

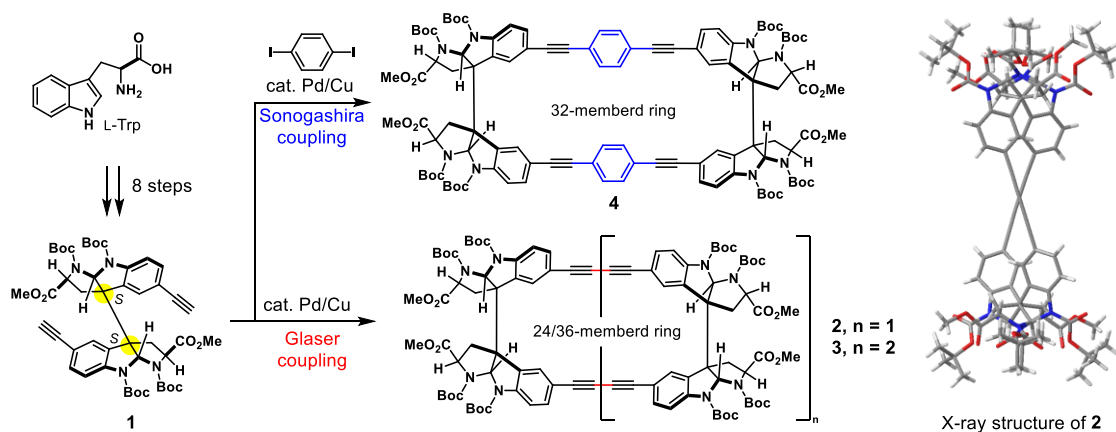
Design, synthesis, and chiroptical properties of macrocyclic oligomers composed of bispyrrolidinoindoline scaffold

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The figure of eight macrocyclic structure bearing D_2 -symmetry has been regarded as the privileged scaffold for displaying strong circular polarized luminescence (CPL). Most of the reported studies employ rigid non-planar aromatic scaffolds, such as helicene,¹ binaphthyl,² para-cyclophane,³ to induce chirality of the π -conjugated macrocycles. In contrast to the reported synthetic studies that require optical resolutions to provide enantiopure macrocycles, we are exploring an alternative approach employing bispyrrolidinoindoline (BPI) scaffold as a key chiral C_2 -symmetric segment for the modular and rapid asymmetric synthesis of the shape-persistent macrocycles bearing π -extended aromatic components.

In this study, we designed and synthesized macrocyclic oligomers composed of chiral C_2 -symmetric BPI unit **1** readily synthesized from L-tryptophane on gram scale.⁴ Glaser coupling of **1** furnished D_2 -symmetric 24-membered figure-eight macrocycle **2** as the major product along with 36-membered macrocycle **3**. Sonogashira coupling reaction of **1** with 1,4-diiodobenzene proceeded smoothly to afford 32-membered macrocycle **4** bearing benzene units as linkers. Further investigations for synthesizing the π -extended macrocycles and for elucidating their optical and chiroptical properties will be reported.



- 1) Kubo, H.; Shimizu, D.; Hirose, T.; Matsuda, K. *Org. Lett.* **2020**, 22, 9276.
- 2) Nojima, Y.; Hasegawa, M.; Hara, N.; Imai, Y.; Mazaki, Y. *Chem. Eur. J.* **2021**, 27, 5923.
- 3) Morisaki, Y.; Chujo, Y. *Bull. Chem. Soc. Jpn.* **2019**, 92, 265.
- 4) Tsuchiya, N.; Ryu, Y.; Muraoka, T.; Oguri, H. *Org. Biomol. Chem.* **2018**, 16, 9305.