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Synthesis and Mesophase Behavior of Rod Like Phenylene Thiophene Based Polyhydroxy Amphiphiles

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Novel rod like phenylene thiophene based polyhydroxy amphiphiles, derivatives of gallic acid combining three hydrophilic 2,3-dihydroxypropyloxy groups and one alkyl chain via central aromatic linking units, have been synthesized by using Ni(II), Pd(0) catalyzed coupling reaction as key steps. The mesophase behavior of such compounds was investigated by POM and DSC. Thereby the influence of the position of the alkyl chains on the mesophase behavior was discussed. All such compounds exhibit smectic A phases. As the alkyl chain moving from the terminal position to the lateral position near the central of the rigid core, the stability of the smectic A phase would be decreased.

Keywords synthesis, amphiphilic, thiophene, C—C-coupling reaction, smectic phase

Introduction

Amphiphilic molecules consisting of a hydrophilic headgroup and a hydrophobic part can form thermotropic and/or lyotropic mesophases,[1,2] which is of great importance for numerous applications to several fields of science and technology, and also a prerequisite for the development of biological structure.[3] Polyhydroxyamphiphiles are interesing amphiphiles, which have turned out to be especially useful for designing soft matter. Here, the mesophase formation is mainly due to the segregation of the lipophilic segments from the polar polyhydoxy groups. The cooperative hydrogen bonding between these hydroxyl groups additionally stabilizes these polymolecular aggregates, whereas the relative space filling of the polar and nonpolar molecular parts is responsible for the observed mesophase morphology. Hence, by controlling the molecular shape, the polar-apolar parity, and the attractive forces, *i.e*., by changing the number and positions of the hydroxygroups and the alkylchains, quite different mesophases (all reversed type mesophases as well as the normal type mesophases including different cubic mesophases) have been realized with these materials.[4]

Thiophene based derivatives are widely studied because of the potential charge carrier properties.[5-13] Among them, thiophene based amphiphilic mesogens are considered as excellent candidates for organic field effect transistors (OFETS), because they could form highly ordered mesophases by a solution process which could be further transferred into organic thin film devices with high charge carrier mobility. However, to the best of our knowledge, there are only few reports about thiophene based amphiphilic mesogens.[14]

Recently we have reported that thienylanisole derivatives **5**, **7** and **11**, which were obtained in the monocoupling reaction between 2-bromo-3-alkylthiophene (or 2,5-dibromo-3-alkylthiophene or 2,5-dibromothiophene) and 4-methoxybenzene boronic acid, can serve as valuable building blocks for designing new mesogens.[14c,15,16] Herein we want to further extend the use of these monocoupling products for the design of new types of polyhydroxyamphiphilic phenylene thiophene based derivatives, in which the thiophene units are incorporated into a rod-like mesogenic unit with a polyhydrophilic group at one end and alkyl chains in different positions on the thiophene ring; and investigate their mesophase behavior in order to understand the relationship between structure and mesomorphic properties of these new polyhydroxyamphiphilic thiophene derivatives.

Results and discussion

Synthesis

Target compounds **18/3**, **18/4** and **18/5** have been obtained from 3,4,5-trihydroxybenzoate (**14**) as shown in Scheme 1. Etherification with excess allyl bromide gave 3,4,5-triallyloxy benzoate (**15**), and basic hydrolysis of **15** gave benzonic acid (**16**), which was esterified in the usual way using DCC/DMAP with corresponding phenol (**6**, **9** or **13**, Scheme 2) to yield 3,4,5-triallyloxy-

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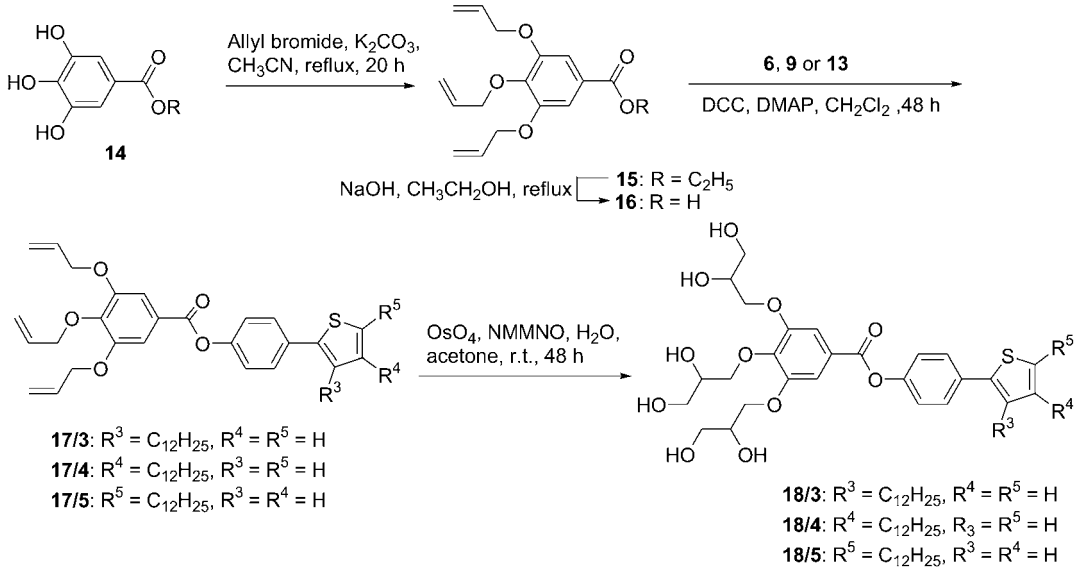
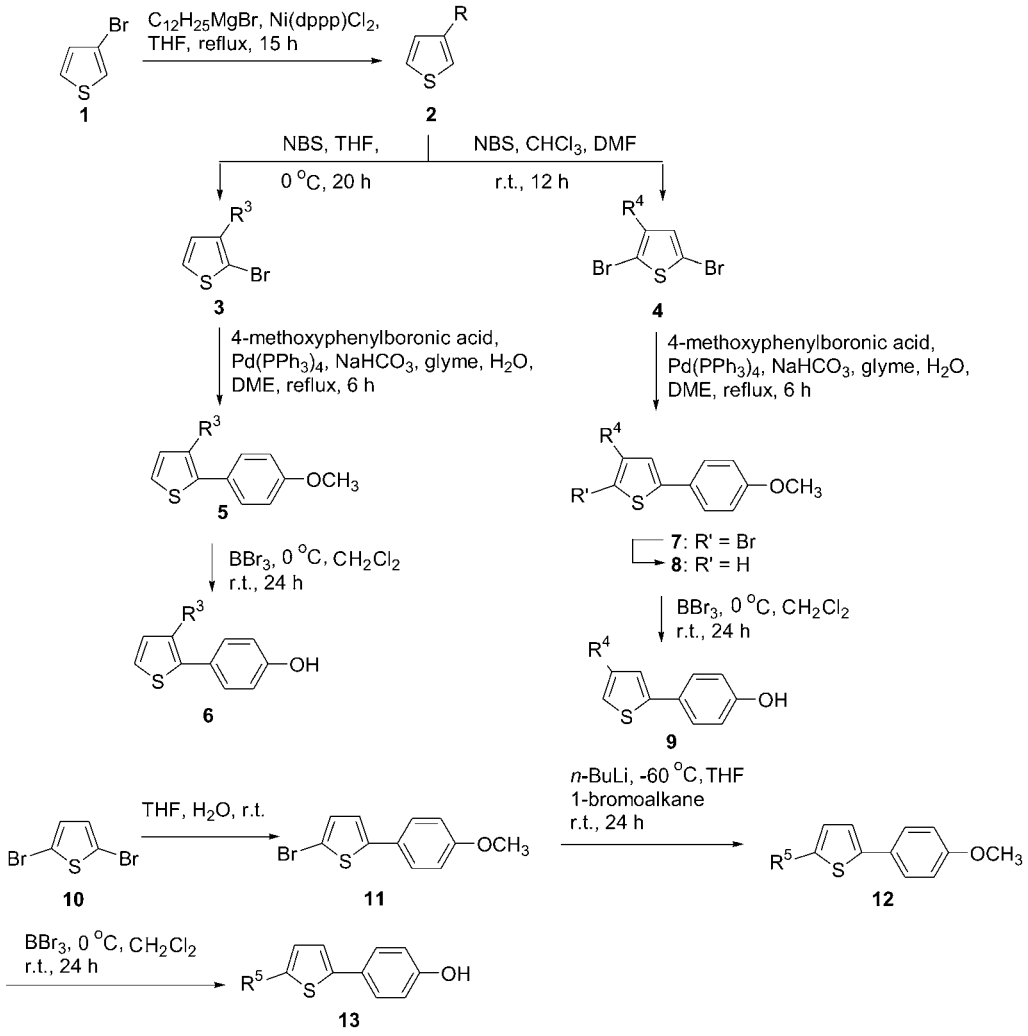
Scheme 1 Synthesis of compound **18**



Scheme 2 Synthesis of phenol **6**, **9** and **13**



benzoyl compounds **17**. Then **17** were completely dihydroxylated using a catalytic quantity of osmium tetroxide and *N*-methylmorpholine-*N*-oxide as reoxydant. The purification of the final compounds was done by means of repeated crystallization. Purity and the structure of the final products were confirmed by thin-layer chromatography, mass spectrometry, elemental analysis and ^{1}H NMR.

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Scheme 2 describes the syntheses of the phenols **6**, **9** and **13** by using Kumada and Suzuki coupling reactions as key steps. Kumada coupling reaction between 3-bromothiophene and *n*-alkyl Grignard reagents resulted in the 3-alkylthiophenes (**2**), which were monobrominated or dibrominated with NBS. The obtained monobromide product **3** and 2,5-dibromo-3-alkylthiophenes (**4**) were then coupled with 4-methoxy benzeneboronic acid under standard Suzuki conditions with $Pd(PPh_3)_4$ respectively. Monocoupling product **7** was debrominated with *n*-BuLi giving **8**. Palladium catalyzed Suzuki cross-coupling between commercially available 2,5-dibromothiophene (**10**) and 4-methoxyphenyl-boronic acid gave monocoupling product **11**, whose bromo substituent was at first exchanged with Li and then coupled with bromoalkanes. Demethylation of **5**, **8** and **12** respectively using BBr_3 at −78 ℃ yielded corresponding phenols **6**, **9** and **13** respectively.

Mesophase behavior

The liquid crystalline properties of compounds **18**/**3**, **18**/**4** and **18**/**5** were investigated by a Mettler FP 82 HT hot-stage-control-unit in conjunction with a Nikonpolarizing optiphot-2 microscope (POM) and for selected compounds by differential scanning calorimeter (perkin-Elmer DSC-7, heating and cooling rate: 10 K•min^{-1}). Their mesophase behaviors are summarized in Table 1. Generally, as all compounds contain three propane-2,3-diol terminal units, the hydrogen bonding between such diol groups leads to cohesive forces in the polar regions which should reinforce micro-segregation and contribute to mesophase stability.

Table 1 Transition temperature

Comp.	R^5	R^4	R^3	Phase behavior (T/℃) and [ΔH/(kJ•mol^{-1})]
18/5	$C_{12}H_{25}$	H	H	Cr 144 (39) SmA＞220 Iso (dec.)[a]
18/4	H	$C_{12}H_{25}$	H	Cr 83 SmA 166 Iso (dec.)[b]
18/3	H	H	$C_{12}H_{25}$	Cr 35 SmA 90 Iso (dec.)[b]

[a] Transition temperature and enthalpy changes were determined by DSC (peak temperature, first heating scan, 5 ℃•min^{-1}). [b] Transition temperature was determined by POM; dec. = decomposition.

Compounds **18**/**3, 18**/**4** and **18**/**5** with alkyl chains at 3-, 4-, 5-position of the thienyl rings respectively, exhibit thermotropic smectic A phases as characterized by textures consisting of both focal-conic and pseudo isotropic regions (Figure 1). The occurrence of focal-conic fans suggests a layered structure, whereas the pseudo isotropic region indicates an on average orthogonal organization of the molecules with respect to the layer planes. Compound **18**/**5** in which the alkyl chain is located at the terminal position of the rigid core exhibits the highest melting and clear temperatures; while compound **18**/**3** in which the alkyl chain is located at the more centrally lateral position of the rigid core shows the lowest melting and clear temperatures. This is obviously because compound **18**/**5** with a terminal chain has more linear conformation, which benefits for the stabilization of the SmA phase. Moving the alkyl chain to the lateral position (3- and 4-positions on the thiophene ring) of the rigid core would disturb the parallel organization of the rigid core and cause a decrease of both the melting and clear temperatures. But as the compounds designed here have an extended aromatic core, moving the alkyl chain to the lateral position induces only the unstability of the mesophase, but the mesophase type remains.

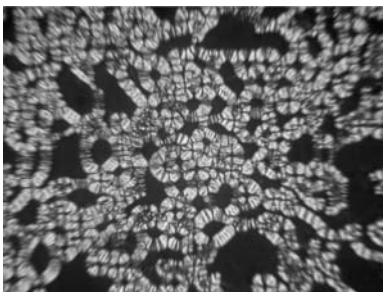

Figure 1 Texture of the smectic A phase of compound **18/5** at 170 ℃.

Therefore, we have successfully designed a new kind of rod like phenylene thiophene based polyhydroxy amphiphiles **18**. The extended aromatic rigid cores in such compounds have implications for the layer organization for such compounds. Therefore all compounds synthesized here exhibit only smectic A phases. Worthy to be noted is that, all compounds **18** decompose near their clear temperatures, the unstable ester bonds in such molecules should be responsible for this phenomenon. According to the literatures,[4] the corresponding amide derivatives should be more stable. Therefore, further work should be concentrated on syntheses of the more stable amide derivatives and changing the number and the length of the alkyl chains in order to get more information about the structure-property relationship in such compounds. The application of such compounds as functional materials would be investigated.

Experimental

Apparatuses and materials

Reactions requiring an inert gas atmosphere were conducted under argon and the glassware was oven-dried (140 ℃). Commercially available chemicals were used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-DRX-500 spectrometer. High resolution MS (HR-MS) data were recorded on a Finnigan MAT 90 spectrometer at an ionization potential of 70 eV. Microanalysis was performed using a Leco CHNS-932 elemental analyzer. Column chromatography was performed with silica gel 60 (230—400 mesh) from Merck.

Preparation

Compound **16** was synthesized according to refer-

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ence. The compounds **5**, **7** and **12** were recently synthesized.[14c]

4-Dodecyl-2-(4-anisyl)thiophene (8) Under an argon atmosphere, 2-bromo-3-dodecyl-5-(4-anisyl)-thiophene (**7**)[14c] (300 mg, 0.69 mmol) was dissolved in dry THF (5 mL) and cooled to −60 ℃. Then *n*-BuLi (1.5 mol/L in *n*-hexane, 0.92 mL, 1.38 mmol) was added dropwise and the solution was stirred for 30 min, then poured into water, the mixture was stirred for 1 h and extracted with ether. The combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated *in vacuo*. The rude product was purified by column chromatography (eluent: petroleum ether). Colorless crystal (229 mg, yield 93%), m.p. 58—59 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.88 (t, J=6.5 Hz, 3H, CH_3), 1.19—1.32 (m, 18H, $9CH_2$), 1.60—1.66 (m, 2H, $ArCH_2CH_2$), 2.59 (t, J=7.5 Hz, 2H, $ArCH_2$), 3.83 (s, 3H, OCH_3), 6.79 (s, 1H, ArH), 6.89 (d, J=8.6 Hz, 2H, ArH), 7.03 (s, 1H, ArH), 7.51 (d, J=8.6 Hz, 2H, ArH).

General procedure for cleavage of methyl ethers Appropriate methyl ether (**5**, **8** or **12**) (4.7 mmol) was dissolved in CH_2Cl_2 (45 mL) and cooled to −78 ℃, BBr_3 (0.49 mL, 5.17 mmol) was added and the solution was stirred at r.t. overnight. Water (30 mL) was carefully added, and the precipitate was filtered and washed with water (10 mL) and petroleum ether (20 mL), respectively, dried *in vacuo* at 40 ℃ for 4 h. The obtained product was used directly for the next step without further purification. Yields of **6**, **9** and **13** were 99%, 98% and 99%, respectively.

4-(3-Dodecylthien-2-yl)phenyl 3,4,5-tris(allyloxy)-benzoate (17/3) 3,4,5-Tris(allyloxy)benzoic acid (**16**) (225 mg, 0.78 mmol), 4-(3-dodecylthien-2-yl) phenol (**6**) (0.52 mmol), DCC (0.78 mmol, 160 mg), and DMAP (a catalytic quantity) were dissolved in CH_2Cl_2 (20 mL) and stirred for 2 d under room temperature. The solvent was evaporated *in vacuo*. The rude product was purified by column chromatography [eluent: *V*(petroleum ether)/*V*(ethyl acetate)=13/1]. Colorless liquid (208 mg, yield 65%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.87 (t, J=6.8 Hz, 3H, CH_3), 1.19—1.31 (m, 18H, $9CH_2$), 1.58—1.64 (m, 2H, $ArCH_2CH_2$), 2.65 (t, J=7.8 Hz, 2H, $ArCH_2$), 4.67 (m, 6H, $3ArOCH_2$), 5.21—5.48 (m, 6H, $3CH_2$=), 6.06—6.12 (m, 3H, 3CH=), 6.98 (d, J=5.2 Hz, 1H, ArH), 7.23 (d, J=8.6 Hz, 2H, ArH), 7.25 (d, J=5.2 Hz, 1H, ArH), 7.45 (s, 2H, ArH), 7.47 (d, J=8.6 Hz, 2H, ArH); IR (KBr) ν: 3083, 3023 (=CH), 2918, 2850 (CH_2, CH_3), 1735 (C=O), 1589, 1506, 1425 (C=C), 1336, 1204, 1120 (C—O—C), 992, 928, 860 (=CH, ArH) cm^{-1}; MS (70 eV) *m/z* (%): 617.3 (M+1, 100). Anal. calcd for $C_{38}H_{48}O_5S$ (616.85): C 73.99, H 7.84; found C 73.51, H 7.48.

4-(4-Dodecylthien-2-yl)phenyl 3,4,5-tris(allyloxy)-benzoate (17/4) 3,4,5-Tris(allyloxy)benzoic acid (200 mg, 0.69 mmol), 4-(4-dodecylthien-2-yl) phenol (**9**) (0.46 mmol), DCC (0.69 mmol, 142 mg), and DMAP (a catalytic quantity) were dissolved in CH_2Cl_2 (20 mL) and stirred for 2 d under room temperature. The solvent was evaporated *in vacuo*. The rude product was purified by column chromatography [eluent: *V*(petroleum ether)/*V*(ethyl acetate)=13/1]. Colorless crystal (206 mg, yield 72%), m.p. 54—55 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.88 (t, J=6.4 Hz, 3H, CH_3), 1.19—1.32 (m, 18H, $9CH_2$), 1.60—1.64 (m, 2H, $ArCH_2CH_2$), 2.61 (t, J=7.4 Hz, 2H, $ArCH_2$), 4.66—4.67 (m, 6H, $3ArOCH_2$), 5.19—5.47 (m, 6H, $3CH_2$=), 6.05—6.12 (m, 3H, 3CH=), 6.87 (s, 1H, ArH), 7.13 (s, 1H, ArH), 7.18 (d, J=8.2 Hz, 2H, ArH), 7.44 (s, 2H, ArH), 7.62 (d, J=7.8 Hz, 2H, ArH); IR (KBr) ν: 3086, 3021 (=CH), 2918, 2850 (CH_2, CH_3), 1734 (C=O), 1589, 1504, 1426 (C=C), 1335, 1201, 1128 (C—O—C), 990, 926, 860 (=CH, ArH) cm^{-1}; MS (70 eV) *m/z* (%): 617.3 (M+1, 100). Anal. calcd for $C_{38}H_{48}O_5S$ (616.85): C 73.99, H 7.84; found C 73.49, H 8.03.

4-(5-Dodecylthien-2-yl)phenyl-3,4,5-tris(allyloxy)-benzoate (17/5) 3,4,5-Tris(allyloxy)benzoic acid (260 mg, 0.9 mol), 4-(5-dodecylthien-2-yl)phenol (**13**) (0.6 mmol), DCC (0.90 mmol, 184 mg), and DMAP (a catalytic quantity) were dissolved in CH_2Cl_2 (20 mL). The solvent was evaporated *in vacuo*. The rude product was purified by column chromatography [eluent: *V*(petroleum ether)/*V*(ethyl acetate)=13/1]. Colorless crystal (255 mg, yield 69%), m.p. 64—65 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.88 (t, J=6.8 Hz, 3H, CH_3), 1.19—1.32 (m, 18H, $9CH_2$), 1.67—1.73 (m, 2H, $ArCH_2CH_2$), 2.82 (t, J=7.6 Hz, 2H, $ArCH_2$), 4.65—4.67 (m, 6H, $ArOCH_2$), 5.20—5.47 (m, 6H, $3CH_2$=), 6.05—6.14 (m, 3H, 3CH=), 6.74 (d, J=3.3 Hz, 1H, ArH), 7.10 (d, J=3.4 Hz, 1H, ArH), 7.18 (d, J=8.5 Hz, 2H, ArH), 7.44 (s, 2H, ArH), 7.59 (d, J=8.5 Hz, 2H, ArH); IR (KBr) ν: 3080, 3020 (=CH), 2918, 2850 (CH_2, CH_3), 1732 (C=O), 1589, 1506, 1425 (C=C), 1335, 1205, 1117 (C—O—C), 989, 931, 861 (=CH, ArH) cm^{-1}; MS (70 eV) *m/z* (%): 617.3 (M+1, 100). Anal. calcd for $C_{38}H_{48}O_5S$ (616.85): C 73.99, H 7.84; found C 74.19, H 7.61.

General procedure for dihyoxylation Trisallyloxy benzoate **17** (0.8 mmol) and NMMNO (2.4 mL, 60% solution in water) were dissolved in acetone. Osmium tetroxide (2.5 mL, 0.004 mol/L solution in *tert*-butanol) was added, and the solution was stirred for 2 d at r.t. Afterwards, saturated aqueous Na_2SO_3 solution was added, and the mixture was stirred for 30 min at r.t. and the mixture was filtered. Ethyl acetate and 10% H_2SO_4 were added into the liquid, the organic layer was separated, washed with saturated $NaHCO_3$ solution and H_2O, dried over Na_2SO_4, and the solvent was evaporated *in vacuo*. Purification of the product was done by crystallization three times from ethyl acetate/methanol (*V*/*V*=1/20).

4-(3-Dodecylthien-2-yl)phenyl-3,4,5-tris(2,3-dihydroxypropoxy)benzoate (18/3) Synthesized from 4-(3-dodecylthien-2-yl)phenyl-3,4,5-tris(allyloxy)benzoate (**17**/**3**) (150 mg, 0.24 mmol) as a colorless solid (79 mg, yield 46%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.82 (t, J=6.6 Hz, 3H, CH_3), 1.17—1.28 (m, 18H, $9CH_2$), 1.46

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—1.52 (m, 2H, $ArCH_2C\mathbf{H}_2$), 2.49 (t, J=7.4 Hz, 2H, $ArCH_2$), 3.71—3.79 (m, 6H, $3C\mathbf{H}_2OH$), 3.84—3.89 (m, 3H, 3CH), 4.10—4.17 (m, 6H, $3OCH_2$), 6.87 (s, J=4.7 Hz, 1H, ArCH), 7.02 (d, J=6.7 Hz, 2H, ArCH), 7.08 (d, J=4.8 Hz, 1H, ArH), 7.16 (s, 2H, ArCH), 7.25 (d, J=6.8 Hz, 2H, ArH); IR (KBr) v: 3395 (OH), 2919, 2851 (CH_2, CH_3), 1720 (C=O), 1593, 1507, 1432 (C=C), 1342, 1205, 1126 (C—O—C), 1052 (C—O), 925, 867, 810 (ArH) cm^{-1}; MS (70 eV) *m/z* (%): 719.3 (M+1, 100). Anal. calcd for $C_{38}H_{54}O_{11}S$ (718.89): C 63.49, H 7.57; found C 63.88, H 7.31.

4-(4-Dodecylthien-2-yl)phenyl 3,4,5-tris(2,3-dihydroxypropoxy)benzoate (18/4) Synthesized from 4-(4-dodecylthien-2-yl)phenyl 3,4,5-tris(allyloxy)benzoate (**17/4**) (150 mg, 0.24 mmol) as a colorless solid (91 mg, yield 53%); ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6) δ: 0.53 (t, J=6.7, 3H, CH_3), 0.91—0.98 (m, 18H, $9CH_2$), 1.29—1.37 (m, 2H, $ArCH_2C\mathbf{H}_2$), 2.67 (t, J=7.6 Hz, 2H, $ArCH_2$), 3.35—3.47 (m, 6H, $3C\mathbf{H}_2OH$), 3.71—3.75 (m, 3H, 3CH), 4.06—4.19 (m, 6H, $3OCH_2$), 6.55 (s, 1H, ArCH), 6.82 (s, 1H, ArCH), 6.85 (d, J=8.1 Hz, 2H, ArH), 7.09 (s, 2H, ArCH), 7.29 (d, J=8.1 Hz, 2H, ArH); IR (KBr) v: 3390 (OH), 2918, 2850 (CH_2, CH_3), 1719 (C=O), 1593, 1506, 1432 (C=C), 1341, 1207, 1126 (C—O—C), 1051 (C—O), 926, 867, 809 (ArH) cm^{-1}; MS (70 eV) *m/z* (%): 719.3 (M+1, 100). Anal. calcd for $C_{38}H_{54}O_{11}S$ (718.89): C 63.49, H 7.57; found C 63.67, H 7.68.

4-(5-Dodecylthien-2-yl)phenyl 3,4,5-tris(2,3-dihydroxypropoxy)benzoate (18/5) Synthesized from 4-(5-dodecylthien-2-yl)phenyl 3,4,5-tris(allyloxy)benzoate (**17/5**) (150 mg, 0.24 mmol) as a colorless solid (96 mg, yield 56%); ^{1}H NMR (500 MHz, DMSO) δ: 0.69 (t, J=6.5 Hz, 3H, CH_3), 1.08—1.15 (m, 18H, $9CH_2$), 1.41—1.47 (m, 2H, $ArCH_2C\mathbf{H}_2$), 2.64 (t, J=7.2 Hz, 2H, $ArCH_2$), 3.67—3.77 (m, 6H, $3C\mathbf{H}_2OH$), 3.79—3.82 (m, 3H, 3CH), 3.87—3.96 (m, 6H, $3OCH_2$), 4.85—4.87 (m, 6H, 6OH), 6.69 (d, J=3.6 Hz, 1H, ArCH), 7.13 (d, J=8.6 Hz, 2H, ArCH), 7.17 (d, J=3.5 Hz, 1H, ArH), 7.26 (s, 2H, ArCH), 7.51 (d, J=8.5 Hz, 2H, ArH); IR (KBr) v: 3392 (OH), 2919, 2850 (CH_2, CH_3), 1721 (C=O), 1593, 1506, 1431 (C=C), 1342, 1207, 1126 (C—O—C), 1050 (C—O), 926, 867, 809 (ArH) cm^{-1}; MS (70 eV) *m/z* (%): 719.3 (M+1, 100). Anal. calcd for $C_{38}H_{54}O_{11}S$ (718.89): C 63.49, H 7.57; found C 63.05, H 7.95.

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