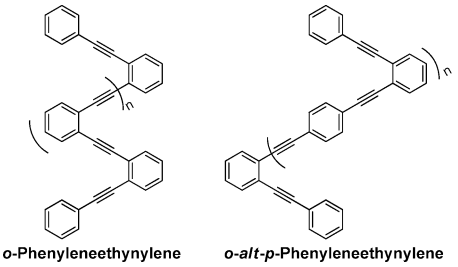


Figure 1. *o*-Phenylene ethynylenes and *o-alt-p*-phenylene ethynylenes, the simplest examples of *o*-arylene ethynylenes and *o-alt-p*-arylene ethynylenes, respectively, have highly unsaturated backbones but low effective conjugation due to their propensity to fold into helices.

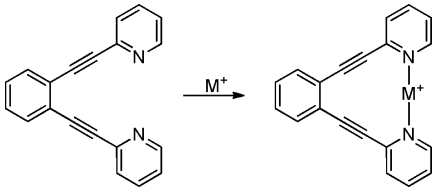


Figure 2. 1,2-Bis(2′-pyridinylethynyl)benzene binds in a bidentate fashion to a variety of metals including Ag(I) and Pd(II).

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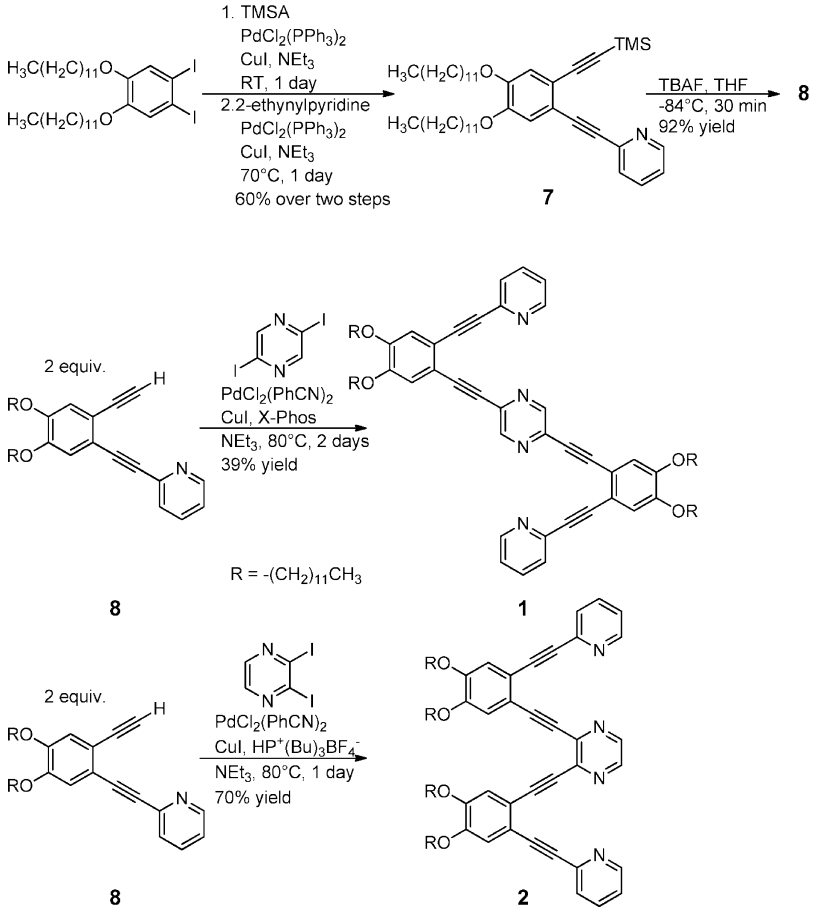
Scheme 1. Generation of Ligands 1 and 2



Two systems, **1** and **2**, should provide insight into the feasibility of enforcing coplanarity in *o*-arylene ethynylenes and *o*-*alt*-*p*-arylene ethynylenes via transition metal coordination (Scheme 1). Sonogashira coupling of terminal alkyne **8**, derived from 1,2-bis(dodecyloxy)-4,5-diiodobenzene, with 2,5-diiodopyrazine and 2,3-diiodopyrazine yields **1** and **2**, respectively. The conditions shown provided the highest conversions to their respective products. Low yields in the generation of **1** are a reflection of difficult chromatographic separations of the product from the homo- and monocoupled byproducts rather than poor conversion. One concern in these reactions was the potential of the products and intermediates to bind to Pd(II) and Cu(I), perhaps interfering with their catalytic viability. It was our hope that the ability of 1,2-bis(2′-pyridinylethynyl)-benzene to function as a ligand for the Heck reaction[26] would carry over to these Sonogashira reactions. To our delight, these reactions proceeded with acceptable conversion, despite likely involvement of our ligands in the catalytic cycle.

To verify that conformational control (i.e., planarity) can be achieved upon introduction of metals to **1** and **2**, there must be evidence of increased conjugation in the presence of metals. Increased conjugation results in a decrease in the HOMO–LUMO gap, which is most often observed as a bathochromic shift for the lowest energy absorption band. Indeed, when dilute samples of ligands **1** and **2** were titrated with silver triflate (AgOTf), significant bathochromic shifts were observed ($\Delta\lambda_{max}$ = 75 nm for **1**, $\Delta\lambda_{max}$ = 50–60 nm for **2**) (Figure 3). As one might expect, an end point is reached once two equivalents of Ag(I) are added to **1** (Figure 3a). Additional metal elicited no

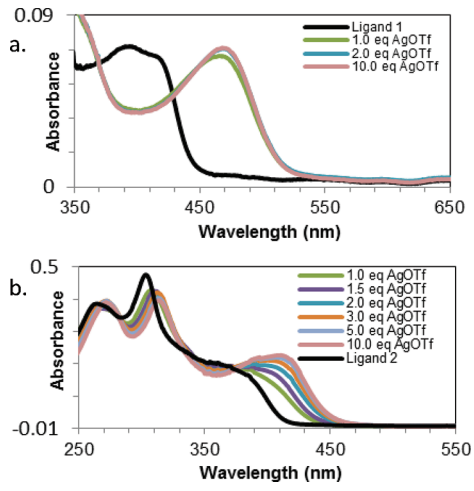


Figure 3. Significant bathochromic shifts are observed for the lowest energy absorption bands when (a) **1** and (b) **2** are treated with AgOTf.

further changes in the absorbance profile. With compound **2** (Figure 3b), more metal was required to reach the end point. The origin of this difference in behavior is not clear at this point, but it may indicate that planarity is less favorable in **2** as this could lead to steric hindrance between alkoxy groups or the creation of a very strong dipole in the metal–ligand complex. Nonetheless, both compounds display behavior indicative of increased conjugation upon metal coordination.

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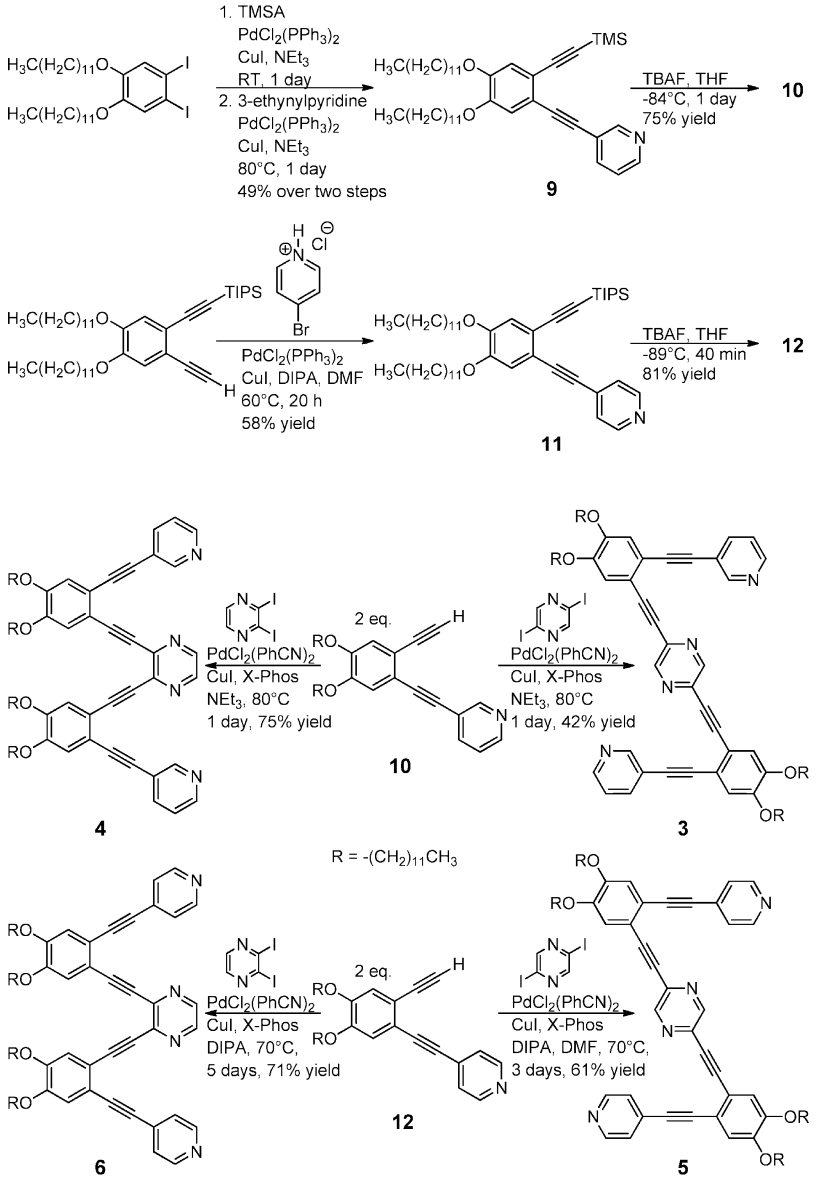
Scheme 2. Generation of Ligands 3−6



To be certain that observed electronic changes are a symptom of increased conjugation rather than electronic interactions with the metal or formation of coordination polymers and/or aggregates, we generated **3**−**6** (Scheme 2), which are very similar to **1** and **2** in terms of their electronic structure and ability to form coordination polymers and aggregates but are mismatched for coordination-driven planarization. The synthetic strategies for these isomers were similar to those employed for **1** and **2**. Careful deprotection of appropriate silyl-protected precursors (**9** and **11**) yielded the desired terminal alkynes (**10** and **12**) necessary for construction of **3**−**6**. Coupling of these alkynes with either 2,3-diiodopyrazine or 2,5-diiodopyrazine yielded the four targeted arylene ethynylenes (**3**−**6**) in reasonable to good yields.

Titration of dilute solutions of **3**−**6** in THF with AgOTf leads to only negligible changes ($\Delta\lambda_{max}$ < 15 nm) in the electronic spectra (see Supporting Information), consistent with our expectation that metal binding in these compounds does not lead to increased conjugation. Moreover, a lack of electronic changes upon attempted saturation of potential pyridine/pyrazine binding sites with excess Ag(I) supports our assertion that the bathochromic shifts observed with **1** and **2** are at least partly due to conformation restrictions rather than electronic metal/ligand interactions.

Attempts to further characterize complexes of **1**−**2** by NMR and GPC were plagued by low solubility in appropriate organic solvents. Lack of solubility could signify enhanced π−π stacking from planarization of the conjugated backbone as complexes of **3**, **4** and **6** are much more soluble than **1** and **2** (ligand **5** is insoluble in most solvents). Nonetheless, ligand/metal/solvent combinations that would allow better characterization of complex formation were sought. $PdCl_2(PhCN)_2$ proved to be a valuable tool for tracking sequential binding of metal cations. UV−vis titration studies of **1** and ^{1}H NMR titration studies of **2** provide evidence of distinct unbound (**1**, **2**), singularly bound (**1-Pd$_1$**, **2-Pd$_1$**) and doubly bound (**1-Pd$_2$**, **2-Pd$_2$**) ligands.

Upon initial introduction of metal to **1** (Figure 4), the signal for the unbound ligand (λ_{max} = 395 nm) decreases, while a signal for what appears to be singly bound ligand (**1-Pd$_1$**) grows in with a λ_{max} = 457 nm. As 2.0 equivalents of metal are

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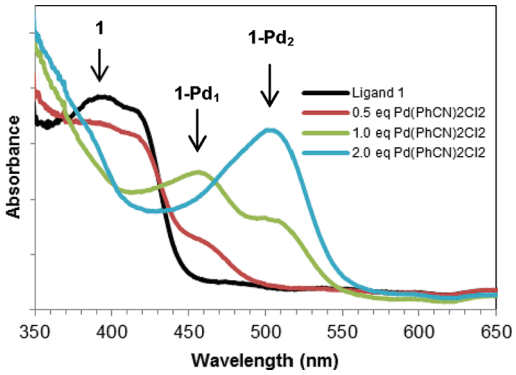

Figure 4. UV−Vis titration study of ligand **1** with Pd(II) indicates three distinct species: unbound **1**, singly bound **1** (**1-Pd$_1$**) and doubly bound **1** (**1-Pd$_2$**).

reached, this intermediate signal goes away while an absorption for doubly bound ligand (**1-Pd$_2$**) grows in with a λ_{max} = 505 nm. It is worth noting that the control molecules (**3**−**6**) also red-shift when $PdCl_2(PhCN)_2$ is introduced. Based on some model calculations with 1,2-bis(2′-pyridinylethynyl)-benzene (see Supporting Information), we tentatively attribute this behavior to mixing of Cl *p*-orbitals with the π/π^* system of the pyridines.[27] However, because complexation does not increase conjugation for these systems, the shifts are less pronounced for **3** ($\Delta\lambda_{max}$ = 55 nm), **4** ($\Delta\lambda_{max}$ = 50 nm), and **5** ($\Delta\lambda_{max}$ = 30 nm) than **1** ($\Delta\lambda_{max}$ = 110 nm) and **2** ($\Delta\lambda_{max}$ = 85 nm). Titration studies with $PdCl_2(PhCN)_2$ were further complicated by the fact that at high metal concentrations all electronic features for ligands **1**-**6** were washed out, yielding broad featureless spectra. This behavior, likely attributable to aggregation, is most evident in the 4-ethynyl pyridine derivatives (**5** and **6**), where this broadening is observed immediately upon Pd(II) introduction (precluding an estimated $\Delta\lambda_{max}$ for **6**).

Solubility issues of metal−ligand complexes prevented systematic NMR studies of metal titrations. Fortunately, compound **2** and its Pd(II) complexes are sparingly soluble in $CDCl_3$, allowing characterization of coordination behavior. With no metal present (Figure 5a), there are two signals for **2** above 8.3 ppm: a singlet (8.52 ppm) corresponding to the pyrazine hydrogen atoms (H_B) and a doublet (8.49 ppm) corresponding to the pyridine hydrogen atoms (H_A). At two equivalents (Figure 5c) of Pd(II), this singlet (H_H: 8.67 ppm) is shifted downfield along with the doublet (H_H: 8.84 ppm). At one equivalent (Figure 5b), all three species (**2**, **2-Pd$_1$** and **2-Pd$_2$**) are present, with four resonances for **2-Pd$_1$** at 8.88 ppm (H_C), 8.72 ppm (H_D), 8.48 ppm (H_E) and 8.37 ppm (H_F). The asymmetry of **2-Pd$_1$** is evident in not only the number of resonances but also splitting of the pyrazine hydrogens (H_D: d, 8.72 ppm, H_E: d, 8.48 ppm).

Compounds **1**−**6** are stable molecules that show no signs of decomposition either in the solid state or in solution. Metal complexes of these ligands, however, show slow discoloration over several days in the solid state. This instability may be indicative of a susceptibility to oxidation/reduction at the metal centers, which would be consistent with our inability to characterize metal complexes of **1**−**6** via ESI-MS. All six reported compounds (**1**−**6**) are emissive (see Supporting Information for spectra). The lowest energy electronic transitions of the six isomers depends on the substitution pattern around the central pyrazine ring and does not seem to be affected by the arrangement of the pyridinyl end groups (i.e.,

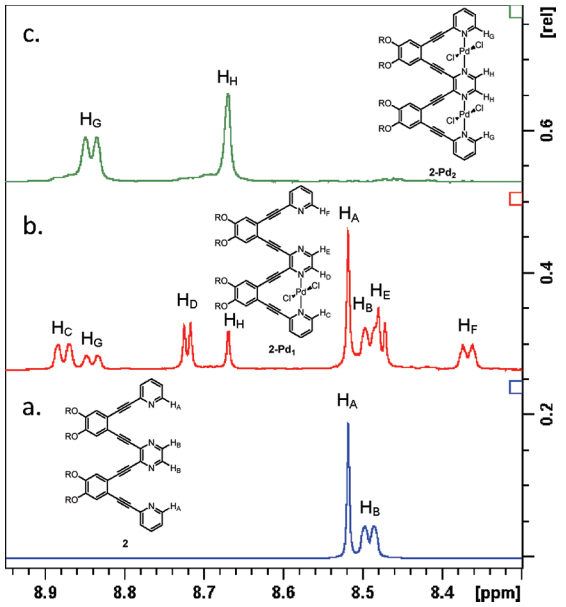

Figure 5. ^{1}H NMR titration study of ligand **2** with Pd(II) reveals a progression from (a) just **2** with no metal, to (b) a mix of **2**, **2-Pd$_1$** and **2-Pd$_2$** with 1.0 equiv of $PdCl_2(PhCN)_2$, to (c) just **2-Pd$_2$** with 2.0 equiv of $PdCl_2(PhCN)_2$.

2-ethynyl, 3-ethynyl, or 4-ethynyl). Ligands **1** (λ_{abs} = 395 nm, λ_{em} = 458 nm), **3** (λ_{abs} = 406 nm, λ_{em} = 463 nm) and **5** (λ_{abs} = 406 nm, λ_{em} = 457 nm), for instance, have very similar absorbance and emission profiles. Likewise, ligands **2** (λ_{abs} = ∼350 nm, λ_{em} = 437 nm), **4** ($\lambda_{abs} \approx$ 350 nm, λ_{em} = 434 nm) and **6** ($\lambda_{abs} \approx$ 350 nm, λ_{em} = 434 nm) have nearly identical electronic profiles. In all isomers, fluorescence is quenched upon introduction of Ag(I) and Pd(II). This is consistent with what has been reported for other 1,2-bis(2′-pyridinylethynyl)-benzene-type systems.[28]

In summary, two arylene ethynylene structures (**1** and **2**) bind to Ag(I) and Pd(II) cations, eliciting behavior that is consistent with increased effective conjugation. Support for this conclusion comes from comparisons of the metal binding behaviors of **1** and **2** to isomeric **3**, **4**, **5** and **6**, which show no signs of increased conjugation upon metal complexation. Continuing studies of these systems will address how this behavior applies to longer arylene ethynylene oligomers with the same pattern of alternating benzene/heterocyclic rings.

EXPERIMENTAL SECTION

Transition Metal Titration Studies. Solutions for UV−vis and fluorescence studies were made by combining dilute solutions of ligands in HPLC grade THF with dilute solutions of AgOTf or $PdCl_2(PhCN)_2$ in HPLC grade THF so that the final ligand concentrations were between 10^{-5} and 10^{-6} M (exact concentrations are listed in Supporting Information). Each of the metal/ligand samples (e.g., 1.0 equiv of AgOTf, 2.0 equiv of AgOTf, etc.) was prepared separately in advance in volumetric glassware, allowing for ample mixing/equilibration time before analysis.

General Coupling Conditions. All Pd coupling reactions were performed under an Ar atmosphere. Generally, three vacuum/purge cycles were applied to the reaction tube to remove air and refill with Ar. Air was displaced from the solvents by bubbling either N_2 or Ar through the liquids for at least 15 min.

2,5-Diiodopyrazine. Commercially available 2,5-dibromopyrazine (1.84 g, 7.75 mmol) was dissolved with sodium iodide (5.81 g, 38.74 mmol) in acetonitrile (15 mL). Small amounts of concentrated H_2SO_4 (8 drops) and glacial acetic acid (20 drops) were added, and the

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mixture was refluxed for 24 h. The reaction mixture was cooled, then diluted with CH_2Cl_2 (50 mL). This organic phase was washed with a saturated $NaHCO_3$ solution (3×), and a saturated sodium bisulfite solution (2×). The remaining organic phase was dried with anhydrous Na_2SO_4, filtered and concentrated to reveal the product as a white solid (2.14 g, 6.45 mmol, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (s, 2H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 154.0, 116.5 ppm. ESI-MS (m/z) calcd for $C_4H_2I_2N_2H^+$ 332.8386; found 332.8359 (small signal due to low solubility in 2-propanol mobile phase).

2,3-Diiodopyrazine. Commercially available 2,3-dichloropyrazine (1.0 g, 6.72 mmol) was refluxed with NaI (5.04 g, 33.6 mmol), glacial acetic acid (0.76 mL), and concentrated sulfuric acid (0.04 mL) in acetonitrile (10 mL) for one day. Upon cooling, the solvent was removed under reduced pressure. The remaining reddish-brown solid was taken up in CH_2Cl_2 (100 mL) and washed sequentially with a saturated sodium bicarbonate solution (50 mL) and a saturated sodium metabisulfite solution. The organic phase was dried with anhydrous Na_2SO_4, filtered and concentrated to reveal a light brown solid (1.82 g, 5.48 mmol, 82% yield). NMR (400 MHz, $CDCl_3$): δ = 8.30 (s, 2H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 142.8, 131.5 ppm. ESI-MS (m/z) calcd for $C_4H_2I_2N_2H^+$ 332.8386; found 332.8367 (small signal due to low solubility in 2-propanol mobile phase).

2-((4,5-Bis(dodecyloxy)-2-((trimethylsilyl)ethynyl)phenyl)-ethynyl)pyridine (7). An oven-dried, side arm storage tube was evacuated and filled with Argon. After addition of $Pd(PPh_3)_2Cl_2$ (0.151 g, 0.22 mmol), CuI (0.041 g, 0.22 mmol) and 1,2-bis(dodecyloxy)-4,5-diiodobenzene[29,30] (3.00 g, 4.3 mmol), the tube was purged with Ar (3×). Following the addition of freshly distilled triethylamine (40 mL) and trimethylsilylacetylene (0.79 mL, 5.6 mmol) via syringe, the reaction tube was sealed and the contents stirred at room temperature for one day. The contents were diluted with CH_2Cl_2 and washed with distilled water until the aqueous layers were colorless (5 washes) then with brine (3×). The organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated. This crude mixture was dissolved in freshly distilled NEt_3 and added to a storage tube containing $Pd(PPh_3)_2Cl_2$ (0.12 g, 1.7 mmol) and CuI (0.033 g, 0.17 mmol) under Ar. After argon was bubbled through this sample for five minutes, 2-ethynylpyridine (0.45 mL, 4.47 mmol) was added via syringe and the tube was sealed and heated at 70 °C for one day. The contents were cooled, diluted with CH_2Cl_2 and washed with distilled water until the aqueous layers were colorless, then with brine. The organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated. The remaining oil was purified via flash chromatography (silica gel) using a gradient mobile phase starting with a 20% CH_2Cl_2/80% hexane mixture with incremental increases in polarity up to 100% CH_2Cl_2. Appropriate fractions were concentrated to reveal the product as a yellowish oil (1.66 g, 2.58 mmol, 60% from 1,2-bis(dodecyloxy)-4,5-diiodobenzene). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (d, J = 4.6 Hz, 1H), 7.65 (td, J = 7.7, 1.5 Hz, 1H), 7.51 (dd, J = 7.7, 0.8 Hz), 7.21 (m, 1H), 7.07 (s, 1H), 6.96 (s, 1H), 4.00 (q, J = 6.4 Hz, 4H), 1.82 (p, J = 6.4 Hz, 4H), 1.4−1.2 (m, 36H), 0.88 (t, J = 6.6 Hz, 6H), 0.27 (s, 9H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 150.4, 149.8, 149.5, 144.1, 136.3, 127.4, 122.8, 119.2, 118.2, 116.4, 116.4, 104.0, 97.1, 91.3, 88.7, 69.4, 32.3, 30.0, 30.0, 29.9, 29.7, 26.3, 26.3, 23.0, 14.4, 0.4 ppm. ESI-MS (m/z) calcd for $C_{42}H_{65}NO_2SiH^+$ 644.4863; found 644.4790.

2-((4,5-Bis(dodecyloxy)-2-ethynylphenyl)ethynyl)pyridine (8). Protected alkyne **7** (0.25 g, 0.38 mmol), dissolved in THF (10 mL), was cooled to −84 °C (EtOAc/N_2) under an argon atmosphere. Tetrabutylammonium fluoride (0.34 mL of 1.0 M solution in THF, 0.34 mmol) was added dropwise via syringe. After 30 min of stirring at this temperature, the reaction flask was allowed to warm to room temperature. Volatile solvents were gently removed (bath temp. < 40 °C) under reduced pressure. The remaining oil was dissolved in CH_2Cl_2. The resulting organic layer was washed with water (2×), dried with Na_2SO_4, filtered and concentrated to reveal **8** as a white solid (0.202 g, 0.35 mmol, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62 (dd, J = 4.8, 0.6 Hz, 1H), 7.66 (td, J = 7.7, 1.8 Hz, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.22 (ddd, J = 7.7, 4.8, 1.1 Hz, 1H), 7.08 (s, 1H), 6.98 (s, 1H), 4.00 (t, J = 6.6 Hz, 2H), 3.99 (t, J = 6.6 Hz, 2H), 3.30 (s, 1H), 1.82 (p, J = 6.8 Hz, 4H), 1.5−1.2 (m, 36H), 0.88 (t, J = 6.6 Hz, 6H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 150.1, 149.6, 149.5, 143.7, 136.0, 127.3, 122.6, 118.1, 117.8, 116.5, 116.3, 91.0, 88.2, 82.3, 79.7, 69.2, 69.2, 31.9, 29.7, 29.7, 29.6, 29.4, 29.0, 29.0, 26.0, 22.7, 14.1, 1.0 ppm. ESI-MS (m/z) calcd for $C_{39}H_{57}NO_2H^+$ 572.4468; found 572.4470.

2,5-Bis((4,5-bis(dodecyloxy)-2-(pyridin-2-ylethynyl)phenyl)-ethynyl)pyrazine (1). To an air-free storage tube (under argon) was added **8** (0.493 g, 0.86 mmol), 2,5-diiodopyrazine (0.152 g, 0.46 mmol), CuI (0.012 g, 0.062 mmol), $PdCl_2(PhCN)_2$ (0.0097 g, 0.025 mmol), and 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (X-Phos, 0.0095 g, 0.020 mmol). The powders were rinsed into the tube with 20 mL freshly distilled triethylamine, and the tube was sealed and heated at 80 °C for two days. After cooling to room temperature, the contents were diluted with CH_2Cl_2. This organic mixture was washed with saturated ammonium chloride solution (3×). The combined aqueous phases were back-extracted with CH_2Cl_2 (3×). The combined organic layers were then washed with distilled water and brine, then dried with anhydrous Na_2SO_4, filtered and concentrated. Sequential flash chromatography columns (silica gel, 1% MeOH/$CHCl_3$, then silica gel, 1% EtOAc/$CHCl_3$) provided enough pure product (yellow solid, 0.208 g, 0.17 mmol, 39% yield, mp = 153−155 °C) for further studies. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.91 (s, 2H), 8.65 (m, 2H), 7.67 (ddd, J = 7.8, 7.3, 1.7 Hz, 2H), 7.63 (m, 2H), 7.23 (ddd, J = 4.9, 1.7, 1.5 Hz, 2H, 7.14 (s, 2H), 7.12 (s, 2H), 4.04 (t, J = 6.6 Hz, 4H), 4.03 (t, J = 6.5 Hz, 4H), 1.85 (p, J = 6.7 Hz, 8H), 1.49 (m, 8H), 1.4−1.2 (m, 64H), 0.88 (t, J = 6.6 Hz, 12H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 150.3, 150.3, 149.7, 147.4, 143.5, 137.8, 136.2, 127.1, 122.8, 118.7, 117.3, 116.0, 94.4, 92.0, 89.3, 87.9, 69.3, 69.2, 31.9, 29.7, 29.7, 29.6, 29.4, 29.0, 29.0, 26.0, 22.7, 14.1 ppm. ESI-MS (m/z) calcd for $C_{82}H_{115}N_4O_4H^+$ 1219.8918; found 1219.8803. λ_{max} nm (ε, $M^{-1}cm^{-1}$) (THF) = 299 (21,920), 395 (8,240).

2,3-Bis((4,5-bis(dodecyloxy)-2-(pyridin-2-ylethynyl)phenyl)-ethynyl)pyrazine (2). To an air-free storage tube (under argon) was added 2,3-diiodopyrazine (0.230 g, 0.67 mmol), $PdCl_2(PhCN)_2$ (0.0195 g, 0.051 mmol), $HP^+(Bu)_3BF_4^-$ (0.0295 g, 0.102 mmol) and CuI (0.0070 g, 0.037 mmol). Freshly distilled triethylamine (20 mL) was added via syringe. In a separate container, terminal alkyne **8** (0.846 g, 1.48 mmol) was dissolved in triethylamine (5 mL) and was transferred via syringe to the reaction tube. An additional five mL triethylamine was added and the tube was sealed and heated at 80 °C for one day. After cooling to room temperature, the contents of the tube were diluted with ethyl acetate. This organic phase was washed with distilled water (3 × 25 mL) and brine (3 × 30 mL), then dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude sample was purified via flash chromatography (silica gel, 40% EtOAc/60% hexane increased to 50% EtOAc/50% hexane). Appropriate fractions were concentrated to reveal the product as a yellow solid (0.576 g, 0.47 mmol, 70% yield, mp = 85−88 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (s, 2H), 8.49 (d, J = 4.5 Hz, 2H), 7.62 (d, J = 7.8 Hz, 2H), 7.54 (td, J = 7.6, 1.7 Hz, 2H), 7.11 (ddd, J = 7.5, 4.9, 1.2 Hz, 2H), 7.04 (s, 2H), 7.01 (s, 2H), 3.97 (t, J = 6.6 Hz, 4H), 3.86 (t, J = 6.6 Hz, 4H), 1.9−1.7 (m, 8H), 1.5−1.2 (m, 72H), 0.88 (t, J = 6.6 Hz, 12H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 150.0, 149.7, 149.4, 143.4, 142.2, 141.9, 135.9, 127.7, 122.4, 118.4, 117.2, 116.3, 115.9, 95.6, 92.0, 88.6, 88.0, 69.2, 69.0, 32.0, 29.8, 29.7, 29.7, 29.7, 29.5, 29.4, 29.4, 29.1, 29.0, 26.0, 26.0, 22.7, 14.1 ppm. ESI-MS (m/z) calcd for $C_{82}H_{115}N_4O_4H^+$ 1219.8918; found 1219.8805. λ_{max} nm (ε, $M^{-1}cm^{-1}$) (THF) = 210 (38,650), 303 (55,180), 350 (23,200).

3-((4,5-Bis(dodecyloxy)-2-((trimethylsilyl)ethynyl)phenyl)-ethynyl)pyridine (9). To an oven-dried storage tube, under argon, was added 1,2-bis(dodecyloxy)-4,5-diiodobenzene (2.0 g, 2.86 mmol), CuI (0.27 g, 0.143 mmol) and $Pd(PPh_3)_2Cl_2$ (0.100 g, 0.143 mmol). Freshly distilled triethylamine (30 mL) was added via syringe, followed by trimethylsilylacetylene (0.45 mL, 3.15 mmol). The tube was sealed and the contents stirred at room temperature for one day. After dilution with CH_2Cl_2, the organic phase was washed with saturated NH_4Cl solution (2 × 20 mL), distilled water (3 × 30 mL), and brine (2 × 20 mL), dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. This crude mixture was taken up in freshly

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distilled triethylamine (20 mL) then added to an air-free (under Ar) storage tube containing $Pd(PPh_3)_2Cl_2$ (0.100 g, 0.143 mmol), CuI (0.027 g, 0.143 mmol), and 3-ethynylpyridine (0.38 g, 3.72 mmol). Additional triethylamine (10 mL) was added before the tube was sealed and heated at 80 °C for one day. After cooling and diluting contents with CH_2Cl_2, the organic phase was washed with saturated NH_4Cl solution (2 × 30 mL), distilled water (3 × 20 mL), and brine (2 × 20 mL), dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude sample was purified via flash chromatography (silica gel, CH_2Cl_2). Appropriate fractions were concentrated to reveal the product as a yellow oil (0.905 g, 1.4 mmol, 49% yield from 1,2-bis(dodecyloxy)-4,5-diiodobenzene). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (d, J = 1.3 Hz, 1H), 8.53 (dd, J = 4.9, 1.4 Hz, 1H), 7.80 (dt, J = 7.9, 1.9 Hz, 1H), 7.27 (m, 1H), 6.98 (s, 1H), 6.97 (s, 1H), 4.00 (m, 4H), 1.83 (p, J = 6.7 Hz, 4H), 1.5−1.2 (m, 36H), 0.88 (t, J = 6.3 Hz, 6H), 0.26 (s, 9H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 152.6, 149.9, 149.7, 148.7, 138.5, 123.3, 121.1, 119.2, 118.5, 116.8, 116.3, 104.0, 97.3, 92.2, 88.6, 69.6, 69.6, 32.3, 30.0, 30.0, 29.9, 29.7, 29.4, 26.3, 23.0, 14.4, 1.3 ppm. ESI-MS (m/z) calcd for $C_{42}H_{65}NO_2SiH^+$ 644.4863; found 644.4880.

3-((4,5-Bis(dodecyloxy)-2-ethynylphenyl)ethynyl)pyridine (10). Protected alkyne **9** (0.90 g, 1.4 mmol) was dissolved in THF (20 mL) and the solution cooled to −84 °C (EtOAc/N_2). Tetrabutylammonium fluoride (2.0 mL, 1.0 M solution in THF, 2.0 mmol) was added dropwise via syringe. The reaction mixture was allowed to slowly warm to room temperature, then stir for one day. After gentle removal of the solvent (bath temp. < 40 °C) under reduced pressure, the crude product was purified via flash chromatography (silica gel, CH_2Cl_2). Concentration of appropriate fractions revealed the product as a greyish/white solid (0.61 g, 1.1 mmol, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (d, J = 1.4 Hz, 1H), 8.53 (dd, J = 4.8, 1.6 Hz, 1H), 7.81 (dt, J = 7.9, 1.8 Hz, 1H), 7.27 (m, 1H), 6.99 (s, 2H), 4.01 (q, J = 6.6 Hz, 4H), 3.29 (s, 1H), 1.82 (m, 4H), 1.46 (m, 4H), 1.4−1.2 (m, 32H), 0.88 (m, 6H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 152.6, 149.8, 149.8, 148.7, 138.6, 123.3, 121.0, 118.6, 118.0, 116.9, 116.1, 91.8, 88.7, 82.6, 80.1, 69.5, 32.2, 30.0, 30.0, 29.9, 29.7, 29.7, 29.4, 26.3, 23.0, 14.4, 1.3 ppm. ESI-MS (m/z) calcd for $C_{39}H_{57}NO_2H^+$ 572.4468; found 572.4471.

2,5-Bis((4,5-bis(dodecyloxy)-2-(pyridin-3-ylethynyl)phenyl)-ethynyl)pyrazine (3). Terminal alkyne **10** (0.300 g, 0.52 mmol) was dissolved in freshly distilled triethylamine (25 mL) and transferred via syringe to an air-free storage tube under argon. 2,5-Diiodopyrazine (0.083 g, 0.24 mmol), CuI (0.0186 g, 0.098 mmol), $PdCl_2(PhCN)_2$ (0.0053 g, 0.0138 mmol), and 2-dicyclohexylphosphino-2′,4′, 6′-triisopropylbiphenyl (X-Phos, 0.0036 g, 0.0076 mmol) were added to the reaction tube and rinsed into solution with 5 mL NEt_3. The tube was sealed and heated at 80 °C for one day. After cooling to room temperature, the mixture was diluted with CH_2Cl_2. This organic mixture was washed with saturated NH_4Cl solution until the aqueous layer was no longer blue. The aqueous phases were then extracted with CH_2Cl_2 (3×). The combined organic layers were washed with distilled water and brine then concentrated under reduced pressure. This crude mixture was purified using consecutive flash chromatography columns (1st: silica gel, CH_2Cl_2 then 5% MeOH/95% CH_2Cl_2. second: silica gel, 1% MeOH in $CHCl_3$). Appropriate fractions were concentrated to reveal the product as a brownish solid (0.124 g, 0.10 mmol, 42% yield, mp = 160−163 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.86 (d, J = 1.4 Hz, 2H), 8.72 (s, 2H), 8.55 (dd, J = 4.9, 1.5 Hz, 2H), 7.91 (dt, J = 7.7, 1.9 Hz, 2H), 7.29 (dd, J = 7.8, 4.9 Hz, 2H), 7.11 (s, 2H), 7.05 (s, 2H), 4.05 (m, 8H), 1.86 (m, 8H), 1.6−1.2 (m, 72H), 0.88 (t, J = 6.8 Hz, 12H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 152.2, 150.4, 149.6, 148.6, 147.0, 138.4, 137.8, 123.1, 120.5, 118.9, 116.9, 116.1, 115.6, 94.4, 91.3, 89.4, 89.1, 69.3, 31.9, 29.7, 29.7, 29.6, 29.4, 29.0, 26.0, 22.7, 14.1 ppm. ESI-MS (m/z) calcd for $C_{82}H_{115}N_4O_4H^+$ 1219.8918; found 1219.8794. λ_{max} nm (ε, $M^{-1}cm^{-1}$) (THF) = 299 (67700), 406 (33900).

2,3-Bis((4,5-bis(dodecyloxy)-2-(pyridin-3-ylethynyl)phenyl)-ethynyl)pyrazine (4). Terminal alkyne **10** (0.300 g, 0.52 mmol) was dissolved in freshly distilled triethylamine (30 mL) and transferred via syringe to an air-free storage tube under argon. 2,3-Diiodopyrazine (0.0801 g, 0.24 mmol), CuI (0.0030 g, 0.016 mmol), $PdCl_2(PhCN)_2$ (0.0047 g, 0.012 mmol), and 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (X-Phos, 0.0034 g, 0.0072 mmol) were added and rinsed into the container with additional triethylamine (5 mL). The tube was sealed and heated at 80 °C for one day. After cooling to room temperature, the contents of the tube were diluted with CH_2Cl_2. This organic layer was washed with saturated NH_4Cl solution (2 × 30 mL), distilled water (3 × 30 mL) and brine (2 × 30 mL), then dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. This crude mixture was purified by flash chromatography (silica gel, 50% EtOAc/50% hexane increasing to 90% EtOAc/10% hexane). Appropriate fractions were concentrated to reveal the product as a brown solid (0.220 g, 0.18 mmol, 75% yield, mp = 85−88 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69 (s, 2H), 8.53 (s, 2H), 8.42 (dd, J = 4.8, 1.2 Hz, 2H), 7.74 (dt, J = 7.9, 1.8 Hz, 2H), 7.13 (dd, J = 7.8, 4.9 Hz, 2H), 7.00 (s, 2H), 6.92 (s, 2H), 4.00 (t, J = 6.6 Hz, 4H), 3.85 (t, J = 6.6 Hz, 4H), 1.84 (p, J = 7.0 Hz, 4 H), 1.78 (p, J = 7.0 Hz, 4H), 1.5−1.2 (m, 72H), 0.88 (t, J = 6.8 Hz, 12H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 152.1, 150.1, 149.3, 148.2, 142.4, 141.8, 138.4, 122.8, 120.4, 118.7, 117.2, 116.3, 115.3, 95.4, 91.4, 89.4, 88.7, 69.3, 69.0, 32.0, 31.9, 29.8, 29.7, 29.7, 29.7, 29.5, 29.4, 29.4, 29.1, 26.0, 26.0, 22.7, 14.1 ppm. ESI-MS (m/z) calcd for $C_{82}H_{115}N_4O_4H^+$ 1219.8918; found 1219.8808. λ_{max} nm (ε, $M^{-1}cm^{-1}$) (THF) = 273 (19800), 303 (21600), 350 (9600).

4-((4,5-Bis(dodecyloxy)-2-((triisopropylsilyl)ethynyl)phenyl)-ethynyl)pyridine (11). $Pd(PPh_3)_2Cl_2$ (0.022 g, 0.031 mmol) and CuI (0.006 g, 0.031 mmol) were added to a storage tube under Ar. After three vacuum/purge cycles (Ar), 4-bromopyridine hydrochloride (0.120 g, 0.616 mmol) was added and rinsed into the container with degassed DMF (2 mL). The terminal alkyne precursor (obtained by methods reported by Zhao)[31] was taken up in degassed diisopropylamine (4 mL) then transferred to the reaction tube, followed by additional DIPA (2 mL). The tube was sealed and heated at 60 °C for 20 h. After cooling to room temperature, the contents were transferred to a separatory funnel with diethyl ether and sat. NH_4Cl solution. The layers were separated and the organic phase washed sequentially with sat. NH_4Cl solution then brine, dried with anhydrous Na_2SO_4, filtered and concentrated. The resulting brown oil was purified via flash chromatography (silica, 25% ether/75% hexane eluent) to reveal a light brown oil (0.261 g, 0.36 mmol, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (m, 2H), 7.35 (m, 2H), 6.98 (s, 1H), 6.96 (s, 1H), 4.01 (m, 4H), 1.83 (m, 4H), 1.5−1.2 (m, 36H), 1.12 (s, 21H), 0.88 (t, J = 6.9 Hz, 6H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 149.8, 149.6, 149.2, 131.8, 125.6, 119.3, 117.5, 116.7, 116.3, 105.2, 93.6, 93.4, 88.6, 69.3, 69.2, 31.9, 29.7, 29.7, 29.6, 29.4, 29.1, 29.1, 26.0, 26.0, 22.7, 18.7, 14.1, 11.4 ppm. ESI-MS (m/z) calcd for $C_{48}H_{77}NO_2SiH^+$ 728.5802; found 728.5739.

4-((4,5-Bis(dodecyloxy)-2-ethynylphenyl)ethynyl)pyridine (12). TIPS-protected alkyne **11** (0.261 g, 0.36 mmol) was dissolved in wet THF (10 mL) then cooled to −89 °C (2-propanol/liq. N_2). TBAF (1 M in THF, 0.36 mL, 0.36 mmol) was added dropwise via syringe. The mixture stirred on the cold bath for 20 min, then was removed from the bath and was allowed to stir for another 20 min. The mixture was rinsed into a separatory funnel with sat. NH_4Cl solution and diethyl ether. The layers were separated and the organic layer was then washed with H_2O and brine, dried with anhydrous Na_2SO_4, filtered and concentrated. The resulting residue was purified via flash chromatography (silica, 50% ether/50% hexane) to yield a white solid (0.166 g, 0.29 mmol, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (m, 2H), 7.38 (m, 2H), 6.99 (s, 1H), 6.99 (s, 1H), 4.01 (m, 4H), 3.30 (s, 1H), 1.83 (m, 4H), 1.5−1.2 (m, 36 H), 0.88 (m, 6H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 149.8, 149.7, 149.5, 131.7, 125.5, 118.1, 117.7, 116.5, 115.9, 93.0, 89.1, 82.2, 79.9, 69.3, 69.2, 31.9, 29.7, 29.7, 29.6, 29.4, 29.1, 29.0, 26.0, 22.7, 17.7, 14.1, 12.3 ppm. ESI-MS (m/z) calcd for $C_{39}H_{57}NO_2H^+$ 572.4468; found 572.4404.

2,5-Bis((4,5-bis(dodecyloxy)-2-(pyridin-4-ylethynyl)phenyl)-ethynyl)pyrazine (5). $PdCl_2(PhCN)_2$ (1.6 mg, 0.0042 mmol), X-Phos (2.0 mg, 0.0042 mmol), 2,5-diiodopyrazine (0.046 g, 0.14 mmol) and CuI (∼1 mg) were added to a reaction tube and oxygen was removed via three vacuum/purge cycles (Ar). Degassed DMF (1 mL)

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was added via syringe. Terminal acetylene **12** (0.166 g, 0.29 mmol) was taken up in degassed diisopropylamine (20 mL) and was transferred to the reaction tube via syringe, followed by additional DIPA (2 mL). The reaction tube was sealed and the contents heated at 70 °C for three days. A yellow precipitate formed during the reaction. This solid was removed via suction filtration and rinsed with ether, sat. NH_4Cl solution, water, then cold ether. The bright yellow solid was air-dried and weighed (0.105 g, 0.086 mmol, 61% yield, mp = 157−160 °C). Despite low solubility in common organic solvents, making characterization difficult, the identity of this compound was verified via ^1H NMR spectroscopy and was analyzed via UV−vis spectroscopy. ^1H NMR (400 MHz, $CDCl_3$): (broad signals due to poor solubility) δ = 8.74 (s, 2H), 8.62 (br s, 4H), 7.48 (br s, 4H), 7.12 (s, 2H), 7.05 (s, 2H), 4.05 (q, J = 6.8 Hz, 8H), 1.86 (m, 8H), 1.49 (m, 8H), 1.5−1.2 (m, 72H), 0.88 (t, J = 6.3 Hz, 12H) ppm. λ_{max} nm (ε, $M^{-1}cm^{-1}$) (THF) = 300 (14400), 406 (7700).

2,3-Bis((4,5-bis(dodecyloxy)-2-(pyridin-4-ylethynyl)phenyl)-ethynyl)pyrazine (6). $PdCl_2(PhCN)_2$ (2.1 mg, 0.0055 mmol), X-Phos (2.6 mg, 0.0055 mmol) and CuI (1.0 mg, 0.0055 mmol) were added to a reaction tube and oxygen removed via three vacuum/purge cycles (Ar). In a separate flask, under Ar, terminal acetylene **12** (0.135 g, 0.24 mmol) was mixed with 2,3-diiodopyrazine (0.0365 g, 0.11 mmol). Degassed diisopropylamine (25 mL) was added to dissolve this mixture and the contents were transferred to the reaction tube via syringe. The reaction tube was sealed and heated at 70 °C for five days. The mixture was rinsed into a separatory funnel with diethyl ether and sat. NH_4Cl solution. The layers were separated and the organic phase was washed with water and brine, dried with anhydrous Na_2SO_4, filtered and concentrated. The reddish residue was purified via flash chromatography (silica, 100% CH_2Cl_2 gradually increased in polarity to 3% CH_3OH/97% CH_2Cl_2) to yield a reddish solid (0.095 g, 0.078 mmol, 71% yield, mp = 83−85 °C). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.55 (s, 2H), 8.46 (m, 4H), 7.29 (m, 4H), 6.93 (s, 2H), 6.92 (s, 2H), 4.00 (t, J = 6.6 Hz, 4H), 3.85 (t, J = 6.6 Hz, 4H), 1.85 (p, J = 6.6 Hz, 4H), 1.79 (p, J = 6.6 Hz, 4H), 1.5−1.2 (m, 72H), 0.88 (t, J = 6.8 Hz, 12H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 150.0, 149.6, 149.4, 142.4, 141.7, 131.2, 125.4, 118.1, 117.6, 116.2, 115.6, 95.3, 92.6, 90.1, 88.7, 69.3, 68.9, 31.95, 31.94, 29.8, 29.7, 29.7, 29.7, 29.5, 29.4, 29.4, 29.1, 29.0, 26.0, 22.7, 14.1 ppm. ESI-MS (m/z) calcd for $C_{82}H_{115}N_4O_4H^+$ 1219.8918; found 1219.8941. λ_{max} nm (ε, $M^{-1}cm^{-1}$) (THF) = 268 (65700), 301 (68300), 350 (31600).

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra (^1H and ^{13}C) for all compounds, UV−vis/fluorescence spectra for all aryleneethynylene isomers (**1**−**6**) and metal complexes thereof, and computational details are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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