CD inversion and fluorescence enhancement in organic nanoparticles of (*R*)-di-2-naphthylprolinol†

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The positive exciton coupling circular dichroism (ECCD) exhibited by monomer of (*R*)-di-2-naphthylprolinol in organic solvent is inverted to be negative upon the formation of its nanoparticles.

CD inversion of organic molecules has attracted great scientific attention in the past decades.[1–5] CD inversion could usually be induced by destruction of the intramolecular hydrogen bonds,[6] changing the temperature or the nature of solvents[7,8] of the systems, *etc*. Recently, it was reported that inversion of molecular chirality can be induced by irradiation[9,10] or redox[11] and may be potentially used as a chiroptical switch. Here, we present a simple strategy to achieve the control of chiroptical characteristics by growing and dissolving (*R*)-di-2-naphthylprolinol (DNP) nanoparticles. The positive exciton coupling circular dichroism (ECCD)[12] exhibited by DNP monomer in organic solvents is inverted to be negative upon formation of the nanoparticle, and the CD inversion process between DNP monomer and nanoparticle is reversible. Moreover, the quantum yield of the nanoparticle (Q = 0.67) is found to be almost 2.5 times that of the monomer (Q = 0.28).

DNP nanoparticles were prepared by the reprecipitation method.[13,14] The average particle size was evaluated to be 150 nm with a polydispersity of 5.2% by the dynamic light scattering (DLS) technique. These values were in agreement with those measured by transmission electron microscope (TEM), as shown in Fig. 1. The selected area electron diffraction taken from an individual particle indicates that DNP particles are amorphous.

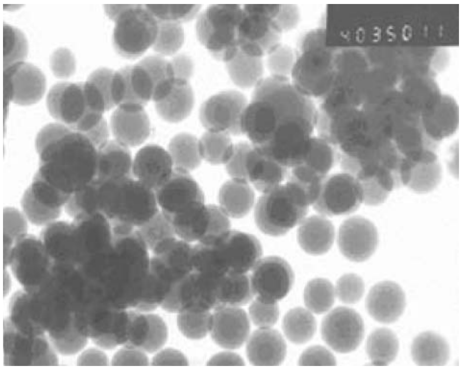

Fig. 1 TEM image of DNP nanoparticles with average size of 150 nm.

It is seen that DNP nanoparticles dispersed in water share the same absorption features with DNP monomers in acetonitrile (inset in Fig. 2). The band centered at 274 nm is due to the ^1L_a transition, which is polarized along the short axis of the naphthalene ring.[15,16] The other ones at 216 and 232 nm are attributed to the coupling of two ^1B_b transitions from the two naphthalene groups in one molecule, which are polarized along their long axes.[16,17] The CD spectrum of DNP monomer in acetonitrile (dashed curve in Fig. 2) exhibits two very strong Cotton effect (CE) bands with opposite signs in the coupling region of the two ^1B_b transitions, as a result of ECCD.[12] Furthermore, a relatively weak and broad positive CE is observed around 274 nm corresponding to the ^1L_a transition. The first ECCD band at λ_{max} = 216 nm and the second one at λ_{max} = 232 nm have mdeg values of −119.61 and +80.45, respectively. The summation of the amplitude of the two ECCD gives an A value of +200.06. This means that the two ^1B_b transition dipole moments in the same molecule are positioned in a right-handed screw manner for DNP monomer.[12] In addition, since the same positive CD signal is observed in a variety of solvents, including cyclohexane, ethanol and acetonitrile, it is concluded that the polarity or hydrogen bond of the solvents does not affect the CD spectrum in a significant way. Most interestingly, DNP nanoparticles present an inverted CD couplet as compared with that of the monomer. The CD spectrum of DNP nanoparticles (solid line in Fig. 2) is actually a mirror image of the spectrum of

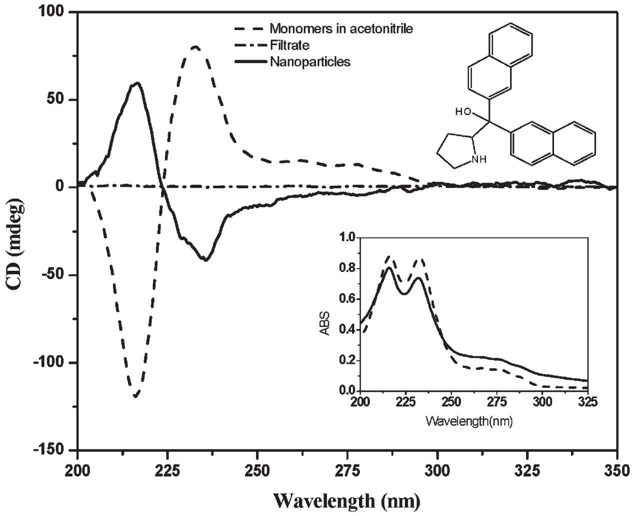

Fig. 2 CD and UV (inset) spectra of DNP monomer (dashed line), nanoparticles (solid line) and the filtrate (dash dot line). See text for details. (The structure of (*R*)-di-2-naphthylprolinol is shown as the inset).

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† Electronic supplementary information (ESI) available: 2D-NMR spectra of DNP molecule and nanoparticles. See http://www.rsc.org/suppdata/cc/b4/b412983k/

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DNP monomer, except for the intensities. The negative ECCD band of the monomer at 216 nm converts to be positive and the positive CE bands at 232 nm and 274 nm convert to be negative upon formation of the nanoparticles. Furthermore, a fluorescence enhancement is observed upon formation of the nanoparticles though there is no great difference between the emission shape of the monomer and the nanoparticles. The fluorescence quantum yield (Q) increases from 0.28 for the monomer to 0.67 for the nanoparticle.

CD inversion between DNP monomer and nanoparticle is identified to be reversible. For example, the positive ECCD of DNP nanoparticle at 216 nm can be returned to the negative one after re-dissolution of the nanoparticles filtered on a 20-nm-pore membrane and dried in vacuum. Repeating the solvent-exchange process, we can get DNP nanoparticles with nearly the same diameter, and the CD signal turns to be positive again. By assuming the concentration equals the average number of molecules per liter, the mdeg value of the nanoparticle suspension is calculated. Fig. 3a shows the reversible inversion of CD signals at 216 and 233 nm by repeating the solvent-exchange process three times, and no decrease in amplitude is found.

To probe the CD inversion process between DNP monomer and nanoparticles in detail, we used different water percentages in the preparation. Curve *a* in Fig. 3b elucidates a gradual inversion process of the ECCD band at 216 nm from negative to positive with increasing water percentage. Its value reaches a constant at a water percentage $\geqslant$ 60%. At the same time, curve *b* displays a gradual increase in fluorescence quantum yield (Q) with increasing water percentage. The yield is determined to be a constant value of 0.67 at water percentage $\geqslant$ 60%, almost 2.5 times that at water percentage = 0%. It should be pointed out that no detectable CD and absorption signals are obtained in the filtrates for the samples with water percentage $\geqslant$ 60%, which were obtained by filtering out the suspension using a 20-nm pore membrane. Therefore, all DNP molecules already join in formation of the particles at a water percentage $\geqslant$ 60%. It is the formation of the nanoparticles that results in the observed CD inversion as well as the fluorescence enhancement.

The spherical and amorphous properties of DNP particles exclude the possibility of both the introduction of Anisotropic Circular Dichroism (ACD) and the artifactual signals caused by birefringence in crystals.[18] The chiral center in the DNP molecule is the carbon next to the nitrogen in the 5-membered prolinol ring, not the carbon which connects the two naphthalene rings. However, the opening and closing of the dihedral angle θ between the two rings in the same molecule could cause the change of CD signal.[19] Fig. 4 displays the conformation of DNP monomer in acetonitrile (left) and the spatial configuration of a DNP-molecule pair in nanoparticles (right). The free-standing DNP molecule possesses a right-handed screwness with a dihedral angle of 74° between the two rings. The optimized structure of a DNP-molecule pair in the nanoparticle suggests that the dihedral angle in molecules 1 and 2 changes to be 92° and 100°, respectively. In fact, the increase in dihedral angle results in a left-handed screwness between the two naphthalene rings in the nanoparticle. This is further clarified by NMR measurements. In DNP/acetonitrile solution, we could identify a kind of interaction between two α-H atoms located in different naphthalene groups. However, the NMR signal from this kind of interaction disappears in the DNP nanoparticle suspensions (see the supporting material). For the free-standing DNP molecule, the distance between two α-H atoms is about 5.45 Å. However the distances increase to 7.13 and 7.45 Å respectively for molecules 1 and 2 in the DNP-molecule pair. In the pair, interaction between the two α-H atoms observed for the monomer will no longer exist. That is to say, opening of the dihedral angle of DNP molecules in the nanoparticles is responsible for the observed CD inversion. As abovementioned, we also observe a fluorescence enhancement upon the formation of DNP nanoparticles, accompanied by no obvious changes in the shapes and positions of absorption and emission bands. Therefore, the fluorescence enhancement of DNP nanoparticles cannot be attributed to J-aggregate formation in the nanoparticles.[20] In fact, the four naphthalene rings in the pair separate and are staggered from each other. The staggered configuration is unfavorable for the formation of H- or J-aggregates in the nanoparticles. Meanwhile, the staggered configuration also restricts the rotation of each naphthalene ring and increases the rigidity of the DNP molecule. This will decrease the probability of a nonfluorescence process,[22] and result in enhanced fluorescence. Moreover, the changes of dihedral angle lead to a decrease in the amplitude of the CD signal of the nanoparticle compared to that of the monomer since the maximum signal corresponds to a dihedral angle of 70°.[20]

In summary, reversible CD inversion of the DNP molecule can be realized upon the formation and re-dissolution of the nanoparticle. Opening of the dihedral angle of DNP molecules in the nanoparticle results in the inversion of the chirality, *i.e.*, from right-handed screwness for the free-standing molecule to left-handed screwness for molecules in the nanoparticle. Moreover, the staggered configuration of the molecules results in fluorescence enhancement of the nanoparticle instead of fluorescence quenching which usually occurs in the condensed phase.

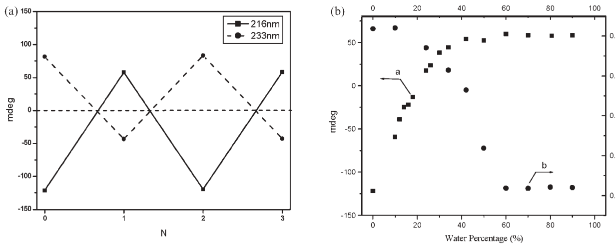

Fig. 3 (a) Plot of ECCD band at 216 nm (solid square) and Q values (solid circle) *versus* the times of the solvent-exchange process. (b) Changes of ECCD band at 216 nm (curve ***a***) and fluorescence quantum yield (curve ***b***) with different water percentages in preparation.

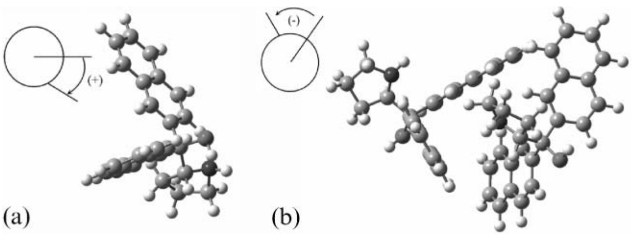

Fig. 4 Optimized molecular configurations of one DNP molecule (a) and a pair of DNP molecules (b).

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