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

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Abstract:

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 are considerable interests 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 opto-electronic devices i.e. field effect transistors[5] and light-emitting diodes[6]. Much progress has been made on 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 fluoro-phores in multi-π-conjugated molecular assemblies, in which chromo- or fluoro-phores are pre-organized and pre-oriented within a molecular framework, to modify and tune the functional properties of a material is largely unexplored.[8]

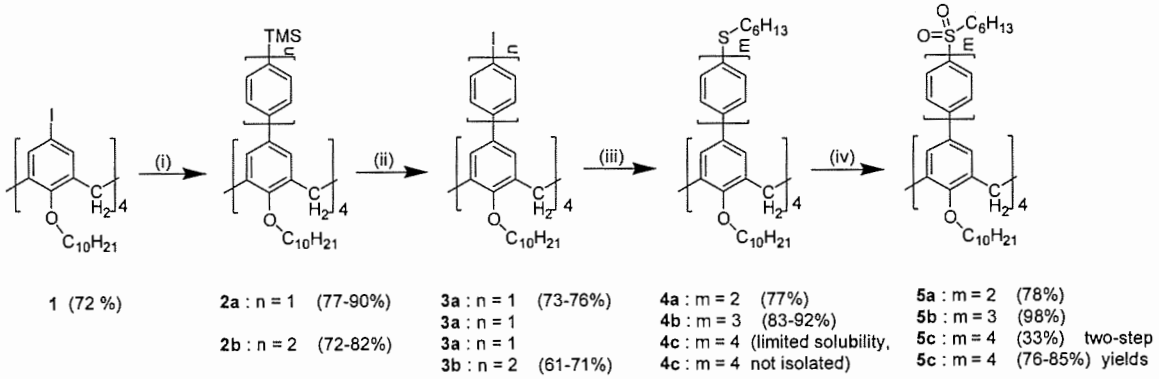
We have previously shown that multi-fluorophoric assemblies based on oligophenylene (OPP)-substituted calix[4]arene assemblies exhibit dramatic difference in the fluorescence properties when compared to that of the corresponding monomeric unit. Interestingly, the donor-acceptor type calix[4]arene assemblies 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 tetraiodobiphenyl–calix[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.

Early attempt to synthesize higher homologous of OPP-substituted calix[4]arene assemblies using the palladium catalysed Suzuki cross-coupling of oligoarylboronic acid

and tetrabromophenyl-calix[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 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.[10] However, there is no facile method of synthesizing iodo-substituted oligoarylcalix[4]arenes reported so far. As a result, method to synthesize tetraiodophenyl– and tetraiodobiphenyl–calix[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,[11] as well as bromide-lithium exchange of tetrabromo-phenylcalix[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)phenyl-calix[4]arene, **2a** was synthesized by cross coupling of tetraiodocalix[4]arene with trimethylsilylphenylboronic acid, which were obtained in a one-pot synthesis by a sequence of lithiation-quenching reactions: mono-transmetalation of 1,4-dibromobenzene with one equiv of *n*-butyl lithium followed by treatment with chlorotrimethylsilane at low temperature and subsequent addition of second equiv of *n*-butyl lithium followed by the reaction with trimethyl borate and then acid hydrolysis (See S. I.), under modified Suzuki protocol. Treatment of **2a** with ICl at various reaction conditions afforded no desired product. However, iododesilylation was achieved smoothly by reaction with

iodine–silver trifluoroacetate in refluxing $CHCl_3$, which afforded tetraiodo-phenylcalix[4]arene, **3a** in good yields. It is important to note that in contrast to other silylated heteroaromatic systems[12], this reaction did not proceed in THF. Cross-coupling of **3a** with 4'-(hexylsulfanyl)-phenylboronic acid and 4'-(hexylsulfanyl)-biphenylboronic acid afforded assembly **4a** and **4b**, respectively in excellent yields (77-92%) as shown in Scheme 1.

Scheme 1 Syntheses of OPP(n)-substituted calix[4]arenes, 4a-b and 5a-c.



Reagents and Conditions: (i) TMS-$(C_6H_4)_n$-$B(OH)_2$, 20 mole% $Pd(OAc)_2$: 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 mole% $Pd(OAc)_2$: 2P(o-tol)$_3$, K_2CO_3, toluene-CH_3OH, 50 °C, 6-40 h; (iv) MCPBA, CH_3Cl, 0 °C, 1h.

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 insoluble reaction mixture that could not be characterized by any spectroscopic techniques. Fortunately, MCPBA-oxidation of this reaction mixture in $CHCl_3$ at low temperature afforded the desired hexylsulfonylquaterphenyl-calix[4]arene **5c**, except in a relatively low yield (33%) for two steps. (Scheme 1) The ^1H 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, corresponding to $[M - H + Na]^+$ 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, tetraiodobiphenyl-calix[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 MCPBA-oxidation, affording **5c** in 76-85% overall isolated yields.

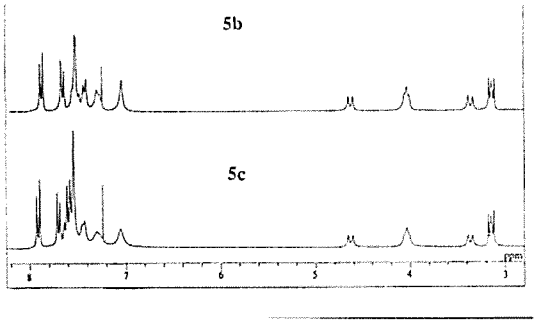


Figure 1 ^{1}H NMR spectra of **5b** and **5c**

The widely employed ligating groups in calixarene-based receptors/ionophores are (crown) ether, keto, ester, and amide, the use of alkylsulfanyl functionality is relatively less.[13] 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 an addition of CF_3COOAg in a $CDCl_3$:CD_3COCD_3 (v/v = 10:1) solution of hexylsulfanyl

end-capped OPP-substituted calix[4]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-methoxy-phenyl-substituted calix[4]arene and the hexylsulfonyl end-capped OPP-substituted series. 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 MALDI-TOF MS analysis in which the spectra of the mixture of **4b** and CF_3COOAg show a peak at m/z 2468 corresponding to [**4b** + Ag]$^+$ ion. 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 3.9×10^4 M^{-1} and 2.8×10^4 M^{-1} for **4a**·Ag^+ and **4b**·Ag^+, respectively. (Figure 2) These binding associations are much stronger than those of the corresponding monomeric counterparts (1.2×10^3 M^{-1} and 1.9×10^3 M^{-1}, respectively as determined by fluorescent titrations) indicating the advantage of cooperation binding.

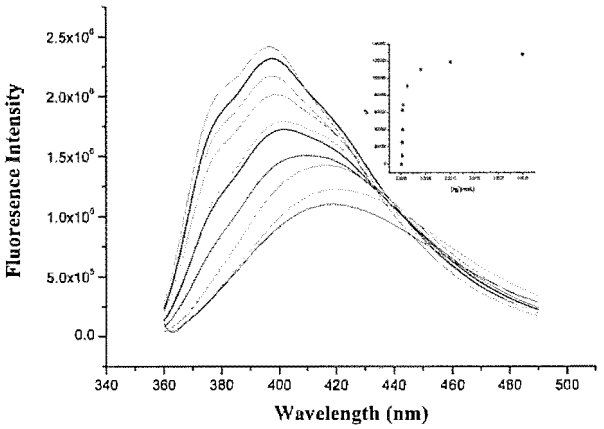
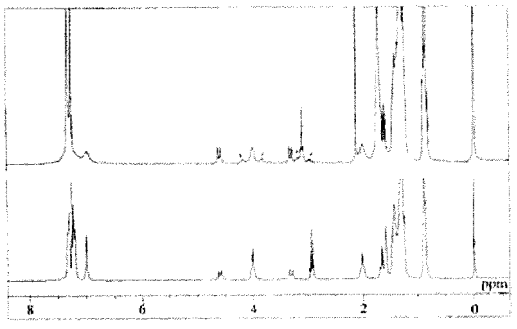


Figure 2. Fluorescence spectra of **4b** (20 μM) upon the addition of various concentrations of silver trifluoroacetate in $CHCl_3/CH_3OH$ (1:1 v/v). The inset shows a plot of ΔF versus $[Ag^+]$ at $\lambda_{max(em)}$ and its theoretical fit.

On the other hand, the changes in chemical shifts of hexylsulfanyl end-capped OPP-substituted calix[4]arene assemblies in the ^1H NMR spectra were apparent upon 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 deuteriated solvent(s) used (i.e., $CDCl_3$), Hg^{2+} and **4a** binding could be kinetically slow compared to NMR timescale. Under such a slow exchange condition, the proton resonances of both OCH_2 and SCH_2 from Hg^{2+}·**4a** complex split into two sets of two magnetically non-equivalent peaks. (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.[14] The association constants, estimated based on fluorescent titrations in $CHCl_3$:CH_3OH (v/v 1:1) were 4.0×10^2 M^{-1} and 1.2×10^2 M^{-1} for **4a**·Hg^{2+} and **4b**·Hg^{2+}, respectively.

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

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. First efficient synthesis of highly extended quaterphenyl-calix[4]arene assembly was also reported. We have shown that the binding affinities of hexylsulfanyl end-capped OPP(n)-substituted calix[4]arene assemblies towards 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 fluoro-ionophores to enhance metal ion binding.

Experimental Section

Improved procedure for Pd-catalysed Suzuki cross-coupling of oligoarylboronic acid and tetraiodoarylcalix[4]arene :

To a stirred solution of tetraiodoaryl-calix[4]arene (0.1 to 0.6 mmole) and about 20 mole % of $Pd(OAc)_2$: 2 $P(o\text{-}tol)_3$ in 15 mL of toluene was added with 5 mL of 2M K_2CO_3 under N_2 and 6 eqv 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 2M

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-tetradecoxycalix[4]arene (2a). ^{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. mp: 86-88 °C.

5,11,17,23-Tetrakis[4'-(trimethylsilyl)biphenyl]-25,26,27,28-tetradecoxy-calix[4]arene (2b). ^{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 $[M]^+$. mp: 195-197 °C.

5,11,17,23-Tetrakis(4-iodophenyl)-25,26,27,28-tetradecoxycalix[4]arene (3a). ^{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. mp: 139-140 °C.

5,11,17,23-Tetrakis(4'-iodobiphenyl)-25,26,27,28-tetradecoxycalix[4]arene (3b). ^1H 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. mp: 130-131.5 °C.

5,11,17,23-Tetrakis[4''-(hexylsulfanyl)biphenyl]-25,26,27,28-tetradecoxy-calix[4]arene (4a). ^1H NMR (400 MHz, $CDCl_3$, 25°C, δ) 7.30-7.33 (m, 16H), 7.20-7.24 (m, 16H), 7.00 (bs, 8H), 4.59 (d, J = 12.8 Hz, 4H), 4.00 (bt, J = 7.0 Hz, 8H), 3.33 (d, J = 13.6 Hz, 4H), 2.94 (t, J = 7.4 Hz, 8H), 2.00 (bt, J = 6.4 Hz, 8H), 1.56-1.70 (m, 8H), 1.29-1.44 (m, 80H), 0.87-0.91 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, δ) 156.3, 140.0, 138.2, 137.8, 135.9, 135.1, 134.6, 128.6, 127.1, 126.9, 126.7, 75.6, 33.4, 32.0, 31.4, 30.4, 30.1, 29.8, 29.5, 29.1, 28.6, 26.4, 22.7, 22.6, 14.1, 14.0. HRMS (MALDI-TOF) Calcd for $C_{140}H_{184}O_4S_4$, 2057.3077, Found: 2057.3072 (M^+). mp: 36 °C.

5,11,17,23-Tetrakis[4''-(hexylsulfanyl)terphenyl]-25,26,27,28-tetradecoxy-calix[4]arene (4b). ^1H NMR (400 MHz, $CDCl_3$, 25°C, δ) 7.48 (s, 16H), 7.41-7.43 (m, 16H), 7.28-7.30 (m, 16 H), 7.05 (bs, 8H), 4.63 (d, J = 12.8 Hz, 4H), 4.04 (bs, 8H), 3.36 (d, J = 13.6 Hz, 4H), 2.97 (t, J = 7.4 Hz, 8H), 2.04-2.05 (m, 8H), 1.66-1.74 (m, 8H), 1.27-

1.50 (m, 80H), 0.86-0.93 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, δ) 156.3, 140.1, 139.4, 138.7, 138.2, 137.5, 136.3, 135.1, 134.6, 128.6, 127.1, 126.8, 75.5, 33.3, 32.0, 31.4, 30.4, 30.1, 29.9, 29.5, 29.0, 28.6, 26.5, 22.7, 22.5, 14.1, 14.0. HRMS (MALDI-TOF) Calcd for $C_{164}H_{200}O_4S_4$, 2361.4329, Found: 2361.4324 $[M]^+$. mp: 203 °C.

5,11,17,23-Tetrakis[4''-(hexylsulfonyl)biphenyl]-25,26,27,28-tetradecoxy-calix[4]arene (5a). ^1H NMR (400 MHz, $CDCl_3$, 25°C, δ) 7.82 (d, J = 8.0 Hz, 8H), 7.57 (d, J = 7.6 Hz, 8H), 7.40 (d, J = 8.0 Hz, 8H), 7.30 (bs, 8H), 7.03 (s, 8 H), 4.63 (d, J = 13.2 Hz, 4H), 4.04 (t, J = 7.0 Hz, 8H), 3.36 (d, J = 13.2 Hz, 4H), 3.13 (t, J = 7.8 Hz, 8H), 2.02 (bt, J = 7.2 Hz, 8H), 1.79-1.69 (m, 8H), 1.26-1.45 (m, 80H), 0.81-0.92 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, δ) 156.7, 145.6, 141.5, 137.7, 136.6, 135.3, 134.0, 128.4, 127.9, 127.3, 127.3, 126.9, 75.6, 56.1, 32.0, 31.4, 31.2, 30.4, 30.0, 29.8, 29.4, 27.9, 26.4, 22.7, 22.4, 22.2, 14.1, 13.9. MS (MALDI-TOF) m/z 2185.3 $[M^+]$. mp: 100.5-102 °C.

5,11,17,23-Tetrakis[4''-(hexylsulfonyl)terphenyl]-25,26,27,28-tetradecoxy-calix[4]arene (5b). ^1H NMR (400 MHz, $CDCl_3$, 25°C, δ) 7.87 (d, J = 8.4 Hz, 8H), 7.65 (d, J = 8.0 Hz, 8H), 7.48-7.53 (m, 16H), 7.41 (bs, 8H), 7.27 (bs, 8H), 7.03 (bs, 8H), 4.62 (d, J = 12.8 Hz, 4H), 4.02 (bs, 8H), 3.35 (d, J = 13.2 Hz, 4H), 3.14 (t, J = 8.0 Hz, 8H), 2.02 (bs, 8H), 1.69-1.79 (m, 8H), 1.26-1.45 (m, 80H), 0.81-0.92 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, δ) 156.5, 145.7, 140.9, 140.6, 137.9, 137.7, 137.4, 135.3, 134.4, 128.6, 128.5, 127.4, 127.3, 127.0, 126.9, 75.6, 56.2, 32.0, 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. HRMS (MALDI-TOF) m/z Calcd for $C_{164}H_{200}O_{12}S_4Na$, 2512.3821, Found: 2512.3826 $[M + Na]^+$. mp: 220-221.5 °C.

5,11,17,23-Tetrakis[4'''-(hexylsulfonyl)quaterphenyl]-25,26,27,28-tetradecoxy-calix[4]arene (5c). ^{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 - H + Na]$^+$. mp: 314 °C (dec).

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Supporting Information Available: General experimental details, spectra data and synthesis of boronic acids, selected fluorescent titration data, and ^{1}H NMR spectra of boronic acids, compounds **2a-5a**, **2b-5b**, and **5c**. This materials is available free of charge via the Internet at http://pubs.acs.org.

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