Palladium Couplings on Metallocalix[4]arenes: A Efficient Synthesis of New Functionalized Cavities

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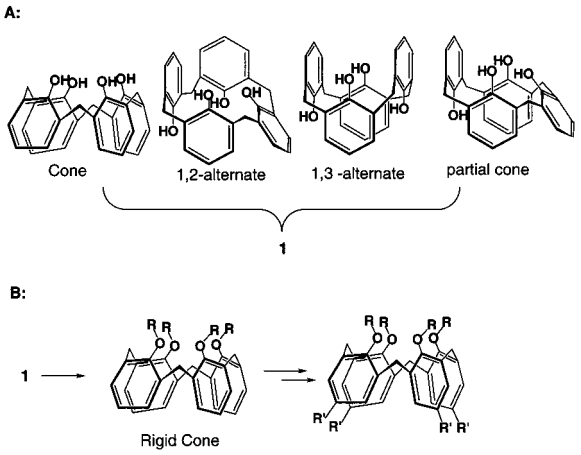
Introduction

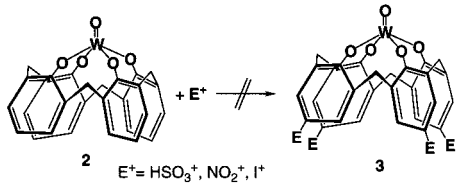
Microenvironments with well-defined geometries are key components for molecular recognition or catalytic processes in both synthetic and biological systems. The design of supramolecular assemblies, which mimic the catalytic and molecular-signaling processes displayed by nature, has generally focused on the construction of functionalized cavities from preorganized rigid molecular building blocks. Among these scaffolds, calix[4]arene (**1**) presents one of the most versatile platforms for the synthesis of diverse supramolecular assemblies with defined structures and functions.[1] Calix[4]arenes also have been found increasing utility in materials research and have been used for the formation of porous monolayers,[2] nonlinear optical chromophores,[3] and bowlic liquid crystals.[4] Both the molecular recognition and materials applications of calix[4]arene make use of its rigid cavity characteristics. Hence, more efficient methods for the formation of calix[4]arenes with functionalized cavities are of interest.

The conformational flexibility (Scheme 1, A)[5] of calix[4]arene has often impeded the formation of functionalized rigid cavities. A rigid cone often is obtained by attaching bulky alkyl groups to the lower-rim of the calix[4]arene, which prohibits the interconversion between conformers (Scheme 1, B).[6] However, in this approach, the yield of the cone conformation is low since it is statistically disfavored. Here we report a new efficient strategy to functionalized calix[4]arenes in rigid cone conformations. Our approach utilizes a metallocalix[4]arene[7] scaffold and provides elaborated calix[4]arenes in few synthetic steps with high overall yields.

Scheme 1



Scheme 2



Results and Discussion

Tungsten(VI) oxo complexes of calix[4]arene[7b] stand out as particularly stable species, and as a result, our initial investigations focused on the electrophilic substitution of these complexes (**2**) (Scheme 2). However, attempted sulfonation of **2** gave decomposition, while nitration (HNO_3/AcOH in CH_2Cl_2) or iodination ($Hg(CF_3COO)_2$ followed by I_2) did not produce characterizable product. Additionally, treament with CF_3COOAg and I_2 only provided di-iodination mixtures and insoluble solids. These failures are attributed to the poor solubility of **2** and the electron-withdrawing character of the tungsten oxo group.

We have previously found dialkoxy tungsten calix[4]arenes (**5a**)[7a,8] to have high solubility and stability. In

(1) (a) Gutsche, C. D. *Aldrichimica Acta* **1995**, *28* (1), 3. (b) *Calixarenes 50th Anniversary*; Vicens, J., Asfari, Z., Harrowfield, J. M., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994. (c) Gutsche, C. D. Calixarenes. In *Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; Royal Society of Chemistry: London, 1989. (d) *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Böhmer, V., Vicens, J., Eds.; Kluwer Academic Publishers: Dordrecht, Germany, 1991. (e) Atwood, J. L.; Orr, G. W.; Juneja, R. K.; Bott, S. G.; Hamada, F. *Pure Appl. Chem.* **1993**, *65*, 1471. (f) Gardiner, M. G.; Raston, C. L. *Coord. Chem. Rev.* **1997**, *166*, 1. (g) Diamond, D.; Mckervey, M. A. *Chem. Soc. Rev.* **1996**, *25*, 15. (h) Böhmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713.

(2) (a) Dedek, P.; Janout, V.; Regen, S. L. *J. Org. Chem.* **1993**, *58*, 6553. (b) Conner, M.; Janout, V.; Regen, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 1178. (c) Markowitz, M. A.; Janout, V.; Castner, D. G.; Regen, S. L. *J. Am. Chem. Soc.* **1989**, *111*, 8192.

(3) Kelderman, E.; Derhaeg, L.; Heesink, G. J. T.; Verboom, W.; Engbersen, J. F. J.; van Hulst, N. F.; Persoons, A.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1075.

(4) (a) Xu, B.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 1159. (b) Xu, B.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 5011. (c) See: Swager, T. M.; Xu, B. in ref 1b and references therein. (d) Komori, T.; Shinkai, S.; *Chem. Lett.* **1993**, 1455.

(5) (a) Fischer, S.; Grootenhuis, P. D. J.; Groenen, L. C.; van Hoorn, W. P.; van Veggel, F. C. J. M.; Reinhoudt, D. N.; Karplus, M. *J. Am. Chem. Soc.* **1995**, *117*, 1611. (b) Baili, S. E.; Böhmer, V.; Brenn, J.; Frings, M.; Thondorf, I.; Vogt, W.; Woehnert, J. *J. Org. Chem.* **1997**, *62*, 8350.

(6) (a) Shinkai, S. *Tetrahedron* **1993**, *49*, 8933. (b) Schmitt, P.; Beer, P. D.; Drew, M. G. B.; Sheen, P. D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1840. (c) Casnati, A.; Ting, Y.; Berti, D.; Fabbi, M.; Pochini, A.; Ungaro, R.; Sciotto, D.; Lombardo, G. G. *Tetrahedron* **1993**, *49*, 9815.

(7) (a) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Chem. Commun.* **1996**, 119. (b) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1991**, *30*, 4465. (c) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1990**, 640. (d) Cameron, B. R.; Van Veggel, F. C. J. M.; Reinhoudt, D. N. *J. Org. Chem.* **1995**, *60*, 0, 2802. (e) Acho, J. A.; Ren, T.; Yun, J. W.; Lippard, S. J. *Inorg. Chem.* **1995**, *34*, 5226. (f) Acho, J. A.; Doerrer, L. H.; Lippard, S. J. *Inorg. Chem.* **1995**, *34*, 2542. (g) Gibson, V. C.; Redshaw, C.; Clegg, W.; Elsegood, M. R. J. *J. Chem. Soc., Chem. Commun.* **1995**, 2371. (h) Giannini, L.; Solari, E.; Zanotti-Gerosa, A.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 85, and references therein. (i) Giannini, L.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1998**, *120*, 823.

(8) (a) Fu, D.-K.; Xu, B.; Swager, T. M. *J. Org. Chem.* **1996**, *61*, 802. (b) Xu, B.; Carroll, P. J.; Swager, T. M. *Angew. Chem., Intl. Ed. Engl.* **1996**, *35*, 2094.

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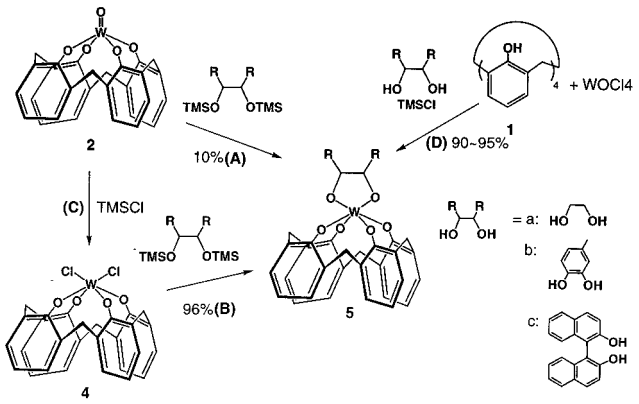
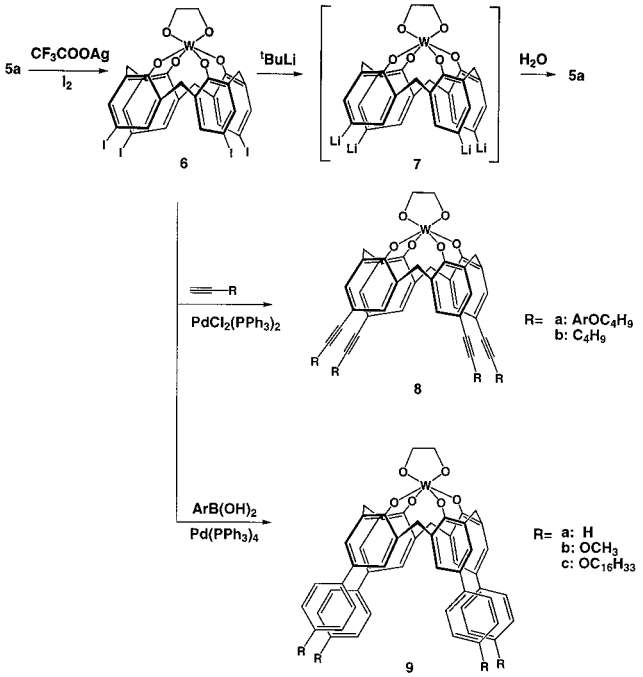
Scheme 3



Scheme 4



contrast to the oxo group of **2**, the dialkoxy functionality in **5a** increases the electron density on the tungsten center, and thereby the phenolic oxygens donate more effectively with the aromatic rings of the calix[4]arene core. The introduction of alkoxy group also prevents efficient stacking of the complexes, which improves solubility of **5a** in organic solvents. The dialkoxy groups also enable a facile entry to a structurally diversed family of complexes. For example, the electronic properties of the tungsten can be changed by replacing an alkoxy with phenoxy group. Moreover, chiral complexes can be generated by using optically active binaphthol groups (vide infra). The dialkoxy tungsten calix[4]arenes also provide a route to other metal-based functionality, and we have developed protocols for their conversion into tungsten oxo or tungsten dichloride compounds.[8b]

Our previous procedure[8b] for the synthesis of **5a** involved the reaction of **2** with 1,2-bis((trimethylsilanyl)-oxy)ethane to give **5a** in 10% yield (Scheme 3, A). We have recently found that dichlorotungsten calix[4]arene (**4**) reacted more efficiently to give **5a** in 96% yield (Scheme 3, B). This led us to a better procedure involving the addition of catalytic amounts of TMSCl to route A to produce **5a** in 95% yield (Scheme 3, C). Further improvements utilize a simplified one-pot process (Scheme 3, D), wherein $WOCl_4$ (1 equiv) and calix[4]arene (**1**) (1 equiv) are refluxed in toluene for 12 h followed by the addition of ethylene glycol (1 equiv) and TMSCl (2.1 equiv) with 12 h of additional reflux. The isolated yield of dialkoxy tungsten calix[4]arene **5a** was 95% in this later procedure. A similar procedure with 4-methyl-1,2-dihydroxy benzene and an extended reaction time (24 h) gave compound **5b** as dark red crystals in 90% yield. We have likewise synthesized the chiral binaphthol complexes **5c** as dark red crystals in 90% yield. Compounds **5a**−**c** all have very distinct ^{1}H NMR patterns for the $ArCH_2Ar$ protons. Compound **5a** has two doublets at 4.62 and 3.36 ppm, compound **5b** has three sets of doublets at 4.67, 4.65, and 3.43 ppm, and compound **5c** has eight sets of doublets ranging from 4.86 to 2.31 ppm. The sharp nature and the number of doublets are consistent with the rigid nonfluxional conformations and the symmetry of the molecules, respectively.

Iodination of **5a** with I^+ by using CF_3COOAg (4 equiv) and I_2 (4 equiv)[9] gave compound **6**, a key intermediate for coupling reaction, in quantitative yield (Scheme 4). The weaker electrophile, $Hg(CF_3COO)_2$, also readily added to the upper rim and is converted to an iodide in near quantitative yields. Both of these results confirm the activated electron-rich nature of the aromatic rings. Lithation of **6** with *tert*-butyllithium in THF may give an unstable tetralithate intermediate (**7**), which was quenched with H_2O to gave compound **5a** in 80% yield. Unfortunately, attempts to react **7** with more interesting electrophiles, such as DMF and TMSCl, failed to give useful product mixtures.

Palladium-catalyzed coupling reactions with **6** generally proceeded in high yields and under mild conditions.[10] Acetylene-coupling reactions (Sonogashira−Hagihara) gave coupling products **8a** or **8b** in excellent yields.[11] Likewise, Suzuki reactions[12] are of interest to provide deep all-aromatic cavities.[13] Attempts to synthesize compounds **9a** and **9b** gave insoluble products which were difficult to characterize. However, under the same reaction conditions and with the addition of a solublizing group (C_{16} carbon chain), compound **9c** was produced as highly soluble complex in 78% yield. Among a variety of Suzuki reaction conditions, we found that Na_2CO_3 in benzene gave the best results.

In conclusion, we have demonstrated a high-yield route to generate functionalized rigid cavities from calix[4]-arene. This methodology should be useful for construc-

(9) Timmerman, P.; Verboom, W.; Reinhoudt, D. N.; Arduini, A.; Grandi, S.; Sicuri, A. R.; Pochini, A.; Ungaro, R. *Synthesis* **1994**, 185.

(10) General review for Pd-catalyzed cross-coupling reactions, see: *Palladium Reagents and Catalysts: Innvotions in Organic Synthesis*; Tsuji, J.; John Wiley & Sons Ltd.: Chichester, England, 1995.

(11) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467. (b) Takahashi, S.; Kuroyama, K.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.

(12) (a) Rehahn, M.; Schlüter, A. D.; Wegner, G.; Feast, W. J. *Polymer* **1989**, *30*, 1060. (b) For recent reviews in biaryl synthesis using Suzuki Reactions, see: Stanforth, S. P. *Tetrhedron* **1998**, *54*, 263. Reference 10.

(13) (a) Khoury, R. G.; Jaquinod, L.; Aoyagi, K.; Olmstead, M. M.; Fisher, Andrew J.; Smith, K. M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2497−2500. (b) Juneja, R. K.; Robinson, K. D.; Johnson, C. P.; Atwood, J. L. *J. Am. Chem. Soc.*, **1993**, *115*, 3818. (c) Atwood, J. L.; Orr, G. W.; Bott, S. G.; Robinson, K. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1093. (d) Gutsche, C. D.; Kwang, H. N. *J. Org. Chem.* **1982**, *47*, 2708. (e) Kwang, H. N.; Gutsche, C. D. *J. Org. Chem.* **1982**, *47*, 2713. (f) Arduini, A.; Pochini, A.; Rizzi, A. R.; Ungaro, R. *Tetrahedron Lett.* **1990**, *31*, 4653.

tion of various supramolecular assemblies requiring an elaborated cavity. The tungsten centers provide a useful group for the control of the calix[4]arene's conformation and reactivity. Other aspects of the metallocalixarenes also merit this investigation. For example, we have previously found tungsten oxo calix[4]arenes to display endohedral Lewis acidity with a strong affinity for formyl amides.[4a] Floriani and co-workers have demonstrated the rich chemistry of metallocalix[4]arenes,[14] therefore elaborated complexes have the potential to display useful catalytic activity.

Experimental Section

General Procedures. Air- and moisture-sensitive reactions were carried out in flame-dried glassware using standard Schlenk-line or drybox techniques under an inert atmosphere of dry argon. All chemicals used were of reagent grade and were purchased from Aldrich Chemical Co. unless otherwise noted. Anhydrous toluene was used from Aldrich Kilo-lab metal cylinders. CH_2Cl_2 and THF were used directly from Aldrich Sure-seal bottles. Diisopropylamine was distilled over solid KOH pellets and degassed by three freeze−pump−thaw cycles. Tetrakis(triphenylphosphine)palladium(0) and *trans*-dichlorobis-(triphenylphosphine)palladium(II) were purchased from Strem chemicals and used as received. ^{1}H NMR spectra were acquired at 250, 300, and 500 MHz. ^{13}C NMR spectra were obtained at 125.66 MHz. All ^{1}H and ^{13}C NMR spectra were taken in $CDCl_3$ with ^{1}H NMR chemical shifts reported relative to internal tetramethylsilane (0.00 ppm) and ^{13}C NMR chemical shifts reported relative to $CDCl_3$ (77.00 ppm). Analytical thin-layer chromatography was performed on Merck 60 F_{254} precoated silica gel plates (250 μm thickness). Flash chromatography was performed on Lagand silica gel 60 stationary phase.

Compound **5a** (route D): A Schlenk flask was charged with calix[4]arene (1.00 g, 2.36 mmol), $WOCl_4$ (0.80 g, 2.34 mmol), and 50 mL of toluene. The suspension was refluxed under inert atmosphere for 12 h to give a red-brown solution. Anhydrous ethylene glycol (0.15 g, 2.42 mmol) and trimethylsilyl chloride (0.60 g, 5.52 mmol) were then introduced via syringe. The reaction mixture was kept at reflux for additional 12 h where the solution became orange-red. The solution was cooled to room temperature and filtered. The filtrate was concentrated, and the resulting solid was purified by flash chromatography (1:1 hexanes/$CHCl_3$) to give 1.47 g of orange-red solid in 95% yield. ^{1}NMR ($CDCl_3$, 250 MHz): δ_H 7.22 (d, J = 7.5 Hz, 4H, ArH), 7.03 (d, J = 7.5 Hz, 4H, ArH), 6.84 (t, J = 7.5 Hz, 2H, ArH), 6.62 (t, J = 7.5 Hz, 2H, ArH), 5.83 (s, 4H, OCH_2), 4.62 (d, J = 13.4 Hz, 4H, ArCH_2Ar), 3.36 (d, J = 13.4 Hz, 4H, ArCH_2Ar). ^{13}C NMR ($CDCl_3$, 125.803 MHz): δ 161.77 (*C*O), 158.07 (*C*O), 136.09, 131.25, 129.38, 126.64, 124.29, 123.70, 81.75 (O*C*H_2*C*H_2O), 33.56 (Ar*C*H_2Ar). HRMS (FAB): found, 664.10828 (M^+); calcd for $C_{30}H_{24}O_6W$, 664.10824 (M^+). Anal. Calcd: C, 54.24; H, 3.64. Found: C, 52.54; H, 3.59.

Compound 5b: The synthetic procedure is similar to that of compound **5a** except that methyl catechol (0.27 g, 2.42 mmol) was used in the reaction instead of ethylene glycol. ^{1}NMR ($CDCl_3$, 250 MHz): δ_H 7.28−6.61 (m, 15H, ArH), 4.67 (d, J = 13.4 Hz, 2H, ArCH_2Ar), 4.65 (d, J = 13.4 Hz, 2H, ArCH_2Ar), 3.43 (d, J = 13.4 Hz, 4H, ArCH_2Ar), 2.51 (s, 3H). ^{13}C NMR ($CDCl_3$, 125.803 MHz): δ 163.43, 158.66, 158.63, 156.20, 154.19, 136.05, 136.02, 135.28, 130.07, 129.95, 129.78, 126.66, 125.49, 125.23, 125.19, 123.72, 116.00, 114.58, 33.49, 33.46, 20.85. HRMS (FAB): found, 726.12405 (M^+); calcd for $C_{35}H_{26}O_6W$, 726.12389 (M^+).

Compound 5c: The synthetic procedure is similar to that of compound **5a** except that (*S*)-(−)-1,1′-bi-2-naphthol (0.67 g, 2.34 mmol) and TMSCl (1.4 g, 13 mmol) were used in the reaction, and the final refluxing period was extended to 24 h. ^{1}NMR ($CDCl_3$, 500 MHz): δ_H 7.92 (d, 1H), 7.86 (d, 1H), 7.71 (d, 1H), 7.40 (t, 1H), 7.32 (d, 1H), 7.29 (t, 1H), 7.23 (d, 1H), 7.20 (d, 1H), 7.17 (d, 1H), 7.12 (d, 1H), 7.06 (d, 1H), 7.00 (d, 1H), 6.96 (d, 1H), 6.90 (d, 1H), 6.88 (t, 1H), 6.79 (d, 1H), 6.65 (t, 1H), 6.48 (t, 1H), 6.39 (t, 1H), 4.86 (d, J = 13.6 Hz, 1H, ArCH_2Ar), 4.73 (d, J = 13.6 Hz, 1H, ArCH_2Ar), 3.60 (d, J = 13.6 Hz, 1H, ArCH_2-Ar), 3.55 (d, J = 13.6 Hz, 1H, ArCH_2Ar), 3.29 (d, J = 13.6 Hz, 1H, ArCH_2Ar), 2.58 (d, J = 13.6 Hz, 1H, ArCH_2Ar), 2.40 (d, J = 13.6 Hz, 1H, ArCH_2Ar), 2.31 (d, J = 13.6 Hz, 1H, ArCH_2Ar). ^{13}C NMR ($CDCl_3$, 125.803 MHz): δ 164.07, 163.60, 160.01, 159.86, 159.19, 137.34, 137.13, 135.74, 135.41, 134.50, 131.97, 131.41, 131.23, 131.14, 131.04, 129.22, 129.06, 128.96, 128.89, 128.75, 128.42, 128.22, 127.79, 126.83, 126.36, 126.29, 126.27, 126.18, 125.90, 125.04, 124.49, 124.17, 123.96, 123.42, 122.23, 121.70, 120.15, 34.10, 33.30, 31.80, 31.67, 29.70 (toluene). HRMS (FAB): found, 888.17115 (M^+); calcd for $C_{48}H_{32}O_6W$, 888.17084 (M^+).

Compound 6: To a three-necked round-bottom flask equipped with reflux condenser were added compound **5a** (0.2 g, 0.30mol), CF_3COOAg (0.29, 1.32 mmol), and 40 mL of $CHCl_3$. The solution was then refluxed for 30 min and cooled to rt; I_2 (0.367 g, 1.44 mmol) was added under a flow of N_2. The resulting red solution was refluxed for an additional 2 h. After cooling to room temperature, the mixture was filtered and the solvent was removed under vacuum. The crude solid was chromatographed on silica gel (1:1 hexanes/$CHCl_3$) to give **6** as an orange/red solid (0.33 g, 90%). ^{1}NMR ($CDCl_3$, 250 MHz): δ_H 7.55 (s, 4H, Ar*H*), 7.35 (s, 4H, Ar*H*), 5.85 (s, 4H, CH_2), 4.45 (d, J = 13.7 Hz, ArCH_2-Ar, 4H), 3.26 (d, J = 13.7 Hz, ArCH_2Ar, 4H). ^{13}C NMR ($CDCl_3$, 125.803 MHz): δ 161.71, 157.71, 138.41, 137.31, 135.63, 133.03, 88.14 (*C*-I), 87.69 (*C*-I), 82.58 (O*C*H_2*C*H_2O), 32.54 (Ar*C*H_2Ar). HRMS (FAB): found, 1167.69499 (M^+); calcd for $C_{30}H_{20}I_4O_6W$, 1167.69485 (M^+).

Compounds 8a and 8b. 8a: To a 50 mL Schlenk flask containing the mixture of **6** (0.1 g, 0.08 mmol), $PdCl_2(PPh_3)_2$ (0.0057 g, 0.008 mmol), CuI (0.003 g, 0.016 mmol), 15 mL of toluene, and 1 mL of $HN(^iPr)_2$ was added butoxylphenylacetylene (0.071 g, 0.4 mmol) via syringe. The resulting dark red solution was allowed to stir overnight at room temperature under inert atmosphere. After the removal of the solvent in vacuo, the residue was purified by column chromatograph (1:3 hexanes/$CHCl_3$) to afford **8a** as a red solid (0.095 g, 86% yield). ^{1}NMR ($CDCl_3$, 500 MHz): δ_H 7.45 (d, 4H, J = 8.8 Hz), 7.43 (s, 4H), 7.32 (d, 4H, J = 8.8 Hz), 7.25 (s, 4H), 6.88 (d, 4H, J = 8.8 Hz), 6.78 (d, 4H, J = 8.8 Hz), 5.88 (s, 4H), 4.56 (d, 4H, J = 13.5 Hz), 3.99 (t, 4H, J = 6.5 Hz), 3.92 (t, 4H, J = 6.5 Hz), 3.38 (d, 4H, J = 13.5 Hz), 1.77 (m, 8H), 1.49 (m, 8H), 0.96 (m, 12H). ^{13}C NMR ($CDCl_3$, 125.803 MHz): 161.90, 159.21, 158.98, 157.87, 135.96, 133.07, 132.97, 132.83, 131.14, 129.86, 128.21, 119.69, 119.04, 115.08, 115.05, 114.49, 114.32, 90.09, 89.22, 87.91, 86.90, 82.24, 67.74, 67.65, 31.25, 31.22, 29.71, 19.23, 19.19, 14.12, 13.85, 13.83. HRMS (FAB): found, 1352.46311 (M^+); calcd for $C_{78}H_{72}O_{10}W$, 1352.46350 (M^+). **8b**: Synthetic procedure is similar to that of **8a** except 4-butoxylphenylacetylene was replaced by 1-hexyne. ^{1}NMR ($CDCl_3$, 250 MHz): δ_H 7.25 (s, 4H, Ar), 7.08 (s, 4H, Ar), 5.81 (s, 4H), 4.46 (d, 4H, J = 13.5 Hz), 3.27 (d, 4H, J = 13.5 Hz), 2.44 (t, 4H, J = 7 Hz), 2.35 (t, 4H, J = 7 Hz), 1.60−1.37 (m, 16H), 0.97 (t, 6H, J = 7 Hz), 0.88 (t, 6H, J = 7 Hz). ^{13}C NMR ($CDCl_3$, 125.803 MHz): δ 161.49, 157.51, 135.75, 132.81, 132.05, 130.94, 129.90, 128.54, 120.01, 119.32, 90.73, 89.82, 82.05, 80.29, 79.37, 33.00, 30.97, 29.70, 22.05, 21.96, 19.11, 18.86, 13.68, 13.61. HRMS (FAB): found, 984.3589 (M^+); calcd for $C_{62}H_{78}O_6W$, 984.3588 (M^+).

Compound 9c: A 50 mL Schlenk flask was charged with compound **6** (0.05 g, 0.041 mmol), 4-((hexyldecyl)oxy)phenylboronic acid (0.088 g, 0.24 mmol), and $Pd(PPh_3)_4$ (0.005 mg, 0.0041 mmol). To this mixture 15 mL of degassed benzene and 1 mL deionized H_2O were introduced via syringe. The resulting heterogeneous reaction mixture was evacuated and refilled with argon five times before it was heated to 75 °C for 24 h. The final two-phase solution was diluted with $CHCl_3$, washed with H_2O, and dried under $MgSO_4$. The organic portion was evaporated, and the crude solid was separated by column chromatog-

(14) (a) Giannini, L.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1998**, *120*, 823. (b) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1998**, *120*, 437. (c) Giannini, L.; Caselli, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C.; Re, N.; Sgamellotti, A. *J. Am. Chem. Soc.* **1997**, *119*, 9709. (d) Giannini, L.; Caselli, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C.; Re, N.; Sgamellotti, A. *J. Am. Chem. Soc.* **1997**, *119*, 9198.

raphy (3:1 $CHCl_3$/hexanes) to give **9c** as a red solid (64 mg, 78%). ^{1}NMR ($CDCl_3$, 250 MHz): δ_H 7.51 (d, 4H, J = 8.7 Hz), 7.43 (s, 4H), 7.31 (d, 4H, J = 8.7 Hz), 7.25 (s, 4H), 6.97 (d, 4H, J = 8.8 Hz), 6.81 (d, 4H, J = 8.8 Hz), 5.86 (s, 4H), 4.71 (d, 4H, J = 13.3 Hz), 4.00 (t, 4H, 6.5 Hz), 3.89 (t, 4H, 6.5 Hz), 3.50 (t, 4H, J = 13.3 Hz), 1.75 (m, 10H), 1.59 (s, 12 H), 1.25 (s, 90 H), 0.87 (m, 20H). ^{13}C NMR ($CDCl_3$, 125.803 MHz): δ 161.33, 158.66, 158.38, 157.35, 137.41, 136.40, 136.05, 133.20, 132.47, 132.07, 131.52, 128.55, 128.46, 128.25, 128.00, 127.74, 125.02, 118.53, 114.69, 114.41, 81.79, 68.13, 68.00, 33.96, 31.93, 29.70, 29.69, 29.62, 29.60, 29.57, 29.44, 29.41, 29.37, 29.32, 29.28, 26.70, 26.08, 26.02, 22.70, 14.13. HRMS (FAB): found, 1929.21539 (M^+); calcd for $C_{118}H_{168}O_{10}W$, 1929.21471 (M^+).

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Supporting Information Available: NMR data for key products and intermediates (13 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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