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Synthesis and Properties of New Chiral Donor-Embedded Polybinaphthalenes for Nonlinear Optical Applications

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ABSTRACT: Eight new chiral, chromophore-functionalized donor-embedded polybinaphthalenes were prepared and characterized for their (nonlinear) optical properties. The polymers were prepared by direct polymerization using a Stille coupling reaction between a chiral bis(trimethyltin) binaphthalene derivative and diiodo-functionalized chromophores. The use of diiodo-functionalized instead of dibromo-functionalized chromophores resulted in a significant increase of molecular weight, as demonstrated by end group analysis, GPC, and MALDI−TOF experiments. The reaction conditions allowed the use of a great variety of chromophores with different DπA structures. The typical treelike macromolecular architecture of the polymers is reflected in the behavior of the glass transition temperature and, more clearly, in the nonlinear optical properties. The nonlinear optical response shows a continuous, linear increase in function of chromophore concentration, indicating that the dipolar interactions between the chromophores are eliminated. Moreover, chiral contributions to the nonlinear optical response were observed and mounted 14% of the highest achiral contribution.

Introduction

Design and synthesis of polymeric materials for second-order nonlinear optical (NLO) applications have received considerable interest. These materials usually consist of dipolar chromophores, embedded in a polymer matrix. A large variety of polymers have been used, but seldom were rigid, helical, chromophore-functionalized polymers studied, although they show some additional advantages compared to their random coil analogues. First, the rigidity of the backbone can greatly diminish unwanted dipolar interactions between the chromophores, allowing a very high chromophore density.[1] Second, when chiral polymers are used, the system can benefit from its chirality,[2] giving rise to the relaxation of the need of polar order and the presence of contributions, inherent to chirality, which can increase the nonlinear optical response.

Polymers containing binaphthalene units can also adopt a helical configuration.[3] Due to the twisted configuration of the binaphthalene moiety, polymers in which these units are connected through rigid groups (in the case of triphenylamine derivatives) are helices. The rigidity of the system gives rise to a rigid, rodlike, helical structure. 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.[4]

Chromophores were introduced to trigger a nonlinear optical response. Here, we have chosen to prepare donor-embedded polybinaphthalenes. The treelike macromolecular design (chromophores (branches) are attached to a rigid backbone (trunk)) is optimal in these materials: the chromophores can still easily be poled in an electric field (in contrast to systems in which the chromophores are part of the main chain), but the chromophores are attached to the backbone as close as possible. This allows a very tight relation between the nonlinearity, originating from the chromophores, and the chirality, situated in the backbone, and chiral contributions to the nonlinear optical response are present.[5] Therefore, the importance of chirality is 2-fold: first, rigid, helical conformations can only be formed if chiral monomers are polymerized, and second, chiral contributions to the nonlinear optical response can only be present in chiral samples. Furthermore, polybinaphthalenes show excellent thermal and (photo)-chemical stability.[5]

We already reported[6] the synthesis of two chiral donor-embedded polybinaphthalenes, functionalized with chromophores. Those polymers were prepared by a Stille coupling between a bis(trimethyltin)binaphthalene monomer and dibromo-functionalized chromophores with rather weak to moderate NLO properties. Here, we report the synthesis and properties of eight new, chiral donor-embedded polybinaphthalenes, functionalized with chromophores with negligible to superb NLO properties. These polymers were prepared in an analogues way, but diiodo-functionalized instead of dibromo-functionalized chromophores were used. One of the polymers (**pol-2-1**) was prepared from a diiodo-functionalized chromophore with the same DπA structure as described earlier (where dibromo-functionalized chromophores were used). As a consequence, this allows the investigation of the influence of the synthetic procedure on the polymer's properties.

Results and Discussion

Synthesis of the Polymers. The synthesis of the chromophores is presented in Schemes 1 and 2. All

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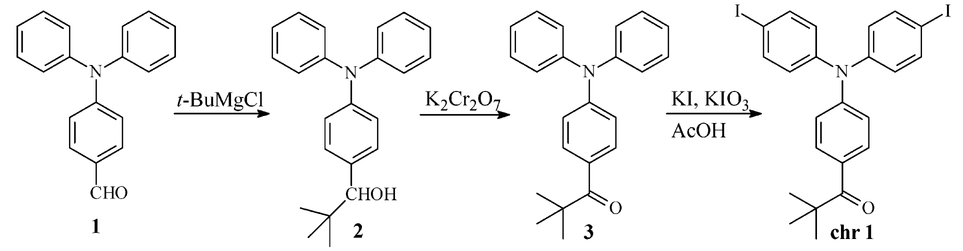
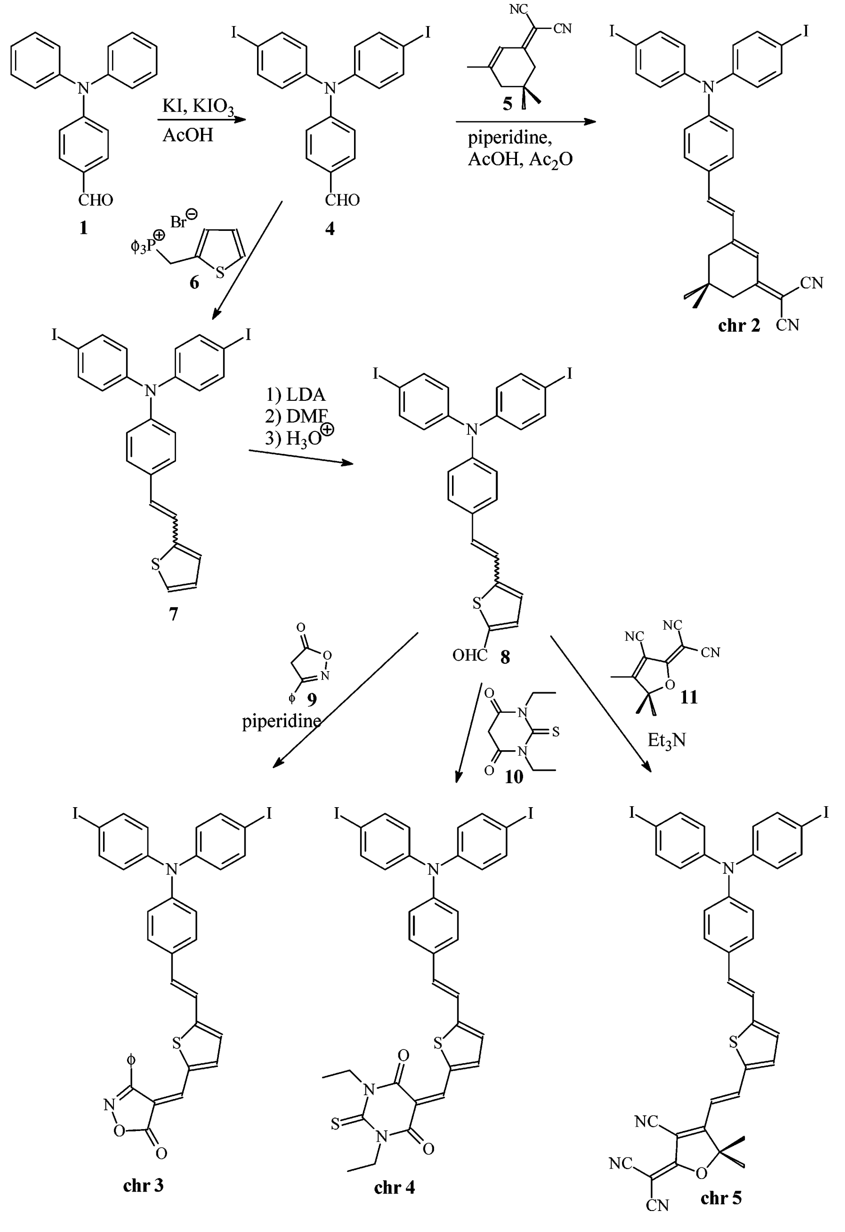
Scheme 1. Synthesis of Chr 1



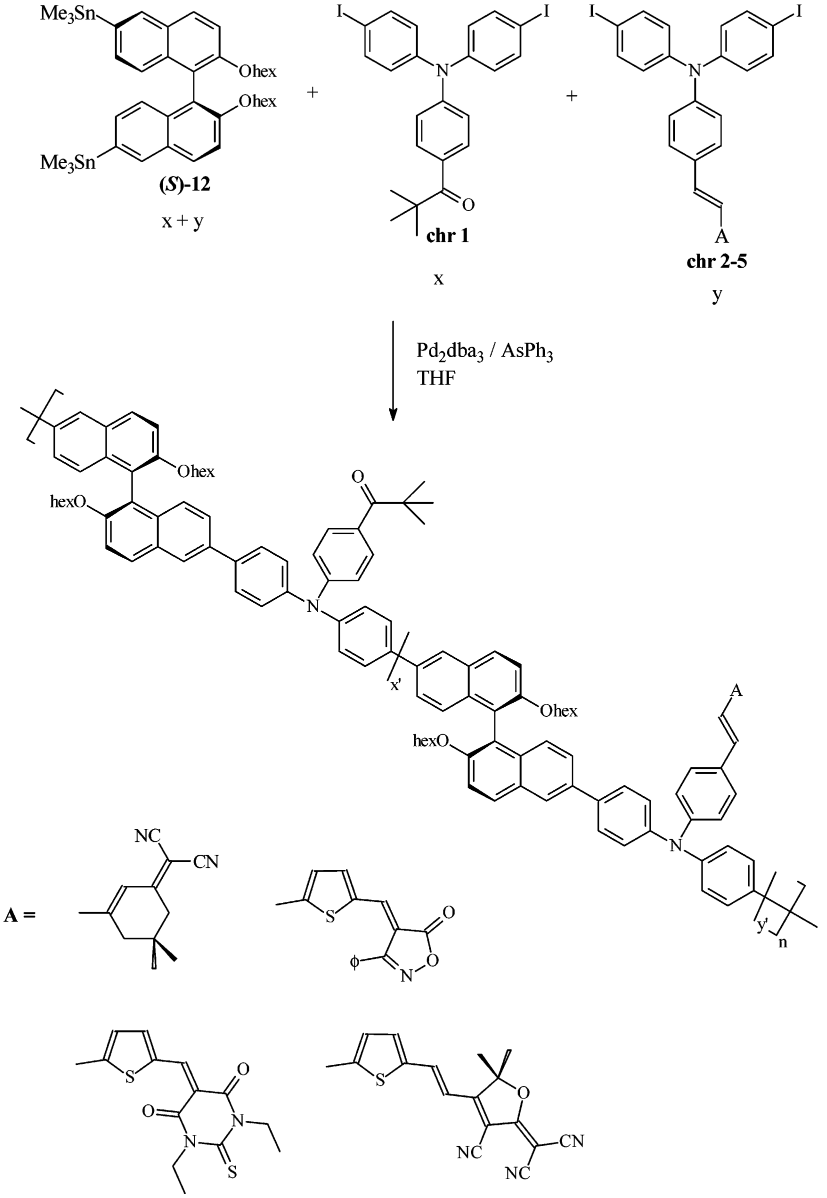
Scheme 2. Synthesis of Chr 2−5



chromophores were prepared starting from the aldehyde **1**. Reaction of **1** with *tert*-butylmagnesium chloride resulted in **2**. **Chr 1** was then prepared by oxidation of the secondary alcohol **2** using $K_2Cr_2O_7/H_2SO_4$, followed by iodation of **3** (Scheme 1). It is worthwhile to note that, if the iodation is performed as the first step, side reactions dominate when the resulting aldehyde (i.e., **4**, Scheme 2) is treated with *tert*-butylmagnesium chloride.

The first step in the synthesis of **chr 2−5** was the iodation of the starting aldehyde **1**. A Knoevenagel condensation of **4** with 2-(3,5,5)-trimethyl-2-cyclohexene-1-ylidenepropanedinitrile **5**[7] resulted in **chr 2**. A Wittig−Horner reaction of the aldehyde **4** and phosphonium salt **6**[8] yielded **7** as a cis/trans mixture. Reaction with lithium diisopropyl amide (LDA), quenching of the lithium derivative with dimethylformamide (DMF) and subsequent hydrolysis resulted in the formation of the target aldehyde **8**, still in a cis/trans mixture. However, it was possible to separate both isomers by careful column chromatography. Finally, **chr 3−5** were prepared by a Knoevenagel condensation under appropriate

Scheme 3. Polymer Synthesis



reaction conditions with 3-phenyl-5-isoxazolone (**9**), diethylthiobarbituric acid (**10**) and 2-dicyanomethylene-3-cyano-4,5,5-trimethyl-(2*H*,5*H*)-furan (**11**),[8] respectively. In the cases of **chr 3** and **chr 5**, only the trans isomer of the chromophore was obtained, starting from a mixture of cis/trans **8**. This is consistent with an increase in bond length alternation in the chromophore, which is observed when stronger withdrawing groups are attached to an aromatic π-conjugated system. In the chromophore, the double bond character of the central vinyl is thus reduced, allowing isomerization to the more stable *trans*-chromophore. Surprisingly,[1,9] this was not the case with **10**: **chr 4** was isolated as a mixture of both isomers, even after heating in an ethanol solution. Pure *trans*-**chr 4** could only be obtained starting from *trans*-**8**.

The polymers were prepared by a Stille coupling between (*S*)-(−)-6,6′-di(trimethyltin)-2,2′-dihexyloxy-[1,1′-binaphthalene] **(*S*)-12**[6] and the diiodo-substituted chromophores **chr 1**−**5** (Scheme 3). Attempts were done to improve the polymerization conditions. In several batches, THF appeared to be a better choice as solvent than DMF ($\bar{M}_w$ = 8.0 and 6.9 kg/mol respectively, GPC, **pol-2-1**). Moreover, sometimes, some degradation of the chromophore seemed to be present, as indicated by UV−vis spectroscopy. As expected,[10] the system Pd_2dba_3/$AsPh_3$ was the catalyst/ligand of choice: with $Pd[PPh_3]_4$, for instance, only oligomers could be isolated ($\bar{M}_w$ = 0.43 kg/mol).

Homopolymers with all 5 chromophores as well as copolymers with **chr 1** and **chr 4** in different ratios were prepared. All chromophores have an analogous build-up: they consist of a triphenylamine moiety, which is substituted in the 4-position with an electron-withdrawing group. Therefore, we can assume that they are all more or less equally reactive in the Stille coupling reaction. As a consequence, the ratio of **chr 1** and **chr 4** in the copolymers can easily be adjusted, simply by varying the feed ratios (Table 1).

Characterization of the Polymers. Composition. In this way, eight new polymers were prepared. Their composition, yields, molecular weights, and polydispersities are presented in Table 1.

In the way described above, all polymers could be prepared in very high yields (except for **pol-1-1**), without any decomposition of the chromophore, as judged by ^1H

Table 1. Composition, Yield, Molecular Weight, and Polydispersity of the Polymers

polymer[a]	**chr 1** (*x*)/**chr i** (*y*), feed[b]	$y'_{\textbf{chr 4}}$, copolymer[c] ^{1}H NMR (UV−vis)	ρ[d]/%	$\bar{M}_w$[e]/(kg/mol)	D[f]
pol-1-1	**chr 1** (1)		32	4.5	2.1
pol-2-1	**chr 1** (0)/**chr 2** (1)		98	8.0	2.1
pol-3-1	**chr 1** (0)/**chr 3** (1)		90	5.9	2.4
pol-4-0.25	**chr 1** (0.75)/**chr 4** (0.25)	0.30 (0.27)	91	4.7	2.2
pol-4-0.50	**chr 1** (0.50)/**chr 4** (0.50)	0.50 (0.54)	91	3.3	2.4
pol-4-0.75	**chr 1** (0.25)/**chr 4** (0.75)	0.75 (0.73)	90	3.6	2.7
pol-4-1	**chr 1** (0)/**chr 4** (1)		95	3.8	2.7
pol-5-1	**chr 1** (0)/**chr 5** (1)		97	6.6	2.3

[a] The code number of the polymers is constituted as follows: the first number denotes for the chromophore used in the homopolymers (in the copolymers, **chr 4**, which shows much better nonlinear optical properties than **chr 1**, is taken); the second number indicates the mole ratio of the **chr i** in the feed of the copolymers. [b] Nature and mole ratio of chromophores in the feed. [c] Mole ratio of **chr 4** in the copolymers, determined by ^{1}H NMR and UV−vis spectroscopy. [d] Yield of the isolated polymers. [e] Weight-average molecular weight, measured GPC. [f] Polydispersity, $\bar{M}_w/\bar{M}_n$,determined by GPC.

NMR and UV−vis spectroscopy. The Stille reaction has already been used for the polymerization of chromophore-functionalized monomers for nonlinear optics, even for chromophores related to **chr 4**.[1,11] Here, we show that the Stille coupling can be expended to a large number of chromophores with several, distinctly different DπA systems and even to chromophores with superb NLO properties (**chr 5**).

The ratio **chr 4**/**chr 1** in the copolymers is measured by ^{1}H NMR and UV−vis spectroscopy and resembles the ratio in the feed. If the high yields are taken into account, this is no proof that the different chromophores are randomly distributed in the chain. However, since they are electronically equal (the ^{1}H and ^{13}C NMR signals, for instance, are the same), we can expect that they are equally reactive and therefore randomly distributed in the polymer chain.

GPC Analysis. The molecular weights were determined by gel permeation chromatography (GPC) toward polystyrene standards in THF. It has been demonstrated that the molecular weights determined in this way are underestimated.[12] In a previous publication, in which the chromophores were functionalized with two bromine atoms instead of iodine, we have determined this parameter by end group analysis with ^{1}H NMR. In the polymers obtained by polymerization of diiodo-substituted chromophores, no peaks or very small peaks of end groups were presented, indicating that these polymers have a significantly higher molecular weight.

To get a better estimation of the molecular weights, **pol-2-1** was fractionated by GPC and the fractions ($D \approx 1.1$) were analyzed by MALDI−TOF. This revealed that the unfractionated sample has an overall polydispersity of 1.5, $\bar{M}_w = 7.4$ kg/mol and $\bar{M}_n = 5.0$ kg/mol, which is about 20% higher than that determined by GPC toward polystyrene standards. These results are in line with those Pu et al. found for analogous polybinaphthalenes by LLS.[12] The same polymer, but prepared from the dibromo-substituted chromophore, showed a much lower molecular weight ($\bar{M}_w = 3.0$ kg/mol, $\bar{M}_n = 1.7$ kg/mol and $D = 1.8$). Therefore, we can conclude that the Stille coupling of diiodo-substituted chromophores produces polymers of significantly higher molecular weights. This is consistent with the fact that Stille couplings proceed better with aryl iodides instead of aryl bromides.[10b]

CD and UV—Vis Spectroscopy and Polarimetry. A representative CD spectrum of **pol-2-1** in THF is shown in Figure 1.

All polymers have essentially the same CD spectrum, both in solution as in thin film. Since the observed Cotton effects are due to the binaphthalene moieties, which constitute the main-chain of the polymers, this means that the chromophore does not influence the supramolecular architecture of the polymers.

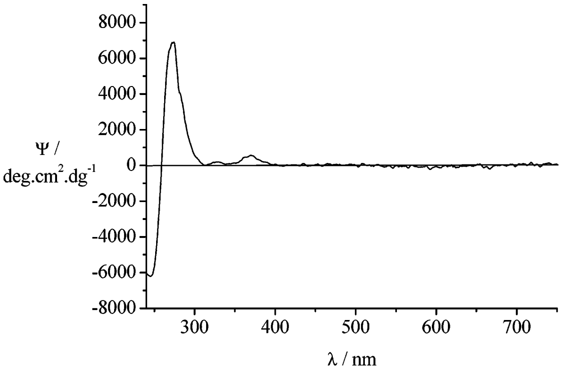


Figure 1. CD spectrum of **pol-2-1**.

A surprising feature of these polymers is the significant red shift of $\lambda_{\max}$ when the chromophores are polymerized. $\lambda_{\max}$ of the chromophores in THF are 318 (**chr 1**), 471 (**chr 2**), 519 (**chr 3**), 538 (**chr 4**), and 568 nm (**chr 5**). As displayed in Table 2, $\lambda_{\max}$ of the chromophores in the polymers is 21−32 nm higher than $\lambda_{\max}$ of the chromophore-monomers. Clearly, polymerization leads to planarization of the triphenylamine unit and, consequently, a better conjugation in the chromophore.

The specific optical rotations of the polymers are summarized in Table 2. The values greatly depend on $\lambda_{\max}$ of the polymers and are therefore resonantly enhanced. Since the CD spectra of all polymers are the same, we can conclude that the macromolecular architecture of the polymers is independent of the chromophore used. The difference in optical rotations can then be ascribed to resonant enhancement and possible differences in end groups.

Molecular Modeling. To visualize the supramolecular (helical) rodlike structure, some molecular modeling was performed. We performed a molecular mechanics simulation modeling of **pol-2-1** (Hyperchem 7.1). Eight repeating units were used. As can be seen in Figure 2, parts a and b, the polymer adopts a helical, rodlike conformation.

DSC Analysis. The glass transition temperatures (T_g) of the polymers were measured by differential scanning calorimetry (DSC) and are listed in Table 2. The observed T_g of rigid, chromophore-functionalized polybinaphthalenes is the T_g of the chromophores in the material and not of the whole polymer material.[1,8] Therefore, the T_g of the polymers depends on the T_g of

Table 2. λ_{max}, Specific Optical Rotations, Glass Transition Temperatures, and NLO Properties of the Polymers

polymer	$\lambda_{max}{}^{a}$/nm	$[\alpha]_D^{20°C}$ ^{b}/deg.dm^{-1}.g^{-1}.mL	$T_g{}^{c}$/°C	$\chi^{(2)}_{zzz}(\omega)$/(pm/V)	$\chi^{(2)}_{zzz}(0)^{d}$/(pm/V)
pol-1-1	349	0.49	157	0	0
pol-2-1	518	1.3	186	99	3.9
pol-3-1	562	71	184	115	9.7
pol-4-0.25	582	4.3	162	22	3
pol-4-0.50	582	66	162	81	11
pol-4-0.75	577	64	165	107	13
pol-4-1	577	71	183	129	16
pol-5-1	625	15	193	98	25

[a] In THF. [b] $c = 0.002$ in THF. [c] Determined by DSC (50 °C/min). [d] Calculated using the two-level model.[13]

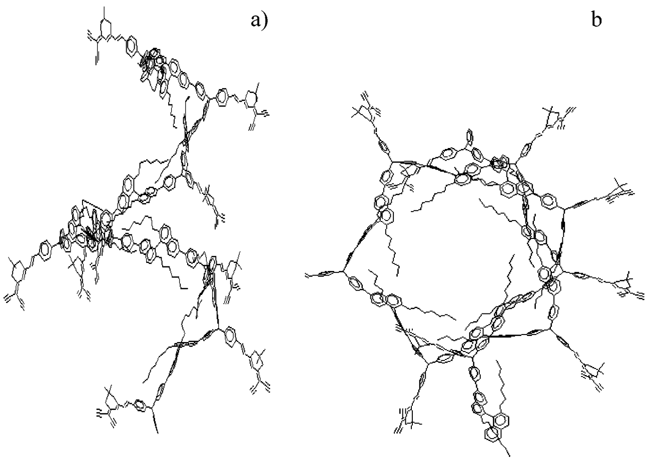


Figure 2. Molecular mechanics simulations: (a) front view and (b) top view of **pol-2-1**.

the incorporated chromophore built in and on the flexibility of the chromophores in the polymer material. The T_g's of the respective chromophores were measured at 49 (**chr 1**), 77 (**chr 2**), 87 (**chr 3**), and 111 °C (**chr 4**) by DSC (30 °C/min). **chr 5** degrades around 275 °C and could not be vitrified. From Table 2, it is clear that the T_g of the homopolymers depends on the T_g of the incorporated chromophores. Moreover, the observed T_g of the copolymers is intermediate to the T_g's of the respective homopolymers. The results confirm the abovementioned phenomenom.

The T_g of the polymer, similar to **pol-2-1**, but prepared from the dibromo-substituted chromophore, was measured under identical conditions and found to be 152 °C.[6] This is 34 °C lower than the T_g of the polymer, prepared from the diiodo-chromophore (Table 2). Since the only difference in both materials is the molecular weight, this means that the molecular weight has a profound influence on the T_g of the polymers, and, as a consequence, on the flexibility of the chromophores in the polymer material. This also explains why the relationship between the T_g of the chromophores and the T_g of the polymers is not very clear. The molecular weight of **pol-2-1**, for instance, is much higher than those of the others, which might explain the fact that **pol-2-1** shows a high T_g, while the T_g of the chromophore is rather low.

Nonlinear Optical Properties. The polymers were spin-coated onto ITO glass slides from chloroform solutions, which resulted in high quality films. Poly(acrylic acid) was spin-coated on top of the polymer film, to prevent bleaching during the poling process. Although a chiral sample is inherently noncentrosymmetric and should therefore, in principle, not be poled, the ordering of the chromophores was insufficient to allow a NLO response. Moreover, electric-dipole second-harmonic generation (SHG) is symmetry-forbidden in isotropic samples. Therefore, a polar ordering of the chromophores remains, in practice, necessary and was achieved by corona poling. We have optimized the poling conditions and found that for this class of polymers, the highest polar order was achieved by poling at 7 °C above T_g during 20 min. The applied voltage was 8.2 kV.

The nonlinear optical properties were analyzed using SHG measurements.[14] Polarized UV–vis showed that the poled films have a C_∞ symmetry. For such samples, there are four nonvanishing susceptibility components, that is, $\chi^{(2)}_{zzz}$, $\chi^{(2)}_{xxz}$, $\chi^{(2)}_{zxx}$, and $\chi^{(2)}_{xyz}$. The first three components originate from the polar ordering, while the latter can only be present in chiral media. The ratio $\chi^{(2)}_{zzz}/\chi^{(2)}_{xxz} = 3$ confirms the symmetry mentioned above.[15]

The macroscopic second-order nonlinear optical response ($\chi^{(2)}$) of chromophore-functionalized polymer materials arises from the hyperpolarizability (β) of the incorporated 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: $\chi^{(2)} \propto N\mu\beta E$ (μ is the dipole moment of the chromophore).[16] Since all polymers are poled at the same voltage and N is always more or less the same in the homopolymers, this implies that $\chi^{(2)}$ should increase with increasing "chromophore strength", i.e. with increasing $\mu\beta$. This is perfectly reflected in the $\chi^{(2)}_{zzz}(0)$ values of the homopolymers: **chr 1** has negligible nonlinear optical properties, while **chr 5** is an excellent chromophore. The nonlinear optical response is very stable at room temperature. After 6 months at room temperature, only 95% of the response of **pol-5-1** is lost, which can be explained by the high T_g.

$\chi^{(2)}_{zzz}(0)$ of **pol-2-1**, prepared from the dibromo-substituted chromophore, was measured at 13.5 pm/V,[5] which is significantly higher than $\chi^{(2)}_{zzz}(0)$ of **pol-2-1**, prepared from the diiodo-substituted chromophore. Since the molecular structure of both samples is identical, this difference cannot be due the chromophore itself, but it must reflect the difference in poling order in both samples. DSC measurements already indicated that the flexibility of the chromophores in the lower molecular weight sample is much higher than in the higher molecular weight samples. Higher mobility allows a better alignment of the chromophore in the poling field, which leads to higher susceptibilities.

As mentioned above, the linear relationship $\chi^{(2)} \propto N\mu\beta E$ only counts when no electrostatic interactions between the chromophores are present. However, good chromophores tend to have high dipole moments and above a critical loading density, electrostatic interactions occur, which favor centrosymmetrical ordering of

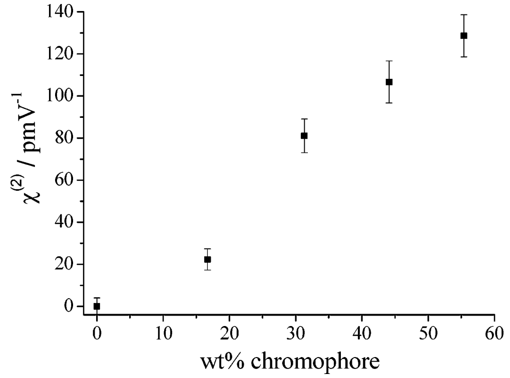


Figure 3. Evolution of $\chi^{(2)}$ of the copolymers with increasing chromophore concentrations.

the chromophores in the polymer matrix. As a result, severe attenuation of $\chi^{(2)}$ as a function of N is expected to occur for chromophores with dipole moments of 7 D and higher. The dipole moment of **chr 4** was determined by capacity measurements and found to be 9 ± 1 D.

We have already shown that the macromolecular architecture of chiral, rigid polybinaphthalenes with chromophores as pendant groups diminishes the electrostatic interactions between the chromophores.[1] Here, we investigate whether the same tendency is present in donor-embedded polybinaphthalenes.

Since **pol-1-1** shows no nonlinear optical response, the nonlinear optical properties of the copolymers **pol-4-0.25** to **pol-4-1** arise from the presence of **chr 4**. As a consequence, the evolution of $\chi^{(2)}$ in function of the chromophore density (N~wt %) can be investigated by plotting the ratio of **chr 4** in the copolymers in function of $\chi^{(2)}$. Figure 3 states a continuous, linear increase of the nonlinear optical response of the copolymers with increasing chromophore concentration, indicating that the electrostatic interactions between the chromophores are more or less eliminated in these materials. In classical systems, the nonlinear optical response reaches a maximum at chromophore concentrations of ~15 wt % ($\mu = 10$ D). Clearly, the electrostatic interactions are in these polymers eliminated by the typical treelike macromolecular structure, which is a unique feature of these polymers. This phenomenon is much more pronounced in donor-embedded polybinaphthalenes than in polybinaphthalenes with chromophores as pendant groups. Finally, we investigated whether the chirality of the system is reflected in its nonlinear optical response. Preliminary results[6] already indicated that chiral contributions are present in chromophore-functionalized polybinaphthalenes, if the donor is embedded in the polymer backbone. $\chi^{(2)}_{xyz}$ (ω) of **pol-2-1** was measured at 14 pm/V, which is 14% of the highest achiral contribution ($\chi^{(2)}_{zzz}$). Therefore, the chirality of the system significantly enhances the nonlinear optical response in two ways: first, by eliminating the dipolar interactions between the chromophores, which allows very high chromophore concentrations, and second, by the presence of chiral contributions.

Conclusion

In this work, we have prepared and studied eight new, chiral, chromophore-functionalized donor-embedded polybinaphthalenes. The use of diiodo-functionalized chromophores resulted in significantly higher molecular weights, compared with materials, prepared from dibromo-substituted chromophores. Furthermore, the polymerization conditions allowed the use of a great variety of chromophores.

The properties, the T_g, and the NLO response of these polymers were compared to those of the lower molecular weights samples, which revealed a reduced flexibility of the chromophores in the higher molecular weight material. The typical treelike macromolecular architecture of the polymers eliminates the dipolar interactions between the chromophores, resulting in a linear increase of the nonlinear optical response as a function of chromophore concentration. Finally, chiral contributions to the nonlinear optical response were observed, which can be ascribed to the donor-embedded structure. We can therefore conclude that these polymers show a unique combination of three assets: first, the possibility to use excellent chromophores, second, the (almost) complete elimination of dipolar interaction between the chromophores, allowing very high chromophore concentration, and third, the presence of chiral contributions, which increase the nonlinear optical response.

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 performed 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. 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. Synthesis of 1-[4-(*N*,*N*-Diphenylamino)]phenyl-2,2-dimethylpropanol, 2. Under argon atmosphere, 100 mL (160 mmol) of *tert*-butylmagnesium chloride (1.6 M in THF) was added to a solution of 41.0 g (150 mmol) of **1** in 100 mL of dry THF at 0 °C. The mixture was refluxed for 2 h, after which it was cooled in an ice bath and 100 mL of a HCl solution (0.1 M) was carefully added. The product was extracted with dichloromethane, and the combined organic layers were washed with a saturated $NaHCO_3$ solution and with brine and dried over $MgSO_4$. After removal of the solvents, the crude reaction product was purified by column chromatography (silica gel; eluent: hexane/ethyl acetate 80/20 (v/v)) and isolated as an oil.

Yield: 18.0 g (36%).

^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.26$ (t; 4H), 7.19 (d; 2H), 7.08 (d; 4H), 7.06 (d; 2H), 7.02 (t; 2H), 4.38 (d; $J = 2.7$ Hz; 1H), 1.83 (d; $J = 2.7$ Hz; 1H), 0.96 (s; 9H).

^{13}C NMR ($CDCl_3$, ppm): $\delta = 147.8$, 146.9, 136.4, 129.2, 128.4, 124.1, 123.0, 122.7, 82.1, 35.7, 26.0.

MS: $m/z = 331$ (M^+), 274 ($M^+ - C_4H_9$).

Anal. Calcd for $C_{23}H_{25}NO$: C, 83.34; H, 7.60; N, 4.23. Found: C, 83.06; H, 7.48; N, 4.12.

Synthesis of 1-[4-(*N*,*N*-Diphenylamino)]phenyl-2,2-dimethylpropanone, 3. A solution of 3.55 g (11.4 mmol) of $K_2Cr_2O_7$ in 3 mL of concentrated sulfuric acid and 100 mL of water was dropwise added to a solution of 18.0 g of **2** in 100 mL of diethyl ether at 0 °C. The reaction mixture was stirred for 2 h at room temperature and then extracted with diethyl ether. The combined organic layers were washed with a saturated $NaHSO_3$ solution, a saturated $NaHCO_3$ solution, and with brine and dried over $MgSO_4$. The crude reaction product was purified by column chromatography (silica gel; eluent: hexane/dichloromethane 70/30 (v/v)) and isolated as a yellow solid.

Yield: 3.20 g (18%).

Mp: 124 °C.

^{1}H NMR (CDCl$_3$, ppm): δ = 7.75 (d; 2H), 7.29 (t; 4H), 7.12 (d; 4H), 7.10 (t; 2H), 6.96 (d; 2H), 1.37 (s; 9H).

^{13}C NMR (CDCl$_3$, ppm): δ = 205.8, 150.7, 146.7, 130.4, 129.6, 129.5, 125.7, 124.3, 119.7, 43.8, 28.5.

MS: m/z = 329 (M^+), 272 ($M^+ - C_4H_9$).

Anal. Calcd for $C_{23}H_{23}NO$: C, 83.85; H, 7.04; N, 4.25. Found: C, 83.48; H, 6.98; N, 4.12.

Synthesis of 1-[4-[*N*,*N*-Di(4-iodophenyl)amino]phenyl-2,2-dimethylpropanone, chr 1. A 3.23 g (19.5 mmol) sample of KI and 6.24 g (29.2 mmol) of KIO$_3$ were added to a solution of 3.20 g (9.72 g) of **3** in 100 mL of glacial acetic acid. The flask was equipped with a CaCl$_2$ tube and the mixture was stirred at 70 °C until completion of the reaction (TLC analysis, takes about 3 h). The reaction mixture was cooled and the salts were filtered off and washed copiously with water and dichloromethane. The aqueous phase was extracted with dichloromethane. The combined organic layers were washed with a diluted ammonia solution until pH $\approx$ 8, with a NaHSO$_3$ solution and with brine, and dried over MgSO$_4$. After removal of the solvents, the crude compound was recrystallized from 2-propanol.

Yield: 2.70 g (48%).

Mp: 105 °C.

^{1}H NMR (CDCl$_3$, ppm): δ = 7.75 (d; 2H), 7.60 (d; 4H), 7.00 (d; 2H), 6.88 (d; 4H), 1.38 (s; 9H).

^{13}C NMR (CDCl$_3$, ppm): δ = 206.1, 149.4, 146.2, 138.6, 131.3, 130.4, 127.0, 121.1, 87.7, 43.9, 28.3.

MS: m/z = 581 (M^+), 524 ($M^+ - C_4H_9$), 397 ($M^+ - C_4H_9I$), 270 ($M^+ - C_4H_9I_2$).

λ_{max} (ϵ): 318.5 nm (2.8×10^4 L·mol^{-1}·cm^{-1}).

Anal. Calcd for $C_{23}H_{21}I_2NO$: C, 47.53; H, 3.64; N, 2.41. Found: C, 47.12; H, 3.51; N, 2.35.

Synthesis of 4-[*N*,*N*-Di(4-iodophenyl)amino]benzaldehyde, 4. Under heavy stirring and slightly warming, 95.0 g (347 mmol) of **1** was dissolved in 1 L of glacial acetic acid. Then, 115 g (693 mmol) of KI and 223 g (1.04 mol) of KIO$_3$ were added, and the reaction mixture was stirred for 3 h at 70 °C. After cooling, the salts were filtered off and washed thoroughly with water (500 mL) and dichloromethane (700 mL). The aqueous phase was extracted several times with dichloromethane. The combined organic phases were washed with a diluted ammonia solution until pH $\approx$ 8, with a NaHSO$_3$ solution, and with brine and dried over MgSO$_4$. After removal of the solvents, the crude compound was stirred for 15 min in 500 mL of boiling ethanol; the solution was cooled, and the pure product was isolated by filtration.

Yield: 133 g (73%).

Mp: 142 °C.

^{1}H NMR (CDCl$_3$, ppm): δ = 9.82 (s; 1H), 7.69 (d; 2H), 7.35 (d; 4H), 7.18 (d; 4H), 7.03 (d; 2H).

^{13}C NMR (CDCl$_3$, ppm): δ = 190.4, 152.2, 145.7, 138.9, 131.4, 130.3, 127.6, 120.7, 88.8.

MS: m/z = 525 (M^+), 398 ($M^+ - I$), 271 ($M^+ - I_2$).

Anal. Calcd for $C_{19}H_{13}I_2NO$: C, 43.46; H, 2.50; N, 2.67. Found: C, 43.21; H, 2.39; N, 2.44.

Synthesis of 2-[3-[2-[4-[*N*,*N*-Di(4-iodophenyl)amino]phenyl]ethenyl]-5,5-dimethyl-2-cyclohexenylidene]-1,3-propanedinitrile, chr 2. To a solution of 13.1 g (25.0 mmol) of **4** and 5.19 (27.8 mmol) of **5** in dry DMF were added 2.5 mL of glacial acetic acid, 2.5 mL of acetic acid anhydride, and 4.5 mL of piperidine. The flask was equipped with a CaCl$_2$ tube, and the mixture was stirred overnight at 60 °C. After cooling, the reaction mixture was poured into iced water. The precipitate was filtered off, thoroughly washed with a NaHCO$_3$ solution and with brine, and dried. The crude reaction product was purified by column chromatography (silica gel; eluent: hexane/dichloromethane 20/80 (v/v)) and recrystallized from toluene/hexane and isolated as a dark red solid.

Yield: 13.5 g (78%).

Mp: 137−139 °C.

^{1}H NMR (CDCl$_3$, ppm): δ = 7.59 (d; 4H), 7.39 (d; 2H), 7.03 (d; 2H), 7.01 (d; J = 16.1 Hz; 1H), 6.88 (d; J = 16.1 Hz; 1H), 6.87 (d; 4H), 6.83 (s; 1H), 2.61 (s; 2H), 2.47 (s; 2H), 1.09 (s; 6H).

^{13}C NMR (CDCl$_3$, ppm): δ = 169.1, 154.0, 148.1, 146.3, 138.6, 130.2, 129.0, 128.9, 128.2, 126.7, 125.3, 123.0, 113.7, 112.9, 87.4, 43.0, 39.2, 32.0, 28.0.

MS: m/z = 693 (M^+).

λ_{max} (ϵ): 471.5 nm (2.1×10^4 L·mol^{-1}·cm^{-1}).

Anal. Calcd for $C_{31}H_{25}I_2N_3$: C, 53.70; H, 3.63; N, 6.06. Found: C, 53.49; H, 3.47; N, 5.98.

Synthesis of 2-[2-[4-[*N*,*N*-Di(4-iodophenyl)amino]phenyl]ethenyl]thiophene, 7. To a solution of 66.5 g (127 mmol) of **4** and 55.5 g (127 mmol) of **6** in 200 mL of dry THF was added 190 mL (190 mmol, 1 M in ethanol) of a NaOEt solution. The reaction mixture was refluxed for 4 h under argon atmosphere. Then, 150 mL of ethanol was added, and THF was evaporated off under reduced pressure. After cooling, the solids were filtered off and redissolved in THF, and the organic layer was washed with water (to remove inorganic salts) and dried over MgSO$_4$. Evaporation of the solvent yielded pure **7** as a mixture of cis and trans isomers (50/50).

Yield: 65.6 g (86%).

Mp: 116 °C (mixture of isomers).

^{1}H NMR (CDCl$_3$, ppm): cis δ = 7.52 (d; 4H), 7.26 (d; 2H), 7.10 (m; 1H), 7.00 (m; 3H), 6.80 (m; 5H), 6.64 (d; J = 11,9 Hz; 1H), 6.48 (d; J = 11,9 Hz; 1H); trans δ = 7.52 (d; 4H), 7.34 (d; 2H), 7.10 (m; 2H), 7.00 (m; 4H), 6.80 (m; 5H).

^{13}C NMR (CDCl$_3$, ppm): δ = 146.9, 146.8, 145.9, 142.9, 139.7, 138.3, 132.5, 130.1, 128.3, 128.1, 127.6, 127.4, 127.3, 126.5, 126.0, 125.4, 124.4, 124.2, 123.0, 120.1, 86.2, 86.0.

MS: m/z = 605 (M^+), 478 ($M^+ - I$), 351 ($M^+ - I_2$).

Anal. Calcd for $C_{24}H_{17}I_2NS$: C, 47.63; H, 2.83; N, 2.31. Found: C, 47.38; H, 2.76; N, 2.26.

Synthesis of 2-[2-[4-[*N*,*N*-Di(4-iodophenyl)amino]phenyl]ethenyl]thien-5-al, 8. Under argon atmosphere, 50 mL (100 mmol, 2 M in THF) of a LDA solution was added dropwise to a solution of 45.4 g (75.0 mmol) of **7** in 150 mL of dry THF at −78 °C. The reaction mixture was warmed to 0 °C and stirred for 30 min. Then, 17 mL of dry DMF was added at −40 °C, and the mixture was stirred for 1 h at room temperature, after which 400 mL of a HCl solution (0.1 M) was carefully added. After 2 h of vigorously stirring, the product was extracted with dichloromethane and the combined organic layers were washed with a saturated NaHCO$_3$ solution and with brine and dried over MgSO$_4$. The crude reaction product was purified by column chromatography (silica gel; eluent: hexane/dichloromethane 40/60 (v/v)) and isolated as a mixture of cis and trans isomers (cis/trans 40/60). Separation of the isomers could be accomplished by column chromatography (silica gel; eluent: hexane/dichloromethane 40/60 (v/v)), if relative small qualities are used (approximately 10 g of **8** for 300 g of silica gel)

Yield: 37.2 g (78%).

Mp: 143.5 °C (trans), 128.2 °C (cis).

^{1}H NMR (CDCl$_3$, ppm): cis δ = 9.82 (s; 1H), 7.58 (d; 4H), 7.56 (d; J = 4.0 Hz; 1H), 7.22 (d; 2H), 7.08 (d; J = 4.0 Hz; 1H), 7.02 (d; 2H), 6.86 (d; 4H), 6.75 (d; J = 11,7 Hz; 1H), 6.65 (d; J = 11,7 Hz; 1H); trans δ = 9.85 (s; 1H), 7.65 (d; J = 4.0 Hz; 1H), 7.56 (d; 4H), 7.38 (d; 2H), 7.12 (d; J = 4.0 Hz; 1H), 7.10 (s; 2H), 7.02 (d; 2H), 6.84 (d; 4H).

^{13}C NMR (CDCl$_3$, ppm): cis δ = 182.8, 149.4, 146.9, 146.6, 142.6, 138.5, 136.0, 133.2, 131.1, 129.9, 129.0, 126.4, 124.1, 122.5, 86.5; trans δ = 182.5, 152.7, 147.2, 146.6, 141.3, 138.5, 137.3, 132.1, 130.8, 128.1, 126.4, 126.3, 123.7, 119.6, 86.8.

MS: m/z = 633 (M^+), 506 ($M^+ - I$).

Anal. Calcd for $C_{25}H_{17}I_2NOS$: C, 47.42; H, 2.71; N, 2.21. Found: C, 47.14; H, 2.58; N, 2.09.

Synthesis of 4-[5-[2-[4-[*N*,*N*-Di(4-iodophenyl)amino]phenyl]ethenyl]2-thienylmethylidene]-3-phenylisoxazol-5-one, chr 3. To a solution of 9.50 g (15.0 mmol) of **8** (mixture of cis and trans) and 3.90 g (24.2 mmol) of **9** in 150 mL of chloroform was added 0.5 mL of piperidine. The flask was equipped with a Soxhlet extraction apparatus, containing a thimble, filled with molecular sieves. The reaction mixture was refluxed overnight. After removal of the solvent, the crude reaction product was recrystallized from ethanol. Pure *trans*-**10** was obtained as a red solid.

Yield: 9.37 g (79%).

Mp: 146.3 °C.

^{1}H NMR (CDCl$_3$, ppm): $\delta = 7.83$ (d; $J = 4.2$ Hz; 1H), 7.68 (s; 1H), 7.60 (m; 5H), 7.57 (d; 4H), 7.42 (d; 2H), 7.29 (d; $J = 16.3$ Hz; 1H), 7.20 (d; $J = 4.2$ Hz; 1H), 7.16 (d; $J = 16.3$ Hz; 1H), 7.05 (d; 2H), 6.88 (d; 4H).

^{13}C NMR (CDCl$_3$, ppm): $\delta = 169.5$, 163.4, 158.4, 147.6, 146.4, 143.8, 140.6, 138.5, 135.1, 133.9, 130.8, 130.6, 129.3, 128.5, 128.4, 127.9, 127.0, 126.6, 123.4, 119.4, 111.5, 87.1.

MS: $m/z = 776$ (M^+).

$\lambda_{\max}$ (ϵ): 519.0 nm (4.2×10^4 L·mol^{-1}·cm^{-1}).

Anal. Calcd for $C_{34}H_{22}I_2N_2O_2S$: C, 52.60; H, 2.86; N, 3.61. Found: C, 52.31; H, 2.74; N, 3.48.

Synthesis of *N,N'*-Diethyl-1-[5-[2-[4-[*N,N*-di(4-iodophenyl)amino]phenyl]ethenyl]2-thienylmethylidene]-(1*H*,3*H*,5*H*)-pyrimidine-2,4-dion-6-thione, chr 4.. A solution of 3.50 g (5.53 mmol) of *trans*-**8** and 1.16 g (5.81 mmol) of **10** was stirred for 2 h at room temperature. The reaction mixture was poured into water and the precipitate was filtered off and washed with water. Finally, the crude reaction product was recrystallized from ethanol to yield a dark purple solid.

Yield: 4.16 g (92%).

Mp: 226−232 °C.

^{1}H NMR (CDCl$_3$, ppm): $\delta = 8.63$ (s; 1H), 7.81 (d; $J = 4.2$ Hz; 1H), 7.59 (d; 4H), 7.43 (d; 2H), 7.37 (d; $J = 16.3$ Hz; 1H), 7.27 (d; $J = 4.2$ Hz; 1H), 7.17 (d; $J = 16.3$ Hz; 1H), 7.05 (d; 2H), 6.88 (d; 4H), 4.61 (m; 4H), 1.35 (m; 6H).

^{13}C NMR (CDCl$_3$, ppm): $\delta = 178.6$, 161.1, 160.4, 160.0, 149.2, 147.7, 147.4, 146.4, 138.6, 136.1, 130.6, 128.4, 127.0, 126.6, 123.3, 119.6, 109.6, 87.1, 44.0, 43.2, 12.5, 12.4.

MS: $m/z = 815$ (M^+), 688 ($M^+ - $ I), 605 ($M^+ - C_9H_{10}N_2O_2S$).

$\lambda_{\max}$ (ϵ): 538.5 nm (5.2×10^4 L·mol^{-1}·cm^{-1}).

Anal. Calcd for $C_{33}H_{27}I_2N_3O_2S_2$: C, 48.60; H, 3.34; N, 5.15. Found: C, 48.37; H, 3.18; N, 5.04.

Synthesis of 2-Dicyanomethylene-3-cyano-4-[2-[5-[2-[4-[*N,N*-di(4-iodophenyl)amino]phenyl]ethenyl]2-thienyl]-ethenyl]-5,5-dimethyl-(2*H*,5*H*)-furan, chr 5. To a solution of 12.7 g (20.0 mmol) of **8** (mixture of cis and trans) and 4.78 g (24.0 mmol) of **11** in 150 mL of chloroform was added 1.0 mL of triethylamine. The flask was equipped with a Soxhlet extraction apparatus, containing a thimble filled with molecular sieves, and the reaction mixture was refluxed overnight. After removal of the solvent, the crude reaction product was purified by column chromatography (silica gel; eluent: dichloromethane), yielding pure *trans*-**14** as a dark blue solid.

Yield: 8.80 g (54%).

Mp: >275 °C dec.

^{1}H NMR (CDCl$_3$, ppm): $\delta = 7.78$ (d; $J = 15.7$ Hz; 1H), 7.59 (d; 4H), 7.40 (m; 3H), 7.11 (d; $J = 5.1$ Hz; 1H), 7.05 (m; 4H), 6.87 (d; 4H), 6.65 (d; $J = 15.7$ Hz; 1H), 1.78 (s; 6H).

^{13}C NMR (CDCl$_3$, ppm): $\delta = 175.5$, 172.9, 152.2, 147.6, 146.4, 138.6, 138.4, 133.0, 130.5, 128.3, 128.0, 126.6, 123.4, 112.0, 111.2, 110.8, 97.3, 97.1, 87.1, 56.8, 26.5.

MS: $m/z = 814$ (M^+), 688 ($M^+ - $ I), 562 ($M^+ - I_2$).

$\lambda_{\max}$ (ϵ): 568.5 nm (4.8×10^4 L·mol^{-1}·cm^{-1}).

Anal. Calcd for $C_{36}H_{24}I_2N_4OS$: C, 53.09; H, 2.97; N, 6.88. Found: C, 52.87; H, 2.86; N, 6.59.

Synthesis of the Polymers. A typical procedure is as follows: A solution of 156 mg (200 μmol) **(*S*)-12**, 200 μmol of diiodo-substituted chromophore (**chr 1**−**5** or a combination thereof), 4.58 mg (5.0 μmol) of Pd$_2$dba$_3$, and 12.3 mg (40.0 μmol) of AsPh$_3$ in 10 mL of dry THF was purged with argon and then refluxed for 64 h. After cooling, the polymer was precipitated in methanol and filtered. For purification, the polymer was redissolved in THF, precipitated in methanol and filtered. This procedure was repeated twice.

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