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Synthesis and Characterization of Novel Optically Active Polyarylene Vinylenes with Controlled Effective Conjugation Length[†]

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New chiral and soluble binaphthyl derivatives (**12** and **13**) endowed with carboxaldehyde or cyanomethyl functional groups have been prepared as suitable building blocks for the synthesis by Knoevenagel condensation of a series of optically active block copolymers (**1**−**7**) with controlled effective conjugation length. A variety of functionalized co-monomers (**14**−**19**) have been prepared by different synthetic procedures to be used in further polymerization reactions with binaphthyl derivatives **12** and **13**. Depending upon the nature of the co-monomers, it is possible to tune the wavelength of the new polymers, which is very close to that of the respective repeating units. Fluorescence measurements on polymers **1**−**3** reveal a strong blue-green emission with Stokes shifts of 74−107 nm. Theoretical calculations at the semiempirical AM-1 level have been carried out on model compounds, and the calculated torsion angles are in agreement with the electronic spectra data. Finally, the redox properties of the polymers prepared (**1**−**7**) were determined by cyclic voltammetry, and an amphoteric behavior with oxidation potentials ranging from 1.1 to 1.6 V and reduction potentials close to −1.5 V was found.

Introduction

The design of tailor-made π-conjugated polymers has been a subject of intensive research during the past decade because of their potential applications as novel materials for optoelectronics[1] given that they combine the optical and electronic properties of semiconductors with the processing advantages and mechanical properties of polymers.

The HOMO−LUMO gap in semiconducting polymers is roughly determined by the extent of π delocalization along the backbone, the so-called effective conjugation length, which is responsible for the emitting properties of these materials. Introduction of nonconjugated segments into conjugated polymer backbones results in the confinement of π electrons in the conjugated fragment. Materials of this type can be seen as long chains of separated small dye molecules connected by a variety of nonconjugated spacer units including ether,[2] ester,[3] amide,[4] or sililene[5] groups.

Binaphthyl derivatives are optically active materials, their chirality being derived from the restricted rotation of the two naphthalene rings. The angle between the rings ranges from 60 to 120°, and therefore conjugation between the two naphthalene units is minimal.[6] Thus, the conjugated system in polymers containing binaphthyl units is confined to the region between two binaphthyl units (Figure 1a).[7−9] In this paper, we describe the synthesis of a family of chiral conjugated−nonconjugated block copolymers containing binaphthyl units in order to efficiently tune the conjugation length. The structure of these block copolymers can be schematically represented as in Figure 1b with consecutive conjugated systems linked to each other in a noncoplanar way.

Although different luminescent fragments as well as hole-transport and electron-transport materials have been integrated in conjugated−nonconjugated polymeric

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[†] This work is dedicated to Professor Michael Hanack on the occasion of his retirement.

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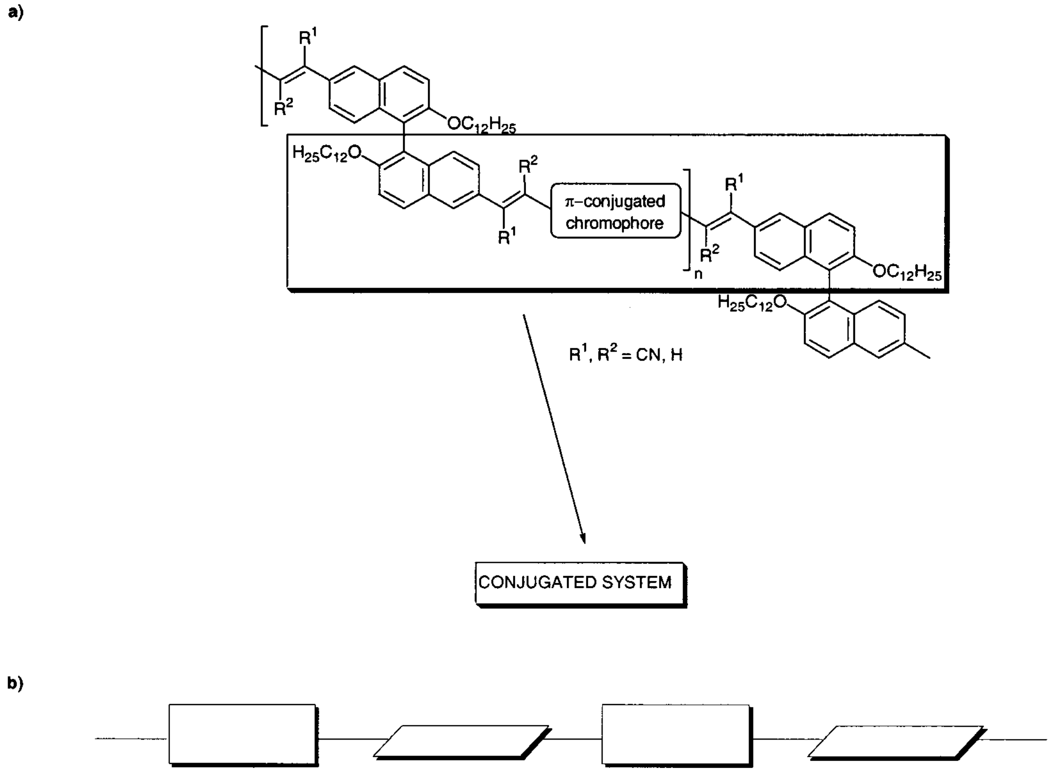

Figure 1. Structure of the conjugated−non-conjugated block copolymers showing the conjugated region.

systems,[1b] conjugated oligomers present special interest from a chemical point of view because of the possibility to tune their wavelength of emission as well as their electron affinity and ionization potential by means of synthetic strategies.[10] Thus, in this paper, we describe a synthetic strategy which allows us to copolymerize bifunctionalized conjugated oligomers and binaphthyl derivatives to yield conjugated−nonconjugated block copolymers in which the HOMO−LUMO band gap can be efficiently tailored by the choice of appropriate conjugated oligomers.

Results and Discussion

The preparation of these main chain chiral cyano-containing binaphthyl-based copolymers **1**−**7** (Figure 2) was carried out using the Knoevenagel condensation[11] of appropriately functionalized monomers.

This type of polymerization allows the introduction of nitrile groups on the vinylene linkages of PPV derivatives.[12] The introduction of the high electron affinity CN group to a π-conjugated polymer system lowers the energy level of the LUMO[13] and reduces the barrier to the electron injection in light-emitting devices (LED). Thus, Holmes and co-workers showed that PPV derivatives containing cyano groups on the vinylene linkage present high electron affinity and therefore exhibit a relatively low threshold voltage and high quantum efficiency in LED devices even using stable aluminum electrodes.[11]

To be able to perform this type of polymerization, appropriate monomeric units have been synthesized.

1. Synthesis of Binaphthyl Monomers. The synthesis of suitably functionalized binaphthyl derivatives (**12** and **13**) is depicted in Scheme 1. The resolution of the (±)-1,1′-bi-2-naphthol was carried out by using (−)-*N*-benzylcinconidinium chloride as the chiral resolution reagent,[14] and the enantiomerically pure *R* isomer was used in the subsequent reactions.

Two different synthetic routes previously described in the literature for analogous compounds have been followed in order to synthesize derivatives (*R*)-**12** and (*R*)-**13**. The first route involves selective bromination of the 1,1′-binaphthalenic unit in the 6,6′ positions by using bromine in dichloromethane to yield derivative (*R*)-**9**. Subsequent Williamson reaction of (*R*)-**9** with dodecyl bromide using potassium carbonate as the base afforded derivative (*R*)-**11**. Compound (*R*)-**11** could be also obtained by first introducing the alkyl chains to yield (*R*)-**10** followed by a selective bromination reaction. In our hands, the first synthetic route has proven to be more

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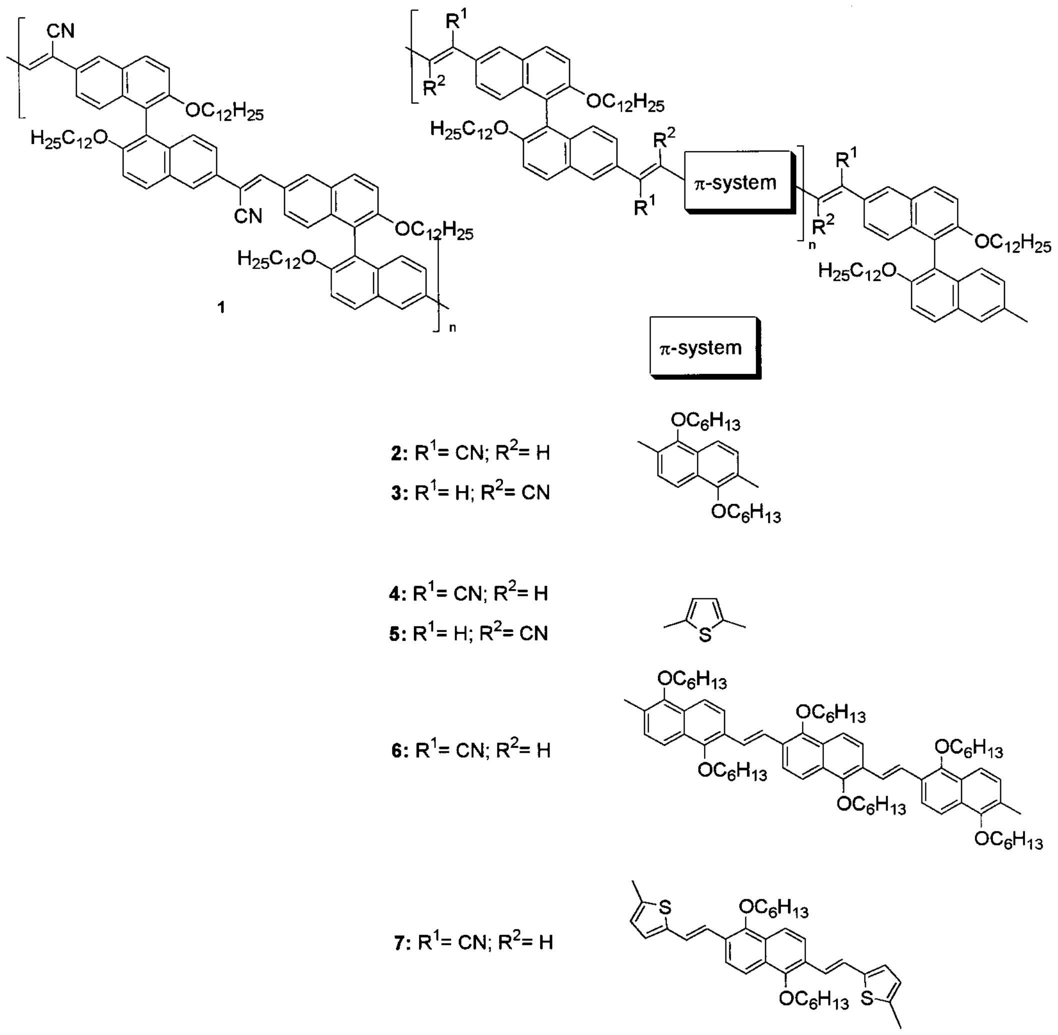

Figure 2. Main chain chiral cyano-containing binaphthyl-based copolymers **1**−**7**.

effective (overall yield 79%) in comparison with the second one (65%), which is in agreement with previous bibliographic data.[15] The presence of the long alkyl chains in the monomeric units is important in order to obtain soluble polymers useful to fabricate large area thin films for LEDs or photovoltaic applications. After the Bouveault formylation reaction[16] of dibromo derivative (*R*)-**11**, the corresponding diformyl derivative (*R*)-**12** was obtained. Finally, the bis(cyanomethyl) derivative (*R*)-**13** could be obtained from dialdehyde (*R*)-**12** upon treatment with tosylmethylisocyanide (TosMIC) and a base.[17] This reaction is carried out in one single step, offering yields similar to those obtained by classical methods that involve reduction of the aldehyde to the corresponding alcohol and transformation of the alcohol to the halogenated derivative by nucleophilic substitution followed by a new nucleophilic substitution to transform the bromomethyl derivative into the corresponding cyanomethyl analogue.

2. Synthesis of Functionalized Co-monomers. The remaining monomers used in the polymerization reactions are depicted in Figure 3.

Naphthalene derivatives **14** and **15** were synthesized by following the multistep synthetic route developed by Hanack and co-workers.[12a] Although 2,5-thiophenedicarboxaldehyde (**16**) was commercially available, the related bis(cyanomethyl) derivative **17** was prepared following a previously described synthetic route.[18] Reduction of **16** to the bis(hydroxymethyl) derivative was followed by chlorination with thionyl chloride in dichloromethane and finally cyanation with sodium cyanide in dimethylformamide. The synthesis of the versatile synthon[19] diformyloligonaphthylenevinylene **18** has been carried out by using the synthetic route recently reported by our group.[20] Finally, oligomer **19** has been synthesized as depicted in Scheme 2. Wittig reaction of commercially available thiophene derivative **21** with 1,5-dihexyloxy-2,6-bis[triphenylphosphonio(methyl)]naphthalene **20** afforded the dibromo derivative **22** as a mixture of the trans,trans isomer together with the cis,trans and cis,cis forms. Iodine-catalyzed thermal isomerization of the mixture was carried out in xylene to afford the pure *trans,trans*-**22**. Treatment of **22** with copper cyanide in

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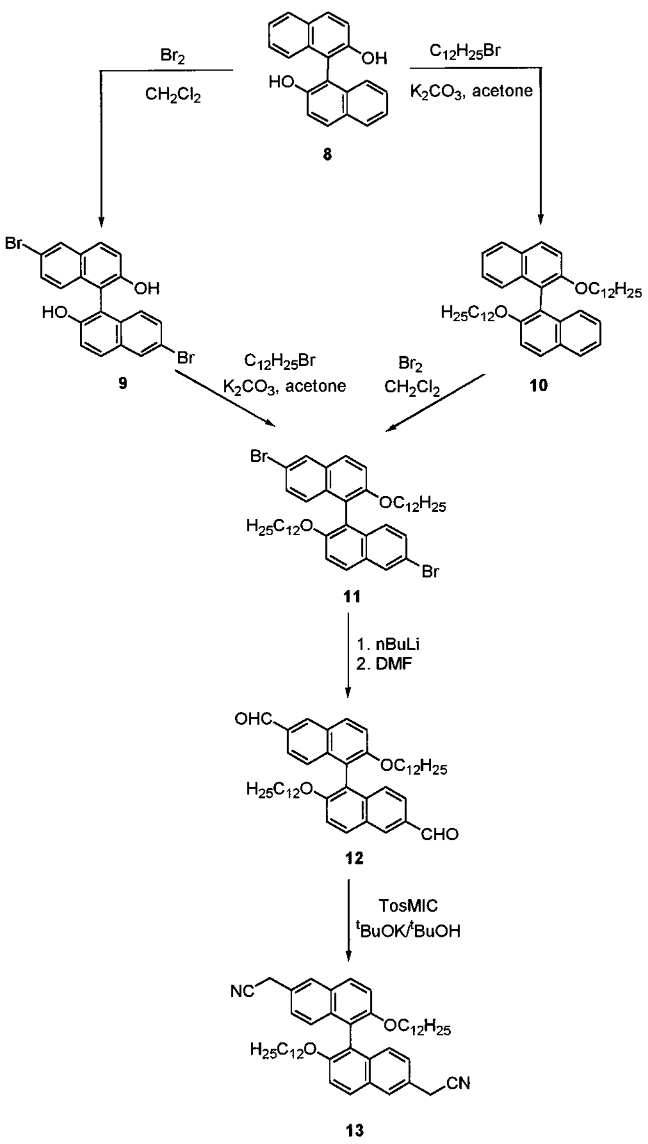
Scheme 1



dimethylformamide[21] led to the dicyano derivative **23**, which upon reduction with DIBAL-H yielded the target compound **19**.

3. Synthesis and Characterization of Binaphthyl-Containing Copolymers. As previously stated, syntheses of polymers **1**−**7** were carried out by using the Knoevenagel condensation polymerization, between suitable monomers containing either two aldehyde groups (**12**, **14**, **16**, **18**, and **19**) or two cyanomethyl functionalities (**13**, **15**, and **17**). Equimolecular amounts of dialdehyde and bis(cyanomethyl) derivative were dissolved in a mixture of *tert*-butyl alcohol and tetrahydrofuran, and the solution was heated to 50 °C. After addition of tetrabutylammonium hydroxide and potassium *tert*-butoxide, a colored solid precipitated in all cases. The resulting pastelike polymeric product was fully precipitated from the solution by further addition of methanol, collected, and thoroughly washed with methanol and diethyl ether to remove ionic species and unreacted compounds. The polymerization results and optical properties of these new compounds are summarized in Table 1.

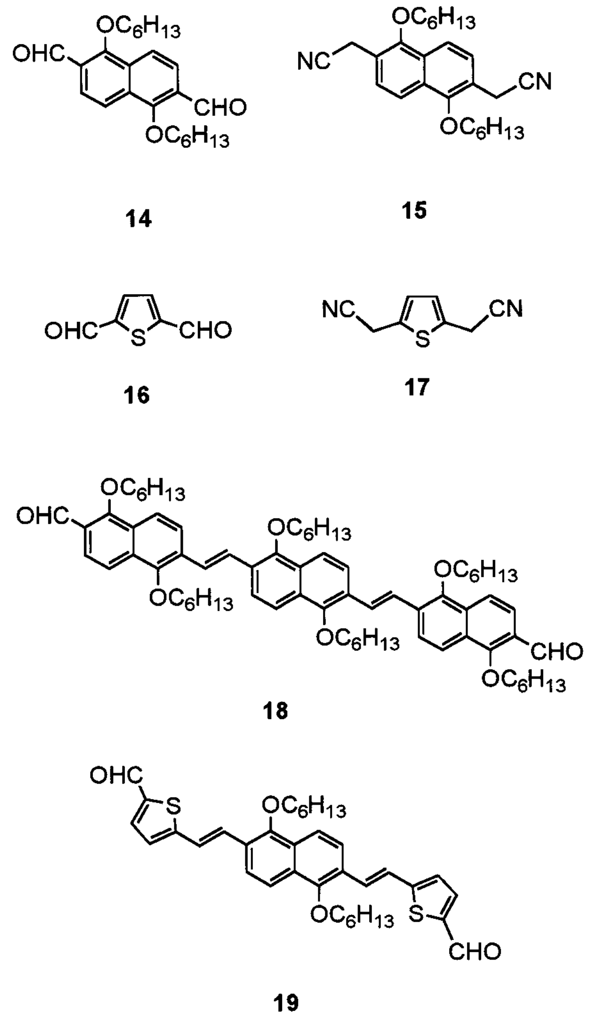


Figure 3. Monomers used in the polymerization reactions.

The average molecular weights (M_w) of the polymers, determined by gel permeation chromatography (GPC) using polystyrene standards, were between 9400 (polydispersity of 1.62) for polymer **2** and 55 185 (polydispersity of 5.61) for polymer **7**. The reaction yields were in all cases above 75%, and the obtained polymers were soluble in common organic solvents such as tetrahydrofuran, chloroform, or dichloromethane. The incorporation of the flexible long alkyl chains both in the naphthalene and binaphthyl units affords rather soluble materials. Furthermore, the lack of planarity of the binaphthyl system can reduce the characteristic chain stiffness of conjugated polymers, thus contributing to the enhanced solubility of these materials.

FTIR, ^{1}H NMR, and UV−vis spectrometry characterized the chemical structures of the resulting polymers. Comparison of the polymers FTIR spectra with that of monomers shows a drastic decrease of the bands at around 1680 cm^{-1}, which is expected to be present for the strong aldehyde−carbonyl stretching band of the dialdehyde monomer. On the other hand, a new sharp absorption peak in the region 2210−2220 cm^{-1} appears in the polymers, corresponding to the conjugated nitrile moiety.

^{1}H NMR spectra of polymers exhibit the characteristic vinylene proton at around δ 8.1 together with the expected signals of the binaphthyl units (one singlet at δ 8.2−8.3 corresponding to the H-5,5′ of the binaphthyl unit and four doublets in the aromatic region because of the four remaining protons on the binaphthyl system).

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Scheme 2

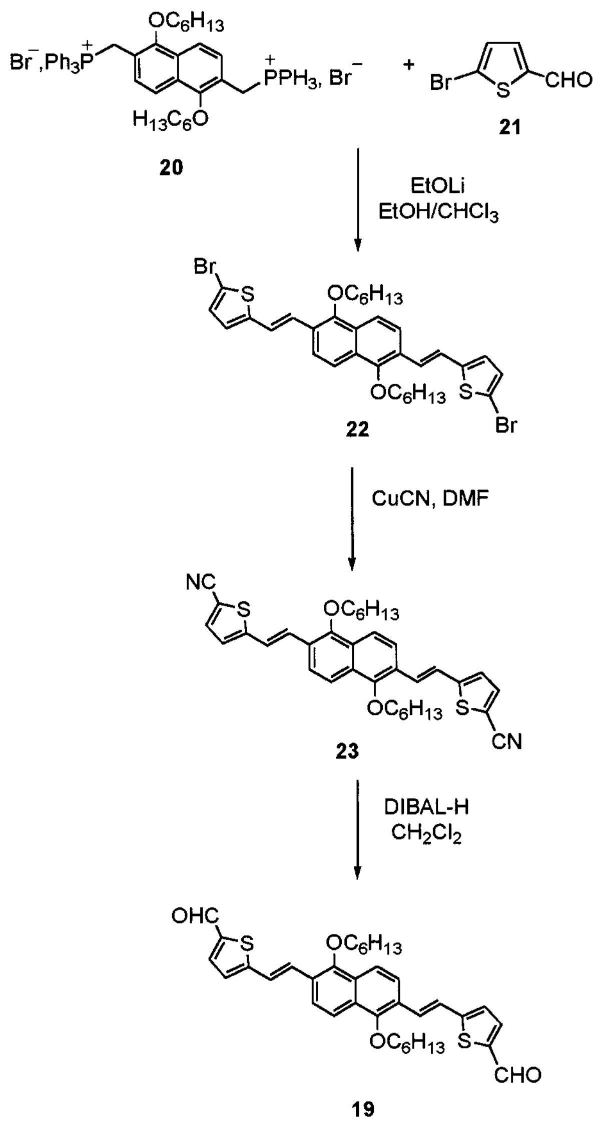

Table 1. Polymerization Results and Optical and Redox Properties of the Novel Compounds 1−7

compd	yield (%)	M_n[a]	M_w[a]	PDI[a]	UV−vis ($\lambda_{max,nm}$)[b]	E_{ox} (V)[c,d]	E_{red} (V)[c,d]
1	90	164 000	22 000	7.62	382	1.19	−1.52
2	80	15 300	9400	1.62	422	1.34	−1.54
3	75	27 500	12 200	2.27	378	1.32	−1.54
4	99	8496	29 440	3.47	472	1.30	−1.55
5	93	9922	33 183	3.34	454	1.62	−1.59
6	90	7210	11 382	1.58	438	1.44	−1.51
7	90	9837	55 185	5.61	482	1.32	−1.61

[a] M_n (number average), M_w (weight average) molecular weights, and PDI (polydispersity) of the polymers were determined by gel permeation chromatography (GPC) using polystyrene standards. [b] In dichloromethane solutions. [c] In dichloromethane solutions using Bu_4NClO_4 (0.3 mg mL^{-1}; SCE reference electrode and glassy carbon as the working electrode). [d] Values indicated correpond respectively to the onset oxidation (E_{ox}) and reduction (E_{red}) potentials.

Dihexyloxynaphthalene-containing polymers show two additional doublets in the aromatic region, whereas thiophene-containing polymers exhibit an additional singlet at δ 7.4. The methylene protons adjacent to the oxygen atom in the hexyloxy and dodecyloxy groups are observed as multiplets at around δ 4.0. The remaining alkyl protons are observed at δ 0.8−1.9.

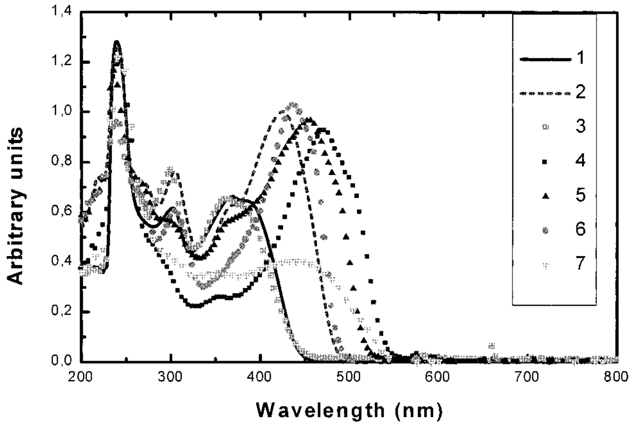

Figure 4. UV−vis spectra of polymers **1**−**7**.

Because the polymers have been synthesized by using enantiomerically pure (*R*)-binaphthyl derivatives (**12** and **13**), main-chain chiral polymers have been obtained with the following observed optical rotations ([α]$_D$): −305 (*c* 0.2, CHCl$_3$) for (*R*)-**1**, −832 (*c* 1.3, CHCl$_3$) for (*R*)-**2**, −220 (*c* 0.7, CHCl$_3$) for (*R*)-**3**, −1800 (*c* 3 × 10^{-4}, CHCl$_3$) for (*R*)-**4**, −516 (*c* 8 × 10^{-4}, CHCl$_3$) for (*R*)-**5**, −490 (*c* 4 × 10^{-4}, CHCl$_3$) for (*R*)-**6**, and −362 (*c* 5 × 10^{-4}, CHCl$_3$) for (*R*)-**7**. Thus, these polymers rotate the plane of polarized light in the direction opposite to that of the binaphthyl dicyanomethyl species (*R*)-**13** {[α]$_D$: +34 (*c* 0.6, CHCl$_3$)} and in the same direction as the binaphthyldicarbaldehyde (*R*)-**12** {[α]$_D$: −56 (*c* 0.7, CHCl$_3$)}. Optically active conjugated polymers are potentially useful in areas such as asymmetric electrosynthesis, polarization-sensitive electro-optical devices, nonlinear optics, and enantioselective sensing.[7] Furthermore, various studies on chiral π-conjugated polymers substituted with enantiomerically pure pendant groups or chiral dopants demonstrate a strong optical rotation and circular dichroism (CD) of the $\pi-\pi^*$ transition.[22] Circularly polarized light can be transformed into linearly polarized light with little loss by using a suitable quarter-wave (λ/4) plate. Devices emitting polarized light have proven to be particularly useful as backlights for conventional liquid crystal displays (LCDs), because they could make the polarizer (with its associated cost, weight, and power inefficient absorptive loss) redundant. Most of the methods used[23] to obtain polarized luminescence from conjugated polymers involve the orientation (mechanical, Langmuir−Blodgett deposition, liquid-crystalline self-organization) of highly anisotropic materials into a specific direction. Thus, the possibility to obtain polarized luminescence from chiral light-emitting polymers in combination with a quarter-wave plate can avoid the complicated orientation step. Preliminary studies on polymers (*R*)-**1**−**7** show that they exhibit circular polarization of the fluorescence, and therefore further studies should be focused on this direction.

The UV−vis absorption spectra observed for these polymers are depicted in Figure 4. It is worth mentioning that the presence of additional naphthalene moieties

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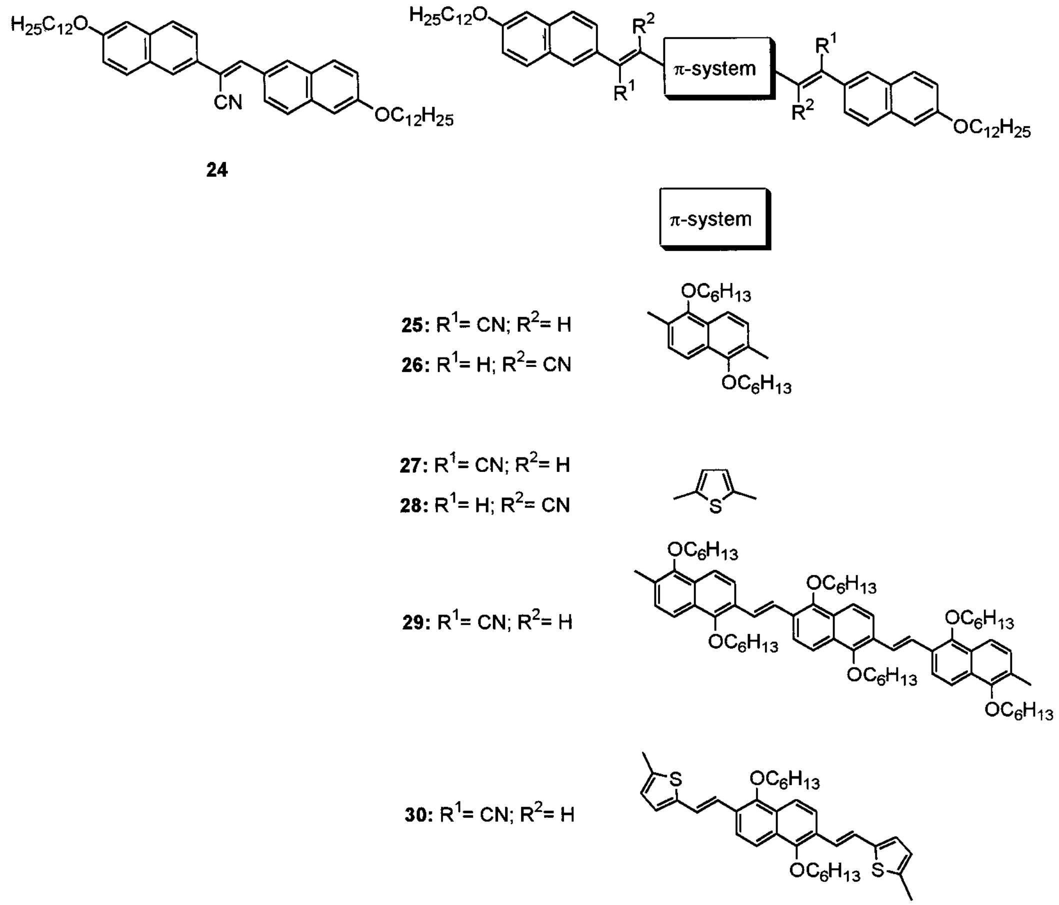


Figure 5. Model compounds **24**–**30** containing the conjugated fragment of the parent polymeric materials **1**–**7**.

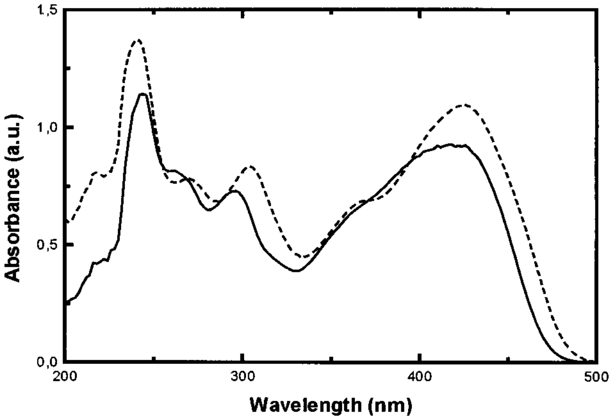
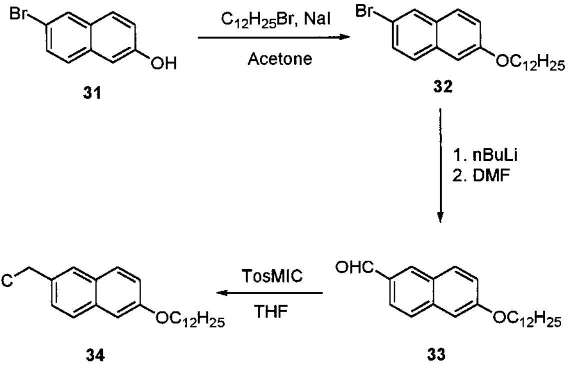


Figure 6. Comparison between the UV–vis spectra of polymer **2** and model compound **25**.

between the binaphthyl units red-shifts the absorption of polymers. Thus, when the two binaphthyl units are linked to each other (polymer **1**), a λ_{max} of 382 nm was observed, whereas λ_{max}'s of 422 and 438 nm were observed after the introduction of one (polymer **2**) and three naphthalene units (polymer **6**), respectively, between the binaphthyl units. We have also introduced the thiophene ring in these systems given that a strong red shift in the absorption values has been reported for polymers containing thienylene vinylene units with nitrile groups on the vinylene moiety.[24] Thus, by simple introduction of one thiophene unit, a 90 nm bathochromic shift was observed (polymer **4**), whereas introduction of the thiophene-containing oligomer **19** between the binaphthyl units shifts the absorption up to 482 nm (polymer **7**). Further red shift may be expected by introduction of longer thienylenevinylene oligomers between the binaphthyl units.

Scheme 3



Compounds **24**–**30** (Figure 5) have been prepared as the repeating units of the binaphthyl-based polymers. Spectroscopic studies show that the absorption wavelengths of these repeating units are very close to those of their corresponding polymers. This demonstrates that the conjugation of the binaphthyl-based polymers is mostly determined by the conjugation within their repeating units, and there is almost no extended conjugation between each adjacent repeating unit in the main

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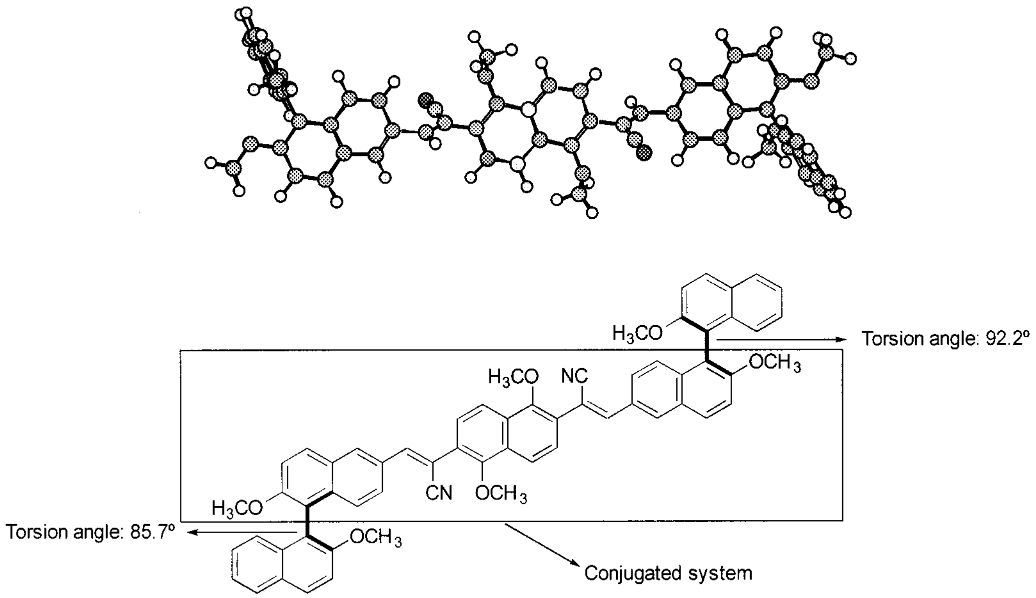

Figure 7. AM1 equilibrium geometry optimized for a model compound of polymer **3**.

chain. In Figure 6 are depicted for comparison purposes the UV−vis spectra of polymer **2** together with that of the model compound **25**.

The synthesis of these compounds has been carried out by Knoevenagel condensation between the monomers **14**−**19** depicted in Figure 3 and the new dodecyloxynaphthalene derivatives **33** and **34**.

The synthesis of these new compounds (**33** and **34**) is depicted in Scheme 3. After reaction of 6-bromo-2-naphthol with dodecylbromide and potassium carbonate with a catalytic amount of sodium iodide in acetone, the corresponding derivative **32** was obtained. Further formylation yielded aldehyde **33**, which upon treatment with TosMIC afforded the cyanomethyl derivative **34**.

To rationalize the above-described UV−vis data for the polymer and model compounds, we have carried out geometry optimization using the Austin Model 1 (AM1) semiempirical technique.[25] We choose this method because previous studies on phenylene and polyene chains have shown that the AM1 method gives good agreement for both bond lengths and torsion angles with data obtained from experimental and Hartree−Fock ab initio calculations.[26] Recently, this method has been successfully used to perform theoretical studies on torsion angles and its effect on the structural and electronic properties of substituted poly(*p*-phenylenevinylene)s.[27] Figure 7 shows the AM1 equilibrium geometry optimized for a model compound of polymer **3** in which the hexyloxy and dodecyloxy chains have been replaced by methoxy substituents.

In agreement with previous bibliographic references, torsion angles of around 90° are observed between both naphthalene units of the binaphthyl moiety, which strongly suggests the lack of conjugation.

AM1 theoretical calculations have been also performed in order to rationalize the blue shift observed in the absorption spectrum of polymer **3** in comparison with polymer **2** (Figure 8).

Although in polymer **2** the nitrile group of the vinylene linkage is close to the naphthalene moiety of the binaphthyl system, in polymer **3** the nitrile group is closer to the dialkoxynaphthalene central ring. In Figure 8 are depicted the AM1-optimized geometries of model compounds of polymers **2** (left) and **3** (right). We have already shown[20] that, in contrast to the parent PPV system, dialkoxy-substituted oligo(naphthylenevinylenes) are not planar because of the steric interactions between the bulk naphthalene system and the vinylene protons. The presence of nitrile groups in the vinylene linkage causes even a larger steric hindrance. Because the steric hindrance of the nitrile group with respect to the alkoxy group in the naphthalene ring is larger than that observed when the nitrile group is closer to the naphthalene ring of the binaphthyl unit, a larger torsion of the chain is observed for polymer **3** (torsion angles of 37 and 50° compared with 35 and 41° observed for polymer **2**). This reduction of the backbone's planarity decreases the degree of conjugation in the system, thus blue-shifting the absorption wavelength values. A different trend is observed for polymers **4** and **5** (Table 1), which can be accounted for by the conjugation of the cyano groups. This finding is in agreement with that observed for the model compounds **27** (λ_{max} 458 nm) and **28** (λ_{max} 432 nm).

Because these polymers emit strong blue-green light under an UV lamp, we decided to carry out fluorescence measurements of selected members of the series (polymers **1**−**3**). The fluorescence spectrum of **1** shows emission maxima at λ_{emi} 475 nm when excited at 382 nm. The fluorescence spectrum of **2** displays λ_{emi} 496 nm when excited at 422 nm, and **3** exhibits an emission maxima of λ_{emi} 485 nm when excited at 378 nm. The Stokes shifts observed are of 93 nm for **1**, 74 nm for **2**, and 107 nm for **3**, which indicates only a small region of coincidence between the absorption and emission (Figure 9). This fact

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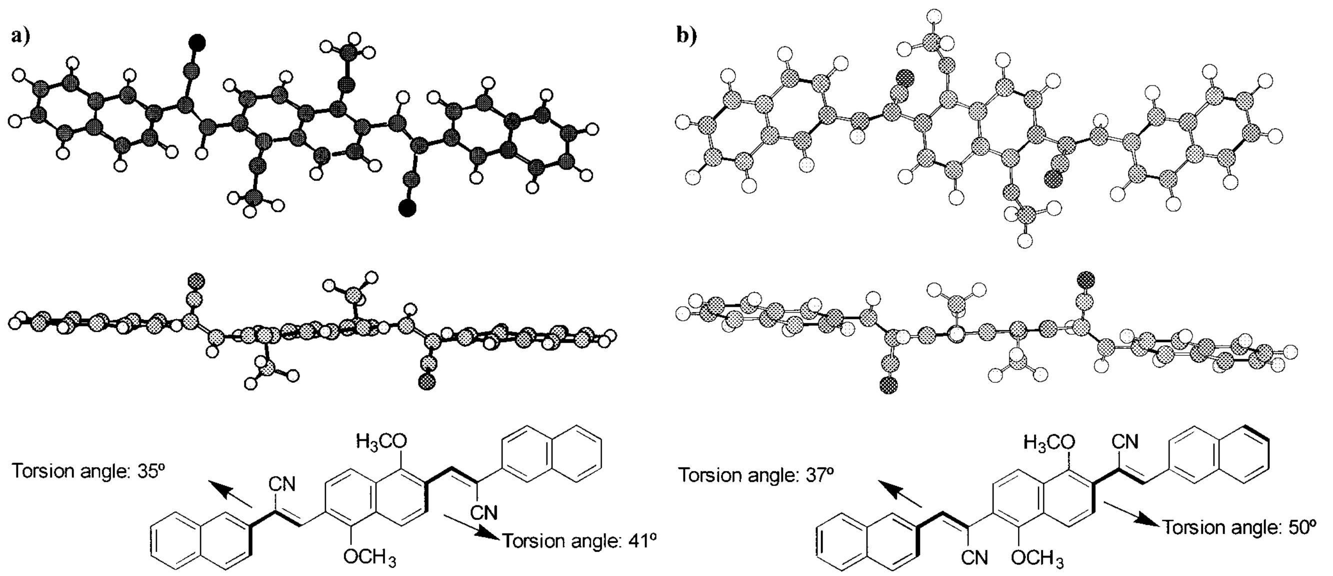

Figure 8. AM1 equilibrium geometry optimized for model compounds showing the steric hindrance of the nitrile group with respect to the alkoxy group in the naphthalene ring.

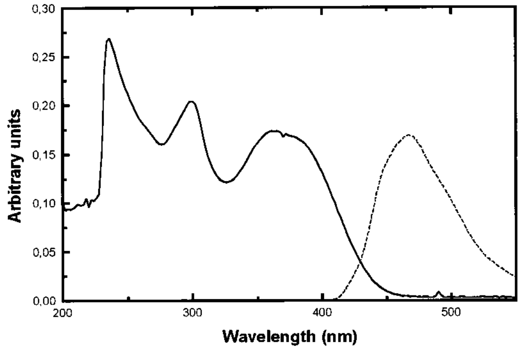

Figure 9. UV–vis and fluorescence spectra obtained for polymer **3**.

indicates that the reabsorption of the emitted light is almost negligible, which is very important in order to avoid undesired loses in the LED performance.

Cyclic voltammetry studies of polymers **1**–**7** were carried out in a three-electrode cell in dichloromethane at room temperature using Bu_4NClO_4 as the supporting electrolyte (0.3 mg mL^{-1}; SCE reference electrode and glassy carbon as the working electrode). It was found that all of the polymers are oxidized at potentials above 1.19 V (vs SCE; Table 1), which is a high value compared with other related polymers (0.6–1.0 V).[24b] On the other hand, all of the polymers were found to be reducible at potentials around −1.5 V (vs SCE). The relatively good acceptor ability of these polymers can be ascribed to the presence of cyanovinylene moieties on the conjugated system. Because of the presence of the π-excedent thiophene system, polymers **4**, **5**, and **7** show the highest reduction potentials.

As previously stated, Holmes and co-workers showed that PPV derivatives containing cyano groups on the vinylene linkage exhibit a relatively low threshold voltage and high quantum efficiency in LED devices, even using stable aluminum electrodes, because of their relatively high electron affinity, which reduces the barrier to the electron injection in light-emitting devices (LED).[11]

Summary

In summary, we have developed a general synthetic route for the preparation of optically active block copolymers containing binaphthyl units. The synthesis of binaphthyl derivatives bifunctionalized with either carboxaldehyde or cyanomethyl groups will allow us to extend this synthetic route to many other difunctionalized chromophores and lumophores. In the present study, we have focused our attention on the preparation of chiral soluble polymers which offer the possibility of tuning both optical and redox properties by means of chemical modification of the monomeric structure. Considering the very large number of functionalized fluorophores synthesized in recent years with specific electrochemical and photophysical properties, we see that a remarkable aspect of this contribution is that it might provide an effective approach to the synthesis of luminescent polymeric materials in which the emission colors, electron affinity, and ionization potentials can be efficiently tailored.

The good solubility imparted by the long alkyl chains and the high electron afinity provided by the cyanovinylene linkage make these types of polymers good candidates for the fabrication of LEDs in which the luminescent properties can be efficiently tailored. Furthermore, because of the main chain chiral character of these polymers, the observation of circularly polarized photo- and electroluminescence can be expected, which may be of use as backlights for conventional liquid crystal displays (LCDs).

Experimental Section

All melting points were measured with a melting point apparatus and are uncorrected. IR spectra were recorded either as KBr pellets or neat films. ^{13}C and ^{1}H NMR spectra were recorded with a 300 MHz for ^{1}H and 75 MHz for ^{13}C spectrometer. Chemical shifts are given as δ values (internal standard: TMS). $[\alpha]_D$ values were determined using the light of a sodium lamp (λ = 589 nm), at room temperature in a cylindric cell with a length of 1 dm and a volume of 1 mL. GPC measurements were carried out using chloroform as the eluent in a system consisting of a pump, a UV detector, and three mStyragel columns of 10^4, 10^3, and 500 Å. The columns were calibrated with a polystyrene standard with a narrow distribution of molecular weights. Semiempirical calculations (AM1) were performed using the program Hyperchem (version 3.0) with a PC compatible at 200 MHz. For each structure, the minimum energy was determined after reminimization. Cyclic voltammograms were recorded on a potentiostat/galvanostat equipped with a software electrochemical analysis by using a GCE (glassy carbon) as working electrode, SCE as reference electrode, Bu_4NClO_4 as supporting electrolyte, and dichloromethane as solvent and at a scan rate of 200 mV/s. (±)-2,2′-Dihydroxy-1,1′-binaphthalene and 6-bromo-2-hydroxynaphthalene are commercially available and were used without further purification. ^{t}BuOH and tetrahydrofuran were dried with sodium, dimethylformamide was dried with calcium hydride, chloroform and dichloromethane were distilled from P_2O_5, and all were distilled before use.

Monomer Syntheses. (*R*)-2,2′-Didodecyloxy-6,6′-diformyl-1,1′-binaphthalene (12). To a solution of 4 g (51 mmol) of (*R*)-6,6′-dibromo-2,2′-didodecyloxy-1,1′-binaphthalene (**11**)[28] in 50 mL of dry tetrahydrofuran (THF) was added dropwise under argon atmosphere 13 mL of a 1.6 M solution of *n*-butyllithium (20 mmol) in hexane, at −78 °C. The reaction was stirred at this temperature for 4 h, and then 2.6 mL (180 mmol) of dry *N*,*N*-dimethylformamide was added. After 1 h, the reaction was allowed to reach room temperature and was poured, under vigorous stirring, on a water/ice/HCl mixture (pH < 1). The mixture was extracted three times with methylene dichloride, and the organic layers were combined and washed twice with water and dried over magnesium sulfate. After vacuum evaporation of the solvent, an orange oil was obtained, which was chromatographically purified (silica gel, hexane/diethyl ether (8:2)) to yield 2.93 g (80%) of **12** as a yellow solid. Mp: 45 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.09 (s, 2 H, CHO), 8.29 (d, 2 H, J = 1.5 Hz), 8.00 (d, 2 H, J = 9.0 Hz), 7.62 (dd, 2 H, J_1 = 8.8, J_2 = 1.6 Hz), 7.49 (d, 2 H, J = 9.0 Hz), 7.19 (d, 2 H, J = 8.8 Hz), 4.01−3.84 (m, 4 H), 1.45−1.00 (m, 40 H), 0.81 (t, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 192.0 (CHO), 157.2, 137.4, 135.0, 132.2, 131.5, 128.0, 126.2, 123.3, 119.8, 115.6, 69.3, 32.0, 29.7, 29.5, 29.4, 29.2, 29.1, 26.0, 22.8, 14.2. FTIR (KBr, cm^{-1}): 3055, 2923, 2852, 1693, 1620, 1593, 1274, 1230. MS (EI) *m*/*z* (%I): 678 (M^+, 100), 510 (30), 342 (59). Anal. Calcd for $C_{46}H_{62}O_4$: C, 81.37; H, 9.21. Found: C, 81.18; H, 9.33.

(*R*)-2,2′-Dicyanomethyl-6,6′-diformyl-1,1′-binaphthalene (13). A solution of 85 mg (43.0 mmol) of tosylmethylisocyanide (TosMIC) in dry THF was added dropwise under argon atmosphere to another solution of 107 mg (0.9 mmol) of potassium *tert*-butoxide in 2 mL of dry THF, and the mixture was cooled to −30 °C. Afterward, a solution of 136 mg (0.2 mmol) of dialdehyde **12** was added and stirred for 30 min at −30 °C. Then 3 mL of methanol was added, and the mixture was heated to 80 °C for 15 min. Then the crude reaction was allowed to reach room temperature, and the solvent was vacuum evaporated. A 1 mL portion of glacial acetic acid and a 20 mL portion of water were added to the solid residue obtained. The mixture was extracted three times with chloroform, and the combined organic layers were washed twice with a 10% $NaHCO_3$ aqueous solution and then with water. After the compound was dried over magnesium sulfate, the solvent was vacuum evaporated to yield an oil residue, which was further purified chromatographically (silica gel, hexane/diethyl ether (7:3)) to afford 70 mg (50%) of **13** as a greenish oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.85 (d, 2 H, J = 9.0 Hz), 7.83 (s, 2 H), 7.36 (d, 2 H, J = 9.0 Hz), 7.07−6.97 (m, 4 H), 3.93 (t, 4 H), 3.82 (s, 4 H), 0.91−0.61 (m, 40 H), 0.54 (t, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 155.0, 133.5, 129.0, 128.9, 126.8, 126.4, 125.8, 124.6, 120.1, 117.9, 116.3, 69.6, 31.9, 30.6, 30.3, 29.7, 29.5, 29.4, 29.3, 29.1, 25.6, 23.5, 22.7, 14.1. FTIR (neat film, cm^{-1}): 2923, 2852, 2252, 1597, 1275, 1248. MS (EI) *m*/*z* (%I): 700 (M^+, 100), 532 (32), 364 (84). Anal. Calcd for $C_{48}H_{64}O_2N_2$: C, 82.24; H, 9.20; N, 4.00. Found: C, 82.30; H, 9.30; N, 3.83.

2,6-Bis[2-(5-bromo-2-thienyl)vinyl]-1,5-bis(hexyloxy)-naphthalene (22). To a stirred solution of 300 mg (0.28 mmol) of triphenylphosphonium salt **20** in 20 mL of dry ethanol, heated to 50 °C and under argon atmosphere, was added 0.07 mL of formylthiophene **21** and 0.7 mL of a 1 M solution of sodium ethoxide in ethanol. The formation of a yellow precipitate which consisted of the pure trans,trans compound **22** was observed. The precipitate was filtered and washed with methanol to afford the pure trans,trans compound. The mother liquors were vacuum evaporated, and the solid residue was chromatographed (silica gel, hexane/dichloromethane (9:1)) to yield a mixture of isomers. This mixture was suspended in 10 mL of xylene and heated to reflux for 24 h, after addition of a catalytic amount of iodine. After the reaction mixture was cooled, methanol was added, leading to a second crop of pure trans,trans isomer. Mp: 167−169 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.78 (d, 2 H, J = 8.8 Hz), 7.60 (d, 2 H, J = 8.9 Hz), 7.32 (d, 2 H, J_{trans} = 16.3 Hz), 7.20 (d, 2 H, J_{trans} = 16.1 Hz), 6.98 (d, 2 H, J = 3.9 Hz), 6.84 (d, 2 H, J = 3.7 Hz), 3.91 (t, 4 H), 1.89 (q, 4 H), 1.59 (m, 4 H), 1.37 (m, 8 H), 0.59 (t, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 153.3, 130.6, 129.7, 126.4, 125.9, 123.4, 122.0, 118.8, 111.3, 75.9, 31.9, 30.5, 26.2, 22.8, 14.2. FTIR (KBr, cm^{-1}): 2926, 2856, 1466, 1260, 1234. EM (EI) *m*/*z* (%I): 702 (M^+, 100), 617 (38), 533 (18), 453 (38). Anal. Calcd for $C_{34}H_{38}Br_2O_2S_2$: C, 58.28; H, 5.47; S, 9.13. Found: C, 57.82; H, 5.55; S, 9.04.

2,6-Bis[2-(5-cyano-2-thienyl)vinyl]-1,5-bis(hexyloxy)-naphthalene (23). A mixture of 100 mg (0.15 mmol) of dibromo derivative **22**, 40 mg (0.45 mmol) of potassium cyanide, and a catalytic amount of sodium iodide suspended in 10 mL of dry *N*,*N*-dimethylformamide was refluxed for 72 h under argon atmosphere. Then the reaction mixture was poured into a 15 wt % aqueous ammonia solution. The yellow precipitate was filtered off, washed with ammonia solution and water, and vacuum dried. Chromatographic purification (silica gel, hexane/dichlorometane (6:4)) yielded 33 mg (37%) of compound **23** as a yellow solid. Mp: 128−130 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.88 (d, 2 H, J = 8.8 Hz), 7.63 (d, 2 H, J = 8.9 Hz), 7.56 (d, 2 H, J_{trans} = 16.3 Hz), 7.54 (d, 2 H, J = 4.0 Hz), 7.29 (d, 2 H, J_{trans} = 16.3 Hz), 7.09 (d, 2 H, J = 4.0 Hz), 3.92 (t, 4 H), 1.90 (q, 4 H), 1.58 (s, 4 H), 1.36 (m, 8 H), 0.89 (t, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 154.0, 150.3, 137.9, 129.8, 126.8, 125.5, 125.4, 123.3, 120.7, 118.9, 114.4, 107.1, 68.2, 31.6, 30.2, 29.5, 29.2, 25.9, 22.5, 13.9. FTIR (KBr, cm^{-1}): 2926, 2856, 2214, 1728, 1275, 1124, 1070. EM (EI) *m*/*z* (%I): 594 (M^+, 29), 510 (10), 426 (45), 149 (100). Anal. Calcd for $C_{36}H_{38}N_2O_2S_2$: C, 72.69; H, 6.44; N, 4.71. Found: C, 72.05; H, 8.13; N, 2.06.

2,6-Bis[2-(5-formyl-2-thienyl)vinyl]-1,5-bis(hexyloxy)-naphthalene (19). To a refluxing solution of 200 mg (0.34 mmol) of dicyano derivative **23** in 25 mL of dry dichloromethane under argon atmosphere was added dropwise 0.68 mL (0.68 mmol) of a 1 M solution of DIBAL-H in dichloromethane. After 5 h, the reaction mixture was allowed to reach room temperature and methanol was added to the crude. The precipitated yellow solid was treated portionwise with concentrated HCl solution until dissolution of the solid. The mixture was extracted with chloroform, and the organic layers were combined and dried over magnesium sulfate. After vacuum evaporation of the solvent, the remaining residue was chromatographically purified (silica gel, hexane/dichloromethane (3:7)) to yield 130 mg (64%) of compound **19** as a yellowish solid. Mp: 150−151 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.89 (s, 2 H, −CHO), 7.89 (d, 2 H, J = 8.8 Hz), 7.72 (d, 2 H, J = 8.8 Hz), 7.67 (d, 2 H, J_{trans} = 15.9 Hz), 7.69 (d, 2 H, J = 3.9 Hz), 7.34 (d, 2 H, J_{trans} = 16.1 Hz), 7.21 (d, 2 H, J = 3.9 Hz), 4.01 (t, 4 H), 1.98 (q, 4 H), 1.65 (s, 4 H), 1.43 (m, 8 H), 0.95 (t, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 182.5, 154.2, 137.2, 130.0, 127.3, 130.0, 127.3, 126.7, 125.7, 123.5, 121.8, 119.1, 76.0, 31.8, 30.4, 26.0, 22.7, 14.1. FTIR (KBr, cm^{-1}): 2926, 2854, 1661, 1226. EM (EI) *m*/*z* (%I): 600 (M^+, 87), 516 (20), 432 (100). Anal. Calcd for $C_{36}H_{40}O_4S_2$: C, 71.97; H, 6.71; S, 10.67. Found: C, 71.29; H, 6.85; S, 9.69.

6-Bromo-2-dodecyloxynaphthalene (32). To a solution of 7.0 g (31 mmol) of 6-bromo-2-hydroxynaphthalene (**31**) in 40 mL of dry acetone was added 8.6 g (62 mmol) of anhydrous potassium carbonate, 23 mL (93 mmol) of 1-bromododecane, and a catalytic amount of sodium iodide, and the mixture was refluxed for 72 h. After the reaction was cooled, 50 mL of water was added, and then the mixture was extracted three times with dichloromethane. The combined organic layers were washed with water and dried with magnesium sulfate. The solvent was vacuum evaporated to yield an oil which was vacuum distilled to remove unreacted 1-bromododecane. After chromatography (silica gel, hexane/dichloromethane (9:1)) of the residue, 11 g (90%) of **32** was obtained as a white solid. Mp: 62−63 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.90 (d, 1 H, J = 1.7 Hz), 7.62 (d, 1 H, J = 8.5 Hz), 7.53 (m, 1 H), 7.48 (dd, 1 H, J_1 = 8.5, J_2 = 1.9 Hz), 7.15 (dd, 1 H, J_1 = 8.8, J_2 = 2.4 Hz), 7.08 (d, 1 H, J = 2.4 Hz), 3.85 (t, 2 H), 1.64 (q, 2 H), 1.08 (s, 18 H), 0.69 (t, 3 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 157.4, 133.0, 129.9, 129.6, 129.4, 128.3, 128.2, 120.0, 116.8, 106.4, 68.0, 31.9, 29.6, 29.6, 29.6, 29.4, 29.3, 29.1, 26.0, 22.6, 14.1. FTIR (KBr, cm^{-1}): 3018, 1627, 1591, 1500, 1261, 1215. MS (EI) *m/z* (%I): 390 (M$^+$, 30), 224 (100). Anal. Calcd for $C_{22}H_{31}OBr$: C, 67.67; H, 8.01. Found: C, 67.60; H, 7.98.

2-Dodecyloxy-6-formylnaphthalene (33). To a solution of 10 g (25 mmol) of **32** in 100 mL of dry THF at −78 °C under argon atmosphere was added 31 mL of a 1.5 M solution of *n*-butyllithium (50 mmol) in hexane. After 6 h, 26.3 mL of dry *N*,*N*-dimethylformamide was added, and the reaction was allowed to stay at −78 °C for an additional 2 h. Then it was poured, under vigorous stirring, on a water/ice/HCl mixture (pH < 1). The mixture was extracted three times with methylene dichloride, and the organic layers were combined and washed twice with water and dried over magnesium sulfate. After vacuum evaporation of the solvent, an orange oil was obtained which was chromatographically purified (silica gel, hexane/diethyl ether (95:5)) to yield 8 g (94%) of **12** as a white solid. Mp: 45−47 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 10.08 (s, 1 H, CHO), 8.23 (s, 1 H), 7.91 (m, 1 H), 7.87 (m, 1 H), 7.79 (d, 1 H, J = 8.4 Hz), 7.24 (dd, 1 H, J_1 = 9.9 Hz, J_2 = 2.5 Hz), 7.16 (d, 1 H, J = 2.2 Hz), 4.14 (t, 2 H), 1.90 (q, 2 H), 1.30 (s, 18 t), 0.91 (t, 3 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 191.8 (CHO), 159.7, 138.2, 134.1, 132.1, 130.9, 127.7, 127.5, 123.4, 120.0, 106.6, 68.1, 31.7, 29.5, 29.4, 29.2, 29.2, 28.9, 25.9, 22.5, 13.9. FTIR (KBr, cm^{-1}): 2954, 2849, 1691, 1625, 1261. MS (EI) *m/z* (%I): 340 (M$^+$, 18), 172 (100). Anal. Calcd for $C_{23}H_{32}O_2$: C, 81.12; H, 9.48. Found: C, 81.19; H, 9.48.

6-Cyanomethyl-2-dodecyloxynaphthalene (34). Under an argon atmosphere, a solution of 2.7 g (14.0 mmol) of tosylmethylisocyanide (TosMIC) in 45 mL of dry THF was added dropwise to another solution of 3.41 g (14 mmol) of potassium *tert*-butoxide in 45 mL of dry THF, and the mixture was cooled to −30 °C. Afterward, a solution of 4 g (12 mmol) of aldehyde **33** in 70 mL of dry THF was added and stirred for 30 min at −30 °C. Then 65 mL of methanol was added, and the mixture was heated to 80 °C for 15 min. Then the crude reaction was allowed to reach room temperature, and the solvent was vacuum evaporated. A 3 mL portion of glacial acetic acid and a 60 mL portion of water were added to the solid residue obtained. The mixture was extracted three times with chloroform, and the combined organic layers were washed twice with 10% NaHCO$_3$ aqueous solution and then with water. After drying over magnesium sulfate, we vacuum evaporated the solvent to yield an oil residue, which was further purified chromatographically (silica gel, hexane/diethyl ether (8:2)) to afford 2.1 g (50%) of **34** as a white solid. Mp: 87−88 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.65 (s, 3 H), 7.28−7.05 (m, 3 H), 3.99 (s, 2 H), 3.80 (s, 2 H), 1.77 (s, 2 H), 1.20 (s, 18 H), 0.81 (s, 3 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 158.2, 134.8, 129.0, 129.0, 127.7, 126.6, 125.8, 125.0, 120.0, 106.4, 68.1, 31.9, 29.6, 29.4, 29.2, 26.1, 23.6, 22.6, 14.1. FTIR (KBr, cm^{-1}): 2918, 2253, 1606, 1265, 1225. MS (EI) *m/z* (%I): 351 (M$^+$, 45), 183 (M$^+$, 100), 157 (19). Anal. Calcd for $C_{24}H_{33}NO$: C, 82.00; H, 9.46; N, 3.98. Found: C, 81.97; H, 9.47; N, 3.88.

Synthesis of Polymers. General Procedure. Under an argon atmosphere, a solution of 0.14 mmol of the dialdehyde in 2 mL of dry THF was added to a solution of the corresponding bis(cyanomethyl) derivative in 5 mL of *tert*-butanol. Then 45 mg (0.14 mmol) of ^{t}BuOK and a few drops of a 1 M solution of tetrabutylammonium hydroxide in methanol were added. The reaction was heated to 50 °C for 20 min and then allowed to cool to room temperature. Afterward, the polymers were precipitated with the addition of methanol. Further purification was accomplished by washing the polymers twice with methanol and once with diethyl ether. Dry vacuuming for a few hours gives the polymers as colored solids.

Characterization of Polymer 1. By following the general procedure and using monomers **12** and **13** as starting materials, we obtained polymer **1** as a dark yellow solid. Yield: 90%. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.40 (s, 2 H), 8.22 (s, 2 H), 8.02 (m, 4 H), 7.80 (d, 2 H, J = 9.0 Hz), 7.67 (s, 2 H), 7.52 (d, 2 H, J = 9.1 Hz), 7.45 (m, 4 H), 7.20 (d, 4 H, J = 8.8 Hz), 3.98 (s, 8 H), 1.60 (s, 4 H), 1.42 (s, 8 H), 1.19 (s, 68 H), 0.83 (s, 12 H). FTIR (film, cm^{-1}): 3050, 2926, 2853, 2213, 1621, 1593. Anal. Calcd for $[C_{94}H_{122}N_2O_4]_n$: C, 84.00; H, 9.15; N, 2.08. Found: C, 83.66; H, 9.25; N, 2.04.

Characterization of Polymer 2. By following the general procedure and using monomers **13** and **14** as starting materials, we obtained polymer **2** as a dark yellow solid. Yield: 80%. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.44 (d, 2 H, J = 9.0 Hz), 8.30 (s, 2 H), 8.18 (s, 2 H), 8.07 (d, 2 H, J = 9.0 Hz), 8.00 (d, 2 H, J = 8.8 Hz), 7.61 (d, 2 H, J = 9.2 Hz), 7.51 (d, 2 H, J = 9.2 Hz), 7.26 (d, 2 H, J = 8.8 Hz), 4.03 (m, 8 H), 1.9 (m, 4 H), 1.5 (m, 4 H), 1.4−0.9 (m, 48 H), 0.8 (m, 12 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 155.9, 155.6, 135.0, 134.2, 130.2, 129.3, 128.8, 126.7, 126.3, 125.0, 124.8, 122.4, 119.8, 119.1, 118.1, 117.5, 116.1, 112.6, 77.1, 69.4, 31.8, 31.6, 30.3, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 25.9, 25.6, 22.6, 22.5, 14.0, 13.9. FTIR (film, cm^{-1}): 3060, 2855, 2214, 1682, 1621. Anal. Calcd for $[C_{72}H_{92}N_2O_4]_n$: C, 82.40; H, 8.83; N, 2.67. Found: C, 81.00; H, 8.84; N, 2.45.

Characterization of Polymer 3. By following the general procedure and using monomers **12** and **15** as starting materials, we obtained polymer **3** as an orange solid. Yield: 90%. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.37 (s, 2 H), 8.04 (d, 2 H), 7.79 (d, 2 H), 7.98 (d, 2 H), 7.78 (s, 2 H), 7.59 (d, 2 H), 7.42 (d, 2 H), 7.07 (d, 2 H), 3.95 (s, 8 H), 1.77 (s, 8 H), 1.38−0.98 (m, 48 H), 0.77 (s, 12 H). FTIR (film, cm^{-1}): 3028, 2969, 2214, 1622. Anal. Calcd for $[C_{72}H_{92}N_2O_4]_n$: C, 82.40; H, 8.83; N, 2.67. Found: C, 82.06; H, 8.77; N, 2.74.

Characterization of Polymer 4. By following the general procedure and using monomers **13** and **16** as starting materials, we obtained polymer **4** as a red solid. Yield: 99%. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.13 (s, 2 H), 7.95 (d, 2 H, J = 8.9 Hz), 7.73 (s, 2 H), 7.58 (s, 2 H), 7.40 (d, 4 H, J = 8.9 Hz), 7.12 (m, 2 H), 3.92 (s, 4 H), 1.36 (s, 4 H), 1.13 (s, 18 H), 0.92 (s, 18 H), 0.78 (t, 6 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 155.8, 141.0, 134.3, 131.6, 131.2, 128.9, 128.4, 126.8, 122.2, 120.0, 118.6, 116.1, 111.8, 110.6, 104.7, 69.2, 31.9, 29.7, 29.4, 29.3, 29.1, 25.7, 22.7, 14.1. FTIR (film, cm^{-1}): 3040, 2923, 2212, 1619, 1593, 1276, 1246. Anal. Calcd for $[C_{54}H_{64}N_2O_2S]_n$: C, 80.55; H, 8.01; N, 3.48; S, 3.98. Found: C, 78.88; H, 8.01; N, 3.72; S, 4.32.

Characterization of Polymer 5. By following the general procedure and using monomers **12** and **17** as starting materials, we obtained polymer **5** as a dark yellow solid. Yield: 93%. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.25 (s, 2 H), 7.96 (d, 2 H, J = 8.8 Hz), 7.75 (d, 2 H, J = 8.9 Hz), 7.40 (s, 4 H), 7.34 (s, 2 H), 7.19−7.12 (m, 2 H), 3.92 (s, 4 H), 1.36 (s, 4 H), 1.13 (s, 18 H), 0.92 (s, 18 H), 0.78 (t, 6 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 156.5, 140.4, 135.2, 131.1, 130.7, 128.7, 128.4, 127.5, 126.3, 125.5, 119.8, 116.8, 115.9, 104.0, 69.4, 32.0, 29.8, 29.8, 29.6, 29.5, 29.3, 29.2, 25.8, 22.8, 14.2. FTIR (film, cm^{-1}): 3052, 2924, 2215, 1618, 1577, 1275, 1250. Anal. Calcd for $[C_{54}H_{64}N_2O_2S]_n$: C, 80.55; H, 8.01; N, 3.48; S, 3.98. Found: C, 79.10; H, 7.94; N, 3.47; S, 3.69.

Characterization of Polymer 6. By following the general procedure and using monomers **13** and **18** (in this case dialdehyde **18** was dissolved in dichloromethane instead of THF) as starting materials, we obtained polymer **6** as a yellow solid. Yield: 90%. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.44 (d, 2 H, J = 9.02 Hz), 8.30 (s, 4 H), 8.18 (s, 4 H), 8.09−7.87 (m, 8 H), 7.79 (s, 4 H), 7.64−7.45 (m, 4 H), 7.17−7.13 (m, 2 H), 4.04 (s, 16 H), 1.99 (s, 14 H), 1.69 (s, 14 H), 1.44 (s, 28 H), 1.21 (s, 16 H), 0.95 (s, 16 H), 0.85−0.79 (m, 24 H). ^{13}C−RMN (CDCl$_3$, 75 MHz): δ 156.1, 155.6, 153.5, 153.3, 135.4, 134.2, 133.6, 131.1, 130.1, 129.8, 129.7, 129.6, 128.9, 128.3, 126.9, 126.8, 126.6, 126.4, 124.6, 123.8, 123.7, 123.5, 122.5, 120.0, 119.0, 118.4, 116.2, 111.8, 76.0, 69.5, 31.9, 31.8, 31.7, 30.6, 30.5, 29.7, 29.6, 29.4, 29.2, 26.2, 26.0, 25.7, 22.7, 22.7, 22.6, 14.1, 14.0. FTIR (film, cm^{-1}): 3068, 2955, 2924, 2215, 1618, 1593, 1275. Anal. Calcd for $[C_{110}H_{156}N_2O_8]_n$: C, 80.83; H, 9.62; N, 1.71. Found: C, 78.99; H, 9.42; N, 1.69.

Characterization of Polymer 7. By following the general procedure and using monomers **13** and **19** as starting materials, we obtained polymer **7** as a red solid. Yield: 90%. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.18 (s, 2 H), 8.01 (d, 2 H, $J = 8.2$ Hz), 7.88 (d, 2 H, $J = 8.4$ Hz), 7.72−7.38 (m, 10 H), 7.21−7.16 (m, 8 H), 3.99 (s, 8 H), 1.59 (s, 8 H), 1.43 (s, 16 H), 1.21 (s, 24 H), 0.94 (s, 8 H), 0.90−0.85 (m, 12 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 155.6, 153.8, 137.0, 134.0, 133.1, 132.5, 130.0, 129.9, 129.8, 128.9, 126.6, 126.3, 126.0, 123.6, 122.3, 120.0, 119.0, 118.4, 116.2, 107.8, 69.5, 31.9, 31.7, 30.4, 29.7, 29.6, 29.4, 29.2, 26.0, 25.7, 22.7, 22.7, 14.1. FTIR (film, cm^{-1}): 3045, 2926, 2209, 1620, 1592, 1277. Anal. Calcd for $[C_{84}H_{100}N_2O_4S_2]_n$: C, 79.70; H, 7.96; N, 2.21; S, 5.07. Found: C, 78.50; H, 7.99; N, 2.33; S, 4.91.

Synthesis of Model Compounds. General Procedure. Under an argon atmosphere, a solution of 0.4 mmol of the monoaldehyde-substituted (or 0.2 mmol of the dialdehyde-substituted) derivative in dry THF was added to a solution of 0.2 mmol of the bis(cyanomethyl)-substituted derivative (or 0.4 mmol of the mono(cyanomethyl)-substituted derivative) in 5 mL of *tert*-butanol. Then 0.4 mmol of ^{t}BuOK and a few drops of a 1 M solution of tetrabutylammonium hydroxide in methanol were added. After heating to 50 °C for 30 min, we allowed the reaction to cool to room temperature, and the model compounds were precipitated with the addition of methanol and then filtered.

Characterization of Model Compound 24. By following the general procedure and using **33** and **34** (in this case, equimolecular amounts of both reactives) as starting materials, we obtained model compound **24** as a white solid. Yield: 90%. Mp: 173 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.05 (s, 1 H), 7.93 (s, 2 H), 7.66−7.94 (m, 6 H), 7.09−6.97 (m, 4 H), 3.91 (s, 4H), 1.69 (s, 4 H), 1.11 (s, 36 H), 0.72 (s, 6 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 158.7, 158.0, 141.1, 135.5, 134.4, 130.0, 129.7, 129.4, 129.0, 128.5, 128.4, 127.4, 127.2, 125.6, 122.8, 120.0, 119.8, 110.0, 106.5, 68.0, 31.7, 29.4, 29.1, 29.0, 25.9, 22.5, 14.0. FTIR (KBr, cm^{-1}): 2955, 2224, 1628, 1603, 1244, 1202. MS (EI) *m*/*z* (%I): 674 (M$^+$, 100). Anal. Calcd for $C_{47}H_{63}NO_2$: C, 83.75; H, 9.43; N, 2.08. Found: C, 83.75; H, 9.25; N, 2.02.

Characterization of Model Compound 25. By following the general procedure and using **14** and **34** as starting materials, we obtained model compound **25** as a yellow solid. Yield: 90%. Mp: 130−133 °C. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 8.49 (d, 2 H, $J = 8.9$ Hz), 8.20 (d, 4 H, $J = 2.3$ Hz), 8.06 (d, 2 H, $J = 8.9$ Hz), 7.88 (s, 2 H), 7.83 (d, 4 H, $J = 2.3$ Hz), 7.30−7.23 (m, 2 H), 7.20 (s, 2 H), 4.16−4.05 (m, 8 H), 2.05−1.83 (m, 8 H), 1.61−1.32 (m, 48 H), 0.90 (t, 12 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 158.1, 155.9, 135.1, 134.7, 130.1, 129.8, 129.3, 128.4, 127.5, 126.0, 124.9, 124.8, 122.6, 119.9, 119.1, 118.1, 112.5, 106.3, 77.0, 67.9, 31.7, 31.5, 30.3, 29.4, 29.2, 29.2, 29.0, 25.9, 25.8, 22.5, 22.4, 13.9, 13.8. FTIR (KBr, cm^{-1}): 2920, 2849, 2215, 1601, 1273. MS (ESI) *m*/*z* (%I): 1073 (M$^+$+ 23, 100), 685 (57). Anal. Calcd for $C_{72}H_{94}N_2O_4$: C, 82.24; H, 9.01; N, 2.66. Found: C, 82.40; H, 8.94; N, 2.61.

Characterization of Model Compound 26. By following the general procedure and using **15** and **33** as starting materials, we obtained model compound **26** as a yellow solid. Yield: 45%. Mp: 119−120 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.04 (s, 2 H), 7.96 (d, 2 H, $J = 8.6$ Hz), 7.82 (d, 2 H, $J = 8.7$ Hz), 7.63 (s, 6 H), 7.46 (d, 2 H, $J = 8.4$ Hz), 7.02 (d, 2 H, $J = 5.7$ Hz), 6.96 (s, 2 H), 3.85 (t, 8 H), 1.65 (s, 8 H), 1.06 (s, 48 H), 0.63 (t, 12 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 158.7, 153.2, 147.3, 135.7, 130.5, 130.2, 128.9, 128.2, 127.3, 126.9, 125.5, 125.3, 119.9, 119.0, 118.5, 106.4, 105.9, 75.0, 68.0, 31.7, 31.4, 30.1, 29.5, 29.2, 29.0, 25.9, 25.7, 22.5, 22.4, 13.9, 13.8. FTIR (KBr, cm^{-1}): 2924, 2852, 2212, 1624, 1605, 1265. MS (ESI) *m*/*z* (%I): 1073 (M$^+$+ 23, 100), 685 (14). Anal. Calcd for $C_{72}H_{94}N_2O_4$: C, 82.24; H, 9.01; N, 2.66. Found: C, 82.17; H, 9.05; N, 2.62.

Characterization of Model Compound 27. By following the general procedure and using **16** and **34** as starting materials, we obtained model compound **26** as a red solid. Yield: 85%. Mp: 131−132 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.02 (s, 2 H), 7.88 (d, 2 H, $J = 8.04$ Hz), 7.80−7.71 (m, 4 H), 7.64−1.43 (m, 4 H), 7.20−7.02 (m, 4 H), 4.09 (t, 4 H), 1.77−1.73 (m, 4 H), 1.20 (s, 36 H), 0.81 (t, 6 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 159.9, 135.6, 132.4, 130.7, 129.3, 128.5, 121.3, 120.9, 120.4, 120.0, 118.8, 118.4, 113.2, 107.3, 68.9, 32.6, 30.3, 30.0, 29.9, 26.8, 23.4, 14.8. FTIR (KBr): 2928, 2852, 2216, 1630, 1473, 1207, 848, 794. EM (ESI) *m*/*z* (%I): 829 (M$^+$+ 23, 48), 685 (100). Anal. Calcd for $C_{54}H_{66}N_2O_2S$: C, 80.35; H, 8.24; N, 3.47; S, 3.97. Found: C, 80.09; H, 8.50; N, 3.65; S, 4.00.

Characterization of Model Compound 28. By following the general procedure and using **17** and **33** as starting materials, we obtained model compound **28** as a red solid. Yield: 85%. Mp: 125−128 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.11 (s, 2 H), 8.00 (s, 2 H), 7.90 (s, 2 H), 7.74 (s, 4 H), 7.56 (s, 4 H), 7.40 (s, 2 H), 4.21 (s, 4 H), 1.98 (s, 4 H), 1.41 (s, 36 H), 1.02 (s, 6 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 159.1, 139.8, 140.5, 136.0, 130.9, 130.5, 128.5, 127.7, 127.3, 125.5, 120.2, 116.7, 106.7, 103.9, 68.3, 32.0, 29.7, 29.4, 29.2, 26.1, 22.8, 14.2. FTIR (KBr, cm^{-1}): 2920, 2850, 2214, 1628, 1276. EM (ESI) *m*/*z* (%I): 829 (M$^+$ + 23, 100), 685 (18). Anal. Calcd for $C_{54}H_{66}N_2O_2S$: C, 80.35; H, 8.24; N, 3.47; S, 3.97. Found: C, 77.92; H, 7.96; N, 3.48; S, 3.98.

Characterization of Model Compound 29. By following the general procedure and using **18** and **34** as starting materials, we obtained model compound **29** as a red solid. Yield: 92%. Mp: 146−148 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.42 (d, 2 H, $J = 9.0$ Hz), 8.20 (s, 2 H), 8.16 (s, 2 H), 8.02 (d, 2 H, $J = 9.3$ Hz), 7.98−7.89 (m, 8 H), 7.84 (s, 2 H), 7.80−7.79 (m, 6 H), 7.23−7.20 (m, 2 H), 7.16 (m, 4 H), 4.08 (t, 16 H), 2.03−1.68 (m, 20 H), 1.68−1.57 (m, 8 H), 1.57−1.56 (m, 8 H), 1.46−0.97 (m, 52 H), 0.89 (t, 12 H), 0.88 (t, 12 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 158.2, 156.2, 153.6, 153.4, 135.8, 134.9, 131.2, 130.0, 129.8, 128.9, 128.7, 128.4, 127.7, 126.8, 126.1, 124.5, 124.5, 123.8, 123.6, 122.9, 120.1, 119.0, 118.5, 111.9, 106.6, 68.2, 31.9, 31.9, 31.7, 30.6, 30.5, 29.6, 29.4, 29.4, 29.2, 26.2, 26.0, 25.9, 22.8, 22.7, 22.7, 14.1, 14.0. FTIR (KBr, cm^{-1}): 2924, 2852, 2224, 1628, 1603. EM (ESI) *m*/*z* (%I): 1777 (M$^+$ + 23, 100).

Characterization of Model Compound 30. By following the general procedure and using **19** and **33** as starting materials, we obtained model compound **30** as a red solid. Yield: 95%. Mp: 174−176 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.03 (s, 2 H), 7.87 (d, 2 H, $J = 8.8$ Hz), 7.74 (d, 2 H, $J = 8.8$ Hz), 7.69−7.65 (m, 4 H), 7.64 (s, 4 H), 7.60−7.58 (m, 2 H), 7.53 (d, 2 H, $J_{\mathrm{trans}} = 16.6$ Hz), 7.31 (d, 2 H, $J_{\mathrm{trans}} = 16.3$ Hz), 7.20−7.10 (m, 6 H), 4.09−3.98 (m, 8 H), 2.03−1.96 (m, 4 H), 1.86−1.81 (m, 4 H), 1.67 (s, 4 H), 1.46−1.44 (m, 44 H), 1.00−0.85 (m, 12 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 158.1, 153.8, 137.0, 134.6, 133.0, 132.5, 129.8, 129.0, 128.7, 127.6, 126.6, 126.0, 123.6, 122.0, 121.9, 120.1, 119.0, 113.5, 112.0, 111.1, 106.6, 67.7, 31.9, 31.8, 30.4, 29.6, 29.4, 26.0, 22.7, 14.1. FTIR (KBr, cm^{-1}): 2922, 2851, 2216, 1628, 1601. EM (ESI) *m*/*z* (%I): 1289 (M$^+$ + 23, 48), 685 (100). Anal. Calcd for $C_{84}H_{102}N_2O_4S_2$: C, 79.58; H, 8.11; N, 2.21; S, 5.06. Found: C, 79.00; H, 8.08; N, 2.29; S, 5.06.

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