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Size-tunable exciton chirality and fluorescence emission in (*R*)-(−)-2,2′-bis-(*p*-toluenesulfonyloxy)-1,1′-binaphthalene nanoparticles

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Abstract

The organic nanoparticles from a chiral auxiliary, (*R*)-(−)-2,2′-bis-(*p*-toluenesulfonyloxy)-1,1′-binaphthalene (R-BTBN), were fabricated with a range of particle size from 40 to 160 nm through the reprecipitation method. The exciton chirality and the fluorescence emission of the particles display size-tunable behaviors. The circular dichroism (CD) spectra of the nanoparticles experience a bathochromic shift with an increase in the particle size and the intensity ratio of the first to the third cotton effect (CE) increases as the nanoparticle size increases to 60 nm. And also the nanoparticles show excimer emission that enhances as the particle size grows. CD spectra accompanied with UV, fluorescence emission spectra, reveal that the size-tunable optical properties are attributed to the synergetic effect of the change of dihedral angle in the initial stage and the more effective formation of excimer between the two naphthalene chromophores in adjacent molecules as nanoparticles grow.

Keywords: Nanoparticle; Chirality; Circular dichroism; Excimer

1. Introduction

The design of chiroptical and fluorescent switches and triggers that operate with efficiency, reversibility, and permanency offers a challenging issue in the area of information science and technology [1]. On the basis of the study of semiconductor and metal nanoparticles, increasing attention is being paid to organic nanoparticles [2,1e,1f]. Motivated by the attractive potential applications of organic nanoparticles in nanosized optoelectronic devices, we select a typical chiral low-molecular-weight compound, (*R*)-(−)-2,2′-bis-(*p*-toluenesulfonyloxy)-1,1′-binaphthalene (R-BTBN), to extend the study. 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 [3]. In this contribution, we fabricated a series of R-BTBN nanoparticles with different average sizes in diameter from 40 to 160 nm by the reprecipitation method [2]. The exciton chirality and the fluorescence emission of the particles display size-tunable behaviors, which are attributed to the synergetic effect of the change of dihedral angle in the initial stage and the more effective formation of excimer between the two naphthalene chromophores in adjacent molecules as nanoparticles grow.

2. Experimental

2.1. Materials

The model compound used in our work, R-BTBN was used as purchased from ACROS. Acetonitrile (for HPLC use) was used to be the good solvent of R-BTBN as purchased from ACROS. Ultrapure water with a resistivity of 18.2 MΩ cm was produced using Milli-Q Apparatus (Millipore, USA).

2.2. Methods

The organic nanoparticles of R-BTBN were prepared as follows: 100 μL of R-BTBN/acetonitrile stock solution (1.0×10^{-3} mol/L) was rapidly injected into 5 mL of water with

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stirring at the ambient temperature of 25 °C. The particles with different sizes were obtained through sampling at different aging time, that is, by changing the time intervals after the stock solution injection, i.e. the particles with an average diameter of 40, 60, 140 and 160 nm were obtained when the system was aged for 0 min, 6 h, 12 h and 24 h after the injection, respectively, at the ambient temperature of 25 °C.

The sizes and distributions of the nanoparticles dispersed in water were evaluated in situ by dynamic light scattering (DLS) technique using a particle size analyser (BI-90Plus, Brookhaven Instruments Corp., Holtsville, NY) with the scattering angle of 90°. The surface electric ξ-potential measurement was conducted with palladium electrode assembly using 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 field emission scanning electron microscope (FESEM, 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.

The UV absorption spectra and the emission fluorescence spectra of the aliquots of R-BTBN nanoparticles dispersions in water were measured in situ using a Shimadzu UV-1601 PC double-beam spectrophotometer and a Hitachi F-4500 fluorospectrometer, respectively. The CD spectra of R-BTBN dilute solution and nanoparticles were recorded on a JASCO J-810 CD spectrophotometer. DLS and FESEM measurement showed that, during the above optical characterization, the average particle sizes and the size distributions did not change much.

3. Results and discussion

3.1. SEM images of R-BTBN nanoparticles

A series of R-BTBN nanoparticles with different average sizes in diameter from 40 to 160 nm were successfully prepared in our experiment by controlling the aging time. The nanoparticles' dispersions into water exhibited an off-white turbidity due to the light scattering of the nanoparticles. Moreover, the color deepened as the nanoparticle size increased.

Fig. 1 presents some FESEM photographs of the R-BTBN nanoparticles, in which the average sizes are 40 and 160 nm, respectively. These values agreed roughly with those determined by DLS with the polydispersity less than 10%. Measurements of surface electric properties indicated that these nanoparticles were all negatively charged, and their ξ-potentials retained a value of about −38 mV for all of the nanoparticles with different sizes.

3.2. UV absorption spectra of R-BTBN nanoparticles and dilute solution in acetonitrile

Fig. 2 presents the UV absorption spectra of R-BTBN nanoparticles with different sizes dispersed in water and R-BTBN dilute solution in acetonitrile. The UV spectrum of the acetonitrile solution shows absorption bands at 225 and 294 nm that can be assigned to ^1B_b and ^1L_a transition, respectively [4–6].

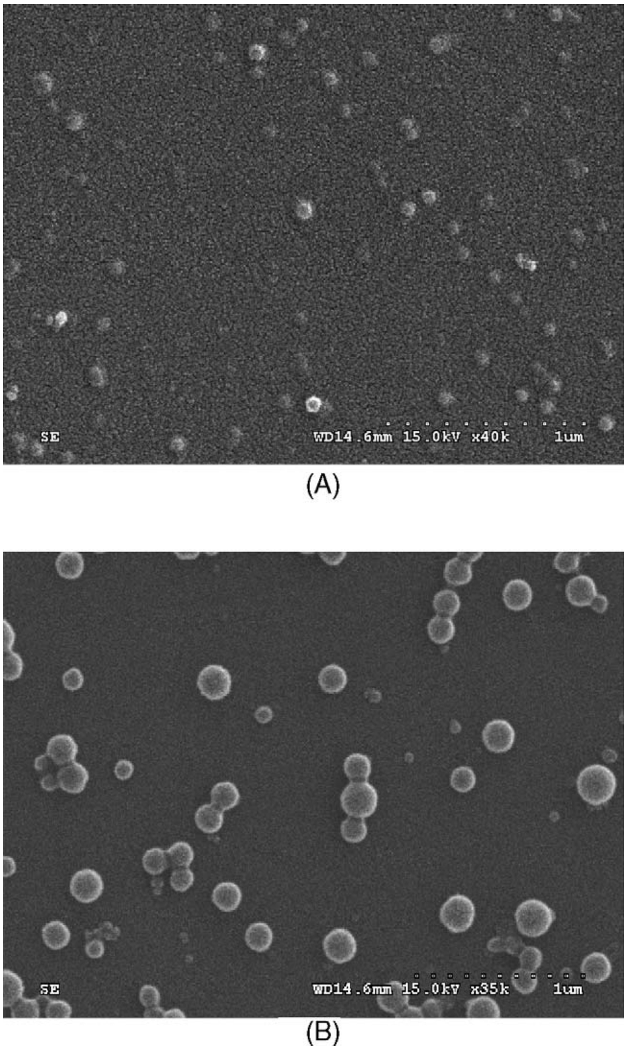

Fig. 1. FESEM images of R-BTBN nanoparticles: (A) 40 nm; (B) 160 nm.

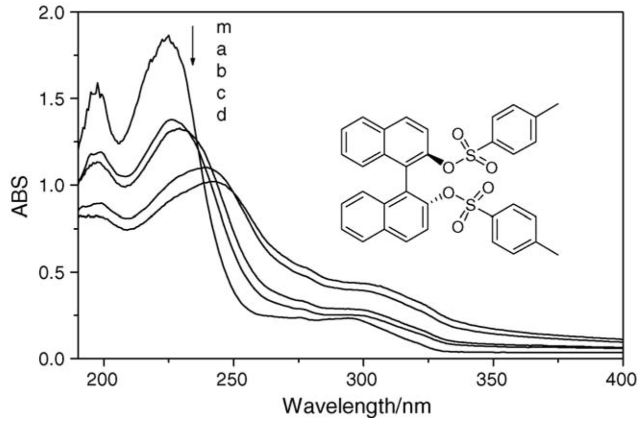

Fig. 2. UV/vis absorption spectra of R-BTBN nanoparticle dispersions with different sizes and R-BTBN dilute solution in acetonitrile: (m) R-BTBN/acetonitrile (2.0×10^{-5} mol/L); (a) 40 nm; (b) 60 nm; (c) 140 nm; (d) 160 nm.

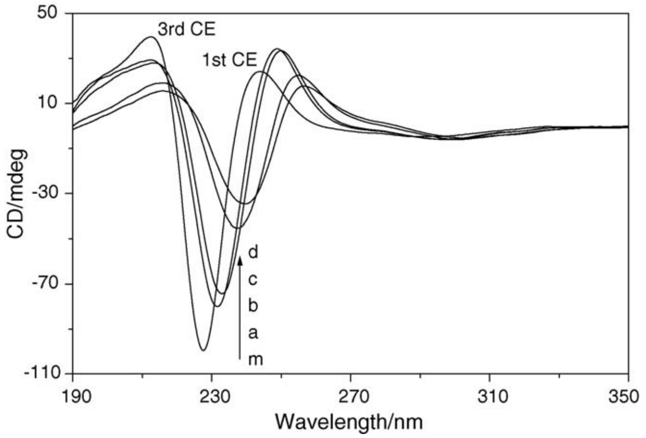

Fig. 3. CD spectra of R-BTBN nanoparticles and the dilute solution in acetonitrile: (m) R-BTBN/acetonitrile (2.0×10^{-5} mol/L); (a) 40 nm; (b) 60 nm; (c) 140 nm; (d) 160 nm.

In the case of nanoparticles dispersions, a new absorption peak gradually appears in the region of 230–250 nm, which experiences a red shift, as the particle size increases from 40 to 160 nm accompanied by a slight red shift in the band at 294 nm. In addition, the trailing edge of the spectra at long wavelengths became more pronounced for the larger particles than for the smaller ones due to Mie scattering effects [7]. The bathochromic bands indicate that the molecules undergo aggregation in R-BTBN nanoparticles.

3.3. CD spectra of R-BTBN nanoparticles and dilute solution in acetonitrile

The CD spectra of R-BTBN nanoparticles and R-BTBN dilute solution in acetonitrile are displayed in Fig. 3. The CD spectrum of the acetonitrile solution shows a dramatic signal inversion of the couplet centered at ca. 225 nm (^1B_b transition of the naphthalene chromophore) with respect to that of other cisoid binaphthyl derivatives [8,9] due to the coupling of the two ^1B_b transitions located on distinct naphthalene rings. This kind of inversion indicates that the single molecules of R-BTBN in CH_3CN adopt transoid conformation [8]. For the dilute solution, the intensity of the third cotton effect (CE) of ^1B_b transition is still stronger than that of the first CE, indicating that the dihedral angle does not exceed the critical value of about 110° over which the CD signals will be inverted [9]. So the dihedral angle in the dilute solution is between 90° and the critical value. It is interesting to find that the intensity ratio of the first to the third CE increases to 1.20 as the particle size grows up to 60 nm compared with the value of 0.61 in R-BTBN dilute solution. This result manifests that the molecular conformation experiences changes, i.e. the dihedral angle increases to some extent [8]. For the nanoparticles with a size of 140 or 160 nm, the intensity ratio of the first and the third CE does not further increase, indicating that there is no obvious increase of the molecular dihedrel angle in the nanoparticles of 140 and 160 nm, i.e. the intramolecular planarization does not further enhance [8]. To exclude the effect of solvent on the chirality of R-BTBN molecules, we recorded the CD spectra of R-BTBN in a series of solvents with different polarities, which are displayed in Fig. 4. It is seen that the solvents do not affect the chirality of R-BTBN molecules obviously. It has been reported that chiral open-chain binaphthyls are not conformationally rigid molecules and for a given conformation they can exist in cisoid or transoid conformation displaying opposite helicity of the two naphthalene groups [8]. The conformation of chiral open-chain binaphthyls in the crystalline state seems to be dependent not only on intramolecular interactions but also on crystal packing effects [10]. It is expected that the intermolecular interactions can also affect the conformation of the R-BTBN molecules.

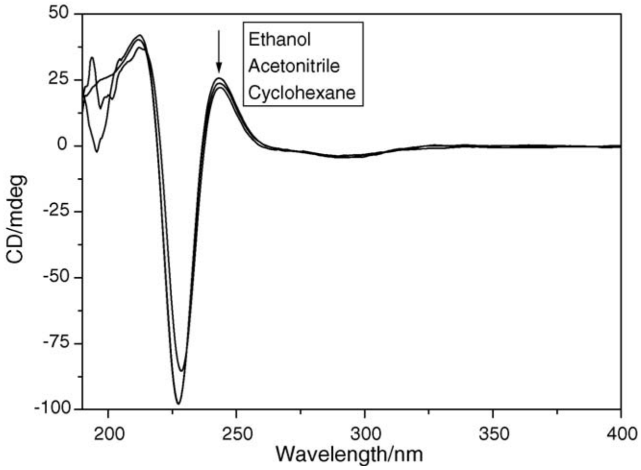

Fig. 4. CD spectra of R-BTBN solutions (1.0×10^{-5} mol/L) in a series of solvents.

3.4. Fluorescence emission spectra of R-BTBN nanoparticles and R-BTBN dilute solution in acetonitrile

The fluorescence emission spectra of R-BTBN nanoparticles and R-BTBN dilute solution in acetonitrile are shown in Fig. 5. R-BTBN molecules in acetonitrile solution show only weak monomer-like fluorescence of the naphthalene group at

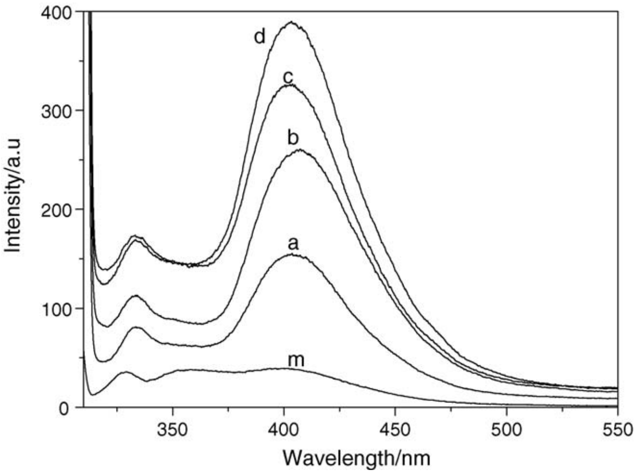

Fig. 5. Fluorescence emission spectra of R-BTBN nanoparticles and R-BTBN dilute solution in acetonitrile: (m) R-BTBN/acetonitrile (2.0×10^{-5} mol/L); (a) 40 nm; (b) 60 nm; (c) 140 nm; (d) 160 nm. The excitation wavelength is at 298 nm.

327 nm. However, the nanoparticles present an excimer emission of the naphthalene group at 400 nm [11] in addition to the monomer-like emission at 333 nm. It is noted that the intensity of the exicimer emission increases as the size of the nanoparticles increases from 40 to 160 nm. The fluorescent enhancement of excimer emission cannot be attributed to the Mie scattering effect. In principle, light scattering phenomenon may have great impact on the absorption spectrum, especially in the colloidal systems. However, light scattering have little influence on the emission spectrum since the scattering light always has the same wavelength with the incident light. Practically, in the measurement of the fluorescence emission spectrum, the starting wavelength is at the longer wavelength of the excitation one which will exclude the impact of the Mie scattering. Here in our measurement the excitation wavelength is 298 nm, while emission peaks are at 333 and 400 nm respectively. In addition, we found no changes in emission peak wavelength and in the evolving trend of emission spectra as the excitation wavelength changes from 236 to 298 nm. So, it can be seen that the fluorescence intensity is not affected by Mie scattering effect. It has been reported that the emission of some specific organic molecules were enhanced in solid state due to the intramolecular conformational changes of chromophores [12]. The twist conformations of chromophores in solution tend to suppress the radiative process whereas planar ones of chromophores induced in the solid state activate the radiation process. For R-BTBN nanoparticles, the increased dihedral angle corresponding to more planar molecular conformation contributes the enhanced fluorescence emission for the particle size of 40 and 60 nm. Simultaneously, the appearance of excimer emission indicates the interaction between naphthalene chromophores. This interaction cannot rise from two naphthalene chromophores in the same molecule. So it is reasonable to deduce that two naphthalene chromophores from adjacent molecules interacts with each other. In fact, due to the nonplanar arrangement of two naphthalene chromophores and the bulky and polar *p*-toluenesulfonyloxy groups in the same R-BTBN molecule, an exact face to face interaction between two naphthalene chromophores in adjacent molecules may be prevented [13]. Generally, the formation of excimer or exciplex necessitates parallel sandwich-pair structure [14]. However, it is not always the case in practical systems. The excimer can also be formed by partial overlap of electron cloud without an exact face-to-face parallel conformation [15]. The intensity of excimer emission is influenced by overlapping extent between chromphores [11,15]. As the sizes of nanoparticles increase, the enhanced intermolecular interactions may bring changes of overlapping extent between two naphthalene chromophores in adjacent molecules [2a,2b,2d,2e], which possibly facilitate more effective excimer formation of naphthalene chromophores in adjacent molecules, resulting in enhanced emission from excimer [11,15]. When the size of the R-BTBN nanoparticles increased from 40 to 60 nm, the synergetic effect of conformational planarization and excimer formation contributes to the fluorescent enhancement. For the 140 and 160 nm nanoparticles, although molecular planarization does not increase further, the enhanced intermolecular interactions may still facilitate more effective excimer formation of naphthalene chromophores in adjacent molecules, resulting in enhanced emission from excimer.

The mechanism of the size-tunable exciton chirality and fluorescence emission is in consistent with the UV absorption measurements. When R-BTBN nanoparticles begin to form, a new absorption band assigned to ^1B_b transition at longer wavelength appears and experiences red-shift to low energy side with increased particle size. The appearance of the new band indicates the formation of aggregate, which favors the intramolecular planarization and intermolecular excimer formation. As the particle size increases, the intramolecular planarization and the enhanced degree of naphthalene chromophores in adjacent molecules would result in their absorption shifting to lower energy [2d].

3.5. *Size-dependent exciton chirality and fluorescence emission in R-BTBN nanoparticles*

It is obvious that the CD and fluorescence emission spectral evolution is the result of particle growth. Such size-dependent chirality and fluorescence emission 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 [16]. It also unlikely originates from the Mie scattering due to the fact that the peak broadening with an increase in the particles in Fig. 2 cannot be elucidated in terms of Mie scattering [7]. To explain the same size dependence of perylene nanoparticles as that in our experimental results, Nakanish suggested two reasons [2a,2b]. One is the change of lattice state due to the decrease in surface area. It is likely that the decrease in surface area causes lattice hardening, and therefore the Coulombic interaction energies between molecules become larger, leading to narrower band gaps. The other reason may be the electric field effect of surrounding media through the surface of nanoparticles. The same potential of R-BTBN nanoparticles with different sizes and the shapes indicates that the latter is not, at least, the principal reason for the optical size dependence of R-BTBN nanoparticles. As the nanoparticle size increased, the enhanced intermolecular interactions [2a,2b,2d,2e] not only affects the molecular planarization of R-BTBN but also gradually enhances the overlapping extent of naphthalene chromphores in adjacent molecules, which contributes to the size-dependent exciton chirality and fluorescence emission in R-BTBN nanoparticles.

4. Conclusion

In summary, R-BTBN nanoparticles with different sizes ranging from 40 to 160 nm have been prepared by using the reprecipitatation method. And it is found that R-BTBN nanoparticles exhibit optical size-tunable exciton chiralty and fluorescence emission that are ascribed to the cooperation of the change of dihedral angle and the change of overlapping extent between two naphthalene chromophores in adjacent molecules as the particle size increases. Such optical tunabilty may have potential application in information areas such as optical switchable device and information storage.

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