

Control over the chirality of (*R*)-1,1'-bi-2-naphthol dibenzoate in nanoparticles

Yanli Zhang, Wensheng Yang¹, Zhiyuan Tian, Jiannian Yao*

Key Laboratory of Photochemistry, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, PR China

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Abstract

Nanoparticles of (*R*)-1,1'-bi-2-naphthol dibenzoate (*R*-BND) ranging from 40 to 170 nm were prepared by using the reprecipitation method. The nanoparticles exhibit size-dependent exciton chirality, where the coupling potential V_{12} of 1B_b transitions increases as nanoparticles grow and simultaneously the exciton chirality peaks exhibit the bathochromic shift. Such size-dependent optical properties can be attributed to the lattice hardening with increased particle size, which leads to a decreased dihedral angle θ between the two naphthyl planes in a *R*-BND molecule. © 2005 Elsevier B.V. All rights reserved.

Keywords: Nanoparticles; Chirality; (*R*)-1,1'-bi-2-naphthol dibenzoate

1. Introduction

The modulation of chirality has been one of the most important research activities because it plays an important role in many fields such as biological systems and optoelectronic devices [1,2]. So far, little was known about size effect on the chirality of nanoparticles made of small chiral organic molecules. In a previous study, we found that chiral inversion occurs in nanoparticles made of (*R*)-(+)-1,1'-bi-2-naphthol dimethyl ether (BNDE) as compared to its dilute solution. Such chiral inversion is caused by the formation of BNDE dimers, which substantially affect the intermolecular exciton coupling between two adjacent BNDE molecules in the nanoparticles [3]. Herein, we select (*R*)-1,1'-bi-2-naphthol dibenzoate (*R*-BND) (Scheme 1) as a model compound to extend our study for further understanding the size effects on the optical properties of nanoparticles made of these chiral 1,1'-binaphthyl derivatives. By using a reprecipitation method, we synthesized *R*-BND nanoparticles with average sizes ranging from 40 to 170 nm in diameter [4]. We then studied the optical properties of these

nanoparticles by using UV–vis absorption and circular dichroism spectroscopy.

2. Experimental

2.1. Materials

The model compound used in our work, (*R*)-1,1'-bi-2-naphthol dibenzoate was purchased from ACROS. Acetonitrile (for HPLC use)—the good solvent for *R*-BND—was purchased from ACROS. Purified water with a resistivity of 18.2 MΩ cm was produced using Milli-Q Apparatus (Millipore, USA).

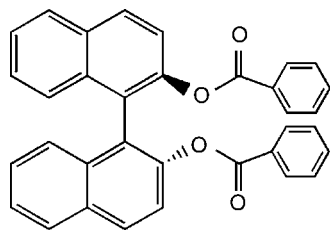
2.2. Methods

R-BND nanoparticles were prepared as follows: 100 μL *R*-BND/acetonitrile stock solution (1.0×10^{-3} mol/L) was rapidly injected (<2 s) into 5 mL of water at room temperature (25 °C). Mixing of the solvent and induces nucleation and growth of *R*-BND nanoparticles. A series of nanoparticles were successfully prepared by controlling the aging time.

The sizes and size distributions of *R*-BND nanoparticles dispersed in water were evaluated in situ by the dynamic light scattering (DLS) technique using a particle size analyser

* Corresponding author. Tel.: +86 10 82616517; fax: +86 10 82616517.
E-mail address: jnyao@iccas.ac.cn (J. Yao).

¹ Present address: College of Chemistry, Jilin University, Changchun 130023, PR China.

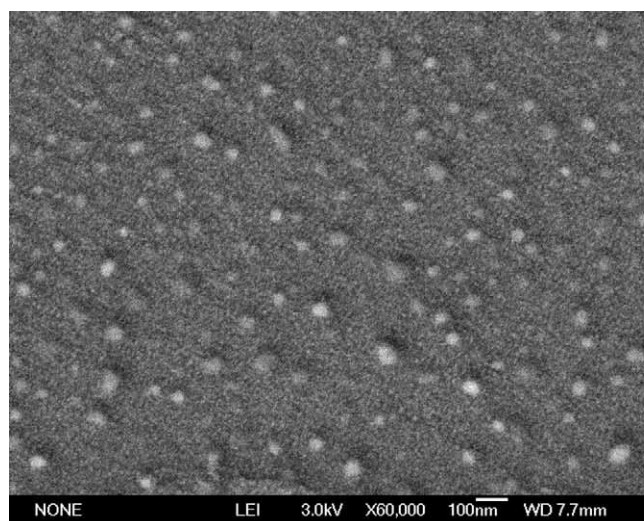
Scheme 1. Structure of *R*-BND.

(BI-90Plus, Brookhaven Instruments Co., Holtsville, NY) with scattering angle of 90° . Surface charge zeta-potentials were measured with palladium electrode assembly using the ZetaPALS (phase analysis light scattering) technique at a pH value of 6.50 at room temperature (25°C). The sizes and shapes of the nanoparticles were observed on a field emission scanning electron microscope (FESEM, JSM-6700F, JEOL) at an accelerating voltage of 3 kV. To enhance the conductivity of the sample, a layer of platinum was sputtered at a current of 5 mA and a pressure of 3 mm Hg.

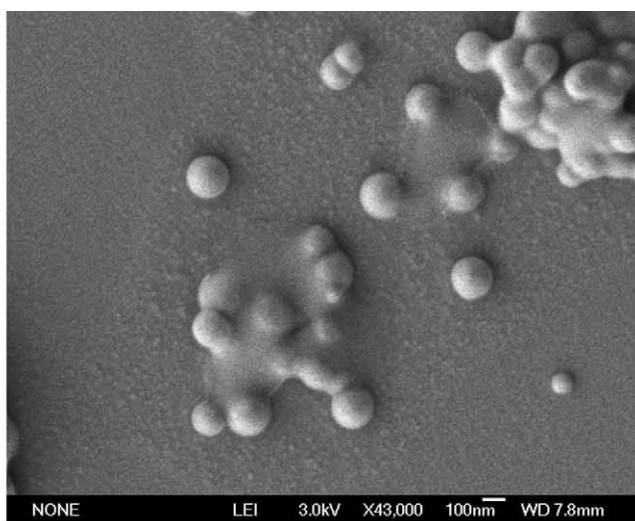
UV absorption spectra of aliquots of *R*-BND nanoparticle dispersions in water were measured in situ using a Shimadzu UV-1601 PC double-beam spectrophotometer. CD spectra of *R*-BND dilute solutions and nanoparticles were recorded on a JASCO J-810 CD spectrophotometer. DLS and FESEM measurements indicate that, during the above optical characterization, the average particle size and size distribution do not experience obvious changes.

3. Results and discussion

A series of *R*-BND nanoparticles ranging from 40 to 170 nm were prepared by using the reprecipitation method through controlling the aging time. Fig. 1 presents some field-emission scanning electron microscopy photographs of the



(a)



(b)

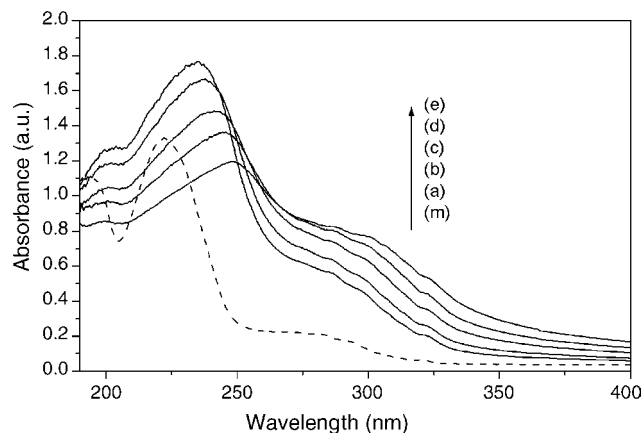
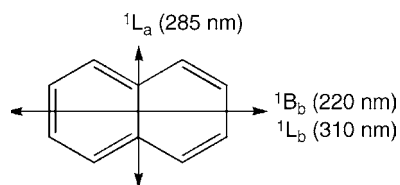
Fig. 1. FESEM photographs of *R*-BND nanoparticles: (A) 40 nm, and (B) 170 nm.

Fig. 2. UV-vis absorption spectra of *R*-BND nanoparticle dispersions with different sizes and *R*-BND solution in acetoneitrile (m). The spectrum of the *R*-BND/acetoneitrile solution (1.0×10^{-5} mol/L): (a) 40 nm, (b) 70 nm, (c) 90 nm, (d) 120 nm, and (e) 170 nm.

R-BND nanoparticles, in which the average sizes were 40 and 170 nm, respectively. These nanoparticle sizes are consistent with those determined by dynamic light scattering (DLS), in which the polydispersity was less than 10%. The measurements of surface electric properties indicate that these nanoparticles are all negatively charged, and their ζ -potentials retains a value of about -38 mV for all of the nanoparticles with different sizes.

Fig. 2 displays UV absorption spectra of *R*-BND nanoparticles of different sizes, dispersed in water (lines a–e) and dilute solution in acetoneitrile (line m). The electronic spectrum of naphthalene chromophore consists of $^1\text{B}_b$, $^1\text{L}_a$ and $^1\text{L}_b$ transitions at 220, 286 and 310 nm, respectively [5]. Scheme 2 displays their polarization directions [6]. In the case of the solution, UV absorption spectra exhibits a vibronically structured band in the 250–350 nm region ($^1\text{L}_a$ and $^1\text{L}_b$ transitions) and a higher energy band at 224 nm ($^1\text{B}_b$



Scheme 2. Polarization directions of the main electronic transition moments of naphthalene.

transition). The evolution of absorption of *R*-BND nanoparticles is studied as a function of the particle size. In the spectra of *R*-BND nanoparticles, both the low-energy absorption centred at 280 nm in the region of 250–350 nm and the 1B_b transition experiences bathochromic shift with increased particle size. Such bathochromic shifts indicate that the molecules undergo aggregation upon the formation of the nanoparticles. In addition, the trailing edge of the spectra at longer wavelength becomes more pronounced for the large particles than the small ones due to Mie scattering effects [7].

Circular dichroism spectra of *R*-BND nanoparticles of different sizes, dispersed in water (lines a–e) and dilute solution in acetonitrile (line m) are shown in Fig. 3. CD spectrum of the *R*-BND in acetonitrile solution consists of an intense exciton couplet from 1B_b transitions (maximum at 215 nm and minimum at 228 nm) with a crossover at 211 nm. The negative sign of the couplet of 1B_b transition indicates that the dihedral angle θ defined by the two naphthyl groups in *R*-BND should be smaller than the critical angle (110°) over which the CD signal will be inverted [8]. In contrast to the intense couplet of 1B_b transitions the compound also shows positive first and negative second cotton effects of medium intensity CD signal in the region of 1L_a transition (around 258 and 280 nm). However, the sequence of the sign of the cotton effects, i.e. positive and negative from longer wavelength side, is in conflict with the negative exciton chirality predicted by a point

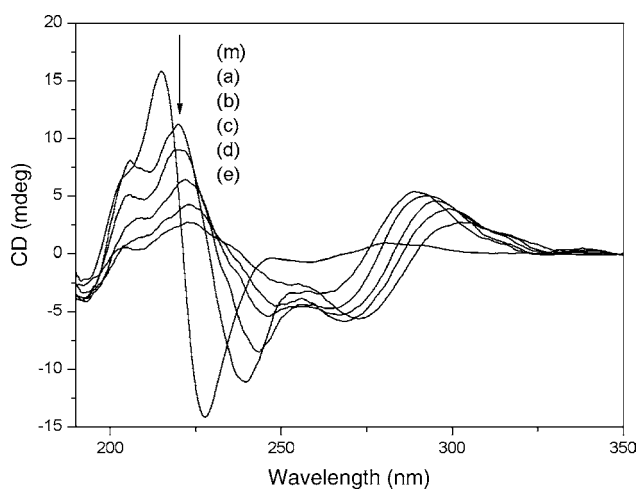


Fig. 3. CD spectra of *R*-BND nanoparticle dispersions with different sizes and *R*-BND solution in acetonitrile (m). The spectrum of the *R*-BND/acetonitrile solution (2.0×10^{-5} mol/L) $\times 0.4$: (a) 40 nm, (b) 70 nm, (c) 90 nm, (d) 120 nm, and (e) 170 nm.

dipole approximation method. Thus, the weak 1L_a transitions are unsuitable for the exciton chirality method. From the CD spectra, we can find that signals in shorter wavelength are more complex than simple 1B_b couplet. This is because 1B_b transitions are also coupled to 1L_a transitions [9]. The evolution of CD spectra of *R*-BND nanoparticles is also studied as a function of nanoparticle size. Compared with the spectrum of the monomer, both the CE of the 1B_b transitions and the couplet in the region of 1L_a transition shift to longer wavelength in case of the nanoparticles. It is more interesting to find that the first CE of the 1B_b transitions shifts more strongly to longer wavelength than the second CE in energy. To exclude off the effect of solvent on the chirality of *R*-BND molecules, we recorded the CD spectra of *R*-BND in a series of solvents with different polarities, which was displayed in Fig. 4. It is seen that the solvents do not affect the chirality of *R*-BND molecules obviously.

It is well known that the conformation of chiral open-chain binaphthyls in the crystalline state does not seem to be dependent on only intramolecular interactions but also on crystal packing effects. For example, in racemic crystals, 1,1'-binaphthyl adopts a cisoid conformation ($\theta = 68^\circ$), while in optically active crystals the transoid conformation is present ($\theta = 103^\circ$) [10]. Other 4, 4'-disubstituted 1,1'-binaphthyls show similar behavior with dihedral angles smaller in the racemic ($\theta = 68^\circ$) and larger in the optically active crystals ($\theta = 80^\circ$ – 102°) [11]. X-ray crystallographic studies for other 1,1'-binaphthyls derivatives report dihedral angles in the range of 68° – 92° [12]. Therefore, it is expected that the *R*-BND molecules present similar conformational changes contributed to the aggregation effect in the nanoparticles.

So far, various methods have been utilized to analyze conformations of 1,1'-binaphthyl compounds [13–15,8,16]. As for the relationship between the absolute conformation of 1,1'-binaphthyl derivatives and the sign of the 220 nm exciton couplet, the analytical function of V_{12} versus the dihedral angle θ has been first calculated by Mason [8]. It is shown that

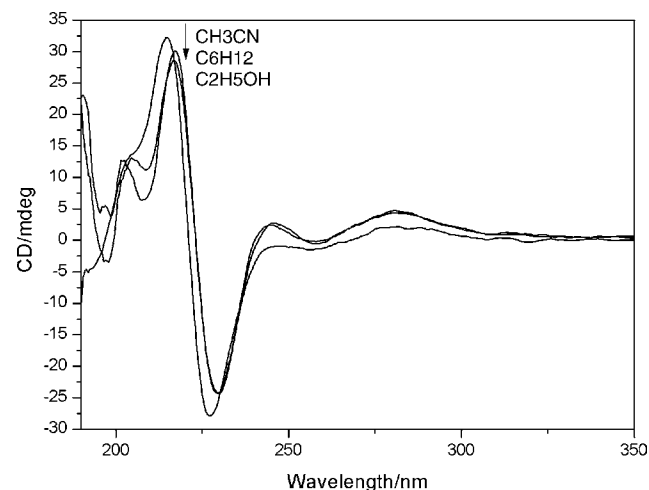


Fig. 4. CD spectra of *R*-BND solution (1.0×10^{-5} mol/L) in a series of solvents.

Table 1

The separations in energy ($\Delta\bar{\nu}$, cm^{-1}) between the two oppositely signed CD bands of ${}^1\text{B}_b$ couple of monomers and nanoparticles

Sample	m	a	b	c	d	e
Nanoparticle size (nm)	–	40	70	90	120	170
$\Delta\bar{\nu}$ (cm^{-1})	2613.4	3794.5	4328.7	4501.3	4585.5	5429.1

V_{12} decreases monotonally with the increase of dihedral angle θ and vanishes at the critical angle, $\theta = 110^\circ$. The separations in energy ($\Delta\bar{\nu}$, cm^{-1}) between the two oppositely signed CD bands of ${}^1\text{B}_b$ couple of monomers and nanoparticles are displayed in Table 1. According to Table 1, as the size of *R*-BND nanoparticles increases from 40 to 170 nm, the separation in energy between the two oppositely signed CD bands of ${}^1\text{B}_b$ couple gradually increases, i.e. the coupling potential V_{12} increases. In term of the empirical rule calculated by Mason, we can deduce that the dihedral angle θ decreases along with the growth of nanoparticles. As the result of this conformational change the CD spectra show integral bathochromic shift. This result is in consistent with the π -SCF calculations, which suggest not only local electronic excitation within each aromatic chromophore but also charge-transfer excitation arising from an occupied orbital of one aromatic residue to an unoccupied orbital of the other should be taken into consideration [8]. In the same way, from the absorption spectra of a 1,1'-binaphthyl calculated by π -SCF method we also find that absorption bands experience bathochromic shifts, which well explains change of UV spectra.

It is obvious that the CD spectral evolution is the result of particle growth. Such size-dependent chirality cannot be attributed to the confinement effect because the radii of Frenkel and CT excitons in organic materials are so small that the quantum size effect should be negligible for particles larger than 10 nm in diameter [17]. It also unlikely originate from the Mie scattering due to that the peak broadening with an increase in the particles in Fig. 2 cannot be elucidated in terms of Mie scattering [7].

The size-dependent optical properties of these *R*-BND nanoparticles can be explained by using a model suggested by, Nakanishi. As the nanoparticle grow, the ratio between the amount of the surface molecules to that of those interior molecules of the nanoparticles decrease. This leads to lattice hardening of *R*-BND crystals, and therefore increased Coulombic interaction energies. The Increased intermolecular interactions will result in the decrease of the dihedral angle θ between the two naphthyl groups in a *R*-BND molecule. As a result, the coupling potential V_{12} is increased. Thus UV-vis absorption peak of these nanoparticles is red shifted with the increase of particle size.

4. Conclusions

In conclusion, we prepared *R*-BND nanoparticles with average diameters from 40 to 170 nm through the reprecipitation method. *R*-BND nanoparticles exhibit the

size-dependent exciton chirality. The coupling potential V_{12} of ${}^1\text{B}_b$ transitions increases along with the bathochromic shift of the exciton chirality peaks as nanoparticles grow. The size-tunable chirality can be attributed to the decreased dihedral angle θ between the two naphthyl groups in *R*-BND with the increase particle size. Such size-dependence chirality could be of interest to the information technology such as optoelectronic switch and information storage and has potential illuminating meaning in analyzing chiral molecular secondary structure in nanoscale so that optimum property can be obtained.

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