

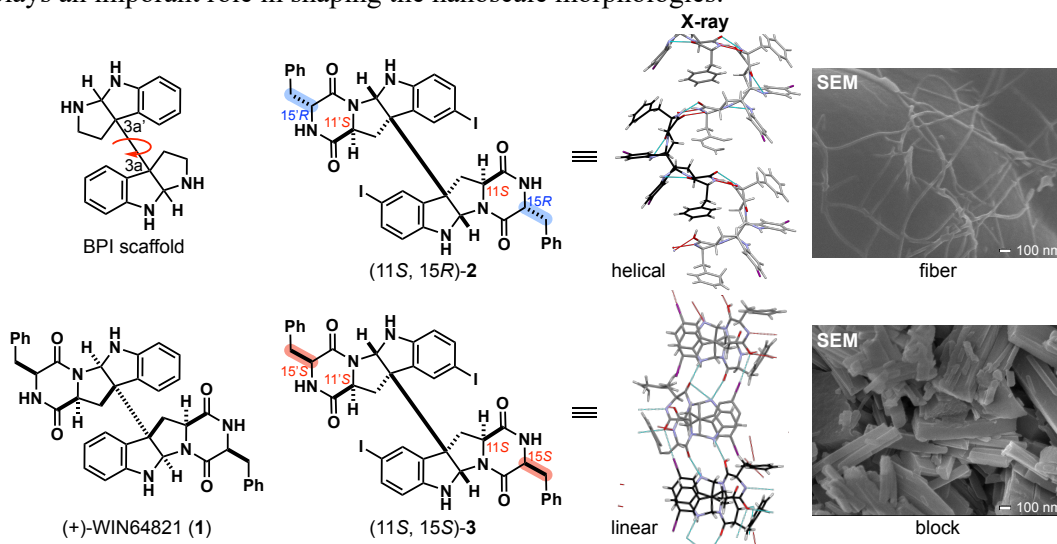
## Control of nanoscale morphologies in self-assembling molecules based on $C_2$ -symmetric alkaloidal scaffolds

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Bispyrrolidinoindoline (BPI) alkaloids, represented by (+)-WIN64821 (**1**), are characterized by chiral  $C_2$ -symmetric dimeric structures, which exhibit flexible conformational behavior due to the rotational freedom around the 3a/3a' bond. Leveraging this unique property of BPI scaffold, our research group has focused on developing functional molecules derived from BPI by controlling its conformation through modifications of the stereochemistry and substituents.<sup>1,2</sup> In this study, we aimed to construct self-assembled nanostructures of the BPI scaffold integrated with diketopiperazine (DKP) rings as hydrogen-bonding units. By systematically modifying the stereochemistry of the DKP moieties and the substituents on the BPI scaffold, we explored the influence of these modifications on nanoscale morphologies.

X-ray crystallographic analysis revealed that the (11*S*, 15*R*)-**2** promotes helical aggregation through single-point intermolecular hydrogen bonding. This relatively flexible interaction led to the formation of fibrous nanostructures, as observed in SEM images. In contrast, the diastereomer (11*S*, 15*S*)-**3** formed linear structures through multiple hydrogen bonding interactions. Reflecting this more rigid assembly, the resulting nanostructures exhibited block-like morphologies. These results suggest that the stereochemistry of DKP rings plays an important role in shaping the nanoscale morphologies.



1) Honda, T.; Ogata, D.; Tsurui, M.; Yoshida, S.; Sato, S.; Muraoka, T.; Kitagawa, Y.; Hasegawa, Y.; Yuasa, J.; Oguri, H. *Angew. Chem. Int. Ed.* **2024**, *63*, e202318548. 2) Taniguchi, T.; Tsubouchi, A.; Imai, Y.; Yuasa, J.; Oguri, H. *J. Org. Chem.* **2018**, *83*, 15284.