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Star-Shaped Molecules Containing Polyalkynyl Groups with Metal Moieties on Benzene and Triphenylene Cores

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A series of star-shaped molecules with a silyl group and an aromatic core surrounded by extended π conjugative arms has been synthesized by the use of Sonogashira coupling methods. They show excellent fluorescence intensity with high quantum yield. These molecules undergo desilylation in the presence of $n\mathrm{Bu_4NF}$ to give terminal polyalkynyl compounds. By incorporating metal moieties such as palladium, platinum and gold into these compounds, star-shaped molecules can be obtained. Photophysical properties of these molecules are investigated spectroscopically in solution. These star-shaped molecules are characterized by IR, NMR (^{1}H, ^{31}P and ^{13}C) spectroscopy, as well as MALDI-TOF mass spectrometry.

Introduction

Since the past decade, there has been a blooming growth in the development of the chemistry of carbon-rich metal-containing systems, in particular those with long sp carbon chain.[1] Such a rapid growth is partly assisted by the urgent demand for new materials in molecular electronics as a result of the inherent limit of the present semiconductor technology. The alkynyl group, with its linear geometry, structural rigidity, extended π-electron delocalization, and ability to interact with metal centers through p_π–d_π overlap, has been an attractive candidate to serve as building blocks for the construction of carbon-rich metal-containing materials that possess potential applications as optical nonlinearity,[2] electrical conductivity,[3] luminescence[4] and liquid crystallinity.[5]

Early works on metal alkynes involve those of polymeric nature, which precluded further purification and characterization. Hagihara and co-workers reported the first soluble polyynylplatinum and -palladium complexes.[6] Subsequent reports on metal-containing polyynes provided important contributions in this area.[7] Despite all these important works, studies on these polymeric systems present difficulties such as the exact arrangement of the structure, molecular-weight distribution, heterogeneity of samples, reproducibility, and many others. All of these would render a direct understanding of the structure–property relationship and the fundamental understanding on the spectroscopic origin of these chromophores less straightforward and less amenable to study. Recent interest in alkynylpalladium(II) and -platinum(II) chemistry has been extended toward platinum-containing hyperbranched molecules and organometallic dendrimers. Stang[8] and Takahashi[9] have shown that 1,3,5-triethynylbenzene could be used as a building block for organoplatinum dendrimers. Yam and her co-workers[10] have explored the luminescence properties of a series of branched alkynyl palladium(II) and alkynylplatinum(II) complexes. With regard to hexaethynylbenzene, Vollhardt et al. first reported its synthesis and derivatives at high-temperature Sonogashira conditions in 1986.[11] Recently, Beck[12] have utilized hexaethynylbenzene as a building block to construct star-shaped molecules containing hexa-platinum and hexa-iron. Despite the growing interests and extensive studies in alkynylmetal compounds in the past decade or so, relatively less attention was focused on the exploration and exploitation of dendritic molecules containing more metal moieties as luminescent materials. Herein, we report the properties of a series of organic star-shaped molecules with four, five and six arms, and then incorporate palladium, platinum and gold metal moieties into them to extend the polyethynylbenzenes in the direction of the long conjugated polyyne system to investigate the properties of these metal acetylide molecules.

Results and Discussion

Synthetic methodologies used for the construction of poly(silylethynyl)benzenes rely on two approaches described as divergent and convergent strategies. The compounds **1**–**4** could be prepared by convergent method by a simple one-pot reaction involving Pd-catalyzed alkynylation of halogenated arenes with 1-ethynyl-4-[2-(triisopropylsilyl)ethynyl]benzene (**A**)[13] under the condition of Sonogashira coup-

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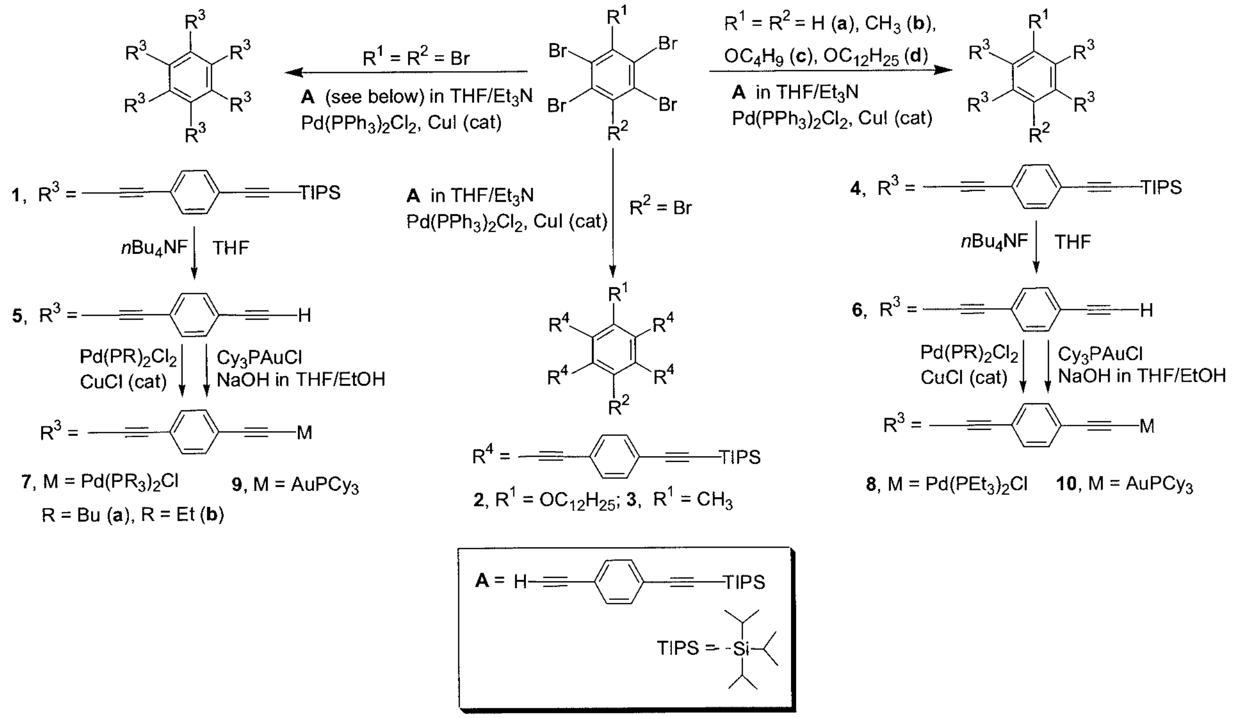
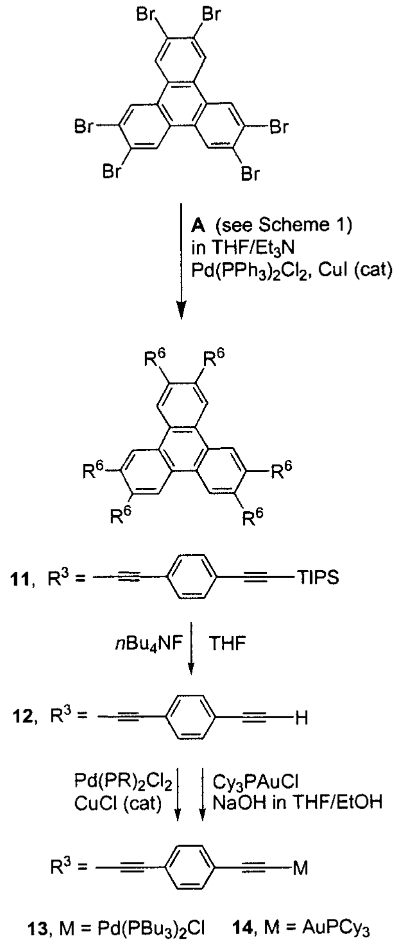


Scheme 1.

ling reaction.[14] The inverse cross-coupling reaction of (4-iodophenyl)ethynyltrimethylsilane with ethynylated arenes also afforded the desired poly(silylethynyl)benzenes compound on divergent approach. However, the intermediate obtained in the divergent method, hexaethynylbenzene could turns brown slowly in the absence of air and rapidly in its presence.[11] Therefore, it is not convenient to utilize it as good precursors for subsequent Sonogashira coupling reaction to form poly(silylethynyl)benzenes. For this reason, the poly(silylethynyl)benzenes **1**–**4** were efficiently prepared by the convergent approach. The preparation of **1**–**4** commenced with tetra-, penta- or hexa-halogenated arenes and excess **A** as outlined in Scheme 1. Compared with the reported preparation of the similar molecules,[15] our preparation uses only 1.1–1.25 equiv. of **A**, and the poly(silylethynyl)arenes **1**–**4** are obtained in 50–90% yield. Desilylation of poly(silylethynyl)benzene **1** and **4** with $n\mathrm{Bu_4NF}$ gave the compounds **5** and **6**, respectively, mostly in quantitative yield with multiple terminal alkynyl groups.

In the reaction of **5** and **6** with *trans*-$\mathrm{Pd(PR_3)_2Cl_2}$ (R = Et, Bu), only a four- or sixfold equivalent of Pd complex was dissolved in THF in the reaction mixture for the formation of the desired product. Multiple Pd metal moieties were added to all terminal carbon atoms of alkyne. The reaction was carried out in the presence of CuCl catalyst and $\mathrm{Et_2NH}$ to yield the palladium acetylide complex **7**. After stirring at room temperature overnight the reaction mixture was processed by chromatography to yield the expected air- and moisture-stable palladium complex in good yield (> 70%). We note that Yam and her co-workers[10] have reported that excess *trans*-$\mathrm{M(PEt_3)_2Cl_2}$ (M = Pd, Pt) was required in the preparation of the branched palladium ace-



Scheme 2.

tylide complexes in the presence of copper(I) catalyst in order to decrease the formation of undesirable insoluble oligomeric materials. They carried out these reactions in CH_2Cl_2. In our cases, the reaction in CH_2Cl_2 gave incomplete incorporation of the metal moieties affording three- or four-substituted product. However, the reaction in THF generally gave much better yield because the organic starting material has a higher solubility in THF. Using the preparation method of gold acetylide in the literature,[16] the gold complexes **9** and **10** are obtained in THF solution from compound **5** and **6**, respectively with a four- or sixfold of $(Cy_3P)AuCl$ in the presence of a strong base KOH. Consequently, we believe that the solvent plays a crucial role in the preparation of alkynylmetal. In addition, complexes **11**–**14** with triphenylene as the core have been synthesized by similar preparation method (Scheme 2).

Spectroscopic Characterization

These star-shaped molecules are characterized by ^1H, ^{13}C, ^{31}P NMR, mass and IR spectroscopy and give satisfactory elemental analysis. The high symmetry of compound **1**, with twelve acetylenic groups and six silyl groups, is manifested by simple signals in the ^1H and ^{13}C NMR spectra. In the ^1H NMR spectrum of **1**, there is only one set of two doublet resonance at δ = 7.51 and 7.47 ppm with J_{H-H} = 8.5 Hz in the aromatic region. In addition to the ^{13}C NMR signals of the triisopropylsilyl group typically at δ = 18.7, 11.3 ppm, five signals (one for the benzene core and four for the C_6H_4 groups) are observed in the region of δ = 134–124 and four signals for the acetylide carbon atoms are observed at δ = 106.5, 99.4, 93.6 and 88.8 ppm indicating the C_6 symmetry. Mass spectra of star-shaped molecules with triisopropylsilyl groups can not be determined by traditional techniques such as FAB and EI. Therefore, MALDI-TOF technique is used to obtain the mass spectra of these compounds. MALDI-TOF mass spectra were obtained using DHB (2,5-dihydroxybenzoic acid) as matrix. The protonated molecular ion $[M + H]^+$ appeared as the parent ion in the spectra of compounds **1**–**4** and **11**.

The ^1H NMR spectrum of palladium complexes **7** shows only one set of two doublet resonance at δ = 7.48 and 7.21 ppm with $^3J_{H-H}$ = 8.2 Hz in the aromatic region and four broad resonances in the region of δ = 2.0–0.9 ppm are rationally assigned to the butyl protons on the $PnBu_3$ ligands. No signal for acetylenic proton was detected, eliminating the possibility of the existence of partially substituted molecules. In the ^{31}P NMR spectrum, only one singlet signal was observed at δ = 10.80 ppm. The ^{13}C resonances of the alkynyl carbon atoms bound to the palladium are at δ = 106.27 ppm with $^2J_{C-P}$ = 5.3 Hz and 101.62 $^2J_{C-P}$ = 15.6 Hz, respectively. Two singlet resonances of internal alkynyl carbon atoms are located at δ = 99.68 and 88.55 ppm. These data are consistent with other palladium acetylide complexes in the literature.[10a]

The ^{13}C NMR spectra of the gold complexes **9** and **10** display two doublets at δ = 140–139 ($^2J_{C-P}$ = 131 Hz) and δ = 103–104 ($^2J_{C-P}$ = 24 Hz) ppm, which are assigned to the α- and β-carbon atoms of the acetylide ligand, respectively.[17] The ^{31}P NMR spectra of **9** and **10** reveal singlet resonances at δ = 56.8 and 56.9 ppm, respectively, which slightly shift downfield from that of $Au(PCy_3)Cl$ at δ = 55.2 ppm.

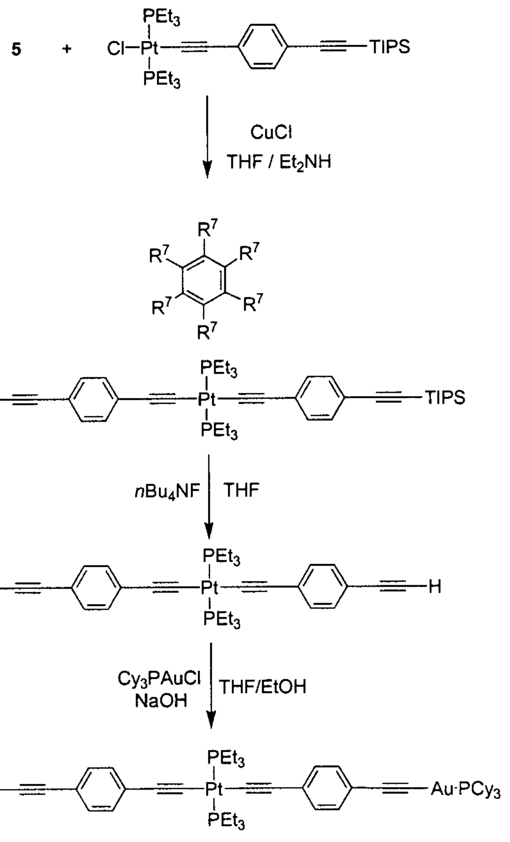
The IR spectra of all organic compounds containing silyl and terminal alkynyl groups show one stretching band at around 2190 cm^{-1} ($\nu_{C\equiv C}$) and terminal acetylenic ends (≡CH) near 3286 cm^{-1}. Additionally, after incorporating metal moieties, these compounds exhibit other stretching band at around 2090 cm^{-1}. It is probably due to π backbonding from metal centers to reduce the stretching frequency of the C≡C bond adjacent to the transition metal. With regard to the mass spectra of these metal acetylide complexes, **8** and **10** with four arms show parent ion $[M + H]^+$ consistent with their formulation in the FAB mass spectra. Nevertheless, metal acetylide complexes with six arms can not been detected by FAB or MALDI-TOF mass.

Heterometallic Polynuclear Complexes

Platinum acetylide complex **15** was prepared by the reaction of compound **A** and *cis*-$Pt(PEt_3)_2Cl_2$ in the presence of CuCl catalyst in Et_3N/toluene.[18] Subsequent reaction of **5** with excess of **15** in the presence of a CuCl catalyst in THF/diethylamine generated the pure complex **16**, which undergoes deprotection in the presence of tetrabutylammonium fluoride to afford complex **17** containing six terminal alkynes. The reaction of **17** with 6 equiv. of $(Cy_3P)AuCl$ in the presence of excess of KOH give the heterometallic complex **18** containing six gold and six platinum metal atoms (Scheme 3).

The ^{31}P NMR spectra of **16** and **17** show both a singlet resonance at δ = 11.78 and 11.80 ppm, respectively, indicative of highly symmetrical structure of the molecules. Platinum satellites with $^1J_{Pt-P}$ = 2359 Hz, which is characteristic of a *trans*-P–Pt–P configuration, are observed in the ^{31}P NMR spectrum.[19] In the ^1H NMR spectrum of **17**, four sets of coupled doublet resonances at δ = 7.45–7.17 ppm with J_{H-H} = 8.2 Hz are located in the aromatic region and the singlet resonance of the terminal alkyne protons is observed at δ = 3.09 ppm. In the IR spectra, the $\nu_{C\equiv C}$ stretching band appears at 2093, 2195 cm^{-1} and the absorption at 3286 cm^{-1} is assigned to the $\nu_{H-C\equiv}$ stretching vibration.

In the ^{31}P NMR spectrum of **18** incorporating gold moieties, the resonance at δ = 11.76 ppm (s, J_{Pt-P} = 2366 Hz) was almost consistent with that of complex **17**, and the singlet peak at δ = 56.91 ppm is assigned to the tricyclohexylphosphane of the gold acetylide moiety. In the ^1H NMR spectrum similar patterns with complex **17** are observed in the aromatic region. No signals for acetylenic proton are detected, eliminating the possibility of partial substitution. However, the mass spectra of these metal acetylide complexes can not obtained by FAB or MALDI mass technique.



Scheme 3.

Photophysical Properties

Table 1 summarizes the photophysical data of star-shaped molecules containing triisopropylsilyl group, palladium and platinum metal moieties. The emission spectra of these compounds are obtained by excitation at their longest wavelength with absorption maximums. The quantum yields were determined while the absorbance is set in the range of 0.1–0.2 to avoid the interference of reabsorption in determining the quantum yield. The wavelength at the intersection point of the absorption spectra of the sample and the reference is taken as the excitation wavelength in determining the quantum yield.

The electronic absorption spectra of triisopropylsilyl-substituted benzene system **1**–**4a** show that the absorption maximum (λ_{max}) for the lowest π–π* transition increases from 340 to 373 nm as the number of arms around the benzene core increases. The photophysical properties of the molecules presented in this report will likely arise from the extended π conjugation and enhanced electron delocalization of these star-shaped systems. The trend is consistent with the phenylethynyl-substituted benzene system[20] and is evidence of extended π conjugation through the benzene core. However, **4b** and **4c** show a shoulder at around 398–400 nm due to the electron-donation effect of the methyl group and the alkoxyl group, respectively. This phenomenon was observed for (1,4-diphenylethynyl-2,5-dialkoxy)-benzene.[21] The absorption band of compound **11** with triphenylene as the core displays much higher extinction coefficient with $2.9 \cdot 10^5\ dm^3 mol^{-1} cm^{-1}$ and a blue shift relative to that of compound **1** with benzene as the core. (Table 1) In general, the introduction of metal moieties makes absorption peaks (275–420 nm) shift to longer wavelength and displays higher extinction coefficient relative to that of **5** with terminal alkyne groups (247–392 nm) in THF. Much higher extinction coefficients of the absorption bands in complex **7** and **16** than their precursor complex, *trans*-$M(PEt_3)_2Cl_2$ (M = Pd, Pt),[22] and the close similarity of its absorption patterns and extinction coefficients with that of compound **1** and **5** are indicative of transitions of predominantly organic complex character. Spectroscopic studies on *trans*-$[L_2M(C{\equiv}CR)_2]$ (L = tertiary phosphane or stibane, M = Ni, Pd, Pt)[23] and trinuclear palladium or platinum acetylide complexes,[9d,10] in which the absorption bands at ca. 300–370 nm were assigned as metal-to-alkynyl MLCT transitions have been reported. It is likely that the electronic absorption bands of these metal acetylide complexes would also involve metal-to-alkynyl MLCT character.

Table 1. Photophysical properties.

Compounds	Absorption spectra λ_{max} [nm] ($10^{-4}\ \varepsilon/\text{M}^{-1}\text{cm}^{-1}$)	Emission spectra λ_{max} [nm]	Quantum yield Φ_{em}
1	294 (4.75), 373[a] (16.01), 399 sh (8.04)	466	0.11
2	288 (3.04), 354[a] (12.36)	460	0.51
3	288 (2.68), 355[a] (12.09)	438	0.46
4a	340[a] (12.54), 374 sh (1.25)	411	0.92
4b	247 (1.11), 339[a] (11.96), 398 (1.57)	417	0.83
4c	263 (2.20), 336[a] (11.69), 400 (3.02)	470	0.52
5	280 (1.24), 366[a] (11.95), 392 sh (5.64)	461	0.17
7	275 (6.28), 307 (4.45), 398[a] (13.76), 420 (9.36)	480	0.14
9	305 (2.93), 388[a] (8.55)	475	0.34
11	268 (3.83), 325 sh (8.79), 361[a] (28.97), 384 sh (19.01)	432	0.21
12	261 sh (1.92), 320 sh (5.56), 356[a] (20.13), 378 sh (12.04)	429	0.29
13	277 (13.66), 312 sh (7.22), 378[a] (35.16), 400 sh (28.42)	439	0.09
14	372[a] (36.72), 395 sh (25.12)	436	0.52
16	300 (20.78), 334 (23.55), 407[a] (30.08)	486	0.06
17	297 (19.90), 333 (24.36), 392[a] (28.62)	487	0.05
18	344 (25.90), 409[a] (25.00)	487	–[b]

[a] Excitation wavelength for the emission spectra. [b] Not observed with very low quantum effciency.

As in the case for the absorption spectra, the emission spectra of triisopropylsilyl-substituted benzene system **1**–**4** also display an analogous red shift as the number of arms increases. Compound **4c** shows the emission data with red shift about 50–60 nm in comparison to those of **4a** and **4b** as a result of incorporating the electron-donating alkoxy groups. Similar to the trend of absorption spectra, the emission spectrum of **11** with triphenylene core is blue-shifted relative to those with benzene core. Compound **4a** shows excellent fluorescence intensity with the highest quantum yield ($\Phi_{em} \approx 0.92$). Due to incorporating the two electron-donating alkoxy groups, complex **4c** show the emission data with red shift about 60 nm and lower quantum yield ($\Phi_{em} \approx 0.52$) in comparison to those of **4a** and **4b**.

On the whole, with incorporation of metal into multiple alkynyl compounds, the emission spectra of metal complexes show a red shift relative to those of alkynyl and silyl compounds. The tendency of wavelength shifts in emission spectra is similar to that of their corresponding absorption spectra due to the same electronic factors.[10b] For example, after incorporation of palladium moieties, the low quantum yield for **13** with triphenylene as a core decreases to 0.09 relative to that for **5** with 0.29. In addition, a red shift in the emission energies is observed for metal complexes on going from the palladium complexes to the platinum analogs; this is indicative of the involvement of the triplet metal-to-alkynyl MLCT character in emissive states.[10a] For the platinum complexes, the emission spectra of **16**–**18** show nearly the same band at 487 nm. Accordingly, the introduction of six electron-rich Cy_3PAu moieties or triisopropylsilyl groups into the platinum acetylide complex seems to have almost no influence on the emission energy. Complexes **16** and **17** display lower quantum efficiency ($\Phi_{em} \approx 0.05$) than that of **7** with palladium moieties ($\Phi_{em} \approx 0.14$). Moreover, when the terminal alkynyl protons of complex **17** are substituted by gold moieties to form complex **18**, the quantum efficiency (ca. 0.005) is even lower. However, gold complex **14** show the highest quantum efficiency ($\Phi_{em} \approx 0.52$) in these metal acetylide complexes.

Conclusions

We use benzene and triphenylene as cores to synthesize a series of star-shaped molecules with extended π conjugative system by Sonogashira reaction. Palladium acetylide complexes can be obtained by appropriate incorporation of the $(PR_3)_2PdCl$ moiety. The photophysical data of metal acetylide complexes show that introduction of electron-rich palladium or triisopropyl groups makes absorption peaks shift to longer wavelength and higher extinction coefficients relative to that of organic molecules. However, the quantum yields of palladium complexes are decreased in comparison with free organic molecules. In organic molecules, the blue-emitting compounds **4a** and **4b** show excellent fluorescence intensity with high quantum yield (Φ_{em} **4a** = 0.92). In addition, gold acetylide complexes can also be obtained from terminal alkynyl ligands with $(Cy_3P)AuCl$ in the presence of appropriate base. Heterometallic polynuclear complex **18** containing Pt and Au metals has also been prepared.

Experimental Section

General Procedures: All manipulations were performed under nitrogen using vacuum-line, dry box, and standard Schlenk techniques. CH_2Cl_2 was distilled from CaH_2 and diethyl ether and THF from Na/diphenyl ketyl. All other solvents and reagents were of reagent grade and were used as received. NMR spectra were recorded with Bruker AC-300 and DMX-500 FT-NMR spectrometers at room temperature (unless states otherwise) and are reported in units of δ with residual protons in the solvents as a standard ($CDCl_3$, δ = 7.24 ppm; CD_2Cl_2, δ = 5.32; $[D_8]THF$, δ = 1.73; 3.58). FAB mass spectra were recorded with a JEOL SX-102A spectrometer. MALDI-mass spectra were collected Voyager DE-PRO (Applied Biosystem, Houston, USA) equipped with a nitrogen laser (337 nm) and operated in the delayed extraction reflector mode. 1-Ethynyl-4-[2-(triisopropylsilyl)ethynyl]benzene, (**A**) was prepared according to the literature methods[13] as were $Au(PCy_3)Cl$[24] and 2,3,6,7,10,11-hexabromotriphenylene.[25] The complex *trans*-dichlorobis(triethylphosphane)palladium(II) was obtained from Aldrich Chemical Co. Absorption spectra were obtained using HP 8453 diode array spectrophotometer. Emission spectra were taken using Hitachi F-4500 luminescence spectrometer. Luminescence quantum yield (Φ_{em}) were calculated relative to quinine sulfate dihydrate in 1 N H_2SO_4(aq) (Φ_{em} = 0.52).[26] Elemental analyses were carried with Perkin–Elmer 2400 CHN elemental analyzer.

Synthesis of 1,2,3,4,5-Pentabromo-6-dodecyloxybenzene (B): 2-Butanone (20 mL) was added to a 50-mL Schlenk flask containing pentabromophenol (977 mg, 2 mmol), 1-bromododecane (700 mg, 2.8 mmol) and K_2CO_3 (553 mg, 4 mmol). The mixture was heated at reflux for 24 h. After cooling to room temperature, the solvent was removed under vacuum. The residue was extracted with EtOAc (2×40 mL), and the solution was dried with $MgSO_4$. After filtration, the organic solution was concentrated under reduced pressure. Column chromatography (silica gel, hexane/EtOAc, 9:1) of the residue removed excess 1-bromododecane and gave 1,2,3,4,5-pentabromo-6-dodecyloxybenzene as a white powder in 60% yield (788 mg) by the eluent with hexane/EtOAc (1:1). Spectroscopic data of **B**: ^{1}H NMR ($CDCl_3$): δ = 3.97 (t, $^3J_{H-H}$ = 6.6 Hz, 2 H, OCH_2), 1.90–1.80 (m, 2 H, CH_2), 1.54–1.44 (m, 18 H, CH_2), 0.86 (t, $^3J_{H-H}$ = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 154.6, 128.3, 124.4, 121.9 (Ph), 73.7 (OCH_2), 31.9, 29.9, 29.6, 29.6, 29.6, 29.4, 29.3, 25.8, 22.7 (CH_2), 14.1 (CH_3) ppm. MS (FAB): *m/z* = 652 [M^+, Br = 79.9]. $C_{18}H_{20}Br_5O$ (651.87): calcd. C 33.16, H 3.09; found C 33.28, H 3.07.

Synthesis of 1,2,4,5-Tetrabromo-3,6-dibutoxybenzene (C): Synthesis of **C** followed the same procedure as that used for the preparation of **B**. Their spectroscopic data are the same as that of literature.[27]

Synthesis of 1,2,4,5-Tetrabromo-3,6-dodecyloxybenzene (D): Synthesis of **D** followed the same procedure as that used for the preparation of **B**, with 77% yield. Spectroscopic data of **D**: ^{1}H NMR ($CDCl_3$): δ = 3.94 (t, $^3J_{H-H}$ = 6.5 Hz, 4 H, OCH_2), 1.89–1.80 (m, 4 H, CH_2), 1.54–1.25 (m, 36 H, CH_2), 0.86 (t, $^3J_{H-H}$ = 6.5 Hz, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 152.0 (C-2), 121.4 (C1), 73.6 (OCH_2), 31.9, 29.9, 29.7, 29.6, 29.4, 25.8, 22.7 (CH_2), 14.1 (CH_3) ppm. $C_{30}H_{50}Br_4O_2$ (762.33): calcd. C 47.27, H 6.61; found C 47.30, H, 6.58.

Preparation of Compound 1: Compound **A** (2.82 g, 10 mmol) was added to a stirred suspension of hexabromobenzene (0.732 g, 1.33 mmol), $PdCl_2(PPh_3)_2$ (93 mg, 0.13 mmol), CuI (25 mg, 0.13 mmol), and PPh_3 (174 mg, 0.67 mmol) in Et_3N (60 mL) under nitrogen. The mixture was stirred at 100 °C for 48 h. After cooling to room temperature, the solvent was removed under vacuum and the resulting residue was washed with hexanes and H_2O/EtOH (1:2) to give the yellow product (1.96 g, 84% yield). Spectroscopic data of **1**: ^1H NMR ($CDCl_3$): $\delta = 7.51$ (d, $^3J_{H-H} = 8.5$ Hz, 12 H, C_6H_4), 7.47 (d, $^3J_{H-H} = 8.5$ Hz, 12 H, C_6H_4), 1.13 (m, 126 H, TIPS) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 132.2$, 131.5, 127.4, 124.2, 122.7 (Ph), 106.5, 99.4, 93.6, 88.8 (C=C), 18.7 (CH_3), 11.3 (CH) ppm. MALDI-TOF-MS (DHB): $m/z = 1761.23$ [$M^+ + 1$]. IR (KBr, cm^{-1}): $\tilde{\nu} = 2144$ ($\nu_{C\equiv C}$). $C_{120}H_{150}Si_6$ (1760.99): calcd. C 81.85, H 8.59; Found C 81.90, H 8.53.

Preparation of Compound 2: Compound **A** (338 mg, 1.2 mmol) was added to a stirred suspension of **B** (131 mg, 0.2 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol), CuI (3.8 mg, 0.02 mmol), and PPh_3 (14 mg, 0.02 mmol) in Et_3N (15 mL) under nitrogen. The mixture was stirred at 100 °C for 48 h. After cooling to room temperature, the solvent was removed and the resulting residue was extracted with THF (3 × 10 mL). The solvent was evaporated and the residue was passed through silica gel using hexanes as the eluent to remove the excess **A**. The crude product was eluted with EtOAc/hexanes (1:1). The solvent was removed under vacuum and the residue washed with EtOH (20 mL) to give bright-yellow solid **2**. (229 mg, 69% yield). Spectroscopic data of **2**: ^1H NMR ($CDCl_3$): $\delta = 7.51$–7.44 (m, 20 H, Ph), 4.34 (t, $^3J_{H-H} = 6.3$ Hz, 2 H, OCH_2), 1.94–1.84 (m, 2 H, CH_2), 1.55–1.22 (m, 18 H, CH_2), 1.12 (m, 105 H, TIPS), 0.86 (t, $^3J_{H-H} = 6.6$ Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 160.7$, 132.2, 132.1, 131.5, 131.3, 128.9, 124.2, 124.0, 123.9, 123.8, 123.1, 122.8, 122.7, 120.1 (Ph), 106.5, 99.4, 99.3, 97.1, 93.5, 93.4, 93.3, 88.9, 88.5, 86.1 (C=C), 75.1 (OCH_2), 31.9, 30.6, 29.6, 29.3, 26.3, 22.67 (CH_2), 18.7 (CH_3), 14.1 (CH_3), 11.3 (CH) ppm. MALDI-TOF-MS (DHB): $m/z = 1665.95$ [$M^+ + 1$]. IR (KBr, cm^{-1}): $\tilde{\nu} = 2144$ ($\nu_{C\equiv C}$). $C_{113}H_{150}OSi_5$ (1644.83): calcd. C 81.52, H, 9.08; found C 81.70, H 9.01.

Preparation of Compound 3: Compound **A** (451 mg, 1.2 mmol) was added to a stirred suspension of 2,3,4,5,6-pentabromotoluene (97 mg, 0.2 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol), CuI (3.8 mg, 0.02 mmol), and PPh_3 (14 mg, 0.02 mmol) in Et_3N (15 mL) under nitrogen. The mixture was stirred at 100 °C for 48 h. After cooling to room temperature, the solvent was removed under vacuum and the resulting residue was extracted with THF (3 × 10 mL). The solvent was removed and the residue was passed through silica gel using hexane as the eluent to remove excess **A**. The desired product was then eluted with EtOAc/hexane (1:1). The solvent was removed and the residue was washed with EtOH (20 mL) to give bright-yellow solid **3** (188 mg, 63% yield). Spectroscopic data of **3**: ^1H NMR ($CDCl_3$): $\delta = 7.51$–7.44 (m, 20 H, Ph), 2.74 (s, 3 H, CH_3), 1.12 (m, 105 H, TIPS) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 142.3$, 132.1, 131.4, 127.4, 125.9, 125.5, 124.0, 123.8, 123.0, 122.9, 122.8(Ph), 106.6, 99.2, 98.8, 93.4, 93.2, 89.5, 88.8, 88.5 (C=C), 20.2 (CH_3), 18.7 (CH_3), 11.3 (CH) ppm. MALDI-TOF-MS (DHB): m/z = 1495.0 [M^+]. IR (KBr, cm^{-1}): $\tilde{\nu} = 2144$ ($\nu_{C\equiv C}$). $C_{102}H_{128}Si_5$ (1494.54): calcd. C 81.97, H 8.63; found C 81.75, H 8.53.

Preparation of Compound 4a: A mixture of tetrabromobenzene (157 mg, 0.4 mmol) and **A** (496 mg, 1.76 mmol) in 30 mL of Et_3N was stirred in the presence of $PdCl_2(PPh_3)_2$ (22 mg, 0.032 mmol) and CuI (6 mg, 0.032 mmol) as catalyst at 100 °C for 36 h. After cooling to room temperature, the solvent was removed and excess **A** was removed by washing with *n*-hexane (2 × 10 mL) and ethyl alcohol (2 × 10 mL) to give the product as yellow solid (317 mg, 66% yield). Spectroscopic data of **4a**: ^1H NMR ($CDCl_3$): $\delta = 7.73$ (s, 2 H, Ph), 7.46 (s, 16 H, Ph), 1.12 (m, 84 H, TIPS) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 134.9$, 132.1, 131.4, 125.3, 124.0, 122.6 (Ph), 106.5, 99.1, 93.3, 89.1 (C=C), 18.7 (CH_3), 14.1 (CH_3), 11.3 (CH) ppm. IR (KBr, cm^{-1}): $\tilde{\nu} = 2144$ ($\nu_{C\equiv C}$). MS (MALDI-TOF): m/z = 1199.7 [M^+]. $C_{82}H_{102}Si_4$ (1200.03): calcd. C 82.07, H 8.57; found C 82.30, H, 8.66.

Preparation of Compound 4b: Compound **A** (496 mg, 1.76 mmol) was added to a stirred suspension of 2,3,5,6-tretabromo-*p*-xylene (169 mg, 0.4 mmol), $PdCl_2(PPh_3)_2$ (22 mg, 0.032 mmol), CuI (6 mg, 0.032 mmol), and PPh_3 (14 mg, 0.02 mmol) in Et_3N (30 mL) under nitrogen. The mixture was heated to reflux for 36 h. After cooling to room temperature, the solvent was removed and the resulting residue was extracted with THF (3 × 10 mL). The solvent was removed and the residue was passed through a silica gel column using *n*-hexane as the eluent to remove excess **A**. The product **4b** was eluted with THF/*n*-hexane (1:2). The solvent was removed and the residue washed with EtOH (20 mL) to give green-yellow solid **4b** in 51% yield (251 mg) Spectroscopic data of **4b**: ^1H NMR ($CDCl_3$): $\delta = 7.47$ (d, $^3J_{H-H} = 8.6$ Hz, 8 H, Ph), 7.44 (d, $^3J_{H-H} = 8.6$ Hz, 8 H, Ph), 2.70 (s, 6 H, CH_3), 1.12 (m, 84 H, TIPS) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 139.9$, 132.1, 131.3, 125.4, 123.8, 123.0 (Ph), 106.6, 98.7, 93.2, 89.2 (C=C), 19.8 (CH_3), 18.7 (CH_3), 11.3 (CH) ppm. IR (KBr, cm^{-1}): $\tilde{\nu} = 2144$ ($\nu_{C\equiv C}$). MS (MALDI-TOF): $m/z = 1227.7$ [M^+]. $C_{84}H_{106}Si_4$ (1228.08): calcd. C 82.15, H 8.07; found C 82.33, H 8.15.

Preparation of Compound 4c: Compound **A** (271 mg, 0.2 mmol) was added to a stirred suspension of 1,2,4,5-tetrabomo-3,6-dibutoxybenzene (108 mg, 0.2 mmol), $PdCl_2(PPh_3)_2$ (11 mg, 0.016 mmol), CuI (3 mg, 0.016 mmol), and PPh_3 (21 mg, 0.08 mmol) in THF/NEt_3 (30 mL, 1:1) under nitrogen. The mixture was stirred at 100 °C for 36 h. After cooling to room temperature, the solvent was removed and the resulting residue was extracted with *n*-hexane (3 × 20 mL). The solvent was removed and the residue was passed through a silica gel packed column using *n*-hexane as the eluent to remove excess **A**. Elution with THF/*n*-hexane gave yellow solid compound **4c** (180 mg, 67% yield). Spectroscopic data of **4c**: ^1H NMR ($CDCl_3$): $\delta = 7.47$ (s, 16 H, Ph), 4.27 (t, $^3J_{H-H}$ = 6.6 Hz, 4 H, OCH_2), 1.92–1.83 (m, 4 H, CH_2), 1.68–1.56 (m, 4 H, CH_2), 1.12 (m, 84 H, TIPS), 0.86 (t, $J = 6.3$ Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 157.4$, 132.1, 131.3, 123.9, 122.9, 121.1 (Ph), 106.5, 99.1, 93.3, 86.3 (C=C), 74.6 (OCH_2), 32.5, 19.5 (CH_2), 18.7 (CH_3), 14.0 (CH_3), 11.3 (CH) ppm. IR (KBr, cm^{-1}): $\tilde{\nu} = 2144$ ($\nu_{C\equiv C}$). MS (MALDI-TOF): $m/z = 1343.9$ [M^+]. $C_{90}H_{118}O_2Si_4$ (1344.24): calcd. C 80.41, H 8.85; found C 80.73, H 8.91.

Preparation of Compound 4d: Synthesis of **4d** followed the same procedure as that used for the preparation of **4c**, with 72% yield. Spectroscopic data of **4d**: ^1H NMR ($CDCl_3$): $\delta = 7.45$ (s, 16 H, Ph), 4.25 (t, $^3J_{H-H} = 6.3$ Hz, 4 H), 1.93–1.83 (m, 4 H, CH_2), 1.61–1.21 (m, 18 H, CH_2), 1.12 (m, 84 H, TIPS), 0.86 (t, $^3J_{H-H} = 6.6$ Hz, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 157.4$, 132.1, 131.3, 123.9, 122.9, 121.1 (Ph), 106.5, 99.1, 93.3, 86.3 (C=C), 75.0 (OCH_2), 31.9, 30.5, 29.6, 29.3, 26.4, 22.7(CH_2), 18.7 (CH_3), 14.1 (CH_3), 11.3 (CH) ppm. MS (MALDI-TOF): m/z = 1568.8 [M^+]. $C_{106}H_{150}O_2Si_4$ (1568.67): calcd. C 81.16, H, 9.64; found C 81.34 H 9.74.

Preparation of Compound 5: A mixture of **1** (1.96 g, 1.11 mmol) in THF (20 mL) and nBu_4NF (1 M THF solution, 13.32 mL) was stirred at 45 °C overnight. The solvent was removed and EtOH (50 mL) was added to give yellow solid which was filtered and dried under vacuum to give **5** (907 mg, 99% yield). Spectroscopic data of **5**: ^1H NMR ([D_8]THF): $\delta = 7.62$ (d, $^3J_{H-H} = 8.3$ Hz, 12 H, C_6H_4), 7.52 (d, $^3J_{H-H} = 8.3$ Hz, 12 H, C_6H_4), 3.77 (s, 6 H, C=CH) ppm. ^{13}C NMR ([D_8]THF): $\delta = 133.3$, 132.8, 128.6, 124.7, 124.0

(Ph), 100.5, 89.4, 83.9, 81.7 (C=C) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3286 ($\nu_{H-C\equiv}$), 2195 ($\nu_{C\equiv C}$). Mass (FAB): *m/z* = 823 [M$^+$ + 1]. HRMS cacld for $C_{66}H_{30}$: 822.2347; found 822.2352. $C_{66}H_{30}$ (822.94): C 96.33, H 3.67; found C 96.37, H 3.66.

Preparation of Compound 6a: A mixture of **4a** (340 mg, 0.28 mmol) and *n*Bu_4NF (1.13 mL, 1 M in THF) in THF (10 mL) was stirred at room temperature for 1 h. The solvent was removed and EtOH (20 mL) was added to give yellow solid which was filtered and dried under vacuum to give **6a** (160 mg, 99% yield). Spectroscopic data of **6a**: ^{1}H NMR ([D$_8$]THF): δ = 7.82 (s, 2 H, Ph), 7.56 (d, $^3J_{H-H}$ = 8.1 Hz, 8 H, C_6H_4), 7.50 (d, $^3J_{H-H}$ = 8.1 Hz, 8 H, C_6H_4), 3.72 (s, 4 H, C≡C*H*) ppm. ^{13}C NMR ([D$_8$]THF): δ = 136.1, 133.2, 132.6, 126.5, 124.4, 124.0 (Ph), 96.2, 89.9, 83.9, 81.4 (C≡C) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3286 ($\nu_{H-C\equiv}$), 2195 ($\nu_{C\equiv C}$). Mass (FAB): *m/z* = 574.2 [M$^+$]. HRMS cacld for $C_{46}H_{22}$: 574.1722; found 574.1719. $C_{46}H_{22}$ (574.67): calcd. C 96.14, H 3.86; found C 96.21, H 3.86.

Preparation of Compound 6c: A mixture of **6c** (269 mg, 0.2 mmol) and *n*Bu_4NF (0.8 mL, 1 M in THF) in THF (10 mL) was stirred at room temperature for 1 h. The solvent was removed and EtOH (20 mL) was added to give yellow solid and dried under vacuum (141 mg, 98% yield). Spectroscopic data of **6c**: ^{1}H NMR ($CDCl_3$): δ = 7.62 (d, $^3J_{H-H}$ = 8.5 Hz, 12 H, C_6H_4), 7.52 (d, $^3J_{H-H}$ = 8.5 Hz, 12 H, C_6H_4), 4.27 (t, $^3J_{H-H}$ = 6.3 Hz, 4 H, OCH_2), 3.19 (s, 4 H, C=CH), 1.89–1.83 (m, 4 H, CH_2), 1.64–1.54 (m, 4 H, CH_2), 0.95 (t, $^3J_{H-H}$ = 6.6 Hz, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 157.4, 132.2, 131.4, 123.5, 122.5, 121.1 (Ph), 98.8, 86.4, 83.1, 79.3 (C=C), 74.7 (OCH_2), 32.5, 19.5 (CH_2), 14.0 (CH_3) ppm. IR (KBr,cm^{-1}): $\tilde{\nu}$ = 3276 ($\nu_{H-C\equiv}$), 2195 ($\nu_{C\equiv C}$). Mass (FAB): *m/z* = 718 [M$^+$]. HRMS calcd. for $C_{54}H_{38}O_2$: 718.2872; found 718.2877. $C_{54}H_{38}O_2$ (718.88): calcd. C 90.22, H 5.33; found C 90.37, H 5.44.

Preparation of Compound 7a: *trans*-$Pd(PBu_3)_2Cl_2$ (174 mg, 0.3 mmol) was dissolved in $HNEt_2$ (10 mL) containing CuI (2 mg). Compound **5** (41 mg, 0.05 mmol) in THF (10 mL) was added and the reaction mixture stirred for 8 h at room temperature under nitrogen. The solvent was then removed under reduced pressure. The residue was extracted with diethyl ether/*n*-hexane (1:1) and the solution was dried with anhydrous $MgSO_4$ followed by filtration with celite. The filtrate was then concentrated under reduced pressure and passed through a short column of basic aluminum oxide using petroleum ether (boiling range 40–65 °C) as the eluent to remove excess *trans*-$Pd(PBu_3)_2Cl_2$. The hexanuclear complex **7a** was eluted with EtOAc and the solvent was removed by rotary evaporator to give pale yellow solid **7a** (162 mg, 79% yield). Spectroscopic data of **7a**: ^{31}P NMR ($CDCl_3$): δ = 10.80. ^{1}H NMR ($CDCl_3$): δ = 7.48 (d, $^3J_{H-H}$ = 8.2 Hz, 2 H, Ph), 7.21 (d, $^3J_{H-H}$ = 8.2 Hz, 2 H, Ph), 1.94–1.88 (m, 6 H, CH_2), 1.57–1.37 (m, 12 H, CH_2), 0.91 (t, $^3J_{H-H}$ = 7.2 Hz, 9 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 131.5, 130.6, 128.7, 127.1, 119.9 (Ph), 106.3 (t, $^3J_{C-P}$ = 5.3 Hz, Cβ), 101.6 (t, $^2J_{C-P}$ = 15.6 Hz, Cα), 99.6, 88.3 (C≡C), 26.4 (CH_2), 24.4 (t, $^2J_{C-P}$ = 6.6 Hz, CH_2), 22.9 (t, J_{C-P} = 13.6 Hz, CH_2), 13.8 (CH_3) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2195 and 2103 ($\nu_{C\equiv C}$). $C_{210}H_{348}Cl_6P_{12}Pd_6$ (4095.93): calcd. C 90.22, H 5.33; found C 90.37, H 5.44.

Preparation of Compound 7b: Synthesis of **7b** followed the same procedure as that used for the preparation of **7a** in 73% yield. Spectroscopic data of **7b**: ^{31}P NMR (CD_2Cl_2): δ = 18.95. ^{1}H NMR (CD_2Cl_2): δ = 7.51 (d, $^3J_{H-H}$ = 8.2 Hz, 12 H, C_6H_4), 7.27 (d, $^3J_{H-H}$ = 8.2 Hz, 12 H, C_6H_4), 2.02–1.93 (m, 72 H, CH_2), 1.26–1.16 (m, 108 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 132.10, 131.40, 129.46, 127.62, 120.20 (Ph), 107.24 (t, $^3J_{C-P}$ = 5.6 Hz, Cβ), 101.72 (t, $^2J_{P-C}$ = 15.8 Hz, Cα), 100.39, 88.62 (C≡C), 16.00 (t, J_{C-P} = 14.0 Hz, CH_2), 8.70 (CH_3) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2195, 2103 ($\nu_{C\equiv C}$). $C_{138}H_{204}Cl_6P_{12}Pd_6$ (3086.02): calcd. C 53.71, H 6.66; found C 53.90, H 6.61.

Preparation of Complex 8a: A mixture of *trans*-$Pd(PEt_3)_2Cl_2$ (125 mg, 0.30 mmol), **6a** (43 mg, 0.075 mmol) and CuCl (2 mg) was dissolved in THF (10 mL) then Et_2NH (5 mL) was added. The reaction mixture stirred overnight at room temperature under nitrogen. The solvent was then removed under reduced pressure. After the residue was extracted with *n*-hexane, the solvent was then concentrated under reduced pressure. The residues was passed through a short column of basic aluminum oxide using CH_2Cl_2/petroleum ether (boiling range 40–65 °C), 1:1, as the eluent to remove excess *trans*-$Pd(PEt_3)_2Cl_2$. The tetranuclear complex **8a** was eluted with THF and the solvent was removed by a rotary evaporator to give complex **8a** as a yellow solid (136 mg, 87% yield). Spectroscopic data of **8a**: ^{31}P NMR ($CDCl_3$): δ = 18.86 ppm. ^{1}H NMR ($CDCl_3$): δ = 7.70 (s, 2 H, Ph), 7.40 (d, $^3J_{H-H}$ = 8.4 Hz, 8 H, C_6H_4), 7.21 (d, $^3J_{H-H}$ = 8.4 Hz, 8 H, C_6H_4), 2.01–1.92 (m, 48 H, CH_2), 1.25–1.13 (m, 72 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 134.8, 131.5, 130.7, 128.3, 125.1, 119.8 (Ph), 106.8 (t, $^3J_{C-P}$ = 5.6 Hz, Cβ), 99.8 (t, $^2J_{C-P}$ = 15.8 Hz, Cα), 95.8, 88.4 (C≡C), 15.5 (t, J_{C-P} = 14.0 Hz, CH_2), 8.3 (CH_3) ppm. Mass (FAB): *m/z* = 2081 [M$^+$, Cl = 35]. $C_{94}H_{138}Cl_4P_8Pd_4$ (2083.38): calcd. C 54.19, H 6.68; found C 54.00, H 6.73.

Preparation of Complex 8c: Et_2NH (5 mL) was added to a mixture of *trans*-$Pd(PEt_3)_2Cl_2$ (83 mg, 0.100 mmol), **6c** (36 mg, 0.025 mmol) and CuCl (1 mg) dissolved in THF (5 mL). The reaction mixture was stirred overnight at room temperature under nitrogen. The solvent was then removed under reduced pressure. The residue was passed through a short column of basic aluminum oxide using CH_2Cl_2/petroleum ether (boiling range 40–65 °C), 1:1, as the eluent to remove excess *trans*-$Pd(PEt_3)_2Cl_2$. The tetranuclear complex **8c** was eluted with THF and the solvent was removed by rotary evaporator to give complex **8c** as orange solid. (35 mg, 62% yield). Spectroscopic data of **8c**: ^{31}P NMR ($CDCl_3$): δ = 18.86 ppm. ^{1}H NMR ($CDCl_3$): δ = 7.41 (d, *J* = 8.2 Hz, 8 H, C_6H_4), 7.21 (d, $^3J_{H-H}$ = 8.2 Hz, 8 H, C_6H_4), 4.24 (t, $^3J_{H-H}$ = 6.3 Hz, 4 H, OCH_2), 2.01–1.91 (m, 48 H, CH_2), 1.88–1.83 (m, 4 H, CH_2), 1.64–1.57 (m, 4 H, CH_2), 1.25–1.13 (m, 72 H, CH_2), 0.95 (t, *J* = 6.6 Hz, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 157.2 (O–*C*, C_6H_4), 131.3, 130.7, 128.2, 120.8, 120.1 (Ph), 106.7 (t, $^3J_{C-P}$ = 5.6 Hz, Cβ), 99.7 (t, $^2J_{C-P}$ = 14.3 Hz, Cα), 99.8, 85.8 (C≡C), 74.4 (OCH_2), 32.5, 19.5 (CH_2), 15.4 (t, J_{C-P} = 14.0 Hz, CH_2), 14.0 (CH_3), 8.4 (s, CH_3) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2195, 2103 ($\nu_{C\equiv C}$). Mass (FAB): *m/z* = 2227 [M$^+$, Cl = 35.45]. $C_{102}H_{154}Cl_4O_2P_8Pd_4$ (2227.59): calcd. C 55.00, H 6.97; found C 55.31, H 6.79.

Preparation of Complex 9a: A mixture of **5** (41 mg, 0.05 mmol), NaOH (36 mg, 0.9 mmol) dissolved in EtOH (2 mL) and $Au(PCy_3)Cl$ (154 mg, 0.3 mmol) dissolved in THF (10 mL) was stirred at room temperature under nitrogen for 3 h. The solvent was then removed, and the residue was washed with EtOH/H_2O (1:1, 10 mL) and acetone to give the yellow solid **9a** (153 mg, 83% yield). Spectroscopic data of **9a**: ^{31}P NMR ($CDCl_3$): δ = 56.81 ppm. ^{1}H NMR ($CDCl_3$): δ = 7.47 (d, $^3J_{H-H}$ = 8.7 Hz, 12 H, C_6H_4), 7.43 (d, $^3J_{H-H}$ = 8.7 Hz, 12 H, C_6H_4), 2.01–1.24 (m, 180 H, P*Cy*$_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 139.9 (d, $^2J_{P-C}$ = 131.2 Hz, C_α (Au*C*≡C)), 132.3, 131.4, 127.2, 125.9, 121.0 (Ph), 103.5 (d, $^3J_{P-C}$ = 24.5 Hz, C_β, (AuC≡*C*)), 99.7, 88.6, (C≡C), 33.2 (d, J_{P-C} = 24.5 Hz, *Cy*$_3$P), 30.7 (s, Cy$_3$P), 27.7 (d, $^2J_{P-C}$ = 11.8 Hz, Cy$_3$P), 25.9 (s, *Cy*$_3$P) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2195, 2103 ($\nu_{C\equiv C}$). $C_{174}H_{222}Au_6P_6$ (3681.27): calcd. C 56.77, H 6.08; found C 56.91, H 6.21.

Preparation of Complex 10c: A mixture of **6c** (36 mg, 0.05 mmol), NaOH (8 mg, 2 mmol) dissolved in EtOH (1.2 mL) and Au-

$\mathrm{(PCy_3)Cl}$ (103 mg, 0.2 mmol) dissolved in THF (10 mL) was stirred at room temperature under nitrogen for 5 h. The solvent was removed under vacuum then the residue was washed with $\mathrm{EtOH/H_2O}$ (1:1, 10 mL) to give a yellow solid identified as **10c** (106 mg, 81% yield). Spectroscopic data of **10c**: ^{31}P NMR ($\mathrm{CDCl_3}$): δ = 56.88. ^{1}H NMR ($\mathrm{CDCl_3}$): δ = 7.41 (d, $^{3}J_{\mathrm{H-H}}$ = 8.4 Hz, 8 H, $\mathrm{C_6H_4}$), 7.21 (d, $^{3}J_{\mathrm{H-H}}$ = 8.4 Hz, 8 H, $\mathrm{C_6H_4}$), 4.22 (t, $^{3}J_{\mathrm{H-H}}$ = 6.3 Hz, 4 H, $\mathrm{OCH_2}$), 2.05–1.19 (m, 128 H, $\mathrm{CH_2}$, $\mathrm{Cy_3P}$), 0.91 (t, $^{3}J_{\mathrm{H-H}}$ = 6.6 Hz, 6 H, $\mathrm{CH_3}$) ppm. ^{13}C NMR ($\mathrm{CDCl_3}$): δ = 157.2 (Ph), 139.8 (d, $^{2}J_{\mathrm{C-P}}$ = 131.3 Hz, Au*C*≡C), 132.3, 131.2, 125.7, 121.2, 120.9 (Ph), 103.3 (d, $^{2}J_{\mathrm{C-P}}$ = 23.8 Hz, AuC≡*C*), 99.5, 85.8 (C≡C), 74.4 ($\mathrm{OCH_2}$), 33.2 (d, $^{2}J_{\mathrm{C-P}}$ = 27.8 Hz, Cy), 32.5 ($\mathrm{CH_2}$), 27.1 (d, $^{2}J_{\mathrm{C-P}}$ = 11.7 Hz, Cy), 25.9 (s, Cy), 19.5 ($\mathrm{CH_2}$), 13.9 ($\mathrm{CH_3}$) ppm. Mass (FAB): *m*/*z* = 2624.1 [M$^+$, Au = 197]. $\mathrm{C_{126}H_{166}Au_4O_2P_4}$ (2624.43): calcd. C 57.66, H 6.38; found: C 56.88, H 6.31.

Preparation of Compound 11: Compound **A** (2.83 g, 7.5 mmol) was added to a stirred suspension of 2,3,6,7,10,11-hexabromotriphenylene (0.702 g, 1 mmol), $\mathrm{PdCl_2(PPh_3)_2}$ (70 mg, 0.1 mmol), CuI (19 mg, 0.1 mmol), and $\mathrm{PPh_3}$ (131 mg, 0.57 mmol) in $\mathrm{THF/Et_3N}$ (50 mL, 1:1) under nitrogen. The mixture was stirred at 100 °C for 48 h. After cooling to room temperature, the solvent was removed and the resulting residue was extracted with THF (3 × 10 mL). The solvent was removed under vacuum and excess **A** was washed with hexanes (2 × 10 mL) and ethyl alcohol (2 × 10 mL) to give a yellow solid (1.74 g, 85%). Spectroscopic data of **11**: ^{1}H NMR ([D$_8$]THF): δ = 8.99 (s, 6 H, triphenylene), 7.65 (d, $^{3}J_{\mathrm{H-H}}$ = 8.3 Hz, 2 H, $\mathrm{C_6H_4}$), 7.55 (d, $^{3}J_{\mathrm{H-H}}$ = 8.3 Hz, 12 H, $\mathrm{C_6H_4}$), 1.19 (m, 126 H, TIPS) ppm. ^{13}C NMR ([D$_8$]THF): δ = 133.1, 132.5, 129.8, 128.6, 125.7, 124.6, 124.3 (Ph), 108.1, 95.1, 93.3, 91.3 (C≡C), 19.2 ($\mathrm{CH_3}$), 12.4 (CH) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2144 ($\nu_{\mathrm{C\equiv C}}$). MALDI-TOF-MS (DHB): *m*/*z* = 1913.6 [M$^+$ + 2]. $\mathrm{C_{132}H_{156}Si_6}$ (1191.16): calcd. C 82.96, H 8.23; found C 83.06, H 8.31.

Preparation of Compound 12: A mixture of **11** (1.74 g, 0.85 mmol) and $n\mathrm{Bu_4NF}$ (10.2 mL, 1 M in THF) in THF (20 mL) was stirred at 45 °C overnight. The solvent was removed under vacuum and EtOH (50 mL) was added to give yellow solid which was filtered and dried under vacuum to give **12** (907 mg, 99%). Spectroscopic data of **12**: ^{1}H NMR ([D$_8$]THF): δ = 8.91 (s, 6 H, triphenylene), 7.61 (d, $^{3}J_{\mathrm{H-H}}$ = 8.1 Hz, 12 H, $\mathrm{C_6H_4}$), 7.51 (d, $^{3}J_{\mathrm{H-H}}$ = 8.1 Hz, 12 H, $\mathrm{C_6H_4}$), 3.77 (C≡CH) ppm. ^{13}C NMR ([D$_8$]THF): δ = 133.1, 132.6, 129.3, 128.1, 125.5, 124.6, 124.5 (Ph), 94.9, 91.4, 83.9, 81.1 (C≡C) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3286 ($\nu_{\mathrm{H-C\equiv}}$), 2205 ($\nu_{\mathrm{C\equiv C}}$). Mass (FAB): *m*/*z* = 974 [M$^+$ + 1]. HRMS cacld for $\mathrm{C_{78}H_{36}}$: 973.2896; found 973.2913. $\mathrm{C_{78}H_{36}}$ (973.12): calcd. C 96.27, H 3.73; found C 963.21, H 3.71.

Preparation of Complex 13: *trans*-$\mathrm{Pd(PBu_3)_2Cl_2}$ (174 mg, 0.3 mmol) was dissolved in $\mathrm{Et_2NH}$ (10 mL) containing CuCl (2 mg). Compound **12** (49 mg, 0.05 mmol) in THF (10 mL) was added and the reaction mixture stirred overnight at room temperature under nitrogen. The solvent was then removed under reduced pressure. The residue was extracted with diethyl ether/hexanes (1:1), the resulting solution was dried with anhydrous $\mathrm{MgSO_4}$ following by filtration using Celite. The filtrate was concentrated under reduced pressure and passed through a short column of basic aluminum oxide using petroleum ether (boiling range 40–65 °C) as the eluent to remove excess *trans*-$\mathrm{Pd(PBu_3)_2Cl_2}$. The product **13** was eluted with EtOAc and the solvent was removed by rotary evaporator to give a pale yellow solid identified as **13** (159 mg, 75% yield). Spectroscopic data of **13**: ^{31}P NMR ($\mathrm{CD_2Cl_2}$): δ = 10.67 ppm. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ = 8.84 (s, 6 H, triphenylene), 7.55 (d, $^{3}J_{\mathrm{H-H}}$ = 8.2 Hz, 12 H, $\mathrm{C_6H_4}$), 7.29 (d, $^{3}J_{\mathrm{H-H}}$ = 8.2 Hz, 12 H, $\mathrm{C_6H_4}$), 1.97–1.91 (m, 36 H, $\mathrm{CH_2}$), 1.60–1.44 (m, 72 H, $\mathrm{CH_2}$), 0.95 (t, $^{3}J_{\mathrm{H-H}}$ = 7.2 Hz, 54 H, $\mathrm{CH_3}$) ppm. ^{13}C NMR ($\mathrm{CD_2Cl_2}$): δ = 132.0, 131.3, 129.4, 129.2, 128.0, 125.4, 120.1 (Ph), 106.6 (t, $^{3}J_{\mathrm{C-P}}$ = 5.5 Hz, Cβ), 102.7 (t, $^{2}J_{\mathrm{C-P}}$ = 15.7 Hz, Cα), 95.5, 89.5 (C≡C), 27.0 (s, $\mathrm{CH_2}$), 25.0 (t, $J_{\mathrm{C-P}}$ = 6.6 Hz, $\mathrm{CH_2}$), 23.5 (t, $J_{\mathrm{C-P}}$ = 6.6 Hz, $\mathrm{CH_2}$), 14.2 (s, $\mathrm{CH_3}$) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2205, 2103 ($\nu_{\mathrm{C\equiv C}}$). $\mathrm{C_{222}H_{354}Cl_6P_{12}Pd_6}$ (4246.11): calcd. C 62.80, H 8.40; found C 62.65, H 8.51.

Preparation of Complex 14: A mixture of **13** (49 mg, 0.05 mmol), NaOH (36 mg, 0.9 mmol) in EtOH (2 mL) and $\mathrm{Au(PCy_3)Cl}$ (154 mg, 0.3 mmol) in THF (10 mL) was stirred at room temperature under nitrogen for 3 h. The solvent was then removed, and then the residue was washed with $\mathrm{EtOH/H_2O}$ (1:1, 10 mL) and acetone to give a yellow solid (153 mg, 80% yield). Spectroscopic data of **14**: ^{31}P NMR ($\mathrm{CDCl_3}$): δ = 56.86 ppm. ^{1}H NMR ($\mathrm{CDCl_3}$): δ = 8.73 (s, 6 H, triphenylene), 7.52 (d, $^{3}J_{\mathrm{H-H}}$ = 8.5 Hz, 12 H, $\mathrm{C_6H_4}$), 7.48 (d, $^{3}J_{\mathrm{H-H}}$ = 8.5 Hz, 12 H, $\mathrm{C_6H_4}$), 2.02–1.24 (m, 180 H, P*Cy*$_3$) ppm. ^{13}C NMR ($\mathrm{CDCl_3}$): δ = 139.7 (d, $^{2}J_{\mathrm{P-C}}$ = 132 Hz, Au*C*≡C), 132.3, 131.4, 128.5, 127.2, 125.7, 124.9, 120.9 (Ph), 103.5 (d, $^{3}J_{\mathrm{P-C}}$ = 24 Hz, AuC≡*C*), 95.0, 89.4, (C≡C), 33.2 (d, $^{1}J_{\mathrm{P-C}}$ = 28 Hz, *Cy*$_3$P), 30.7 (s, Cy$_3$P), 27.1 (d, $^{2}J_{\mathrm{P-C}}$ = 12 Hz, Cy$_3$P), 25.9 (s, *Cy*$_3$P) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2205, 2103 ($\nu_{\mathrm{C\equiv C}}$). $\mathrm{C_{186}H_{228}Au_6P_6}$ (3831.44): calcd. C 58.31, H 6.00; found C 58.55, H 6.11.

Synthesis of Cl(Et$_3$P)$_2$Pt(C≡CC$_6$H$_4$C≡CTIPS) (15): *trans*-Dichlorobis(triethylphosphane)platinum (201 mg, 0.40 mmol) was treated with compound **A** (113 mg, 0.4 mmol) in the presence of 2 mg of CuCl as catalyst in 20 mL of toluene/$\mathrm{Et_3N}$ (1:1) at 90 °C. After 24 h the solvent was removed under vacuum, and the residue was extracted with hexanes. Then the solvent was removed to afford oily residue. The residue was passed through a short column of basic aluminum oxide using hexanes as the eluent to give a colorless oily product **15** (284 mg, 95% yield). Spectroscopic data of **15**: ^{31}P NMR ($\mathrm{CDCl_3}$): δ = 15.47 (s, $J_{\mathrm{Pt-P}}$ = 2379 Hz) ppm. ^{1}H NMR ($\mathrm{CDCl_3}$): δ = 7.30 (d, $^{3}J_{\mathrm{H-H}}$ = 8.2 Hz, 12 H, $\mathrm{C_6H_4}$), 7.13 (d, $^{3}J_{\mathrm{H-H}}$ = 8.2 Hz, 12 H, $\mathrm{C_6H_4}$), 2.08–1.98 (m, 72 H, $\mathrm{CH_2}$), 1.17 (dt, $^{2}J_{\mathrm{P-H}}$ = 16.0 Hz, $^{3}J_{\mathrm{H-H}}$ = 8.0 Hz, 108 H, $\mathrm{CH_3}$), 1.10 (m, 126 H, TIPS) ppm. ^{13}C NMR ($\mathrm{CDCl_3}$): δ = 131.7, 130.5, 128.8, 120.0 (Ph), 107.5 (C≡*C*Si), 101.9 (s, *C*≡CPt), 90.9 (*C*≡CSi), 85.7 (t, $^{3}J_{\mathrm{C-P}}$ = 29 Hz, C≡*C*Pt), 18.7 ($\mathrm{CH_3}$), 14.5 (t, $^{3}J_{\mathrm{C-P}}$ = 18 Hz, $\mathrm{CH_2}$), 11.3 (CH), 8.0 ($\mathrm{CH_3}$) ppm. MS (FAB): *m*/*z* = 748.3 [M$^+$] (Cl = 35.45). $\mathrm{C_{31}H_{55}ClP_2PtSi}$ (748.33): calcd. C 49.75, H 7.41; found C 49.88, H 7.51.

Preparation of Complex 16: A mixture of **5** (41 mg, 0.05 mmol) in THF (15 mL) and **15** (299 mg, 0.40 mmol) in $\mathrm{Et_2NH}$ (10 mL) was stirred at room temperature in the presence of CuCl (2 mg) for 24 h. The solvent was then removed under vacuum. The residue was passed through alumina column using $\mathrm{CH_2Cl_2}$/hexanes (1:4) as the eluent to remove excess **15**. The complex **16** was eluted with EtOAc and the solvent was removed by rotary evaporator to give the yellow solid **16** (211 mg, 83% yield). Spectroscopic data for **16**: ^{31}P NMR ($\mathrm{CDCl_3}$): δ = 11.80 (s, $J_{\mathrm{Pt-P}}$ = 2359 Hz) ppm. ^{1}H NMR ($\mathrm{CDCl_3}$): δ = 7.47 (d, $^{3}J_{\mathrm{H-H}}$ = 8.2 Hz, 12 H, $\mathrm{C_6H_4}$), 7.31 (d, $^{3}J_{\mathrm{H-H}}$ = 8.2 Hz, 12 H, $\mathrm{C_6H_4}$), 7.25 (d, $^{3}J_{\mathrm{H-H}}$ = 8.2 Hz, 12 H, $\mathrm{C_6H_4}$), 7.18 (d, $^{3}J_{\mathrm{H-H}}$ = 8.2 Hz, 12 H, $\mathrm{C_6H_4}$), 2.22–2.12 (m, 72 H, $\mathrm{CH_2}$), 1.22 (dt, $^{2}J_{\mathrm{P-H}}$ = 16.0 Hz, $^{3}J_{\mathrm{H-H}}$ = 8.0 Hz, 108 H, $\mathrm{CH_3}$), 1.10(m, 126 H, TIPS) ppm. ^{13}C NMR ($\mathrm{CDCl_3}$): δ = 131.7, 131.5, 130.9, 130.6, 129.3, 128.8, 127. 0, 119.8, 119.5 (Ph), 112.0 (t, $^{2}J_{\mathrm{C-P}}$ = 28 Hz, C≡*C*Pt), 110.8 (t, $^{2}J_{\mathrm{C-P}}$ = 28 Hz, C≡*C*Pt), 110.0 (*C*≡CPt), 109.9 (*C*≡CPt), 107.6, 99.9, 90.8, 88.3 (C≡C), 18.7 ($\mathrm{CH_3}$), 16.4 (t, $^{3}J_{\mathrm{C-P}}$ = 18 Hz, $\mathrm{CH_2}$), 11.3 (CH), 8.3 ($\mathrm{CH_3}$) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2093, 2195 ($\nu_{\mathrm{C\equiv C}}$). $\mathrm{C_{252}H_{354}P_{12}Pt_6Si_6}$ (5094.17): calcd. C 59.41, H 7.00; found C 59.37, H 7.02.

Preparation of Complex 17: Complex **16** (211 mg, 0.041 mmol) was dissolved in THF (10 mL), and $n\mathrm{Bu_4NF}$ (0.4 mL, 1 M in THF) was added. The mixture was stirred at room temperature for 2 h and then the solvent was removed under vacuum. The residue was purified by washing with EtOH to afford the deprotected alkyne **17** as yellow solid (171 mg, 99% yield). Spectroscopic data for **17** are as follows: ^{31}P NMR (CDCl$_3$): δ = 11.77 ($J_{\text{Pt–P}}$ = 2359 Hz) ppm. ^{1}H NMR (CDCl$_3$): δ = 7.47 (d, $^{3}J_{\text{H–H}}$ = 8.2 Hz, 12 H, C$_6$H$_4$), 7.32 (d, $^{3}J_{\text{H–H}}$ = 8.2 Hz, 12 H, C$_6$H$_4$), 7.25 (d, $^{3}J_{\text{H–H}}$ = 8.2 Hz, 12 H, C$_6$H$_4$), 7.19 (d, $^{3}J_{\text{H–H}}$ = 8.2 Hz, 12 H, C$_6$H$_4$), 3.09 (s, C≡C*H*), 2.19–2.14(m, 72 H, CH$_2$), 1.22 (dt, $J_{\text{P–H}}$ = 16.0 Hz, $J_{\text{H–H}}$ = 8.0 Hz, 108 H, CH$_3$) ppm. ^{13}C NMR (CDCl$_3$): δ = 131.8, 131.5, 130.9, 130.7, 129.4, 127.0, 119.5, 118.2 (Ph), 112.0 (t, $^{2}J_{\text{C–P}}$ = 30 Hz, C≡*C*Pt), 111.2 (t, $^{2}J_{\text{C–P}}$ = 30 Hz, C≡*C*Pt), 110.0 (*C*≡CPt), 109.9 (*C*≡CPt), 107.6, 99.9, 88.2, 84.1 (C≡C), 77.2 (C≡*C*H), 16.4 (t, $J_{\text{C–P}}$ = 18 Hz, CH$_2$), 8.3 (CH$_3$) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3286 ($\nu_{\text{H–C≡}}$), 2185, 2093 ($\nu_{\text{C≡C}}$). $C_{198}H_{234}P_{12}Pt_6$ (4156.13): calcd. C 57.22, H 5.67; found C 57.47, H 5.82.

Preparation of Complex 18: To a mixture of **17** (20 mg, 4.8 × 10^{-3} mL) and Au(PCy$_3$)Cl (15 mg, 0.029 mmol) in THF (10 mL) was added excess NaOH (2 mg,0.048 mmol) in EtOH (1 mL). The mixture was stirred at room temperature for 3 h. The solvent was removed under vacuum and the residue was washed with EtOH/H$_2$O (1:1, 10 mL) and acetone to give a yellow solid (29 mg, 86% yield). Spectroscopic data for **18**: ^{31}P NMR (CDCl$_3$): δ = 56.91 (Cy$_3$PAu), 11.76 ($J_{\text{Pt–P}}$ = 2366 Hz) ppm. ^{1}H NMR (CDCl$_3$): δ = 7.45 (d, $^{3}J_{\text{H–H}}$ = 8.2 Hz, 12 H, C$_6$H$_4$), 7.32 (d, $^{3}J_{\text{H–H}}$ = 7.8 Hz, 12 H, C$_6$H$_4$), 7.23 (d, $^{3}J_{\text{H–H}}$ = 7.8 Hz, 12 H, C$_6$H$_4$), 7.10 (d, $^{3}J_{\text{H–H}}$ = 7.8 Hz, 12 H, C$_6$H$_4$), 2.17–1.15 (m, 360 H, PCy$_3$ and PEt$_3$) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2185, 2083 ($\nu_{\text{C≡C}}$). $C_{306}H_{426}Au_6P_{18}Pt_6$ (7014.45): calcd. C 52.40, H 6.12; found C 52.68, H 7.20.

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