

Size-Dependent Exciton Chirality in (*R*)-(+)-1,1'-Bi-2-naphthol Dimethyl Ether Nanoparticles

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Abstract: Organic nanoparticles from a chiral auxiliary, (*R*)-(+)-1,1'-bi-2-naphthol dimethyl ether (BNDE), with a range of particle sizes from 25 to 100 nm were fabricated through the reprecipitation method. It is found that BNDE nanoparticles exhibit positive exciton chirality in 200–260 nm region in circular dichroism (CD) spectra, which are completely opposite to CD spectra of the dilute solution. The exciton chirality of the particles displays size-dependent behavior; that is, the exciton chirality peaks evolve to the low-energy side with increase in particles size. CD spectra accompanied with UV, fluorescence spectra, lifetime measurements of the excited states, and quantum mechanical calculations reveal that the chirality inversion results from intermolecular exciton coupling between two adjacent BNDE molecules in the nanoparticles, and the bathochromic shift of the peaks is attributed to the increased intermolecular interaction with increasing particle size.

Introduction

The manipulation of chirality has received a great deal of attention because it plays a pivotal role in life science and material science. Chirality is expressible at every level of the structures of biological systems and can emerge cooperatively at the molecular scale in chiral supramolecular assemblies.^{1–12} A change in exciton chirality has been realized in many organic systems in the nanometer regime. Chirality in such systems can be achieved either by assembly of chiral molecules^{1,2} or by combination of chiral and achiral molecules.^{3–5} Generally speaking, chirality inversion can be generated through solvent

effect,¹³ temperature change,¹⁴ redox,¹⁵ and different vortex direction.⁹ In a previous study of size effects on the properties of organic nanoparticles, we found that the optical absorption and emission transition behavior of organic nanoparticles are tunable simply by changing particle size. These effects arise from aggregation and increased intermolecular interaction as a function of particle size.^{16–18}

Inspired by the aforementioned works, we herein extend the organic model compound to a chiral one and select a typical chiral auxiliary, (*R*)-(+)-1,1'-bi-2-naphthol dimethyl ether (BNDE), to investigate the effect of particle size on exciton chirality in organic nanoparticles. 1,1'-Binaphthyl derivatives have a nonplanar arrangement of naphthalene moieties, and the dihedral angle between the two chromophores plays a crucial role in determining the discrimination ability of 1,1'-binaphthyl-derived auxiliaries in enantioselective reactions. They are widely used in chiral recognition processes and especially as auxiliaries in asymmetric organic synthesis.^{19,20} According to the exciton model of optical activity, exciton chirality is related to the angle between two transition dipole moments. A feature of BNDE is

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that the splitting of exciton chirality is dependent on the dihedral angle between the two component naphthyl chromophores.

In the work reported in this paper, we turned our interest to the chiroptical properties of BNDE in the solid state in the nanometer regime. A series of BNDE nanoparticles with a range of sizes from 25 to 100 nm were prepared through the reprecipitation method. Chirality of the as-prepared nanoparticles was investigated through a series of characterization methods such as UV spectra and circular dichroism (CD) spectra, combined with quantum mechanical semiempirical calculations. It is found that BNDE nanoparticles exhibit positive exciton chirality that is completely opposite to that of the solution, and the exciton chirality of the particles displays size-tunability. That is, exciton chirality peaks evolve to the low-energy side with increasing particle size. To the best of our knowledge, this is the first report on the evolution of chiroptical spectroscopy as a function of size of organic particles.

Experimental Section

Materials. The model compound used in our work, (*R*)-(+)-1,1'-bi-2-naphthol dimethyl ether (BNDE), was used as purchased from ACROS. Acetonitrile (for HPLC use), which was used as a good solvent for BNDE, was purchased from ACROS. Purified water with a resistivity of 18.2 M Ω ·cm was produced using a Milli-Q apparatus (Millipore, Billerica, MA) and was filtered using an inorganic membrane with a pore size of 0.02 μ m (Whatman International Ltd., U.K.) just before use.

Methods. BNDE nanoparticles were prepared as follows: 100 μ L of BNDE–acetonitrile stock solution (5.0×10^{-4} mol/L) was rapidly injected into 5 mL of water with stirring at the ambient temperature of 25 $^{\circ}$ C. The BNDE–acetonitrile solution was filtered by using an inorganic membrane filter with 0.02 μ m pore size (Whatman International Ltd.) before the injection. Control over the particle size was achieved by changing the aging time.

The sizes and size distributions of BNDE nanoparticles dispersed in water were evaluated in situ by the dynamic light scattering (DLS) technique using a particle size analyzer (BI-90Plus, Brookhaven Instruments Corp., Holtsville, NY) with a scattering angle of 90 $^{\circ}$. Surface charge zeta-potentials were measured with a palladium electrode assembly using the ZetaPALS (phase analysis light scattering) technique at a pH value of 6.50 at room temperature (25 $^{\circ}$ C). The sizes and shapes of the nanoparticles were observed on a scanning electron microscope (SEM, Hitachi S-4300) at an accelerating voltage of 15 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 mmHg.

UV absorption spectra and steady-state excitation and emission fluorescence spectra of aliquots of BNDE nanoparticle dispersions in water were measured in situ using a Shimadzu UV-1601 PC double-beam spectrophotometer and a Hitachi F-4500 fluorospectrometer, respectively. Time-resolved fluorescence measurements were carried out at the ambient temperature of 25 $^{\circ}$ C on a FLS920 time-resolved spectrofluorometer with a single-photon counting system (Edinburgh Analytical Instruments, U.K.). CD spectra of BNDE 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.

The molecular geometries of an isolated BNDE molecule and its dimer were drawn, and the minimum energy configuration was optimized using the semiempirical AM1 (Austin Model 1) method²¹ as implemented in the AMPAC program package.²² In actual nano-

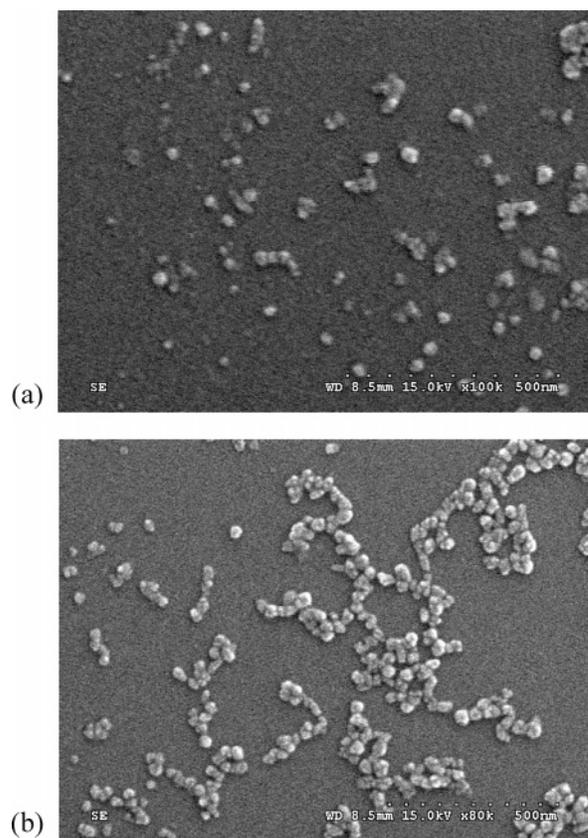


Figure 1. SEM images of BNDE nanoparticles with average sizes of (a) 25 and (b) 40 nm.

particles, a number of different intermolecular separations and relative orientations of the molecules are likely to be present. To investigate the dependence of the results on the choice of intermolecular geometric parameters, we repeated the same calculations by varying the intermolecular position and by using different packing models. Within the framework of the intermediate neglect of diatomic overlap (INDO) Hamiltonian²³ in the single and double configuration interaction (SDCI) approach to describe the exciton states, we have developed a formalism²⁴ to calculate the magnetic dipole operator: first in the atomic orbital basis, the Slater-type orbital is transformed into the INDO molecular orbital, and finally to the magnetic dipole transition moment between the ground and excited states. On the basis of the isolated molecular and dimeric geometric structures, their CD spectra were obtained by combining electric and magnetic dipole transition moments. The active space includes the 20 highest occupied molecular orbitals and the 20 lowest unoccupied molecular orbitals for a single molecule, and the 40 highest occupied molecular orbitals and the 40 lowest unoccupied molecular orbitals for a dimer. It was found that such a choice of active space retains the dominant molecular orbitals in the expansion of the excited states of interest and leads to converging excitation energies.

Results and Discussion

SEM Images of BNDE Nanoparticles. A series of BNDE nanoparticles with different average sizes in diameters from 25 to 100 nm were successfully prepared in our experiment by controlling the aging time. Figure 1 displays some field emission scanning electron microscope images of the as-prepared BNDE

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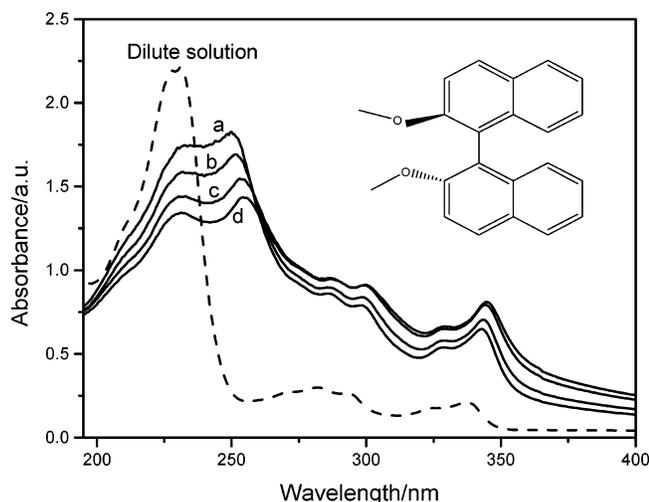


Figure 2. Absorption spectra of BNDE nanoparticle aqueous suspensions and BNDE dilute solution (1.0×10^{-5} mol/L): (a) 25, (b) 40, (c) 70, and (d) 100 nm. Inset: Molecular structure of BNDE.

nanoparticles, in which the average sizes are 25 (a) and 40 nm (b), respectively. DLS evaluation of the aliquots indicates that the size distributions of the particles are very narrow. Polydispersivities of the samples are less than 0.1 (10%). Measurements of surface electric properties indicate that these nanoparticles are all negatively charged, and their zeta-potentials retain a value of ca. -44.2 mV for all nanoparticles of different sizes under the conductance of $10 \mu\text{S}$ and electric field of 10.42 V/cm at pH 6.50. XRD measurements show no characteristic diffraction peaks for the samples with different diameters, and electron diffraction patterns displayed two halos for the samples with diameters of 25 and 40 nm. These results confirm that the particles are unambiguously amorphous.

UV Absorption Spectra of BNDE Nanoparticles and Dilute Solutions. Figure 2 shows UV absorption spectra of BNDE nanoparticle aqueous dispersions with a range of particle sizes and its dilute solution in acetonitrile. The dilute solution shows absorption bands at 230, 280, and 336 nm, respectively, which can be assigned as $^1\text{B}_b$ (230 nm), $^1\text{L}_a$ (280 nm), and $^1\text{L}_b$ (336 nm) transitions of the binaphthyl group. It is reported that $^1\text{B}_b$ and $^1\text{L}_b$ bands correspond to the long axis of the naphthyl group, while the $^1\text{L}_a$ band corresponds to the short axis.²⁵ In contrast, in BNDE nanoparticles, a new absorption peak as compared to the monomeric absorption appears at ca. 250 nm, linked with the original band at 230 nm, and this new peak undergoes a slightly bathochromic shift to the lower energy side as the particle size increases from 25 to 100 nm. At the same time, the other two bands at 282 and 339 nm also experience a slightly bathochromic shift with increased particle size. In addition, the trailing edge of the spectra at longer wavelength becomes more pronounced for the larger particles than for the smaller ones due to Mie scattering effects.²⁶

The bathochromic bands indicate that the molecules undergo aggregation in BNDE nanoparticles. It should be noted that, as far as the new peak is concerned, it may not be due to the increased intermolecular dipole–dipole interaction arising from the aggregation effect. It is known that strong coupling between

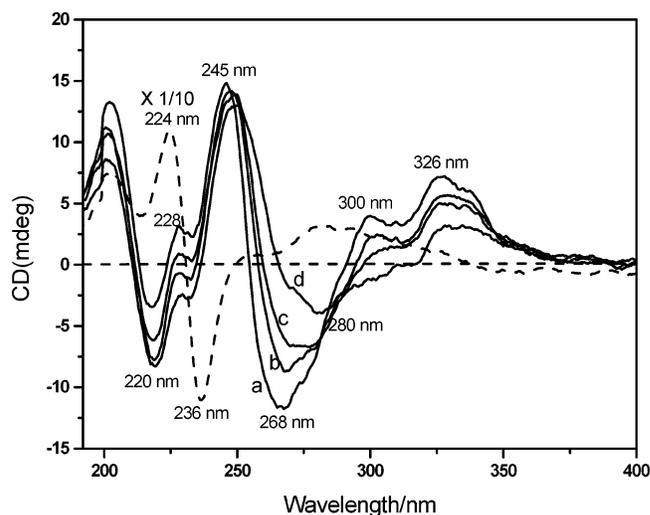


Figure 3. CD spectra of BNDE nanoparticle aqueous suspensions and BNDE dilute solution (1.0×10^{-5} mol/L): (a) 25, (b) 40, (c) 70, and (d) 100 nm.

two chromophores usually results in pronounced band splitting.^{19,20} Thus, it is proposed that the new peak in the absorption spectra may potentially originate from a strong intermolecular coupling effect between adjacent molecules in BNDE nanoparticles.

CD Spectra of BNDE Nanoparticles and Dilute Solution.

Figure 3 shows CD spectra of aqueous dispersions of BNDE nanoparticles in comparison with that of the dilute solution in acetonitrile. The spectrum of the BNDE dilute solution consists of an intense exciton couplet (maximum at 224 nm and minimum at 236 nm) with a crossover at 230 nm. This exciton couplet is assigned to the coupling of $^1\text{B}_b$ transitions of the two naphthyl moieties.^{19,20} The absence of a coupling couplet in the region of 250–350 nm is due to the fact that the dipole moments of $^1\text{L}_a$ transitions of two naphthyl groups are parallel. It is interesting to note that BNDE nanoparticles exhibit three strong split circular dichroism effects. The first positive bisignate band corresponds to the coupling of the $^1\text{B}_b$ transition on the high-energy side with one Cotton effect (CE) from 220 to 254 nm with the superposition of a weak negative exciton couplet (maximum at 228 nm and minimum at 233 nm for the 25 nm nanoparticles). This band shows an inverted CD couplet as compared to that of the dilute solution. The second positive bisignate band corresponds to the coupling interaction of the $^1\text{L}_a$ transition from 260 to 340 nm. In contrast to the signal of the BNDE dilute solution, this band turns into a bisignate one. This means that the coupling effect of transition dipoles corresponding to $^1\text{L}_a$ occurs in BNDE nanoparticles. The third one corresponds to the $^1\text{L}_b$ transition from 300 to 370 nm. The complexity of CD spectra in the region of 290–370 nm is due to the overlap of the exciton couplets of the $^1\text{L}_a$ and $^1\text{L}_b$ transitions. It should be noted that CD spectra of BNDE nanoparticles are dependent on particle size. That is to say, with an increase in particle size, all the exciton peaks experience bathochromic shifts, and the crossovers corresponding to these peaks also shift to the low-energy side. At the same time, the amplitude (ΔCD) of the CD spectra decreases with increasing particle size. It is concluded that the exciton chirality of BNDE nanoparticles is indeed inverted, and the change in exciton chirality originates from the formation of BNDE nanoparticles (see Supporting Information for details).

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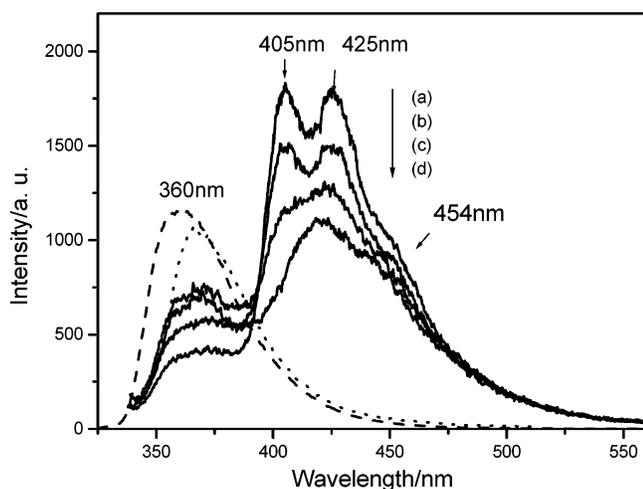


Figure 4. Emission spectra of BNDE nanoparticle aqueous suspensions (solid line), BNDE bulk crystals (dotted line), and BNDE dilute solution (1.0×10^{-5} mol/L, dashed line): (a) 25, (b) 40, (c) 70, and (d) 100 nm. The excitation wavelength is at 340 nm.

Fluorescence Emission Spectra of BNDE Dilute Solution and BNDE Nanoparticles. To clarify the aggregation structure of adjacent molecules in BNDE nanoparticles, we recorded the fluorescence spectra of the nanoparticles with different sizes and the dilute solution in acetonitrile at an excitation wavelength of 340 nm (Figure 4). The emission spectrum of the dilute solution, which is asymmetric, shows a maximum at about 360 nm, and the low-energy tail of the spectrum extends to about 450 nm. The emission spectra of BNDE nanoparticles are distinctly different from that of the dilute solution. In nanoparticles, the emission at 365 nm remains stable. It is interesting to note that there is a broad emission with resolved peaks at ca. 405, 425, and 454 nm, and the low-energy tail extends to ca. 520 nm. Moreover, as the nanoparticles' size increases, the relative intensity of the emission at 405 nm decreases compared to that at 365 nm. The emission spectrum of BNDE bulk crystals presents only an emission peak at 365 nm, which is slightly shifted to the low-energy side as compared to that of the solution, and is similar to the part around 365 nm in the nanoparticle state.

To assign the emission peaks of BNDE nanoparticles, we further conducted fluorescence lifetime measurement of BNDE solutions and nanoparticles at the excitation wavelength at 340 nm, monitored at 365 and 405 nm (see Supporting Information), respectively. The fluorescence decay curve of a BNDE dilute solution monitored at 365 nm is monoexponential, with a lifetime of 4.973 ns, which is ascribed to emission of the naphthyl group. The 25 nm BNDE nanoparticle shows a similar monoexponential decay curve at 365 nm, with a lifetime of 1.595 ns, which is in accordance with the emission of the naphthyl group.²⁷ The shortened lifetime as compared to that of the solution may arise from the aggregation quenching due to formation of the aggregate state. The decay curve monitored at 405 nm for the nanoparticles was fitted with a dual-exponential function by use of the nonlinear least-squares method with a deconvolution technique, corresponding to lifetimes of 1.931 (42.75%) and 7.160 ns (57.25%), respectively. The species with longer lifetime is ascribed to the aggregate

Table 1. Summary of the Lifetime Values of BNDE Dilute Solution and the 25 nm Nanoparticles

sample	λ_{em}/nm	τ_1/ns	$Q_1/\%$	τ_2/ns	$Q_2/\%$	χ^2
monomer	365	4.973	100			1.162
particles	365	1.595	100			1.242
	405	1.931	42.75	7.160	57.25	1.219

state.²⁸ The lifetime results are summarized in Table 1. It should be noted that the lifetimes of the nanoparticles are independent of particle size.

For organic molecules, the complex state generally exhibits a long decay time as compared to that of the initially excited state.²⁹ The long lifetime component monitored at 405 nm confirms the existence of a complex state, while the one with short lifetime is assigned to emission from the naphthyl chromophore. The above spectral features, accompanied with the molecular shape of BNDE, lead us to conclude that there exists a complex in the nanoparticles and the complex is an intermolecular excimer, which is caused by the molecular packing in the particles. It is known that the complex state is prone to form on the surface in the solid state³¹ because of the molecular freedom to rotate. This suggestion is in good accordance with the emission spectra. With increasing particle size, the specific surface area is reduced, and the amount of excimers is also decreased, leading to the decreased intensity of the emission at 405 nm. This is also consistent with the evolution of CD spectra of the nanoparticles as a function of particle size, in which the amplitudes of the spectra keep decreasing with increase in particle size due to decreased surface area of the particles.

Optimized Structure of BNDE Molecular Dimer Pair in the Nanoparticles. For BNDE monomer in a vacuum, the calculated dihedral angle between two naphthyl chromophores is ca. 87.5° (Figure 5A), which roughly agrees with the quasi-orthogonal conformation in solution.^{19,20} The dihedral angle may be subject to change in a wide range in different systems. It has been reported^{30,31} that the dihedral angle between the two moieties in crystals changes from 60 to 100° in binaphthyl derivatives. This means that the dihedral angle can be substantially modified in the solid state. With consideration of the split band at 228 nm with small amplitude in the CD spectra, and the relationship between the angle and the wavelength splitting, it is estimated that the dihedral angle between the two binaphthyl chromophores in one BNDE molecule in the nanoparticles is 60 – 70° . Thus, the angle is taken as 65° in the following discussion.

It is established^{19,20} that in binaphthyl systems there exists a critical value of 110° . When the dihedral angle exceeds this value, the CD signal will be inverted. As shown in Figure 3, the positive couplet at 245 and 220 nm suggests that in the nanoparticles there exist two coupling chromophores whose dihedral angle exceeds 110° . Considering the aforementioned fact that the dihedral angle between the two binaphthyl chromophores in one BNDE molecule is in the range of 60 –

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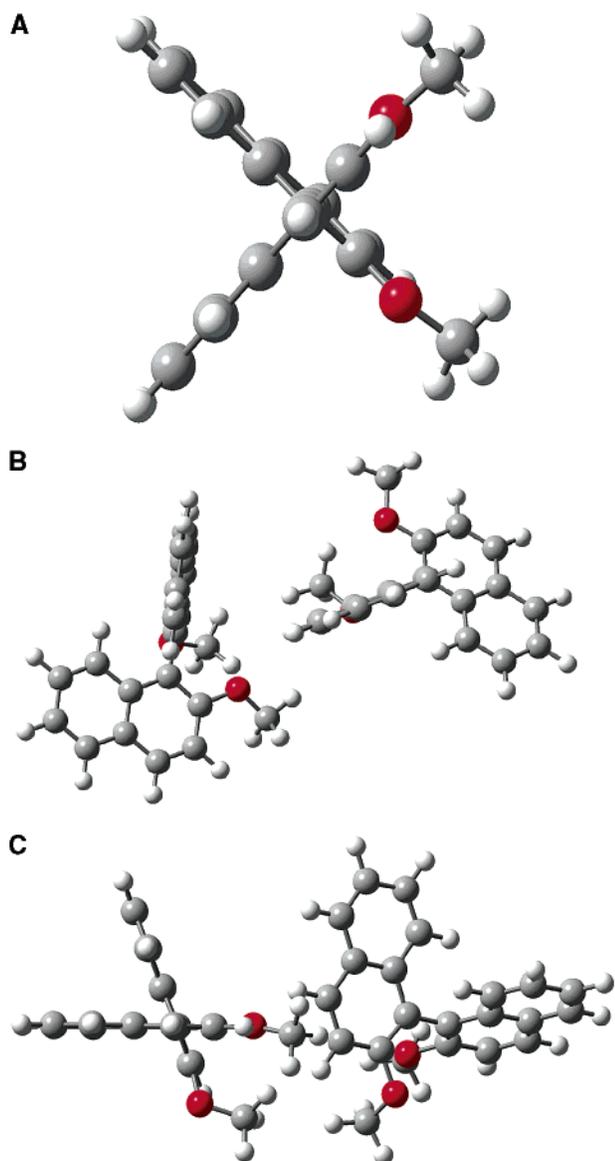


Figure 5. Energy-optimized BNDE (A) monomer and (B, C) dimeric pair. The chromophores are numbered as 1, 2, 3, and 4 respectively from left to right. B and C represent projection of the same pair from two different directions.

70°, it is thus proposed that two naphthyl moieties from two adjacent molecules facilitate the formation of an angle between two transition moments, which exceeds the critical value of 110°. That is to say, the positive CD signal in BNDE nanoparticles as compared to the negative one in the monomer results from intermolecular coupling effect in the nanoparticles. This is also supported by observation of the excimer emission, which needs the formation of a dimer as a precursor of the excimer in BNDE nanoparticles.

In principle, the formation of an excimer or exciplex necessitates face-to-face stacking of two moieties.^{30,31} In effect, it is not the case in practical systems. Complexes can also be formed even when the chromophores are not stacked in this way. For example, it has been reported³² that the fluorescence spectrum of anthracene microcrystals exhibits excimer emission with vibrational progressions, which is caused by displaced

anthracene molecules. The authors also suggested that the broadness is not a necessary criterion for excimer bands. The structured emission peaks in the 400–500 nm region in Figure 4 lead us to expect that, in BNDE nanoparticles, two naphthyl chromophores from two adjacent molecules are stacked not strictly face-to-face, but in a displaced mode. It should also be noted that, in contrast to the signal of BNDE dilute solution, the 1L_a transition from 260 to 340 nm turns out to be a bisignate one, which means the occurrence of coupling of transition dipole corresponding to 1L_a in BNDE nanoparticles. This means that the angle between short axes of the two molecules is also not zero any more, which also lends support to the existence of displaced dimeric molecular pairs in BNDE nanoparticles.

To further envisage the dimeric conformation of the two adjacent BNDE molecules, we conducted a modeling calculation using the AM1 semi-empirical quantum mechanical method. With consideration of the CD spectra, we set the dihedral angle between two naphthyl moieties in one molecule as 65°. In light of the existence of the intermolecular excimer in BNDE nanoparticles deduced by the spectral investigation, we used the BNDE dimeric pair as a model to perform the calculation. A number of different dimers may be constructed. To investigate the dependence of the results on intermolecular geometric parameters, we repeated the same calculation by variation of the intermolecular position and different packing models. The pair with optimized energy is obtained as shown in Figure 5, in which B and C display projection of the dimer from two different directions. The chromophores in C are labeled as 1, 2, 3, and 4 respectively from left to right. It can be determined that the angles between transition dipole moments of the corresponding naphthyls are 145° (1 and 4), 98° (1 and 3), 77° (2 and 4), and 31° (2 and 3), respectively. It is obvious that the angle between chromophores 1 and 4 exceeds the critical value of 110°. This leads us to conclude that the formation of the dimeric structure is responsible for the inversion of exciton chirality in BNDE nanoparticles. Furthermore, the angle between the short axes of the two chromophores exceeds 0°, which determines the coupling splitting in the region of 268–400 nm.

Quantum Mechanical Calculation of the CD Spectrum of the BNDE Dimeric Pair. Quantum mechanical calculations of CD spectra were performed to further confirm the supposition that CD inversion is a result of the formation of the BNDE dimeric pair, as shown in Figure 5. For comparison, a calculation on the monomer was also performed. The calculated CD spectrum of the monomer (Figure 6) presents a bisignate Cotton effect with a positive part at 201 nm and a negative part at 210 nm, which is considered to be in satisfactory agreement with the observed spectrum of the BNDE monomer in acetonitrile, as shown in Figure 3. In contrast, the dimer pair presents an inverted calculated CD spectrum (Figure 6) with a positive part at 260 nm and a negative part at 207 nm, with the superposition of signal of the monomer (positive part at 229 nm and negative part at 245 nm). The calculated spectrum of the dimer pair is also in good agreement with the experimental results.

Size-Dependent Exciton Chirality in BNDE Nanoparticles. From the fluorescence spectra, molecular modeling, and quantum mechanical calculations, it is proposed that the chirality inversion is the result of intermolecular exciton coupling by formation of a displaced molecular dimer pair in BNDE nanoparticles. The size-dependent absorption spectra and exciton

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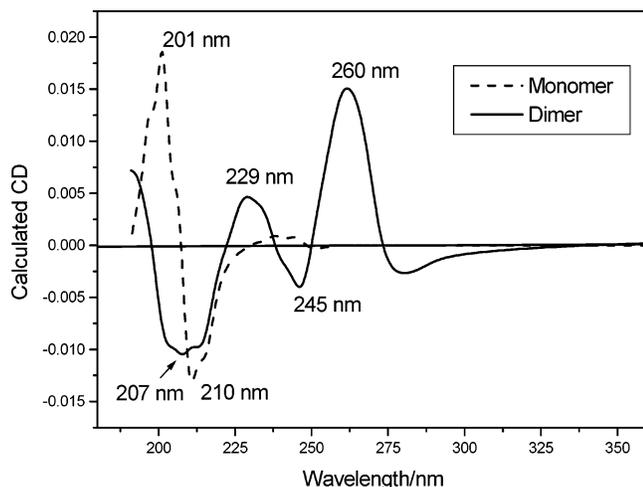


Figure 6. Calculated CD spectra of BNDE monomer and the dimeric pair as displayed in Figure 5.

chirality of BNDE nanoparticles are, therefore, related to existence of the dimeric structure. The bathochromic shift of the 1B_b , 1L_a , and 1L_b bands indicates that the molecules experience aggregation behavior in the nanoparticles. A similar phenomenon has been observed in other organic solid systems, for example, LB films³³ of bi-2-naphthol derivatives. As Nakanishi et al. suggested, the decrease in surface area of the nanoparticles leads to lattice hardening, and therefore increased Coulombic interaction energies. Increased intermolecular interaction will result in the bathochromic shift of 1B_b , 1L_a , and 1L_b bands in both UV absorption and CD spectra.

As far as the size-dependent amplitude of CD signals is concerned, it can be interpreted in terms of surface effects. It is known that, with increase in particles size, the specific surface area will be reduced. The dimer pair is prone to form on the

surface of the particles because the conformation of the molecules can be adjusted freely on the surface. With increasing BNDE particle size, the relative amount of the dimers formed will be decreased, leading to the decreased amplitude of CD signals of the nanoparticles. This is also consistent with the decreased intensity of the excimer emission of BNDE nanoparticles with increased particle size.

Conclusion

In summary, we have prepared BNDE nanoparticles with different sizes using the reprecipitation method. The nanoparticles exhibit inverted exciton chirality as compared to that of BNDE in acetonitrile solution. The chirality inversion has been identified to originate from formation of the dimer pairs in the nanoparticles. The exciton chirality of the particles displays size-tunability; that is, the exciton chirality peak evolves to the low-energy side as the particles grow larger. This work presents a successful paradigm for manipulation of exciton chirality simply by changing the size of the organic particles. This degree of chirality control might be of practical value, for example, in the use of the particles as active components or optically switchable devices.

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Supporting Information Available: Discussion which lends support to the hypothesis that the inversion of exciton chirality and the evolution of CD spectra can be attributed to the formation of BNDE nanoparticles and increase in particle size (page S1 and Figure S1), and fluorescence decay curves (Figure S2) of BNDE nanoparticle aqueous suspensions and BNDE dilute solutions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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