

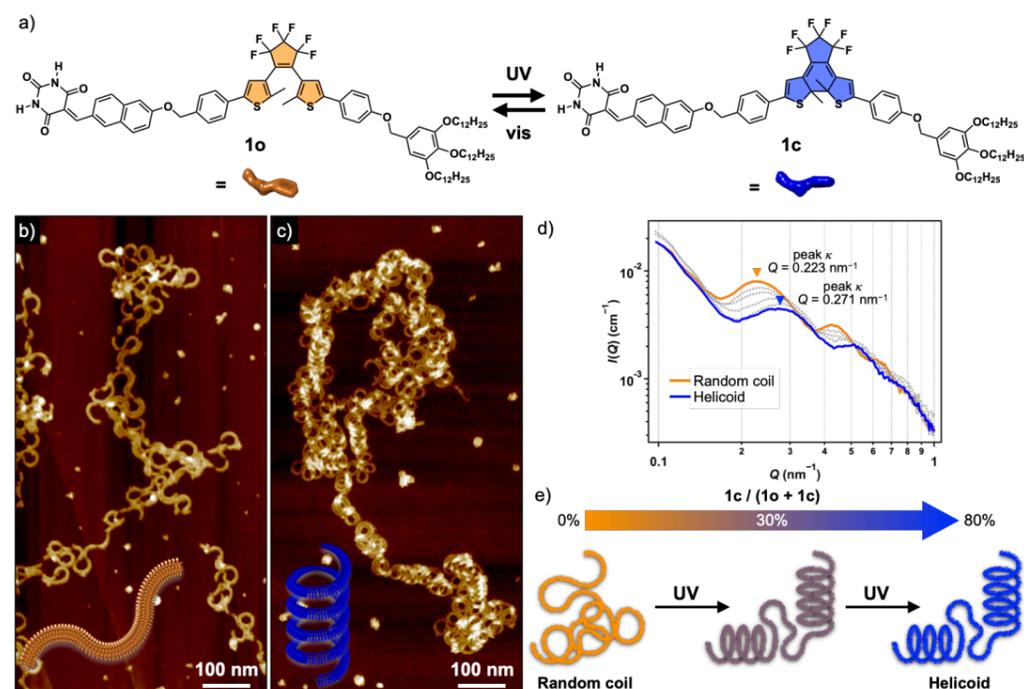
## Reversible Folding/Unfolding of Diarylethene-Incorporated Supramolecular Polymers by Light

Helical folding of randomly coiled polymers is an essential organization process not only for natural protein but also for synthetic polymers, but realizing this dynamic process in supramolecular polymers (SPs) is a formidable challenge. Herein, we achieved photo-induced reversible folding/unfolding of SPs driven by photo-isomerization of diarylethene (DAE). A DAE-functionalized supramolecular monomer (open isomer) affords randomly coiled SPs in a nonpolar solvent. Irradiation of the solution with UV light causes ring-closure reaction of the DAE moieties, inducing helical folding of the SP chains. Subsequent visible-light irradiation to the resultant helical SPs induces their unfolding. These dynamic structural transition processes can be studied by in-situ small-angle X-ray scattering measurements.

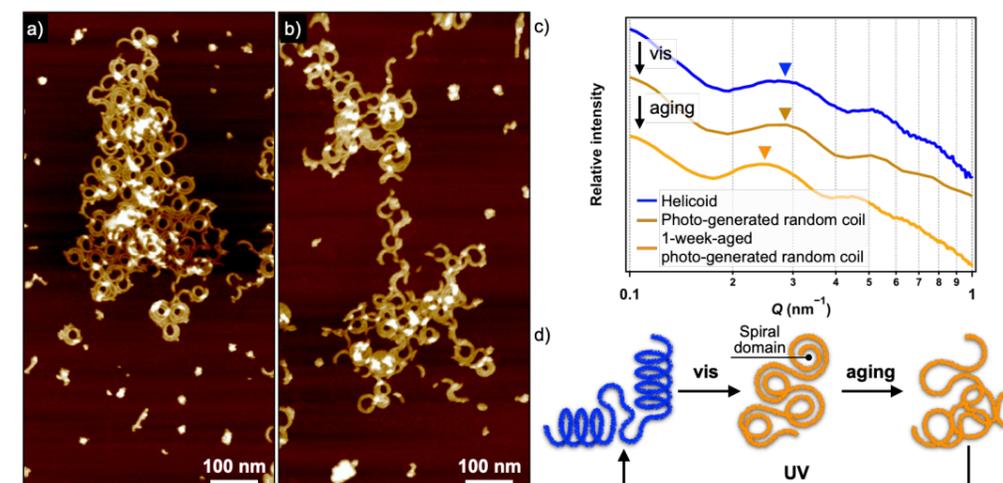
We have been exploring unique self-assembling properties of a variety of barbiturated  $\pi$ -conjugated molecules [1, 2]. These molecules initially organize into six-membered cyclic hexamers referred to as rosettes by self-complementary hydrogen-bonding. The resulting rosettes subsequently stack with rotational and translational displacements to afford intrinsically curved supramolecular polymers (SPs) including toroids and catenanes [3, 4], random coils [5, 6], waves [7], spirals [5], and helicoids [5, 6]. Furthermore, incorporating a photochromic unit into the monomer allows us to control the higher-order structures of the corresponding SPs by light [5]. Herein, we studied the photoresponsive behavior of SPs formed by diarylethene (DAE)-incorporated monomer **1** [Fig. 1a] [8]. Our studies using atomic force microscopy (AFM) and *in-situ* small-angle X-ray scattering (SAXS) revealed that ring-closure and ring-opening reactions of DAE units enable fine-tuning of curvature to realize reversible photoinduced folding/unfolding of SPs.

We prepared SP solutions of the open isomer of

**1** (**1o**) by cooling its hot monomer solutions in methylcyclohexane (MCH). AFM images of the resulting SPs of **1o**, spin-coated onto highly oriented pyrolytic graphite (HOPG), showed randomly coiled SPs with well-defined curvatures [Fig. 1b]. The failure to form helicoids by **1o** was presumably due to the formation of kinetically trapped structural defects during polymerization. Upon irradiation of these MCH solutions with UV light, the growth of a visible absorption band that indicates the ring-closure reaction of DAE moieties was observed.  $^1\text{H}$  NMR analysis revealed that 80% of **1o** was isomerized into the closed isomer (**1c**). AFM imaging of the UV-irradiated samples visualized helically folded SPs [Fig. 1c]. The average radius of curvature ( $r_{\text{ave}}$ ) in SPs, measured by manually fitting a circle along each curve, decreased upon this light-induced folding from  $15.6 \pm 0.3$  to  $13.6 \pm 0.2$  nm. Reflecting this change in  $r_{\text{ave}}$ , SPs in solution displayed different SAXS profiles [Fig. 1d]. Both random coils and helicoids in MCH showed similar nonperiodic oscillatory features in the  $Q$  range of



**Figure 1:** a) Chemical structure of **1** (**1o** and **1c**). b, c) AFM images of random coils (b) and helicoids (c). d) Time-dependent SAXS profiles from random coils (orange line) to helicoids (blue line) in MCH upon UV irradiation. e) Schematic illustration of folding process by UV irradiation.



**Figure 2:** a, b) AFM images of photo-generated random coils with partial spiral domains (a) and photo-generated random coils after 10 days of aging (b). c) SAXS profiles of helicoids (blue), photo-generated random coils (brown) and 1-week aged photo-generated random coils (orange). d) Schematic representation of unfolding process of helicoids into random coils by visible-light irradiation.

0.2–1.0  $\text{nm}^{-1}$ , which are characteristic of our curved SPs [2]. However, their smallest- $Q$  scattering peaks (peak  $\kappa$ ) were observed at  $Q = 0.223$  and  $0.271$   $\text{nm}^{-1}$  for random coils and helicoids, respectively. The difference clearly indicates the reduction of  $r_{\text{ave}}$  upon folding in solution. Data fits using a hollow cylinder model provided  $r_{\text{ave}}$  values of 16.5 nm for random coils and 14.2 nm for helicoids, which qualitatively agree well with the AFM results. Furthermore, it was found from AFM and SAXS analyses that the morphological transition from random coils to helicoids occurred in a phase transition manner when the **1o/1c** ratio reached 70/30. This suggests that the light-induced folding is a direct process driven by internal structural change of DAE moieties, and is not a consequence of reorganization of aggregates through dissociation/reassociation of monomers [Fig. 1e]. According to the thermodynamic parameters estimated by means of pseudo van't Hoff plots, the light-induced folding of the SP chains is most likely driven by repairing of the structural defects through ordering of the internal structure through additional  $\pi$ - $\pi$  stacking interaction between ring-closed DAE moieties, and by the interloop van der Waals interactions occurring only for the resulting helicoids.

When the solution of helicoids was exposed to visible light, quantitative ring-opening isomerization from **1c** to **1o** was confirmed by spectroscopic measurements. In line with the smooth photoisomerization, AFM imaging immediately showed randomly coiled structures, but they contained some of the spirally folded domains [Fig. 2a]. The  $r_{\text{ave}}$  value estimated by AFM at this time was  $14.2 \pm 0.2$  nm, which was still much closer to that of helicoids and largely different from that of the original random coils. SAXS analysis also showed that the  $r_{\text{ave}}$  value of the photo-generated random coils was 14.2 nm, which was almost the same value as that of helicoids [Fig. 2c]. However, the  $r_{\text{ave}}$  value in

SAXS gradually increased over a week and eventually reached 16.3 nm, which is comparable to that of the original random coils. AFM imaging after 10 days of aging showed that all SPs were unfolded to a similar degree as the original random coils [Fig. 2b]. When this photo-generated random coil solution was irradiated with UV light, we could again see helicoids by AFM, indicating reversibility of the light-induced folding/unfolding processes [Fig. 2d]. The hysteresis between the folding and unfolding is presumably due to the interloop van der Waals interactions of the helicoidal structures that render the latter process slow.

### REFERENCES

- [1] S. Yagai, Y. Kitamoto, S. Datta and B. Adhikari, *Acc. Chem. Res.* **52**, 1325 (2019).
- [2] S. Datta, S. Takahashi and S. Yagai, *Acc. Mater. Res.* **3**, 259 (2022).
- [3] S. Yagai, Y. Goto, X. Lin, T. Karatsu, A. Kitamura, D. Kuzuhara, H. Yamada, Y. Kikkawa, A. Saeki and S. Seki, *Angew. Chem. Int. Ed.* **51**, 6643 (2012).
- [4] S. Datta, Y. Kato, S. Higashiharaguchi, K. Aratsu, A. Isobe, T. Saito, D. D. Prabhu, Y. Kitamoto, M. J. Hollamby, A. J. Smith, R. Dalgliesh, N. Mahmoudi, L. Pesce, C. Perego, G. M. Pavan and S. Yagai, *Nature* **583**, 400 (2020).
- [5] B. Adhikari, Y. Yamada, M. Yamauchi, K. Wakita, X. Lin, K. Aratsu, T. Ohba, T. Karatsu, M. J. Hollamby, N. Shimizu, H. Takagi, R. Haruki, S. Adachi and S. Yagai, *Nat. Commun.* **8**, 15254 (2017).
- [6] D. D. Prabhu, K. Aratsu, Y. Kitamoto, H. Ouchi, T. Ohba, M. J. Hollamby, N. Shimizu, H. Takagi, R. Haruki, S. Adachi and S. Yagai, *Sci. Adv.* **4**, eaat8466 (2018).
- [7] K. Tamaki, T. Aizawa and S. Yagai, *Chem. Commun.* **57**, 4779 (2021).
- [8] T. Fukushima, K. Tamaki, A. Isobe, T. Hirose, N. Shimizu, H. Takagi, R. Haruki, S. Adachi, M. J. Hollamby and S. Yagai, *J. Am. Chem. Soc.* **143**, 5845 (2021).

### BEAMLIN

BL-10C

K. Tamaki<sup>1</sup>, A. Isobe<sup>1</sup>, T. Fukushima<sup>1</sup>, N. Shimizu<sup>2</sup>, H. Takagi<sup>2</sup>, R. Haruki<sup>2</sup>, S. Adachi<sup>2</sup>, M. J. Hollamby<sup>3</sup> and S. Yagai<sup>1</sup> (<sup>1</sup>Chiba Univ., <sup>2</sup>KEK-IMSS-PF, <sup>3</sup>Keele Univ.)