

Impact of Symmetry/Asymmetry on Aggregate Properties of Aryleneethynylenes having Amino-Acid-based Diamides

(¹Graduate School of Science, Nagoya University, ²Integrated Research Consortium on Chemical Sciences, ³Institute of Transformative Bio-Molecules, Nagoya University)

○Saeko Yamada,¹ Soichiro Ogi,² Takeshi Yanai,^{1,3} Shigehiro Yamaguchi^{1,2,3}

Keywords: Self-assembly; Supramolecular polymers; π -Conjugated molecules; Molecular orientation; Photophysical properties

Supramolecular polymers composed of π -conjugated molecules exhibit diverse photophysical properties distinct from those of monomers. The establishment of molecular design strategies for controlling the packing structure of aromatic moieties is essential to realize supramolecular polymers with desired photophysical properties. In this context, seed-initiated supramolecular polymerization has received particular attention as it enables kinetic control over the structural parameters of π -stacked assemblies. We have reported that amino-acid-based diamide groups are useful for achieving seeded growth of various π -conjugated molecules.^{1,2} However, the effect of symmetric/unsymmetric introduction of the diamide on aromatic interactions have not been fully elucidated.

Herein, we synthesized aryleneethynylenes **1** and **2** having leucine-based diamide groups on either one or both of the terminal phenyl moieties (Figure 1a). Microscopic studies revealed that both **1** and **2** form fibrous aggregates in low-polarity solvents (Figure 1b). While the UV-vis absorption spectra in their monomeric states were identical, the spectrum in the aggregated state of **1** exhibits a bathochromic shift, which is distinct from that of **2** showing a hypsochromic shift (Figure 1c). In addition, a circular dichroism (CD) spectrum with a bisignate Cotton effect was observed for the aggregates of **2**, while the aggregates of **1** showed a negative CD signal without a Cotton effect. We employed theoretical methodology to connect the results obtained from spectroscopic means to potential supramolecular packing models. Furthermore, we have demonstrated that the symmetrical/unsymmetrical introduction of leucine-based diamide influences not only the packing structure but also the self-assembly pathway, enabling elucidation of self-sorting behavior under non-equilibrium conditions.

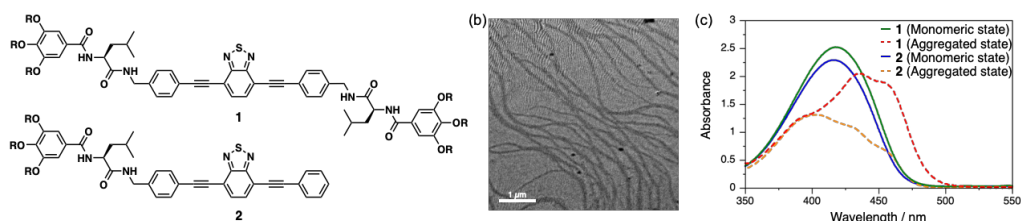


Figure 1. (a) Chemical structures of **1** and **2**, (b) TEM image of **1** in the aggregated state, and (c) UV-vis absorption spectra of **1** and **2** in the monomeric and aggregated states.

1) H. Choi, S. Ogi, N. Ando, S. Yamaguchi, *J. Am. Chem. Soc.* **2021**, *143*, 2953; 2) K. Matsumoto, N. Bäumer, S. Ogi, S. Yamaguchi, *Angew. Chem. Int. Ed.* **2024**, *63*, e202416361.