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Optically Active BINOL Core-Based Phenyleneethynylene Dendrimers for the Enantioselective Fluorescent Recognition of Amino Alcohols

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A dramatic enhancement in fluorescence intensity from 1,1′-bi-2-naphthol (BINOL) to dendritic phenyleneethynylenes containing the BINOL core was observed. The strong fluorescence of the dendrimers allows a very small amount of the chiral materials to be used for sensing. The light harvesting antennas of the dendrimer funnel energy to the center BINOL unit, whose hydroxyl groups upon interaction with a quencher molecule lead to fluorescence quenching. This mechanism makes the dendrimers have much more sensitive fluorescence responses than corresponding small molecule sensors. The fluorescence of these dendrimers can be enantioselectively quenched by chiral amino alcohols. It is observed that the fluorescence lifetime of the generation two dendrimer does not change in the presence of various concentrations of 2-amino-3-phenyl-1-propanol. This demonstrates that the fluorescence quenching is entirely due to static quenching. Thus, formation of nonfluorescent ground-state hydrogen-bond complexes between the dendrimers and amino alcohols is proposed to account for the fluorescent quenching. A linear relationship has been established between the Stern−Völmer constant of the generation two dendrimer and the enantiomeric composition of 2-amino-3-phenyl-1-propanol. Such enantioselective fluorescent sensors may allow a rapid determination of the enantiomeric composition of chiral molecules and are potentially useful in the combinatorial search of asymmetric catalysts and reagents.

Introduction

Since the initial reports on the synthesis of dendritic molecules,[1,2] tremendous amounts of research have been conducted in this area.[3] Among the many unique properties of dendrimers, their light harvesting effects have received special attention recently.[4] For example, Moore and co-workers have demonstrated that phenyleneethynylene-derived dendritic arms can function as antennas to absorb as well as transfer light energy to the more conjugated center.[5] Fréchet-type aryl ether-based dendrons were also found to be able to carry out energy transfer and light harvesting.[6,7] Such a light-harvesting process of dendrimers mimics that found in the photosynthetic systems of nature.[8]

Optically active dendrimers capable of light harvesting were not studied until our recent work.[9−11] We are interested in using the light harvesting and the energy migration properties of chiral dendrimers[12] to develop efficient enantioselective fluorescent sensors. Chiral den-

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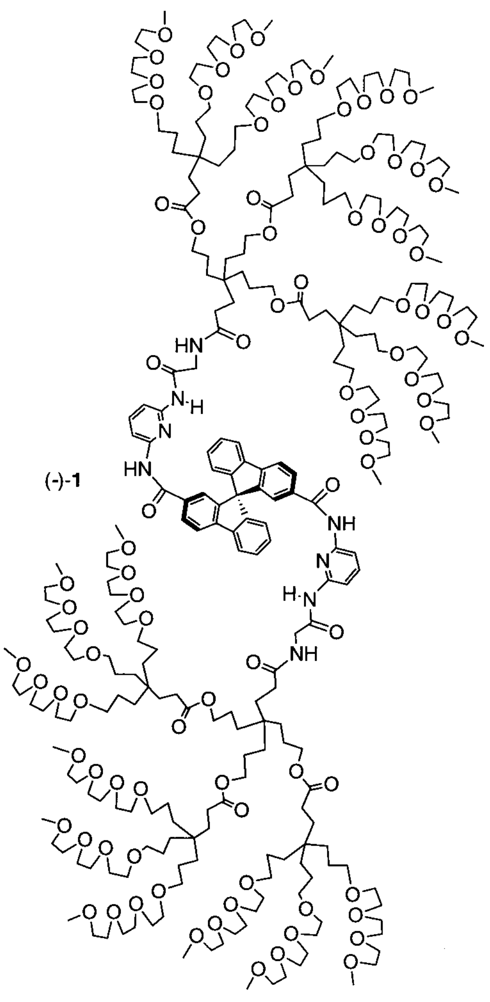
drimers such as **1** have been investigated by Diederich and co-workers for enantioselective recognition with the use of ^{1}H NMR and CD spectroscopy.[13] Using luminescence for chiral discrimination has also been studied during the past two decades.[14−17] A variety of chiral luminescent materials including inorganic complexes,[14] organic molecules,[15,16] and enzymes[17] have shown enantioselective responses when treated with chiral quenchers or enhancers. The relationship between the fluorescence properties of luminophores and the enantiomeric purity of substrates have been established in a few cases.[14b,15g,16a,b,17b] Recently, we have used optically pure 1,1′-bi-2-naphthol (BINOL) to build chiral dendrimers (*S*)-**2**−(*S*)-**4** as potential enantioselective fluorescent sensors.[9,18] These materials have shown very efficient energy migration from the cross-conjugated diphenyleneethynylene units to the more conjugated BINOL core. As the dendrimer generation increases, the fluorescence intensity increases significantly. Herein, our work on using chiral dendrimers (*S*)-**2**−(*S*)-**4** as fluorescent sensors for the enantioselective recognition of chiral amino alcohols is reported.[19]



(-)-**1**

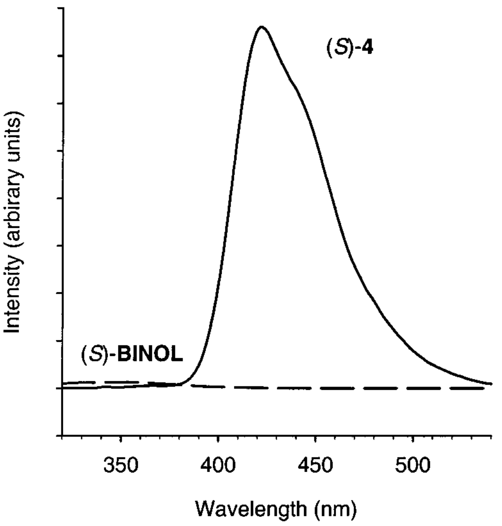


Figure 1. Fluorescence spectra of (*S*)-BINOL and dendrimer (*S*)-**4** (uncorrected).

Results

In 1992, Iwanek and Mattay found that the fluorescence of BINOL can be quenched by amines and amino alcohols.[15e] Under certain conditions, enantioselective fluorescence responses were also observed. We have compared the fluorescence spectrum of (*S*)-BINOL with that of the generation-two dendrimer (*S*)-**4**. Figure 1 shows the fluorescence spectra of (*S*)-BINOL and (*S*)-**4** each with a concentration of 4.0×10^{-8} M in benzene/hexane (20:80). It demonstrates that the introduction of the dendritic arms to the BINOL core has greatly enhanced the fluorescence signal. This strong fluorescence intensity at low concentration should make these dendrimers more suitable sensors when used to interact with fluorescent quenchers.

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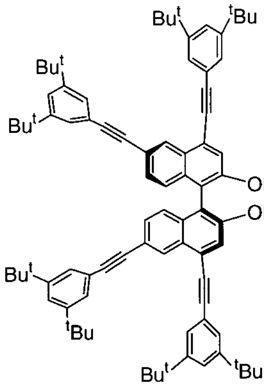
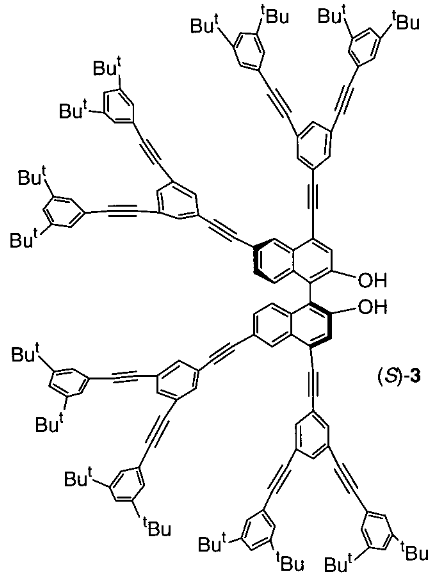
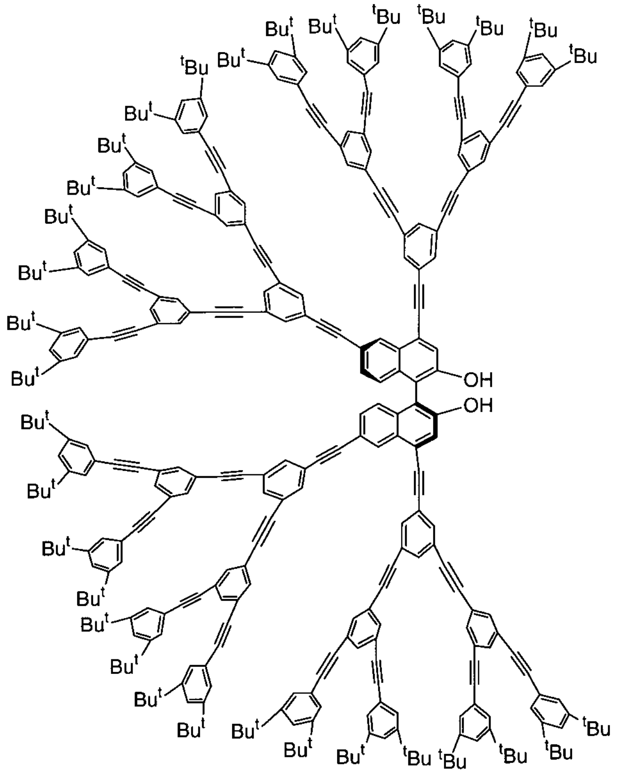


(*S*)-**2**



(*S*)-**3**



(*S*)-**4**

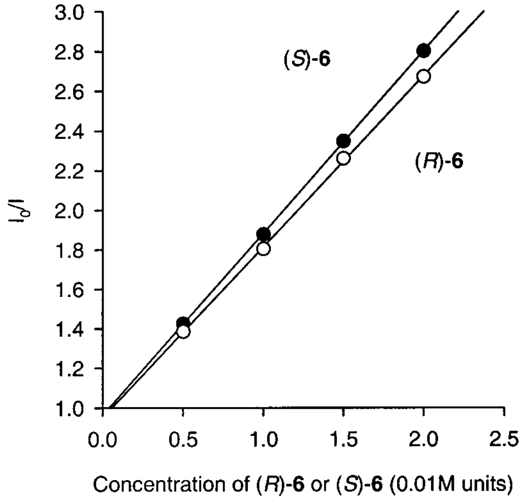
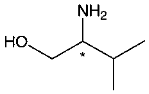


Figure 2. Stern–Völmer plots of (*S*)-**4** in the presence of (*R*)- and (*S*)-**6**.

The chirality-dependent quenching of the dendrimers in the presence of both enantiomers of chiral amino alcohols, including 2-amino-3-methyl-1-butanol (**5**), 2-amino-4-methyl-1-pentanol (**6**), and 2-amino-3-phenyl-1-propanol (**7**), have been studied. All these molecules were found to efficiently quench the fluorescence of the dendrimers. In the concentration range studied, the fluorescence quenching follows the Stern–Völmer equation[20]

$$I_0/I = 1 + K_{SV}[Q]$$

where I_0 is the fluorescence intensity in the absence of a quencher and I the fluorescence intensity in the presence of a quencher. [Q] is the quencher concentration. K_{SV} is the Stern–Völmer constant, which measures the efficiency of quenching. The Stern–Völmer constants for the luminescence quenching of the dendrimers in the presence of the amino alcohols are listed in Tables 1–3, and their units are M^{-1}. In these tables, $K_{SV}^{(S_D,S_Q)}$ is the quenching constant when the *S* enantiomer of a dendrimer interacts with the *S* enantiomer of the amino alcohol, and $K_{SV}^{(S_D,R_Q)}$ is the quenching constant when the *S* enantiomer of a dendrimer interacts with the *R* enantiomer of the amino alcohol. The uncertainties in the Stern–Völmer constants are approximately ±4%. As an example, Figure 2 shows the Stern–Völmer plots of (*S*)-**4** ($c = 4.0 \times 10^{-8}$ M) in the presence of (*R*)- and (*S*)-**6** in methylene chloride.



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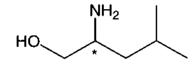

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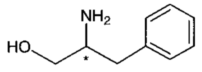

7

The effective Stern–Völmer constants of dendrimer (*S*)-**4** as a function of the enantiomeric composition of amino alcohol **7** in benzene/hexane (20:80) have been studied, and a linear relationship has been observed (Figure 3). The concentration of (*S*)-**4** was 4.0×10^{-8} M,

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[20] Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic/Plenum: New York, 1999.

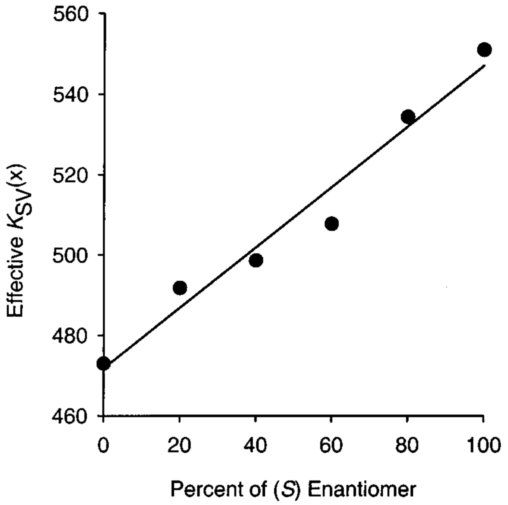

Figure 3. Effective Stern−Völmer quenching constant, $K_{SV}(x)$, versus the enantiomeric composition of quencher **7**.

Table 1. Stern−Völmer Quenching Constants for the Dendrimers in the Presence of (*R*)- and (*S*)-5 in Methylene Chloride

dendrimer[a]	$K_{SV}^{(S_D,S_Q)}$	$K_{SV}^{(S_D,S_Q)}$	$K_{SV}^{(S_D,S_Q)}/K_{SV}^{(S_D,R_Q)}$
(*S*)-**2**	47	43	1.09
(*S*)-**3**	63	57	1.11
(*S*)-**4**	83	80	1.04

[a] Concentration = 4.0 × 10^{-8} M.

and the total concentration of amino alcohol **7** remained constant at 2.0 × 10^{-3} M. Each point shown is the average of two experimental determinations.

For truly chiral interactions, there exists a mirror-image relation such that the luminescence quenching of the *S* dendrimer by the *S* amino alcohol is exactly the same as the luminescence quenching of the *R* dendrimer by the *R* amino alcohol under otherwise identical and nonchiral conditions. This provides a check to ensure that the measured differences in quenching arise from chiral interactions and not impurities or systematic errors. Several experiments on the expected mirror-image relations were performed, which indicate that chiral interactions were primarily responsible for the measured differences between *S* and *R* amino alcohols. One such experimental check is shown in Table 4. In this experiment, the fluorescence quenching of (*S*)-**4** and (*R*)-**4** by (*S*)- and (*R*)-**6** in methylene chloride was studied. The Stern−Völmer quenching constants show the expected mirror-image relationships.

The fluorescence lifetime of the generation two dendrimer (*S*)-**4** in the presence of (*R*)- and (*S*)-**7** was studied. It was found that in the absence of quencher, the fluorescence lifetime of (*S*)-**4** is 1.6 ± 0.2 ns. There was essentially no change in the fluorescence lifetime when the dendrimer was treated with the amino alcohol at various concentrations.

Table 2. Stern−Völmer Quenching Constants for the Dendrimers in the Presence of (*R*)- and (*S*)-6 in Methylene Chloride

dendrimer[a]	$K_{SV}^{(S_D,S_Q)}$	$K_{SV}^{(S_D,R_Q)}$	$K_{SV}^{(S_D,S_Q)}/K_{SV}^{(S_D,R_Q)}$
(*S*)-**2**	61	54	1.13
(*S*)-**3**	92	73	1.26
(*S*)-**4**	90	82	1.10

[a] Concentration = 4.0 × 10^{-8} M.

Table 3. Stern−Völmer Quenching Constants for the Dendrimers and BINOL in the Presence of (*R*)- and (*S*)-7 in Benzene/Hexane (20:80)

dendrimer	$K_{SV}^{(S_D,S_Q)}$	$K_{SV}^{(S_D,R_Q)}$	$K_{SV}^{(S_D,S_Q)}/K_{SV}^{(S_D,R_Q)}$
(*S*)-**2**[a]	305	253	1.21
(*S*)-**3**[a]	445	351	1.27
(*S*)-**4**[a]	520	426	1.22
(*S*)-**4**[b]	561	461	1.22
(*S*)-BINOL[c]	111	109	1.02

[a] Concentration = 1.0 × 10^{-6} M. [b] Concentration = 4.0 × 10^{-8} M. [c] Concentration = 1.0 × 10^{-4} M.

Table 4. Stern−Völmer Quenching Constants (M^{-1}) of (*S*)-4 and (*R*)-4 in the Presence of (*S*)- and (*R*)-6 in Methylene Chloride

dendrimer	(*S*)-**6**	(*R*)-**6**
(*S*)-**4**	90	82
(*R*)-**4**	80	93

Discussion

The luminescence quenching data presented in Tables 1−3 indicate a measurable difference in chirality-dependent interactions between the dendrimers and chiral amino alcohols. The observed quenching constants show that the *S* enantiomer of the amino alcohols is more effective than the *R* enantiomer in quenching the luminescence of the *S* dendrimers at equal concentrations. The extent of the chiral interaction is measured by the ratio of the Stern−Völmer constants $K_{SV}^{(S_D,S_Q)}/K_{SV}^{(S_D,R_Q)}$, where a ratio other than 1 indicates an asymmetric interaction. These data show that the chiral differential interactions are similar in signs and magnitudes for the quenching of the zeroth-, first-, and second-generation dendrimers. There is a significant difference between the chiral recognition abilities of the dendrimers and the core BINOL molecule, as evidenced in Table 3. Also of note is the rapid increase in the Stern−Völmer constants with increasing dendrimer generation. Thus, the higher generation dendrimers have higher sensitivity toward the fluorescence quenchers than the lower generation ones. The much higher fluorescence signal of the dendrimer over the parent BINOL molecule also makes the dendrimer more sensitive sensors toward fluorescence quenchers over the small BINOL molecule.

The expected mirror-image relationships between the experimental Stern−Völmer quenching constants (and relative intensity measurements) of the enantiomeric fluorophores in the presence of the enantiomeric quenchers are well obeyed, as shown by the example in Table 4. Thus, the measured differences in the quenching of chiral dendrimers by chiral amines are indeed of a chiral origin. The observed linear response between the change in the luminescence of (*S*)-**4** and the enantiomeric composition of amino alcohol **7** implies that the enantiomeric composition of an unknown sample can be determined from the measurement of the luminescence responses of the chiral dendrimers.

The observation that the fluorescence lifetime of dendrimer (*S*)-**4** does not change when treated with the amino alcohol quencher **7** demonstrates that only static quenching occurs. This static quenching may be originated from the formation of ground-state hydrogen bond complexes between the hydroxyl groups of the dendrimer core and the amino alcohol. When both (*S*)-BINOL and the dendrimers are treated with 2.0 × 10^{-3} M NaOH, a new peak in the UV–vis spectra appears to the red of the lowest absorption (by 50 nm) due to deprotonation. However, the UV–vis spectra of the dendrimers in the presence of amino alcohol **7** were only slightly different from those in the absence of the amino alcohol. This indicates that the amino alcohol cannot deprotonate the dendrimer core but probably forms a hydrogen-bond complex. We have also found that the hydroxyl groups of (S)-**4** are necessary for efficient quenching by amino alcohols as there was no significant quenching by (*S*)-**7** when the two hydroxyl groups of (*S*)-**4** are converted to two methoxy groups. Thus, the hydrogen-bonded complex may be nonfluorescent, leading to the observed static quenching of the dendrimer.

The fluorescence lifetime study also indicates that the observed dependence of the K_{SV} of the dendrimers on the dendritic generation and solvent reflects the ground-state association constants between the dendrimers and the amino alcohols. That is, the increase of K_{SV} with increasing dendritic generation can be attributed to higher association constant between the higher generation dendrimers and amino alcohols, and the increase of K_{SV} as the solvent polarity decreases from methylene chloride to benzene/hexane can be attributed to stronger ground-state hydrogen bonding interaction between the BINOL core and amino alcohols in the less polar solvent.

Summary

We have observed a dramatic enhancement in fluorescence intensity from BINOL to the phenyleneethynylene dendrimers containing the BINOL core. The strong fluorescence of the dendrimers allows a very small amount of the chiral materials to be used for sensing. The light-harvesting antennas of the dendrimer funnel energy to the center BINOL unit whose hydroxyl groups upon interaction with a quencher molecule lead to fluorescence quenching. This mechanism makes the dendrimers have much more sensitive fluorescence responses than corresponding small molecule sensors. Therefore, fluorescence signal amplification has been provided by the cross-conjugated dendrimer arms.[21] The fluorescence of these dendrimers can be enantioselectively quenched by chiral amino alcohols. It is observed that the fluorescence lifetime of dendrimer (*S*)-**4** does not change in the presence of various concentrations of amino alcohol **7**. This demonstrates that the fluorescence quenching is entirely due to static quenching. Thus, formation of nonfluorescent ground-state hydrogen-bond complexes between the dendrimers and the amino alcohols is proposed to account for the fluorescent quenching. A linear relationship has been established between the effective Stern–Völmer constant of dendrimer (*S*)-**4** and the enantiomeric composition of amino alcohol **7**. Such enantioselective fluorescence sensors may allow a rapid determination of the enantiomeric composition of chiral molecules and is potentially useful in the combinatorial search of asymmetric catalysts and reagents.[22–25] We are currently working on extending the observed enantioselective fluorescence response of this class of chiral dendrimers to other chiral organic substrates in order to develop sensors for practical applications.

Experimental Section

The amino alcohols used were purchased from Aldrich and stored under nitrogen gas. The liquid amino alcohols (*S*)-/(*R*)-**5** and (*S*)-/(*R*)-**6** were vacuum distilled prior to use. The solid amino alcohols (*S*)-/(*R*)-**7** were individually dissolved in methanol, filtered through silica gel, and then recrystallized from ethyl acetate/hexane solution (2.5:1) prior to use. All solutions were prepared using volumetric syringes, pipets, and/or volumetric flasks. For each series of experiments, a single stock dendrimer solution was prepared and used.

The uncertainty in the precision of the dendrimer concentration within a given series of experiments should be <0.3% because of the technique used. The uncertainty in the dendrimer concentration is <5%. The uncertainties in the precision of the amino alcohol concentrations are estimated to be <0.4% and the uncertainties in accuracy to be <1.0%. The fluorescence properties of the solutions were measured within a few hours of mixing the dendrimers and amino alcohols; day-old samples showed some changes in the shape of the emission spectra.

All fluorescence measurements were performed on a Perkin-Elmer LS50B spectrofluorimeter. Filters were used in the excitation pathway when necessary to reduce the excitation light intensity from the spectrometer. Relative emission intensities were determined from the integrated peak intensities from the standard Perkin-Elmer instrumental software.

Fluorescence singlet lifetimes were measured on a Photon Technologies International LS-1 single photon counting apparatus with a gated hydrogen arc lamp using a scatter solution to profile the instrument response function. Nonlinear least-squares fitting of the decay curves were performed with the Levenburg–Marquardt algorithm as described by James et al.[26] as implemented by the Photon Technologies International Timemaster (version 1.2) software. Goodness of fit was determined by judging the χ^2-(<1.3 in all cases). Samples are excited at 310 nm and detected at 418 nm.

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