

Synthesis and study of binaphthyl-based chiral dendrimers

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Received 4 September 2002; accepted 17 September 2002

Abstract

1,1-Binaphthyl and bisbinaphthyl core-based optically active dendrimers containing phenylene or phenyleneethynylene dendrons have been synthesized and characterized. These materials have exhibited efficient light-harvesting properties with greatly increased fluorescence intensity as the dendritic generation increases. The fluorescent responses of these materials in the presence of chiral substrates such as amino alcohols and mandelic acid have been studied. Good enantioselective fluorescent recognitions have been observed. The light-harvesting effects of the dendrimers are found to greatly amplify their fluorescence responses towards both the fluorescent quenchers and enhancers. Thus, highly sensitive as well as enantioselective fluorescent sensors have been obtained. These sensors will be useful in the high throughput combinatorial chiral catalyst screening.

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Keywords: Chiral dendrimers; 1,1-Binaphthyls; Fluorescent sensors; Chiral recognition

1. Introduction

Dendrimers are hyperbranched macromolecules with well-defined size and composition. In the past two decades, the study of dendrimers has attracted a broad range of research activity because of their unique structures and potential applications [1,2]. Chirality has also been introduced to the cores, the branches, and the peripheries of dendrimers to generate chiral dendrimers with diverse structures [3–9]. Applications of these materials in areas such as catalysis, separation, sensing, and molecular recognition are currently under active investigation.

In our laboratory, we have used optically active 1,1'-binaphthyl molecules to build new chiral materials because of the stable chiral configuration of the binaphthyl compounds and their high asymmetric induction in many processes [10,11]. Fig. 1 shows a few examples of the 1,1'-binaphthyl-based polymers prepared in our laboratory. Polymer **1** can catalyze several highly enantioselective organic reactions [12]. Polymer **2** represents a class of chiral non-linear optical materials [13]. Polymer **3** is used to prepare efficient electroluminescent devices [14].

We have also constructed chiral binaphthyl core-based dendrimers for the enantioselective fluorescent recognition of chiral organic compounds. Using fluorescence in chiral

recognition has the advantages of real time response, high sensitivity, and many modes of detection. They could be used in the high throughput combinatorial screening of chiral catalysts. We have used the light-harvesting effect of chiral dendrimers to amplify their fluorescent responses toward chiral amino alcohols and α -hydroxycarboxylic acids. Both highly sensitive and highly enantioselective fluorescent sensors have been obtained. Herein, this work is summarized.

2. Synthesis and study of BINOL core-based phenyleneethynylene dendrimers [15]

In order to use the binaphthyl structure to build the core of chiral dendrimers, we have synthesized the 4,4',6,6'-tetrabrominated binaphthyl compounds **4** and **5** starting from (*S*)-1,1'-bi-2-naphthol [(*S*)-BINOL] according to Scheme 1. Following the procedure of Moore and co-workers, we have prepared the phenyleneethynylene dendrons **6**, **7** and **8** (Fig. 2) [16]. These compounds are reacted with the tetrabromobinaphthyl compound **5** in the presence of Pd(PPh₃)₄ and CuI catalysts. After hydrolysis, the generation zero (G0) dendrimer **9**, the generation one (G1) dendrimer **10**, and the generation two (G2) dendrimer **11** are obtained (Fig. 3). These materials are soluble in common organic solvents such as THF, methylene chloride and chloroform. Because of the dendritic structure and the periphery tertiary

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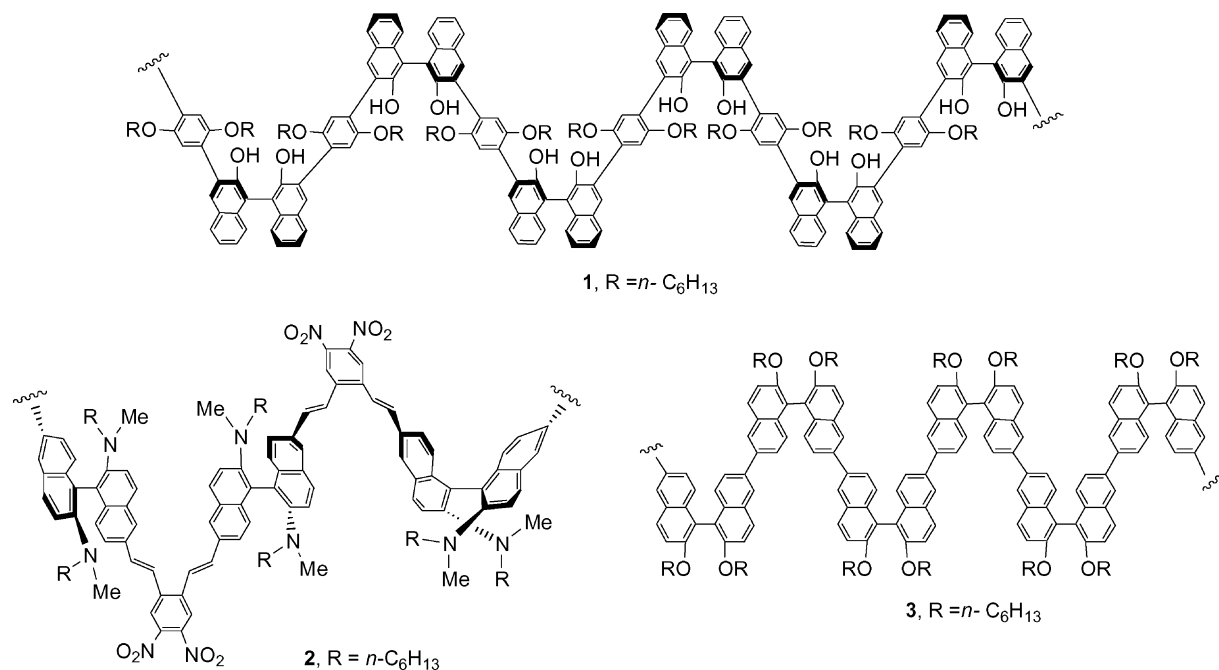


Fig. 1. Examples of 1,1'-binaphthyl-based polymers.

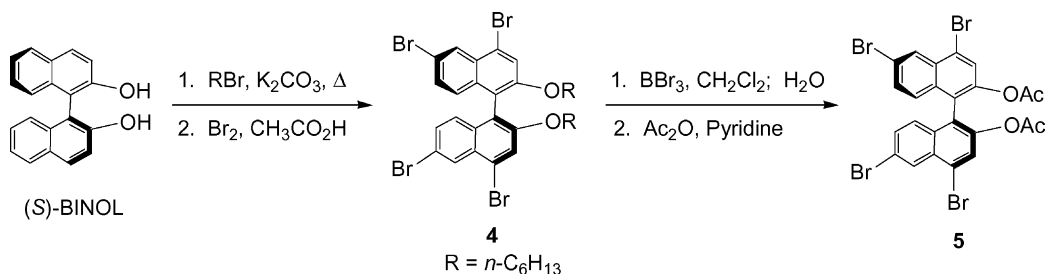
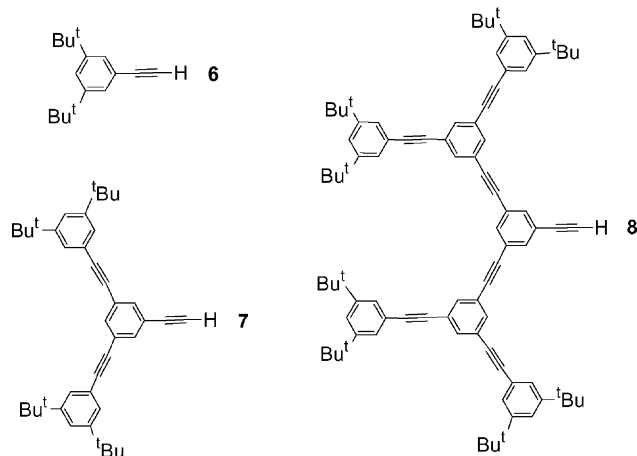
Scheme 1. Synthesis of the optically active 1,1'-binaphthyl compounds **4** and **5**.

Fig. 2. Phenyleneethynylene dendrons.

butyl groups, nonpolar solvents such as hexane can also dissolve these compounds.

NMR and mass (EI, FAB and MALDI-TOF) spectroscopic analyses have confirmed the molecular structures of these dendrimers. For example, in the ¹³C NMR spectra, dendrimers **9**, **10**, and **11** give 4, 8 and 12 signals, respectively, between $\delta = 85$ and 98 for their alkyne carbons, consistent with their C₂ symmetric structures. HPLC-chiral column analysis shows that these materials maintain the high optical purity of BINOL. Their specific optical rotations ($[\alpha]_D$) are 114.4 for **9**, 67.5 for **10** and 36.2 for **11** in methylene chloride at $c = 1.0$. As the dendrimer generation increases, the specific optical rotations decrease. The CD spectra of these dendrimers are all very similar. These data indicate that with the increasing number of the rigid phenyleneethynylene units from G₀ to G₂ there is no chiral amplification. Thus, the cross-conjugated units do not achieve a chiral order, but have random conformations, leading to the reduced specific optical rotation. Only their core units

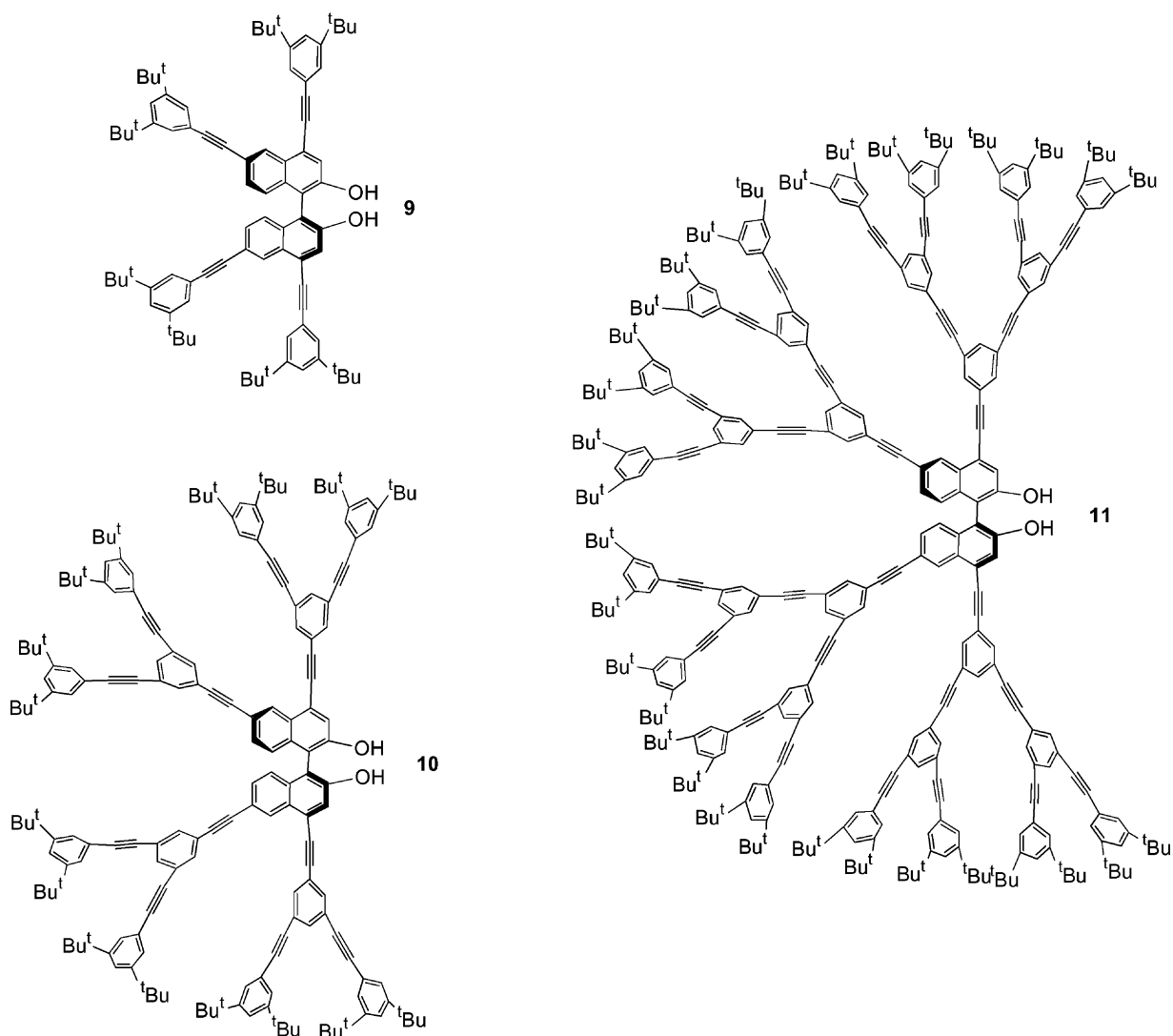


Fig. 3. Binaphthyl core-based chiral phenyleneethynylene dendrimers.

contribute to the CD signals. The molar optical rotations are 1299, 1609 and 1769, respectively, for the dendrimers G0, G1 and G2. This increase in molar optical rotation as the dendrimer generation increases is very modest.

Two bands are observed in the UV-Vis absorption spectra of these dendrimers in methylene chloride: one strong band around 250–330 nm and one weak band around 340–400 nm. The strong band is due to both the phenyleneethynylene dendrons and the binaphthyl core, and the weak band is due to the more extendedly conjugated 4,4',6,6'-tetraphenylethynyl-1,1'-bi-2-naphthol core. As the dendritic generation increases, a large increase in absorption is observed in the band of 250–330 nm, while the absorption band due to the core remains almost the same. The molar extinction coefficient at ca. 310 nm increases nine times going from the G0 dendrimer to the G2 dendrimer. This is because of the increased number of diphenylethyne units. The *meta*-phenylene linkage of the dendritic arms does not

change the conjugation of the dendrimers as shown by their absorption spectra.

When these compounds are excited at 310 nm where the phenyleneethynylene dendrons absorb, there is a large increase in the emission intensity from the G0 dendrimer **9** to the G2 dendrimer **11**. Dendrimer **11** emits 12 times more strongly than **9**. No emission due to the dendrons **7** and **8** is observed in **10** and **11**. It indicates that the light absorbed by the dendrons is completely transferred to the core, leading to the light-harvesting effect and greatly enhanced emission. This is also supported by the excitation spectra of the dendrimers. While the emission is set at 422 nm, the absorption at 310 nm increases greatly from **9** to **11**. A similar light-harvesting effect has been observed by Moore and co-workers in their achiral phenyleneethynylene-based dendrimers [16]. The fluorescence quantum yields of the 1,1'-binaphthyl-based chiral dendrimers are measured by using quinine sulfate in 1 N sulfuric acid as the reference. It

is found that the quantum yields of the G0, G1 and G2 dendrimers are approximately 0.30, 0.32 and 0.40, respectively.

Dendrimer **11** is used to catalyze the reaction of diethylzinc with benzaldehyde. It is found that this dendrimer is much more active as a catalyst than the small BINOL molecule. In the presence of 5 mol% of **11** in toluene, the reaction proceeds with ca. 99% conversion in 24 h at room temperature. Under the same conditions, BINOL can only catalyze this reaction to 37% conversion. Both of the dendrimer and BINOL show low enantioselectivity for this reaction. The aggregation of the BINOL–Zn complex through the bridging –O–Zn–O– bonds probably have greatly reduced the Lewis acidity of the zinc center and decreased the catalytic activity. However, when the bulky dendrimer is used, because it is almost impossible for it to aggregate through the BINOL core, it shows much higher catalytic activity. When the reaction of diethylzinc with benzaldehyde is carried out in the presence of excess $\text{Ti}(\text{O}^i\text{Pr})_4$, both the dendrimer and BINOL showed similar high catalytic activity and high enantioselectivity (up to 90% ee). It indicates that the catalytically active species of the dendrimer and BINOL under this condition are similar and are probably made of a monobinaphthyl titanium complex. This study demonstrates that although the dendritic arms are bulky, the chiral BINOL core is still approachable by small organic compounds and capable of good chiral induction.

The fluorescence of **11** is compared with that of BINOL. At 4.0×10^{-8} M, the fluorescence intensity of BINOL is almost at the base line, but that of the dendrimer is very strong. This demonstrates that the dendrimer should serve as a much better sensor when interacting with a chiral quencher. Iwanek and Mattay studied the fluorescence quenching of BINOL by chiral amines and amino alcohols [17]. They found that under certain conditions, there were some enantioselective fluorescence responses.

We have investigated the interaction of the dendrimers with chiral amino alcohols including 2-amino-3-methyl-1-butanol (**12**), 2-amino-4-methyl-1-pentanol (**13**) and 2-amino-3-phenyl-1-propanol (**14**). All these compounds are found to efficiently quench the fluorescence of the dendrimers. The fluorescence quenching follows the Stern–Völmer equation. The Stern–Völmer constants increase with increasing dendrimer generation. The fluorescence intensity change of the higher generation dendrimers in the presence of the amino alcohols is also much larger than the lower generation one. Therefore, the dendritic branches lead to more sensitive fluorescent sensor. The fluorescent quenching is also found to be enantioselective. The *S* enantiomer of the amino alcohols quenches the fluorescence of the (*S*)-dendrimers more effectively than the *R* enantiomer under the same conditions. The ratio of the Stern–Völmer constants K_{SV}^S/K_{SV}^R is found to be up to 1.27. When the (*R*)-dendrimers are used, a mirror image relationship in the fluorescence quenching is observed which confirms the enantioselective response. The effective Stern–Völmer constants of dendrimer **11** (4.0×10^{-8} M

in 20:80 benzene:hexane) is found to be linear with the enantiomeric composition of the amino alcohol **14** in benzene:hexane (20:80). Thus, from the fluorescence intensity of the sensor, we will be able to determine the enantiomeric composition of the amino alcohol.

In collaboration with Lewis' laboratory, the fluorescence lifetime of dendrimer **11** in the presence of the amino alcohol (*R*)- and (*S*)-**14** is studied. In the absence of a quencher, the fluorescence lifetime of **11** is 1.6 ± 0.2 ns. Almost no change is observed for the fluorescence lifetime of the dendrimer when treated with the amino alcohol at various concentrations. This demonstrates that only static quenching occurs. We thus propose that the formation of nonfluorescent ground state hydrogen bond complexes between the hydroxyl groups of the dendrimer core and the amino alcohol is probably responsible for the fluorescence quenching. In the presence of strong base such as NaOH, both the dendrimer and (*S*)-BINOL exhibit a new peak in the UV-Vis spectra ca. 50 nm to the red of the lowest absorption maximum because of deprotonation. However, when the dendrimers are treated with the amino alcohol **14**, their UV-Vis spectra only show a slight difference from their original spectra. Thus, the dendrimer core cannot be deprotonated by the amino alcohol, but probably only forms a hydrogen bond complex. The hydroxyl groups of **11** are also found to be necessary for efficient quenching by amino alcohols. No fluorescence quenching by an amino alcohol is observed when the two hydroxyl groups of (*S*)-**4** are methylated. The static quenching mechanism indicates that the observed K_{SV} represent the ground state association constants between the dendrimers and the amino alcohols. We have observed that K_{SV} increases as the solvent polarity decreases from methylene chloride to benzene/hexane. This can be attributed to stronger ground state hydrogen bonding interaction between the BINOL core and amino alcohols in the less polar solvent. The observed increase of K_{SV} with increasing dendritic generation can be also attributed to higher association constant between the higher generation dendrimers and amino alcohols.

Study of the BINOL core-based phenyleneethynylene dendrimers demonstrates that the light-harvesting effect of dendrimers can be used to greatly amplify the fluorescence signal for the development of highly sensitive fluorescent sensors over the small molecules. In addition, the chirality of these dendrimers can also lead to enantioselective fluorescent recognition.

3. Synthesis and study of BINOL core-based phenylene dendrimers [18]

We have synthesized the phenylene-based dendritic boronic acids **15**, **16** and **17**, by using a procedure similar to that of Miller et al.'s (Fig. 4) [19]. The Suzuki coupling of **15–17** with (*R*)-**4** in the presence of 3 mol% of $\text{Pd}(\text{PPh}_3)_4$ and 2 M K_2CO_3 (aq) followed by treatment with BBr_3 and hydrolysis gives the G0 dendrimer **18**, the G1 dendrimer **19**

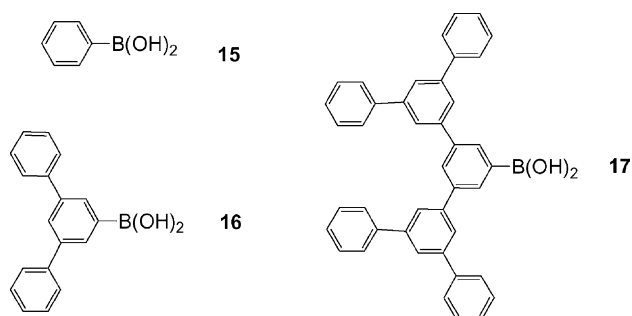


Fig. 4. Phenylene boronic acid-based dendrimers.

and the G2 dendrimer **20**, respectively (Fig. 5). These compounds are pale yellow solids and soluble in common polar organic solvents such as acetone, ethyl acetate, methylene chloride, chloroform and THF, but insoluble in nonpolar solvents such as hexane and toluene. They are characterized by ¹H and ¹³C NMR, and various mass spectrometries (CI, EI and FAB). In the ¹H NMR spectra of these dendrimers, signals at $\delta = 8.18$ (d, $J = 1.8$ Hz), $\delta = 8.49$ (s) and $\delta = 8.59$ (s) are assigned to the 5,5'-protons of **18**, **19** and **20** respectively, indicating a C₂ symmetric structure of these compounds in solution.

The specific optical rotations ($[\alpha]_D$) of these compounds are -66.3 for **18**, -51.6 for **19** and -31.2 for **20** in THF at $c = 1.0$. As the dendrimer generation increases, their specific optical rotations decrease. The molar optical rotations are -391 , -704 and -754 , respectively, for dendrimers **18**, **19** and **20**. The molar optical rotation is almost doubled as the molecular weight increases about four times from the generation zero dendrimer to the generation two dendrimer. Earlier, Chen et al. [20], and Peerlings and others [21] have

studied the effect of the Fréchet type dendritic branches at the 2,2'-positions of the 1,1'-binaphthyls on the optical rotation of the chiral binaphthyl core-based dendrimers. They found that the growing steric interaction between the dendritic branches at the 2,2'-positions from the lower generation binaphthyl dendrimers to the higher generations increased the dihedral angle of the 1,1'-binaphthyl core which significantly increased the molar optical rotation. However, as we have discussed earlier there is only 30% increase in molar optical rotation for the phenyleneethynylene-based dendrimers from the generation zero **9** to the generation two **11**. This indicates that substitution at the 4,4',6,6'-positions of the binaphthyl core as in **11** cannot significantly change the 1,1'-binaphthyl dihedral angle at least from G0 to G2. Therefore, the observed large increase in molar optical rotation from the phenylene dendrimers **18–20** might also not be due to the change of the binaphthyl dihedral angle. Instead, the chiral binaphthyl core might have induced a chiral conformation for the dendrons of the higher generation dendrimers, leading to the significant increase in optical rotation. The difference in the observed optical rotation change between the phenylene-based dendrimers and the phenyleneethynylene-based dendrimers probably arises from their difference in steric interaction. The steric interaction between the adjacent arylene units in the dendrons of **18–20** is expected to be much larger than that in the phenyleneethynylene dendrimers. This might have allowed the chiral bias of the binaphthyl core in dendrimers **18–20** to propagate better along the dendritic branches.

The CD spectra of the phenylene dendrimers show 15 nm red-shift for the major CD signal from **18** to **20**. The intensity is decreased to 54% of the original value. This is in contrast to what is observed for the phenyleneethynylene-based

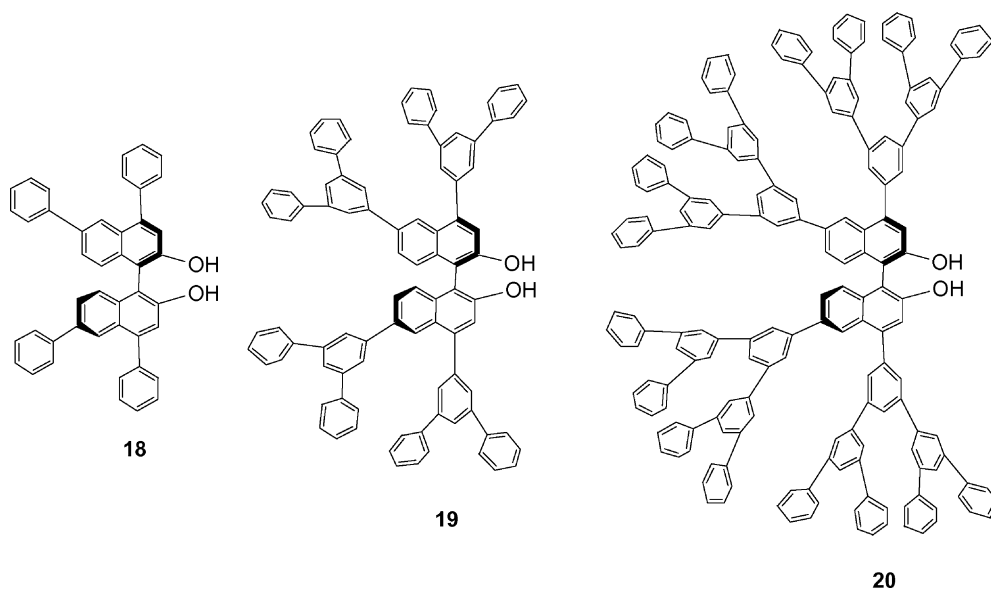


Fig. 5. Binaphthyl cored-based chiral phenylene dendrimers.

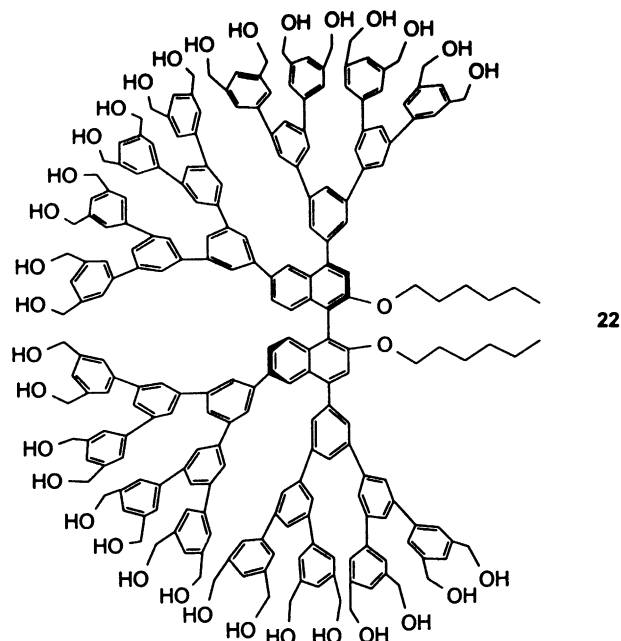
dendrimers **9–11**. There is no significant change in the CD spectra of **9–11**. Both the CD spectra and the molar optical rotations of **18–20** suggest that the dendritic arms of these materials might have contributed to their chiral optical effects probably because of the increased steric interaction between the adjacent arylene units in the dendrons.

Dendrimers **18–20** show two major absorption bands in their UV spectra: one at 250–300 nm and another at 300–370 nm. The short wavelength band is attributed to both the phenylene dendrons and the binaphthyl moieties. Its intensity increases significantly as the dendritic generation grows because of the increased phenylene units. The second absorption band is attributed to the conjugated 4,4',6,6'-tetraphenyl-1,1'-bi-2-naphthol core. No significant change in its intensity is observed as the dendrimer generation increases. These dendrimers are strong blue light emitters under UV irradiation. They show emissions at 395–405 nm when excited at 256 nm, where the absorption is mostly due to the benzene units of the dendrons. At the same molar concentration, from the G0 dendrimer to G2, the fluorescence intensity has increased about 7.5 times. No emission due to the dendritic phenylene units **6–8** is observed. This indicates that there is an efficient energy migration from the dendritic light absorbing antenna to the more conjugated core, leading to the observed enhanced fluorescence at high generations. The excitation spectra also support an efficient intramolecular energy migration. When the emission is set at 405 nm, there is a large increase for the excitation maximum at 256 nm from **18** to **19** and **20**. The fluorescence of the dendrimers is also much stronger than that of BINOL.

The fluorescence of the G2 dendrimer **20** in the presence of chiral amino alcohols is studied. No significant fluorescence quenching is observed when the dendrimer is treated with 2-amino-1-propanol (**21**) in methylene chloride solution. However, when hexane is added as a co-solvent, the amino alcohol can efficiently quench the fluorescence of the dendrimer. This is probably because a less polar solvent provides a better environment for the hydrogen bonding interaction between the hydroxyl groups of the dendrimer and the amino alcohol. It is found that the fluorescence quenching of **20** by the optically pure amino alcohol (*R*)- and (*S*)-**21** obeys the Stern–Völmer equation with $K_{SV}^R = 243.5 \text{ M}^{-1}$ and $K_{SV}^S = 216.0 \text{ M}^{-1}$. Thus, the fluorescence quenching of **20** by the amino alcohol is enantioselective with $K_{SV}^R/K_{SV}^S = 1.13$. The *R* enantiomer of the amino alcohol quenches the fluorescence of the dendrimer more efficiently than the *S* enantiomer. The fluorescence quenching of the G0 dendrimer **18** and the G1 dendrimer **19** by (*R*)- and (*S*)-**21** also follow the Stern–Völmer equation with $K_{SV}^R = 75.5 \text{ M}^{-1}$ and $K_{SV}^S = 63.5 \text{ M}^{-1}$ for **18**, and $K_{SV}^R = 99.9 \text{ M}^{-1}$ and $K_{SV}^S = 88.4 \text{ M}^{-1}$ for **19**, respectively. The fluorescence quenching of dendrimer **20** in the presence of other amino alcohols such as leucinol and 2-amino-3-methyl-butanol are also enantioselective with K_{SV}^R/K_{SV}^S in the range of 1.09–1.18. The higher generation

dendrimers are found to be much more sensitive toward the chiral quenchers and show greater fluorescence intensity change.

We have synthesized the micelle-like chiral dendrimer **22** by introducing periphery polyhydroxyl groups [18b]. This dendrimer is found to be more soluble in H₂O/THF than in THF. The UV spectrum of **22** in H₂O/THF (3:1) is much broader than in THF. It indicates that this dendrimer may have a tighter conformation in THF than in H₂O/THF. Such a solvent effect is probably due to a different degree of intermolecular hydrogen bonding versus intramolecular hydrogen bonding in different solvents. More intramolecular hydrogen bonding between the periphery hydroxyl groups in the less polar THF solution than in the H₂O/THF solution should lead to its tighter conformation. Dendrimer **22** is potentially useful for the chiral recognition carried out in highly polar media.



4. Synthesis and study of bisbinaphthyl core-based phenylene dendrimers [22]

Chiral α -hydroxycarboxylic acids are very useful synthons for many organic natural products and drug molecules. Fluorescent sensors that can distinguish the enantiomers of an α -hydroxycarboxylic acid will be useful in the high throughput screening of chiral catalysts for the asymmetric synthesis of these chiral compounds. The chiral bisbinaphthyl molecule **23** is designed for the fluorescent recognition of α -hydroxycarboxylic acids (Fig. 6). Structure **24** shows a proposed complex between **23** and (*S*)-mandelic acid featuring three specific hydrogen bonds. In compound **23**, a nitrogen atom is introduced to quench the fluorescence

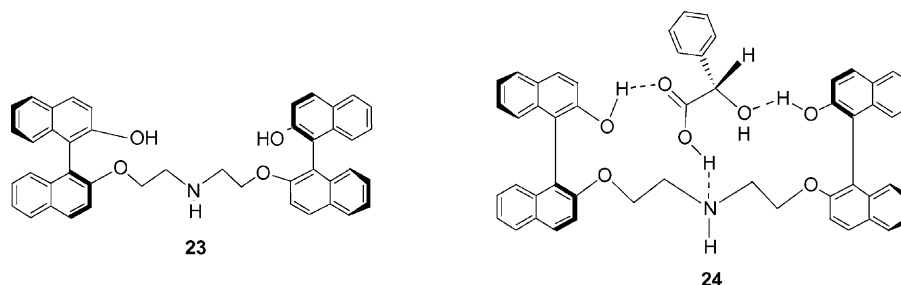


Fig. 6. A bisbinaphthyl receptor for mandelic acid.

of the binaphthyl units by a photoinduced electron transfer (PET) process [23,24]. When **23** is treated with an α -hydroxycarboxylic acid, the interaction of the nitrogen with the acid proton as shown in the proposed complex **24** is expected to inhibit the PET process and enhance the fluorescence.

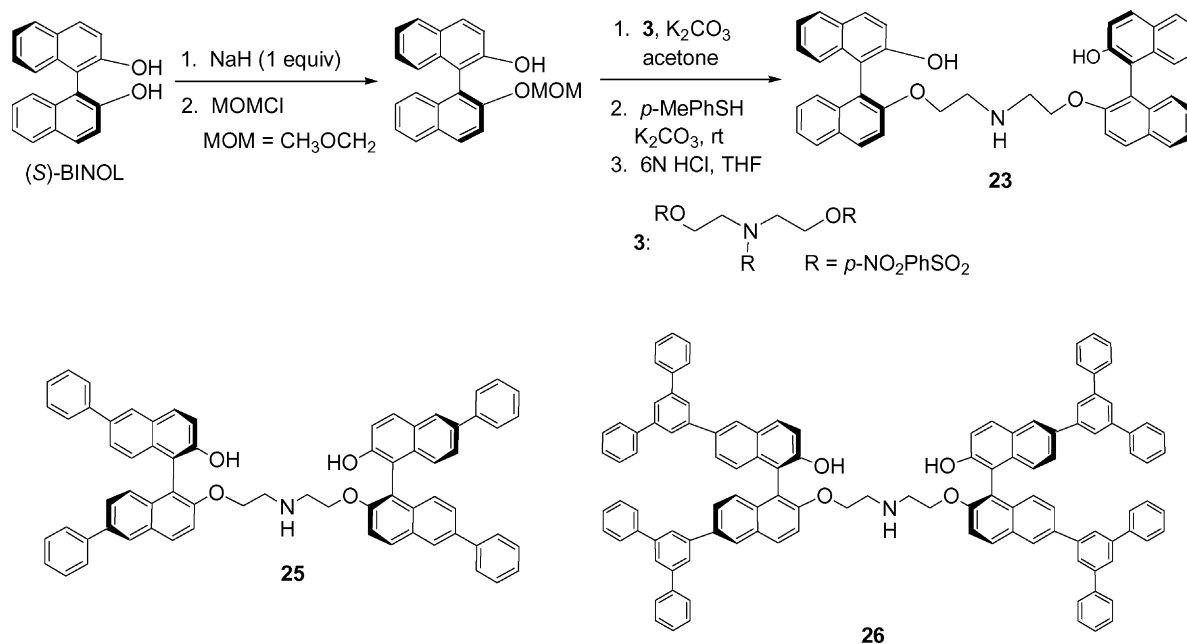
Compound **23** is readily prepared from the optically pure BINOL as shown in Scheme 2. Compounds **25** and **26**, the dendritic derivatives of **23** with phenylene dendrons, are also synthesized. Compound **25** is the G0 dendrimer and compound **26** is the G1 dendrimer.

The NMR spectra of these bisbinaphthyl compounds are consistent with their C_2 symmetry. Their UV spectra show that there are large increases in absorption for the signals at the short wavelengths (<300 nm) from the core to G0 and G1 because of the absorptions of the increasing number of branching phenyl rings at the 6,6'-positions of the binaphthyl units, but much smaller changes at the long wavelengths. The absorption maxima and extinguish coefficients for these compounds are 280 nm (16,500) and 334 nm (10,600) for the

core **23**; 263 nm (168,700), 297 nm (sh, 53,200) and 343 nm (sh, 9800) for **25**; and 267 nm (257,100), 304 nm (sh, 58,600) and 343 nm (sh, 9800) for **26**, respectively.

The dendritic branching benzene rings of the G0 and G1 compounds have greatly increased their fluorescence intensity over the core **23**. This indicates an efficient intramolecular energy transfer from the phenyl rings to the naphthyl core. The fluorescence maxima are observed at 372 nm for both **25** and **26** and 368 nm for **23**. In the excitation spectra, the most intense absorptions for **25** and **26** are observed at 270 nm where the phenyl rings absorb. This supports the efficient intramolecular energy migration.

The fluorescence response of these compounds toward mandelic acid is studied. When **23** is treated with (*R*)- or (*S*)-mandelic acid, it exhibits a significant fluorescence enhancement because of a suppressed PET quenching when the acidic proton of the acid interacts with the nitrogen of the bisbinaphthyl compound. This fluorescence enhancement is found to be very enantioselective. In benzene solution (containing 2% dimethoxyethylene (DME)), the

Scheme 2. Synthesis of the chiral bisbinaphthyl compound **23**.

fluorescence intensity of **23** (9.5×10^{-5} M) is increased to 2.87 times of the original value by (*S*)-mandelic acid (5.0×10^{-3} M). However, (*R*)-mandelic acid (5.0×10^{-3} M) only increases the fluorescence intensity of **23** to 1.75 times. That is, the enantiomeric fluorescence difference ratio, *ef* ($ef = (I_S - I_0)/(I_R - I_0)$), is 2.49. With this large difference in the enantiomeric fluorescence enhancement, compound **23** is practically useful for the enantioselective recognition of the chiral α -hydroxycarboxylic acid.

The fluorescence enhancement of the sensor follows the Benesi–Hildebrand type equation which gives the association constant of **23**+(*S*)-mandelic acid 348 M^{-1} , and that of **23**+(*R*)-mandelic acid 163 M^{-1} . The Job plot of the sensor in the presence of the acid indicates the formation of a 1:1 complex between the sensor and the acid. The fluorescence enhancement of the enantiomer of **23** in the presence of (*R*)- and (*S*)-mandelic acid confirms that the observed different fluorescence enhancement between the two enantiomers of mandelic acid is indeed due to chiral recognition by the fluorescent sensor. When **23** is treated with mandelic acid with various enantiomeric compositions, a linear relationship between I/I_0 and the percent of the *S* component of mandelic acid is observed. Thus, the enantiomeric composition of the α -hydroxycarboxylic acid can be readily determined by measuring the fluorescence intensity of sensor **23** in the presence of the substrate.

The interaction of mandelic acid with the G0 and G1 dendritic derivatives **25** and **26** is studied. We find that as the dendritic generation increases, the fluorescence enhancement of the chiral bisbinaphthyl compounds in the presence of the acid increases greatly. The fluorescence signals of the G0 and G1 compounds in the presence of the acid are much stronger than the unbranched core **23**. The fluorescence enhancement ($I - I_0$) of **25** by (*R*)-mandelic acid is ca. 14 times that of **23**, and the fluorescence enhancement of **26** by (*R*)-mandelic acid is ca. 22 times that of **23**. That is, the dendritic branches of the G0 and G1 compounds have amplified the fluorescence responses of the core toward the α -hydroxycarboxylic acid. They make the G0 and G1 molecules much more sensitive fluorescent sensors than the core. The enantioselectivity of the G0 molecule **25** is similar to that of the core with an *ef* value of 2.05. The enantioselectivity of the G1 molecule **26** is lower with an *ef* of 1.49. Through this study, we have identified the G0 dendrimer **25** as a highly sensitive as well as highly enantioselective fluorescent sensor for the recognition of mandelic acid.

5. Summary

We have designed and synthesized various types of optically active 1,1'-binaphthyl-based dendrimers for the fluorescent recognition of chiral amino alcohols and mandelic acid. The optically active binaphthyl cores lead to enantioselective recognition of the chiral substrates. The

light-harvesting effects of dendrimers are used to amplify the fluorescence responses of these compounds. Highly sensitive as well as enantioselective fluorescent sensors have been obtained. These sensors will be useful in the high throughput combinatorial chiral catalyst screening.

Acknowledgements

We thank the support of this work from the National Institute of Health (R01GM58454), and a partial support provided by the donors of the Petroleum Research Fund Administered by the American Chemical Society. I am most grateful to my post-doctorals and graduate students, whose names are cited in the references, for their excellent contributions.

References

- [1] G.R. Newkome, C.N. Moorefield, F. Vögtle, *Dendritic Molecules. Concepts, Synthesis, Perspectives*, VCH, Weinheim, 1996.
- [2] J.M.J. Fréchet, C.J. Hawker, in: S.L. Aggarwal, S. Russo (Eds.), *Comprehensive Polymer Science*, 2nd ed., Pergamon Press, Oxford, 1996, pp. 71–132.
- [3] B. Romagnoli, W.J. Hayes, *Mater. Chem.* 12 (2002) 767–799.
- [4] F. Vögtle, S. Gesteremann, R. Hesse, H. Schwierz, B. Windish, *Prog. Polym. Sci.* 25 (2000) 987.
- [5] K. Inoue, *Prog. Polym. Sci.* 25 (2000) 453.
- [6] D. Seebach, P.B. Rheiner, G. Greiveldinger, T. Butz, H. Sellner, *Top. Curr. Chem.* 197 (1998) 125–164.
- [7] M. Fischer, F. Vögtle, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 884.
- [8] H.-F. Chow, T.K.-K. Mong, M.F. Nongrum, C.W. Wan, *Tetrahedron* 54 (1998) 8543.
- [9] A. Archut, R. Moors, F. Vögtle, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 2413.
- [10] L. Pu, *Chem. Rev.* 98 (1998) 2405–2494.
- [11] L. Pu, *Macromol. Rapid Commun.* 21 (2000) 95–809.
- [12] (a) W.-S. Huang, Q.-S. Hu, L. Pu, *J. Org. Chem.* 64 (1999) 7940–7956;
(b) L. Pu, *Chem. Eur. J.* 5 (1999) 2227–2232.
- [13] (a) L. Ma, Q.-S. Hu, D. Vitharana, C. Wu, C.M.S. Kwan, L. Pu, *Macromolecules* 30 (1997) 204;
(b) S.V. Elshocht, T. Verblest, L. Ma, H. Cheng, K.Y. Musick, L. Pu, A. Persoons, *Chem. Phys. Lett.* 309 (1999) 315.
- [14] A.K.-Y. Jen, Y. Liu, Q.-S. Hu, L. Pu, *Appl. Phys. Lett.* 75 (24) (1999) 3745–3747.
- [15] (a) Q.-S. Hu, V. Pugh, M. Sabat, L. Pu, *J. Org. Chem.* 64 (1999) 7528–7536;
(b) V. Pugh, Q.-S. Hu, L. Pu, *Angew. Chem. Int. Ed. Engl.* 39 (2000) 3638–3641;
(c) V. Pugh, Q.-S. Hu, X.-B. Zuo, F.D. Lewis, L. Pu, *J. Org. Chem.* 66 (2001) 6136–6140.
- [16] C. Devadoss, P. Bharathi, J.S. Moore, *J. Am. Chem. Soc.* 118 (1996) 9635.
- [17] W. Iwanek, J. Mattay, *J. Photochem. Photobiol. A: Chem.* 67 (1992) 209–226.
- [18] (a) L.-Z. Gong, Q.-S. Hu, L. Pu, *J. Org. Chem.* 66 (2001) 2358–2367;
(b) L.-Z. Gong, L. Pu, *Tetrahedron Lett.* 42 (2001) 7337–7340.
- [19] T.M. Miller, T.X. Neenan, R. Zayas, H.E. Bair, *J. Am. Chem. Soc.* 114 (1992) 1018–1025.
- [20] Y.-M. Chen, C.-F. Chen, F. Xi, *Chirality* 10 (1998) 661.

- [21] (a) H.W. Peerlings, E.W. Meijer, *Eur. J. Org. Chem.* 4 (1998) 573–577;
(b) C. Rosini, S. Superchi, H.W.I. Peerlings, E.W. Meijer, *Eur. J. Org. Chem.* 1 (2000) 61–71.
- [22] (a) J. Lin, Q.-S. Hu, M.H. Xu, L. Pu, *J. Am. Chem. Soc.* 124 (2002) 2088–2089;
(b) M.H. Xu, J. Lin, Q.-S. Hu, L. Pu, *J. Am. Chem. Soc.*, in press.
- [23] (a) M.A. Fox, M. Chanon (Eds.), *Photoinduced Electron Transfer: A–D*, Elsevier, Amsterdam, 1988;
(b) R.A. Bissell, A.P. de Silva, H.Q.N. Gunaratna, P.L.M. Lynch, G.E.M. Maguire, C.P. McCoy, K.R.A.S. Sandanayake, *Top. Curr. Chem.* 168 (1993) 223–264.
- [24] (a) R.A. Bissell, A.P. de Silva, H.Q.N. Gunaratna, P.L.M. Lynch, G.E.M. Maguire, K.R.A.S. Sandanayake, *Chem. Soc. Rev.* 21 (1992) 187–195;
(b) A.W. Czarnik, *Acc. Chem. Res.* 27 (1994) 302–308.