

Photo-induced Racemization and Polymerization of (R)-1,10-Bi(2-naphthol)

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Interactions between substances and light play important roles in life. One of the most important aspects is photosynthesis by plants and other organisms. In photosynthesis, sugars and molecular oxygen are produced from carbon dioxide and water where photon energy drives the reaction. Moreover, in artificial chemical synthesis, light promotes various reactions that are not driven by thermal energy. Further, in reactions where chiral compounds are produced, non-racemic products can be obtained using circularly polarized light (CPL). We recently reported that a preferred-handed helical conformation is induced for a polyfluorene derivative in the solid state when the polymer is irradiated with CPL [1-3]. The mechanism of this chirality induction involves a twisted-coplanar transition (TCT) of an aromatic–aromatic junction in the polymer where one of the enantiomeric, right- and left-handed twists is preferentially excited into the coplanar conformation. TCT through photo excitation was first predicted for biphenyl through theoretical calculations [4].

In this work, in order to examine the applicability and limitations of the photo-induced TCT for a molecule with a higher rotational barrier, we irradiated optically active (R)-1,10-bi(2-naphthol) (BINOL) with non-polarized light and investigated the structures of the products (Fig. 1). BINOL has been used as an effective chiral ligand and as a building block for chiral functional molecules and polymers; its stability has been considered to be sufficient under normal conditions for organic synthesis. However, the present study indicated that BINOL is readily racemized and polymerized at the same time upon photo irradiation. As indicated in Fig. 2, CD spectral

intensity remarkably decreased on irradiation, and at the same time, formation of a polymer was confirmed by size-exclusion chromatography. Such stereo chemical and chemical transformations of BINOL occurring simultaneously are unprecedented.

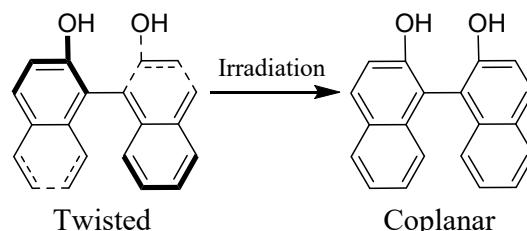


Fig.1 Twisted-coplanar transition (TCT) of BINOL.

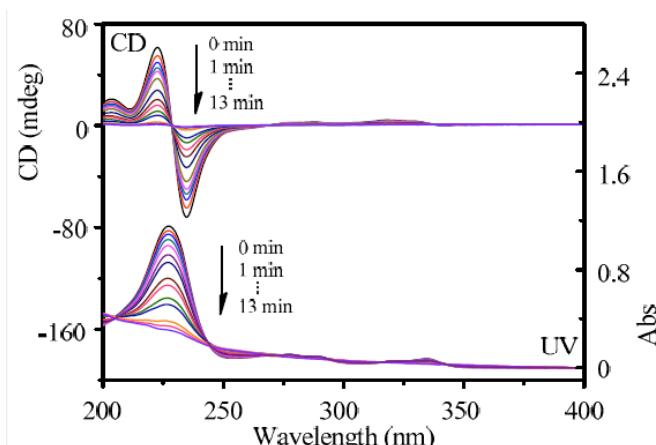


Fig. 2. Changes in CD (top) and UV (bottom) spectra of (R)-BINOL in CH_3CN solution upon irradiation ($[\text{BINOL}]_0 = 1.0 \times 10^{-4} \text{ M}$, cell path 1 mm, room temperature).

REFERENCES

- [1] Wang, Y.; Sakamoto, T.; Nakano, T. *Chem. Commun.* **2012**, 48, 1871–1873.
- [2] Pietropaolo, A.; Wang, Y.; Nakano, T. *Angew. Chem. Int. Ed.* **2015**, 54, 2688–2692.
- [3] Wang, Y.; Kanibolotsky, A.L.; Skabara, P.J.; Nakano, *Chem. Commun.* **2016**, 52, 1919–1922.
- [4] Imamura, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1968**, 90, 5379–5385..