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Facile Synthesis of Oligophenylene-Substituted Calix[4]arenes and Their Enhanced Binding Properties

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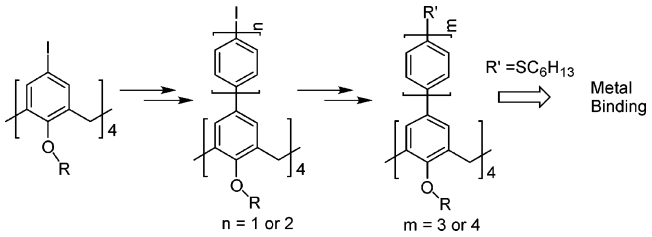

A facile and efficient protocol for the synthesis of oligophenylene OPP(n)-substituted calix[4]arenes (with n up to 4) via iodo-substituted oligoarylcalix[4]arenes has been developed. The cooperation effect of the proximate fluoroionophores in hexylsulfanyl end-capped OPP(n)-substituted calix[4]arene assemblies leads to metal ion binding enhancement.

There is considerable interest in developing novel π-conjugated molecular systems, i.e., oligomers[1] or dendrimers[2] or assemblies,[3] into useful functional materials for various technological applications such as sensors[4] and optoelectronic devices, i.e., field effect transistors[5] and light-emitting diodes.[6] Much progress has been made toward tuning/enhancing the various functional/material properties of these π-conjugated molecules by means of structural modifications.[7] On the other hand, the use of intramolecular interaction or cooperation effect of the proximate chromo- or fluorophores in multi-π-conjugated molecular assemblies, in which chromo- or fluorophores are preorganized and preoriented within a molecular framework, to modify and tune the functional properties of a material is largely unexplored.[8]

We have previously shown that multifluorophoric assemblies based on oligophenylene (OPP)-substituted calix[4]arene assemblies exhibit a dramatic difference in the fluorescence properties when compared to that of the corresponding monomeric unit. Interestingly, the donor−acceptor type calix[4]arene assemblies exhibit strong and enhanced fluorescence as compared to those of the donor−donor type assemblies.[9] Continuing our effort in investigating the structural factor(s) that can enhance a functional property of an assembly, we report herein a more efficient protocol for the synthesis of OPP(n)-substituted calix[4]arene assemblies with n up to 4 via tetraiodophenyl- or tetraiodobiphenylcalix[4]arenes and an investigation of the cooperation effect of the proximate fluoroionophores for soft metal ion binding in hexylsulfanyl end-capped OPP(n)-substituted calix[4]arene assemblies.

Although various aryl-substituted calix[4]arenes have been synthesized in good yields by various metal-catalyzed cross-coupling protocols,[10] our early attempt to synthesize higher homologous of OPP-substituted calix[4]arene assemblies using the palladium-catalyzed Suzuki cross-coupling of oligoarylboronic acid and tetrabromophenylcalix[4]arene as well as to improve the efficiency of such a strategy was not so successful. It was attributed to the increased steric crowdedness of the multiple reaction sites and the low reactivity of tetrabromophenylcalix[4]arene employed. As the oxidative addition step is often considered to be the rate-determining step in the Suzuki cross-coupling reaction, the use of aryl iodide would certainly increase the efficiency and reactivity of the coupling.[11] However, there is no facile method of synthesizing iodo-substituted oligoarylcalix[4]arenes reported so far. As a result, method to synthe-

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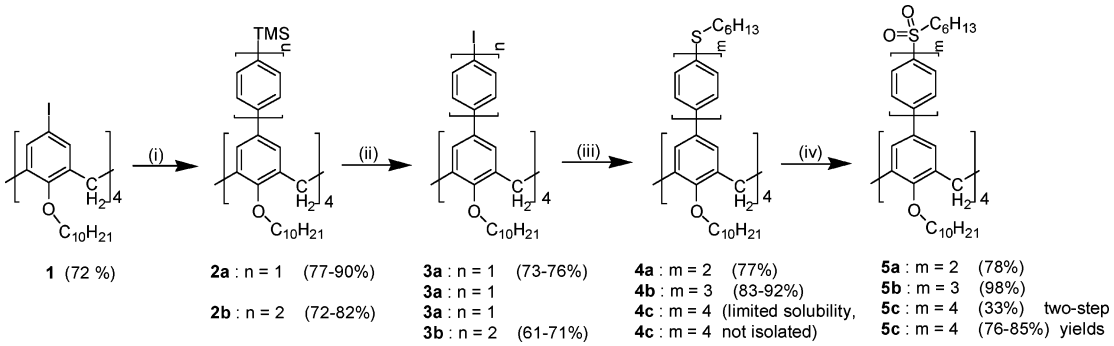
SCHEME 1. Syntheses of OPP(n)-Substituted Calix[4]arenes 4a,b and 5a−c[a]



[a] Reagents and conditions: (i) TMS-$(C_6H_4)_n$-B$(OH)_2$, 20 mol % Pd$(OAc)_2$/2P(o-tol)$_3$, K_2CO_3, toluene−CH_3OH, 45−65 °C, overnight; (ii) I_2, $CF_3COO^-Ag^+$, $CHCl_3$, 75 °C, 2−4 h; (iii) $C_6H_{13}S$-$(C_6H_4)_{m-n}$-B$(OH)_2$, 20 mol % Pd$(OAc)_2$/2P(o-tol)$_3$, K_2CO_3, toluene−CH_3OH, 50 °C, 6−40 h; (iv) m-CPBA, $CHCl_3$, 0 °C, 1 h.

size tetraiodophenyl- and tetraiodobiphenylcalix[4]arenes was first explored.

Classical iodination strategies such as direct iodination of tetraphenylcalix[4]arene by means of iodine−silver trifluoroacetate in refluxing chloroform, which is often used to prepare tetraiodocalix[4]arene,[12] as well as bromide−lithium exchange of tetrabromophenylcalix[4]-arene followed by subsequent quenching with iodine were not useful. Taking advantage of the facile ipso substitution of arylsilane by electrophile, iododesilylation of tetra(trimethylsilyl)oligoarylcalix[4]arenes was investigated. Following the same synthetic strategy used previously, tetra(trimethylsilyl)phenylcalix[4]arene, **2a**, was synthesized by cross-coupling of tetraiodocalix[4]arene with trimethylsilylphenylboronic acid, which was obtained in a one-pot synthesis by a sequence of lithiation−quenching reactions: mono-transmetalation of 1,4-dibromobenzene with 1 equiv of n-butyllithium followed by treatment with chlorotrimethylsilane at low temperature and subsequent addition of a second equivalent of n-butyllithium followed by the reaction with trimethyl borate and then acid hydrolysis (see the Supporting Information), under modified Suzuki protocol. Treatment of **2a** with ICl under various reaction conditions afforded no desired product. However, iododesilylation was achieved smoothly by reaction with iodine−silver trifluoroacetate in refluxing $CHCl_3$, which afforded tetraiodophenylcalix[4]arene, **3a**, in good yields. It is important to note that in contrast to other silylated heteroaromatic systems,[13] this reaction did not proceed in THF. Cross-coupling of **3a** with 4-(hexylsulfanyl)phenylboronic acid and 4′-(hexylsulfanyl)biphenylboronic acid afforded assembly of **4a** and **4b**, respectively, in excellent yields (77−92%) as shown in Scheme 1. This confirms that iodo-substituted phenylcalix-[4]arene was more reactive and efficient for coupling. Interestingly, cross-coupling of **3a** and 4″-(hexylsulfanyl)-terphenylboronic acid gave an insoluble reaction mixture that could not be characterized by any spectroscopic techniques. Fortunately, m-CPBA oxidation of this reaction mixture in $CHCl_3$ at low temperature afforded the desired hexylsulfonylquaterphenylcalix[4]arene **5c**, except in a relatively low yield (33%) for two steps (Scheme 1). The ^{1}H NMR spectrum of **5c** is very similar to that of **5b** except with more aromatic proton resonances, which correspond to an increase in phenylene units (Figure 1). The MALDI-TOF mass spectrum of **5c** showed a base peak at m/z 2818.10, corresponding to $[M + Na]^+$ ion. The poor conversion was presumably due to the increased steric hindrance between partially oligophenylene-substituted calix[4]arene and the highly extended terphenylboronic acid. To improve the synthesis further, tetraiodobiphenylcalix[4]arene, **3b** was pursued and prepared according to the newly developed protocol as shown in Scheme 1. Great improvement was indeed achieved by cross-coupling of **3b** and 4′-(hexylsulfanyl)biphenylboronic acid followed by subsequent m-CPBA oxidation, affording **5c**[14] in 76−85% overall isolated yields.

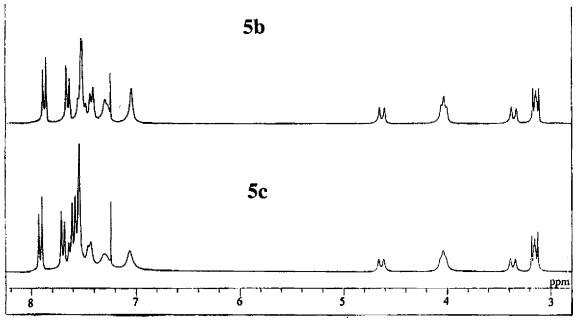


FIGURE 1. ^{1}H NMR spectra of **5b** and **5c**.

The widely employed ligating groups in calixarene-based receptors/ionophores are (crown) ether, keto, ester, and amide.[15] Some of these receptors show good affinity for Ag^+ and Hg^{2+} ions;[16] on the other hand, the use of alkylsulfanyl functionality is relatively less. According to the soft−hard acid−base principle, the ionophore containing sulfur atom(s) would have an affinity for soft metal ions such as Ag^+ and Hg^{2+}. Upon addition of CF_3COOAg in a $CDCl_3/CD_3COCD_3$ (v/v = 10:1) solution of hexylsulfanyl end-capped OPP-substituted calix[4]-

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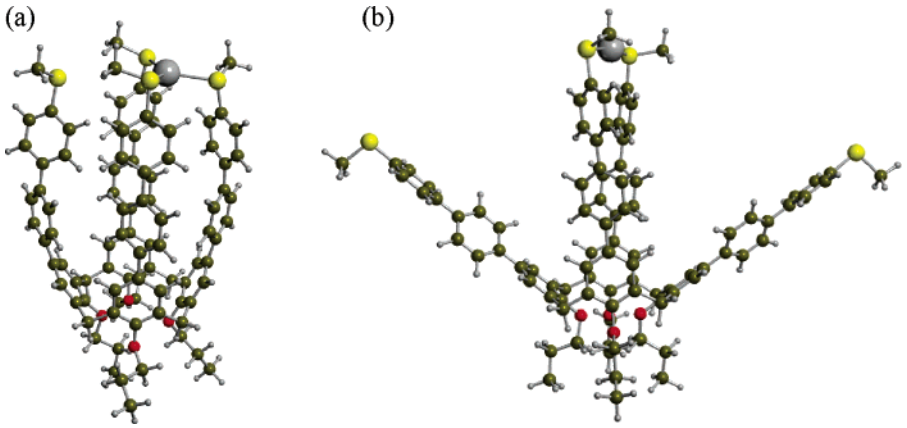

FIGURE 2. DFT-optimized geometries of an analogue of **4a**·Ag^+ complex for the (a) pseudo-C_{4v} binding mode and (b) near the C_{2v} binding mode. The drawings were performed by MOLDRAW.[19]

arene assemblies, there were substantial shifts of the proton resonances and peak broadening in the ^{1}H NMR spectra indicating the presence of interaction between the calix[4]arene assemblies and Ag^+ ion. Such a change in chemical shifts or peak broadening was not observed for 4-methoxyphenyl-substituted calix[4]arene and the hexylsulfonyl end-capped OPP-substituted series as well as for phenyl-substituted calix[4]arene, which excludes the involvement of π-cation interactions. Of a particular large downfield shift of proton resonance comes from the methylene adjacent to the sulfur atom ($\Delta\delta$ = 0.17−0.25 ppm), suggesting that the binding site is at the sulfur atoms. The binding stoichiometry of **4b**·Ag^+ complex determined by Job plot using the fluorescent titrations of **4b** with CF_3COOAg in $CHCl_3/CH_3OH$ (v/v 1:1) supported a 1:1 binding mode. This was further confirmed by high-resolution MALDI-TOF MS analyses in which the spectra of the mixture of alkylsulfanyl end-capped OPP-substituted calix[4]arenes and CF_3COOAg show a peak at *m/z* 2164.3030 and 2468.4402 with expected isotopic distribution, which correspond to [**4a** + Ag]$^+$ and [**4b** + Ag]$^+$ ions, respectively (see the Supporting Information). The association constants, estimated by nonlinear curve fitting analysis using data obtained from fluorescent titrations in $CHCl_3/CH_3OH$ (v/v 1:1), were 23.5×10^4 and 2.0×10^4 M^{-1} for **4a**·Ag^+ and **4b**·Ag^+, respectively (see the Supporting Information). These binding associations are much stronger than those of the corresponding monomeric counterparts[17] in which their association constants as determined by fluorescent titrations are 1.2×10^3 and 1.9×10^3 M^{-1}, respectively, indicating the advantage of cooperation binding. In the monomeric system, an increase in a phenylene unit leads to an enhancement of the Ag^+ ion binding indicating the contribution of π-conjugation in facilitating complexation. On the other hand, the binding association of the OPP-substituted calix[4]arene decreases with an increase in a phenylene unit. This is attributed to the increased degrees of freedom of extended oligophenylene arms in the longer homologues hindering the cooperation binding. The moderate increase in binding association of **4b**·Ag^+ may additionally be due to the crowdedness around the sulfur binding sites imposed by the solubilizing hexyl groups, which hinders the effectiveness of cooperation binding as compared to their monomeric counterparts.

Attempt to grow single crystals of the complexes was not so successful. To probe the binding behavior, ab inito quantum chemical calculations using Gaussian03[18] (B3LYP 6-31G(d) with ECP for the Ag atom from LANL2DZ) were pursued. For the computational simplicity, an analogue of **4a** bearing propoxy cone-stabilizing substituents and methylsulfanyl endcaps was used. It is interesting to find that the pseudo-C_{4v} binding mode, in which the three sulfur atoms on the oligophenylene scaffolds cooperatively bind to Ag^+ ion with the fourth arm being slightly swayed away, is 3.28 kcal/mol enthalpically more stable than the near C_{2v} binding mode, in which the Ag^+ ion is cooperatively bound by the two opposite methylsulfanyl groups conforming to a pinched structure (Figure 2). These results further confirm the importance of the cooperative effect in binding.

On the other hand, the changes in chemical shifts of hexylsulfanyl end-capped OPP-substituted calix[4]arene assemblies in the ^{1}H NMR spectra were apparent upon

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(17) The monomer of **4a** is 4-decyloxy-3,5-dimethyl-4″-hexylsufanylterphenyl and the monomer of **4b** is 4-decyloxy-3,5-dimethyl-4‴-hexylsufanylquaterphenyl.

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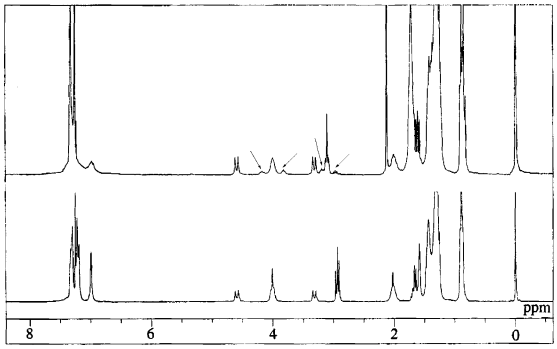

FIGURE 3. ^{1}H NMR spectra of **4a** in $CDCl_3$ (below) and **4a** with an addition of solid sample of $Hg(OAc)_2$ (top).

an addition of one equivalent of Hg^{2+} salt in contrast to their corresponding monomeric counterparts, which show no significant change in chemical shifts. These results indicate that the Hg^{2+} binding is also enhanced in the calix[4]arene assemblies. Interestingly, dependent on the deuterated solvent(s) used (i.e., $CDCl_3$), Hg^{2+} and **4a** binding could be kinetically slow compared to NMR time scale. Under such a slow exchange condition, the proton resonances of both OCH_2 and SCH_2 from **4a**·Hg^{2+} complex split into two sets of two magnetically nonequivalent peaks[20] (Figure 3). This splitting pattern suggests that Hg^{2+} ion was bound by two sulfur atoms leading to a conformationally stable pinched cone structure, analogous to the *tert*-butyl-1,3-dihydroxy-2,4-disulfanylcalixarene-Hg^{2+} complex.[21] The association constants, estimated based on fluorescent titrations in $CHCl_3/CH_3OH$ (v/v 1:1) were 4.0×10^2 and 1.2×10^2 M^{-1} for **4a**·Hg^{2+} and **4b**·Hg^{2+}, respectively.

In summary, we have developed a facile and mild protocol for iodination of oligoaryl-substituted calix[4]-arenes for the improved synthesis of highly extended OPP-substituted calixarenes. The first efficient synthesis of highly extended quaterphenylcalix[4]arene assembly was also reported. We have shown that the binding affinities of hexylsulfanyl end-capped OPP(n)-substituted calix[4]arene assemblies toward Ag^+ and Hg^{2+} ions are stronger than those of the corresponding monomeric units because of the cooperation effect of the proximate fluoroionophores. This result provides an alternatively useful approach to design chromo- and fluoroionophores to enhance metal ion binding.

Experimental Section

Improved Procedure for Pd-Catalyzed Suzuki Cross-Coupling of Oligoarylboronic Acid and Tetraiodoarylcalix-[4]arene. To a stirred solution of tetraiodoarylcalix[4]arene (0.1−0.6 mmol) and about 20 mol % of $Pd(OAc)_2/2P(o\text{-tol})_3$ in 15 mL of toluene were added 5 mL of 2 M K_2CO_3 under N_2 and 6 equiv of arylboronic acid in 10 mL of methanol, respectively. After being heated to 50−65 °C for overnight, the reaction mixture was added with 50 mL of 2 M Na_2CO_3 and then extracted twice with CH_2Cl_2 (50 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and evaporated to dryness. The crude product was purified by silica gel column chromatography using petroleum ether and CH_2Cl_2 as eluent.

5,11,17,23-Tetrakis(4-trimethylsilylphenyl)-25,26,27,28-tetradecyloxycalix[4]arene (2a): mp 86−88 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ) 7.43 (d, J = 8.0 Hz, 8H), 7.26 (d, J = 8.0 Hz, 8H), 7.00 (s, 8H), 4.61 (d, J = 12.8 Hz, 4H), 4.03 (t, J = 7.4 Hz, 8H), 3.38 (d, J = 12.8 Hz, 4H), 2.08 (bs, 8H), 1.34−1.46 (bs, 56H), 0.92 (bs, 12H), 0.27 (s, 36 H); ^{13}C NMR (67.8 MHz, $CDCl_3$, 25 °C, δ) 157.6, 141.8, 137.5, 135.3, 134.7, 133.3, 127.1, 126.3, 75.6, 32.1, 31.6, 30.5, 30.2, 29.9, 29.6, 26.5, 22.8, 14.2, −0.85; MS (FAB) m/z 1578.6 $[M]^+$. Anal. Calcd for $C_{104}H_{152}O_4Si$: C, 79.13; H, 9.70. Found: C, 79.47; H, 10.01.

5,11,17,23-Tetrakis[4′-(trimethylsilyl)biphenyl]-25,26,-27,28-tetradecyloxycalix[4]arene (2b): mp 195−197 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ) 7.48 (s, 16 H), 7.42 (d, J = 8.0 Hz, 8H), 7.26 (d, J = 7.6 Hz, 8H), 7.03 (s, 8H), 4.62 (d, J = 13.2 Hz, 4H), 4.03 (t, J = 7.4 Hz, 8H), 3.34 (d, J = 13.2 Hz, 4H), 2.05 (bs, 8H), 1.27−1.44 (bs, 56H), 0.89 (t, J = 6.6 Hz, 12H), 0.29 (s, 36 H); ^{13}C NMR (67.8 MHz, $CDCl_3$, 25 °C, δ) 157.3, 141.2, 140.3, 138.9, 138.7, 135.1, 134.8, 133.7, 127.2, 127.1, 127.0, 126.3, 75.6, 32.0, 31.8, 30.4, 30.1, 29.9, 29.7, 29.5, 26.5, 22.7, 14.2, −1.0; HRMS (MALDI-TOF) calcd for $C_{128}H_{168}O_4Si$ 1881.2020, found 1881.2117 $[M]^+$.

5,11,17,23-Tetrakis(4-iodophenyl)-25,26,27,28-tetradecyloxycalix[4]arene (3a): mp 139−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, δ) 7.45 (d, J = 8.0 Hz, 8H), 6.85 (s, 8H), 6.83 (d, J = 8.0 Hz, 8H), 4.53 (d, J = 13.2 Hz, 4H), 3.96 (t, J = 7.2 Hz, 8H), 3.25 (d, J = 13.2 Hz, 4H), 1.96−1.98 (m, 8H), 1.29−1.41 (m, 56H), 0.87 (t, J = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, δ) 156.4, 140.3, 137.3, 135.1, 133.8, 128.3, 126.6, 92.0, 75.5, 32.1, 31.2, 30.4, 30.1, 30.1, 29.9, 29.5, 26.5, 22.8, 14.2; MS (FAB) m/z 1793.2 $[M]^+$. Anal. Calcd for $C_{92}H_{116}O_4I_4$: C, 61.61; H, 6.52. Found: C, 61.74; H, 6.82.

5,11,17,23-Tetrakis(4′-iodobiphenyl)-25,26,27,28-tetradecyloxycalix[4]arene (3b): mp 130−131.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, δ) 7.59 (d, J = 8.4 Hz, 8H), 7.27 (bs, 8H), 7.23 (bs, 8H), 7.10 (d, J = 7.6 Hz, 8H), 6.99 (s, 8H), 4.60 (d, J = 13.2 Hz, 4H), 4.00 (t, J = 7.2 Hz, 8H), 3.32 (d, J = 13.2 Hz, 4H), 1.96−2.04 (m, 8H), 1.29−1.44 (m, 56H), 0.90 (t, J = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, δ) 156.5, 140.5, 139.9, 137.7, 137.6, 135.2, 134.3, 128.4, 127.1, 126.9, 126.7, 92.8, 75.6, 32.0, 31.4, 30.4, 30.0, 29.8, 29.5, 26.4, 22.7, 14.1. Anal. Calcd for $C_{116}H_{132}O_4I_4$: C, 66.41; H, 6.34. Found: C, 66.35; H, 6.17.

5,11,17,23-Tetrakis[4‴-(hexylsulfonyl)quaterphenyl]-25,26,27,28-tetradecyloxycalix[4]arene (5c): mp 314 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, δ) 7.91 (d, J = 8.4 Hz, 8H), 7.70 (d, J = 8.0 Hz, 8H), 7.62 (d, J = 8.0 Hz, 8H), 7.54−7.58 (m, 24H), 7.45 (bs, 8H), 7.31 (bs, 8H), 7.06 (bs, 8H), 4.64 (d, J = 13.2 Hz, 4H), 4.02 (bs, 8H), 3.37 (d, J = 13.2 Hz, 4H), 3.16 (t, J = 8.0 Hz, 8H), 2.05 (bs, 8 H), 1.72−1.80 (m, 8H), 1.25−1.46 (m, 80H), 0.85−0.93 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, δ) 156.4, 145.7, 140.8, 140.3, 140.0, 138.4, 138.0, 137.6, 135.2, 134.5, 128.6, 127.6, 127.4, 127.2, 127.1, 127.1, 126.9, 75.6, 56.2, 32.0, 31.6, 31.2, 30.4, 30.0, 29.8, 29.7, 29.5, 27.9, 26.4, 22.7, 22.5, 22.3, 14.1, 13.9; MS (MALDI-TOF) m/z calcd for $C_{188}H_{215}O_{12}S_4Na$ 2818.03, found 2818.10 $[M + Na]^+$.

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Supporting Information Available: General experimental details, spectra data, and synthesis of boronic acids; selected fluorescent titration data; ^{1}H NMR spectra of boronic acids, compounds **2a**−**5a**, **2b**−**5b**, and **5c**; and MALDI-TOF MS spectra of **4a**·Ag^+ and **4b**·Ag^+ complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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