Cross-Linked Liquid-Crystalline Materials − A Possible Strategy to Ordered Organic Semiconductors

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Received April 22, 2004. Revised Manuscript Received August 16, 2004

Ideal materials used in organic electronics should possess both a high order to exhibit high charge carrier mobility and easy processability to achieve low cost production. While single crystals only meet the first property, polymers usually only meet the second. To combine both, it would be desirable to conserve the order of liquid-crystalline phases over a wide temperature range as needed for practical use. In this paper, a synthesis of different liquid-crystalline materials is reported that incorporate both an aromatic heterocyclic core responsible for the semiconductor character and a cross-linkable group to freeze in the liquid-crystal order at a suitable temperature. The liquid-crystalline phases are investigated, and cross-linking experiments are performed. The structure of the prepared films is investigated by X-ray diffraction.

Introduction

The field of organic electronics is divided into two groups of materials: polymers and small molecules. Both of these have their advantages and disadvantages. On one hand, small molecules are quite easy to synthesize with the required high degree of purity. Chemical structure modifications can be done with comparatively low efforts. Their main advantage can be seen in the high charge carrier mobility found in single crystals of such materials. Because single crystals are hard to process, their use is restricted to research work only. Active layers for a real device have to be fabricated by vapor deposition, which always yields polycrystalline layers. Grain boundaries in such polycrystalline layers reduce the carrier mobility significantly.

On the other hand, polymers can be processed very easily, for example, by spin coating or printing. Yet their charge transport properties are not as good as observed for crystalline materials. Also, they are not so easily synthesized with a defined structure. Often chemical modifications are necessary to obtain soluble materials. Another problem is the complex purification process necessary to remove impurities in the ppm range.

For both types of materials, the crucial point for charge carrier mobility is, however, the exchange interaction between the molecules and therewith related overlap of the involved orbitals. Such an interaction is weak in amorphous layers, but can be high in ordered systems, at least, in specific directions where $\pi-\pi$-stacking occurs. The main goal is to enhance the exchange interaction in the transport direction by a directed control over the structural order. In this respect, surface alignment effects can be utilized to optimize such a $\pi-\pi$-stacking.[1,2]

From the point of structural ordering, liquid-crystalline substances are a very interesting class of material. As polycrystalline films, they show a poor carrier mobility that increases noticeable when transferred into the higher ordered liquid-crystalline phase.[3,4] Processing such materials can be done similar to polymers, which exhibit a LC phase. Unfortunately, the liquid-crystalline state is only present in a small temperature range that in most cases does not match the desired operating temperature of a device made thereof. A possible solution to overcome such a mismatch is to conserve the order found in the LC phase down to practically used temperatures.

In the present paper, it is demonstrated that such conservation can be achieved by attaching reactive groups such as epoxy-, acrylate-, or oxetane-groups to the molecule, which then can be permanently cross-linked in the liquid-crystalline phase.

As the first step, a molecule has to be selected that can act as a mesogen as well as exhibit semiconducting properties. In this respect, it is known that liquid-crystalline diarylheterodiazoles, used as electron-transporting materials, undergo a noticeable increase in their electron mobility when in the LC phase.[3] For diarylbenzthiazole, which is a hole-transporting material, a similar behavior has been observed.[4] As the cross-

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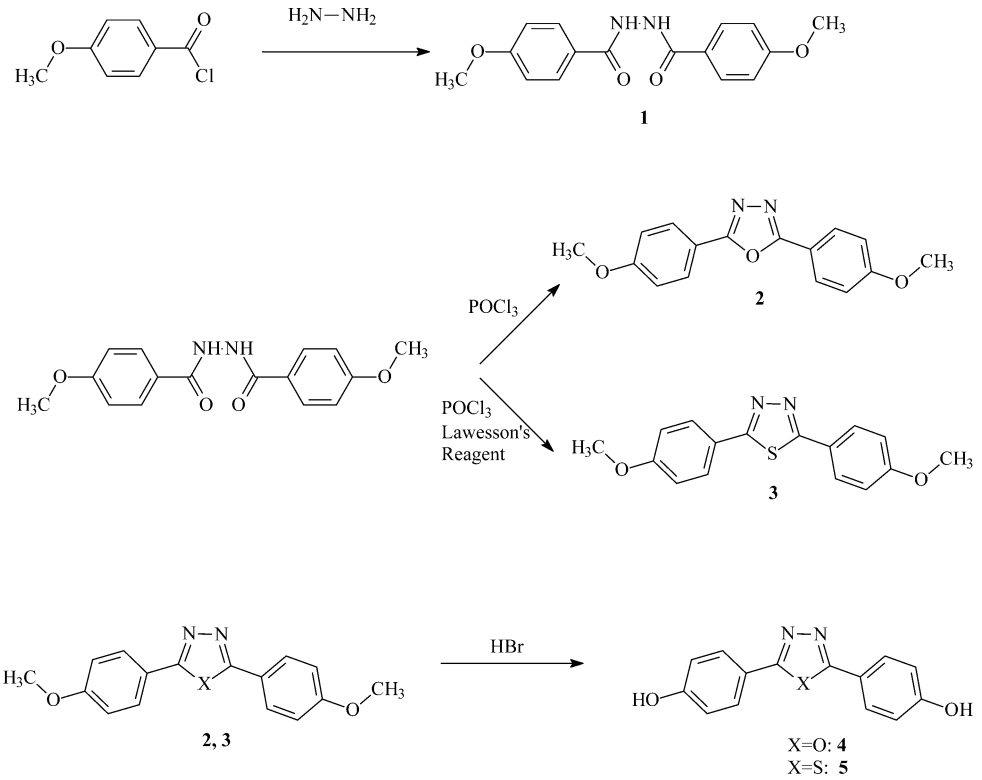
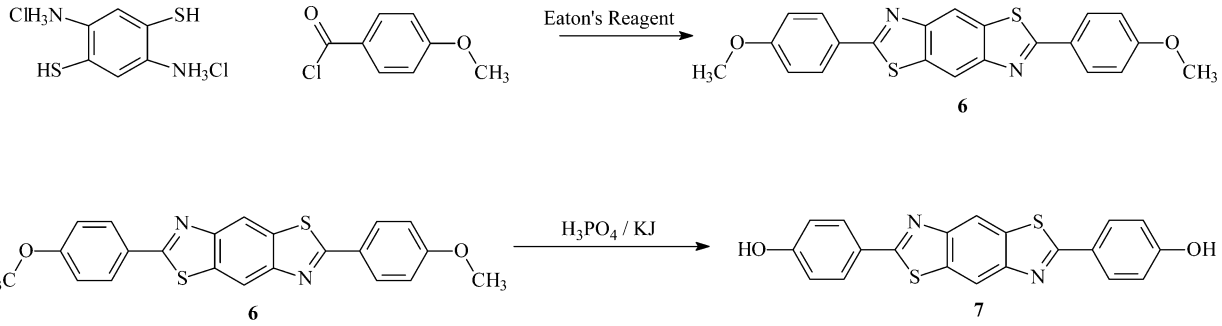
10.1021/cm049352l CCC: $27.50
Published on Web 10/09/2004

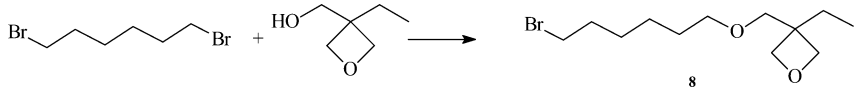
Scheme 1. Synthesis of the Heterodiazoles



Scheme 2. Synthesis of the Bisbenzthiazole



Scheme 3. Synthesis of the Cross-Linker



linking system, an alkoxy-oxetane system was chosen.[5] The group was attached to the end of the mesogen (see Scheme 4). Cross-linking was performed by adding a cationic photoinitiator, triarylsulfonium hexafluoroantimonate. Subsequent heating to temperatures above 80 °C led to a highly ordered film.

Results and Discussion

Synthesis. *2,5-Bis-(4-hydroxy-phenyl)-oxadiazole* ***5*** *and -thiadiazole* ***6***. To synthesize the heterodiazoles, the usual synthetic route via a bishydrazide,[6,7] as shown in Scheme 1, was used.

Because the last step of this route requires a hydroxy group, the anisoyl chloride was used as the starting material, which was reacted with hydrazinium hydrate to yield the bishydrazide **1**. Cyclization took place in the presence of phosphorus oxychloride to form the oxadiazole **2**, and adding Lawesson's Reagent resulted in the bismethoxy-substituted thiadiazole **3**.

The methoxy groups were cleaved with hydrobromic acid, forming the dihydroxy compounds **4** and **5**.

2,6-Bis-(4-hydroxy-phenyl)-benzo-[1,2-d-4,5-d′]-bisthiazole **7**. The bisbenzthiazoles were obtained following a route given by Arnold et al.[8] A summary can be seen in Scheme 2.

The 1,4-diamino-2,5-dithiolobenzene-dihydrochloride was reacted with anisoyl chloride, yielding the dimethoxy

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Scheme 4. Attaching the Cross-Linker

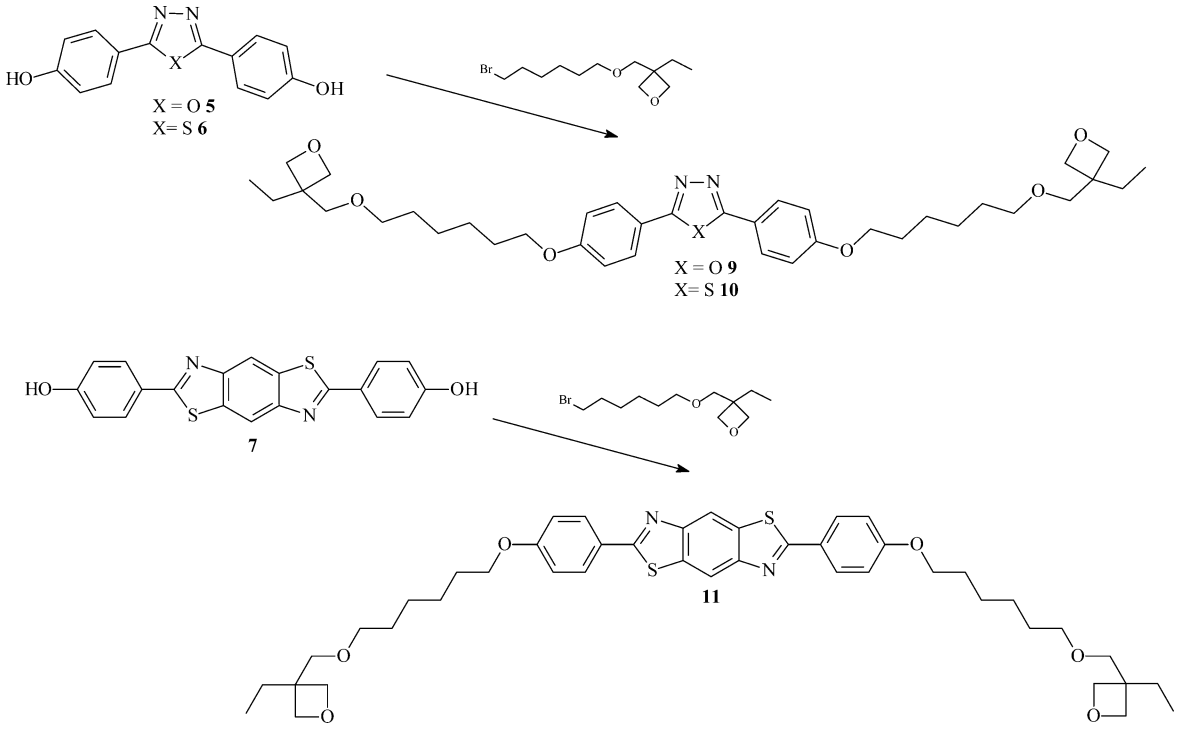

Table 1. Phase Transitions of the Synthesized Materials

compound	phase transition [K] by DSC
9	K 358 I
10	K 350 Sm 374 I
11	K 381 SmA 401 N 425 I

compound **6**. To obtain the dihydroxy compound **7**, the methoxy groups were cleaved with a mixture of phosphoric acid and potassium iodide.

*1-Bromo-6-(3-ethyl-3-methyleneoxy-oxetan)hexane **8**.* The cross-linking agent **8** which also includes the flexible side chain was synthesized by a method given by Nyken (Scheme 3).[5] Dibromohexane was reacted with a hydroxymethyl ethyl- oxetane.

*2,5-Bis-(4-[6-(3-ethyl-3-methyleneoxy-oxetan)hexyl -phenyl)-oxadiazole **9** and -thiadiazole **10** and 2,6-Bis-(4-[6-(3-ethyl-3-methyleneoxy-oxetan)hexyl]-phenyl)-benzo-[1,2-d-4,5-d′]-bisthiazole **11**.* As shown in Scheme 4, the spacer groups with the affixed cross-linker were attached by a reaction between the hydroxy-substituted heterocyclic core and the bromo-substituted alkyl chain with the cross-linker. As a result, the corresponding ether is formed. The reaction is catalyzed by K_2CO_3 and is initiated by adding a small amount of KI. While the heterodiazoles react easily, the benzobisthiazole requires long reaction times and the reaction product needs excessive cleaning.

Thermal Analysis and Characterization of the LC Phases. The phase transition temperatures of the synthesized materials were determined by DSC measurements. Additionally, the liquid-crystalline phases were characterized using polarized microscopy. As shown in Table 1, the investigated materials display different thermal behavior. While the oxadiazole **9** forms no liquid-crystalline phases, the analogue thiadiazole **10** shows one and the bisbenzthiazole **11** shows two liquid-crystalline phases. Further investigation by polarized microscopy indicates that **10** exhibits a broken fan-shaped texture that, along with the simultaneous occurrence of Schlieren texture, points to a smectic C phase. The first LC phase of **11** is a smectic A phase, indicated by fanlike textures visible under polarized light, while the second phase shows the Schlieren texture of a nematic phase. The micrographs of the smectic phases are shown in Figure 1.

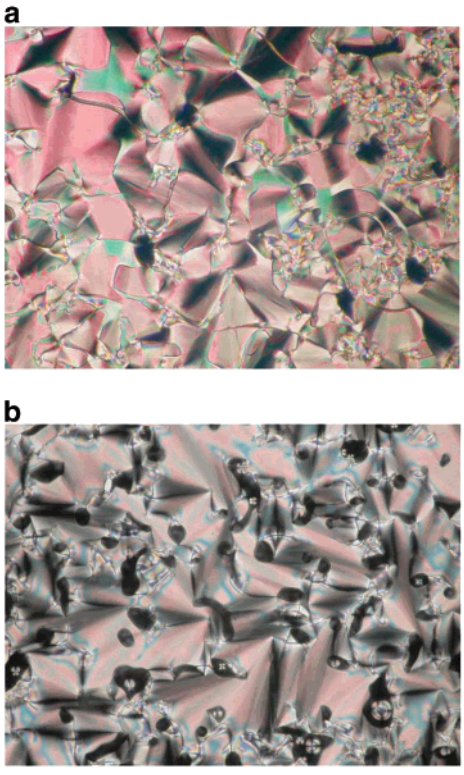

Figure 1. Polarizing micrograph of **10** (a) and **11** (b) in the smectic phase (40×).

Because of their order, the presence of smectic phases is of special interest for the above-discussed $\pi-\pi$-

stacking. Usually such structures are ordered perpendicular or at least tilted to the surface in the smectic A phase. In such a configuration, preferred charge transport should occur via $\pi-\pi$ interaction.

Layer Formation and Cross-Linking. Thin layers of compound **10** and **11** were fabricated from solution to study the cross-linking properties. Therefore, the monomer was solved in chloroform (ca. 7.5×10^{-2} M). Under exclusion of light, 5−7% of triarylsulfonium hexafluoroantimonates (Aldrich) relative to the monomer was added, which acts as an initiator for the cross-linking. This solution was utilized to spin-cast a 200 nm layer on a silicon (100) substrate. After the layer preparation, the sample was heated to a temperature within the isotropic phase and then slowly cooled to the LC phase (see Table 1). Subsequently, the sample was kept in the LC phase for 10 min. During the last 3 min, the sample either continued to be in the dark or was irradiated with UV-light from a xenon-lamp. Finally, the layers were cooled to room temperature in the dark. The whole process was performed under inert atmosphere. The resulting structural order was investigated by X-ray diffraction at a wavelength of 0.154 nm in a $\theta-2\theta$ configuration.

To obtain a deeper understanding of the cross-linking effect, the samples were prepared in four different ways:

(1) Thin layers of compounds **10** and **11** were spin-coated without initiator and then characterized in the pristine state to act as a reference.

(2) To investigate the order properties of the pristine materials, compounds **10** and **11** were tempered without initiator as described above.

(3) To check if the cross-linking can be initiated by thermal activation, compounds **10** and **11** were tempered with initiator but kept in the dark.

(4) Finally, compounds **10** and **11** with initiator were tempered and irradiated by UV-light, which was expected to be the optimal process with respect to light-induced cross-linking.

The pristine layers from experiment 1 show only weak reflexes in the X-ray diagram (not shown), which indicate a low degree of order. However, the hazy appearance of the layer is a strong indication for precipitation of small crystalline grains in an otherwise amorphous layer.

After experiment 2, the silicon surface is no longer covered completely, meaning that the material agglomerates to little droplets. The degree of order has, however, increased drastically, which manifests itself in sharp peaks in the X-ray diagram shown in Figure 2. This pattern is expected after the phase transition of the well-ordered LC phase to the polycrystalline phase upon cooling.

In contrast to experiment 2, the surface of the silicon substrate remains well covered by a thin layer after experiments 3 and 4. The fact that such layers are insoluble in chloroform and, in addition, exhibit a vitreous appearance is a strong indication for a successful cross-linking. From the X-ray pattern in Figure 2, it can be seen that experiment 3 results in a significantly ordered film whereas experiment 4 yields only a weak order, which will be discussed later. From the position of the structural order, it can be stated that the lattice plain distance in the layers resulting from

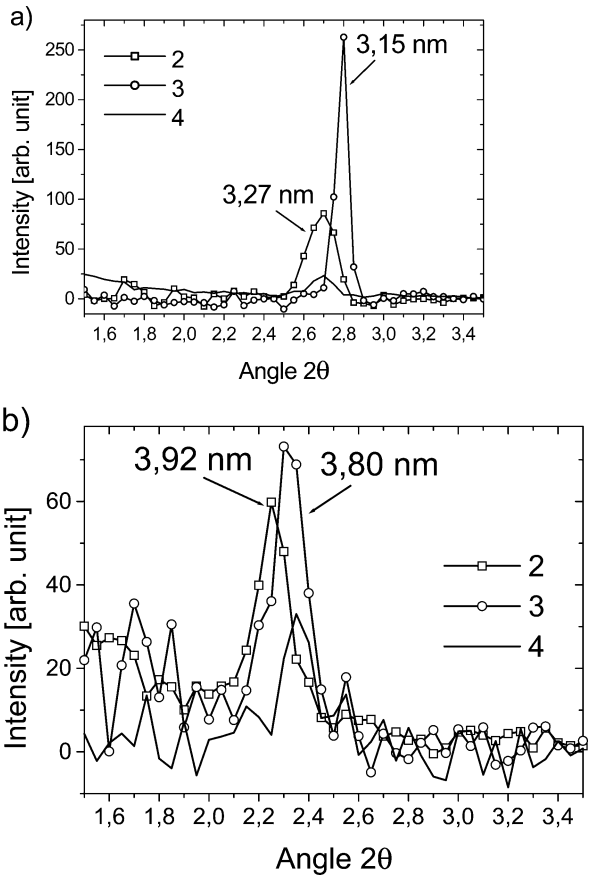

Figure 2. X-ray diffraction results for scenarios 2−4 for compound **10** (a) and compound **11** (b).

experiment 3 is slightly smaller than that obtained in experiment 2. The lattice constant decreases from 3.27 to 3.15 nm and from 3.92 to 3.80 nm in compounds **10** and **11**, respectively. This decrease could result from cross-linking. A comparison of the lattice constants with the estimated length of the molecules, which are 3.6 nm for **10** and 4.2 nm for **11**, indicates that the experimental and calculated values are of the same order of magnitude. This indicates that the layer structure of the original Sm phase of **10** and **11** is preserved during film formation and final cross-linking. However, there is no definite experimental evidence regarding macroscopic domain formation.

The fact that the cross-linking has occurred in experiment 3 proves that cross-linking is strongly temperature induced. Usually the first step of such a cross-linking process is assumed to be a photolysis of the initiator by UV irradiation at room temperature. This process then leads to the generation of protons that open the oxetane ring and start the polymerization.[9,10] The formed layers are then tempered afterward to assist curing.[11] In the present case, the materials were cross-linked at high temperatures (approximately 120 °C), making it more probable that the dissociation of the initiator is thermally induced and not optically induced.

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Under such conditions, the cross-linking occurs rather in the phase of increasing temperature than in the cooling phase from the isotropic phase to the LC phase. There is presently no clear evidence why the material irradiated with UV-light in experiment 4 shows hardly any order (see Figure 2). According to the conclusions of experiment 3, the order of the cross-linked material must be destroyed during UV-exposure. On the other hand, the insolubility of the layer after optical treatment still indicates a successful cross-linking. Therefore, a photodegradation of the chemical structure under UV-irradiation has to be assumed. Further investigations are necessary to clarify such a degradation.

The hole-transport properties of compound **11** were investigated by applying a cross-linked layer to a field effect transistor substrate consisting of a silicon wafer with a thermal grown oxide-layer and gold contacts as source and drain electrodes. It was, however, not possible to accumulate holes in the channel, and no source drain current was observed. Such a bad transport behavior can be caused by residual impurities from the synthesis, such as those from the initiator triarylsulfonium hexafluoroantimonates.

Conclusions

New organic molecules have been synthesized with the property to thermally cross-link in the ordered liquid-crystalline phase. It has been shown by X-ray diffraction that the order of molecules in the LC phase can be conserved by thermal-activated cross-linking. Under the condition that the activation of the cross-linking takes place in the temperature range of the LC phase, the order can be "frozen-in" at room temperature. To initiate the cross-linking by irradiation with UV-light is not feasible because the thermal cross-linking is dominant for the present systems. Also, the order of the cross-linked materials was destroyed by UV-irradiation. Although an improved electrical performance after cross-linking could not be demonstrated for the investigated materials, it is nevertheless believed that the idea of freezing-in the structural order during the LC phase of a suitable material may be advantageous not only to improve the structural order but also to improve the electrical performance.

Experimental Section

General. All reagents were purchased from Fluka or Aldrich Chemical Co. and were used without further purification. All solvents were dried under standard conditions. Melting points were recorded on a NAGEMA K8 melting point apparatus and were uncorrected.

All NMR spectra were recorded on a Varian INOVA 500 at 295 K in $CDCl_3$ as solvent. The ^1H NMR spectra were obtained at 500 MHz, and the ^{13}C NMR spectra were obtained at 125 MHz.

The DSC-scans were done on Netzsch DSC 204 equipment. The heating rate was 10 or 20 K/min. Around 10 mg of the material was placed in a 40 μL Al-pan. Nitrogen was used as the protective and purge gas.

Elemental analysis was performed on a EA 1110 CHNS-O (Ceinstruments). Infrared spectra were obtained using FTIR Digilab Excalibur.

Synthesis of the Mesogens. *Bis-anisoyl-hydrazide **1**.* Under intense stirring at a temperature of 10 °C, a mixture of 0.5 g (5 mmol) of hydrazinium hydrate and 1 mL of methanol was added dropwise to 1.71 g (10 mmol) of anisoyl chloride. In a vigorous reaction, a white suspension formed. When the mixture became too viscous, a total of 3 mL of toluene was added as a dilutor. After being stirred for 1 h, the mixture was poured into 300 mL of water and the crude product was collected by filtration. The hydrazide was recrystallized from methanol (252 °C).

Yield: 1.4 g (47%). Anal. Calcd for $C_{16}H_{16}N_2O_4$ (300.31): C, 63.99; H, 5.37; N, 9.33; O, 21.31. Found: C, 64.14; H, 5.29; N, 9.68; O, 21.06.

*Bis-anisoyl-oxadiazole **2**.* A solution of 1.5 g (5 mmol) of **1** in 30 mL of dry toluene was heated to 80 °C. After 1 mL of phosphorus oxychloride was added, the mixture was refluxed for 2 h. The mixture was allowed to cool to room temperature, and the solvent was removed under reduced pressure. The crude product was recrystallized from ethanol (157 °C).

Yield: 1 g (70%). Anal. Calcd for $C_{16}H_{14}N_2O_3$ (282.29): C, 68.08; H, 5.00; N, 9.92; O, 17.00. Found: C, 67.78; H, 5.12; N, 9.57; O, 17.24.

*Bis-anisoyl-thiadiazole **3**.* Together with 1.5 g of Lawesson's Reagent, 1.5 g (5 mmol) of **1** was dissolved in 30 mL of dry toluene and heated to 80 °C. To this solution was added 1 mL of phosphorus oxychloride, and the mixture was refluxed for 2 h. After being cooled to room temperature, the solvent was removed under reduced pressure and the crude product was recrystallized from ethanol (138 °C).

Yield: 1 g (67%). Anal. Calcd for $C_{16}H_{14}N_2O_2S$ (298.35): C, 64.41; H, 4.73; N, 9.39; O, 10.72; S, 10.75. Found: C, 64.49; H, 4.61; N, 9.71; O, 10.95; S, 10.51.

*Bis-(4-hydroxyphenyl)-oxadiazole **4** and -thiadiazole **5**.* A suspension of 0.875 g (3 mmol) of **2** or 0.895 g (3 mmol) of **3** in 100 mL of 48% hydrobromic acid was stirred at 120 °C for 24 h. The product was precipitated in 400 mL of water, collected, and recrystallized from ethanol (**4** 185 °C, **5** 162 °C).

4 Yield: 0.56 g (75%). Anal. Calcd for $C_{16}H_{14}N_2O_3$ (254.24): C, 66.14; H, 3.96; N, 11.02; O, 18.88. Found: C, 66.05; H, 4.09; N, 10.75; O, 18.59.

5 Yield: 0.55 g (68%). Anal. Calcd for $C_{16}H_{14}N_2O_2S$ (270.30): C, 62.21; H, 3.73; N, 10.36; O, 11.84; S, 11.86. Found: C, 62.47; H, 3.78; N, 10.51; O, 11.78; S, 11.61.

*2,6-Bis-(-anisoyl)-benzo-[1,2-d-4,5-d′]-bisthiazole **6**.* Under a stream of argon was stirred 2.45 g (10 mmol) of 1,4-diamino-2,5-dithiolo-benzene-dihydrochloride into 20 mL of Eaton's Reagent. The suspension was heated to 90 °C until it became a nearly clear solution while HCl was formed. At 120 °C, 3.41 g (20 mmol) of anisoyl-chloride was added. After 4 h of stirring at this temperature, the mixture was stirred into 400 mL of cold water. The product precipitated and was purified by recrystallization from propylene carbonate.

Yield: 3.5 g (86%). Anal. Calcd for $C_{22}H_{16}N_2O_2S_2$ (404.5): C, 65.33; H, 3.99; N, 6.93; O, 7.91; S, 15.85. Found: C, 65.15; H, 4.09; N, 6.72; O, 8.02; S, 15.78.

*2,6-Bis-(4-hydroxy-phenyl)-benzo-[1,2-d-4,5-d′]-bisthiazole **7**.* After 3.0 g (7.4 mmol) of **6** was stirred into 75 mL of 85% phosphoric acid and then 5 g of KI was added, the resulting suspension was heated to 120 °C. At that temperature, the mixture was stirred for 5 h. After being cooled to room temperature, the product was precipitated by adding 500 mL of water. The solid was collected, washed three times with acetone to remove traces of iodine, and then purified by recrystallization from propylene carbonate.

Yield: 2.44 g (82%). Anal. Calcd for $C_{20}H_{12}N_2O_2S_2$ (376.44): C, 63.81; H, 3.21; N, 7.44; O, 8.50; S, 17.03. Found: C, 63.71; H, 3.54; N, 7.36; O, 8.21; S, 17.15.

Synthesis of the Cross-Linker. *3-(6-Bromhexyloxymethyl)-3-ethyloxetane **8**.* To a mixture of 105 g of 50% aqueous NaOH, 100 mL of *n*-hexane, and 1.3 g of tetrabutylammoniumbromide were added 9.3 g (80 mmol) of 3-ethyl-3-hydroxymethyloxetane and 58.5 g (240 mmol) of 1,6-dibromohexane, and the suspension was refluxed for 5 h. After cooling, 200 mL of water was added, and the resulting mixture was extracted three times with 150 mL of diethyl ether. The organic layers were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The product was purified by distillation under reduced pressure (110 °C/5 $\times$ 10^{-1} mbar).

Yield: 16.8 g (75%). Anal. Calcd for $C_{12}H_{23}BrO_2$ (279.21): C, 51.62; H, 8.30; O, 11.46. Found: C, 51.81; H, 8.17; O, 11.21.

Synthesis of the Target Compounds. *2,5-Bis-(4-[6-(3-ethyl-3-methyleneoxy-oxetan)hexyl]-phenyl)-oxadiazole* ***9*** *and -thiadiazole* ***10***. To a solution of 1.02 g (4 mmol) of **4** (1.08 g (4 mmol) of **5**, respectively) and 11.16 g (40 mmol) of **8** in 75 mL of dry cyclohexanone were added 2 g (15 mmol) of dried and powdered K_2CO_3 and 0.06 g (0.4 mmol) of KI under a stream of argon. The resulting suspension was refluxed for 5 h. The hot mixture was filtered, and the residue was washed twice with 50 mL of cyclohexanone.

After the solvent and the excess of **8** were removed by distillation under reduced pressure, the crude product was purified by column chromatography (eluent: *n*-hexane/ethylacetate 10/1 v/v).

9 Yield: 1.56 g (60%). Anal. Calcd for $C_{38}H_{54}N_2O_7$ (650.85): C, 70.13; H, 8.36; N, 4.30; O, 17.21. Found: C, 70.03; H, 8.52; N, 4.19; O, 17.31.

10 Yield: 1.540 g (58%). Anal. Calcd for $C_{38}H_{54}N_2O_6S$ (666.91): C, 68.44; H, 8.16; N, 4.20; O, 14.39; S, 4.81. Found: C, 68.27; H, 7.98; N, 4.07; O, 14.54; S, 4.68.

2,6-Bis-(4-[6-(3-ethyl-3-methyleneoxy-oxetan)hexyl]-phenyl)-benzo-[1,2-d-4,5-d′]-bisthiazole ***11***. To a solution of 1.51 g (4 mmol) of **7** and 11.16 g (40 mmol) of **8** in 75 mL of dry cyclohexanone were added 2 g (15 mmol) of dried and powdered K_2CO_3 and 0.06 g (0.4 mmol) of KI under a stream of argon. The resulting suspension was refluxed for 72 h. The hot mixture was filtered, and the residue was washed twice with 50 mL of cyclohexanone.

After the solvent and the excess of **8** were removed by distillation under reduced pressure, the crude product was purified by column chromatography (eluent: $CHCl_3$/ethylacetate/acetic acid 4/1/1 v/v/v).

Yield: 0.46 g (15%). Anal. Calcd for $C_{44}H_{56}N_2O_6S_2$ (773.05): C, 68.36; H, 7.30; N, 3.62; O, 12.42; S, 8.29. Found: C, 68.11; H, 7.34; N, 3.75; O, 12.18; S, 8.17.

Acknowledgment. We are grateful to the DFG (SPP 1121) for financial support.

CM049352L