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## COMMUNICATION

# Aggregation-induced Chirality Amplification of Optically Active Fluorescent Polyurethane and Cyclic Dimer in the Ground and Excited States

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**Optically active linear polyurethane and cyclic dimer were synthesized from 2,7-diisocyanatofluorene and 2,2'-dihydroxy-1,1'-binaphthyl. Circular dichroism (CD) spectral intensity of polymer was amplified at a higher concentration through aggregate formation while circularly polarized light (CPL) emission was not enhanced. Cyclic dimer's CPL emission was largely amplified ( $g_{lum}$   $1.1 \times 10^{-2}$ ) due to intermolecular excimer formation through aggregation while CD intensity was not affected.**

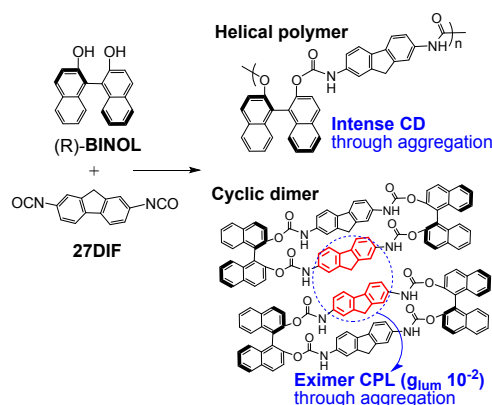
Chiral polymers are an important class of materials because of their wide scope of applications, and those having helical conformation are of particular interest to which various synthetic and analytical methods have been studied.<sup>1-4</sup> Helical polymers with single- or preferred-handed screw sense can be prepared by asymmetric polymerization of chiral or achiral monomers where helicity is generated through the polymerization (helix-sense-selective polymerization, asymmetric helix-chirogenic polymerization). In such polymerization, single-handedness of helix can arise from chiral ligands or chiral monomeric units. With such a background, we have recently reported that polyurethanes based on 1,4-diisocyanatobenzene and (+)-(R)- or (-)-(S)-2,2'-dihydroxy-

1,1'-binaphthyl (BINOL) form single-handed helical conformation of BINOL.<sup>5,6</sup>

BINOL has been used as chirality source in various chiral molecular and polymer systems.<sup>7-14</sup>

We herein report an optically active, helical polyurethane and a cyclic dimer synthesized from (R)- or (S)-BINOL and 2,7-diisocyanatofluorene (27DIF) which are fluorescent and envisioned to emit circularly polarized light (CPL) (Scheme 1). In spite of the fact that polyurethanes can be readily prepared through facile polyaddition and find broad applications,<sup>15,16</sup> precise control of their stereochemistry has been rarely reported. In this work, aggregation was found to amplify chiroptical properties of the urethane compounds with controlled stereostructure.

The polyaddition was conducted between (R)- or (S)-BINOL and 2,7-diisocyanatofluorene (27DIF) in the presence of Et<sub>3</sub>N as catalyst under various conditions (Scheme 1, Table S1 in ESI). Under all examined conditions, the products were composed of a linear polymer and a cyclic dimer (11% to 64%) which were separated by preparative size exclusion chromatography (SEC). Dimer formation was favored at lower monomer concentrations. The chemical structure of the linear polymer was supported by NMR and mass spectrometry (Figs. S2 and S3 in ESI).



**Scheme 1.** Synthesis of helical polyurethane and urethane cyclic dimer by polyaddition between 27DIF and BINOL and their chirality amplification.

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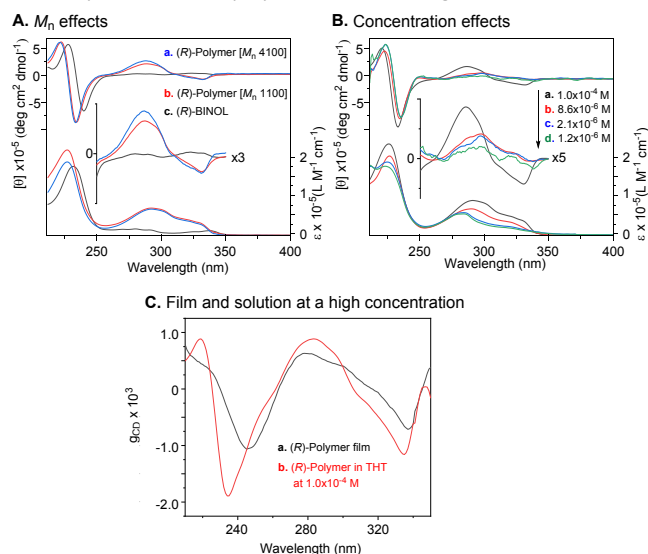
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Stereochemistry of the linear polymer was assessed by circular dichroism (CD) spectra as well as theoretical calculations. **Fig. 1A** shows CD and UV spectra of two linear polymers having different averaged molar masses ( $M_n$ 's) prepared from (*R*)-BINOL and 27DIF in acetone at 23 °C (run 6 in Table S1 in ESI) and separated by preparative SEC separation and that of (*R*)-BINOL. The polymers showed broad absorption and intense CD bands with a negative splitting pattern in the range of about 270–350 nm which are not clearly observed for (*R*)-BINOL in addition to the negative Cotton splitting centered at around 225 nm based on the 1,1'-binaphthyl-2,2'-diyl unit's chirality. The UV bands in the 270–350-nm range were ascribed to the -C(O)NH-fluorenyl-NHC(O)- moieties on the basis of the spectrum of *N,N'*-(fluorene-2,7-diyl)diacetamide as a unit model (**Fig. S11A** in ESI), and the intense CD of these bands indicate that the main chain has a single-handed helical conformation based on the axial chirality of BINOL units. Evidentially, the polymers obtained using (*R*)- and (*S*)-BINOL exhibited mirror image CD spectra (**Fig. S6** in ESI). The negative splitting in CD in the 270–350-nm range may reflect interactions between neighboring -C(O)NH-fluorenyl-NHC(O)- units in a twisted spatial arrangement. In addition, linear dichroism (LD) spectra of the polymer solution did not show any clear signals, supporting that the observed CD spectra are based on molecular chirality.

Molar mass had negligible effects on the spectra, indicating that the helical conformation is stable even for short chains. Further, polymerization solvent and temperature did not obviously affect UV and CD spectra of linear polymers (**Table S1**, **Figs. S7–S10** in ESI).



**Fig. 1.** CD-UV spectra of poly(*R*)-BINOL-*alt*-27DIFs of  $M_n$ 's 4100 (a) and 1100 (b) and (*R*)-BINOL (c) in THF (conc. =  $1.0 \times 10^{-4}$  M) [A], those of poly(*R*)-BINOL-*alt*-27DIF of  $M_n$  4100 in THF at  $1.0 \times 10^{-4}$  M (a),  $8.6 \times 10^{-6}$  M (b),  $2.1 \times 10^{-6}$  M (c), and  $1.2 \times 10^{-6}$  M (d) [B], and those of poly(BINOL-*alt*-27DIF) of  $M_n$  4100 in cast film (a) and in a THF solution at  $1.0 \times 10^{-4}$  M [C]. Concentrations in A and B are based on residue composed of a BINOL-based unit and a 27DIF-based unit. [cell path = 1 mm]

The CD and UV spectral intensity and shape in the 270–350-nm range remarkably changed depending on concentration of sample solution in tetrahydrofuran (THF) (**Fig. 1B**). At  $8.6 \times 10^{-6}$  M and lower

concentrations, UV signals were weaker and blue shifted, and the CD spectra lost the splitting pattern and changed into a positive, monotonous pattern with much lower intensities which were still different from the spectrum of BINOL. These results strongly suggest that chain aggregation affected the helical shape of poly(*R*)-BINOL-*alt*-27DIF, and aggregation enhanced chirality of the polymer. It is notable that the polymer showed very similar CD spectra in solution at  $1 \times 10^{-4}$  M and in film (**Fig. 1C**), suggesting that helix in aggregate in solution and in film have similar shapes. Also, the almost unchanged CD patterns and intensities at around 225 nm based on the 1,1'-binaphthyl-2,2'-diyl units support that chirality of this groups is unaffected by aggregation.

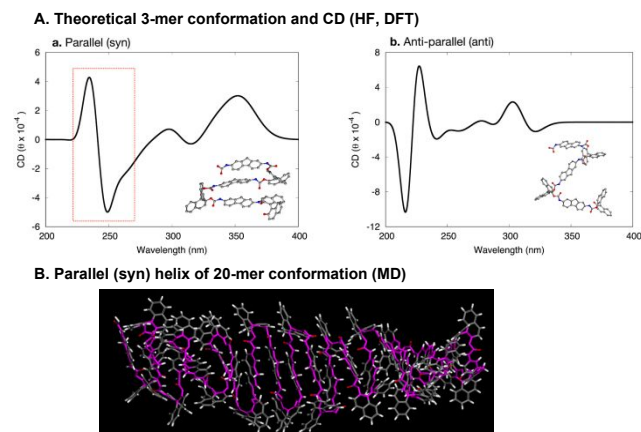
Aggregation of the polymer was detected by dynamic light scattering (DLS) experiments in THF (**Fig. S14** in ESI). Aggregates with a mean diameter of 100–200 nm were found in addition to much smaller particles of around 10 nm corresponding to single chain at  $1.0 \times 10^{-4}$  M, whereas aggregates were not detected at  $1.0 \times 10^{-6}$  M. TEM observation and XRD analysis were also attempted to obtain information on the structure of aggregates, which did not lead to significant information on intramolecular structures (**Figs. S22** and **S23** in ESI). In addition, CD and UV spectra were measured in the presence of acetic acid and imidazole as additives which would break intermolecular H-bonding; however, no clear changes were induced to the spectra, suggesting that H-bonding is not the main interaction to form aggregates (**Figs. S18** and **S19** in ESI).

Polymer conformation was also studied by theoretical calculations (**Fig. 2**). 2/1-Helix models were studied by HF calculations and molecular dynamics (MD) simulations (**Fig. 2**). 2/1-Helix has been proposed for a polyurethane prepared from BINOL and 1,4-diisocyanatobenzene.<sup>5,6</sup> In the modeling, two relative orientations of neighboring fluorene-2,7-diyl units in the main chain needed to be considered, *i.e.*, parallel (*syn*) and anti-parallel (*anti*) orientations. The model 3-mers with the two orientations were optimized at the HF/6-31G\* level of theory, followed by 50 steps of ab-initio MD calculations in the framework of Atom Centered Density Matrix Propagation<sup>17,18</sup> at 300 K at the same level of theory, and CD spectra were calculated within ZINDO for the optimized structures (**Fig. 2A**). The theoretical CD spectrum of the parallel (*syn*) 3-mer was rather similar to the experimental spectra of the linear polymer (**Fig. 1A,B**) with common features including an intense *negative splitting centered at around 225 nm* and a positive band in the longer wavelength range where excitation energies may be underestimated by systematic errors.<sup>19,20</sup> In a sharp contrast, the theoretical CD spectrum of the anti-parallel (*anti*) 3-mer had a *positive splitting centered at around 225 nm*, which does not coincide with the experimental spectra. The parallel (*syn*) orientation of fluorene-2,7-diyl units may thus be preferred.

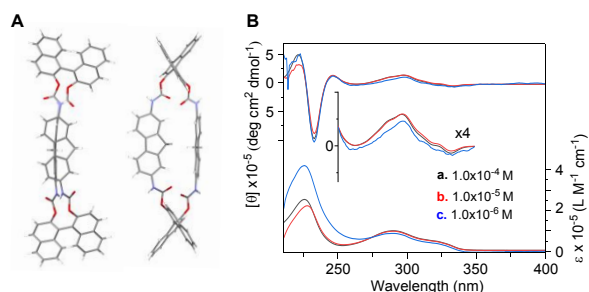
**Fig. 2B** shows the 2/1-helical 20-mer model with parallel orientation of fluorene-2,7-diyl units obtained through MD simulations. The conformation did not remarkably change through the simulation, suggesting its stability. This is in line with the fact that experimental CD spectra of the polymers did not substantially change on standing.

The *ab initio* and MD calculations predicted conformations in which the -C(O)NH-fluorenyl-NHC(O)- units are  $\pi$ -stacked in an accumulated form.<sup>21</sup> This aspect was experimentally supported by the remarkable hypochromicity of the polymer UV signals in the range of 270–350 nm with respect to *N,N'*-(fluorene-2,7-diyl)diacetamide as a unit model (**Fig. S9 A** in ESI) and also by XRD profiles showing d spacings of around 4.2 Å and 7.7 Å (**Fig. S23** in ESI).

Further, in connection with the MD model of the polymer, the hypochromicity in UV both at around 225 nm and in the 270-350-nm range at lower concentrations may be interpreted that the polymer chain has a more contracted conformation with chromophores located in closer vicinity to each other in a single chain form while it as a more stretched conformation in aggregate leading to more separated chromophore alignments. The bathochromic shifts of the -C(O)NH-fluorenyl-NHC(O)- signals at a higher concentrations may reflect stronger interactions between the units in a chain with a more contracted conformation in aggregate.



**Fig. 2.** Theoretical CD spectra and *ab initio*-optimized structures of 3-mer models of poly((*R*)-BINOL-*alt*-27DIF) having parallel (*syn*) (a) and anti-parallel (*anti*) (b) orientations of fluorene-2,7-diyl units [A] and helical conformation of 20-mer with parallel fluorene-2,7-diyl units orientations obtained through MD simulations (B). [MD conditions: NVT ensemble, temp. 300K, duration = 20 nsec, force field = COMPASS].



**Fig. 3.** Crystal structure of (*S*)-BINOL-27DIF cyclic dimer (A) and CD-UV spectra of (*R*)-BINOL-27DIF cyclic dimer (B).  $[\theta]$  and  $[\theta]_{\text{per residue}}$  are based on the molarity of cyclic dimer and that of the residue composed of a BINOL unit and a 27DIF unit, respectively, in A. [Experimental spectral measurement conditions: THF,  $1.1 \times 10^{-4}$  M, 1-mm cell].

The structure of the cyclic dimer was unambiguously decided by crystallography (Fig. 3A). The two fluorene-2,7-diyl units are oriented almost perpendicularly to each other in the cyclic structure. The cyclic dimer obtained from (*R*)-BINOL and 27DIF spectra exhibited UV and CD which were not affected by the sample concentration unlike the case of the polymer (Fig. 3B). DLS analysis of the cyclic dimer indicated a much lower intensity based on larger particles compared with the polymer even at a higher concentration ( $1.0 \times 10^{-4}$  M) (Fig. S15 in ESI), indicating that intermolecular aggregation is not likely for the dimer.

In the UV spectra, hypochromicity was observed at around 225 nm for the binaphthyl signals at a higher concentration suggestive of  $\pi$ -stacking interactions between 1,1'-binaphthyl-2,2'-diyl units. The interactions

did not induce large aggregates as indicated by the DLS results and also did not affect molecular chirality of the dimer in the ground state as indicated by the almost unchanged CD spectra.

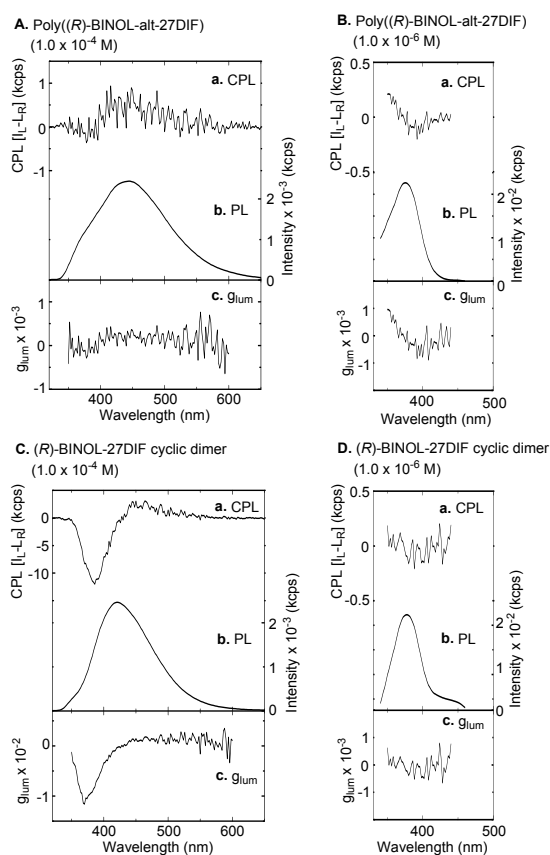
Next, fluorescence and CPL emission properties of linear polymer and cyclic dimer were examined in THF solution where remarkable concentration effects were found (Fig. 4).<sup>22</sup> Poly((*R*)-BINOL-*alt*-27DIF) showed a broad emission peak at around 430 nm associated with a minor shoulder at around 380 nm at  $1.0 \times 10^{-4}$  M (Fig. 4A) while it only showed a band at around 380 nm at  $1.0 \times 10^{-6}$  M (Fig. 4B). The bands at around 380 nm and 430 nm may be based on unimer and intramolecular excimer emission of fluorene units, respectively. The unimer emission is supported by the fact that *N,N'*-(fluorene-2,7-diyl)diacetamide as a unit model emitted in the range of 330-400 nm (Fig. S11B in ESI). At  $1.0 \times 10^{-4}$  M, aggregation may lead to a relative alignment between neighboring fluorene-2,7-diyl units suited for excited-state interactions. Intermolecular excimer formation of linear polymer may not be likely considering the predicted 20-mer structure with high steric hindrance (Fig. 2B). The CPL of the polymer was rather weak. At  $1.0 \times 10^{-4}$ , negative and positive CPL's for the 380-nm and 440-nm bands, respectively, were observed with anisotropy factor,  $g_{\text{lum}}$ , of the order of  $10^{-4}$  ( $g_{\text{lum}} = (2I_L - I_R)/(I_L + I_R)$  where  $I_L$  and  $I_R$  are emission intensities of L-CPL and R-CPL, respectively) (Fig. 4A). At  $1.0 \times 10^{-6}$  M, negative CPL responses with  $g_{\text{lum}}$  of the order of  $10^{-4}$  were observed at around 380 nm (Fig. 4B).

The (*R*)-BINOL-27DIF cyclic dimer showed a broad emission peak at around 420 nm which may arise from intermolecular excimer of two molecules with intense bisignate CPL responses with  $g_{\text{lum}}$  of  $-1.1 \times 10^{-2}$  (370 nm) and  $-1.1 \times 10^{-3}$  (450 nm) (Fig. 4C). In the excimer, two fluorene-2,7-diyl moieties of two molecules may be in a twisted arrangement. Intramolecular excimer may not be likely considering the crystal structure with the perpendicular arrangement of two fluorene-2,7-diyl units and the rigidity of the ring structure. On the other hand, at  $1.0 \times 10^{-6}$  M, the cyclic dimer only showed an emission peak at around 380 nm with rather weak CPL responses with  $g_{\text{lum}}$  of the order of  $10^{-4}$ . This order of  $g_{\text{lum}}$  may be considered to be the anisotropy inherent to single molecule of the cyclic dimer and also the linear polymer. Chirality of the cyclic dimer was thus remarkably amplified due to intermolecular excimer formation through aggregation. This is supported also by the clear discrepancy in the sign of CD and CPL of the cyclic dimer: the CD and CPL signs are considered to reflect intramolecular chirality in the ground state and intermolecular chirality in excited states, respectively.

TD-DFT optimization of the dimer in the lowest excited state ( $S_1$ ) indicated a molecular geometry very similar to that in the ground state ( $S_0$ ) with the two fluorene-2,7-diyl units oriented perpendicularly; however, electric dipole moment significantly increased from 3.44 Debye in the  $S_0$  state to 4.66 Debye in the  $S_1$  state (Fig. S17 in ESI). These results suggest that dipole-dipole interactions have a role in aggregate formation.

In conclusion, remarkable effects of aggregation leading to chirality amplification were found for the linear polyurethane in the ground state and for the cyclic dimer in excited states. The linear polymer may assume a more stretched form in aggregate where the twist between which the -C(O)NH-fluorenyl-NHC(O)- units is more significant leading to the observed chirality amplification in the ground state. On the other hand, the cyclic dimer forms aggregate in excited states possibly through dipole-dipole interactions, and the molecular structure is not

affected by aggregation. The dimer aggregates emitted highly efficient CPL based on an intermolecular excimer in excited states in which a chiral intermolecularly twisted arrangement between the -C(O)NH-fluorenyl-NHC(O)- units showed the sign of CPL which was opposite to that of CD based on intramolecular chirality in the ground state.



**Fig. 4.** CPL spectra (a), total emission (PL) spectra (b), and  $g_{lum}$  spectra (c) of poly((R)-BINOL-*alt*-27DIF) at  $1.0 \times 10^{-4}$  M (A) and  $1.0 \times 10^{-6}$  M (B) and those of (R)-BINOL-27DIF cyclic dimer at  $1.0 \times 10^{-4}$  M (C) and  $1.0 \times 10^{-6}$  M (D). [THF, 10-mm cell,  $\lambda_{ex}$  260 nm]

In a sharp contrast to the dimer, the polymer showed rather inefficient CPL emission based on intramolecular twist chirality between the -C(O)NH-fluorenyl-NHC(O)- units based on the axial chirality of the 1,1'-binaphthyl-2,2'-diyl units which may undergo a transient loss of chirality in excited states. BINOL molecule is known to decrease its anisotropy through twisted-coplanar transition (TCT) in excited states leading to a loss of chirality.<sup>23-29</sup>

Molecular aggregation has been known to enhance photo emission through restriction of molecular motions in excited states.<sup>30,31</sup> Aggregation also amplifies chirality of materials in the ground and excited states.<sup>32</sup> In this work, the fluorescent polyurethane and the cyclic dimer were found to amplify chirality through aggregation which occurs in solution at a rather low concentration.

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## Conflicts of interest

There are no conflicts to declare.

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