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Aryl Trihydroxyborate Salts: Thermally Unstable Species with Unusual Gelation Abilities

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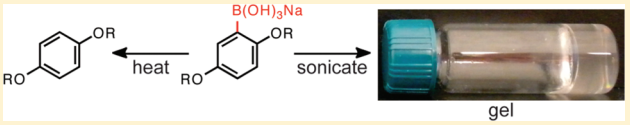
Supporting Information

ABSTRACT: A series of aryl trihydroxyborate salts were synthesized and found to form gels in benzene. The compounds were thermally unstable and readily underwent protodeboronation in solution and the solid state. Gelation could be induced without decomposition via sonication. Subsequent characterization studies revealed an unusual dependence of gel properties on alkyl chain length.

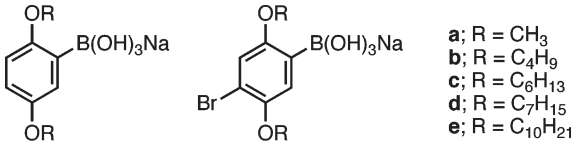


Aryl trihydroxyborate salts have recently emerged as convenient reagents for a variety of metal-catalyzed reactions,[1] including Pd-catalyzed Suzuki−Miyaura cross-couplings and Rh-catalyzed conjugate additions. Aryl trihydroxyborate salts were first utilized by Vaultier and co-workers in solid-phase reactions in 2001.[2] More recently, Cammidge and co-workers reported a simple procedure for synthesizing aryl trihydroxyborate salts and provided examples of their use in solution-phase reactions.[3] Since these early reports, a number of other researchers have used aryl trihydroxyborate salts in a variety of synthetic transformations.[1] Aryl trihydroxyborate salts have also been postulated to be the active, transmetalating species in base-mediated Suzuki−Miyaura cross-couplings using either boronic acids[4,5] or trifluoroborates[6] in the presence of water, although this hypothesis has recently come into question.[7]

Given their synthetic utility, we recently prepared a series of brominated aryl trihydroxyborates (**2a**−**e**) and investigated their use as difunctional monomers for preparing π-conjugated polymers. During these studies, we discovered that these aryl trihydroxyborate salts are unstable to prolonged heating and readily undergo protodeboronation. In addition, we observed that these complexes formed gels in aromatic solvents. As such, these compounds join a growing class of organometallic gelators.[8−10] Gelation typically occurs when molecules self-assemble to form anisotropic fibers, which entangle and entrap solvent through surface tension and capillary forces.[11,12] Because molecular gels can be stimuli-responsive and have nano- and micrometer-scale architectures, they are being explored for many different applications, including sensing,[13] remediation,[14] and materials synthesis.[15]

Herein, we report the synthesis, thermal instability, and unusual gelation ability of aryl trihydroxyborate salts (Chart 1). Compounds **1a**−**e** and **2a**−**e** were synthesized in high yields from their corresponding boronic acids via treatment with 1 equiv of NaOH in benzene. ^{11}B NMR spectroscopic studies revealed the anticipated upfield shift for the tetravalent boron (0−5 ppm) compared to the boronic acids (25−30 ppm), supporting formation of the aryl

Chart 1



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trihydroxyborate salts.[2] During these studies, we observed evidence of decomposition, including changes in the aromatic region of the ^{1}H NMR spectrum and brown discoloration of the NMR sample. We suspected protodeboronation was occurring because it was previously reported for *boronic acids* under base-catalyzed conditions.[16,17] Fields and Doyle first reported on the instability of isolated *aryl trihydroxborate salts* in 1974.[18] They observed an onset of weight loss for the sodium salt of benzene trihydroxyborate at 170 °C using thermal gravimetric analysis. Consistent with these previous reports, heating **1c** in the solid state for 30 min at 200 °C led to quantitative conversion to 1,4-bis(hexyloxy)benzene (Figure 1). To determine the decomposition rate in solution, the formation of 1,4-bis(butyloxy)benzene was monitored via HPLC analysis (relative to an internal standard) for samples of **1b** and **2b** heated in benzene. While **2b** was 70% decomposed within 1 h at 60 °C, **1b** was remarkably more stable. However, heating **1b** at an elevated temperature (100 °C) for 1 h led to a 64% conversion to 1,4-bis(butyloxy)benzene. These results are consistent with Frohn and co-workers, who observed that the rates of base-catalyzed protodeboronation of boronic acids in solution depended on both the number and position of fluorine atoms on the aromatic ring.[16c]

Compounds **1a**−**e** and **2b**−**d** form gels by heating and cooling samples in benzene. However, this method was not reproducible due to the thermal instability of these materials. To induce gelation without heating, an alternative sonication-based

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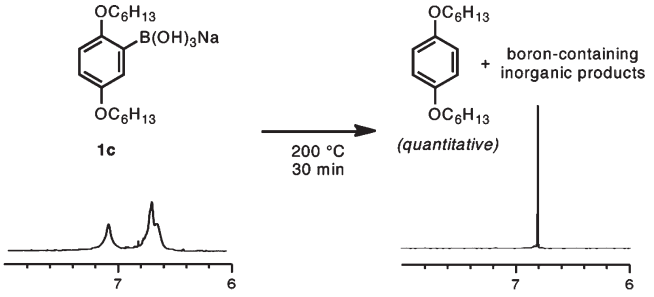

Figure 1. ^{1}H NMR spectra of compound **1c** in CD_3OD before (left) and after (right) heating in the solid state at 200 °C for 30 min.

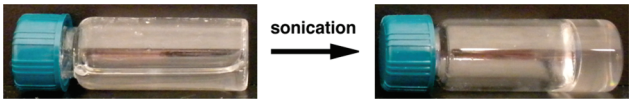

Figure 2. Gels of **1c** (12 mg) form in benzene (1 mL) with sonication for 5 min at rt.

Table 1. Characterization Data for Gelators 1a−e and 2b−d[a]

gelator	chain	cgc (mg/mL)	cgc (mM)	G'/G'' (Pa)
1a	CH_3	22 ± 2	100 ± 10	200/70
1b	C_4H_9	15 ± 1	49 ± 3	300/200
1c	C_6H_{13}	10 ± 2	28 ± 6	4000/1000
1d	C_7H_{15}	26 ± 1	67 ± 3	6000/1500
1e	$C_{10}H_{21}$	44 ± 2	98 ± 4	250/40
2b	C_4H_9	24 ± 2	62 ± 5	15000/9000
2c	C_6H_{13}	30 ± 2	68 ± 5	1400/220
2d	C_7H_{15}	32 ± 2	68 ± 4	4000/900

[a] All data represent an average of three runs. The G'/G'' measurements were performed at concentrations of 2 × cgc.

procedure was explored.[19] Indeed, gels were formed by adding solid sodium hydroxide to a vial, followed by a benzene solution of the boronic acid precursor and sonication for 5 min at rt (Figure 2). Using this procedure, aryl trihydroxyborate salts **1a−e** and **2b−d** also form gels in other solvents, including toluene, *p*-cymene, styrene, and cyclohexane. Compounds **2a** and **2e** did not form gels under any conditions examined.

As seen in Table 1 and Figure 3A, the critical gel concentration (cgc), which is the minimum concentration needed to form a stable gel, for **1a−e** shows an unusual dependence on alkyl chain length. For example, when the alkyl chain is changed from methyl to hexyl, the cgc drops from 22 to 10 mg/mL. However, the trend does not continue as further increases in chain length (decyl) led to a substantial increase in cgc (44 mg/mL). Chain-length-dependent cgcs have previously been observed; however, they typically fall into one of two classes: (1) Increasing chain lengths correlate with decreasing cgcs, which is generally attributed to increased van der Waals interactions and/or hydrophobic interactions.[20] (2) Odd−even effects of chain length are observed.[21] For example, Steed, Clarke and co-workers reported that bis(ureas) with odd-numbered linkers did not form gels, whereas molecules with even-numbered linkers did.[21a] These results are generally attributed to differences in packing densities for odd and even-length alkyl chains.[22] Neither of these trends is

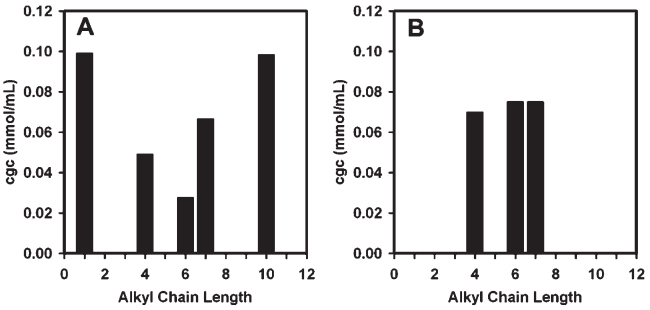

Figure 3. Plot of the cgc (in benzene) versus alkyl chain length for aryl trihydroxyborate salts (A) **1a−e** and (B) **2b−d**.

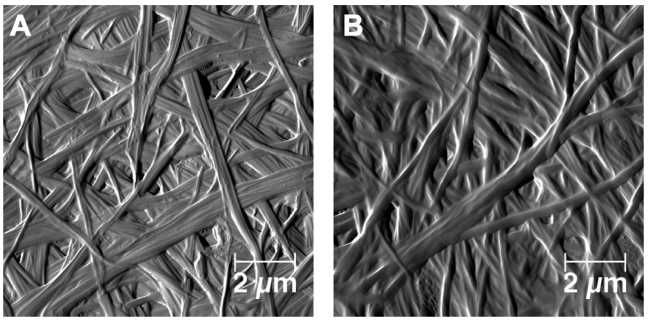

Figure 4. AFM images of gels from (A) **1c** (12 mg/mL) and (B) **2c** (32 mg/mL) in benzene.

observed herein. However, Dey and co-workers recently reported a similar trend in cgc for histidine-based gelators in water, with a C8 chain giving the lowest cgc compared to C6 and C10.[23] They attributed this result to the hydrophilic−lipophilic balance of the amphiphilic gelator. Given that the gels reported herein are formed in benzene, the observed relationship between cgc and chain length is not easily rationalized. It is interesting to note that the same chain-length dependence is not observed with brominated aryl trihydroxyborate salts **2b−d**, suggesting that the bromine atoms alter the molecular packing in the gel.

The strength and resilience of a gel to deformation by an external force is characterized by the loss (G') and storage (G'') moduli. The majority of the aryl trihydroxyborate gels reported herein show relatively large values for the modulus (G' > 1000 Pa) when compared to other organometallic gelators.[9] Strong gels typically result from highly cross-linked microstructures. To understand this effect, the gel structure was examined via microscopy. Scanning electron microscope images were unreliable because the gel samples decomposed when exposed to the electron beam (see the Supporting Information). Instead, atomic force microscopy (AFM) was used to generate high-resolution images of the aryl trihydroxyborate gels. The AFM images for gels **1a−e** and **2b−d** revealed that the gel microstructures contain physically cross-linked fibers (see Figure 4 and the Supporting Information). This dense fibrous network is consistent with the unusually strong gels observed via rheology. Despite these results, it was surprising that the gel-to-solution transition temperatures (measured by the falling-ball method) had almost no correlation with the gel strength (see the Supporting Information). These differences are likely due to the low melting temperature of the salts and competing decomposition reactions occurring during the T_{gel} measurements.

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The 3D orientation of molecules within the gel fiber can be elucidated if the powder X-ray diffraction (PXRD) pattern of the gel matches a single-crystal diffraction pattern of the gelator. Although we were unable to grow single crystals of **1a**−**e** and **2b**−**d** from benzene, Cammidge and co-workers obtained a single crystal of a structurally related compound, sodium 4-methoxyphenylborate salt, from H_2O.[3] In this compound, the sodium ions formed a linear hydrated chain $[Na(H_2O)_5]_n$ wherein significant hydrogen-bonding interactions between the H_2O and the B−OH were observed. We hypothesize that a similar chainlike structure may be present in our gel fibers because the PXRD pattern for the xerogel of **1a** exhibited a Bragg reflection at a *d*-spacing of 15.6 Å, which is similar to the (002) peak that corresponds to the distance between the chains of sodium ions in the reported structure (Supporting Information).[3,24]

In summary, a series of aryl trihydroxyborate salts with increasing alkyl chain lengths were synthesized. These compounds were found to be thermally unstable, undergoing quantitative protodeboronation with heating both in solution and the solid state. These results suggest a limited utility for these compounds as stoichiometric reagents in metal-catalyzed reactions. Some of these salts formed gels in organic solvents. The resulting gels are interesting because of their unusual strength and the observed chain-length dependence on gel properties. The origins of the chain-length dependence remain unclear at this time. Excitingly, these novel gelators may prove useful for preparing new materials, as the localization of difunctional gelators **2b**−**d** may lead to higher molecular weight polymers via Suzuki−Miyaura cross-coupling polymerizations in the gel state. Alternatively, free-radical polymerization of a styrene- or divinylbenzene-based solvent could lead to porous materials after removal of the aryl trihydroxyborate salt.

EXPERIMENTAL SECTION

Representative Procedure for Gel Formation. An aliquot (0.50 mL) of a NaOH solution (0.10 M in CH_3OH) was added to a 4 mL vial. The CH_3OH was removed in vacuo, and the resulting solid NaOH was held under vacuum overnight. Subsequently, (2,5-bis(hexyloxy)phenyl)boronic acid (1.0 mL, 0.06 M in benzene) was added to the vial. The heterogeneous mixture was sonicated for 5 min to create a homogeneous solution of **1c**. Gel formation occurred if the solution was left undisturbed for approximately 5 min.

General Procedure for the Synthesis of 1,4-Dialkoxybenzene. Hydroquinone (20.02 g, 0.1818 mol, 1.0 equiv), 1-bromobutane (48.0 mL, 0.454 mol, 2.5 equiv), and DMF (120 mL) were added under N_2 to a 500 mL flask and the mixture heated to 80 °C with vigorous stirring. K_2CO_3 (62.77 g, 0.4542 mol, 2.5 equiv) was then added, and the reaction mixture was stirred for 3 d. The reaction was cooled to rt, filtered, and washed with hexanes. The filtrate was washed with water (2 × 200 mL) and brine (2 × 200 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude product was recrystallized from hot CH_3OH to give 24.10 g of product as a white crystalline solid (60% yield): HRMS (ESI) $[M + H]^+$ calcd for $C_{14}H_{22}O_2$ 223.1698, found 223.1696; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 4H), 3.91 (t, J = 6.4 Hz, 4H), 1.75 (m, 4H), 1.49 (m, 4H), 0.98 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 115.4, 68.3, 31.5, 19.2, 13.9; NMR spectral data agree well with previously reported values;[25] mp 43.8−44.4 °C (lit.[25] mp 45−47 °C).

1,4-Bis(hexyloxy)benzene. Following the general procedure described above, 1,4-bis(hexyloxy)benzene was obtained after purification by recrystallization as a white crystalline solid (16.06 g, 63% yield): HRMS (ESI) $[M + H]^+$ calcd for $C_{18}H_{30}O_2$ 279.2324, found 279.2328; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 4H), 3.90 (t, J = 6.8 Hz, 4H), 1.76 (m, 4H), 1.47−1.32 (br, 12H), 0.91 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 115.4, 68.6, 31.6, 29.4, 25.7, 22.6, 14.0; NMR spectral data agree well with previously reported values;[26] mp 43.4−44.3 °C (lit.[27] mp 45 °C).

1,4-Bis(heptyloxy)benzene. Following the general procedure described above, 1,4-bis(heptyloxy)benzene was obtained after purification by recrystallization as a white crystalline solid (11.59 g, 42% yield): HRMS (ESI) $[M + H]^+$ calcd for $C_{20}H_{34}O_2$ 307.2637, found 307.2634; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 4H), 3.90 (t, J = 6.8 Hz, 4H), 1.75 (m, 4H), 1.46−1.28 (br, 16H), 0.90 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 115.4, 68.6, 31.8, 29.4, 29.1. 26.0, 22.6, 14.1; mp 56.5−57.1 °C (lit.[28] mp 57.6−58 °C).

1,4-Bis(decyloxy)benzene. Following the general procedure described above, 1,4-bis(decyloxy)benzene was obtained after purification by recrystallization as a white crystalline solid (27.03 g, 76% yield): HRMS (ESI) $[M]^+$ calcd for $C_{26}H_{46}O_2$ 390.3498, found 390.3500; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 4H), 3.90 (t, J = 6.8 Hz, 4H), 1.73 (m, 4H), 1.46−1.27 (m, 28H), 0.88 (t, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 115.4, 68.7, 31.9, 29.57, 29.55, 29.4, 29.3, 26.1, 22.7, 14.1; some carbons on the decyl chains are unresolved; mp 68.0−69.0 °C.

General Procedure for the Synthesis of 2-Bromo-1,4-dialkoxybenzene. Sequentially, 1,4-dibutoxybenzene (5.039 g, 0.0226 mol, 1.0 equiv), acetonitrile (38.5 mL), NH_4NO_3 (0.180 g, 0.0022 mol, 0.1 equiv), and *N*-bromosuccinimide (4.029 g, 0.0226 mol, 1.0 equiv) were added to a 100 mL round-bottom flask with a stir bar. The reaction was stirred at rt for 2 h and then quenched with water (50 mL). The aqueous mixture was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with water (2 × 50 mL) and brine (2 × 50 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography using 14.95/85.00/0.05 toluene/hexanes/EtOAc as the eluent to give 3.96 g of product as a clear colorless oil (58% yield): MS (EI) m/z = 300.2 $[M(^{79}Br)]^+$ 302.2 $[M(^{81}Br)]^+$; HRMS (ESI) $[M]^+$ calcd for $C_{14}H_{21}BrO_2$ 300.0725, found 300.0722; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 2.4 Hz, 1H), 6.82 (m, 2H), 3.96 (t, J = 6.4 Hz, 2H), 3.89 (t, J = 6.4 Hz, 2H), 1.76 (m, 4H), 1.50 (m, 4H), 0.97 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 149.8, 119.5, 114.7, 114.4, 112.8, 69.9, 68.5, 31.4, 31.3, 19.24, 19.19. 13.9, 13.8; NMR spectral data agree well with previously reported values.[29]

2-Bromo-1,4-bis(hexyloxy)benzene. Following the general procedure described above, 2-bromo-1,4-bis(hexyloxy)benzene was obtained after purification by column chromatography as a clear colorless oil (2.808 g, 35% yield): MS (EI) m/z = 356.2 $[M(^{79}Br)]^+$, 358.2 $[M(^{81}Br)]^+$; HRMS (ESI) $[M]^+$ calcd for $C_{18}H_{29}BrO_2$ 356.1351, found 356.1336; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 2.8 Hz, 1H), 6.79 (m, 2H), 3.95 (t, J = 6.8 Hz, 2H), 3.88 (t, J = 6.8 Hz, 2H), 1.77 (m, 4H), 1.83−1.31 (br, 12H), 0.91 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 149.8, 119.5, 114.7, 114.4, 112.8. 70.2, 68.8, 31.6, 29.22, 29.23, 25.7, 22.6, 14.0. Some carbons on the hexyl chains are unresolved. NMR spectral data agree well with previously reported values.[30]

2-Bromo-1,4-bis(heptyloxy)benzene. Following the general procedure described above, 2-bromo-1,4-bis(heptyloxy)benzene was obtained after purification by column chromatography as a clear colorless oil (2.964 g, 34% yield): MS (EI) m/z = 384.3 $[M(^{79}Br)]^+$, 386.3 $[M(^{81}Br)]^+$; HRMS (ESI) $[M]^+$ calcd for $C_{20}H_{33}BrO_2$ 384.1664, found 384.1677; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 2.8 Hz, 1H), 6.79 (m, 2H), 3.95 (t, J = 6.4 Hz, 2H), 3.88 (t, J = 6.4 Hz, 2H), 1.76 (m, 4H), 1.49−1.30 (br, 16H), 0.91 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 149.8, 119.5, 114.7, 114.4, 112.8, 70.2, 68.8, 31.77, 31.76, 29.27, 29.25, 29.0, 26.0, 22.6, 14.07, 14.06. Some carbons on the heptyl chains are unresolved.

2-Bromo-1,4-bis(decyloxy)benzene. Following the general procedure described above, 2-bromo-1,4-bis(decyloxy)benzene was obtained after purification by column chromatography using

19.95/80.0/0.05 toluene/hexanes/EtOAc as the eluent to give a clear crystalline solid (1.43 g, 40% yield): MS (EI) m/z = 468.4 $[M(^{79}Br)]^+$, 470.4 $[M(^{81}Br)]^+$; HRMS (ESI) $[M]^+$ calcd for $C_{26}H_{45}BrO_2$ 468.2603, found 468.2598; ^1H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 2.8 Hz, 1H), 6.81 (m, 2H), 3.95 (t, J = 6.4 Hz, 2H), 3.88 (t, J = 6.4 Hz, 2H), 1.76 (m, 4H), 1.49−1.27 (br, 28H), 0.88 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 149.8, 119.5, 114.7, 114.4, 112.8, 70.2, 68.8, 31.9, 29.6, 29.5, 29.4, 29.32, 29.26, 29.25, 26.0, 22.7, 14.1. Some carbons on the decyl chains are unresolved; mp 37.0−39.0 °C.

General Procedure for the Synthesis of 1,4-Dibromo-2,5-dialkoxybenzene. Dimethoxybenzene (2.009 g, 0.0146 mol, 1.0 equiv) was dissolved in $CHCl_3$ and cooled to 0 °C under N_2, and the pressure was vented through a 10% aq Na_2SO_3 solution (~100 mL). Bromine (1.9 mL, 0.04 mol, 2.5 equiv) was added dropwise via syringe. The ice bath was then removed and the reaction continued to stir at rt for 3 h. The reaction was quenched with 10% aq Na_2SO_3 (50 mL) and extracted with CH_2Cl_2 (2 × 50 mL). The organic layer was washed with brine (2 × 50 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude product was recrystallized from CH_2Cl_2/MeOH to give 2.894 g of product as white crystals (67% yield): MS (EI) m/z = 294.0 $[M(^{79}Br,^{79}Br)]^+$, 296.0 $[M(^{79}Br, ^{81}Br)]^+$, 298.0 $[M(^{81}Br, ^{81}Br)]^+$; HRMS (ESI) $[M]^+$ calcd for $C_8H_8Br_2O_2$ 293.8891, found 293.8882; ^1H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 2H), 3.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 117.1, 110.5, 57.0; NMR spectral data agree with previously reported values;[31] mp 143.9−145.0 °C (lit.[31] mp 140−143 °C).

1,4-Dibromo-2,5-dibutoxybenzene. Following the general procedure described above, 1,4-dibromo-2,5-dibutoxybenzene was obtained after purification by recrystallization as white crystals (2.804 g, 81% yield): MS (EI) m/z = 378.1 $[M(^{79}Br,^{79}Br)]^+$, 380.1 $[M(^{79}Br, ^{81}Br)]^+$, 382.1 $[M(^{81}Br, ^{81}Br)]^+$; HRMS (ESI) $[M]^+$ calcd for $C_{14}H_{20}Br_2O_2$ 377.9830, found 377.9829; ^1H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 2H), 3.96 (t, J = 6.8 Hz, 4H), 1.80 (m, 4H), 1.53 (m, 4H), 0.98 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 118.5, 111.1, 70.0, 31.2, 19.2, 13.8; NMR spectral data agree well with previously reported values;[25] mp 73.0−74.0 °C (lit.[25] mp 76−77 °C).

1,4-Dibromo-2,5-bis(hexyloxy)benzene. Following the general procedure described above, 1,4-dibromo-2,5-bis(hexyloxy)benzene was obtained after purification by recrystallization as white crystals (2.758 g, 88% yield): MS (EI) m/z = 434.3 $[M(^{79}Br,^{79}Br)]^+$, 436.3 $[M(^{79}Br, ^{81}Br)]^+$, 438.3 $[M(^{81}Br, ^{81}Br)]^+$; HRMS (ESI) $[M]^+$ calcd for $C_{18}H_{28}Br_2O_2$ 434.0456, found 434.0448; ^1H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 2H), 3.95 (t, J = 6.4 Hz, 4H), 1.80 (m, 4H), 1.49 (m, 4H), 1.35 (m, 8H), 0.91 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 118.5, 111.1, 70.3, 31.5, 29.1, 25.6, 22.6, 14.0; NMR spectral data agree well with previously reported values.[26,32] mp 51.3−53.1 °C.

1,4-Dibromo-2,5-bis(heptyloxy)benzene. Following the general procedure described above, 1,4-dibromo-2,5-bis(heptyloxy)benzene was obtained after purification by recrystallization as white crystals (2.835 g, 93% yield): MS (EI) m/z = 462.1 $[M(^{79}Br,^{79}Br)]^+$, 464.1 $[M(^{79}Br, ^{81}Br)]^+$, 466.1 $[M(^{81}Br, ^{81}Br)]^+$; HRMS (ESI) $[M]^+$ calcd for $C_{20}H_{32}Br_2O_2$ 462.0769, found 462.0779; ^1H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 2H), 3.95 (t, J = 6.8 Hz, 4H), 1.79 (m, 4H), 1.48 (m, 4H), 1.38−1.31 (br, 12H), 0.90 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 118.5, 111.1, 70.3, 31.6, 29.1, 29.0, 26.0, 22.6, 14.1; NMR spectral data agree well with previously reported values;[33] mp 62.0−64.0 °C (lit.[33] mp 63 °C).

1,4-Dibromo-2,5-bis(decyloxy)benzene. Following the general procedure described above, 1,4-dibromo-2,5-bis(decyloxy)benzene was obtained after purification by recrystallization as white crystals (2.557 g, 91% yield): MS (EI) m/z = 546.1 $[M(^{79}Br,^{79}Br)]^+$, 548.1 $[M(^{79}Br, ^{81}Br)]^+$, 550.1 $[M(^{81}Br, ^{81}Br)]^+$; HRMS (ESI) $[M]^+$ calcd for $C_{26}H_{44}Br_2O_2$ 546.1708, found 546.1707; ^1H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 2H), 3.94 (t, J = 6.4 Hz, 4H), 1.80 (m, 4H), 1.54−1.27 (br, 28H), 0.90 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 118.5, 111.1, 70.3, 31.9, 29.5, 29.31, 29.29, 29.1, 25.9, 22.7, 14.1; some carbons on the decyl chains are unresolved; mp 75.0−76.5 °C.

General Procedure for (2,5-Bis(alkoxy)phenyl)boronic Acid. An oven-dried 50 mL Schlenk flask was equipped with a stir bar and septum, cooled to rt under vacuum, and filled with N_2. 2-Bromo-1,4-dibutoxybenzene (1.002 g, 0.0033 mol, 1.0 equiv) and THF (32 mL) were added to the flask. The solution was then cooled to −78 °C. Then *n*-BuLi (2.3 mL, 1.6 M, 1.1 equiv) was added via syringe. After 20 min, triisopropyl borate (2.3 mL, 1.0 mmol, 3.0 equiv) was added. The reaction was gradually warmed to rt and stirred for 24 h. The mixture was cooled to 0 °C, aqueous HCl (5 mL, 2 M) was added, and the mixture was stirred for 20 min. The aqueous mixture was extracted with ether (2 × 50 mL). The combined organic layers were washed with brine (1 × 50 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography using 5/15/80 EtOAc/CH_2Cl_2/hexanes as the eluent to give 477 mg of product as a white solid (53% yield): HRMS (ESI) $[M]^+$ calcd for $C_{14}H_{23}BO_4$ 266.1689, found 266.1697; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.24; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 3.2 Hz, 1H), 6.97 (dd, J = 8.8, 3.2 Hz, 1H), 6.84 (d, J = 8.8 Hz, 1H), 6.49 (s, 2H), 4.03 (t, J = 6.8 Hz, 2H), 3.96 (t, J = 6.8 Hz, 2H), 1.77 (m, 4H), 1.48 (m, 4H), 0.98 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 153.3, 121.3, 119.3, 112.1, 68.7, 68.3, 31.43, 31.35, 19.3, 19.2, 14.0, 13.8; C *ipso* to B is not observed; mp 71.5−73.0 °C.

(2,5-Bis(hexyloxy)phenyl)boronic Acid. Following the general procedure described above, (2,5-bis(hexyloxy)phenyl)boronic acid was obtained after column chromatography as a white solid (400 mg, 26% yield): HRMS (ESI) $[M + Na]^+$ calcd for $C_{18}H_{31}BO_4$ 345.2213, found 345.2222; ^{11}B NMR (128 MHz, CD_3OD) δ 29.67; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 3.2 Hz, 1H), 6.96 (dd, J = 8.8, 3.2 Hz, 1H), 6.84 (d, J = 8.8 Hz, 1H), 6.16 (s, 2H), 4.02 (t, J = 6.4 Hz, 2H), 3.94 (t, J = 6.8 Hz, 2H), 1.79 (m, 4H), 1.48−1.31 (br, 12H), 0.91 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 153.3, 121.4, 119.3, 112.1, 69.0, 68.6, 31.6, 31.5, 29.26, 29.29, 25.71, 25.69, 22.6, 22.5, 14.03, 13.97; C *ipso* to B is not observed; mp 73.7−74.2 °C.

(2,5-Bis(heptyloxy)phenyl)boronic Acid. Following the general procedure described above, (2,5-bis(heptyloxy)phenyl)boronic acid was obtained after column chromatography as a white solid (713 mg, 62% yield): HRMS (ESI) $[M]^+$ calcd for $C_{20}H_{35}BO_4$ 350.2628, found 350.2635; ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.87; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 3.2 Hz, 1H), 6.96 (dd, J = 8.8, 3.2 Hz, 1H), 6.84 (d, J = 8.8 Hz, 1H), 5.97 (s, 2H), 4.02 (t, J = 6.8 Hz, 2H), 3.94 (t, J = 6.8 Hz, 2H), 1.77 (m, 4H), 1.48−1.30 (br, 16H), 0.89 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 153.3, 121.4, 119.3, 112.1, 69.0, 68.6, 31.8, 31.7, 29.4, 29.1, 29.0, 26.0, 22.61, 22.56, 14.08, 14.05; C *ipso* to B is not observed, some carbons on the heptyl chains are unresolved; mp 74.0−76.5 °C.

(2,5-Bis(decyloxy)phenyl)boronic Acid. Following the general procedure described above, (2,5-bis(decyloxy)phenyl)boronic acid was obtained after column chromatography as a white solid (404 mg, 43% yield): HRMS (ESI) $[M + Na]^+$ calcd for $C_{26}H_{47}BO_4$ 457.3465, found 457.3460; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.13; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 3.2 Hz, 1H), 6.97 (dd, J = 8.8, 3.2 Hz, 1H), 6.84 (d, J = 8.8 Hz, 1H), 5.90 (s, 2H), 4.02 (t, J = 6.8 Hz, 2H), 3.94 (t, J = 6.8 Hz, 2H), 1.78 (m, 4H), 1.45−1.27 (br, 28H), 0.88 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 153.3, 121.4, 119.3, 112.1, 69.0, 68.6, 31.89, 31.87, 29.55, 29.50, 29.4, 29.34, 29.32, 29.28, 26.0, 22.7, 14.1; C *ipso* to B is not observed, some carbons on the decyl chains are unresolved; mp 89.8−91.2 °C.

(2,5-Dimethoxyphenyl)boronic Acid. Following the general procedure described above, (2,5-dimethoxyphenyl)boronic acid was obtained after column chromatography (20/80 EtOAc/hexanes) as a white solid (490 mg, 58% yield): HRMS (ESI) $[M]^+$ calcd for $C_8H_{11}BO_4$

182.0750, found 182.0757; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 3.2 Hz, 1H), 7.00−6.97 (dd, J = 8.8, 3.2 Hz, 1H), 6.86 (d, J = 8.8 Hz, 1H), 6.72 (s, 2H), 3.87 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 153.8, 120.6, 118.6, 111.2, 56.0, 55.7; C *ipso* to B not observed; NMR spectral data agree well with previously reported values;[34] mp 91.2−92.7 °C (lit.[35] mp 91−93 °C).

(4-Bromo-2,5-dibutoxyphenyl)boronic Acid. Following the general procedure described above, (4-bromo-2,5-dibutoxyphenyl)boronic acid was obtained after column chromatography as a white solid (420 mg, 46% yield): MS (EI) m/z = 344.1 $[M(^{79}Br)]^+$, 346.1 $[M(^{81}Br)]^+$; HRMS (ESI): $[M]^+$ calcd for $C_{14}H_{22}BBrO_4$, 344.0795; found 344.0796. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.05; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s,1H), 7.10 (s, 1H), 5.80 (s, 2H), 4.02 (m, 4H), 1.80 (m, 4H), 1.5 (m, 4H), 0.98 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 150.1, 120.7, 116.6, 116.5, 69.7, 69.0, 31.3, 31.2, 19.2, 13.9, 13.8; C *ipso* to B is not observed, some carbons on the butyl chains are unresolved; mp 110.0 − 112.5 °C.

(4-Bromo-2,5-bis(hexyloxy)phenyl)boronic Acid. Following the general procedure described above, (4-bromo-2,5-bis(hexyloxy)-phenyl)boronic acid was obtained after column chromatography as a white solid (525 mg, 57% yield): MS (EI) m/z = 400.1 $[M(^{79}Br)]^+$, 402.1 $[M(^{81}Br)]^+$; HRMS (ESI) $[M]^+$ calcd for $C_{18}H_{30}BBrO_4$ 400.1421, found 400.1434; ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.78; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.10 (s, 1H), 5.91 (s, 1H), 4.02 (m, 4H), 1.81 (m, 4H), 1.50−1.34 (br, 12H), 0.91 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 150.0, 120.7, 116.5, 70.0, 69.3, 31.5, 31.4, 29.20, 29.17, 25.64, 25.63, 22.6, 22.5, 14.02, 13.95; C *ipso* to B is not observed; mp 106.0−108.0 °C.

(4-Bromo-2,5-bis(heptyloxy)phenyl)boronic Acid. Following the general procedure described above, (4-bromo-2,5-bis(heptyloxy)-phenyl)boronic acid was obtained after column chromatography as a white solid (315 mg, 34% yield): MS (ES) m/z = 451.2 $[M + Na(^{79}Br)]^+$, 453.2 $[M + Na(^{81}Br)]^+$; HRMS (ESI) $[M + Na]^+$ calcd for $C_{20}H_{34}BBrO_4$ 451.1626, found 451.1640; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.04; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.10 (s, 1H), 6.32 (s, 1H), 4.01 (m, 4H), 1.81 (m, 4H), 1.48−1.31 (br, 16H), 0.89 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 150.0, 120.6, 116.5, 116.4, 69.9, 69.3, 31.8, 31.7, 29.23, 29.19, 29.0, 28.9, 25.92, 25.90, 22.60, 22.55, 14.1, 14.0; C *ipso* to B is not observed; mp 90.2−92.4 °C.

(4-Bromo-2,5-bis(decyloxy)phenyl)boronic Acid. Following the general procedure described above, (4-bromo-2,5-bis(decyloxy)-phenyl)boronic acid was obtained after column chromatography as a white solid (193 mg, 20% yield): MS (EI) m/z = 512.3 $[M(^{79}Br)]^+$, 514.3 $[M(^{81}Br)]^+$; HRMS (ESI) $[M]^+$ calcd for $C_{26}H_{46}BBrO_4$ 512.2672, found 512.2665; ^{11}B NMR (128 MHz, $CDCl_3$) δ 26.44; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.10 (s, 1H), 5.93 (s, 2H), 4.01 (m, 4H), 1.81 (m, 4H), 1.57−1.27 (br, 28H), 0.88 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 150.0, 120.7, 116.6, 116.5, 70.0, 69.3, 31.90, 31.86, 29.56, 29.55, 29.49, 29.48, 29.4, 29.34, 29.32, 29.27, 29.25, 29.2, 26.0, 22.7, 14.1; C *ipso* to B is not observed, some carbons on the decyl chains are unresolved; mp 85.0−88.2 °C.

(4-Bromo-2,5-dimethoxyphenyl)boronic Acid. Following the general procedure described above, (4-bromo-2,5-dimethoxyphenyl)boronic acid was obtained after column chromatography (20/80 EtOAc/hexanes) as a white solid (556 mg, 63% yield): MS (EI) m/z = 260.1 $[M(^{79}Br)]^+$, 262.1 $[M(^{81}Br)]^+$; HRMS (ESI) $[M]^+$ calcd for $C_8H_{10}BBrO_4$ 259.9856, found 259.9862; ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.96; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.13 (s, 1H), 6.08 (s, 2H), 3.89 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 150.5, 119.1, 116.0, 115.7, 56.7, 56.3; C *ipso* to B is not observed; mp 105−109 °C.

General Procedure for 2,5-Dialkoxyphenylboronic Acid Sodium Salt (1a). (2,5-Dimethoxyphenyl)boronic acid (359 mg, 1.97 mmol, 1.0 equiv) was dissolved in benzene (10.0 mL), and then NaOH (77.2 mg, 1.93 mmol, 0.98 equiv) was added. The reaction was stirred for 20 h at rt, and the solution turned into a white suspension. The mixture was concentrated in vacuo isolating 390 mg of a white solid (89% yield): ^{11}B NMR (128 MHz, CD_3OD) δ 4.63; ^{1}H NMR (400 MHz, CD_3OD) δ 7.12 (br, 1H), 6.74−6.65 (br, 2H) 3.74 (br, 6H); ^{13}C NMR (125 MHz, CD_3OD) δ 158.1, 154.7, 122.4, 112.3, 111.1, 56.1, 56.0; C *ipso* to B is not observed; mp 99 °C dec.

(2,5-Dibutoxyphenyl)boronic Acid Sodium Salt (1b). Following the general procedure described above, (2,5-dibutoxyphenyl)boronic acid sodium salt was obtained as a white solid (405 mg, 99% yield): ^{11}B NMR (128 MHz, CD_3OD) δ 4.76; ^{1}H NMR (400 MHz, CD_3OD) δ 7.08 (br, 1H), 6.70 (br, 2H), 3.92 (t, J = 6.4 Hz, 4H), 1.7 (m, 4H), 1.5 (m, 4H), 0.99 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.5, 154.1, 123.2, 121.9, 113.6, 113.1, 69.7, 69.3, 32.9, 32.7, 20.4, 14.4, 14.3; mp 80−82 °C.

(2,5-Bis(hexyloxy)phenyl)boronic Acid Sodium Salt (1c). Following the general procedure described above, (2,5-bis(hexyloxy)-phenyl)boronic acid sodium salt was obtained as a white solid (450 mg, 100% yield): ^{11}B NMR (128 MHz, CD_3OD) δ 4.51; ^{1}H NMR (400 MHz, CD_3OD) δ 7.08 (br, 1H), 6.71−6.65 (br, 2H), 3.90 (m, 2H), 1.71 (m, 4H), 1.47−1.34 (br, 12H), 0.91 (m, 6H); ^{13}C NMR (125 MHz, CD_3OD) δ 157.4, 154.4, 123.2, 122.2, 114.0, 113.2, 70.1, 69.7, 33.1, 33.0, 30.8, 27.1, 23.9, 14.6; some carbons on the hexyl chains are unresolved; mp 60−62 °C.

(2,5-Bis(heptyloxy)phenyl)boronic Acid Sodium Salt (1d). Following the general procedure described above, (2,5-bis(heptyloxy)-phenyl)boronic acid sodium salt was obtained as a white solid (488 mg, 80% yield): ^{11}B NMR (128 MHz, CD_3OD) δ 4.65; ^{1}H NMR (400 MHz, CD_3OD) δ 7.08 (br, 1H), 6.69−6.62 (br, 2H), 3.94 (m, 4H), 1.71 (m, 4H), 1.47−1.27 (br, 16H), 0.90 (m, 6H); ^{13}C NMR (125 MHz, CD_3OD) δ 157.3, 154.1, 123.4, 122.0, 113.6, 113.0, 70.0, 69.6, 33.0, 30.7, 30.5, 30.4, 30.3, 27.2, 23.7, 14.4; some carbons on the heptyl chains are unresolved; mp 59−62 °C.

(2,5-Bis(decyloxy)phenyl)boronic Acid Sodium Salt (1e). Following the general procedure described above, (2,5-bis(decyloxy)-phenyl)boronic acid sodium salt was obtained as a clear oil (429 mg, 97% yield): ^{11}B NMR (128 MHz, CD_3OD) δ 4.41; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (br, 1H), 6.98−6.63 (br, 2H), 3.91 (t, J = 6.4 Hz, 4H), 1.73 (m, 4H), 1.46−1.29 (br, 28H), 0.89 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.4, 154.1, 123.7, 122.0, 113.5, 113.1, 70.0, 69.6, 33.1, 30.7, 30.6, 30.5, 27.2, 27.1, 23.8, 14.5; some carbons on the decyl chains are unresolved.

General Procedure for (4-Bromo-2,5-dialkoxyphenyl)boronic Acid Sodium Salt (2a). (4-Bromo-2,5-dimethoxyphenyl)boronic acid (414 mg, 1.59 mmol, 1.0 equiv) was dissolved in benzene (10.0 mL) and CH_2Cl_2 (5.0 mL). Then NaOH (64.4 mg, 1.61 mmol, 1.0 equiv) was added. The reaction was stirred for 11−24 h at rt. The mixture was concentrated in vacuo isolating 437 mg of product as a white solid (92% yield): ^{11}B NMR (128 MHz, CD_3OD) δ 4.88; ^{1}H NMR (500 MHz, CD_3OD) δ 7.22 (br, 1H), 6.94 (br, 1H) 3.81 (br, 3H), 3.73 (br, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 159.3, 151.0, 121.2, 115.5, 109.4, 57.3, 56.4; C *ipso* to B is not observed; mp 134 °C dec.

(4-Bromo-2,5-dibutoxyphenyl)boronic Acid Sodium Salt (2b). Following the general procedure described above, (4-bromo-2,5-dibutoxyphenyl)boronic acid sodium salt was obtained as a white solid (337 mg, 99% yield); ^{11}B NMR (128 MHz, CD_3OD) δ 4.57; ^{1}H NMR (400 MHz, CD_3OD) δ 7.17 (br, 1H), 6.91 (br, 1H), 3.99 (m, 2H), 3.92−3.89 (br, 2H), 1.74 (m, 4H), 1.52 (m, 4H), 0.98 (m, 6H); ^{13}C NMR (125 MHz, CD_3OD) δ 158.0, 150.5, 123.0, 121.7, 117.0, 110.7, 70.9, 69.7, 32.8, 32.6, 20.4, 14.3, 14.2; some carbons on the butyl chains are unresolved; mp 98−100 °C.

(4-Bromo-2,5-bis(hexyloxy)phenyl)boronic Acid Sodium Salt (2c). Following the general procedure described above, only

dissolved in benzene, (4-bromo-2,5-bis(hexyloxy)phenyl)boronic acid sodium salt was obtained as a white solid (438 mg, 94% yield): ^{11}B NMR (128 MHz, CD_3OD) δ 4.53; ^{1}H NMR (400 MHz, CD_3OD) δ 7.19 (br, 1H), 6.88 (br, 1H), 3.98 (t, J = 6.4 Hz, 2H), 3.89 (m, 2H), 1.75 (m, 4H), 1.54−1.33 (br, 12H), 0.92 (m, 6H); ^{13}C NMR (125 MHz, CD_3OD) δ 158.0, 150.4, 123.4, 121.9, 116.9, 110.2, 71.2, 70.0, 32.9, 32.8, 30.6, 30.4, 26.9, 23.7, 14.4; some carbons on the hexyl chains are unresolved; mp 35−37 °C

(4-Bromo-2,5-bis(heptyloxy)phenyl)boronic Acid Sodium Salt (2d). Following the general procedure described above, only dissolved in benzene, (4-bromo-2,5-bis(heptyloxy)phenyl)boronic acid sodium salt was obtained as a white solid (310 mg, 90% yield): ^{11}B NMR (128 MHz, CD_3OD) δ 4.49; ^{1}H NMR (400 MHz, CD_3OD) δ 7.21 (br, 1H), 6.88 (br, 1H), 3.98 (t, J = 6.8 Hz, 2H), 3.91 (t, J = 6.8 Hz, 2H), 1.75 (m, 4H), 1.53−1.27 (br, 16H), 0.90 (m, 6H); ^{13}C NMR (125 MHz, CD_3OD) δ 158.0, 150.4, 123.6, 121.8, 116.9, 110.1, 71.1, 70.0, 33.0, 30.7, 30.3, 30.2, 27.2, 27.1, 23.7, 14.5; some carbons on the heptyl chains are unresolved; mp 48−50 °C.

(4-Bromo-2,5-bis(decyloxy)phenyl)boronic Acid Sodium Salt (2e). Following the general procedure described above, (4-bromo-2,5-bis(decyloxy)phenyl)boronic acid sodium salt was obtained as a white solid (193 mg, 95% yield): ^{11}B NMR (128 MHz, CD_3OD) δ 4.35; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (br, 1H), 6.89 (br, 1H), 3.98 (m, 2H), 3.89 (br, 2H), 1.75 (m, 4H), 1.52−1.29 (br, 28H), 0.89 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0, 150.4, 123.4, 121.8, 116.9, 110.3, 71.1, 70.0, 33.1, 30.73, 30.68, 30.6, 30.5, 27.2, 23.7, 14.5; some carbons on the decyl chains are unresolved; mp 46−48 °C.

■ ASSOCIATED CONTENT

Supporting Information. Spectroscopic data; microscope images; rheological data; powder X-ray diffraction patterns; thermal gravimetric analysis data; T_{gel} data. This material is available free of charge via the Internet at http://pubs.acs.org.

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