非対称にπ拡張した[4.3.3]プロペランの合成と光学特性

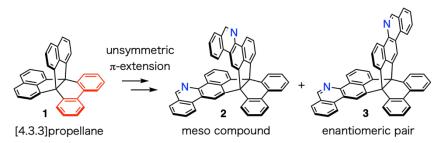
(京大院工 ¹・金沢大院自然 ²・金沢大 WPI-NanoLSI³) ○加藤 研一 ¹・瀬戸 延欣 ¹・和田 圭介 ²・Shixin Fa¹・生越 友樹 ¹,³

Synthesis and Optical Properties of Unsymmetrically π -Extended [4.3.3]Propellanes (1 Graduate School of Engineering, Kyoto University, 2 Graduate School of Natural Science and Technology, Kanazawa University, 3 WPI-NanoLSI, Kanazawa University) \bigcirc Kenichi Kato, 1 Nobuyoshi Seto, 1 Keisuke Wada, 2 Shixin Fa, 1 Tomoki Ogoshi 1,3

Chiral arrangement of two or more π -conjugated planes in a three-dimensional molecule is an attractive strategy for development of chiroptical organic compounds because such oligomers are systematically prepared with ease¹⁾, as compared with twisted π -conjugated frameworks such as helicenes. In this work, we used [4.3.3]propellane 1 as a rigid three-dimensional core and synthesized unsymmetrically π -extended [4.3.3]propellanes 2 and 3 via functionalization on their naphthalene segments.²⁾ The products were obtained as a set of stereoisomers, which were different in spatial arrangement of two 5-azachrysene units. The isomers were isolated using a chiral column and were characterized by electronic absorption and fluorescence spectroscopy. Chiral isomers 3 exhibited chiroptical response originating from through-space interaction between two 5-azachrysenes in skew position.

Keywords: Propellane; Fused-ring System; Nitrogen; Circular Dichroism; Optical Properties

優れたキラル光学特性を有する有機分子の開発において、複数の π 共役平面を立体的に配置した多量体は、ヘリセンなどのねじれた縮環 π 共役化合物に比べて簡便かつ系統的に合成可能な点で魅力的である $^{1)}$ 。本研究では、剛直な立体構造をもつ[4.3.3] プロペラン 1 に着目し $^{2)}$ 、ナフタレン環への修飾反応を行うことで非対称に π 拡張された新規 π 共役化合物を合成した。得られた立体異性体の組を光学分割することで、二つの 5 -アザクリセン骨格の相対配置が異なる分子 2 3 が得られた。これらの吸収・蛍光スペクトルおよびねじれの位置で空間を介して相互作用する二つの 5 -アザクリセンに起因したキラル光学特性について報告する。



- 1) a) T. Kawai, K. Kawamura, H. Tsumatori, M. Ishikawa, M. Naito, M. Fujiki, T. Nakashima, *ChemPhysChem* **2007**, *8*, 1465; b) K. Takaishi, R. Takehana, T. Ema, *Chem. Commun.* **2018**, *54*, 1449.
- Efficient synthesis of propellanes fused with naphthalene units. a) G. Dyker, J. Körning, P. G. Jones,
 P. Bubenitschek, *Angew. Chem. Int. Ed. Engl.* 1993, 32, 1733; b) T. Kubo, S. Miyazaki, T. Kodama,
 M. Aoba, Y. Hirao, H. Kurata, *Chem. Commun.* 2015, 51, 3801.