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Redox-Driven Molecular Switches Consisting of Bis(benzodithiolyl)bithienyl Scaffold and Mesogenic Moieties: Synthesis and Complexes with Liquid Crystalline Polymer

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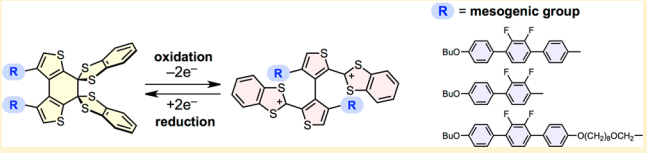
Supporting Information

ABSTRACT: Molecular switches composed of a benzodithiolylbithienyl scaffold and biphenyl or terphenyl mesogenic substituents were designed and synthesized. The molecular switches could undergo redox-triggered interconversion between the cationic form and cyclized neutral form, and this was confirmed using cyclic voltammetry and UV−vis spectroscopy. Binary complexes consisting of the molecular switches and a liquid crystalline polymer (LCP) were prepared to investigate the function of these redox-active molecular switches as actuating dopants. X-ray diffraction measurements were performed to determine the differences between the layer spacings of the complexes in the liquid crystalline phase with the oxidized and reduced states of the molecular switches. The LCP that was doped with the oxidized cationic form of the molecular switch had layer spacings that were up to 4% larger than the layer spacings in the polymer that was doped with the reduced cyclized molecular switch. Our approach will allow stimulus-responsive deformable materials to be constructed and give an impetus for fabricating redox-driven soft actuators.



INTRODUCTION

Molecular switches, or molecular machines,[1] undergo a structural change when an external stimulus, such as a change in pH,[2−4] the presence of light,[5−12] an electrochemical reaction,[13−24] an ionic interaction,[25,26] or a chemical treatment,[27] is applied. There has been much interest in using molecular switches to prepare novel actuating or sensing materials. The assembly and operation of stimulus-responsive molecules in an ordered molecular field is required to develop their performance in terms of deformation and stress. Ordered molecular architecture plays a key role in biological systems[28] that exhibit specific and amplified functions, a typical example being myosin II, which plays a role in muscle contraction.[29] A well-ordered structure is crucial to the production of synthetic sensing[30,31] or actuating systems.[32,33]

We have focused our attention on the unique nature of liquid crystals (LCs) for forming well-ordered molecular fields. LCs have recently become widely known as functional materials that form self-assembled highly ordered anisotropic structures.[34,35] Using LCs will allow to gain insights into how novel intrinsically anisotropic soft actuators can be fabricated. The utilization of the stimulus-induced changes of the ordered structures of liquid crystals has a potential to achieve stimulus-triggered deformable materials. Previously, controls of the layer spacings of smectic liquid crystals driven by photoisomerization of azobenzene unit,[36] tilting of directors by electroclinic effect,[37] and molecular reorientation by phase transition[38] have been reported. A wide variety of soft actuators based on the properties of LCs have been developed using polymers and gels. Liquid crystalline elastomers (LCEs) and liquid crystalline polymer (LCP) gels are materials that can change shape and combine the anisotropic properties of LCs with the properties of cross-linked rubber-like polymers and gels.[39] The changes in the shapes of LCEs and LCP gels are, in most cases, driven by phase transitions,[40−42] photoisomerization,[43−47] or electric field.[37,48−50] However, a few examples of redox responsive LC molecules have been reported,[51] although, from the practical point of view, electrochemically controlled actuating systems have advantages that include low operating voltages and precise control.

We have attempted to prepare redox-driven molecular switches that are capable of propagating their conformational changes to the surrounding polymer matrix, causing enhanced changes in their ordered nanostructures. This would be a promising method of constructing redox-driven deformable materials. We have previously reported the electrochemically mediated conformational interconversion of bis(benzodithiolyl)bithienyl (BDTBT), as shown in Scheme 1.[52] An electrochemical stimulus can induce C−C bonds to form or break, through an electron transfer mechanism. Similar redox-driven interconversion have been studied by Yamashita et al. and Suzuki et al.[13−18] In this study, we designed functional molecular switches **1**, **2**, and **3**, which were based on a

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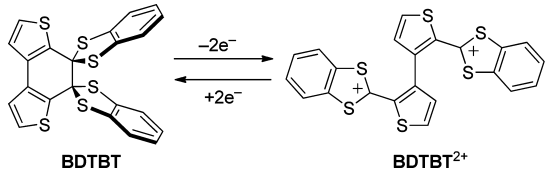
Scheme 1. Redox-Triggered Structural Interconversion of Bis(benzodithiolyl)bithienyl



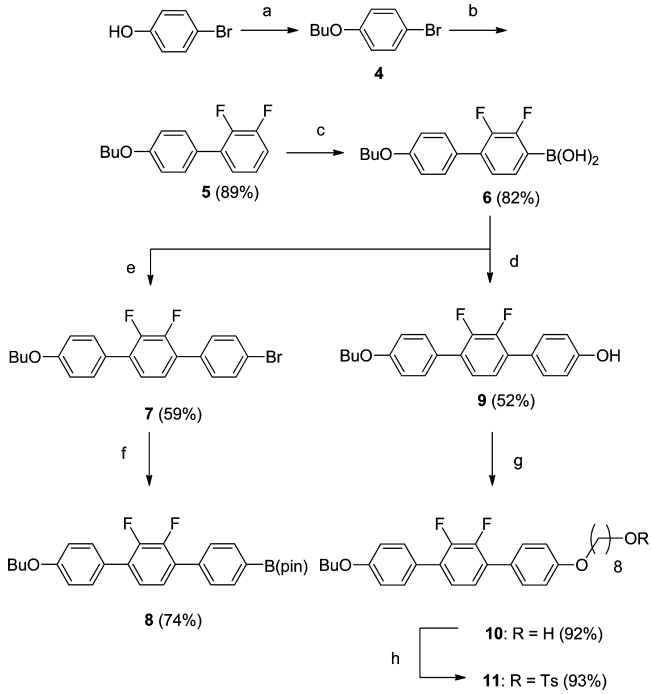
benzodithiolylbithienyl scaffold and rigid terphenyl or biphenyl substituents (mesogenic moieties). These molecular switches could undergo redox-triggered C−C bond forming and bond breaking reactions. We wished to evaluate the functions of these molecular switches as dopants for inducing changes in the molecular order of surrounding molecules, and, to achieve this, we designed a side-chain LCP to act as a host polymer. Complexes of the molecular switches **1**−**3** with LCP were then prepared (Scheme 2). Pure LCP formed a smectic ordered structure and was suitable for evaluating the differences in the smectic ordered structures when it was complexed with the molecular switches. Here, we report the synthesis, electrochemical response, and liquid crystalline properties of the redox-driven molecular switches **1**−**3** and the results of examination of the nanostructures of the molecular switch/LCP complexes in the oxidized and reduced states.

RESULTS AND DISCUSSION

Synthesis and Characterization. The mesogenic units and bis(benzodithiolyl)bithienyl moiety were prepared separately, then they were attached to each other using either Suzuki−Miyaura coupling reaction or Wiliamson etherification reaction. Laterally fluorinated biphenyl or terphenyl were used as the mesogenic units. The presence of lateral fluorine substituents would be expected to decrease the melting point of the mesogenic unit,[53] which should offer practical advantages.

Scheme 3 shows the synthetic route for the mesogenic units, which were synthesized from 4-bromophenol. The alkylation of 4-bromophenol by butyl bromide in the presence of potassium carbonate afforded 1-bromo-4-butoxybenzenes **4**,[54] which was then coupled with 2,3-difluorophenylboronic acid, using the

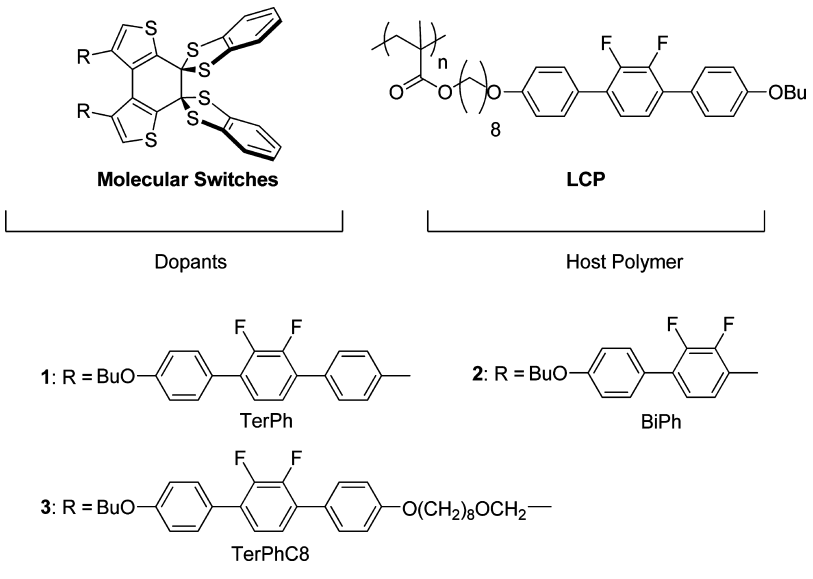
Scheme 3. Synthesis of Mesogenic Units[a]



[a]Reagents and conditions: (a) 1-bromooctane, K_2CO_3, acetone, reflux; (b) 2,3-difluorophenylboronic acid, $Pd(PPh_3)_4$, Na_2CO_3, DME/EtOH/H_2O, reflux; (c) (1) butyllithium, $B(OMe)_3$, THF, −78 °C; (2) HCl; (d) 4-bromophenol, $Pd(PPh_3)_4$, Na_2CO_3, DME/EtOH/H_2O, reflux; (e) 1-bromo-4-iodobenzene, $Pd(PPh_3)_4$, Na_2CO_3, benzene/EtOH/H_2O, 95 °C; (f) $(Bpin)_2$, $PdCl_2(dppf)$, KOAc, DMF, 80 °C; (g) 8-bromo-1-octanol, K_2CO_3, KI, DMF, 80 °C; (h) TsCl, Et_3N, CH_2Cl_2, rt.

Suzuki−Miyaura coupling reaction, to give biphenyl **5**. After **5** had been converted to the corresponding boronic acid **6**, cross-coupling of **6** with 1-iodo-4-bromobenzene[55] or 4-bromophenol afforded **7** or **9**, respectively. Terphenyl **7** was transformed into the corresponding boronate **8**.[56] Attempts to prepare the boronic acid from **7** through lithiation or using the Grignard

Scheme 2. Chemical Structures of Molecular Switches (Dopants) and Host Liquid Crystalline Polymer (LCP)



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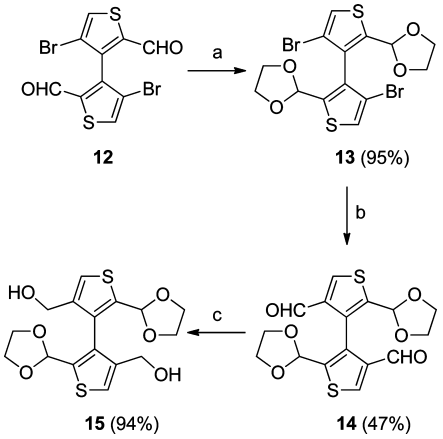
reaction[57] were not successful. An alkylene spacer was incorporated into **9**,[58] then the corresponding tosylate **11** was obtained by treating **10** with tosyl chloride in the presence of triethylamine.[59]

The synthetic route used to prepare the bithienyl moiety is shown in Scheme 4. Dialdehyde **12**[60,61] was used as a starting material for preparation of diol **15**. The carbonyl groups in **12** were protected with ethylene glycol to form **13**, then **13** was formylated by treating it with BuLi followed by DMF, to give **14**, which was then reduced by the treating it with $NaBH_4$ in ethanol, to afford diol **15**.

Scheme 4. Synthesis of Bithienyl Moiety[a]

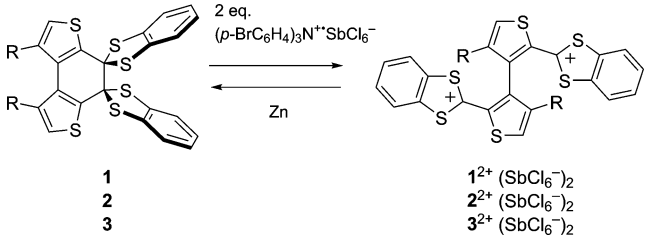


[a]Reagents and conditions: (a) ethylene glycol, TsOH, benzene, reflux; (b) (1) butyllithium, THF, −78 °C; (2) DMF; (3) HCl; (c) $NaBH_4$, EtOH, rt.

The mesogenic moieties were incorporated into the benzodithiolyl moiety as shown in Scheme 5. The biphenyl derivative **6** and terphenyl derivative **8** were directly attached to dialdehyde **12**, through palladium-catalyzed cross-coupling reactions, to give **17** and **16**, respectively. However, the preparation of **18**, in which the terphenyl units are connected to the bithienyl moiety through alkylene spacers, was achieved by conventional etherification.[62] We incorporated the benzodithiolyl units through condensation of the dialdehydes **16**, **17**, and **18** with 1,2-benzenedithiol in the presence of *p*-toluenesulfonic acid, to afford **19**, **20**, and **21**, respectively. The oxidation of **19**, **20**, and **21** with 4 equiv of $(p\text{-}BrC_6H_4)_3N^{+\bullet}SbCl_6^-$ yielded the corresponding $SbCl_6$ salts $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, and $\mathbf{3}^{2+}$. The reductive cyclization of these $SbCl_6$ salts using zinc gave cyclized compounds **1**, **2**, and **3**.

The dications $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, and $\mathbf{3}^{2+}$ were also obtained, in moderate yields, from the chemical oxidation of **1**, **2**, and **3**, respectively, with 2 equiv of $(p\text{-}BrC_6H_4)_3N^{+\bullet}SbCl_6^-$ (Scheme 6). This confirmed that the redox-triggered interconversion between the cyclic form and dicationic form was reversible.

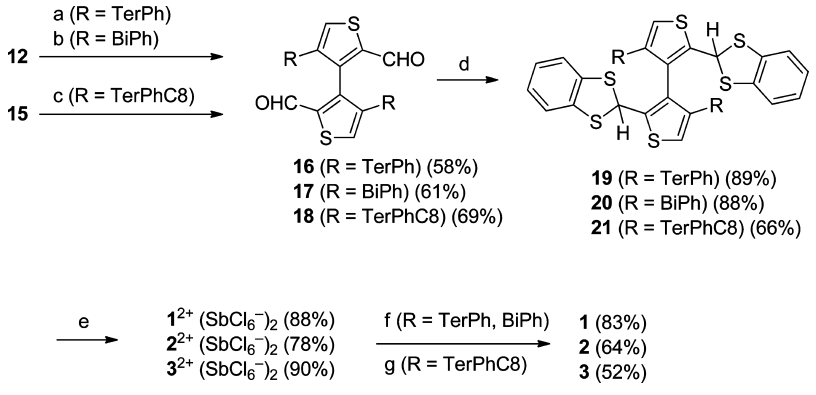
Scheme 6. Structural Interconversion between Oxidized and Reduced Forms through Chemical Treatment



UV−vis spectra of the molecular switches and their corresponding dications, in dichloromethane, are shown in Figure 1. Characteristic absorption bands corresponding to $\pi-\pi^*$ electronic transitions in the aromatic cores were observed in the UV region for the molecular switches **1**, **2**, and **3** (Figure 1A). The maximum absorption (λ_{max}) of **1** was found at 292 nm, and this was higher than that found for **2** (λ_{max} = 279 nm) or **3** (λ_{max} = 287 nm). This may have been caused by the extension of the π-conjugation system. However, new absorption bands close to 450 nm were found for $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, and $\mathbf{3}^{2+}$ (Figure 1B). The hypochromic effect could be seen close to 300 nm when **1** and **2** were oxidized to their corresponding dications, but no such effect was seen for **3**. The absorption edges in the visible region were 512, 634, and 663 nm for $\mathbf{3}^{2+}$, $\mathbf{1}^{2+}$, and $\mathbf{2}^{2+}$, respectively. A noticeable red shift was observed for the absorption edges of $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ relative to the absorption edge for $\mathbf{3}^{2+}$.

As shown in Figure 2A, **1** had the longest conjugated π-bonds (consisting of terphenyl units and thiophene ring), **2** had π-conjugation over the biphenyl units and thiophene ring, and

Scheme 5. Synthesis of Molecular Switches 1, 2, and 3[a]



[a]Reagents and conditions: (a) **8**, $PdCl_2$(dppf), Na_2CO_3, DMF/H_2O, 95 °C; (b) **6**, $Pd(PPh_3)_4$, Na_2CO_3, DME/EtOH/H_2O, reflux; (c) (1) **11**, NaH, DMF, 75 °C; (2) HCl; (d) 1,2-benzenedithiol, TsOH, benzene, reflux; (e) 4 equiv of $(p\text{-}BrC_6H_4)_3N^{+\bullet}SbCl_6^-$, MeCN/$CH_2Cl_2$, rt; (f) Zn, MeCN/THF, rt; (g) Zn, CH_2Cl_2/THF, rt.

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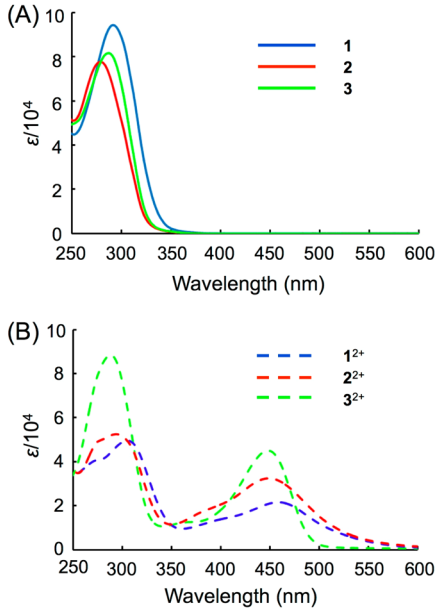

Figure 1. UV−vis spectra for (A) the molecular switches and (B) their dications ($SbCl_6$ salts) in dichloromethane. The spectra for **1** and $\mathbf{1}^{2+}$ are in blue, for **2** and $\mathbf{2}^{2+}$ in red, and for **3** and $\mathbf{3}^{2+}$ in green.

3 had π-conjugation over terphenyl units. The increasing π-bond conjugation length order matched the increasing λ_{max} order. The bathochromic shift in the absorption maximum when the π-conjugation was lengthened was confirmed for our molecular switches. The longer absorption edge wavelengths for $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ than for $\mathbf{3}^{2+}$ could be attributed to the extension of the π-conjugation system in the dications through the direct attachment of the terphenyl or biphenyl units to the thiophene ring (Figure 2B). The π-conjugation system in $\mathbf{3}^{2+}$ was interrupted between the terphenyl unit and thiophene ring because of the presence of the alkylene spacer, but this had no effect on the absorption properties.

We attempted to investigate the structures of the molecular switches using X-ray crystallography. Single crystals suitable for X-ray crystallography were obtained only for **2**. Attempts to prepare single crystals of **1** and **3** were not successful. Single crystals of **2** suitable for X-ray crystal analysis were recrystallized from a CH_2Cl_2/methanol solution by slow evaporation (Figure 3). The crystals of **2** crystallized in the space group $P\bar{1}$.

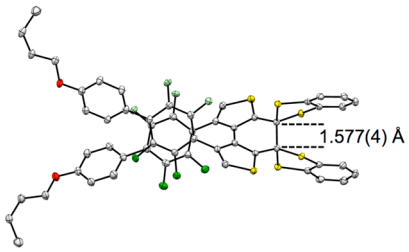

Figure 3. ORTEP view of **2**. Hydrogen atoms are omitted for clarity. The lower occupancy disordered fluorine atoms are shown in light green.

Both 2,3-difluorophenylene rings were statistically disordered by 180° rotation in the crystal. The dihedral angle of the bithienyl moiety in **2** was 27.1°, which is much larger than that of the unsubstituted 1,1′-benzodithiolyl bithienyl (8.3°)[52] and oligothiophene derivative (1.4°),[18] suggesting that the biphenyl mesogenic unit that was incorporated caused the bithienyl moiety conformation to be more twisted than it was in the unsubstituted molecule. The C−C bond formed through electrochemical reduction reaction was 1.577(4) Å long, which is approximately the length we found previously (1.583(3) Å).[52]

Electrochemical Studies. The electrochemical behaviors of the cyclized compounds **1**, **2**, and **3** were examined using cyclic voltammetry (CV). CV analyses were performed in PhCN, with Bu_4NBF_4 as the supporting electrolyte, on a Pt button electrode. Figure 4 shows CV results for the cyclized compounds. Similar redox curves were obtained for all the compounds, with oxidation peaks at approximately 1.3 V and reduction peaks at 0.1 V. According to our previous results,[52] the oxidation peaks could be attributed to the oxidative bond-breaking process involving the cyclized compounds, and the reduction peaks could be attributed to reductive C−C bond-forming in the dications. CV results from the analyses confirmed that the same reversible bond-breaking and bond-forming reactions were driven by the electrochemical process. The electrochemical properties of **1**, **2**, and **3** are summarized in Table 1. No distinct differences were found between the E_{pa}

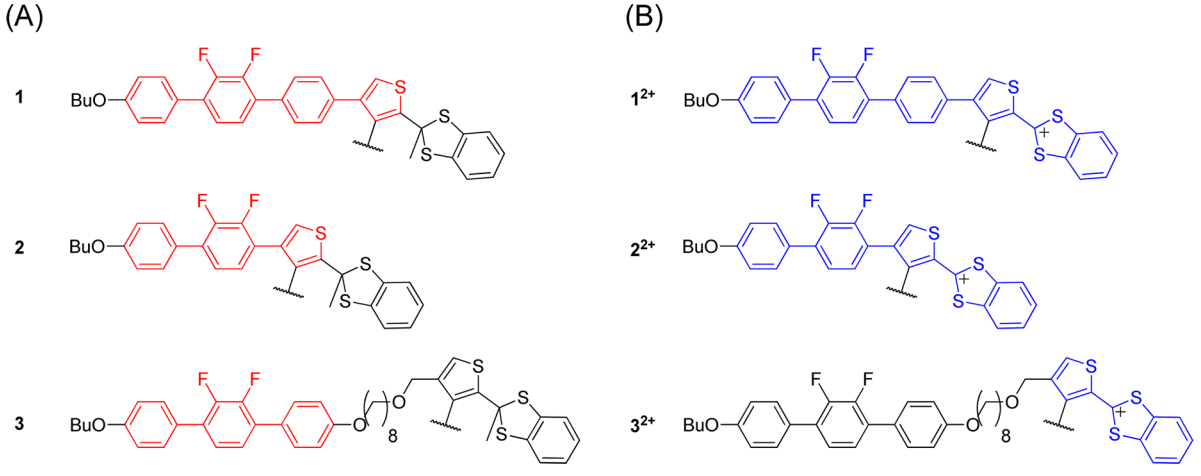

Figure 2. π-Conjugation systems determined from UV−vis spectra (red indicates cyclized molecules and blue indicates the corresponding dications). (A) Cyclized molecules **1**, **2**, and **3**. (B) Dications $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, and $\mathbf{3}^{2+}$.

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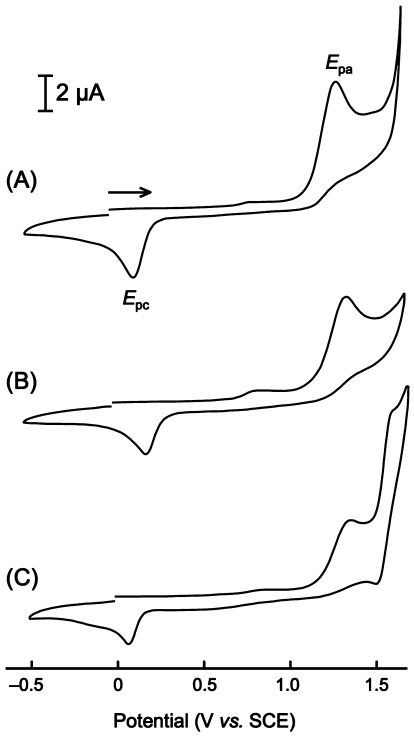

Figure 4. Cyclic voltammograms for (a) **1**, (b) **2**, and (c) **3** in benzonitrile solution containing 0.1 M Bu_4NBF_4. The scan rate was 100 mV/s.

Table 1. Redox Potentials of 1, 2, and 3[a]

compound	E_{pa}[b] (V)	E_{pc}[c] (V)
1	+1.33	+0.13
2	+1.37	+0.19
3	+1.37	+0.08

[a]Peak potentials in V versus SCE; electrolyte: 0.1 M Bu_4NBF_4; solvent: PhCN; Pt electrode, scan rate: 100 mV/s. [b]Anodic peak potentials of **1**, **2**, and **3**. [c]Cathodic peak potentials of $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, and $\mathbf{3}^{2+}$.

values for the compounds, and the values were close to that for the unsubstituted parent molecule (1.33 V).[52] However, the E_{pc}s varied between 0.08 and 0.19 V. The E_{pc} for **3** was distinctly lower than that for the unsubstituted parent molecule (0.16 V), suggesting that the oxidized dication $\mathbf{3}^{2+}$ was stabilized by being attached to the electron donating alkylene spacer. Another redox couple at 1.56 V was observed only for **3**. A similar redox couple was found for the dialdehyde **18**, which contained mesogenic moieties (Figure S1, Supporting Information). This could be attributed to the redox response of the mesogenic moieties.

Spectroelectrochemical measurements were also performed, to determine the electrochemical response. All redox pairs clearly showed electrochromism. Figure 5 shows the changes in the absorption spectra of **2** in CH_2Cl_2 as the applied potential was changed. Oxidation caused absorption in the UV region to decrease and new absorption peaks in the visible region to simultaneously develop (Figure 5A), and the opposite spectral changes were found when the samples were reduced (Figure 5B). The isosbestic point at 302 nm indicates clean transformation between **2** and $\mathbf{2}^{2+}$. Similar spectral changes were observed for **1** and **3** (Figures S2 and S3, Supporting Information). These results support the conclusion that structural interconversion between the reduced cyclic form

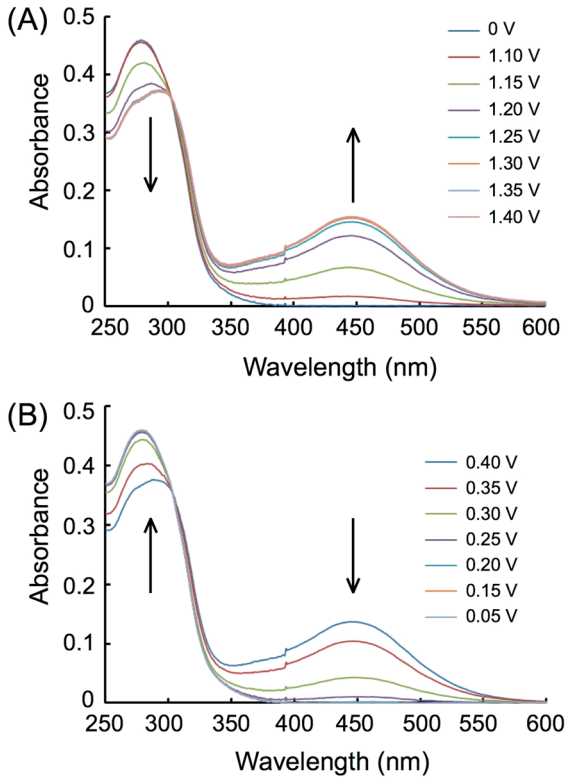

Figure 5. (A) UV–vis spectra of **2** in CH_2Cl_2 solution containing 0.1 M Bu_4NBF_4 as a function of the applied potential, from 0.0 to 1.40 V, against SCE. (B) UV–vis spectra of $\mathbf{2}^{2+}$ in CH_2Cl_2 solution containing 0.1 M Bu_4NBF_4 as a function of the applied potential, from 0.40 to 0.05 V, against SCE.

and opened dicationic form occurred and also confirm that mesogenic moieties being attached to the thiophene ring did not prevent the redox-triggered interconversion, as was observed for BDTBT.[52]

Mesomorphic Behavior. The mesomorphic behaviors of the cyclized compounds were examined using differential scanning calorimetry, X-ray diffractometry (XRD), and polarized optical microscopy. Compound **3** only exhibited liquid crystalline phases, whereas **1** and **2** did not show any mesophases. A focal conic fan texture, which is a characteristic of a smectic phase, a striated texture (Figure 6A), and a schlieren texture typical of a nematic phase (Figure 6B) were observed. It should be noted that incorporating the alkyl spacer to connect the mesogenic moieties and bithienyl scaffold played an important role in the formation of stable liquid crystalline phases.

For the $SbCl_6$ salts of these compounds, a birefringent mesophase (Figure 6C) could be seen only for $\mathbf{3}^{2+}(SbCl_6^-)_2$, but we could not identify the type of liquid crystalline phase that was present. Ionic compounds that exhibit liquid crystalline phases have previously been intensively studied as ionic liquid crystals.[63−65] The ionic parts, in either rigid cores[64] or flexible spacers,[65] can contribute to the formation of ordered structures in liquid crystalline phases. The ionic parts of the benzodithiolyl moieties may have had an effect on the mesomorphism of $\mathbf{3}^{2+}(SbCl_6^-)_2$ in our study.

The nanostructure of **3** in the liquid crystalline phase was examined using XRD. Figure 7 shows the XRD patterns for **3** at 89 °C (Figure 7A) and 70 °C (Figure 7B) during cooling. A sharp diffraction peak at 2θ = 4.09° (d = 21.6 Å) and broad

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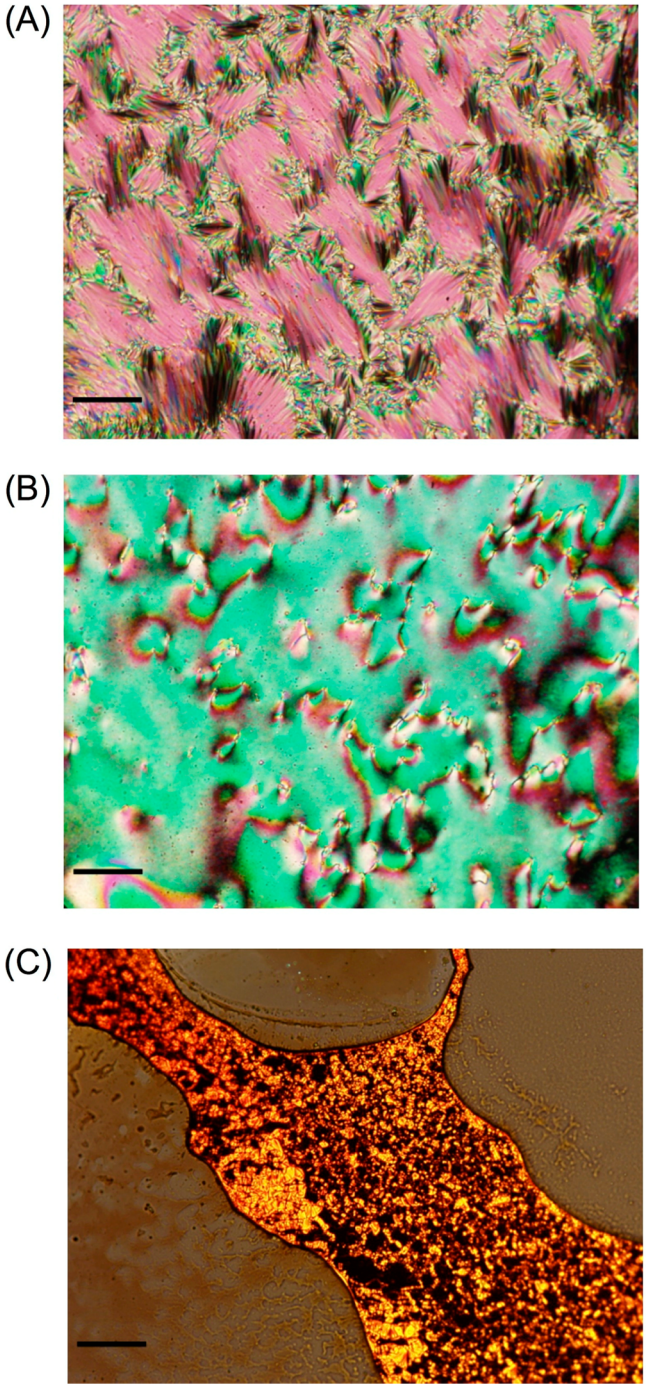

Figure 6. Polarized photomicrographs of (A) **3** at 102 °C on heating; (B) **3** at 118 °C on heating; and (C) $3^{2+}(SbCl_6^-)_2$ at 127 °C on cooling. The scale bar indicates 50 μm.

halo around 2θ = 20°, which are characteristics of a one-dimensional lamellar structure of a smectic A phase, were observed at 89 °C. The broad halo around 20° may have been caused by melting of the alkyl spacer. The XRD pattern for **3** at 70 °C had seven diffraction peaks, at 27.5, 21.3, 21.0, 16.6, 14.0, 12.0, and 10.6 Å (Figure 7B inset). The lattice parameters a = 42.6 Å and b = 36.1 Å were calculated assuming that the peaks at 27.5, 21.3 Å, and 21.0 Å were (110), (200), and (001) reflections, respectively, and the other four diffraction peaks were assigned to (120), (300), (030), and (400) reflections for a two-dimensional rectangular lattice. The possible molecular

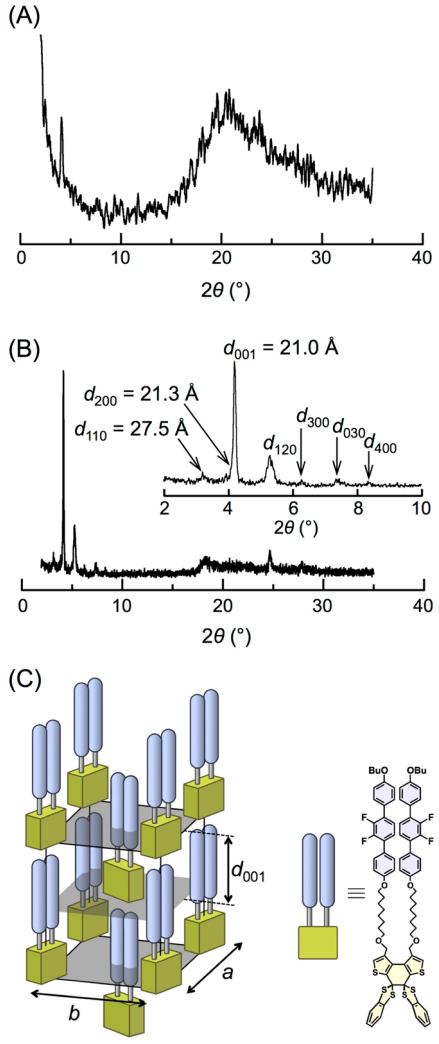

Figure 7. X-ray diffraction patterns for **3** at (A) 89 °C, (B) 70 °C during cooling, and (C) the possible packing structures for **3** in smectic E (crystal E) phase. The directors of **3** in the unit cell are drawn in the same direction for clarity.

packing of **3** in this mesophase was determined from these XRD results and is illustrated schematically in Figure 7C. As previously reported,[66−68] the smectic phase with a rectangular lattice structure that was observed for **3** could be identified as a smectic E (crystal E) phase.

Nanostructures of Molecular Switch/LCP Complexes. The nanostructures of the molecular switch/LCP complexes in liquid crystalline states were analyzed by XRD to assess the abilities of the molecular switches to change the ordered structures of the host polymers. Feringa et al. recently demonstrated that the ordered structure of host cholesteric liquid crystalline molecules could be photochemically tuned by doping with a photoresponsive molecular rotor.[69] In that case, the conformational change in the molecular rotor caused the ordered structure of the host LC molecules to change because of strong host−guest interactions. Other successful examples of orientations of host LCs and the helical structures and helical twisting powers of cholesteric LCs being controlled by photoresponsive molecular switches have also been reported.[70,71] Inspired by the above-mentioned studies, we expected that our redox-driven molecular switches could induce changes in the local order of the host polymer. Host polymeric

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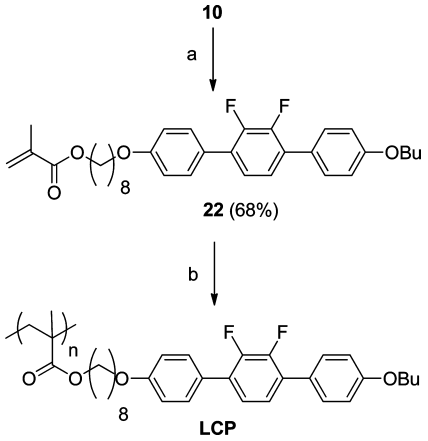
materials or functional gels that could undergo macroscopic deformations could be achieved if such structural changes could be effectively enhanced.

The host polymer LCP was prepared by conventional radical polymerization of **22**, as shown in Scheme 7. Complexes

Scheme 7. Synthesis of Host LCP[a]



[a]Reagents and conditions: (a) methacryloyl chloride, Et_3N, THF, 0 °C; (b) AIBN, toluene, 95 °C.

consisting of molecular switch dopants (**1**, $\mathbf{1}^{2+}$, **2**, $\mathbf{2}^{2+}$, **3**, $\mathbf{3}^{2+}$, BDTBT, or $BDTBT^{2+}$) and host LCP were prepared and their nanostructures were analyzed. All molecular switches and their corresponding $SbCl_6$ salts except $BDTBT^{2+}(SbCl_6^-)_2$ (Figure S6, Supporting Information) formed homogeneous complexes with LCP. The XRD patterns for **3**/LCP and $\mathbf{3}^{2+}$/LCP are shown as examples in Figure 8. Pure LCP and all the complexes showed diffraction patterns that were characteristic of a smectic A phase, indicating that the original smectic order structure of LCP was maintained even after complexes with molecular switches were formed (Figure S7, S8, S9, and S10, Supporting Information). The layer spacings for all the complexes and pure LCP are listed in Table 2 and shown in Figure 9. A distinctly

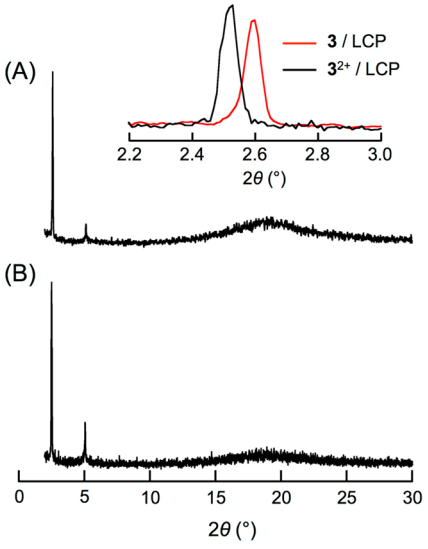


Figure 8. X-ray diffraction patterns for (A) **3**/LCP at 177 °C and (B) $\mathbf{3}^{2+}$/LCP at 178 °C during cooling. The inset shows diffraction peaks for **3**/LCP and $\mathbf{3}^{2+}$/LCP in small-angle region.

Table 2. Layer Spacings of Complexes[a] of LCP with Molecular Switches and Their $SbCl_6$ Salts in Smecic A Phases

complex	T^b (°C)	layer spacing d (Å)
Pure LCP	104	33.8
1/LCP	175	32.8
$\mathbf{1}^{2+}(SbCl_6^-)_2$/LCP	175	34.2
2/LCP	177	33.6
$\mathbf{2}^{2+}(SbCl_6^-)_2$/LCP	175	33.4
3/LCP	177	33.9
$\mathbf{3}^{2+}(SbCl_6^-)_2$/LCP	178	34.9
BDTBT/LCP	147	35.0
$BDTBT^{2+}(SbCl_6^-)_2$/LCP	148	34.3

[a]Each complex contained 0.1 μmol of molecular switch or corresponding $SbCl_6$ salt per milligram of LCP. [b]Except for $\mathbf{2}^{2+}$/LCP, the layer spacings and temperatures reported were determined during cooling.

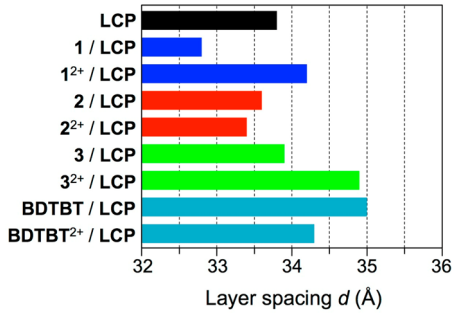


Figure 9. Layer spacings d for all complexes and pure LCP.

smaller layer spacing was observed for **1**/LCP than for pure LCP, but such remarkable decrease in the layer spacings were not found for **2**/LCP and **3**/LCP compared with that for pure LCP. On the other hand, BDTBT/LCP showed a larger layer spacing than pure LCP.

This result can be explained as follows. The terphenyl units of **1** in **1**/LCP are directly attached to the bithienyl scaffold, forming a rigid structure, and the conformation of the polymer backbone of the host LCP may strongly depend on the conformation of dopant **1** because of the attractive $\pi-\pi$ interactions between the terphenyl units, which cause the shrunken nanostructure of the smectic layer structure. We speculate that intermolecular interactions between biphenyl units attached to the thiophene moieties and terphenyl pendant group of the LCP in **2**/LCP are not strong enough to change the nanostructure of the host LCP.[72] A structural resemblance between the dopant and host molecules is a crucial factor for homogeneous complexes being formed.[69] Strong attractive $\pi-\pi$ interactions between the terphenyl units may exist in the complex **3**/LCP, similar to **1**/LCP, but the LCP nanostructure is probably less affected in **3**/LCP than in **1**/LCP because of the flexible spacer connecting the terphenyl units and thiophene rings.[73] In the case of BDTBT, there is no structural resemblance between BDTBT and terphenyl mesogenic units of LCP, and this results in poor molecular interaction between BDTBT and mesogenic moieties of LCP.[69] Consequently, BDTBTs may be intercalated not inside the layer of mesogenic moieties but outside the layer of mesogenic moieties of LCP leading to the expansion of interlayer distance.

Larger layer spacings were found for complexes $\mathbf{1}^{2+}$/LCP and $\mathbf{3}^{2+}$/LCP than for complexes **1**/LCP and **3**/LCP (indicated by

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lower diffraction angles, see Figure 8A inset), but the layer spacings were smaller for the complexes $\mathbf{2}^{2+}$/LCP and BDTBT^{2+}/LCP than for complexes **2**/LCP and BDTBT/LCP. The layer spacings for $\mathbf{1}^{2+}$/LCP and $\mathbf{3}^{2+}$/LCP were higher than those for **1**/LCP and **3**/LCP by 1.4 and 1.0 Å, respectively. The ionic pairs $\mathbf{1}^{2+}(SbCl_6^-)_2$ and $\mathbf{3}^{2+}(SbCl_6^-)_2$ could expand the LCP smectic layer spacing parallel to the normal layer. As depicted schematically in Figure 10, the formation of molecular switch ionic pairs requires a large free volume of LCP because of the intercalation of counteranions and changes in the molecular shape compared with that of the cyclized form.[74] This could cause the LCP layer spacing to increase, but the influence of the counteranions may not be dominant because of the small differences in the nanostructures of **2**/LCP and $\mathbf{2}^{2+}$/LCP. In contrast to $\mathbf{1}/\mathbf{1}^{2+}$ and $\mathbf{3}/\mathbf{3}^{2+}$, BDTBT^{2+}/LCP showed smaller layer spacings than those of BDTBT/LCP. Such decrease in layer spacings suggests that the oxidization of BDTBT to BDTBT^{2+} causes a reduction in orientational order of smectic structures[75] of LCP. To investigate the effects of temperatures on the stability of the smectic layer structures of the complexes, the layer spacings of **3**/LCP and $\mathbf{3}^{2+}$/LCP were measured with different temperatures (Table S1 and S2, Supporting Information). As reported by Lemieux et al.,[76] both complexes did not show drastic changes of the layer spacings in smectic A phases. This suggests that the complexes formed stable orientational order structures in smectic A phase and tilting of mesogenic units like smectic C phase[76] did not occur.

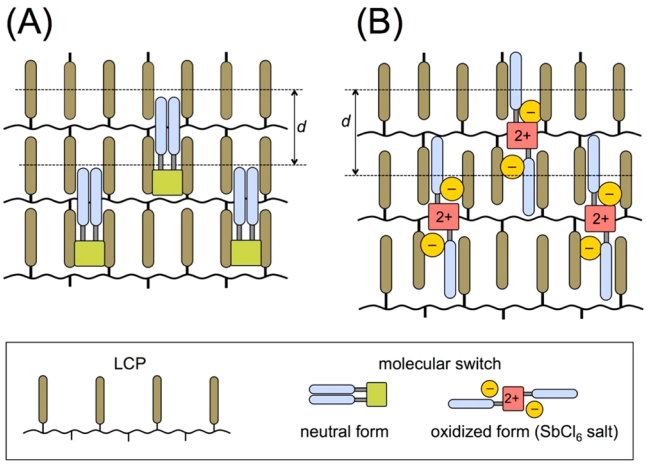

Figure 10. Schematic illustration of change in layer spacings of LCP complexes based on the redox-induced interconversion of guest molecular switches. (A) Complexes of LCP with cyclized molecular switch and (B) complexes of LCP with oxidized cationic salt of molecular switch.

These results suggest that the ordered structures of polymer matrices can be changed by the redox-triggered interconversion between a molecular switch and its corresponding oxidized dication.

CONCLUSIONS

Redox-driven molecular switches consisting of a benzodithiolylbithienyl scaffold and rigid biphenyl or terphenyl units were designed and synthesized for use as functional dopants to induce changes in the nanostructures of host polymers. UV and CV studies confirmed that the interconversion between the cationic form and neutral cyclized form occurred. Binary complexes of the molecular switch and host LCP were prepared, and the changes in smectic layer structures of these complexes were examined using XRD. Layer spacings for the redox pairs $\mathbf{1}/\mathbf{1}^{2+}$ and $\mathbf{3}/\mathbf{3}^{2+}$ complexes with LCP were larger when molecular switches were in the oxidized cationic form than when they were in the neutral cyclized form. In this study, we demonstrated the potential for molecular switches to be used as functional dopants for tuning the nanostructures of host polymeric materials. This should be a crucial factor in constructing soft actuators consisting of deformable host media (polymers or gels) and actuating dopants (molecular switches). For future challenges to prepare redox-driven actuators, the design of electrode that can achieve the effective electron transfer between molecular switches and electrode should be optimized. The molecular switches presented here should provide a useful impetus for development of redox-driven molecular actuators in practical applications.

EXPERIMENTAL SECTION

General Procedures. Unless otherwise noted, all reactions were run under nitrogen atmosphere. CH_2Cl_2 and CH_3CN were distilled from CaH_2 before use. Most ^1H and ^{13}C were recorded at 25 °C on a 400 and 100 MHz spectrometer, respectively. Chemical shifts are in parts per million (ppm) using either the solvent's residual protons or TMS employed as the internal standard. For mesomorphic compounds, DSC measurements were carried out to determine phase transition temperatures. Heating and cooling rates were 10 °C/min. The transition temperatures were determined by the minimum of exothermic and maximum point of endothermic peaks, respectively. A polarizing microscope equipped with hot stage and crossed polarizers were used for visual observation of mesophases. The following abbreviations are used to describe the phase transition behaviors. Cr: crystal; N: nematic; S_A: smectic A; S_E: smectic E; S_X: ordered smectic; I: isotropic liquid. Polymer molecular weights and polydispersity indexes (PDI) were determineed by gel permeation chromatography (GPC). Polystyrene standards were used for calibration, and THF was used as an eluent at a flow rate of 1.0 mL/min. XRD scans of polymers or molecular switch were performed to determine the type of liquid-crystalline phases and layer spacing of polymers. Cyclic voltammetry was carried out in a three-compartment cell. All solutions were purged with nitrogen and retained under inert atmosphere during experiments.

2,3-Difluoro-4-(4-butoxyphenyl)benzene (5). A suspension of $Pd(PPh_3)_4$ (1.06 g, 0.92 mmol) and **4** (7.00 g, 30.6 mmol) in DME (60 mL) was stirred at room temperature for 10 min. To this suspension were added subsequently a solution of 2,3-difluorophenylboronic acid (4.96 g, 31.4 mmol) in ethanol (15 mL) and aqueous Na_2CO_3 (2 M solution, 30 mL, 60 mmol). The mixture was heated to reflux for 22 h, cooled to room temperature, and extracted with CH_2Cl_2 three times. The combined extracts were washed with water and brine, dried over Na_2SO_4, and filtered. The solvent was evaporated and the residue was purified by column chromatography (silica gel, eluent: hexane followed by hexane/CH_2Cl_2 = 10/1) to afford **5** (7.13 g, 27.2 mmol): yield 89%; white solid; mp 33−34 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 0.99 (t, J = 7.4 Hz 3H), 1.47−1.56 (m, 2H), 1.76−1.83 (m, 2H), 4.01 (t, J = 6.5 Hz, 2H), 6.96−7.00 (AA'BB', 2H), 7.06−7.18 (m, 3H), 7.45−7.48 (AA'BB', 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.9 (s), 19.4 (s), 31.4 (s), 67.8 (s), 114.7 (s), 115.4 (d, J = 17 Hz), 124.0 (dd, J = 8.1 Hz, J = 4.9 Hz), 125.1 (dd, J = 3.3 Hz, J = 2.3 Hz), 126.9 (dd, J = 2.9 Hz, J = 1.0 Hz), 130.2 (d, J = 3.9 Hz), 131.2 (d, J = 10 Hz), 148.0 (dd, J = 13 Hz, J = 247 Hz), 151.3 (dd, J = 14 Hz, J = 247 Hz), 159.4 (s); HR-MS (APCI) $C_{16}H_{16}F_2O$ $[M]^+$ calcd m/z 262.1169, found m/z 262.1165.

2,3-Difluoro-4-(4-butoxyphenyl)phenylboronic acid (6). A solution of **5** (2.57 g, 9.78 mmol) in THF (20 mL) was stirred at −78 °C. BuLi (1.66 M in hexane, 8 mL, 13.3 mmol) was added dropwise to the solution. The reaction mixture was stirred at the same condition for 3 h, then trimethyl borate (3.36 g, 32.3 mmol) was added to the

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mixture. The mixture was allowed to warm to room temperature overnight and quenched with 4 M HCl solution (30 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O three times. The combined organic extracts were washed with water and brine, dried over Na_2SO_4, and filtered. The solvent was evaporated, and the residue was purified by column chromatography (silica gel, eluent: hexane/ethyl acetate = 3/2) to give **6** (2.44 g, 7.97 mmol): yield 82%; white solid; mp 129−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.99 (t, J = 7.4 Hz 3H), 1.47−1.56 (m, 2H), 1.76−1.83 (m, 2H), 4.02 (t, J = 6.5 Hz, 2H), 5.09 (d, J = 5.6 Hz, 2H), 6.97−7.01 (AA'BB', 2H), 7.22−7.26 (m, 1H), 7.48−7.53 (AA'BB', 2H), 7.56−7.60 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 13.7 (s), 18.8 (s), 30.8 (s), 67.3 (s), 114.7 (s), 124.5 (s), 126.1 (d, J = 2.1 Hz), 129.7 (s), 129.99 (s), 130.02 (s), 131.2 (d, J = 10 Hz), 147.0 (dd, J = 15 Hz, J = 246 Hz), 153.5 (dd, J = 12 Hz, J = 243 Hz), 158.9 (s); IR (KBr, cm^{-1}) 1358 (ν BO); HR-MS (ES) $C_{16}H_{18}BF_2O_3$ $[M + H]^+$ calcd m/z 307.1317, found m/z 307.1309.

1-Bromo-4-[2,3-difluoro-4-(4-butoxyphenyl)phenyl]-benzene (7). The experimental procedure was as described for the preparation of **5** except that benzene was used as a solvent, and the reaction time was 1.5 h. Quantities: 1-iodo-4-bromobenzene (1.45 g, 5.11 mmol), **6** (1.72 g, 5.61 mmol), $Pd(PPh_3)_4$ (0.18 g, 0.15 mmol), aqueous Na_2CO_3 (2 M solution, 5.0 mL, 10.0 mmol). The crude product was purified by column chromatography (silica gel, eluent: hexane/CH_2Cl_2 = 7/1) to afford **7** (1.25 g, 3.00 mmol): yield 59%; white solid; phase transition temperature/°C (DSC on second heating) Cr 116 S_X 122 S_A 145 N 182 I; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.00 (t, J = 7.4 Hz 3H), 1.47−1.57 (m, 2H), 1.77−1.84 (m, 2H), 4.02 (t, J = 6.5 Hz, 2H), 6.98−7.01 (AA'BB', 2H), 7.18−7.24 (m, 2H), 7.44−7.47 (AA'BB', 2H), 7.49−7.53 (AA'BB', 2H), 7.58−7.62 (AA'BB', 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.00 (s), 19.4 (s), 31.5 (s), 68.0 (s), 114.9 (s),122.6 (s), 124.57 (dd, J = 28 Hz, J = 2.4 Hz), 124.61 (dd, J = 28 Hz, J = 3.7 Hz), 126.7 (d, J = 1.7 Hz), 128.0 (d, J = 4.5 Hz), 128.1 (d, J = 4.5 Hz), 130.2 (d, J = 2.3 Hz), 130.6 (d, J = 2.1 Hz), 132.0 (s), 133.8 (s), 148.6 (dd, J = 16 Hz, J = 250 Hz), 159.5 (s); HR-MS (ES) $C_{22}H_{19}BrF_2O$ $[M]^+$ calcd m/z 416.0587, found m/z 416.0579.

1-(4-Butoxyphenyl)-4-[4-(pinacolboronato)phenyl]-2,3-difluorobenzene (8). A mixture of **7** (833 mg, 2.00 mmol), bis(pinacolato)diboron (609 mg, 2.40 mmol), KOAc (590 mg, 6.01 mmol), and $PdCl_2$(dppf) (49 mg, 0.06 mmol) in DMF (12 mL) was stirred at 80 °C for 4 h. After cooling the reaction mixture to room temperature, the mixture was diluted with CH_2Cl_2 and water. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic extracts were washed with water and brine, dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure. Purification by column chromatography (silica gel, eluent: hexane/CH_2Cl_2 = 1/1) afforded **8** (682 mg, 1.47 mmol): yield 74%; white solid; mp 143−144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.00 (t, J = 7.3 Hz, 3H), 1.37 (s, 12H), 1.47−1.57 (m, 2H), 1.77−1.84 (m, 2H), 4.02 (t, J = 6.6 Hz, 2H), 6.98−7.02 (AA'BB', 2H), 7.21−7.27 (m, 2H), 7.51−7.53 (AA'BB', 2H), 7.59−7.61 (AA'BB', 2H), 7.90−7.93 (AA'BB', 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.0 (s), 19.4 (s), 25.0 (s), 31.4 (s), 67.9 (s), 84.1 (s), 114.8 (s), 124.6 (dd, J = 3 Hz, 4 Hz), 124.8 (dd, J = 3.9 Hz, J = 4.3 Hz), 126.9 (dd, J = 1 Hz, J = 2 Hz), 128.3 (d, J = 3 Hz), 129.2 (d, J = 10 Hz), 130.0 (d, J = 10 Hz), 130.2 (d, J = 3 Hz), 135.2 (s), 137.6 (d, J = 1 Hz), 137.6 (d, J = 1 Hz), 148.6 (dd, J = 14 Hz, J = 247 Hz), 148.7 (dd, J = 12 Hz, J = 246 Hz), 159.4 (s); IR (KBr, cm^{-1}) 1358 (ν BO); HR-MS (EI) $C_{28}H_{31}BF_2O_3$ $[M]^+$ calcd m/z 464.2334, found m/z 464.2324.

1-Hydroxy-4-[2,3-difluoro-4-(4-butoxyphenyl)phenyl]-benzene (9). The experimental procedure was as described for the preparation of **5** except that the reaction time was 21.5 h. Quantities: **6** (4.73 g, 15.5 mmol), 4-bromophenol (2.42 g, 14.0 mmol), $Pd(PPh_3)_4$ (0.48 g, 0.42 mmol), DME (90 mL). The crude product was purified by column chromatography (silica gel, eluent: hexane/ethyl acetate = 15/1 followed by 5/1) to give **9** (2.58 g, 7.28 mmol): yield 52%; white powder; phase transition temperature/°C (DSC on first cooling) I 175 S_X 173 Cr; (DSC on second heating) Cr 191 I; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.00 (t, J = 7.2 Hz 3H), 1.47−1.57 (m, 2H), 1.77−1.84 (m, 2H), 4.02 (t, J = 6.5 Hz, 2H), 4.83 (brs, 1H), 6.92−6.95 (AA'BB', 2H), 6.98−7.01 (AA'BB', 2H), 7.17−7.23 (m, 2H), 7.47−7.53(m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 13.7 (s), 18.7 (s), 30.7 (s), 67.3 (s), 114.7 (s), 115.6 (s), 124.4 (s), 124.6 (s), 124.68 (d, J = 4 Hz), 124.73 (s), 126.0 (s), 127.9 (d, J = 4 Hz), 128.6 (s), 129.9 (dd, J = 1.6 Hz, J = 1.7 Hz), 147.5 (dd, J = 7 Hz, J = 248 Hz), 147.7 (dd, J = 7 Hz, J = 248 Hz), 157.7 (s), 158.8 (s); IR (KBr, cm^{-1}) 3429 (ν OH); HR-MS (APCI) $C_{22}H_{19}F_2O_2$ $[M - H]^+$ calcd m/z 353.1353, found m/z 353.1349.

1-(8-Hydroxyoctyl-1-oxy)-4-[2,3-difluoro-4-(4-butoxyphenyl)phenyl]benzene (10). A mixture of **9** (1.11 g, 3.13 mmol), KI (0.13 g, 0.77 mmol), K_2CO_3 (0.88 g, 6.36 mmol), and 8-bromo-1-octanol (1.22 g, 5.84 mmol) in DMF (20 mL) was heated and stirred at 85 °C for 20 h. The resulting mixture was poured into water (100 mL), and then the precipitate was collected by filtration and washed with ethanol several times. The crude product was purified by column chromatography (silica gel, eluent: CH_2Cl_2 followed by CH_2Cl_2/methanol = 20/1) to give **10** (1.39 g, 2.89 mmol): yield 92%; white solid; phase transition temperature/°C (DSC on second heating) Cr 117 N 162 I; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.00 (t, J = 7.4 Hz, 3H), 1.33−1.62 (m, 12H), 1.77−1.85 (m, 4H), 3.65 (t, J = 6.6 Hz, 2H), 4.01 (t, J = 6.2 Hz, 2H), 4.02 (t, J = 6.2 Hz, 2H), 6.97−7.01 (AA'BB', 4H), 7.20−7.21 (m, 2H), 7.50−7.53 (AA'BB', 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.0 (s), 19.4 (s), 25.8 (s), 26.1 (s), 29.4 (s), 29.5 (s), 31.5 (s), 32.9 (s), 63.2 (s), 67.9 (s), 68.2 (s), 114.8 (s), 124.4 (s), 124.5 (s), 124.5 (s), 127.01 (s), 127.04 (s), 128.98 (s), 129.01 (s), 129.1 (s), 130.1 (s), 148.6 (dd, J = 15 Hz, J = 249 Hz), 159.26 (s), 159.30 (s); IR (KBr, cm^{-1}) 3323 (ν OH), 1053 (ν CO); HR-MS (ES) $C_{30}H_{36}F_2O_3Na$ $[M + Na]^+$ calcd m/z 505.2530, found m/z 505.2541.

1-(8-*p*-Toluenesulfonyloxyoctyloxy)-4-[2,3-difluoro-4-(4-butoxyphenyl)phenyl]benzene (11). To a solution of **10** (1.32 g, 2.74 mmol) in CH_2Cl_2 (60 mL) were added *p*-toluenesulfonyl chloride (0.79 g, 4.16 mmol), 4-dimethylaminopyridine (36 mg, 0.30 mmol), and triethylamine (0.42 g, 4.16 mmol), and the solution was stirred at room temperature for 18 h. Then the reaction mixture was quenched with sat. NH_4Cl aqueous solution and extracted with $CHCl_3$ three times. The combined organic extracts were dried over Na_2SO_4, filtered. The solvent was evaporated, and the residue was purified by column chromatography (silica gel, eluent: $CHCl_3$/hexane = 3/1 followed by $CHCl_3$) to afford **11** (1.62 g, 2.55 mmol): yield 93%; white waxy solid; phase transition temperature/°C (DSC on second heating) Cr 72 S_A 95 N 101 I; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.00 (t, J = 7.6 Hz, 3H), 1.26−1.36 (m, 6H), 1.41−1.57 (m, 4H), 1.62−1.69 (m, 2H), 1.75−1.84 (m, 4H), 2.45 (s, 3H), 3.98−4.05 (m, 6H), 6.97−7.00 (m, 4H), 7.20−7.21 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.6 Hz, 4H), 7.80 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.0 (s), 19.4 (s), 21.8 (s), 25.4 (s), 26.1 (s), 28.95 (s), 28.98 (s), 29.25 (s), 29.32 (s), 31.5 (s), 67.9 (s), 68.1 (s), 70.8 (s), 114.77 (s), 114.78 (s), 124.30 (s), 124.32 (s), 126.9 (s), 127.0 (d, J = 1 Hz), 127.1 (d, J = 1 Hz), 128.0 (s), 129.1 (s), 120.0 (s), 130.10 (s), 130.12 (s), 130.14 (s), 133.4 (s), 144.8 (s), 148.6 (dd, J = 16 Hz, 250 Hz), 159.2 (s), 159.3 (s); IR (KBr, cm^{-1}) 1358 (ν_{as} SO_2), 1178 (ν_s SO_2); HR-MS (APCI) $C_{37}H_{41}F_2O_5S$ $[M - H]^+$ calcd m/z 635.2643, found m/z 635.2651.

4,4′-Dibromo-2,2′-bis(1,3-dioxolan-2-yl)-3,3′-bithienyl (13). To a solution of **12** (1.33 g, 3.50 mmol) in benzene (50 mL) were added ethylene glycol (1.21 g, 19.4 mmol) and *p*-toluenesulfonic acid monohydrate (0.22 g, 1.17 mmol). The mixture was heated to reflux using a Dean−Stark apparatus to remove water for 3 h and cooled to room temperature. The mixture was diluted with CH_2Cl_2, washed with sat. $NaHCO_3$ aqueous solution, dried over Na_2SO_4, and filtered. The solvent was evaporated, and the residue was purified by column chromatography (silica gel, eluent: CH_2Cl_2) to afford **13** (1.56 g, 3.32 mmol): yield 95%; light yellow solid; mp 149−150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.89−3.97 (m, 4H), 4.04−4.12 (m, 4H), 5.80 (s, 2H), 7.39 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 65.46 (s), 65.49 (s), 99.1 (s), 112.9 (s), 123.2 (s), 133.3 (s), 141.5 (s); IR (KBr, cm^{-1}) 1076 (ν CO); HR-MS (ES) $C_{14}H_{13}Br_2O_4S_2$ $[M + H]^+$ calcd m/z 466.8622, found m/z 466.8601.

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2,2′-Bis(1,3-dioxolan-2-yl)-4,4′-diformyl-3,3′-bithienyl (14). A solution of **13** (988 mg, 2.11 mmol) in THF (6 mL) was added dropwise to a mixture of BuLi (1.65 M in hexane, 3.1 mL, 5.12 mmol) and THF (6 mL) at −78 °C. Then the mixture was stirred for 1 h. To the mixture was added DMF (1.3 mL, 16.8 mmol), and the reaction mixture was further stirred for 1 h. The reaction mixture was allowed to warm to room temperature and treated with sat. NH_4Cl aqueous solution. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography (silica gel, eluent: CH_2Cl_2/ethyl acetate = 5/1) to afford **14** (367 mg, 1.00 mmol): yield 47%; light yellow powder; mp 140−143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.85−3.94 (m, 4H), 4.00−4.12 (m, 4H), 5.78 (s, 2H), 8.23 (s, 2H), 9.57 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 65.5 (s), 65.7 (s), 98.4 (s), 131.6 (s), 135.3 (s), 141.2 (s), 142.3 (s), 184.8 (s); IR (KBr, cm^{-1}) 1687 (ν C═O); HR-MS (EI) $C_{16}H_{14}O_6S_2$ $[M]^+$ calcd m/z 366.0232, found m/z 366.0226.

2,2′-Bis(1,3-dioxolan-2-yl)-4,4′-bishydroxymethyl-3,3′-bithienyl (15). To a solution of **14** (118 mg, 0.32 mmol) in ethanol (5 mL) was added $NaBH_4$ (51 mg, 1.35 mmol) at room temperature. The reaction mixture was stirred for 2.5 h and concentrated. The residue was diluted with CH_2Cl_2 and water. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated to afford pure **15** (112 mg, 0.30 mmol): yield 94%; light yellow powder; mp 121−123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.95 (dd, J = 4.2 Hz, J = 8.1 Hz, 2H), 3.86−3.92 (m, 4H), 3.97−4.07 (m, 4H), 4.18−4.33 (m, 4H), 5.72 (s, 2H), 7.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 58.6 (s), 65.2 (s), 65.9 (s), 99.2 (s), 125.1 (s), 133.6 (s), 139.5 (s), 142.8 (s); HR-MS (EI) $C_{16}H_{18}O_6S_2$ $[M]^+$ calcd m/z 370.0545, found m/z 370.0537.

2,2′-Diformyl-4,4′-bis{4-[2,3-difluoro-4-(4-butoxyphenyl)-phenyl]phenyl}-3,3′-bithienyl (16). A flask charged with **12** (73 mg, 0.19 mmol), **8** (195 mg, 0.42 mmol), $PdCl_2$(dppf) (11 mg, 0.013 mmol) was flashed with N_2. DMF (6 mL) was added to the mixture, and the mixture was stirred at room temperature. Then aqueous Na_2CO_3 (2 M, 1 mL, 2.00 mmol) was added to the mixture. The suspension was stirred at 80 °C for 26 h. After cooling to room temperature, the resulting suspension was filtered over Celite pad and diluted with CH_2Cl_2, washed with water and brine, dried over Na_2SO_4, filtered and concentrated. Purification on column chromatography (silica gel, eluent: $CHCl_3$) gave **16** (95 mg, 0.11 mmol): yield 58%; light yellow solid; mp 211−214 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.00 (t, J = 7.4 Hz, 6H), 1.47−1.57 (m, 4H), 1.77−1.84 (m, 4H), 4.02 (t, J = 6.5 Hz, 4H), 6.83 (d, J = 8.1 Hz, 4H), 7.00 (d, J = 8.7 Hz, 4H), 7.16−7.26 (m, 4H), 7.34 (d, J = 7.9 Hz, 4H), 7.52 (d, J = 8.3 Hz, 4H), 7.77 (s, 2H), 9.83 (s, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.0 (s), 19.4 (s), 31.4 (s), 67.9 (s), 114.8 (s), 124.5 (dd, J = 3.3 Hz, J = 3.8 Hz), 124.7 (dd, J = 3.5 Hz, J = 4.0 Hz), 126.7 (s), 128.2 (s), 129.0 (s), 129.1 (s), 130.1 (s), 130.2 (s), 132.2 (s), 133.7 (s), 134.3 (s), 139.9 (s), 143.0 (s), 144.6 (s), 148.5 (dd, J = 13 Hz, J = 250 Hz), 148.7 (dd, J = 15 Hz, J = 250 Hz), 159.4 (s), 183.1 (s); IR (KBr, cm^{-1}) 1668 (ν C═O); HR-MS (APCI) $C_{54}H_{42}O_4F_4S_2$ $[M]^+$ calcd m/z 894.2461, found m/z 894.2465.

2,2′-Diformyl-4,4′-bis[2,3-difluoro-4-(4-butoxyphenyl)-phenyl]-3,3′-bithienyl (17). The experimental procedure was as described for the preparation of compound **5**. Quantities: **12** (0.99 g, 2.60 mmol), **6** (2.09 g, 6.83 mmol), $Pd(PPh_3)_4$ (0.18 g, 0.16 mmol), aqueous Na_2CO_3 (2 M, 5.8 mL, 11.6 mmol). The crude product was purified by column chromatography (silica gel, eluent: hexane/ethyl acetate = 5/1) to give **17** (1.17 g, 1.57 mmol): yield 61%; yellow solid; mp 160−163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.99 (t, J = 7.4 Hz, 6H), 1.46−1.55 (m, 4H), 1.76−1.83 (m, 4H), 4.01 (t, J = 6.5 Hz, 4H), 6.39 (t, J = 6.9 Hz, 2H), 6.92 (t, J = 6.9 Hz, 2H), 6.95−6.99 (AA'BB', 4H), 7.41−7.44 (AA'BB', 4H), 7.79 (s, 2H), 9.83 (d, J = 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.0 (s), 19.3 (s), 31.4 (s), 67.9 (s), 114.8 (s), 121.5 (d, J = 12 Hz), 124.35 (s), 124.38 (s), 124.41 (s), 126.20 (s), 126.22 (s), 130.06 (s), 130.09 (s), 131.0 (s), 131.1 (s), 134.4 (d, J = 3 Hz), 136.6 (d, J = 2 Hz), 139.8 (s), 143.1 (s), 148.0 (dd, J = 13 Hz, J = 250 Hz), 148.4 (dd, J = 15 Hz, J = 249 Hz), 159.6 (s), 182.9 (s); IR (KBr, cm^{-1}) 1666 (ν C═O); HR-MS (EI) $C_{42}H_{34}O_4F_4S_2$ $[M]^+$ calcd m/z 742.1835, found m/z 742.1829.

2,2′-Diformyl-4,4′-bis(8-{4-[2,3-difluoro-4-(4-butoxyphenyl)-phenyl]phenyloxy}octyl-1-oxymethoxy)-3,3′-bithienyl (18). To a solution of **15** (272 mg, 0.74 mmol) in DMF (5 mL) was added NaH (98 mg, 60 wt % in mineral oil, 2.45 mmol), and the mixture was stirred at room temperature for 1.5 h. Next, a solution of **11** (1.046 g, 1.64 mmol) in DMF (5 mL) was added to the mixture, and then the mixture was heated to 75 °C and stirred for 21 h. After cooling to the room temperature, the reaction mixture was quenched with sat. $NaHCO_3$ aqueous solution and extracted with CH_2Cl_2 three times. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated. The residue was dissolved in THF and treated with 6 M HCl (20 mL). The mixture was stirred at room temperature for 2 h and extracted with CH_2Cl_2 three times. The combined organic extracts were washed with water and brine, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography (silica gel, eluent: $CHCl_3$) to give **18** (621 mg, 0.51 mmol): yield 69%; white waxy solid; phase transition temperature/°C (DSC on second heating) Cr 94 S_A 136 N 142 I; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.99 (t, J = 7.4 Hz, 6H), 1.23−1.39 (m, 12H), 1.42−1.56 (m, 12H), 1.76−1.83 (m, 8H), 3.29 (t, J = 6.6 Hz, 4H), 3.98−4.02 (m, 8H), 4.14 (d, ^2J = 12 Hz, 2H), 4.20 (d, ^2J = 12 Hz, 2H), 6.97−6.99 (AA'BB', 8H), 7.18−7.19 (m, 4H), 7.50 (d, J = 8.6 Hz, 8H), 7.78 (d, J = 0.8 Hz, 2H), 9.53 (d, J = 0.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.0 (s), 19.4 (s), 26.11 (s), 26.13 (s), 29.36 (s), 29.40 (s), 29.45 (s), 29.51 (s), 31.4 (s), 66.6 (s), 67.9 (s), 68.1 (s), 71.4 (s), 114.7 (s), 124.40 (d, J = 2 Hz), 124.44 (d, J = 2 Hz), 124.5 (d, J = 2 Hz), 126.96 (d, J = 1 Hz), 127.02 (d, J = 1 Hz), 128.9 (s), 129 (s), 128.99 (s), 129.03 (s), 130.1 (s), 132.6 (s), 140.8 (s), 141.5 (s), 142.3 (s), 148.6 (dd, J = 249 Hz, J = 16 Hz), 159.2 (s), 159.3 (s), 182.9 (s); IR (KBr, cm^{-1}) 1672 (ν C═O); HR-MS (APCI) $C_{72}H_{79}O_8F_4S_2$ $[M + H]^+$ calcd m/z 1211.5147, found m/z 1211.5140.

2,2′-Bis(1,3-benzodithiol-2-yl)-4,4′-bis{4-[2,3-difluoro-4-(4-butoxyphenyl)phenyl]phenyl}-3,3′-bithienyl (19). A solution of **16** (66 mg, 74 μmol), 1,2-benzenedithiol (37 mg, 260 μmol), and *p*-toluenesulfonic acid monohydrate (24 mg, 126 μmol) in benzene (12 mL) was heated to reflux for 4.5 h. To the solution was added sat. $NaHCO_3$ aqueous solution, and then the mixture was extracted with CH_2Cl_2 three times. The combined extracts were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (alumina, eluent: hexane/CH_2Cl_2 = 4/1 followed by 1/1) and recrystallized from toluene/hexane to give **19** (75 mg, 66 μmol): yield 89%; colorless solid; mp 202−204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.00 (t, J = 7.4 Hz, 6H), 1.48−1.57 (m, 4H), 1.77−1.84 (m, 4H), 4.03 (t, J = 6.5 Hz, 4H), 5.99 (s, 2H), 6.98−7.02 (AA'BB', 4H), 7.05−7.10 (m, 8H), 7.13−7.15 (m, 2H), 7.22−7.27 (m, 6H), 7.36 (s, 2H), 7.42−7.44 (AA'BB', 4H), 7.50−7.54 (AA'BB' 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.0 (s), 19.4 (s), 31.5 (s), 50.6 (s), 67.9 (s), 114.8 (s), 122.3 (s), 122.4 (s), 123.4 (s), 124.58 (d, J = 3 Hz), 124.64 (d, J = 3 Hz), 126.2 (d, J = 1 Hz), 126.9 (dd, J = 1.2 Hz, J = 2.0 Hz), 128.2 (s), 128.9 (d, J = 11 Hz), 129.1 (d, J = 3 Hz), 129.8 (d, J = 10 Hz), 130.1 (s), 130.2 (s), 131.1 (s), 133.9 (s), 135.2 (s), 136.8 (s), 137.2 (s), 141.4 (s), 144.5 (s), 148.7 (dd, J = 19 Hz, J = 255 Hz), 159.4 (s); HR-MS (APCI) $C_{66}H_{51}O_2F_4S_6$ $[M + H]^+$ calcd m/z 1143.2144, found m/z 1143.2140.

2,2′-Bis(1,3-benzodithiol-2-yl)-4,4′-bis[2,3-difluoro-4-(4-butoxyphenyl)]phenyl-3,3′-bithienyl (20). The experimental procedure was as described for the preparation of compound **19**. Quantities: **17** (848 mg, 1.14 mmol), 1,2-benzenedithiol (485 mg, 3.41 mmol), *p*-toluenesulufonic acid monohydrate (128 mg, 0.67 mmol). The crude product was purified by column chromatography (alumina, eluent: toluene/hexane = 1/1 followed by 2/1) to give **20** (989 mg, 1.00 mmol): yield 88%; colorless solid; mp 193−195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.99 (t, J = 7.4 Hz, 6H), 1.47−1.56 (m, 4H), 1.76−1.83 (m, 2H), 4.01 (t, J = 6.5 Hz, 4H), 6.20 (s, 2H), 6.45−6.49 (m, 2H), 6.91−6.95 (m, 2H), 6.95−7.00 (AA'BB', 4H), 7.07−7.14 (m, 4H), 7.16−7.20 (m, 4H), 7.33 (s, 2H), 7.44−7.46 (AA'BB', 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.0 (s), 19.4 (s), 31.4 (s), 50.9 (s),

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67.9 (s), 114.7 (s), 122.4 (s), 122.6 (s), 122.9 (d, J = 11 Hz), 124.1 (s), 124.5 (s), 126.0 (d, J = 4 Hz), 126.4 (d, J = 3 Hz), 126.8 (s), 130.06 (s), 130.13 (d, J = 3 Hz), 131.4 (s), 133.4 (d, J = 2 Hz), 136.8 (s), 137.0 (s), 144.1 (s), 148.2 (dd, J = 14 Hz, J = 248 Hz), 148.6 (dd, J = 14 Hz, J = 249 Hz), 159.4 (s); HR-MS (APCI) $C_{54}H_{43}O_2F_4S_6$ [M + H]$^+$ calcd m/z 991.1518, found m/z 991.1506.

2,2′-Bis(1,3-benzodithiolyl)-4,4′-bis (8-{4-[2,3-difluoro-4-(4-butoxyphenyl)phenyl]phenyloxy}octyl-1-oxymethoxy)-3,3′-bithienyl (21). The experimental procedure was as described for the preparation of compound **19**. Quantities: **18** (464 mg, 0.38 mmol), 1,2-benzenedithiol (121 mg, 0.85 mmol), *p*-toluenesulfonic acid monohydrate (17 mg, 0.09 mmol). Purification by column chromatography (alumina, eluent: CH_2Cl_2/hexane = 1/1) gave **21** (360 mg, 0.25 mmol): yield 66%; white powder; phase transition temperature/°C (DSC on first cooling) I 122 N 116 S_A 104 S_X 79 Cr; (DSC on second heating) Cr 92 Cr 93 S_A 116 N 124 I; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.99 (t, J = 7.4 Hz, 6H), 1.26−1.56 (m, 24H), 1.76−1.83 (m, 8H), 3.29−3.39 (m, 4H), 3.97−4.03 (m, 8H), 4.08 (s, 4H), 6.01 (s, 2H), 6.96−7.00(m, 8H), 7.05−7.07 (m, 4H), 7.18−7.24 (m, 10H), 7.49−7.52 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.0 (s), 19.4 (s), 26.16 (s), 26.21 (s), 29.4 (s), 29.5 (s), 29.6 (s), 29.7 (s), 31.5 (s), 50.3 (s), 67.5 (s), 67.9 (s), 68.2 (s), 71.1 (s), 114.8 (s), 122.2 (s), 122.5 (s), 123.6 (s), 124.40 (s), 124.44 (s), 124.5 (s), 126.1 (s), 126.2 (s), 127.0 (s), 129.0 (s), 129.1 (s), 130.1 (s), 131.1 (s), 136.99 (s), 137.03 (s), 138.8 (s), 144.7 (s), 148.6 (dd, J = 16 Hz, 249 Hz), 159.25 (s), 159.28 (s); HR-MS (APCI) $C_{84}H_{85}F_4O_6S_6$ [M − H]$^+$ calcd m/z 1457.4601, found m/z 1457.4602.

1-(8-Methacryloyloxyoctyl-1-oxy)-4-[2,3-difluoro-4-(4-butoxyphenyl)phenyl]benzene (22). Alcohol **10** (1.01 g, 2.09 mmol) and Et_3N (438 mg, 4.33 mmol) were dissolved in THF (30 mL) at 0 °C. Then methacryloyl chloride (540 mg, 5.17 mmol) was added to the solution, and the mixture was stirred for 4.5 h. The reaction mixture was quenched with water and extracted with CH_2Cl_2 three times. The combined organic extracts were washed with water and brine, dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography (silica gel, eluent: CH_2Cl_2/hexane = 3/1) to afford acrylate **22** (776 mg, 1.41 mmol): yield 68%; white waxy solid; phase transition temperature/°C (DSC on second heating) Cr 81 S_A 116 N 136 I; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.00 (t, J = 7.5 Hz, 3H), 1.39−1.57 (m, 10H), 1.65−1.71 (m, 2H), 1.77−1.85 (m, 4H), 1.95 (dd, J = 1.0 Hz, J = 1.4 Hz, 3H), 4.01 (t, J = 6.4 Hz, 2H), 4.03 (t, J = 6.5 Hz, 2H), 4.15 (t, J = 6.7 Hz, 2H), 5.54−5.56 (m, 1H), 6.09−6.11 (m, 1H), 6.97−7.01 (AA'BB', 4H), 7.19−7.21 (m, 2H), 7.50−7.53 (AA'BB', 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.0 (s), 18.5 (s), 19.4 (s), 26.07 (s), 26.12 (s), 28.7 (s), 29.3 (s), 29.36 (s), 29.39 (s), 31.5 (s), 64.9 (s), 67.9 (s), 68.1 (s), 114.8 (s), 124.4 (s), 124.4 (s), 124.5 (s), 125.3 (s), 127.00 (s), 127.04 (s), 127.1 (s), 129.1 (d, J = 3 Hz), 130.1 (s), 136.7 (s), 148.6 (dd, J = 249 Hz, J = 15 Hz), 159.26 (s), 159.30 (s), 167.7 (s); IR (KBr, cm^{-1}) 1720 (ν C═O); HR-MS (ES) $C_{34}H_{40}F_2O_4Na$ [M + Na]$^+$ calcd m/z 573.2792, found m/z 573.2802.

Dication Salt $1^{2+}(SbCl_6^-)_2$. To a solution of **19** (114 mg, 99.7 μmol) in CH_2Cl_2 (5 mL)/MeCN (0.2 mL) was added tris(4-bromophenyl)aminium hexachloroantimonate (326 mg, 399 μmol) at room temperature, and the mixture was stirred for 3 h. To the reaction mixture was added ether (100 mL). The precipitate was filtered, washed and dried in vacuo to afford $\mathbf{1}^{2+}(SbCl_6^-)_2$ (61 mg, 87.3 μmol): yield 88%; brown powder; mp 195−200 °C (dec.); ^{1}H NMR (400 MHz, CD_3CN) δ = 0.99 (t, 7.4 Hz, 6H), 1.45−1.55 (m, 4H), 1.74−1.81 (m, 4H), 4.05 (t, J = 6.5 Hz, 4H), 7.01−7.05 (AA'BB', 4H),7.06−7.09 (AA'BB', 4H), 7.27−7.36 (m, 4H), 7.47 (d, J = 8.4 Hz, 4H), 7.54 (d, J = 8.4 Hz, 4H), 7.91−7.96 (m, 4H), 8.41−8.43 (m, 4H), 8.73 (s, 2H); ^{13}C NMR (125 MHz, CD_3CN) δ = 14.1 (s), 19.9 (s), 31.9 (s), 68.6 (s), 115.6 (s), 125.71 (s), 125.73 (s), 125.80 (s), 125.82 (s), 127.1 (s), 128.6 (s), 128.7 (s), 129.1 (s), 130.2 (d, J = 2 Hz), 131.0 (d, J = 2 Hz), 132.1 (s), 132.7 (s), 133.0 (s), 136.2 (s), 139.6 (s), 141.9 (s), 142.3 (s), 146.4 (s), 160.3 (s), 187.1 (s); HR-MS (APCI) $C_{66}H_{49}O_2F_4S_6$ [M − 2Sb12Cl + H]$^+$ calcd m/z 1141.1987, found m/z 1141.1979.

Compound 1. To a solution of $\mathbf{1}^{2+}(SbCl_6^-)_2$ (116 mg, 64 μmol) in the mixture of MeCN (4 mL)/THF (4 mL) was added Zn powder (115 mg, 1.76 mmol). Then the mixture was stirred at room temperature for 3 h, and filtered to remove Zn powder. The filtrate was concentrated, and the residue was purified by column chromatography (alumina, eluent: CH_2Cl_2/hexane = 1/2 followed by CH_2Cl_2) to give **1** (61 mg, 67.2 μmol): yield 83%; colorless solid; mp 250−254 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.99 (t, J = 7.4 Hz, 6H), 1.48−1.55 (m, 4H), 1.77−1.82 (m, 4H), 4.01 (t, J = 6.5 Hz, 4H), 6.89−6.92 (AA'BB', 4H), 6.96−7.00 (AA'BB', 4H), 7.01−7.07 (m, 10H), 7.15−7.17 (m, 6H), 7.19 (s, 2H), 7.48−7.51 (AA'BB', 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 14.0 (s), 19.4 (s), 31.5 (s), 67.9 (s), 80.2 (s), 114.8 (s), 121.3 (d, J = 5 Hz), 124.49 (s), 124.51 (s), 125.5 (s), 125.8 (s), 126.1 (s), 126.9 (s), 128.1 (s), 128.6 (s), 129.0 (d, J = 9 Hz), 129.6 (d, J = 9 Hz), 130.1 (d, J = 2 Hz), 130.7 (s), 133.1 (s), 136.6 (d, J = 5 Hz), 138.2 (s), 141.3 (s), 144.5 (s), 148.5 (dd, J = 248 Hz, J = 15 Hz), 148.6 (dd, J = 250 Hz, J = 15 Hz), 159.4 (s); HR-MS (APCI) $C_{66}H_{49}O_2F_4S_6$ [M + H]$^+$ calcd m/z 1141.1987, found m/z 1141.1982.

Dication Salt $2^{2+}(SbCl_6^-)_2$. The experimental procedure was as described for the preparation of $\mathbf{1}^{2+}(SbCl_6^-)_2$. Quantities: **20** (320 mg, 323 μmol), tris(4-bromophenyl)aminium hexachloroantimonate (1.054 g, 1.29 mmol). The mixture of CH_2Cl_2 (20 mL) and MeCN (6 mL) was used as a solvent. The resulting precipitate was filtered, washed and dried in vacuo to afford $\mathbf{2}^{2+}(SbCl_6^-)_2$ (417 mg, 251 μmol): yield 78%; brown powder; mp 227−231 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.98 (t, J = 7.4 Hz, 6H), 1.45−1.54 (m, 4H), 1.74−1.81 (m, 4H), 4.01 (t, J = 6.5 Hz, 4H), 6.45−6.49 (m, 2H), 6.98 (d, J = 8.6 Hz, 4H), 7.12−7.15 (m, 2H), 7.46 (d, J = 8.6 Hz, 4H), 7.96 (s, 4H), 8.54 (s, 4H), 8.59 (s, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 13.7 (s), 19.3 (s), 31.3 (s), 68.0 (s), 114.9 (s), 118.9 (s), 119.0 (s), 124.49 (s), 124.50 (s), 124.53 (s), 125.39 (s), 125.40 (s), 125.53 (s), 125.55 (s), 125.56 (s), 126.8 (s), 130.2 (d, J = 3 Hz), 132.2 (s), 132.7 (s), 132.9 (s), 133.0 (s), 139.0 (s), 139.2 (s), 140.5 (s), 143.37 (d, J = 1 Hz), 143.39 (d, J = 1 Hz), 160.1 (s), 184.4 (s); HR-MS (APCI) $C_{54}H_{40}O_2F_4S_6$ [M − 2Sb12Cl]$^+$ calcd m/z 988.1283, found m/z 988.1276.

Compound 2. The experimental procedure was as described for the preparation of **1**. Quantities: $\mathbf{2}^{2+}(SbCl_6^-)_2$ (237 mg, 143 μmol), Zn powder (226 mg, 1.68 mmol). The mixture of CH_3CN (10 mL) and THF (10 mL) was used as a solvent. The crude product was purified by column chromatography (alumina, eluent: toluene/hexane = 2/3 followed by 3/1) to give **2** (91 mg, 92 μmol): yield 64%; white solid; mp 250−252 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.99 (t, J = 7.4 Hz, 6H),1.47−1.56 (m, 4H), 1.76−1.83 (m, 4H), 4.00 (t, J = 6.5 Hz, 4H), 6.62 (brs, 2H), 6.91 (d, J = 8.5 Hz, 6H), 7.01−7.08 (m, 8H), 7.24−7.35 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 14.0 (s), 19.4 (s), 31.5 (s), 67.9 (s), 114.6 (s), 121.31 (s), 121.34 (s), 124.2 (s), 124.3 (d, J = 5 Hz), 124.5 (d, J = 5 Hz), 125.5 (s), 125.8 (s), 126.6 (s), 128.0 (s), 130.1 (s), 136.5 (s), 159.2 (s); HR-MS (ESI) $C_{54}H_{41}O_2F_4S_6$ [M + H]$^+$ calcd m/z 989.1367, found m/z 989.1342.

Dication Salt $3^{2+}(SbCl_6^-)_2$. The experimental procedure was as described for the preparation of $\mathbf{1}^{2+}(SbCl_6^-)_2$. Quantities: **21** (76 mg, 52 μmol), tris(4-bromophenyl)aminium hexachloroantimonate (171 mg, 209 μmol). The mixture of CH_2Cl_2 (4 mL) and MeCN (1.5 mL) was used as solvent. The resulting precipitate was filtered, washed and dried in vacuo to afford $\mathbf{3}^{2+}(SbCl_6^-)_2$ (99 mg, 47 μmol): yield 90%; brown powder; phase transition temperature/°C (DSC on second heating) Cr 78 S_X 122 I; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.99 (t, J = 7.4 Hz, 6H), 1.04−1.29 (m, 16 H), 1.35−1.56 (m, 8H), 1.71−1.83 (m, 8H), 3.30 (t, J = 6.5 Hz, 4H), 3.99 (t, J = 6.4 Hz, 4H), 4.02 (t, J = 6.5 Hz, 4H), 4.35 (d, ^2J = 12 Hz, 2H), 4.37 (d, ^2J = 12 Hz, 2H), 6.97−7.01 (AA'BB', 8H), 7.21−7.26 (AA'BB', 4H), 7.50−7.54 (m, 8H), 7.90−7.92 (m, 4H), 8.40−8.42 (m, 4H), 8.57 (s, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 13.8 (s), 19.4 (s), 26.1 (s), 29.31 (s), 29.34 (s), 29.4 (s), 29.7 (s), 31.4 (s), 66.8 (s), 68.0 (s), 68.2 (s), 72.0 (s), 114.8 (s), 124.6 (s), 124.59 (s), 124.60 (s), 124.64 (s), 126.5 (s), 130.1 (d, J = 3 Hz), 130.2 (d, J = 3 Hz), 131.9 (s), 132.1 (s), 140.7 (s), 141.8 (s), 143.7 (s), 159.3 (s), 159.5 (s), 184.9 (s); HR-MS (ES) $C_{84}H_{84}O_6F_4S_6$ [M − Sb_2Cl_{12}]$^{2+}$ calcd $m/2z$ 728.2264, found $m/2z$ 728.2289.

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Compound 3. The experimental procedure was as described for the preparation of **1**. Quantities: $3^{2+}(SbCl_6^-)_2$ (277 mg, 130 μmol), Zn powder (110 mg, 1.68 mmol). The mixture of dry CH_2Cl_2 (5 mL) and THF (3 mL) was used as solvent. The crude product was purified by column chromatography (alumina, eluent: CH_2Cl_2/hexane = 2/3 followed by 1/1) to give **3** (98 mg, 67.2 μmol): yield 52%; ivory solid; phase transition temperature/°C (DSC on first cooling) I 107 N 103 S_A 87 S_E 59 Cr; (DSC on second heating) Cr 87 S_E 106 S_A 115 N 122 I; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.99 (t, J = 7.3 Hz, 6H), 1.25−1.55 (m, 24 H), 1.73−1.83 (m, 8H), 3.31−3.41 (m, 4H), 3.94 (td, J = 6.5 Hz, J = 2.1 Hz, 4H), 4.01 (t, J = 6.3 Hz, 4H), 4.58 (d, ^2J = 13 Hz, 2H), 4.74 (d, ^2J = 13 Hz, 2H), 6.93−7.00 (m, 16H), 7.18−7.19 (m, 4H), 7.33 (s, 2H), 7.48−7.51 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.0 (s), 19.4 (s), 26.1 (s), 26.2 (s), 29.4 (s), 29.46 (s), 29.52 (s), 30.0 (s), 31.5 (s), 67.9 (s), 68.2 (s), 68.5 (s), 70.2 (s), 80.1 (s), 114.8 (s), 121.1 (s), 121.2 (s), 124.40 (s), 124.44 (s), 124.5 (s), 125.4 (s), 125.58 (s), 125.62 (s), 126.97 (d, J = 1 Hz), 127.00 (d, J = 1 Hz), 128.99 (s), 129.04 (s), 129.1 (d, J = 2 Hz), 130.10 (s), 130.11 (s), 131.2 (s), 136.6 (s), 138.3 (s), 139.0 (s), 143.5 (s), 148.6 (dd, J = 16 Hz, J = 250 Hz), 159.26 (s), 159.29 (s); HR-MS (APCI) $C_{84}H_{84}O_6F_4S_6$ $[M]^+$ calcd m/z 1456.4523, found m/z 1456.4533.

$1^{2+}(SbCl_6^-)_2$ by the Oxidation of 1. To a solution of **1** (47 mg, 41 μmol) in the mixture of CH_2Cl_2 (2 mL) and MeCN (0.1 mL) was added tris(4-bromophenyl)aminium hexachloroantimonate (68 mg, 83 μmol) at room temperature, and the mixture was stirred for 4 h. To the reaction mixture was added ether (40 mL). The precipitate was filtered, washed and dried in vacuo to afford $1^{2+}(SbCl_6^-)_2$ (54 mg, 30 μmol): yield 73%.

$2^{2+}(SbCl_6^-)_2$ by the Oxidation of 2. To a solution of **2** (41 mg, 41 μmol) in CH_2Cl_2 (2.5 mL) was added tris(4-bromophenyl)-aminium hexachloroantimonate (68 mg, 83 μmol) at room temperature, and the mixture was stirred for 2 h. To the reaction mixture was added ether (40 mL). The precipitate was filtered, washed and dried in vacuo to afford $2^{2+}(SbCl_6^-)_2$ (53 mg, 32 μmol): yield 78%.

$3^{2+}(SbCl_6^-)_2$ by the Oxidation of 3. The experimental procedure was as described for the preparation of $2^{2+}(SbCl_6^-)_2$. Quantities: **3** (78 mg, 54 μmol), tris(4-bromophenyl)aminium hexachloroantimonate (88 mg, 108 μmol), CH_2Cl_2 (1 mL), yield 87% (101 mg, 47 μmol).

LCP. A mixture of azobis(isobutyronitrile) (AIBN) (5.8 mg, 35.1 μmol) and **22** (650 mg, 1.18 mmol) in toluene (0.8 mL) was degassed by three freeze/pump/thaw cycles, and the reaction mixture was heated at 95 °C for 20 h. The reaction mixture was concentrated and dissolved in the minimum amount of THF. The solution was poured into acetone, and the resulting precipitate was collected by filtration and dried to give LCP (509 mg): white powder; phase transition temperature/°C (DSC on second heating) Cr 86 S_A 200 I; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.95 (br, 6H), 1.35−1.94 (br, 18H), 3.92 (br, 6H), 6.88 (br, 4H), 7.05 (br, 2H), 7.39 (br, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 14.0 (s), 19.4 (s), 26.3 (s), 28.3 (s), 28.4 (s), 29.4 (s), 29.5 (s), 29.6 (s), 31.5 (s), 67.8 (s), 68.1 (s), 114.7 (s), 124.3 (s), 126.9 (s), 128.8 (s), 130.0 (s), 148.5 (dd, J = 15 Hz, J = 248 Hz), 159.2 (s); GPC M_n = 23832, M_w = 67695, M_w/M_n = 2.84.

X-ray Structure Analysis of 2. X-ray diffraction data were collected with a graphite−monochromated Mo Kα (λ = 0.7107 Å) radiation. The structures were solved by direct methods using SIR2004.[77] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using SHELXL97.[78] All the H atoms were geometrically positioned and refined using a riding model with C−H = 0.95, 0.99, and 0.98 Å for aromatic, methylene, and methyl C, respectively; U_{iso}(H) = 1.2U_{eq}(C) except for methyl H [1.5U_{eq}(C)]. All calculations were performed using the WinGX program package.[79]

Crystal Data. $C_{54}H_{40}F_4O_2S_6$, M = 989.22, T = 123 K, triclinic, space group $P\bar{1}$, a = 7.2094(9), b = 16.0529(17), c = 20.751(2) Å, α = 72.471(3), β = 89.382(3), γ = 79.536(3)°, V = 2249.5(4) Å^3, Z = 2, D_{calcd} = 1.46 g cm^{-3}, 19021 reflections measured, 10987 unique, 635 parameters refined, GOF = 0.908, R_1 = 0.0499 [$I > 2\sigma(I)$], wR = 0.1604 (all data).

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for all compounds, GPC chart of LCP, cyclic voltammogram of **18**, Spectroelectrochemical studies of **1** and **3**, phase diagram of complexes of **3**/**7**, polarized micrographs of complex of **2**/**7**, XRD patterns for LCP and other complexes (**1**/LCP, **2**/LCP, BDTBT/LCP, 1^{2+}/LCP, 2^{2+}/LCP, and BDTBT^{2+}/LCP), and crystal data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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