Synthesis and Properties of Chiral Chromophore-Functionalized Polybinaphthalenes for Nonlinear Optics: Influence of Chromophore Concentration

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ABSTRACT: A series of chromophore-functionalized polybinaphthalenes have been prepared and characterized for their (nonlinear optical) properties. The polymers were prepared by direct polymerization using a Stille coupling between a bis(trimethyltin) compound and dibromo-substituted binaphthalene monomers. The chromophores were attached to the binaphthalene unit via an alkyl spacer. The influence of the chromophore concentration, spacer length, and number of chromophores per binaphthalene unit was studied. The typical treelike macromolecular architecture of these molecules gives rise to a unique behavior in the glass transition temperature, NMR, and nonlinear optical properties. The nonlinear optical response shows a continuous increase in function of the chromophore content. In this way, the nonlinear optical properties can be increased in a way that is not possible with other chromophore-functionalized polymer materials.

Introduction

Design and synthesis of polymeric materials for second-order nonlinear optical applications have received considerable attention. These materials usually consist of dipolar chromophores, embedded in a polymer matrix. To be useful for nonlinear optical applications, the chromophores must be oriented in a noncentrosymmetrical way. This is usually achieved by electric field poling. A major problem associated with these materials is the tendency for dipolar aggregation, which compromises the nonlinearity of the system, especially at high chromophore loading.

The macroscopic second-order nonlinear optical response (second-order susceptibility $\chi^{(2)}$) of most polymer materials arises from the hyperpolarizability (β) of incorporated dipolar chromophores. As a consequence, in the absence of intermolecular interactions, $\chi^{(2)}$ is directly proportional to the hyperpolarizability and the number density of the chromophores, N. Furthermore, if the polar ordering is achieved by orienting the dipolar chromophores in an external electrical field E, $\chi^{(2)}$ depends also on the dipole moment and the orienting field: $\chi^{(2)} \propto N\mu\beta E$ (when no electrostatic interactions are encountered, μ is the dipole moment of the chromophore). This implies that the nonlinear optical properties of these materials can be increased by (i) applying a higher poling field, (ii) using chromophores with higher hyperpolarizabilities and dipole moments, and (iii) increasing the loading densities. The first approach is limited, since already very high voltages are applied. The second solution has led to the synthesis of highly efficient chromophores and materials derived thereof. The last way to increase the macroscopic nonlinear optical response is to increase the chromophore concentration. However, chromophores tend to have high dipole moments, and above a critical loading density, electrostatic interactions occur, which favor centrosymmetrical ordering of the chromophores in the polymer matrix. As a result, $\chi^{(2)}$ will not increase linearly with chromophore loading N, but it will show a maximum at relatively low loading levels (typically around 15 wt % of loading for dipole moments of 10 D) and will decrease at higher chromophore concentrations.

Several approaches have been investigated to diminish the dipolar interactions. Dalton et al. have studied[1,2] the influence of the shape of the chromophore on the dipolar interaction and concluded that a spherical shape inhibits dipolar interactions. This can be achieved by derivatization of chromophores with bulky groups. Another approach consists of the use of chromophore-functionalized dendrimers in which the dendrons effectively decrease the interactions among the chromophores due to steric hindrance.[2]

Our approach consists of the attachment of the chromophores as a side chain to a rigid, nonbendable backbone. The result is a treelike structure: flexible branches (chromophores) are attached to a rigid trunk (backbone). On one hand, this structure prevents the undesired centrosymmetrical ordering of the chromophores, but on the other hand, the chromophores are flexible enough to induce the noncentrosymmetry by electrical poling.

A chiral, helical polybinaphthalene matrix was used, since the backbone of these polymers consists of a rigid, nonbendable (one-handed) helix when chiral monomers are polymerized.[3] A helix is a highly regular structure in which all bonds that form the helix have the same configuration (either *S* or *R*). As a consequence, if both *R* and *S* monomers are incorporated in the same backbone, no helical configuration can be formed. Therefore, the importance of chirality lies in the fact that only

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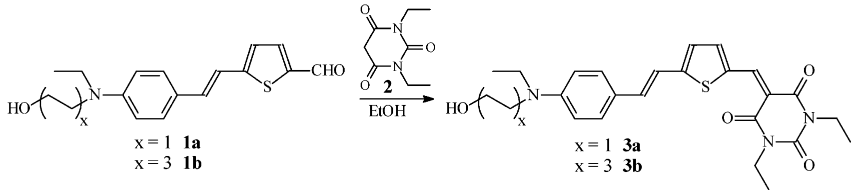
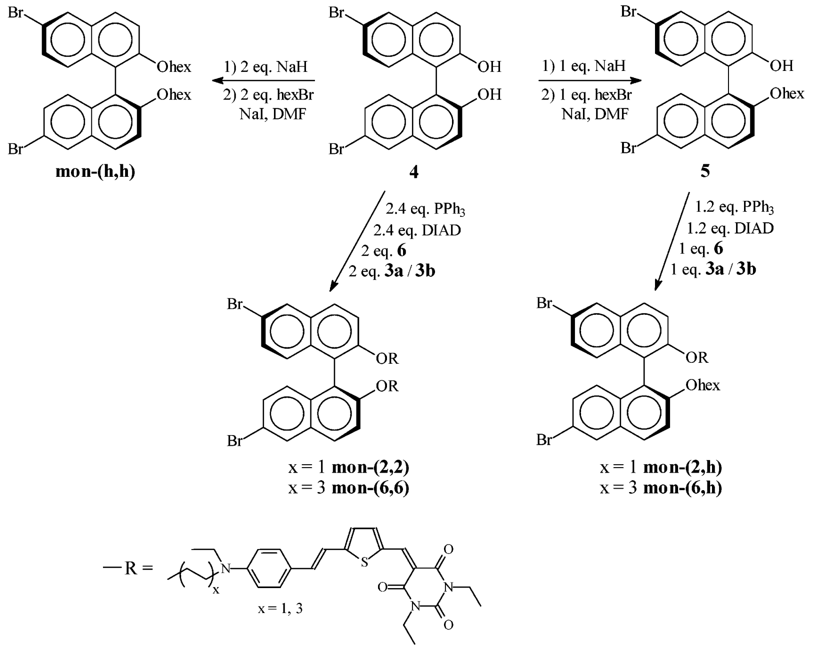
Scheme 1. Synthesis of Chromophores 3a,b



Scheme 2. Synthesis of the Binaphthalene Monomers



helical conformations can be formed if only chiral monomers are polymerized. Furthermore, these materials show excellent thermal and (photo)chemical stability.[4]

Results and Discussion

Synthesis of the Chromophore-Functionalized Polybinaphthalenes by Direct Homo- and Copolymerization of Binaphthalene Monomers. To investigate the influence of the chromophore concentration, we copolymerized binaphthalene monomers containing chromophore with a binaphthalene monomer without chromophore. The polymers were prepared by means of a Stille coupling reaction. To prevent chromophore degradation during polymerization, we limited our chromophore choice to one DπA system, which has proved to withstand the polymerization conditions.[5]

The chromophores differ from each other only in the spacer length, i.e., the group between the actual DπA system and the (alcohol) functionality. The synthesis of the chromophores is presented in Scheme 1. A modified pathway[6] was followed to prepare the key compounds **1a,b** from the 4-aminobenzaldehyde derivatives. With the exception of the necessary protection/deprotection steps, our method essentially consists of the coupling of the thiophene moiety by a classic Wittig reaction (instead of a Horner reaction) and the introduction of the carbonyl functionality by treatment with *n*-butyllithium, followed by *N*,*N*-dimethylformamide (DMF) and hydrolysis (as an alternative for a Vilsmeyer reaction). In this way, **1a,b** were prepared in much higher yields (8 times), and they, as well as their intermediates, could more easily be purified. Finally, the chromophores were obtained by a Knoevenagel condensation[5] with *N*,*N*′-diethylbarbituric acid (**2**).[7]

Subsequently, the chromophores were attached to the binaphthalene derivatives **4**[8] and **5**. **5** itself was prepared by a simple nucleophilic substitution on hexyl bromide and can easily be separated from the disubstituted and unsubstituted analogues (**mon-(h,h**) and **4**, respectively) by column chromatography.[9] The coupling of the chromophores to **4** and **5** to form the chromophore-functionalized binaphthalene monomers was achieved via a Mitsunobu reaction[10] and is presented in Scheme 2. However, under classic reaction conditions (triphenylphosphine, diisopropylazodicarboxylate (DIAD)), the structure of the isolated compound was **7a,b**. By addition of 2,2-dimethylpropanol (**6),** the unwanted side reaction was suppressed and the desired monomers were obtained.

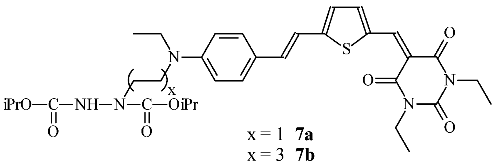


Figure 1. Structure of **7a,b**.

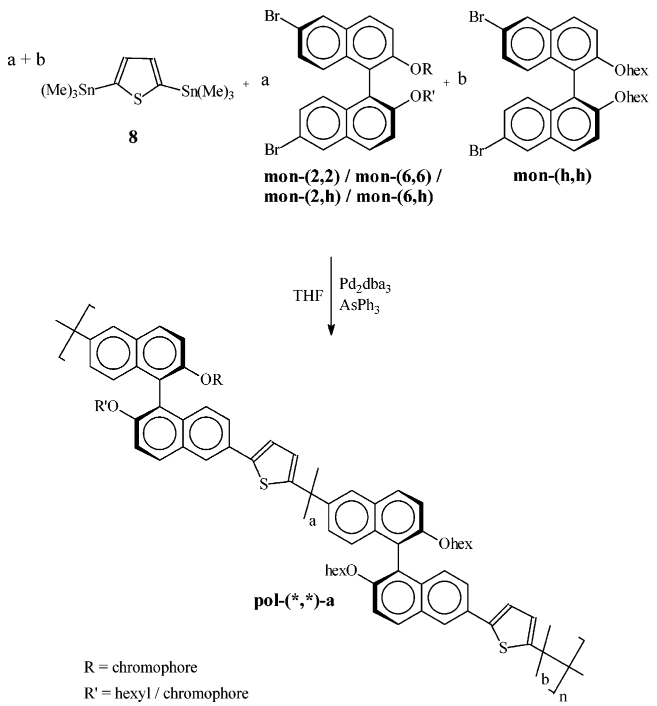
Finally, the polymers were prepared by a Stille coupling reaction between 2,5-bis(trimethyltin)thiophene (**8)**[11] and the dibromo-substituted binaphthalene monomers, **mon-(*,*)** (Scheme 3). $Pd_2dba_3/AsPh_3$ was used as a catalyst and ligand, since this system has shown to give the best results.[12,13] The reaction was carried

Table 1. Composition, Glass Transition, and Nonlinear Optical Properties of the Polymers

polymer[a]	$a_{\mathbf{mon(*,*)},\mathrm{feed}}$[b]	$a_{\mathbf{mon(*,*)},\ \mathrm{polymer}}$[c]	T_g/°C[d]	$\chi^{(2)}_{zzz}(\omega)$/pm V^{-1}	λ_{max}/nm
pol-(h,h)	0	0	*e*	*f*	*g*
pol-(2,2)-1	1	1	186	165	547
pol-(2,2)-0.5	0.5	0.5	160	143	555
pol-(2,2)-0.25	0.25	0.3	140	60	558
pol-(2,h)-1	1	1	145	57	560
pol-(2,h)-0.5	0.5	0.5	144	46	565
pol-(2,h)-0.25	0.25	0.25	123	17	574
pol-(6,6)-1	1	1	115	125	562
pol-(6,6)-0.5	0.5	0.6	107	115	565
pol-(6,6)-0.25	0.25	0.3	102	*f*	565
pol-(6,h)-1	1	1	93	57	571
pol-(6,h)-0.5	0.5	0.7	95	25	580
pol-(6,h)-0.25	0.25	0.25	81	21	572

[a] The code number of the polymers is constituted as follows: the symbols between parentheses denote the two substituents on the two naphthol functions of one binaphthalene moiety. "h" denotes hexyl; "2" and "6" denote the chromophore with 2 and 6 C atoms in the spacer. The number after the parentheses (i.e., 0.25, 0.50, or 1) indicates the mole ratio of chromophore-functionalized binaphthalene monomer in the feed. [b] Mole ratio of chromophore-functionalized binaphthalene monomer in the feed. [c] Mole ratio of chromophore-functionalized binaphthalene monomer incorporated in the polymer, determined by ^{1}H NMR and UV−vis spectroscopy. [d] Determined by DSC (50 °C/min). [e] No glass transition was detected between 50 and 230 °C. [f] No high-quality films could be spin-coated. [g] No absorption in the chromophore region is present.

Scheme 3. Polymer Synthesis



out in tetrahydrofuran (THF), instead of in DMF, because running the reaction in DMF leads to (partial) chromophore degradation.

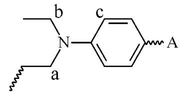
Since all binaphthalene monomers have a 6,6′-dibromo-2,2′-dialkoxybinaphthalene structure, it can be assumed that they are equally reactive in the Stille reaction. As a consequence, it is possible to control the chromophore concentration in the polymers by adjusting the ratio of binaphthalene monomers with and without chromophore in the feed, which has also experimentally been verified (Table 1).

Characterization of the Polymers. a. Composition and Glass Transition of the Polymers. In the way described above, 13 polymers were prepared. The composition, glass transition temperatures, and nonlinear optical properties are listed in Table 1. It is remarkable that the chromophore-functionalized polymers show a very clear glass transition, while the polymers without chromophore (**pol-(h,h)**) do not. Furthermore, the glass transition temperature (T_g) shows a clear dependence on the number of chromophores per binaphthalene unit (**pol-(*,h)** vs **pol-(*,*)**), the spacer length (2 vs 6 C atoms), and the chromophore concentration. Hence, we believe that the observed process is the glass transition of *the chromophores attached to the polymer backbone* and not of the whole material. Indeed, the T_g of the chromophore is measured at 64 and 31 °C (**3a** and **3b**, respectively, measured by DSC at a heating rate of 30 °C/min). In classical systems, when chromophores are introduced in a polymer matrix, Fox's law counts and the T_g of the system decreases; the chromophore acts as a plasticizer. In the systems studied, the opposite tendency is observed: the T_g increases with increasing amounts of chromophores. This can however be explained with the proposed (treelike) molecular structure. The less flexible and mobile the chromophore gets in the polymer, the more the T_g increases. Hence, the T_g increases when two instead of only one chromophore is attached to one binaphthyl unit (**pol-(*,*)** vs **pol-(*,h)**), with shorter spacer lengths (**pol-(2,*)** vs **pol-(6,*)**) and with increasing amounts of chromophore, which is observed.

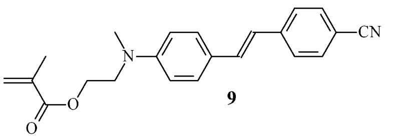
b. GPC Analysis. The molecular weights and polydispersities of these materials were determined by GPC in THF against polystyrene standards. Although they are quite low ($\bar{M}_w = 1.4-8.1$ kg/mol), it must be stated that it has been shown[14a] that the molecular weights, determined in this way, are largely underestimated and that this is a general feature for rodlike macromolecules.[14b] Moreover, the large discrepancy in the molecular weights does not seem to affect their physical properties (T_g). Polydispersities range from 1.6 to 2.4.

c. NMR and CD Spectroscopy. Another intriguing characteristic of the chromophore-containing polymers is the remarkable upfield shift of the ^{1}H nuclei in the ortho and α-position with respect to the N donor (Table 2). The shift of these nuclei is also present in the chromophore-functionalized binaphthalene monomers and is less pronounced if longer spacer lengths are used. Taken the magnitude of the shift into account, this phenomenon can only be explained by assuming that those nuclei are close to an aromatic naphthalene ring. In that case, magnetic anisotropy, arising from aromatic ring flow effects, can cause the dramatic upfield shift. To prove that this shift is not a common feature in

Table 2. Comparison of the Chemical Shift of ^{1}H in the Ortho and α-Position of N Donor in the Free Chromophores and the Chromophores Attached to the Binaphthalene Moiety



	δ_a (ppm)	δ_b (ppm)	δ_c (ppm)
chromophore **3a**	3.5	3.5	6.7
monomer and polymer spacer 2 C	2.7	3.4	6.3
chromophore **3b**	3.3	3.4	6.6
monomer and polymer spacer 6 C	3.1	3.4	6.6



9

Figure 2. Structure of **9**.

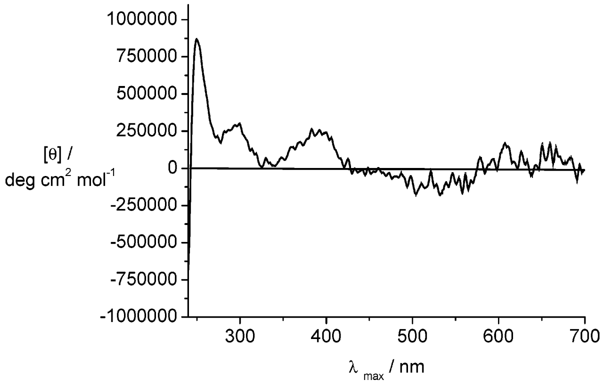


Figure 3. CD spectrum of **pol-(2,2)-1**.

chromophore-functionalized polymers, we have compared the chemical shift of **9**[15] and the corresponding polymethacrylate. The difference of chemical shift of the considered ^{1}H in these systems is limited to 0.15 ppm.

We have tried to determine the exact orientation of the chromophores with respect to the binaphthalene moiety in the monomers as well as in the polymers by means of 2D NMR spectroscopy. NOESY experiments on similar chromophore-functionalized polybinaphthalenes revealed that the chromophores are close to the polymer backbone in these systems.[9] The chromophores do not point away, but instead they are tilted (just like in a tree). Unfortunately, the results of NOESY and ROESY experiments on these systems were unclear because of overlapping of the absorptions in the aromatic region. Nevertheless, the results again strongly indicate a similar treelike structure.

Furthermore, the NMR absorptions of the binaphthalene ^{1}H are extraordinary narrow for polymers. This feature originates from the high regularity and has also been observed in other (chiral) helical polybinaphthalenes.[16]

A representative CD spectrum of pol-(2,2)-1 is presented in Figure 3. It strongly resembles the CD spectrum of other polybinaphthalenes,[16] which were shown to adapt a helical, rodlike macromolecular structure. Those polymers had a similar backbone but did not contain any chromophores. This resemblance indicates that our chromophore-functionalized polybinaphthalenes have a similar macromolecular structure.

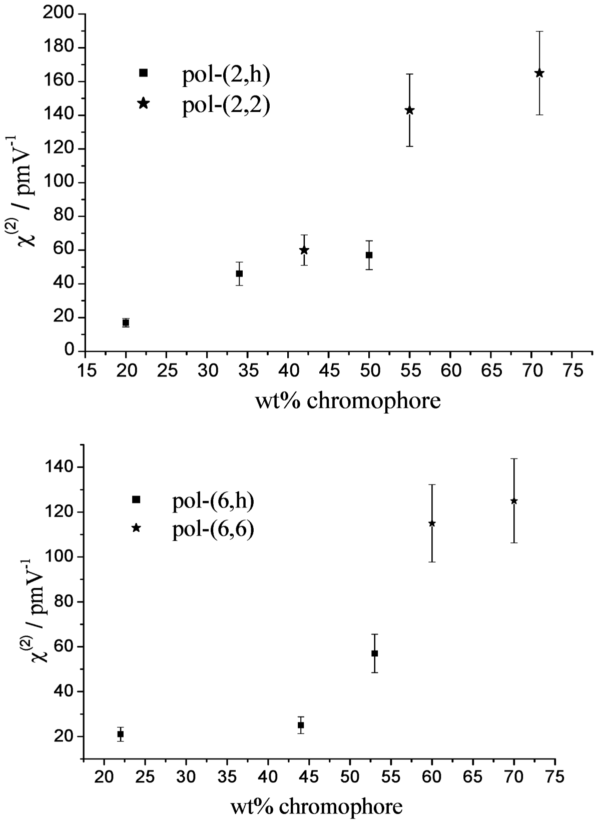


Figure 4. Evolution of $\chi^{(2)}$ of the chromophore-functionalized polybinaphthalenes with increasing chromophore loading densities.

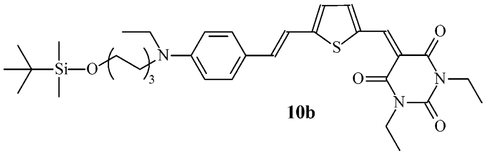
d. Nonlinear Optical Properties. Because of the flexibility of the chromophores in the polymer material, they can easily be poled by an external electric field. Therefore, thin films were spin-coated on an ITO–glass substrate from a concentrated chloroform solution. With the exception of **pol-(6,6)-0.25**, all polymer samples could be easily spin-coated, yielding stable high-quality films. To prevent bleaching of the chromophore during electrical poling, poly(acrylic acid) was spin-coated on top of the polymer sample after drying. The samples were corona-poled at T_g for 15 min.

The second-order susceptibility was measured using a standard second-harmonic generation setup, operated with a Nd:YAG laser (1064 nm, 50 Hz, 5 ns pulses). Absolute values of the susceptibilities were obtained by calibration against a quartz wedge.

Since the chromophore absorption is close to the second harmonic (≈560 and 532 nm), the susceptibilities are resonantly enhanced. The exact λ_{max} are displayed in Table 1. The nonlinear optical response is stable at room temperature for several months, which can be explained by the relative high T_g.

Figure 4a,b shows a continuous increase in nonlinear optical response with increasing chromophore concentration, for both short and long spacer lengths. Furthermore, the nonlinear optical response depends only on the chromophore concentration and not on the spacer length or monomer functionality (mono- or disubstituted).

The dipole moment, determined using capacity measurements, of the chromophore was 10.7 D. Severe attenuation of $\chi^{(2)}$ as a function of N is expected to occur for chromophores with dipole moments of 7 D and higher.[1] However, in the polybinaphthalenes, $\chi^{(2)}$ increases up to loading levels of 70 wt %, the maximum loading level that can be achieved in these polymers.



10b

Figure 5. Structure of **10b**.

To prove that this feature is unique for these materials, we dissolved **10b** (**10b** was preferred over **3b** because of its better solubility in the PMMA matrix) in a polymethacrylate matrix in different loading densities (9, 17, 24, and 36 wt %). We observed that $\chi^{(2)}$ reaches a maximum at a loading level of 17 wt % ($\chi^{(2)} = 49$ pm/V), followed by a drastic decrease at 24 and 36 wt % loading densities ($\chi^{(2)} = 15$ and 13 pm/V). This behavior can be attributed to detrimental chromophore aggregation. When the magnitude of the nonlinear optical response of both systems is compared, we notice that at low chromophore concentration (17 wt %) the blend gives the best results. This can be explained by the higher flexibility of the chromophore in this systems, which leads to a better polar alignment. Hence, these results indicate that the linear increase of the nonlinear optical response with the chromophore concentration in our systems does not originate from the specific nature of the chromophore but is due to the specific treelike supramolecular structure of the polybinaphthalenes.

Conclusion

In this work, we have studied a new class of chromophore-functionalized polymers. The materials show a particular treelike supramolecular structure: flexible chromophores were attached to a rigid backbone. This structure gives rise to some unique physical properties, i.e., their thermal (T_g) and spectral (^{1}H NMR) behavior. Furthermore, this supramolecular structure almost eliminates the dipolar electrostatic interactions between the chromophores, resulting in a quasi-linear increase of the nonlinear optical response as a function of chromophore concentration.

Experimental Section

Reagents. All reagents were purchased from Aldrich Chemical Co., Acros Organics, Merck, Fluka, and Avocado. Reagent grade solvents were dried when necessary and purified by distillation.

The glass transition temperatures were measured with a DSC-7 apparatus from Perkin-Elmer at a heating rate of 50 °C/min (polymers) or 30 °C/min (chromophores). Gel permeation chromatography (GPC) measurements were done with a Waters apparatus with a tunable absorbance detector and a differential refractometer in tetrahydrofuran (THF) as eluent toward polystyrene standards. ^{1}H nuclear magnetic resonance (NMR) measurements were carried out with a Bruker Avance 300 MHz (1D) and a Bruker AMX 400 MHz (2D experiments). UV−vis spectra were recorded with a Varian Cary 400. The optical rotations were measured with an Analis Optical Activity Polaar 20.

Synthesis of the Chromophores. a. Synthesis of *N,N′*-Diethyl-1-[5-[2-[4-[*N*-ethyl-*N*-(2-hydroxyethyl)amino]phenyl]ethenyl]-2-thienylmethylideen]-2,4,6-(1*H*,3*H*,5*H*)pyrimidinetrion (3a). A solution of 9.69 g (32.0 mmol) of **1a** and 7.10 g (38.0 mmol) of **2** in 150 mL of absolute ethanol was stirred overnight and 50 °C. After cooling, the precipitate was filtered off and recrystallized from choroform/hexane. Yield: 14.5 g (97%); mp: 203 °C. ^{1}H NMR (CDCl$_3$, ppm): $\delta = 8.60$ (s; 1H), 7.76 (d; $J = 4.0$ Hz; 1H), 7.43 (d; 2H), 7.35 (d; $J = 15.7$ Hz; 1H), 7.18 (d; $J = 4.0$ Hz; 1H), 7.06 (d; $J = 15.7$ Hz; 1H), 6.74 (d; 2H), 4.10 (q +q; 4H), 3.86 (t; 2H), 3.52 (m; 4H), 1.30 (t + t; 6H), 1.22 (t; 3H). ^{13}C NMR (CDCl$_3$, ppm): $\delta = 162.7$, 161.8, 161.1, 150.7, 149.0, 148.0, 147.2, 135.1, 134.7, 129.0, 125.8, 124.0, 116.3, 112.2, 108.2, 60.3, 52.3, 45.6, 37.4, 36.6, 13.5, 13.4, 12.0. MS: $m/z = 467$ (M$^+$), 436 (M$^+$ − CH$_3$O).

b. Synthesis of *N,N′*-Diethyl-1-[5-[2-[4-[*N*-ethyl-*N*-(6-hydroxyhexyl)amino]phenyl]ethenyl]-2-thienylmethylideen]-2,4,6-(1*H*,3*H*,5*H*)-pyrimidinetrion (3b). The procedure, described for **3a**, was followed, starting from 44.4 g (100 mmol) of **1b**. The product was “recrystallized” from ethanol and isolated as a glass. Yield: 10.6 g (81%). ^{1}H NMR (CDCl$_3$, ppm): $\delta = 8.58$ (s; 1H), 7.74 (d; $J = 4.0$ Hz; 1H), 7.40 (d; 2H), 7.34 (d; $J = 15.7$ Hz; 1H), 7.15 (d; $J = 4.0$ Hz; 1H), 7.02 (d; $J = 15.7$ Hz; 1H), 6.64 (d; 2H), 4.07 (q + q; 4H), 3.67 (t; 2H), 3.42 (q; 2H), 3.31 (t; 2H), 1.59 (m; 4H), 1.41 (m; 4H), 1.28 (t + t; 6H), 1.20 (t; 3H). ^{13}C NMR (CDCl$_3$, ppm): $\delta = 162.8$, 161.8, 161.1, 150.7, 149.0, 148.1, 147.2, 135.1, 134.6, 129.0, 125.8, 124.1, 116.3, 112.2, 108.1, 62.8, 50.3, 45.0, 37.4, 36.6, 32.7, 27.6, 27.0, 25.7, 13.5, 13.4, 12.4. MS: $m/z = 523$ (M$^+$), 436 (M$^+$ − C$_5$H$_{11}$O).

c. Synthesis of (*S*)-(−)-6,6′-Dibromo-2′-hexyloxy-[1,1′-binaphthalene]-2-ol (5). Under an argon atmosphere a solution of 14.4 g (32.4 mmol) of **4**, dissolved in 70 mL of dry DMF, was slowly added to a suspension of 0.78 g (32.4 mmol) of NaH in 30 mL of dry DMF. After 15 min, 4.6 mL of hexyl bromide (32.4 mmol) and 100 mg of anhydrous NaI were added. The mixture was stirred overnight at 50 °C. After cooling, the mixture was poured into 200 mL of water and extracted with dichloromethane. The organic layer was washed with a saturated NaHCO$_3$ solution and with brine and dried over MgSO$_4$. After removal of the solvents, the crude compound was purified by column chromatography (silica gel; eluent: hexane/dichloromethane (60:40 v/v)) and isolated as an oil. Yield: 8.2 g (48%); $[\alpha]_D^{25} = +32.4$ deg dm^{-1} mol^{-1} L ($c = 0.06$ in CHCl$_3$). ^{1}H NMR (CDCl$_3$): $\delta = 8.05$ (d; $J = 1.5$ Hz; 1H), 8.00 (d; $J = 1.5$ Hz; 1H), 7.93 (d; 1H), 7.80 (d; 1H), 7.46 (d; 1H), 7.34 (d; 1H), 7.34 (dd; 1H), 7.28 (dd; 1H), 7.02 (d; 1H), 6.86 (d; 1H), 4.89 (d; 1H), 3.99 (m; 2H), 1.43 (qu; 2H), 1.01 (m; 6H), 0.75 (t; 3H). ^{13}C NMR (CDCl$_3$, ppm): $\delta = 155.7$, 151.6, 132.5, 132.2, 130.6, 130.4, 130.2, 130.1, 130.0, 129.6, 128.9, 126.6, 126.5, 118.7, 118.1, 117.0, 116.2, 115.7, 114.9, 69.6, 31.2, 29.0, 25.2, 22.4, 13.9. MS: $m/z = 528$ (M$^+$), 444 (M$^+$ − C$_6$H$_{12}$), 364 (M$^+$ − C$_6$H$_{12}$, −Br), 284 (M$^+$ − C$_6$H$_{12}$, −Br$_2$).

d. Synthesis of (*S*)-(−)-6,6′-Dibromo-2,2′-dihexyloxy-[1,1′-binaphthalene] (mon-(h,h)). The procedure, described for **5** was followed, starting from 22.2 g (50.0 mmol) of **4**, 2.40 g (100 mmol) of NaH, and 14.0 mL of hexyl bromide. The product was purified by column chromatography (silica gel; eluent: hexane/dichloromethane (60:40 v/v)) and recrystallized from ethanol. Yield: 28.8 g (94%); mp: 75.2 °C; $[\alpha]_D^{25} = -25.0$ deg dm^{-1} mol^{-1} L ($c = 0.5$ in THF). ^{1}H NMR (CDCl$_3$, ppm): $\delta = 8.00$ (d; $J = 1.5$ Hz; 2H), 7.83 (d; 2H), 7.40 (d; 2H), 7.35 (dd; 2H), 6.97 (d; 2H), 3.92 (m; 4H), 1.39 (qu; 4H), 0.90 (m; 12H), 0.74 (t; 6H). ^{13}C NMR (CDCl$_3$, ppm): $\delta = 154.7$, 132.5, 130.2, 129.7, 129.4, 128.4, 127.1, 120.0, 117.2, 116.3, 69.5, 31.3, 29.2, 25.3, 22.5, 13.9. MS: $m/z = 612$ (M$^+$), 528 (M$^+$ − C$_6$H$_{12}$), 444 (M$^+$ − C$_{12}$H$_{24}$), 364 (M$^+$ − C$_{12}$H$_{24}$, −Br), 284 (M$^+$ − C$_{12}$H$_{24}$, −Br$_2$).

Synthesis of Chromophore-Functionalized Binaphthalene Monomers. A general procedure is as follows: A solution of 3.00 mmol of binaphthalene derivative (**4** or **5**), 3.00 mmol/6.00 mmol of chromophore (**3a** or **3b**), 3.00 mmol/6.00 mmol of 2,2-dimethylpropanol (**6**)**,** and 3.60 mmol/7.20 mmol of triphenylphosphine in 60 mL of dry THF was cooled in an ice bath and purged with argon. To this solution, 3.60 mmol/7.20 mmol of DIAD was dropwise added, and the reaction mixture was stirred for 24 h at room temperature. Then, the reaction mixture was poured into water, and the reaction product was extracted (three times) with dichloromethane. The combined organic layers were dried over MgSO$_4$. After removal of the solvents, the crude compound was purified by column chromatography (silica gel; eluent: dichloromethane/ethyl acetate (95:5 v/v)).

a. mon-(2,2). Yield: 0.550 g (14%); $[\alpha]_D^{25} = +1.1 \times 10^4$ deg dm^{-1} mol^{-1} L ($c = 0.013$ in THF). ^{1}H NMR (CDCl$_3$, ppm): $\delta =$ 8.59 (s; 2H), 8.02 (d; $J = 2.2$ Hz; 2H), 7.84 (d; 2H), 7.75 (d;

J = 4.4 Hz; 2H), 7.35 (d; 2H),7.29 (d; J = 16.1 Hz; 2H), 7.25 (dd; 2H), 7.22 (d; 4H), 7.17 (d; J = 4.4 Hz; 2H), 7.01 (d; J = 16.1 Hz; 2H), 6.95 (d; 2H), 6.30 (d; 4H), 4.08 (m; 12H), 3.32 (q; 4H), 2.65 (m; 4H), 1.30 (m; 12H), 0.78 (t; 6H). ^{13}C NMR ($CDCl_3$, ppm): δ = 162.6, 161.8, 161.2, 154.3, 150.7, 148.1, 147.9, 147.3, 135.2, 134.6, 132.4, 130.5, 129.9, 129.8, 128.8, 128.7, 126.9, 125.7, 123.4, 120.1, 117.8, 116.2, 116.0, 111.4, 108.1, 67.8, 49.0, 44.6, 37.4, 36.6, 13.5, 13.4, 11.6.

b. mon-(2,h). Yield: 1.28 g (43%); $[\alpha]_D^{25} = +1.1 \times 10^4$ deg dm^{-1} mol^{-1} L (c = 0.013 in THF). ^{1}H NMR ($CDCl_3$, ppm): δ = 8.58 (s; 1H), 7.99 (d + d; J = 2.2 Hz; 2H), 7.82 (d + d; 2H), 7.74 (d; J = 4.4 Hz; 1H), 7.35 (d + d; 2H), 7.30 (d; J = 16.1 Hz; 1H), 7.25 (m; 4H), 7.17 (d; J = 4.4 Hz; 1H), 7.00 (d; J = 16.1 Hz; 1H), 6.96 (d; 1H), 6.93 (d; 1H), 6.33 (d; 2H), 4.08 (m; 6H), 3.86 (m; 2H), 3.55 (q; 2H), 2.73 (t; 2H), 1.29 (m; 9H), 0.98 (m; 4H), 0.83 (m; 4H), 0.78 (t; 3H). ^{13}C NMR ($CDCl_3$, ppm): δ = 162.7, 161.8, 161.4, 154.7, 154.4, 150.7, 148.2, 147.9, 147.3, 135.4, 134.6, 132.5, 130.5, 130.2, 129.8, 129.6, 128.9, 128.6, 128.5, 127.1, 126.9, 125.7, 125.6, 123.3, 120.4, 119.6, 117.7, 117.3, 116.3, 116.2, 115.9, 111.4, 108.0, 69.5, 67.7, 49.1, 44.7, 37.3, 36.6, 31.2, 29.2, 25.3, 22.4, 13.9, 13.5, 13.4, 11.7.

c. mon-(6,6). Yield: 1.58 g (36%); $[\alpha]_D^{25} = +1.0 \times 10^4$ deg dm^{-1} mol^{-1} L (c = 0.015 in THF). ^{1}H NMR ($CDCl_3$, ppm): δ = 8.59 (s; 2H), 7.97 (d; J = 1.8 Hz; 2H), 7.81 (d; 2H), 7.75 (d; J = 4.0 Hz; 2H), 7.37 (d; 2H), 7.36 (d; J = 13.9 Hz; 2H), 7.29 (dd; 2H), 7.22 (d; 4H), 7.16 (d; J = 4.0 Hz; 2H), 7.04 (d; J = 13.9 Hz; 2H), 7.00 (d; 2H), 6.58 (d; 4H), 4.08 (m; 12H), 3.38 (q; 4H), 3.11 (t; 4H), 1.34 (qu; 4H), 1.28 (m; 12H), 1.17 (t; 6H), 0.98 (t + t; 12H). ^{13}C NMR ($CDCl_3$, ppm): δ = 162.7, 161.8, 161.5, 154.7, 150.7, 148.7, 147.8, 147.3, 135.5, 134.5, 132.5, 130.2, 129.8, 129.5, 129.1, 128.5, 127.1, 125.6, 123.0, 120.0, 117.3, 116.4, 115.6, 111.6, 107.9, 69.4, 50.1, 45.0, 37.3, 36.6, 29.2, 27.3, 26.5, 25.6, 13.5, 13.4, 12.4.

d. mon-(6,h). Yield: 2.16 g (70%); $[\alpha]_D^{25} = +1.3 \times 10^4$ deg dm^{-1} mol^{-1} L (c = 0.011 in THF). ^{1}H NMR ($CDCl_3$, ppm): δ = 8.61 (s; 1H), 8.02 (d; J = 1.8 Hz; 1H), 7.97 (d; J = 2.2 Hz; 1H), 7.82 (d; 1H), 7.80 (d; 1H), 7.76 (d; J = 4.0 Hz; 1H), 7.50 (d; 2H), 7.40 (d; 1H), 7.37 (d; J = 16.8 Hz; 1H), 7.29 (m; 3H), 7.22 (d; J = 4.0 Hz; 1H), 7.05 (d; J = 16.8 Hz; 1H), 7.01 (dd; 1H), 6.99 (dd; 1H), 6.59 (d; 2H), 3.95 (m; 8H), 3.37 (q; 2H), 3.12 (t; 2H), 1.32 (m; 6H), 1.28 (t + t; 6H), 1.18 (t; 3H), 0.97 (m; 10H), 0.76 (t; 3H). ^{13}C NMR ($CDCl_3$, ppm): δ = 162.7, 161.8, 161.6, 154.8, 154.6, 150.7, 148.8, 134.5, 132.6, 132.5, 130.2, 130.1, 129.7, 129.5, 129.4, 129.1, 128.4, 127.2, 127.1, 123.0, 120.0, 117.3, 117.2, 111.6, 107.9, 69.5, 69.4, 37.3, 31.3, 29.2, 27.3, 26.5, 25.6, 25.3, 22.5, 13.9, 13.5, 13.4, 12.4.

Synthesis of the Polymers. A general procedure is as follows: 400 μmol of **8**, 400 μmol of binaphthalene monomer (**mon-(*,*)**), 9.2 mg (12.5 μmol) of Pd_2dba_3, and 30.6 mg (100 μmol) of $AsPh_3$ were dissolved in 30 mL of dry THF. The mixture was purged with argon and refluxed for 60 h. After cooling, the polymer was precipitated in methanol, collected by filtration, and dried. Finally, the polymer was redissolved in THF, precipitated in methanol, and dried under vacuum. This procedure was repeated twice.

a. Synthesis of *N*,*N*′-Diethyl-1-[5-[2-[4-[*N*-ethyl-*N*-[6-(*tert*-butyldimethyl)silyloxyhexyl]amino]phenyl]ethenyl]2-thienylmethylideen]-2,4,6-(1*H*,3*H*,5*H*)-pyrimidinetrion (10b). In a 20 mL flask, equipped with a $CaCl_2$ tube, 156 mg (298 μmol) of **3b** and 54.0 mg (358 μmol) of *tert*-butyldimethylsilyl chloride were dissolved in 5 mL of dry DMF. The solution was cooled in an ice bath, and 48.7 g (715 mmol) of imidazole was added in several portions. The reaction mixture was stirred overnight at 40 °C. After cooling, water was added, and the mixture was extracted with diethyl ether. The combined organic layers were washed with a saturated $NaHCO_3$ solution and with brine and dried over $MgSO_4$. After evaporation of the solvent, the product was purified by column chromatography (silica gel; eluent: dichloromethane/ethyl acetate (95:5 v/v)) and isolated as a glass. Yield: 14.5 g (97%). ^{1}H NMR ($CDCl_3$, ppm): δ = 8.60 (s; 1H), 7.75 (d; J = 4.4 Hz; 1H), 7.41 (d; 2H), 7.35 (d; J = 16.1 Hz; 1H), 7.17 (d; J = 4.4 Hz; 1H), 7.04 (d; J = 16.1 Hz; 1H), 6.65 (d; 2H), 4.10 (q +q; 4H), 3.63 (t; 2H), 3.42 (q; 2H), 3.32 (t; 2H), 1.60 (m; 2H), 1.2 (m; 6H), 1.30 (t + t; 6H), 1.22 (t; 3H), 0.92 (s; 9H), 0.07 (s; 6H). ^{13}C NMR ($CDCl_3$, ppm): δ = 162.8, 161.8, 161.1, 150.7, 149.0, 148.1, 147.2, 135.1, 134.6, 129.0, 125.8, 124.1, 116.3, 112.2, 108.1, 62.8, 50.3, 45.0, 37.4, 36.6, 32.7, 27.6, 27.0, 25.7, 24.7, 17.3, 13.5, 13.4, 12.4, −4.6. MS: m/z = 637 (M^+), 436 ($M^+ - C_{11}H_{25}OSi$).

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Supporting Information Available: A representative UV−vis spectrum of a spin-coated film of **pol-(2,2)-0.25**. This material is available free of charge via the Internet at http://pubs.acs.org.

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