Glass-Forming Binaphthyl Chromophores

Jacek C. Ostrowski, Raymond A. Hudack, Jr., Matthew R. Robinson, Shujun Wang, and Guillermo C. Bazan*[a]

Abstract: The use of the binaphthyl framework to synthesize glass-forming organic chromophores is described. Suzuki coupling reactions of racemic 6,6′-dibromo-2,2′-dialkoxy-1,1′-binaphthyl with 1,1-diphenyl-2-(4-dihydroxyboronphenyl)-ethene using $[Pd(dppf)Cl_2]$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) as the catalyst provide a set of chromophores with the 4-(2,2′-diphenylvinyl)-1-phenyl group at the 6- and 6′-positions and a range of groups on the oxygen atom. Starting with enantiomerically enriched (*R*)-6,6′-dibromo-2,2′-dihexyloxy-1,1′-binaphthyl ((***R***)**-2Hex**), one can obtain (***R***)**-3Hex**. Heck coupling reactions of 6,6′-dibromo-2,2′-dialkoxy-1,1′-binaphthyl compounds with styrene provide chromophores of the type 2,2′-dialkoxy-1,1′-binaphthyl-6,6′-bis(2-phenyl-vinyl). Starting with enantiomerically enriched (***R***)**-2Hex**, one obtains (***R***)**-4Hex**. Molecules of the type **4** contain two 1-naphthyl-2-phenyl ethylene chromophores with a pseudo-orthogonal relationship. Similar procedures can be used to obtain fragments with more extended conjugation length. Thus, the Heck coupling reaction of **2Hex** with 4-(4′-*tert*-butylstyryl)styrene, 1-(4′-*tert*-butylstyryl)-4-(4′-vinylstyryl)-benzene, and 1-(3′,5′-dihexyloxystyryl)-4-(4′-vinylstyryl)benzene provides **5Hex**, **6Hex**, and **7Hex**, respectively. DSC measurements and powder diffraction experiments indicate that the binaphthol chromophores show a resistance to crystallization. In some cases, considerably different thermal behavior is observed between enantiomerically enriched samples and their racemic counterparts. Increasing the size of the conjugated fragment on the binaphthol core leads to materials with higher glass-transition temperatures and a less pronounced tendency to crystallize. Fluorescence spectroscopy gives evidence of “excimer”-type interactions in the solid state, except for the chromophores with 4-(2,2′-diphenylvinyl)-1-phenyl groups. It is possible to obtain amorphous films of these chromophores directly from solution, and to fabricate light-emitting diodes, in which the electroluminescent layer corresponds to the binaphthyl chromophore.

Keywords: amorphous materials · chromophores · electroluminescence · fluorescence · glasses

Introduction

There is intense current interest in finding well-defined organic chromophores of intermediate dimensions that form stable glasses. Much of the motivation derives from the emerging use of organic materials in new optoelectronic technologies.[1] Amorphous materials eliminate complications from grain boundaries and poor metal–organic interfaces that are associated with crystalline samples.[2] They also facilitate simpler manufacturing procedures because of their ability to form homogeneous films directly from solution. Conjugated polymers exist that fit these criteria,[3] however structural imperfections within chains, coupled with the statistical nature of polymerization reactions,[4] provide materials that are not as well defined as low mass organic molecules.[5] Another practical advantage of optical materials based on small molecules[6] is that they can be purified by standard organic methodologies.

Attaching long aliphatic side groups around the periphery of a given chromophore can minimize crystallization.[7] However, these nonpolarizable groups reduce the charge transport ability of the bulk material.[3] In the case of light-emitting diodes (LEDs), the devices need to be operated at elevated potentials, which lower their lifetime under operating conditions.[8]

An alternative approach to amorphous organic molecules that does not resort to using large aliphatic fragments takes advantage of molecular shapes, which can be considered “awkward” for packing. With this geometrical feature, the rate of crystallization can be considerably reduced, leading to supercooled solutions and stable amorphous phases.[9] Representative molecular examples include “starburst” structures (**Sb**), spiro compounds (**Sp**), and tetrahedral arrangements (**Th**) such as those shown below.

Molecules such as 4,4′,4″-tris[*N*-(3-methylphenyl)-*N*-phenylamino]-triphenylamine[10] (**Sb**) correspond to an ever-

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[a] Prof. G. C. Bazan, J. C. Ostrowski, R. A. Hudack, Jr., M. R. Robinson, Dr. S. Wang
Departments of Chemistry and Materials
University of California, Santa Barbara, CA 93106 (USA)
Fax: (+1) 805-893-4120
E-mail: bazan@chem.ucsb.edu

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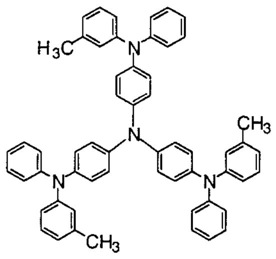

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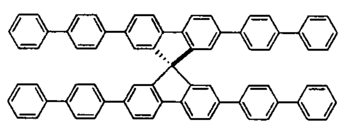

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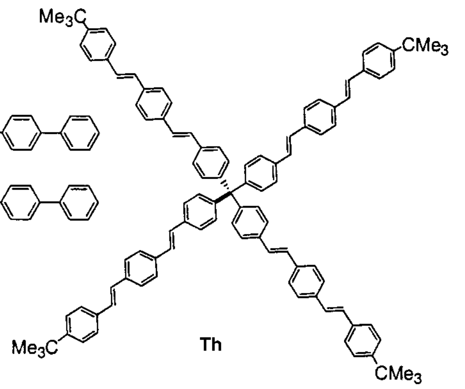
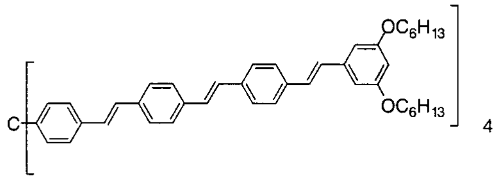


Th

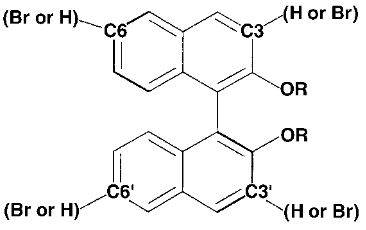
growing family of triarylamine-based hole transport materials that find use in LED fabrication.[11] Spiro-shaped 2,2′,7,7′-tetrakis(biphenyl-4-yl)-9,9′-spirofluorene (**Sp**) is interesting because it exhibits amplified spontaneous emission in the solid state.[12] Whereas tetrakis(*tert*-butylstyrylstilbenyl)methane (**Th**) exhibits a glass-transition temperature, the distyrylbenzene components, on their own, are highly crystalline.[13, 14] These attributes of the tetrahedral complexes make them useful for LED applications. In fact, LEDs prepared using tetrakis(4-(4′-(3″,5″-dihexyloxystyryl)styryl)stilbenyl)-methane (**T-4R-OC$_6$H$_{13}$**) as the electroluminescent layer exhibit low turn on voltages.[15]



T-4R-OC$_6$H$_{13}$

It is noteworthy that the choice of a given framework as a design principle stems from the intuitive feel of chemists for the three-dimensional structure of molecules (sometimes referred to as the molecular topology),[16] and how this parameter relates to the ability of the collective ensemble to arrange in a well-ordered fashion.

Consideration of the issues raised above led us to target binaphthol as a suitable core for synthesizing amorphous organic chromophores. Three attributes of the structure and reactivity of binaphthol were compelling. First, as a consequence of the mutual pseudo-orthogonality of the two planar naphthyl fragments, the molecule can be thought of as comprising half of a spiro compound.[17, 18] Second, there is a versatile and well-developed substitution chemistry, which allows for modifications at the 3,3′- and 6,6′-positions, in addition to the oxygen substituent.[18] Finally, chiral C_2-symmetric, starting materials are readily available by standard procedures, which can be used to synthesize enantiomerically enriched chromophores.[19] Comparison against their racemic analogues gives insight into how molecular chirality, a fundamental topological attribute, can frustrate the ability of the bulk material to crystallize. It should also be noted that there is considerable recent interest in the study of the binaphthol framework to create optically coupled chromophore pairs and networks.[20]

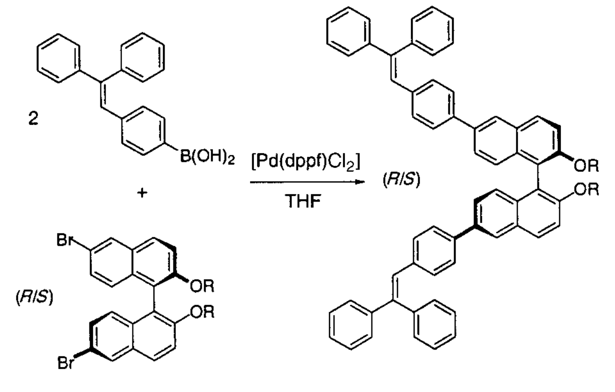


In this contribution, we report the synthesis of organic chromophore pairs that are connected by way of the 6- and 6′-positions in the binaphthol framework. We show by differential scanning calorimetry (DSC) analysis, powder diffraction measurements, and comparison against the monomeric counterpart that the shape of the binaphthyl molecules indeed endows the material with resistance toward crystallization. The effect of chromophore structure and conjugation length, as well as the size of ether groups, on bulk morphology is examined.[21] By synthesizing enantiomerically enriched molecules and comparing their properties against racemic counterparts, we probe the effect of chirality on the ability of the material to reach a stable amorphous state.[22] Finally, we show that it is possible to build organic LEDs, in which binaphthol chromophores are the electroluminescent layer.

Results and Discussion

Synthesis: The compounds in this study were synthesized starting with 6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthyl (**1**), which is available in 95 % yield from 1,1′-binaphthol.[23, 24] Treatment of **1** with the appropriate alkyl- or benzylbromide and K_2CO_3 in acetone provides the corresponding alkyl[25] and benzyl[26] derivatives in greater than 90 % yield. The methoxymethyl ether (**2MOM**) was synthesized in 70 % yield by reaction of **1** in the presence of excess dimethoxymethane with phosphorous pentoxide.[27] This procedure eliminates the use of the hazardous alkylating agent methoxymethylchloride.

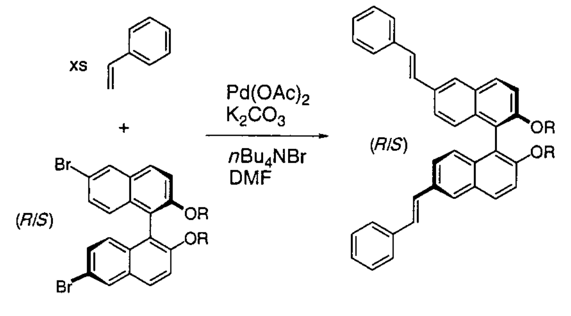
As shown in Scheme 1, a set of compounds containing the 4-(2,2′-diphenylvinyl)-1-phenyl side group[28] at the 6- and 6′-positions was readily prepared by Suzuki coupling[29] of the binaphthyl bromides with 1,1-diphenyl-2-(4-dihydroxyboron-



2Bu, R = C_4H_9
2Bz, R = CH_2Ph
2Hex, R = C_6H_{13}
2MOM, R = CH_2OCH_3
2Me, R = CH_3

3Bu, R = C_4H_9
3Bz, R = CH_2Ph
3Hex, R = C_6H_{13}
3MOM, R = CH_2OCH_3
3Me, R = CH_3

Scheme 1. Preparation by Suzuki coupling of a set of compounds with the 4-(2,2′-diphenylvinyl)-1-phenyl side group.



2Bu, R = C_4H_9
2Bz, R = CH_2Ph
2Hex, R = C_6H_{13}
2Me, R = CH_3

4Bu, R = C_4H_9
4Bz, R = CH_2Ph
4Hex, R = C_6H_{13}
4Me, R = CH_3

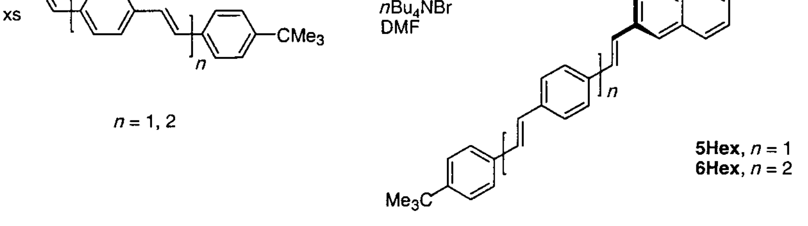
Scheme 2. Preparation of series **4** by Heck coupling of **2Bu**, **2Bz**, **2Hex**, and **2Me** with styrene.

phenyl)-ethene. These reactions used 4% [Pd(dppf)Cl_2] (dppf = 1,1′-bis(diphenylphosphino)ferrocene) in THF with saturated aqueous $NaHCO_3$ in yields of 30–60%. It is possible to begin with enantiomerically enriched (*R*)- or (*S*)-1,1′-binaphthol (>99% *ee*)[30] by using the chiral resolving agent, (8*S*,9*R*)-(−)-*N*-benzylcinchonidinium. Such a sequence was carried out for O*R* = OC_6H_{13}, (**(*R*)-3Hex**). HPLC analysis using chiral supports shows that the final enantiomer purity after resolution of the core and the Suzuki (or Heck, vide infra) reaction conditions corresponds to 90–80% *ee*. High-temperature conditions bring about the loss of enantiopurity during the Heck coupling reactions. The series of chromophores with structure **3** (Scheme 1) will be useful when we examine the effect of the ether side group on T_g.

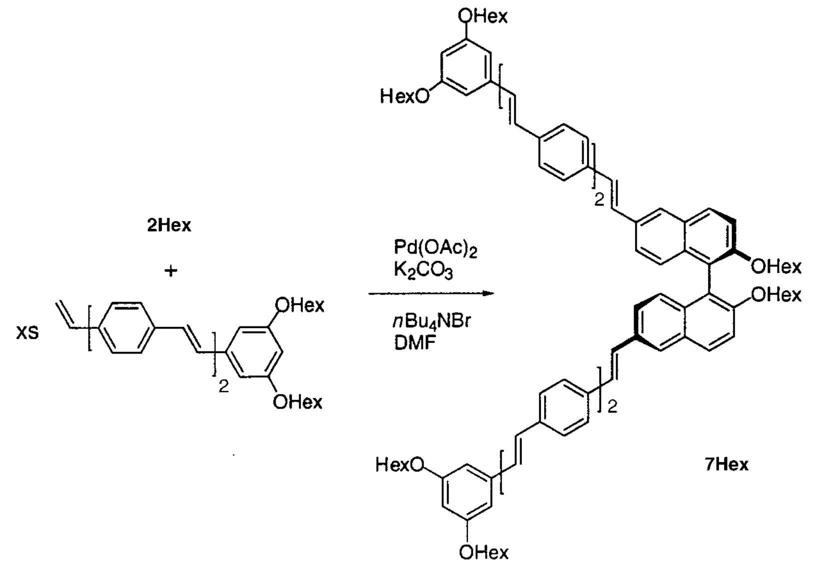
Chromophores containing 2-phenyl-vinyl side groups at the C6 and C6′ sites, the series **4** in Scheme 2, can be conveniently obtained by Heck coupling of **2Bu**, **2Bz**, **2Hex**, and **2Me** (**2Bu**, R = C_4H_9; **2Bz**, R = CH_2Ph; **2Hex**, R = C_6H_{13}; **2MOM**, R = CH_2OCH_3; **2Me**, R = CH_3) with styrene. For example, the reaction of **2Me** with six equivalents of styrene in the presence of 5% Herrmann's catalyst[31] and 4.5 equivalents of sodium acetate in dimethylacetamide at 140 °C for two days affords, after workup, **4Me** in 42% yield. Previous work with tetrahedral chromophores showed that glass-forming tendencies are reduced with a *decrease* in the molecular dimensions of the chromophore.[32, 33] Thus, the series **4** is expected to provide materials with borderline tendencies.

Three additional molecules were prepared to examine the effect of conjugation length and substituent structure. Use of 4-(4′-*tert*-butylstyryl)styrene[32] and 1-(4′-*tert*-butylstyryl)-4-(4′-vinylstyryl)benzene[33] instead of styrene, as shown in Scheme 3, allows for the attachment of groups with longer conjugation lengths. The syntheses of **5Hex** (2,2′-dihexyloxy-6,6′-bis(4-(4′-*tert*-butylstyryl)styryl)-1,1′-binaphthyl) and **6Hex** (2,2′-dihexyloxy-6,6′-bis(4-(4′-(4″-*tert*-butylstyryl)styryl)styryl)-1,1′-binaphthyl) were carried out under an inert atmosphere. For example, compound **2Hex** can be treated with four equivalents of 4-(4′-*tert*-butylstyryl)styrene in the presence of palladium acetate, tetrabutylammonium bromide, and excess potassium carbonate in dimethylformamide. As the reaction proceeds, the appearance of strong blue-green fluorescence is observed when the reaction flask is illuminated by a handheld UV lamp. The product is obtained after the reaction is run at 80 °C for 2.5 days and is easily separated from unreacted starting materials by chromatography. In the synthesis of **6Hex**, the product is contaminated by the monosubstituted species. Separation by chromatography is complicated due to the low solubility of **6Hex** in most organic solvents. After isolation, **6Hex** is photoisomerized to the all-*trans* form by irradiating a degassed benzene solution for 45 minutes.

Problems associated with the low solubility of **6Hex** prompted us to synthesize **7Hex** (2,2′-dihexyloxy-6,6′-bis-(4-(4′-(3″,5″-dihexyloxystyryl)styryl)styryl)-1,1′-binaphthyl)



Scheme 3. The syntheses of **5Hex** and **6Hex**.



Scheme 4. The synthesis of **7Hex**.

in Scheme 4. The requisite 1-(3′,5′-dihexyloxystyryl)-4-(4′-vinylstyryl)benzene was available from previous studies,[33] and the reaction conditions were analogous to those described for **5Hex**. As in the other procedures, best results were obtained when oxygen was rigorously excluded during the reaction. Compound **7Hex** was obtained in 42 % yield and is freely soluble in common organic solvents.

Model compounds **m-3Hex**, **m-4Hex**, **m-5Hex**, and **m-7Hex**, were synthesized to highlight changes in the bulk morphology of the material upon bringing together two chromophores through the binaphthol core. These monomeric derivatives contain the hexyloxy functionality, and the protocols for attaching the arm to 6-bromo-2-hexyloxynaphthalene were adapted from those in Schemes 2, 3, and 4. Attempts of the synthesis of the parent compound for **6Hex** were unsuccessful because 2-hexyloxy-6-(4-(4′-(4″-*tert*-butylstyryl)styryl)styryl)naphthalene is highly insoluble. Interestingly, it was found that all monomers were considerably less soluble than their dimer counterparts.

Morphology: Powder diffraction analysis of samples from the **3** series revealed no diffraction peaks, consistent with a lack of long-range order. DSC measurements in the temperature range 40 to 400 °C only gave evidence of glass transitions. No melting or crystallization was observed for these compounds, regardless of sample history. Throughout the studies, the heating and cooling rates are at 10 °C min^{-1} unless otherwise indicated. The glass-transition temperature can be tuned by choice of the alkyl group on the oxygen atom (Figure 1). The lowest T_gs correspond to the hexyl derivatives **3Hex** (65 °C), while the methyl containing compound **3Me** (**3Me**, R = CH$_3$) displays the highest T_g (137 °C). The butyl (**3Bu**, R = C$_4$H$_9$, T_g = 85 °C), benzyl (**3Bz**, R = CH$_2$Ph, T_g = 90 °C), and methoxymethyl (**3MOM**, R = CH$_2$OCH$_3$, T_g = 108 °C) containing molecules provide intermediate values. Note that there is little difference between enantiomerically enriched **(*R*)-3Hex** and racemic **3Hex** (**3Hex**, R = C$_6$H$_{13}$). Compound **m-3Hex** shows a sharp melting point at 163 °C and during the cooling cycle crystallizes at 100 °C. Altogether, these observations indicate that the binaphthyl framework can be used to enforce an amorphous morphology and that the glass-transition temperature, and therefore film stability, can be controlled by choice of the ether fragment.

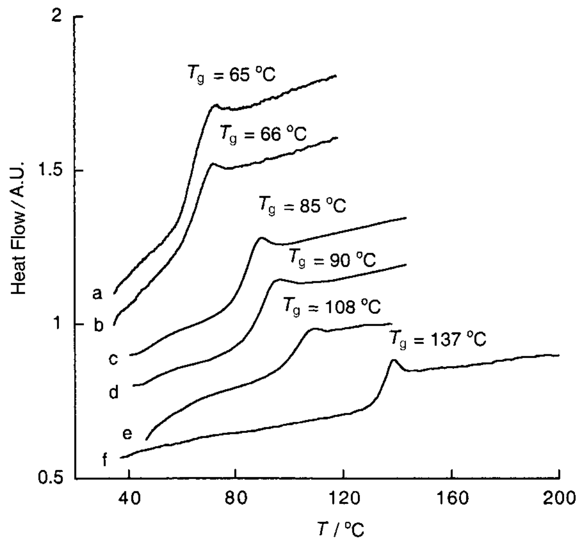
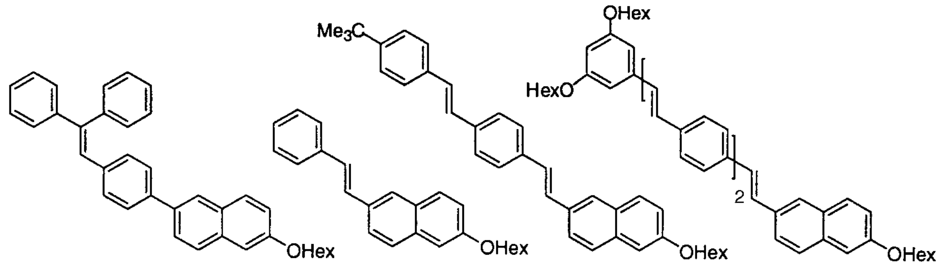


Figure 1. DSC data for the **3** series: a) **3Hex**; b) **(*R*)-3Hex**; c) **3Bu**; d) **3Bz**; e) **3MOM**; f) **3Me**.

Figure 2 shows the DSC traces obtained for **(*S*)-4Bu**, **(*R*)-4Bu**, and the racemic compound **4Bu** (**4Bu**, R = C$_4$H$_9$). As in the case of the **3** series, there is no evidence that **4Bu** crystallizes, and enantiomeric purity makes no observable impact. Analogous data for the benzyl derivative **4Bz** (**4Bz**, R = CH$_2$Ph) also shows no evidence for crystalline regions; however the glass-transition temperature of the racemic



m-3Hex **m-4Hex** **m-5Hex** **m-7Hex**

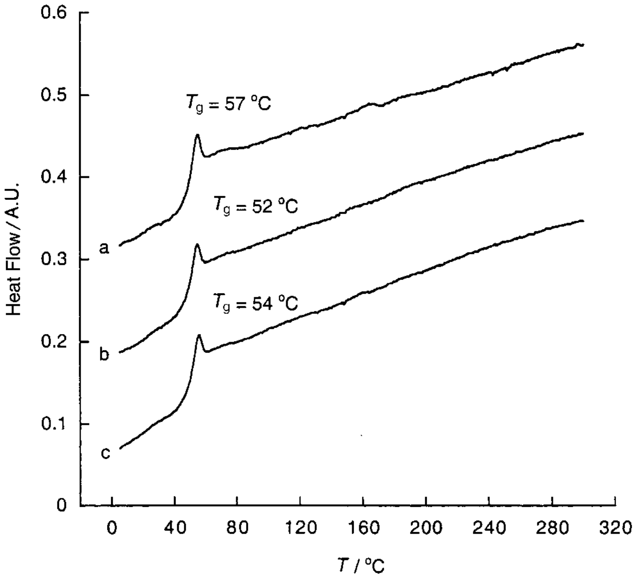


Figure 2. DSC data for the **4Bu** series: a) **4Bu**; b) **(*R*)-Bu**; c) **(*S*)-Bu**.

mixture (**4Bz**, $T_g = 71\,^\circ$C) is slightly higher than that observed for either the *R* or *S* enantiomerically enriched samples (**(*S*)-4Bz**, $T_g = 55\,^\circ$C; **(*R*)-4Bz**, $T_g = 52\,^\circ$C, Figure 3). Therefore chirality affects intermolecular interactions within the sample, and consequently bulk properties.[34]

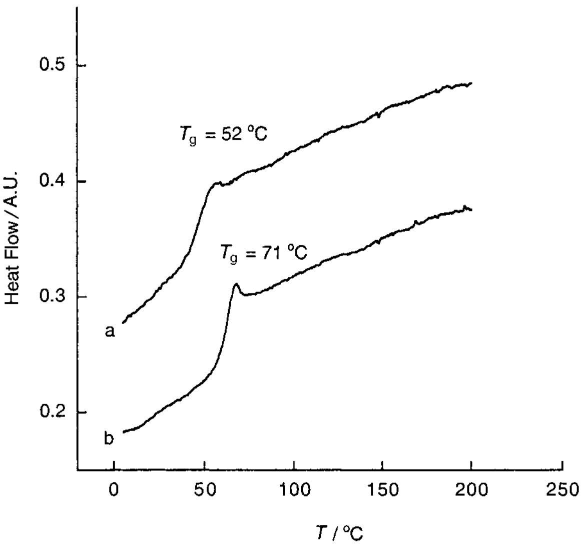


Figure 3. DSC data for the **4Bz** series: a) **(*R*)-4Bz**; b) **4Bz**.

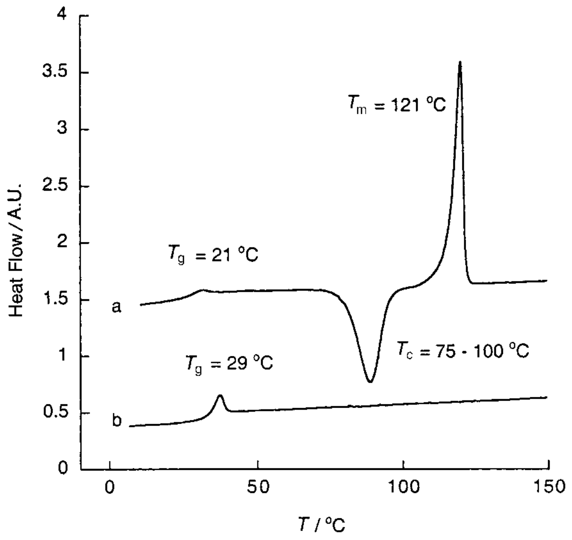


Figure 4. DSC data for **4Hex** (a) and **(*R*)-4Hex** (b).

For the hexyl derivative **4Hex** (**4Hex**, R = C_6H_{13}), there is considerable difference between the racemic and the enantiomerically enriched materials. The heating curve of thermally annealed **4Hex** (Figure 4a) shows a T_g at 21 °C, followed by crystallization in the 75 – 100 °C range, and finally a melting transition at ≈120 °C. No crystallization is observed when **4Hex** is cooled back to room temperature at a rate of 1 °C min^{-1}. These transitions are reproducible, even after repeated cycles. Therefore, compound **4Hex** forms a supercooled solution at room temperature, but at higher temperatures there is sufficient thermal energy to allow relocation of the molecules into a crystalline lattice. In the case of **(*R*)-4Hex**, a T_g similar to that of **4Hex** is observed (Figure 4b). However, 18 – 20 cooling/heating cycles in the range 40 to 150 °C failed to give evidence of crystallization and/or melting. *Therefore the enantiomerically enriched **4Hex** resists crystallization more effectively and provides more stable amorphous materials when compared with the racemic **4Hex**.*

Examination of the heating trace of **4Me** (**4Me**, R = CH_3) reveals a glass transition at 110 °C, a crystallization point at 157 °C, and a melting transition at 255 °C (Figure 5a). Also observed is a weak exotherm at 202 °C, which may be due to a liquid crystal type transition.[35] The cooling curve, in Figure 5b at a rate of 1 °C min^{-1}, reveals a transition from isotropic to glassy state at approximately 100 °C. In the heating trace of **(*R*)-4Me**, only a broad melting transition at 260 °C is observed (Figure 6a). During the cooling cycle, a sharp crystallization transition is observed at 188 °C (Figure 6b). Similar data are obtained for **(*S*)-4Me**. *Thus, in*

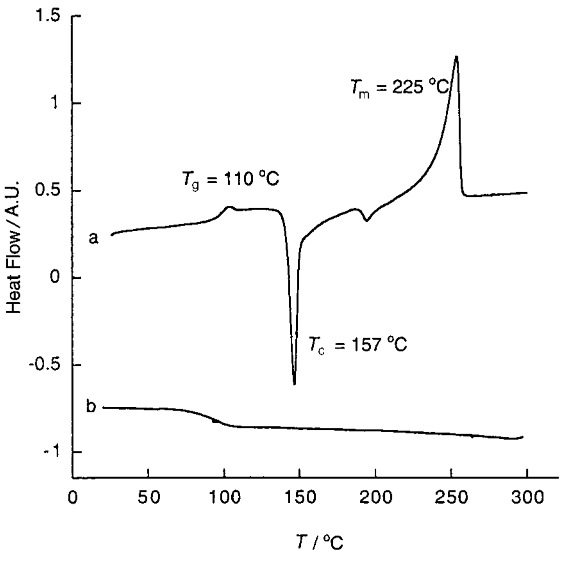


Figure 5. DSC data for **4Me**: a) heating cycle; b) cooling cycle.

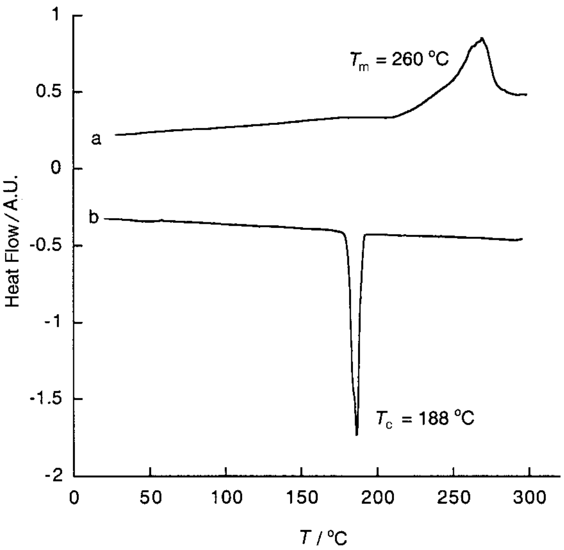


Figure 6. DSC data for **(*R*)-4Me**: a) heating cycle; b) cooling cycle.

contrast to the behavior of the **4Hex** *compound, enantiomerically enriched samples of* ***4Me*** *crystallize more readily.*

It is possible to investigate the changes in the DSC characteristics of **(*R*)-4Me** as a function of multiple heating/cooling cycles, and the resulting calorimetry traces are shown in Figure 7. For these measurements, the heating and cooling rates were 1 °C min^{-1}. In the first scan one observes a T_m at 260 °C. The sample was taken to a maximum temperature of 300 °C. On the first cooling cycle, the T_c occurs at 188 °C. During the second cycle, a decrease in both the T_m (258 °C) and T_c (168 °C) is observed. Subsequent DSC measurements show a progressive increase in the complexity of the traces. There is a general decrease in the intensity and temperature of the original melting transition, and multiple poorly defined transitions are observed in the temperature range 190–260 °C. Note the appearance of a T_g at 98 °C after four cycles. In the cooling cycles, crystallization becomes progressively less pronounced. After 20 cycles, the DSC traces no longer change and are identical to the data of racemic **4Me** in Figure 6. Therefore, the thermal energy at 300 °C is sufficient to rotate the two binaphthyl rings in the melt, thereby racemizing the molecules and changing the morphology of the sample. It is also interesting to note the complex thermal transitions observed at intermediate levels of enantiomeric purity.

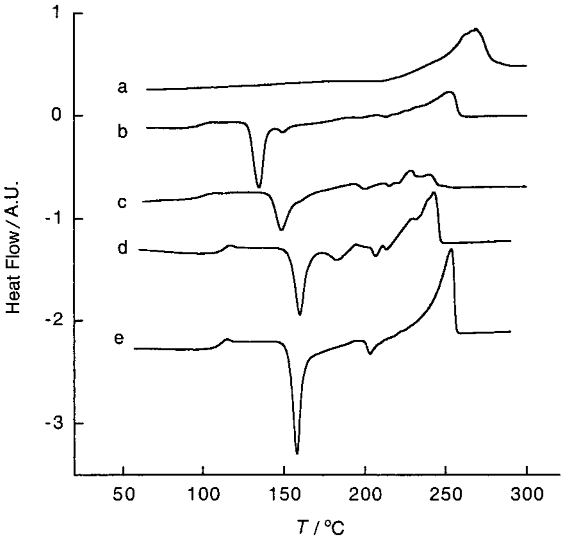


Figure 7. The DSC traces for **(*R*)-4Me**: a) is the third heating cycle; b) is the fourth heating cycle; c) is the eighth heating cycle; d) is the twelfth heating cycle; e) is the trace after twenty heating cycles.

The DSC trace of **m-4Hex** shows a weak crystallization exotherm at 101 °C, followed by two melting transitions at 119 °C and 150 °C. The first endotherm corresponds to a transition from solid to a liquid crystal, while the second suggests a liquid crystal to isotropic transition. The cooling trace shows similar behavior with an exotherm at 146 °C, corresponding to the transition to liquid crystal, followed by a crystallization exotherm at 76 °C.

While **m-5Hex** shows a melting transition at 229 °C, the binaphthyl counterpart **5Hex** is an amorphous solid with a T_g at 89 °C (Figure 8). Correspondingly, the powder diffraction data for **m-5Hex** show diffraction peaks, while those of **5Hex** indicate an amorphous state. Compound **(*R*)-5Hex** shows a slightly increased T_g (94 °C) relative to **5Hex**. DSC analysis gave no indications of thermal transitions for **6Hex** in the range 30–350 °C, even after thermal annealing.

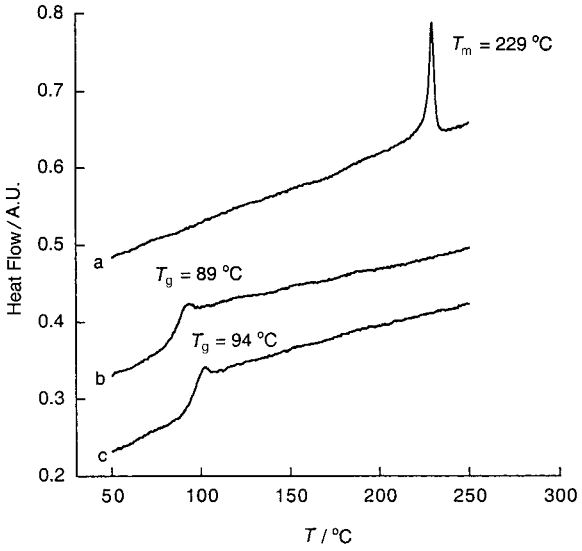


Figure 8. DSC data for **5Hex** series: a) **m-5Hex**; b) **5Hex**; c) **(*R*)-5Hex**.

Compound **m-7Hex** melts at a lower temperature (219 °C, Figure 9) than **m-5Hex**, probably as a result of the large aliphatic chains. The properties of **7Hex** and **(*R*)-7Hex** (Figure 9) parallel those observed for **4Hex** and **(*R*)-4Hex**. In the heating curve, the racemic material crystallizes at 90 °C, and melts at 150 °C. For **(*R*)-7Hex**, only a glass transition is observed at 71 °C.

Optical properties: Table 1 has the collected spectral data for the chromophores prepared in this study. Compounds of the **3** series are soluble in a variety of organic solvents, display absorption maxima at ≈340 nm, and emit in the blue region of

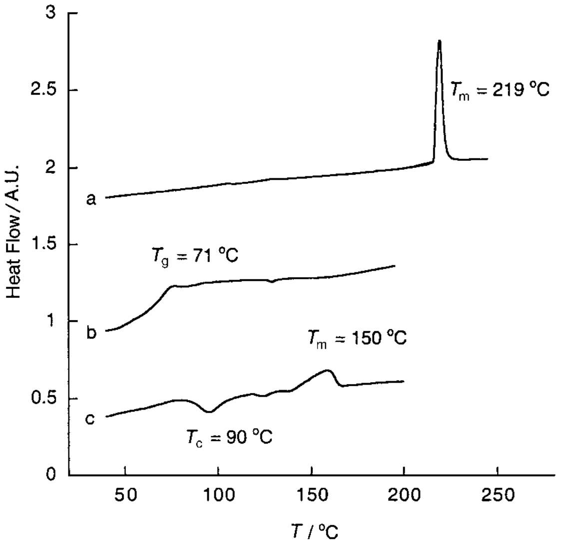


Figure 9. DSC data for **7Hex** series: a) **m-7Hex**; b) **(*R*)-7Hex**; c) **7Hex**.

Table 1. Collected optical data.

Compound	Absorption Maximum [nm]	Absorption Onset [nm]	Solution Emission Maximum [nm]	Film Emission Maximum [nm]
3Hex	340	384	452	452
(*R*)-3Hex	345	384	450	451
3Bz	342	388	449	455
3Bu	345	390	448	450
3MOM	340	387	451	451
3Me	340	391	452	456
m-3Hex	340	384	439	438
4Hex	330	383	398	441
(*R*)-4Hex	333	384	398	440
(*S*)-4Hex	333	384	399	465
4Bz	331	383	403	470
(*R*)-4Bz	333	383	394	465
(*S*)-4Bz	332	384	397	472
4Bu	333	384	399	472
(*R*)-4Bu	334	384	400	464
(*S*)-4Bu	332	385	397	478
4Me	331	383	394	454
(*R*)-4Me	331	384	395	452
(*S*)-4Me	331	383	393	450
m-4Hex	328	379	390	419
5Hex	376	420	429	486
(*R*)-5Hex	375	420	427	472
m-5Hex	374	415	435	465
6Hex	393	444	469	478
7Hex	395	441	471	491
(*R*)-7Hex	394	441	469	490
m-7Hex	396	442	465	464

the spectrum. The different alkoxy substituents have no observable effect on the optical properties. It is possible to cast thin films directly from solution, and the resulting optical properties are identical to those recorded in solution (Figure 10). The lack of intermolecular perturbations in the solid is a phenomenon that has been noted in other chromophores of this type and is likely a result of effective insulation from the environment by the three aryl rings on the olefin unit.[33]

Figure 11 shows that the solution absorbance and emission spectra of **4Hex** are identical to those of **(*R*)-4Hex**. Similar results are obtained for the other compounds in the **4** series. Film emission is considerably red-shifted, relative to the solution emission, probably from the formation of excimers or ground-state complexes in the solid.[36] The emission **m-4Hex** in solution is blue-shifted by approximately 22 nm, relative to that of **4Hex**. For **5Hex** and **m-5Hex** in solution, the difference in emission is less pronounced (Figure 12). Therefore, increasing the conjugation length of the chromophore minimizes the effect of the "contact" across the binaphthyl framework.

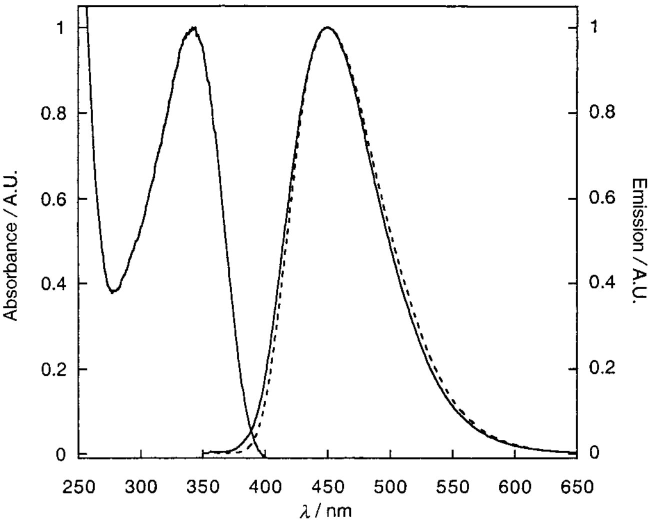


Figure 10. For **3Hex**, absorbance and photoluminescence spectra (λ_{exc} = 340 nm) in solution (solid lines) and from films (dashed lines).

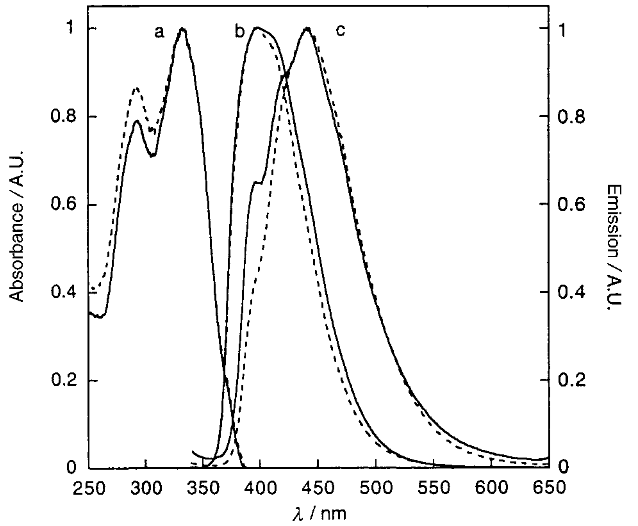


Figure 11. Absorbance (a) and photoluminescence (b: solution; c: film) spectra for **4Hex** (solid line) and **(*R*)-4Hex** (dashed line).

Except for the **3** series, the film emission is red-shifted relative to solution emission (Table 1).[37] There are no observable changes in the absorption spectra, suggesting that the red-shift is a result of excimer-type interactions in the solid.

Electroluminescence: The potential use of binaphthyl-based organic glasses in device fabrication was examined by fabrication of LEDs with the binaphthyl bichromophores as

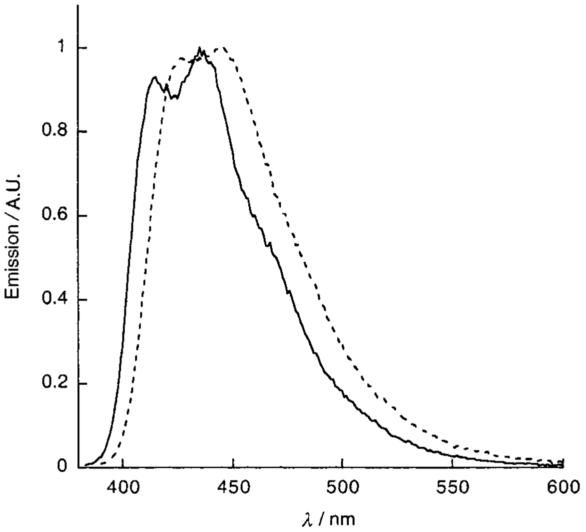


Figure 12. Photoluminescence spectra ($\lambda_{exc} = 374$ nm) for **5Hex** (dashed line) and **m-5Hex** (solid line).

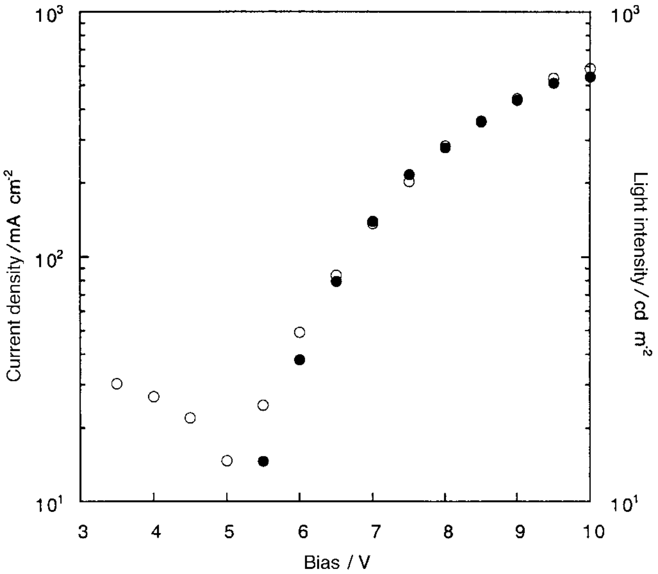


Figure 13. The current density (open circles) and the emission intensity (solid circles) as a function of bias.

the electroluminescent layer. The devices were constructed according to previously established procedures.[38] These studies were made from the proof of principle point of view, and did not include full optimization of the electrode work function to the orbital energies of the organic materials.[39] We focused on **5Hex** because of its superior solubility, relative to **6Hex**, and its lower aliphatic content than the more soluble **7Hex**.

Devices were fabricated with the configurations of ITO/**5Hex**/Ba/Al, ITO/**5Hex**/Ca, ITO/PVK/**5Hex**/Ba/Al, ITO/PVK/**5Hex**/Ca, Au/**5Hex**/Nd, and ITO/PEDT/PVK/**5Hex**/Ba/Al, where PVK refers to poly(vinylcarbazole) and PEDT to poly(ethylenedioxythiophene). Devices without PEDT showed strictly ohmic behavior, with no light output. However, devices using PEDT (ITO/PEDT(300 Å)/PVK(300 Å)/**5Hex**/Ba/Al) exhibited modest efficiency (0.1 cd A^{-1}) and low turn-on voltage (3.5 V, near the HOMO–LUMO energy difference), despite minor current leakage prior to turn-on (see Figure 13). A typical EL (electroluminescence) spectrum displays a maximum at 503 nm, slightly red-shifted from that observed from the PL (photoluminescence) (Figure 14). Substantially more efficient devices should be accessible by optimization of device architecture.

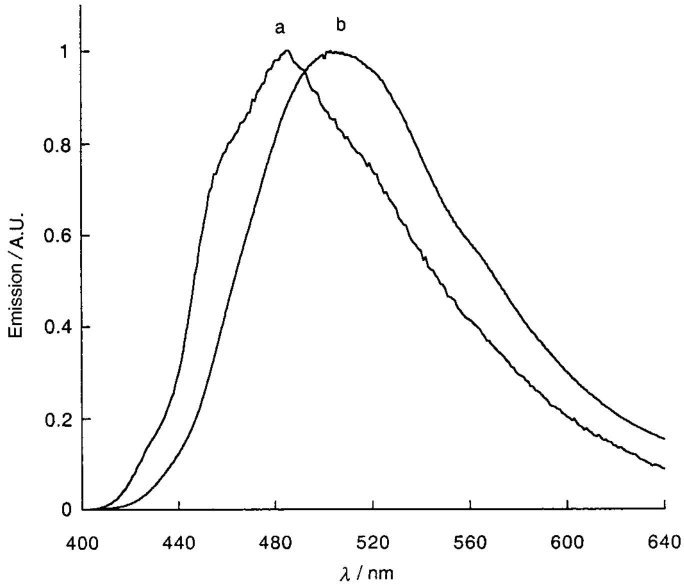


Figure 14. Comparison of PL (a) and EL (b) of the LED in Figure 13.

Conclusion

In summary, we have shown that the molecular topology of the binaphthyl framework makes it suitable for designing noncrystallizable organic chromophores. Oxygen substituents provide a handle to fine-tune glass-transition temperatures. For a given chromophore, increasing the aliphatic content of the molecule reduces the glass-transition temperature. Furthermore, for the molecules involved in this study, as the dimensions of the conjugated fragment *decrease*, there is an *increased* tendency for bulk crystallization.

Molecular chirality emerges from these studies as another parameter that can be used to control crystallization tendencies. At this stage, however, no clear trends have emerged. For **4Hex** and **7Hex**, the enantiomerically enriched molecules lead to samples that resist crystallization to a greater extent than their racemic analogues. The opposite trend is observed for **4Me**. Samples of intermediate enantiomeric purity show complex thermal behavior (Figure 7).

Finally, we have shown that the amorphous features of **5Hex** allow the fabrication of LEDs, in which the electroluminescent layer is cast directly from solution. Current efforts in our group are focused on the optimization of device performance in a study of how the film quality of these binaphthyl chromophores depends on molecular structure.

Experimental Section

General: All metal-mediated coupling reactions were conducted in oven-dried glassware under an argon atmosphere. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Inova 400 NMR spectrometer operating at 400.1 (RT) and 100.6 MHz (RT), respectively. ^{1}H and ^{13}C{^{1}H} NMR spectra were also recorded on a Varian Inova 500 NMR spectrometer operating at 500.1 (RT) and 125 MHz (RT), respectively. UV/Vis absorption spectra were recorded by using a Shimadzu UV-2401PC spectrophotometer. Fluorescence spectra were measured on a Spex Fluorolog 2 spectrometer in spectral grade chloroform using 90 degree angle detection for solution samples and front-face detection for films. High-resolution mass spectrometry was performed by the UC Santa Barbara Mass Spectrometry Lab. Differential scanning calorimetry data were recorded on a Netzsch DSC 204. Purity was analyzed on a Shimadzu HPLC equipped with a photodiode array detector. Optical rotations were done on a Perkin Elmer Polarimeter 341 with a sodium lamp set at 589 nm. Reagents were obtained from Aldrich Co. and used as received.

Compounds **2Bz**,[26] **2Hex**,[24] **2Me**,[25] **2MOM**,[25], [27] 1,1-diphenyl-2-(4′-pinacolatoboronphenyl)-ethene,[33] (4′-*tert*-butylstyryl)styrene,[32] 1-(4′-*tert*-butylstyryl)-4-(4′-vinylstyryl)benzene,[33] and 1-(3′,5′-dihexyloxystyryl)-4-(4′-vinylstyryl)benzene[15] were prepared according to literature procedures.

6,6′-Dibromo-2,2′-dihexyloxy-1,1′-binaphthyl (2Hex): A single-neck round bottom flask (50 mL), equipped with a magnetic stir bar and reflux condenser, was charged with 6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthyl (l0.5 g, 1.13 mmol, 1.0 equiv)[40] and acetone (7 mL). Potassium carbonate (0.715 g, 5.52 mmol, 4.6 equiv) and 1-bromohexane (0.825 mL, 5.85 mmol, 5.2 equiv) were added to the solution. The resulting slurry was refluxed overnight. The mixture was then allowed to cool to room temperature, and then the solvent was removed in vacuo. After dilution with water, the aqueous phase was extracted three times with ethyl acetate (25 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated to afford **2Hex** (0.664 g, 96 %). The ^{1}H NMR (400 MHz, $CDCl_3$) data matched previous assignment.[24, 40]

(*R*)-6,6′-Dibromo-2,2′-dihexyloxy-1,1′-binaphthyl ((*R*)-2Hex): (*R*)-6,6′-Dibromo-2,2′-dihydroxy-1,1′-binaphthyl (1.55 g, 3.5 mmol)[24] was treated according to the general procedure described above for **2Hex** to afford **(*R*)-2Hex** (2.04 g, 95 %).

6,6′-Dibromo-2,2′-dibutyloxy-1,1′-binaphthyl (2Bu): 6,6′-Dibromo-2,2′-dihydroxy-1,1′-binaphthyl (0.744 g, 1.7 mmol) was treated with 1-bromobutane according to the procedure described above for **2Hex** to afford **2Bu** (0.844 g, 91 %).

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.01$ (d, $J = 2.1$ Hz, 2H), 7.85 (d, $J = 9.1$ Hz, 2H), 7.42 (d, $J = 9.1$ Hz, 2H), 7.27 (dd, $J_1 = 9.1$ Hz, $J_2 = 2.1$ Hz, 2H), 6.98 (d, $J = 9.1$ Hz, 2H), 3.94 (m, 4H), 1.40 (m, 4H), 1.00 (m, 4H), 0.67 (t, $J = 7.4$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.0$, 132.8, 130.4, 129.9, 129.6, 128.6, 127.3, 120.2, 117.4, 116.6, 69.4, 31.5, 18.9, 13.8; exact mass (EI) for [MH]$^{+\bullet}$ calcd for $C_{28}H_{28}Br_2O_2$: 554.0456; found: 554.0460.

6-Bromo-2-hexyloxynaphthalene: A round bottom flask (150 mL) was charged with 6-bromo-2-naphthol (2.09 g, 9.4 mmol, 1 equiv), potassium hydroxide (12.4 g, 221.1 mmol, 24 equiv), potassium carbonate (10.5 g, 10.6 mmol, 76.3 equiv), 1-bromohexane (7.605 g, 46.1 mmol, 4.9 equiv), and DMSO (80 mL). The reaction mixture was stirred for 24 hours at room temperature and then was worked up with water and chloroform. The chloroform layer was washed three times with water, dried over $MgSO_4$, filtered, and the solvent was removed under vacuum. The material was purified by column chromatography (100 % hexanes) to yield 6-bromo-2-hexyloxynaphthalene (2.35 g, 94 % yield).

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.92$ (d, $J = 2.0$ Hz, 1H), 7.62 (dd, $J_1 = 25.6$ Hz, $J_2 = 2.0$ Hz, 2H), 7.50 (dd, $J_1 = 8.7$ Hz, $J_2 = 2.0$ Hz, 1H), 7.17 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.6$ Hz, 4H), 7.09 (d, $J = 2.4$ Hz, 1H), 4.06 (t, $J = 6.6$ Hz, 2H), 1.86 (m, 4H), 1.38 (m, 4H), 0.94 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 157.6$, 133.3, 130.1, 129.8, 128.6, 128.5, 120.3, 117.1, 106.7, 68.3, 31.8, 29.4, 26.0, 22.8, 14.3; exact mass (FAB, NBA) for [MH]$^{+\bullet}$ calcd for $C_{15}H_{19}BrO$: 306.0619; found: 306.0620.

2,2′-Dihexyloxy-6,6′-bis(4-(2,2′-diphenyl-vinyl)-1-phenyl)-1,1′-binaphthyl (3Hex): A single-neck round bottom flask (100 mL), equipped with a magnetic stir bar and a rubber septum secured with copper wire, was charged with **2Hex** (0.50 g, 0.82 mmol, 1.0 equiv), 1,1-diphenyl-2-(4-dihydroxyboronphenyl)-ethene (0.74 g, 2.4 mmol, 3.0 equiv), [Pd(dppf)Cl_2] (30 mg, 0.04 mmol, 0.05 equiv), and THF (36 mL). Sodium bicarbonate (sat. aq., 9 mL) was added to the solution. The resulting slurry was sparged with argon for 15 minutes prior to heating to 75 °C for two days. After cooling, the reaction was placed under vacuum to remove THF. Water was added to the resulting solid, and the aqueous phase was extracted three times with methylene chloride (40 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated under vacuum to afford a crude product. The resulting solid was purified by chromatography on silica gel (35 % CH_2Cl_2/65 % hexanes) to afford **3Hex** (0.40 g, 50 %).

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.03$ (d, $J = 2.0$ Hz, 2H), 7.95 (d, $J = 8.8$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 4H), 7.44 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz, 2H), 7.42 (d, 9.2 Hz, 2H), 7.32 (m, 20H), 7.21 (d, $J = 8.8$ Hz, 2H), 7.11 (d, $J = 8.4$ Hz, 4H), 7.02 (s, 2H), 3.96 (m, 4H), 1.41 (m, 4H), 0.98 (m, 20H), 0.71 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.9$, 143.7, 142.7, 140.7, 139.6, 136.3, 135.6, 133.6, 130.6, 130.2, 129.6, 128.9, 128.4, 128.0, 127.8, 127.7, 126.8, 126.2. 125.6, 125.5, 120.6, 116.3. 69.9, 31.5. 29.5, 25.5, 22.7, 14.1; exact mass (FAB, NBA) for [MH]$^{+\bullet}$ calcd for $C_{72}H_{66}O_2$: 962.5063; found: 962.5109.

2,2′-Dihexyloxy-6,6′-bis(4-(2,2′-diphenyl-vinyl)-1-phenyl)-1,1′-binaphthyl ((*R*)-3Hex): The procedure described for **3Hex** was repeated starting with **(*R*)-2Hex** (0.11 g, 0.18 mmol). After purification by chromatography on silica gel (35 % CH_2Cl_2/65 % hexanes), **(*R*)-3Hex** (0.11 g, 60 %) was obtained.

$[\alpha]_D = -6.0$ ($c = 0.50$ in THF); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.03$ (d, $J = 2.0$ Hz, 2H), 7.95 (d, $J = 8.8$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 4H), 7.44 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz, 2H), 7.42 (d, $J = 9.2$ Hz, 2H), 7.32 (m, 20H), 7.21 (d, $J = 8.8$ Hz, 2H), 7.11 (d, $J = 8.4$ Hz, 4H), 7.02 (s, 2H), 3.96 (m, 4H), 1.41 (m, 4H), 0.98 (m, 20H), 0.71 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.9$, 143.7, 142.7, 140.7, 139.6, 136.3, 135.6, 133.6, 130.6, 130.2, 129.6, 128.9, 128.4, 128.0, 127.8, 127.7, 126.8, 126.2, 125.6, 125.5, 120.6, 116.3, 69.9, 31.5, 29.5, 25.5, 22.7, 14.1; exact mass (FAB, NBA) for [MH]$^{+\bullet}$ calcd for $C_{72}H_{66}O_2$: 962.5063; found: 962.5074.

2,2′-Dibenzyloxy-6,6′-bis(4-(2,2′-diphenyl-vinyl)-1-phenyl)-1,1′-binaphthyl (3Bz): The reaction described for the synthesis of **3Hex** was carried out starting with **2Bz** (0.50 g, 0.80 mmol). After chromatographic separation on silica (40 % CH_2Cl_2/60 % hexanes), **3Bz** (0.33 g, 42 %) was obtained.

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.04$ (d, $J = 1.6$ Hz, 2H), 7.95 (d, $J = 8.8$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 4H), 7.46 (m, 2H), 7.43 (d, $J = 9.2$ Hz, 2H), 7.33 (m, 18H), 7.25 (m, 4H), 7.10 (m, 10H), 6.99 (m, 6H), 5.07 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.5$, 143.6, 142.7, 140.7, 139.4, 137.7, 136.4, 135.9, 133.6, 130.6, 130.2, 129.8, 129.0, 128.4, 128.3, 128.0, 127.8, 127.7, 127.5, 126.9, 126.8, 126.3, 125.9, 125.7, 120.7, 116.6, 71.3; exact mass (FAB, NBA) for [MH]$^{+\bullet}$ calcd for $C_{74}H_{54}O_2$: 974.4124; found: 974.4138; elemental analysis calcd (%) for $C_{74}H_{54}O_2$ (975.15): C 91.14, H 5.58; found: C 91.62, H 5.39.

2,2′-Dibutyloxy-6,6′-bis(4-(2,2′-diphenyl-vinyl)-1-phenyl)-1,1′-binaphthyl (3Bu): The reaction described for the synthesis of **3Hex** was carried out starting with **2Bu** (0.091 g, 0.164 mmol). After purification by chromatography on silica gel (50 % $CHCl_3$/50 % hexanes), **3Bu** (0.086 g, 46 %) was obtained.

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.03$ (d, $J = 2.0$ Hz, 2H), 7.96 (d, $J = 8.8$ Hz, 2H), 7.48 (d, $J = 8.8$ Hz, 4H), 7.44 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz, 2H), 7.42 (d, $J = 9.2$ Hz, 2H), 7.32 (m, 20H), 7.21 (d, $J = 8.8$ Hz, 2H), 7.12 (d, $J = 8.8$ Hz, 4H), 7.02 (s, 2H), 3.96 (m, 4H), 1.42 (m, 4H), 1.00 (m, 4H), 0.66 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.9$, 143.7, 142.7, 140.7, 139.06, 136.3, 135.5, 133.6, 130.6, 130.2, 129.6, 129.0, 128.4, 128.0, 127.8, 127.7, 126.8, 126.2, 125.6, 125.5, 120.6, 116.3, 69.6, 31.6, 19.0, 13.8; exact mass (FAB, NBA) for [MH]$^{+\bullet}$ calcd for $C_{68}H_{58}O_2$: 906.4437; found: 906.4465.

2,2′-Bis(methoxymethoxy)-6,6′-bis(4-(2,2′-diphenyl-vinyl)-1-phenyl)-1,1′-binaphthyl (3MOM): The reaction described for the synthesis of **3Hex** was carried out starting with **2MOM** (0.100 g, 0.188 mmol). After purification by chromatography on silica gel (60 % CH_2Cl_2/40 % hexanes), **3MOM** (0.065 g, 39 %) was obtained.

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.05$ (d, $J = 1.6$ Hz, 2H), 7.98 (d, $J = 9.2$ Hz, 2H), 7.60 (d, $J = 9.2$ Hz, 2H), 7.48 (d, $J = 8.0$ Hz, 2H), 7.46 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz, 2H), 7.30 (m, 22H), 7.21 (d, $J = 8.8$ Hz, 2H), 7.11 (d,

$J = 8.4$ Hz, 4H), 7.01 (s, 2H), 5.11 (d, $J = 6.8$ Hz, 2H), 5.00 (d, $J = 6.8$ Hz, 2H), 3.17 (s, 6H); exact mass (FAB, NBA) for $[M]^{+\bullet}$ calcd for $C_{64}H_{50}O_4$: 882.3709; found: 882.3729.

2,2′-Dimethoxy-6,6′-bis(4-(2,2′-diphenyl-vinyl)-1-phenyl)-1,1′-binaphthyl (3Me): The procedure for the synthesis of **3Hex** was duplicated starting with **2Me** (0.376 g, 0.796 mmol). Purification by chromatography on silica gel (40% CH_2Cl_2/60% hexanes) gave **3Me** (0.278 g, 42%).

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.04$ (d, $J = 1.8$ Hz, 2H), 8.00 (d, $J = 8.9$ Hz, 2H), 7.45 (m, 8H), 7.32 (m, 20H), 7.16 (d, $J = 8.9$ Hz, 2H), 7.10 (d, $J = 8.1$ Hz, 4H), 7.02 (s, 2H), 3.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.3$, 143.6, 142.7, 140.7, 139.4, 136.4, 135.7, 133.4, 130.6, 130.2, 130.0, 129.6, 129.0, 128.4, 128.0, 127.8, 127.7, 126.8, 125.9. 125.8, 119.5, 114.8, 57.1; exact mass (FAB, NBA) for $[MH]^{+\bullet}$ calcd for $C_{62}H_{46}O_2$: 822.3498; found: 822.3510.

2-Hexyloxy-6-(4′-(2′,2″-diphenyl-vinyl)-1′-phenyl)naphthalene (m-3Hex): The conditions for the synthesis of **3Hex** were duplicated starting with 6-bromo-2-hexyloxynaphthalene (0.19 g, 0.62 mmol, 1 equiv), 1,1-diphenyl-2-(4′-pinacolatoboronphenyl)-ethene (0.35 g, 0.92 mmol, 1.5 equiv), $[Pd(dppf)Cl_2]$ (0.05 g, 0.06 mmol, 0.1 equiv), sodium bicarbonate (0.84 g, 10 mmol, 16 equiv), THF (8 mL), and water (2.5 mL). The crude material was purified by chromatography on silica gel (20% $CHCl_3$/80% hexanes) to yield of **m-3Hex** (0.22 g, 72%).

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 1.5$ Hz, 1H), 7.76 (d, $J = 8.6$ Hz, 2H), 7.68 (dd, $J_1 = 1.8$ Hz, $J_2 = 8.6$ Hz, 1H), 7.51 (dt, $J_1 = 8.4$ Hz, $J_2 = 1.8$ Hz, 2H), 7.43 (m, 10H), 7.15 (m, 4H), 7.04 (s, 1H), 4.10 (t, $J = 6.6$ Hz, 2H), 1.87 (m, 2H), 1.53 (m, 2H), 1.41 (m, 4H), 0.95 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 157.5$, 143.6, 142.7, 140.7, 139.5, 136.4, 135.7, 134.0, 130.6, 130.3, 129.8, 129.3, 128.9, 128.4, 127.9, 127.8, 127.7, 127.4, 126.8, 125.8, 125.5, 119.7, 106.5, 68.3, 31.8, 29.4, 26.0, 22.9, 14.3; exact mass (FAB, NBA) for $[MH]^{+\bullet}$ calcd for $C_{36}H_{34}O$: 482.2610; found: 482.2603; elemental analysis calcd (%) for $C_{36}H_{34}O$ (482.62): C 89.58, H 7.10; found: C 89.58, H 7.09.

2,2′-Dihexyloxy-6,6′-bis(2-phenyl-vinyl)-1,1′-binaphthyl (4Hex): A single-neck round bottom flask (50 mL), equipped with a magnetic stir bar and a rubber septum secured with copper wire, was charged with **2Hex** (70 mg, 0.114 mmol, 1.0 equiv), Herrmann's catalyst[31] (5 mg, 0.005 mmol, 0.05 equiv), sodium acetate (42 mg, 0.500 mmol, 4.5 equiv), and dimethyl acetamide (3 mL). The solution was sparged with argon for 15 minutes prior to addition of styrene (80 µL, 0.685 mmol, 6.0 equiv). The resulting slurry was heated to 140 °C for two days. After cooling, the reaction was diluted with water. The aqueous phase was extracted three times with portions (20 mL) of methylene chloride. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated to afford crude product. Purification by chromatography on silica gel (30% CH_2Cl_2/70% hexanes) gave **4Hex** (22 mg, 29%).

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 9.2$ Hz, 2H), 7.89 (s, 2H), 7.54 (d, $J = 7.6$ Hz, 4H), 7.49 (dd, $J_1 = 8.8$ Hz, $J_2 = 1.6$ Hz, 2H), 7.41 (d, $J = 9.2$ Hz, 2H), 7.37 (m, 4H), 7.26 (m, 4H), 7.17 (d, $J = 8.8$ Hz, 2H), 7.12 (d, $J = 16.4$ Hz, 2H), 3.96 (m, 4H), 1.42 (m, 4H), 1.00 (m, 12H), 0.74 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.0$, 137.8, 134.0, 132.7, 129.5, 129.4, 129.2, 128.9, 128.0, 127.6, 126.9, 126.6, 126.1, 124.0, 120.8, 116.2, 69.9, 31.5, 29.5, 25.5, 22.7, 14.2; exact mass (FAB, NBA) for $[MH]^{+\bullet}$ calcd for $C_{48}H_{50}O_2$: 658.3811; found: 658.3799.

(*R*)-2,2′-Dihexyloxy-6,6′-bis(2-phenyl-vinyl)-1,1′-binaphthyl ((*R*)-4Hex): The procedure for the synthesis of **4Hex** was duplicated starting with **(*R*)-2Hex** (1.20 g, 1.9 mmol). After purification by chromatography on silica gel (30% CH_2Cl_2/70% hexanes), **(*R*)-4Hex** (1.05 g, 81%) was obtained.

$[\alpha]_D = -341.5$ ($c = 0.50$ in THF); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 8.8$ Hz, 2H), 7.89 (s, 2H), 7.54 (d, $J = 7.2$ Hz, 4H), 7.49 (dd, $J_1 = 8.8$ Hz, $J_2 = 1.6$ Hz, 2H), 7.41 (d, $J = 8.8$ Hz, 2H), 7.37 (m, 4H), 7.26 (m, 4H), 7.17 (d, $J = 8.8$ Hz, 2H), 7.13 (d, $J = 16.4$ Hz, 2H), 3.96 (m, 4H), 1.43 (m, 4H), 1.00 (m, 12H), 0.74 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 155.0, 137.8, 134.0, 132.7, 129.5, 129.4, 129.2, 128.9, 128.0, 127.6, 126.9, 126.6, 126.1, 124.0, 120.8, 116.2, 69.9, 31.5, 29.5, 25.5, 22.7, 14.2; exact mass (FAB, NBA) for $[MH]^{+\bullet}$ calcd for $C_{48}H_{50}O_2$: 658.3811; found: 658.3811; elemental analysis calcd (%) for $C_{48}H_{50}O_2$ (658.86): C 87.67, H 7.36; found: C 87.73, H 7.33.

(*R*)-2,2′-Dibutyloxy-6,6′-bis(2-phenyl-vinyl)-1,1′-binaphthyl ((*R*)-4Bu): The procedure for the synthesis of **4Hex** was duplicated starting with **(*R*)-2Bu** (0.94 g, 1.7 mmol). After purification by chromatography on silica gel (20–60% $CHCl_3$/80–40% hexanes), **(*R*)-Bu** (0.563 g, 55%) was obtained

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 8.8$ Hz, 2H), 7.90 (d, $J = 1.6$ Hz, 2H), 7.55 (d, $J = 7.3$ Hz, 4H), 7.50 (dd, $J_1 = 1.8$ Hz, $J_2 = 8.8$ Hz, 2H), 7.42 (d, $J = 8.9$ Hz, 2H), 7.37 (dd, $J_1 = 7.5$ Hz, $J_2 = 7.8$ Hz, 4H), 7.27 (d, $J = 16.3$ Hz, 2H), 7.18 (d, $J = 8.9$ Hz, 2H), 7.14 (d, $J = 16.3$ Hz, 2H), 3.98 (m, 4H), 1.45 (m, 4H), 1.03 (m, 4H), 0.68 (t, $J = 6.7$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.03$, 137.79, 134.05, 132.61, 129.51, 129.42, 129.15, 128.86, 128.04, 127.58, 126.92, 126.60, 126.12, 123.96, 120.80, 116.16, 69.49, 31.56, 18.96, 13.79; exact mass (FAB, NBA) for $[M]^{+\bullet}$ calcd for $C_{44}H_{42}O_2$: 602.3180; found: 602.3185.

(*S*)-2,2′-Dibutyloxy-6,6′-bis(2-phenyl-vinyl)-1,1′-binaphthyl ((*S*)-4Bu): The procedure for the synthesis of **4Hex** was duplicated starting with **(*S*)-2Bu** (0.9 g, 1.62 mmol). After purification by chromatography on silica gel (20–60% $CHCl_3$/80–40% hexanes), **(S)-4Bu** (0.488 g, 50%) was obtained.

$[\alpha]_D = +346.5$ ($c = 0.58$ in THF); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 8.8$ Hz, 2H), 7.90 (d, $J = 1.6$ Hz, 2H), 7.55 (d, $J = 7.3$ Hz, 4H), 7.50 (dd, $J_1 = 1.8$ Hz, $J_2 = 8.8$ Hz, 2H), 7.42 (d, $J = 8.9$ Hz, 2H), 7.37 (dd, $J_1 = 7.5$ Hz, $J_2 = 7.8$ Hz, 4H), 7.27 (d, $J = 16$ Hz, 2H), 7.18 (d, $J = 8.9$ Hz, 2H), 7.14 (d, $J = 16.3$ Hz, 2H), 3.98 (m, 4H), 1.45 (m, 4H), 1.03 (m, 4H), 0.68 (t, $J = 6.9$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.03$, 137.79, 134.05, 132.61, 129.51, 129.42, 129.15, 128.86, 128.04, 127.58, 126.92, 126.60, 126.12, 123.96, 120.80, 116.16, 69.49, 31.56, 18.96, 13.79; exact mass (FAB, NBA) for $[M]^{+\bullet}$ calcd for $C_{44}H_{42}O_2$: 602.3180; found: 602.3185.

(*R*)-2,2′-Dibenzyloxy-6,6′-bis(2-phenyl-vinyl)-1,1′-binaphthyl ((*R*)-4Bz): The procedure for the synthesis of **4Hex** was duplicated starting with **(*R*)-2Bz** (1.41 g, 2.26 mmol). After purification by chromatography on silica gel (30–60% $CHCl_3$/70–40% hexanes), **(*R*)-4Bz** (0.681 g, 45%) was obtained.

$[\alpha]_D = -265.1$ ($c = 0.31$ in THF); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 8.9$ Hz, 2H), 7.92 (d, $J = 1.3$ Hz, 2H), 7.55 (d, $J = 7.3$ Hz, 4H), 7.52 (dd, $J_1 = 1.9$ Hz, $J_2 = 8.9$ Hz, 2H), 7.43 (d, $J = 9.1$ Hz, 2H), 7.38 (dd, $J_1 = 7.5$ Hz, $J_2 = 7.8$ Hz, 4H), 7.26 (m, 6H), 7.14 (m, 8H), 7.00 (d, $J = 8.1$ Hz, 4H), 5.08 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.57$, 137.73, 137.65, 133.98, 132.99, 129.78, 129.65, 129.02, 128.88, 128.38, 128.32, 127.65, 127.53, 126.96, 126.87, 126.65, 126.16, 124.27, 120.93, 116.45, 71.30; exact mass (FAB, NBA) for $[M]^{+\bullet}$ calcd for $C_{50}H_{38}O_2$: 670.2864; found: 670.2872; elemental analysis calcd (%) for $C_{50}H_{38}O_2$ (670.78): C 89.52, H 5.71; found: C 90.15, H 5.72.

(*S*)-2,2′-Dibenzyloxy-6,6′-bis(2-phenyl-vinyl)-1,1′-binaphthyl ((*S*)-4Bz): The procedure for the synthesis of **4Hex** was duplicated starting with **(*S*)-2Bz** (0.78 g, 1.25 mmol). After purification by chromatograpy on silica gel (30–60% $CHCl_3$/70–40% hexanes), **(*S*)-4Bz** (0.418 g, 50% yield) was obtained.

$[\alpha]_D = +222.4$ ($c = 0.57$ in THF); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 8.9$ Hz, 2H), 7.92 (d, $J = 1.3$ Hz, 2H), 7.55 (d, $J = 7.3$ Hz, 4H), 7.52 (dd, $J_1 = 1.9$ Hz, $J_2 = 8.9$ Hz, 2H), 7.43 (d, $J = 9.1$ Hz, 2H), 7.38 (dd, $J_1 = 7.5$ Hz, $J_2 = 7.8$ Hz, 4H), 7.26 (m, 6H), 7.14 (m, 8H), 7.00 (d, $J = 8.1$ Hz, 4H), 5.08 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.57$, 137.73, 137.65, 133.98, 132.99, 129.78, 129.65, 129.02, 128.88, 128.38, 128.32, 127.65, 127.53, 126.96, 126.87, 126.65, 126.16, 124.27, 120.93, 116.45, 71.30; exact mass (FAB, NBA) for $[M]^{+\bullet}$ calcd for $C_{50}H_{38}O_2$: 670.2864; found: 670.2872.

2,2′-Dimethoxy-6,6′-bis(2-phenyl-vinyl)-1,1′-binaphthyl (4Me): The procedure for the synthesis of **4Hex** was duplicated starting with **2Me** (2.4 g, 5.08 mmol). After purification by chromatography on silica gel (40–60% $CHCl_3$/60–40% hexanes), **4Me** (1.105 g, 42%) was obtained.

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.00$ (d, $J = 9.0$ Hz, 2H), 7.90 (d, $J = 1.8$ Hz, 2H), 7.54 (d, $J = 7.0$ Hz, 4H), 7.50 (dd, $J_1 = 8.8$ Hz, $J_2 = 1.8$ Hz, 2H), 7.47 (d, $J = 8.8$ Hz, 2H), 7.40 (m, 4H), 7.26 (m, 4H), 7.14 (d, $J = 6.6$ Hz, 2H), 7.11 (s, 2H), 3.80 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 155.4$, 137.7, 133.8, 132.8, 129.8, 129.6, 129.0, 128.9, 128.2, 127.6, 127.0, 126.6, 125.9, 124.3, 119.8, 114.6, 57.1; exact mass (FAB, NBA) for $[MH]^{+\bullet}$ calcd for $C_{38}H_{30}O_2$: 518.2246; found: 518.2238.

(*R*)-2,2′-Dimethoxy-6,6′-bis(2-phenyl-vinyl)-1,1′-binaphthyl ((*R*)-4Me): The procedure for the synthesis of **4Hex** was duplicated starting with **(*R*)-2Me** (1.44 g, 3.05 mmol). After purification by chromatography on silica gel (40–60% $CHCl_3$/60–40% hexanes), **(*R*)-4Me** (0.71 g, 45%) was obtained.

$[\alpha]_D = -411.9$ ($c = 0.50$ in THF); ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 8.00$ (d, $J = 9.0$ Hz, 2H), 7.90 (d, $J = 1.8$ Hz, 2H), 7.54 (d, $J = 7.0$ Hz, 4H), 7.50 (dd, $J_1 = 8.8$ Hz, $J_2 = 1.8$ Hz, 2H), 7.47 (d, $J = 8.8$ Hz, 2H), 7.40 (m, 4H), 7.26 (m, 4H), 7.14 (d, $J = 6.6$ Hz, 2H), 7.11 (s, 2H), 3.80 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$): $\delta = 155.4$, 137.7, 133.8, 132.8, 129.8, 129.6, 129.0, 128.9, 128.2, 127.6, 127.0, 126.6, 125.9, 124.3, 119.8, 114.6, 57.1; exact mass (FAB, NBA) for $[M\text{H}]^{+\bullet}$ calcd for $C_{38}H_{30}O_2$: 518.2246; found: 518.2238; elemental analysis calcd (%) for $C_{38}H_{30}O_2$ (518.60): C 87.99, H 5.83; found: C 87.75, H 5.87.

(*S*)-2,2′-Dimethoxy-6,6′-bis(2-phenyl-vinyl)-1,1′-binaphthyl ((*S*)-4Me): The procedure for the synthesis of **4Hex** was duplicated starting with **(*S*)-2Me** (0.59 g, 1.25 mmol). After purification by chromatography on silica gel (40–60% CHCl$_3$/60–40% hexanes), **(*S*)-4Me** (0.259 g, 40%) was obtained.

^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 8.00$ (d, $J = 9.0$ Hz, 2H), 7.90 (d, $J = 1.8$ Hz, 2H), 7.54 (d, $J = 7.0$ Hz, 4H), 7.50 (dd, $J_1 = 8.8$ Hz, $J_2 = 1.8$ Hz, 2H), 7.47 (d, $J = 8.8$ Hz, 2H), 7.40 (m, 4H), 7.26 (m, 4H), 7.14 (d, $J = 6.6$ Hz, 2H), 7.11 (s, 2H), 3.80 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$): $\delta = 155.4$, 137.7, 133.8, 132.8, 129.8, 129.6, 129.0, 128.9, 128.2, 127.6, 127.0, 126.6, 125.9, 124.3, 119.8, 114.6, 57.1; exact mass (FAB, NBA) for $[M\text{H}]^{+\bullet}$ calcd for $C_{38}H_{30}O_2$: 518.2246; found: 518.2238.

2-Hexyloxy-6-(2-phenyl-vinyl)naphthalene (m-4Hex): A round bottom flask (10 mL) was charged with 6-bromo-2-hexyloxynaphthalene (0.23 g, 0.76 mmol, 1 equiv), styrene (0.28 mL, 2.4 mmol, 3.2 equiv), potassium carbonate (0.49 g, 3.5 mmol, 4.6 equiv), tetrabutylammonium bromide (0.46 g, 1.4 mmol, 1.9 equiv), palladium acetate (0.03 g, 0.131 mmol, 0.17 equiv), and DMF (5 mL). This reaction mixture was degassed, placed under argon, and heated to 80 °C. After 2.5 days, the reaction mixture was worked up with water and chloroform. The chloroform layer was washed three times with water, dried over MgSO$_4$, filtered, and the solvent was removed under vacuum. The crude material was purified by chromatography on silica gel (20–30% CHCl$_3$/80–70% hexanes) to yield **m-4Hex** (120 mg, 47%).

^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.79$ (s, 1H), 7.72 (m, 3H), 7.56 (d, $J = 7.2$ Hz, 2H), 7.39 (t, $J = 7.5$ Hz, 2H), 7.26 (m, 2H), 7.21 (s, 1H), 7.15 (m, 2H), 4.08 (t, $J = 6.5$ Hz, 2H), 1.86 (sext, 2H), 1.52 (m, 2H), 1.38 (m, 4H), 0.94 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 157.5$, 137.8, 139.5, 132.8, 129.6, 129.2, 129.1, 128.9, 128.1, 127.7, 127.3, 126.7, 126.6, 124.2, 119.6, 106.9, 68.3, 31.8, 29.4, 26.0, 22.8, 14.3; exact mass (FAB, NBA) for $[M\text{H}]^{+\bullet}$ calcd for $C_{24}H_{26}O$: 330.1984; found: 330.1984; elemental analysis calcd (%) for $C_{24}H_{26}O$ (330.44): C 87.50, H 7.65; found: C 87.00, H 7.73.

2,2′-Dihexyloxy-6,6′-bis(4-(4′-*tert*-butylstyryl)styryl)-1,1′-binaphthyl (5Hex): A round bottom flask (25 mL) was charged with **2Hex** (0.125 g, 0.205 mmol, 1 equiv), 4-(4′-*tert*-butylstyryl)styrene (0.215 g, 0.820 mole, 4 equiv), palladium acetate (0.005 g, 0.021 mmol, 0.1 equiv), potassium carbonate (0.142 g, 1.03 mmol, 5 equiv), tetrabutylammonium bromide (0.132 g, 0.410 mmol, 2 equiv), and DMF (5 mL). This slurry was degassed, placed under argon, and heated to 80 °C for 2.5 days. After cooling, the slurry was diluted with chloroform (50 mL). This solution was washed three times with water (50 mL), dried over MgSO$_4$, filtered, and concentrated to yield a crude product. Purification by column chromatography on silica gel (20–50% CHCl$_3$/80–50% hexanes), yielded **5Hex** (153 mg, 77%).

^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.94$ (d, $J = 8.8$ Hz, 2H), 7.89 (s, 2H), 7.51 (m, 14H), 7.41 (m, 6H), 7.28 (d, $J = 16$ Hz, 2H), 7.18 (d, $J = 8.8$ Hz, 2H), 7.11 (m, 6H), 3.96 (m, 4H), 1.35 (m, 22H), 1.04 (m, 12H), 0.75 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 155.1$, 151.0, 137.0, 136.9, 134.8, 134.0, 132.7, 129.6, 129.4, 129.0, 128.4, 127.8, 127.7, 127.0, 126.95, 126.91, 126.4, 126.2, 125.8, 123.9, 120.8, 116.2, 69.8, 34.8, 31.54, 31.50, 29.5, 25.5, 22.7, 14.21; exact mass (FAB, NBA) for $[M\text{H}]^{+\bullet}$ calcd for $C_{72}H_{78}O_2$: 974.6002; found: 974.6009; elemental analysis calcd (%) for $C_{72}H_{78}O_2$ (975.32): C 88.66, H 8.04; found: C 89.35, H 7.89.

(*R*)-2,2′-Dihexyloxy-6,6′-bis(4-(4′-*tert*-butylstyryl)styryl)-1,1′-binaphthyl ((*R*)-5Hex): The procedure for the synthesis of **5Hex** was duplicated starting with **(*R*)-2Hex** (0.126 g, 0.205 mmol). After purification by chromatography on silica gel (20–50% CHCl$_3$/80–50% hexanes), **(*R*)-5Hex** (139 mg, 68%) was obtained.

$[\alpha]_D = -403$ ($c = 0.30$ in THF); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.94$ (d, $J = 8.9$ Hz, 2H), 7.90 (s, 2H), 7.56 (m, 14H), 7.42 (m, 6H), 7.30 (d, $J = 16$ Hz, 2H), 7.21 (d, $J = 8.9$ Hz, 2H), 7.12 (m, 6H), 3.96 (m, 4H), 1.31 (m, 22H), 1.03 (m, 12H), 0.76 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 155.0$, 150.9, 137.0, 136.8, 134.8, 134.0, 132.7, 129.6, 129.5, 128.9, 128.4, 127.7, 126.94, 126.90, 126.4, 126.1, 125.8, 123.9, 120.8, 116.1, 69.80, 34.80, 31.53, 31.49, 29.50, 25.50, 22.70, 14.20; exact mass (FAB, NBA) for $[M\text{H}]^{+\bullet}$ calcd for $C_{72}H_{78}O_2$: 974.6002; found: 974.6009.

2-Hexyloxy-6-(4-(4′-*tert*-butylstyryl)styryl)naphthalene (m-5Hex): The procedure for the synthesis of **m-4Hex** was duplicated starting with 2-hexyloxy-6-bromonaphthalene (0.135 g, 0.440 mmol, 1 equiv) and 4-(4′-*tert*-butylstyryl)styrene (0.222 g, 0.848 mmol, 1.9 equiv). After purification by chromatography on silica gel (20–50% CHCl$_3$/80–50% hexanes), **m-5Hex** (0.229 g, 73%) was obtained.

^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.78$ (m, 3H), 7.53 (m, 4H), 7.47 (d, $J = 8.3$ Hz, 2H), 7.39 (d, $J = 8.6$ Hz, 2H), 7.26 (m, 1H), 7.12 (m, 6H), 4.08 (t, $J = 6.7$ Hz, 2H), 1.86 (m, 2H), 1.53 (m, 2H), 1.32 (m, 15H), 0.93 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 157.6$, 137.0, 134.8, 134.5, 132.8, 129.7, 129.2, 128.9, 128.5, 127.8, 127.7, 127.3, 127.0, 126.9, 126.7, 126.5, 124.2, 119.6, 106.9, 68.3, 34.9, 31.8, 31.5, 29.4, 26.0, 22.8, 14.3; exact mass (FAB, NBA) for $[M\text{H}]^{+\bullet}$ calcd for $C_{36}H_{40}O$: 488.3079; found: 488.3074.

2,2′-Dihexyloxy-6,6′-bis(4-(4′-(4″-*tert*-butylstyryl)styryl)styryl)-1,1′-binaphthyl (6Hex): The procedure for the synthesis of **5Hex** was duplicated with **2Hex** (0.103 g, 0.17 mmol, 1 equiv) and 1-(4′-*tert*-butylstyryl)-4-(4′-vinylstyryl)benzene (0.242 g, 0.66 mmol, 3.9 equiv). After purification by chromatography on silica gel (40–60% CHCl$_3$/60–40% hexanes), **6Hex** (15 mg, 8%) was obtained.

^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.92$ (m, 3H), 7.42 (m, 29H), 7.17 (m, 17H), 3.95 (m, 4H), 1.35 (m, 20H), 1.00 (m, 4H), 0.76 (m, 6H); ^{13}C NMR could not be done because the compound was too insoluble; exact mass (FAB, NBA) for $[M\text{H}]^{+\bullet}$ calcd for $C_{88}H_{90}O_2$: 1178.6941; found: 1178.6970.

2,2′-Dihexyloxy-6,6′-bis(4-(4′-(3″,5″-dihexyloxystyryl)-styryl)styryl)-1,1′-binaphthyl (7Hex): The conditions for the synthesis of **5Hex** were duplicated with **2Hex** (0.286 g, 0.467 mmol, 1 equiv), 1-(3′,5′-dihexyloxystyryl)-4-(4′-vinylstyryl)benzene (0.923 g, 1.82 mmol, 3.9 equiv), palladium acetate (0.004 g, 0.016 mmol, 0.3 equiv), potassium carbonate (0.355 g, 2.56 mmol, 5.5 equiv), tetrabutylammonium bromide (0.311 g, 0.96 mmol, 2 equiv), and DMF (5 mL). After purification by column chromatography on silica gel (30–50% CHCl$_3$/70–50% hexanes), **7Hex** (287 mg, 42%) was obtained.

^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.92$ (m, 3H), 7.52 (m, 16H), 7.41 (d, 3H), 7.26 (d, 4H), 7.15 (m, 12H), 6.69 (d, $J = 2$ Hz, 4H), 6.39 (t, $J = 2.16$ Hz, 2H), 3.98 (t, $J = 6.5$ Hz, 12H), 1.80 (m, 8H), 1.39 (m, 30H), 0.98 (m, 22H), 0.79 (t, $J = 7$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 160.7$, 155.1, 139.4, 137.3, 137.0, 136.8, 136.6, 134.1, 132.7, 129.6, 129.1, 128.9, 128.8, 128.5, 128.2, 127.6, 127.1, 127.0, 126.9, 126.2, 123.9, 120.8, 119.9, 116.2, 107.3, 105.3, 101.2, 69.9, 68.3, 31.8, 31.7, 31.5, 29.5, 29.4, 26.0, 25.9, 25.6, 22.8, 22.7, 14.3, 14.2, 14.1; exact mass (FAB, NBA) for $[M\text{H}]^{+\bullet}$ calcd for $C_{104}H_{122}O_6$: 1466.9241; found: 1466.9280; elemental analysis calcd (%) for $C_{104}H_{122}O_6$ (1467.96): C 85.08, H 8.38; found: C 84.34, H 8.18.

(*R*)-2,2′-Dihexyloxy-6,6′-bis(4-(4′-(3″,5″-dihexyloxystyryl)-styryl)styryl)-1,1′-binaphthyl ((*R*)-7Hex): The procedure for the synthesis of **7Hex** was duplicated with **(*R*)-2Hex** (0.099 g, 0.1620 mmol). After purification by column chromatography on silica gel (30–50% CHCl$_3$/80–50% hexanes), **(*R*)-7Hex** (73 mg, 31%) was obtained.

^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.92$ (m, 3H), 7.52 (m, 16H), 7.41 (d, 3H), 7.30 (s, 4H), 7.13 (m, 12H), 6.67 (d, $J = 2.1$ Hz, 4H), 6.43 (t, $J = 1.9$ Hz, 2H), 3.98 (t, $J = 6.5$ Hz, 12H), 1.80 (m, 8H), 1.35 (m, 30H), 0.95 (m, 22H), 0.74 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 160.6$, 155.1, 139.4, 137.3, 137.0, 136.8, 136.6, 134.1, 132.7, 129.52, 129.5, 129.2, 128.9, 128.8, 128.4, 128.2, 127.6, 127.0, 126.9, 123.9, 120.8, 116.2, 105.3, 101.2, 94.6, 69.8, 68.3, 31.8, 31.6, 29.9, 29.6, 29.5, 26.0, 25.6, 22.9, 22.7, 14.3, 14.2; exact mass (FAB, NBA) for $[M\text{H}]^{+\bullet}$ calcd for $C_{104}H_{122}O_6$: 1466.9241; found: 1466.9280.

2-Hexyloxy-6-(4-(4′-(3″,5″-dihexyloxystryryl)styryl)styryl)-napthalene (m-7Hex): The procedure for the synthesis of **m-4Hex** was duplicated with 6-bromo-2-hexyloxynaphthalene (0.21 g, 0.67 mmol, 1 equiv) and 1-(3′,5′-dihexyloxystyryl)-4-(4′-vinylstyryl)benzene (0.647 g, 1.3 mmol, 1.9 equiv). After purification by column chromatography on silica gel (40–60% CHCl$_3$/60–40% hexanes), **m-7Hex** (267 mg, 54%) was obtained.

^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.78$ (s, 1H), 7.72 (m, 3H), 7.52 (m, 8H), 7.23 (m, 1H), 7.14 (m, 5H), 7.06 (m, 2H), 6.67 (d, $J = 2.0$ Hz, 2H), 6.41 (t, $J = 2.0$ Hz, 1H), 4.08 (t, $J = 6.6$ Hz, 2H), 3.98 (t, $J = 6.6$ Hz, 4H), 1.81 (m, 6H), 1.49 (m, 6H), 1.37 (m, 12H), 0.93 (m, 9H); ^{13}C NMR (100 MHz,

$CDCl_3$): $\delta = 160.7$, 157.6, 139.4, 137.2, 137.0, 136.8, 136.7, 134.5, 132.8, 129.7, 129.2, 129.0, 128.9, 128.8, 128.4, 128.2, 127.6, 127.4, 127.1, 127.08, 127.04, 126.96, 126.8, 124.2, 119.9, 106.9, 105.3, 101.1, 68.3, 31.8, 29.5, 29.4, 26.0, 25.9, 22.8, 14.3; exact mass (FAB, NBA) for $[MH]^{+\cdot}$ calcd for $C_{52}H_{62}O_3$: 734.4699; found: 734.4727; elemental analysis calcd (%) for $C_{52}H_{62}O_3$ (734.99): C 84.97, H 8.50; found: C 85.73, H 8.37.

Acknowledgements

Financial support from NSF (DMR 9500627) and the Office of Naval Research is gratefully acknowledged.

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Received: February 14, 2001 [F3073]

0947-6539/01/0720-4511 $ 17.50+.50/0