Supporting Information

Formation of hierarchical platelets with morphological control by self-assembly of an azobenzene-containing liquid crystalline diblock copolymer

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1. Materials

RAFT chain transfer agent (CTA), 2-(dodecylthiocarbonothioylthio)-2-methyl propionic acid (DMA), was purchased from TCI and used without further purification. 2,2′-azobis(isobutyronitrile) (AIBN) was used as initiator and recrystallized from anhydrous ethanol twice. 6-[4-(4-butylphenylazo) phenoxy] hexyl methacrylate (AzoMA) was synthesized according to the procedure reported by Stewart and our previous work.[1,2] Poly(ethylene glycol) methyl ether (PEG-OH, $M_n \approx 2000$ g mol^{-1}) was purchased from Sigma-Aldrich and purified by precipitation in ethyl ether prior to use. 4-(dimethylamino)pyridine (DMAP) and dicyclohexylcarbodiimide (DCC) were purchased from Sigma-Aldrich and used as initial. Deionized water was collected from Milli-Q system with the resistance of 18.25 MΩ. Other reagents were commercially available and used as supplied without further purification.

2. Measurements

^{1}H Nuclear Magnetic Resonance (NMR). ^{1}H NMR was recorded by MERCURY plus 400 spectrometer (Varian, Inc., USA) at 30 °C in $CDCl_3$ with tetramethylsilane internal standard.

Gel Permeation Chromatography (GPC). Relative molecular weights and molecular weight distributions were measured by a GPC system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (HR3 (500-30,000), HR4 (5,000-600,000), and HR5 (50,000-4,000,000), 7.8×300 mm, particle size 5 μm). GPC measurements were carried out at 35 °C using THF as eluents with a flow rate of 1.0 mL min^{-1}. The system was calibrated with linear poly(methyl methacrylate) standards.

Differential scanning calorimetry (DSC). DSC was performed on a TA Q200 DSC instrument in N_2 with a heating rate of 10 °C min^{-1}.

Transmission Electron Microscopy (TEM). The morphologies of assemblies at various stages were measured by Transmission Electron Microscopy on JEM-1400 JEOL at an accelerating voltage of 100 kV. 6 μL of the self-assemblies solution was dropped onto a grid coated with pure carbon film and then dried under ambient conditions.

Field Emission Scanning Electron Microscope (FESEM). The surface morphology of the films was observed by a Field Emission Scanning Electron Microscope (Hitachi S4800) with an accelerating voltage of 5.0 kV.

Ultraviolet-Visible spectrophotometer (UV-Vis). The UV-Vis absorbance spectra were obtained using UV-2550 SHIMADZU using a quartz cell.

Atomic Force Microscopy (AFM). AFM images were taken by a JPK NanoWizard Sense system in the AC mode of dropping the aggregates' solution onto a silicon wafer.

Optical Microscopy (OM) and Polarized Optical Microscope (POM). The microscope was Cryo-CSS450 (Nikon) equipped with a CCD camera. The samples were prepared by dropping the aggregates solution onto a silicon wafer, dried under ambient conditions and observed directly.

X-ray Diffraction (XRD). XRD patterns were recorded using on Ultima IV X-ray diffractometer.

3. Synthesis of Poly(ethylene glycol)-*block*-Poly(6-(4-butyl-4′-oxyazobenzene) hexyl methacrylate) (PEG-*b*-PAzoMA)

The synthesis of PEG-based macroRAFT chain transfer agent was prepared according to previous work[3]. PEG-OH ($M_n \approx 2{,}000$ g mol^{-1}), DCC, DMAP, the RAFT chain transfer agent DMA and CH_2Cl_2 (50 mL) were first added to a 250 mL flask sealed with a rubber septum under N_2 at 0 °C. The mixture was stirred under N_2 for 30 min at 0 °C and for another 20 h at room temperature. Subsequently, CH_2Cl_2 was rotary evaporated after filtration and the crude product was precipitated into cold diethyl ether three times. Finally, yellow powder, PEG$_{45}$-DMA RAFT-CTA, was obtained after drying in vacuo overnight.

Target diblock copolymer PEG-*b*-PAzoMA was synthesized via a typical reversible addition-fragmentation chain transfer (RAFT) polymerization of AzoMA monomer with PEG-DMA and initiated by AIBN. The reaction lasted 24 hours at 70 °C. The crude product was purified by reprecipitating three times from dichloromethane to cold diethyl ester and dried in vacuum at room temperature overnight.

The corresponding ^{1}H NMR spectra of PEG-CTA, AzoMA monomer, and PEG-*b*-PAzoMA copolymers are shown in **Figure S2**.

4. Preparation of Self-Assembled Micelles

First of all, the polymer powder, PEG-*b*-PAzoMA, was evenly distributed in ethanol by ultrasonication for 10 min. Then the solution was heated to 85 °C and kept for 2 h to ensure the polymer could absolutely dissolve in ethanol because thermal treatment of polymers could dramatically change their physiochemical properties, resulting in distinctive transform in solubility. The solution was cooled down subsuquently and the change of polymer solubility provided a driving force for self-assembly. For the study of the effect of concentration and cooling rate on self-assembly, solution with various concentration, different cooling manner were prepared, respectively.

In addition, the cooling manners mentioned in manuscript is as follows. Rapid cooling rate is placing the solution to 15 °C condition immediately after heating and the solutiong would cool to 15 °C within 10 min. Natural cooling rate means solution is cooled in ambient condition and the temperature will cool to 15 °C within 1 h. Gradient cooling is that the temperature of solution drops 10 °C every hour from 85 °C to 15 °C which carried in the heated metal bath.

5. Light-Responsiveness of Assemblies

For the study of light-responsiveness of assemblies, the aggregates solution was irradiated using a LED lamp with 365 nm UV light (intensity: 90 mW cm^{-2}). Besides, the solution was kept at an ice-water bath to exclude the photothermal effect on the self-assembly process during irradiation.

6. Supplementary Figures

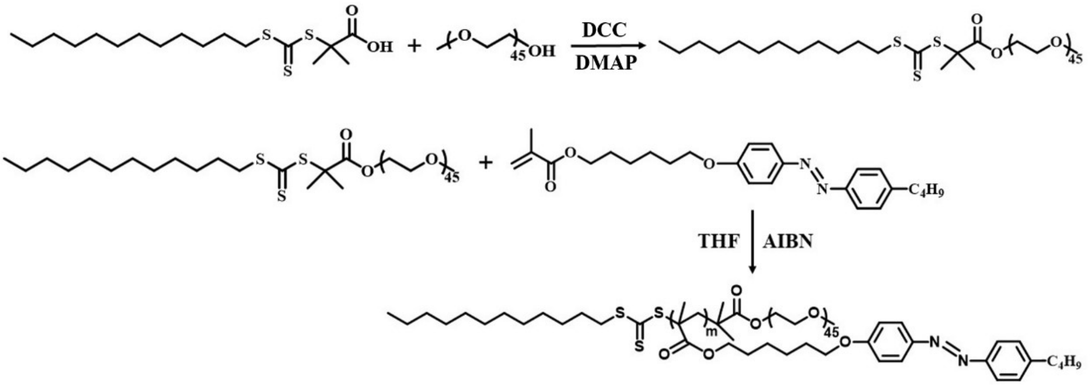

Figure S1. Synthetic routes of PEG_{45}-CTA and PEG-*b*-PAzoMA diblock copolymer.

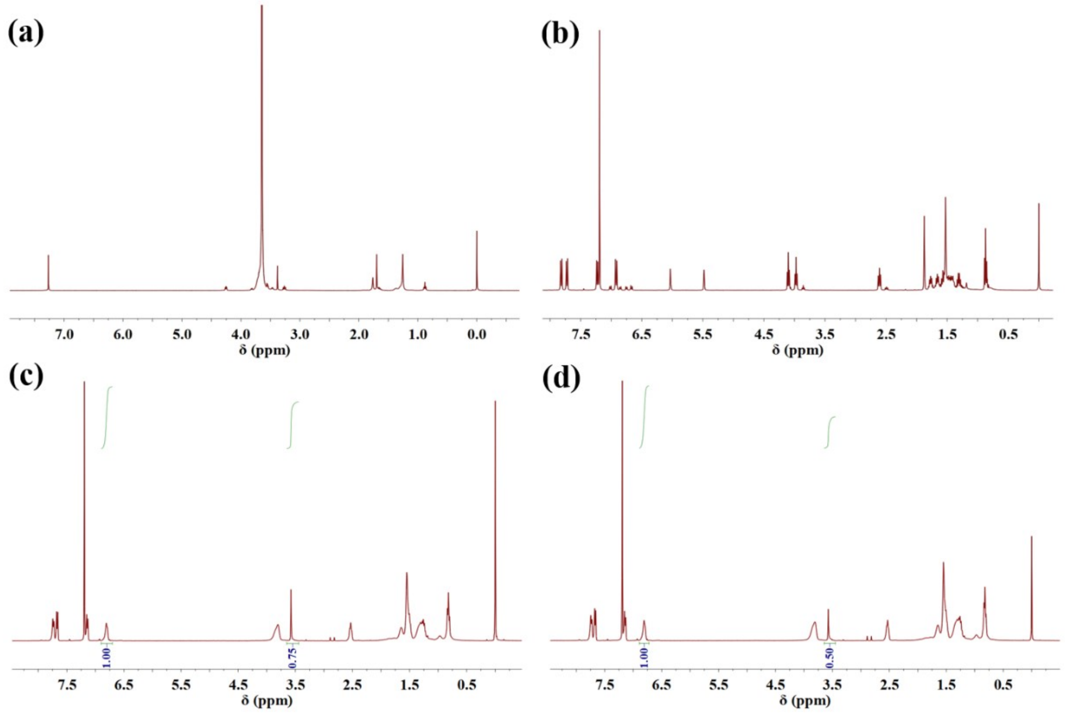

Figure S2. ^1H NMR spectra of (a) PEG_{45}-CTA, (b) AzoMA monomer, and block copolymers (c) PEG_{45}-*b*-$PazoMA_{120}$ and (d) PEG_{45}-*b*-$PazoMA_{180}$ in $CDCl_3$.

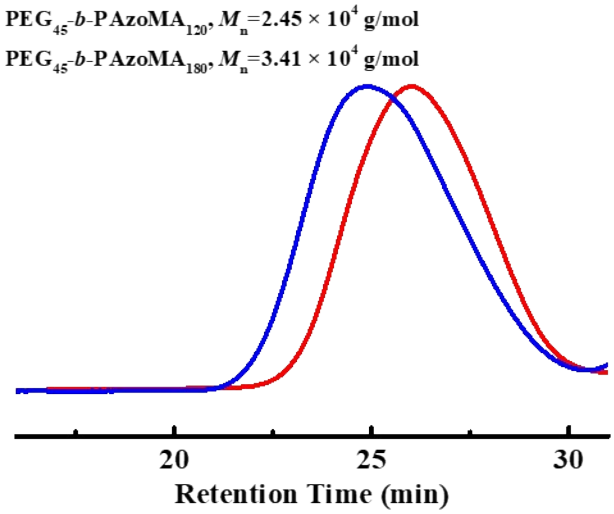

Figure S3. GPC traces of diblock copolymers PEG$_{45}$-b-PAzoMA$_{120}$ and PEG$_{45}$-b-PAzoMA$_{180}$.

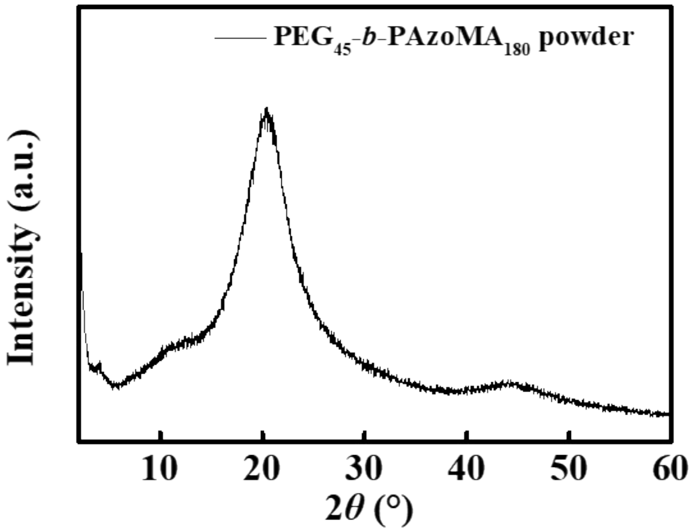

Figure S4. XRD pattern of PEG$_{45}$-b-PAzoMA$_{180}$ polymer powders.

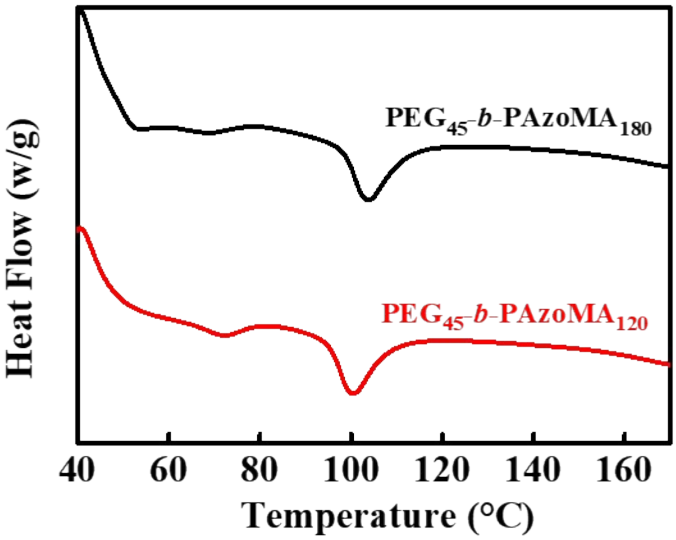

Figure S5. DSC curves of PEG$_{45}$-*b*-PAzoMA$_{120}$ and PEG$_{45}$-*b*-PAzoMA$_{180}$ diblock copolymers.

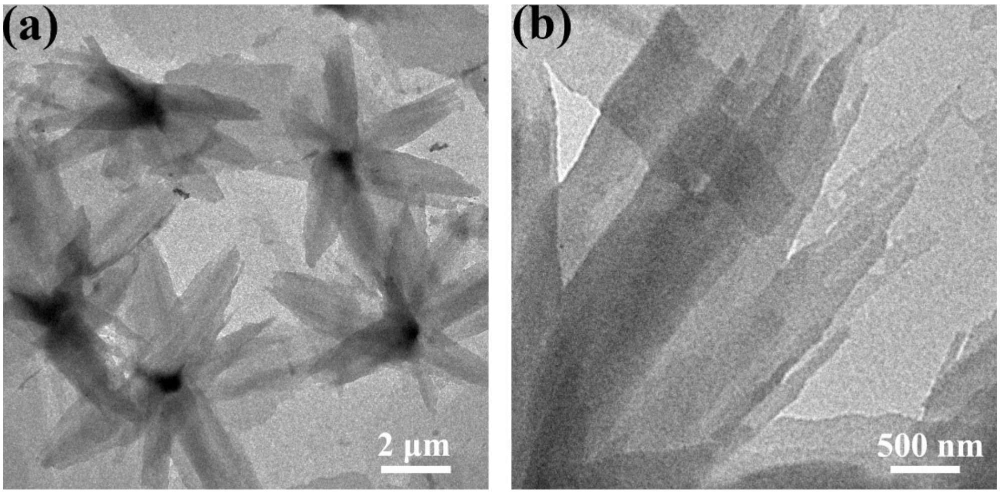

Figure S6. TEM images of micro-flowers in a higher magnification.

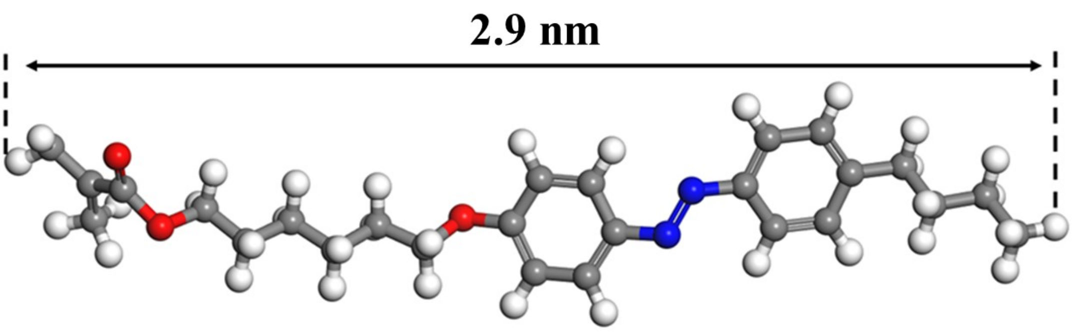

Figure S7. Schematic representation of the structure of AzoMA monomer and calculated by Materials Studio (MS).

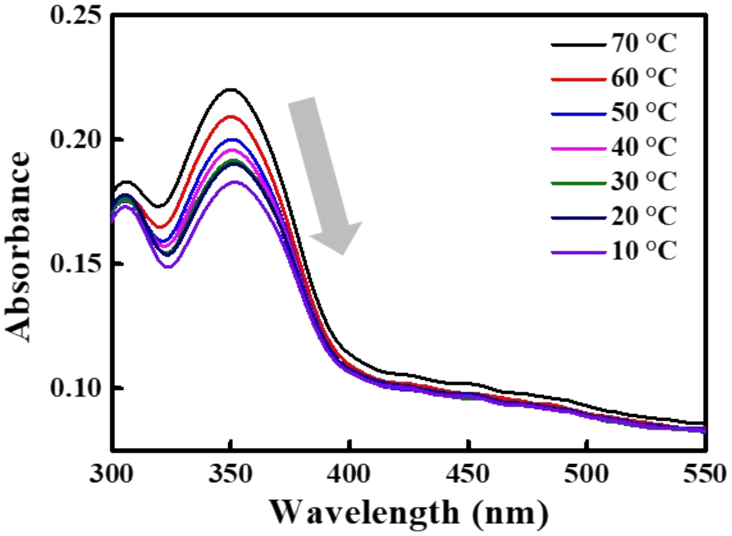

Figure S8. UV-Vis absorption changes of PEG$_{45}$-*b*-PAzoMA$_{180}$ in ethanol solution during cooling process.

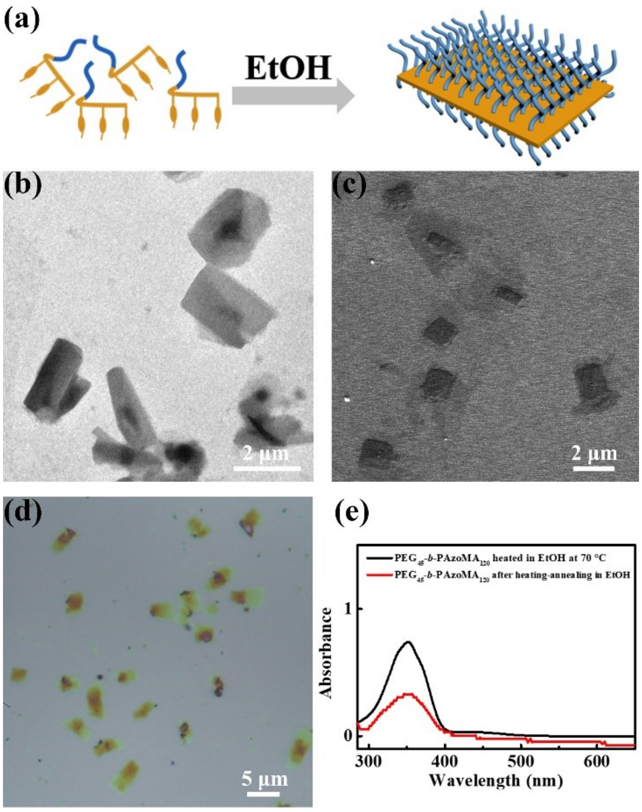

Figure S9. (a) Schematic representation of the formation of orthogon platelet of PEG$_{45}$-*b*-PAzoMA$_{120}$. (b) TEM image, (c) SEM image, and (d) OM image of orthogon platelets. (e) UV−Vis absorption spectra of PEG$_{45}$-*b*-PAzoMA$_{120}$ in ethanol solution (0.10 mg mL^{-1}) heating at 70 °C and cooling to 15 °C for 24 h.

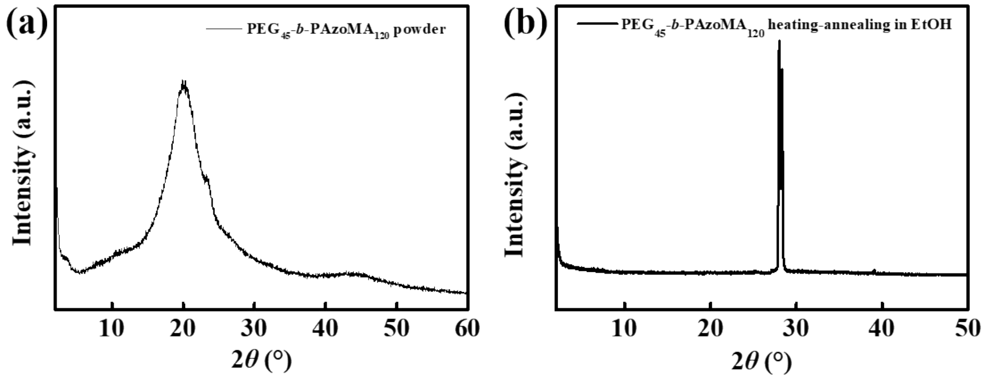

Figure S10. XRD patterns of PEG$_{45}$-*b*-PAzoMA$_{120}$ (a) polymer powders and (b) orthogon platelets after heating-annealing process in ethanol.

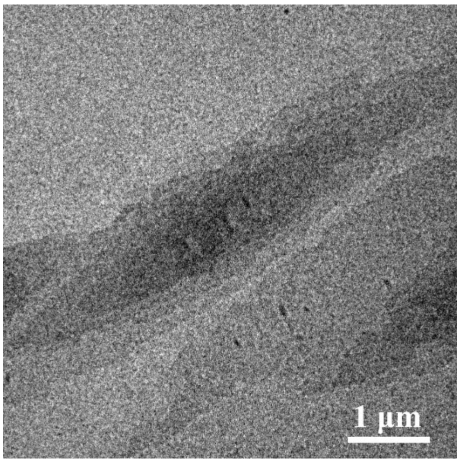

Figure S11. TEM images of the stacked leaf-typed platelets formed in ethanol (0.02 mg mL^{-1}) after heating and keeping at 15 °C for 1 h.

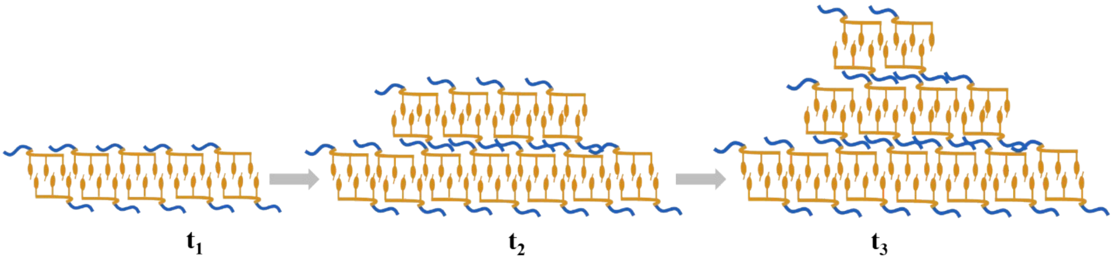

Figure S12. Mechanism for the formation of multi-level platelets on a stack of lamellae. Here $t_1 < t_2 < t_3$.

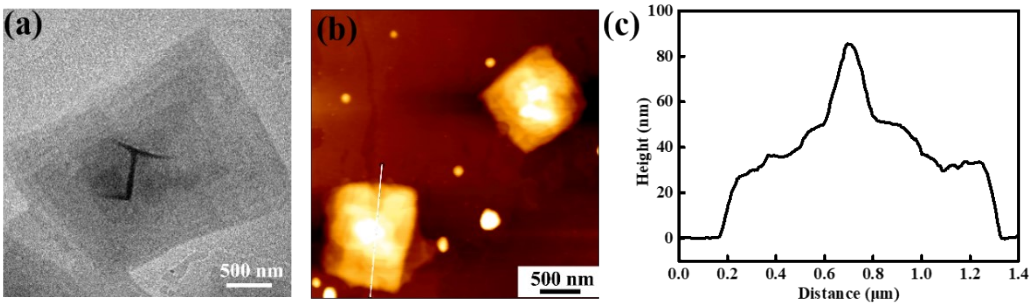

Figure S13. (a) Enlarged TEM image of stacked rectangle platelets. (b) AFM image of stacked rectangle platelets and (c) the height profile across the white line.

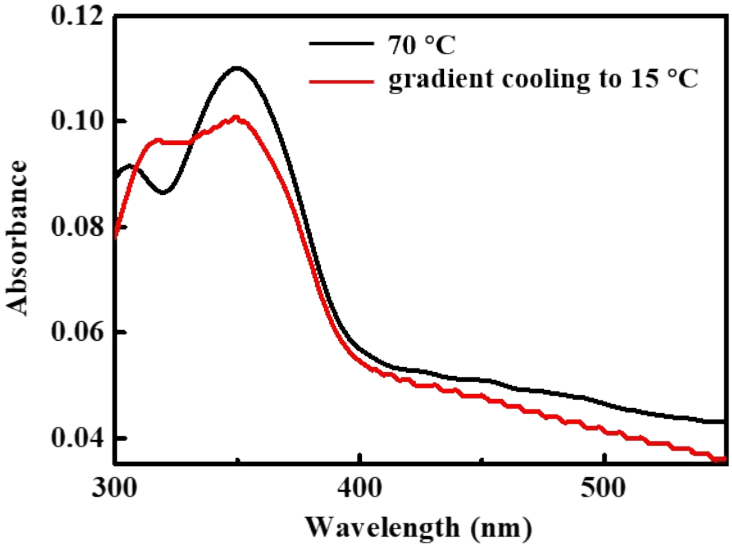

Figure S14. UV−Vis absorption of PEG$_{45}$-*b*-PAzoMA$_{180}$ in ethanol solution (0.02 mg mL^{-1}) heating at 70 °C, after gradient cooling to 15 °C and aging for 24 h.

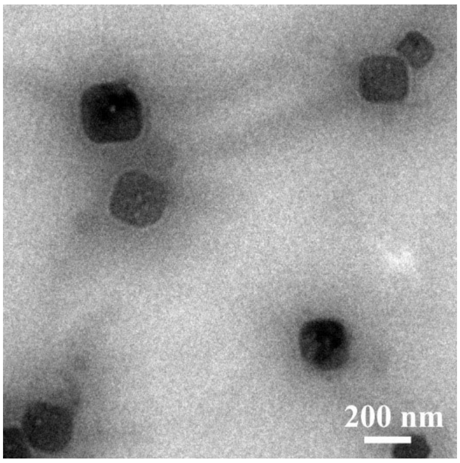

Figure S15. TEM image of rectangular crystal nuclei formed at 40 °C during gradient cooling proecss of PEG_{45}-*b*-$PAzoMA_{180}$ with the concentration of 0.02 mg mL^{-1}.

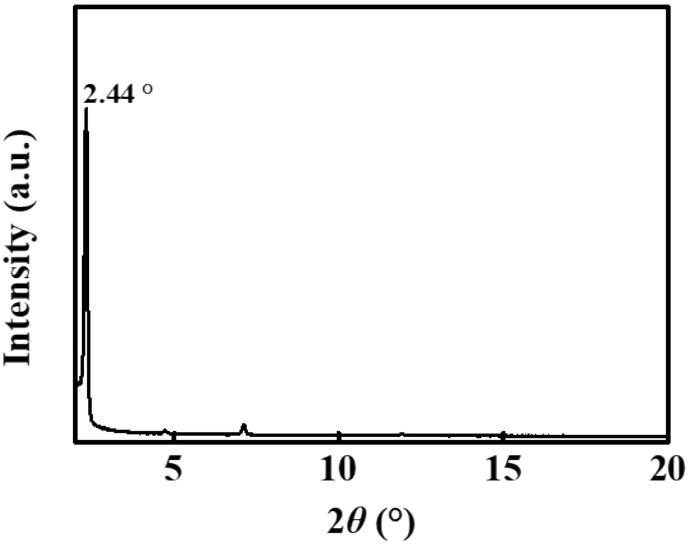

Figure S16. XRD pattern of stacked rectangle platelets formation by gradient cooling process.

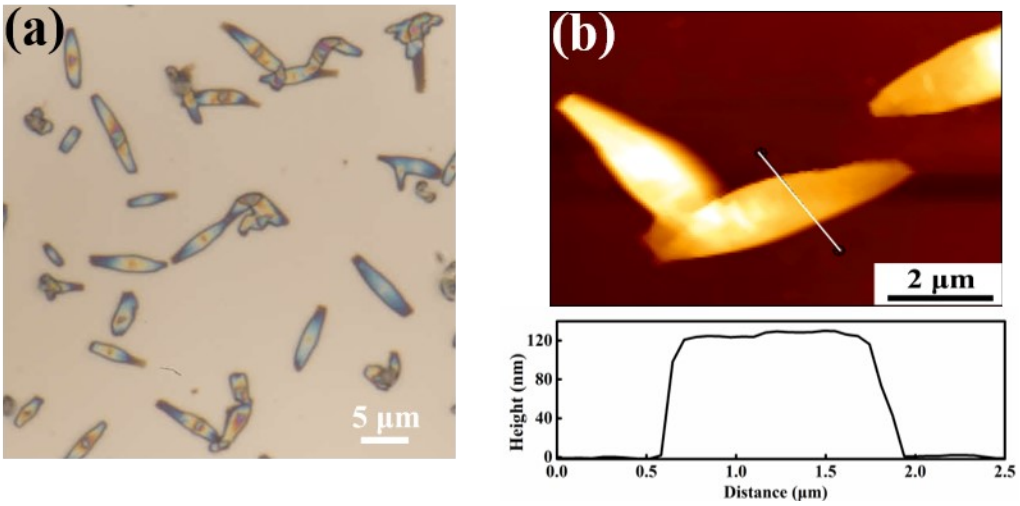

Figure S17. Self-assemblies by rapid cooling rate within 10 min and imaged by (a) OM and (b) AFM. The concentration of the solution was maintained at 0.02 mg mL^{-1}.

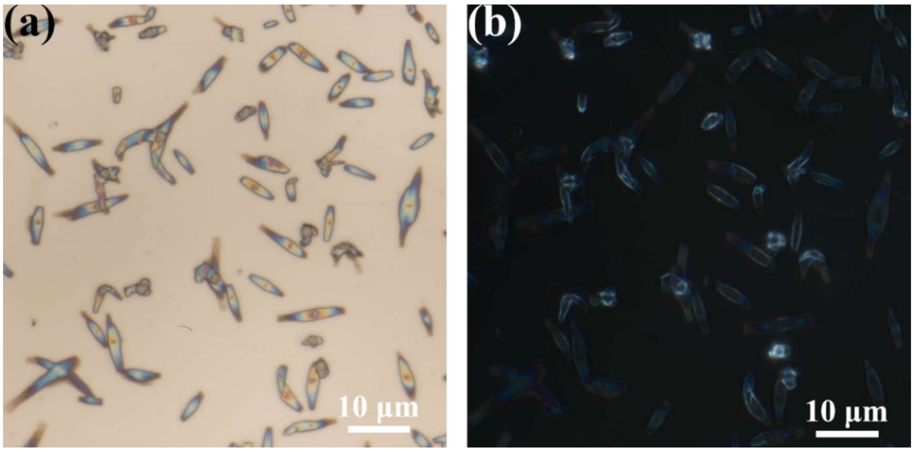

Figure S18. OM image and corresponding POM image of PEG$_{45}$-*b*-PAzoMA$_{180}$ assemblies by rapidly cooling within 10 min with the concentration of 0.02 mg mL^{-1}.

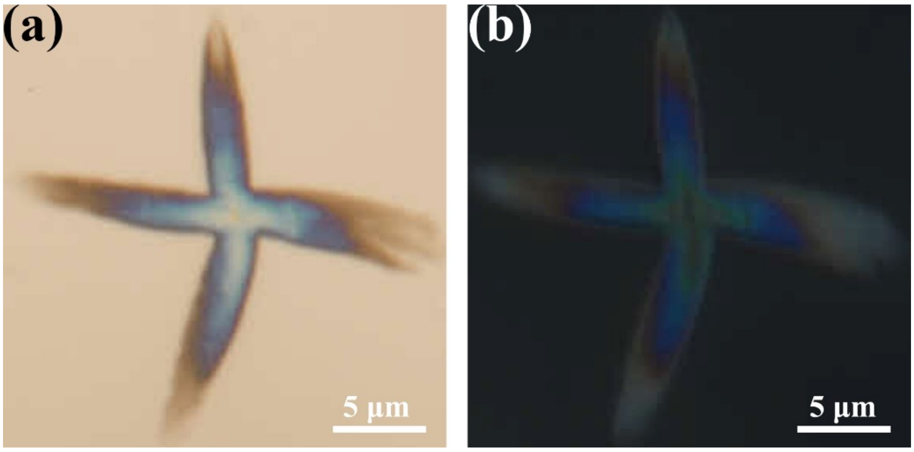

Figure S19. OM and corresponding POM images of in-situ growth micro-flower with the concentration of 0.08 mg mL^{-1}, revealing petals grow from the central body.

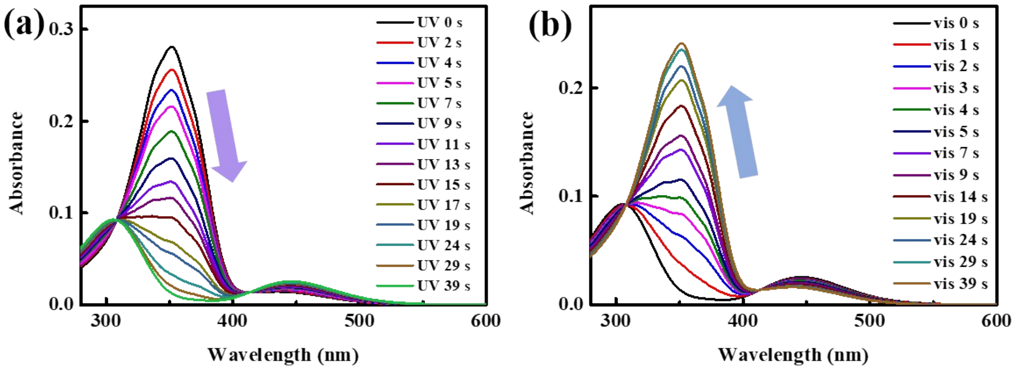

Figure S20. UV-Vis absorption spectra of PEG$_{45}$-*b*-PAzoMA$_{180}$ copolymer after thermal treatment in ethanol and upon (a) 365 nm light irradiation, (b) following 450 nm light irradiation.

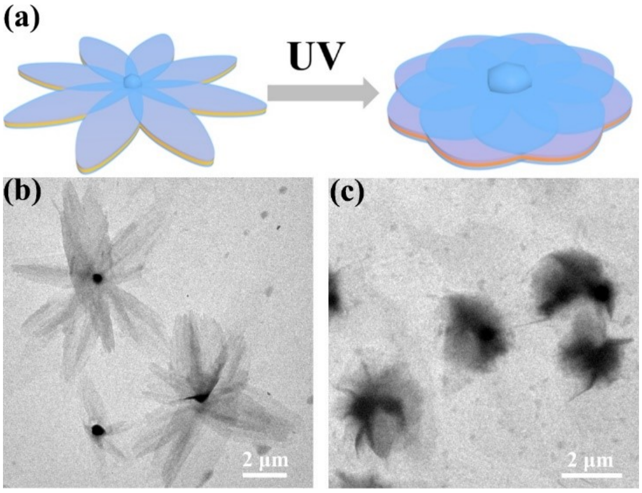

Figure S21. (a) Schematic representation of the disassembly of micro-flower under 365 nm irradiation for 30 min. TEM images of (b) micro-flowers, (c) following irradiation by 365 nm for 30 min.

7. REFERENCES

1. W. Wang, C. Du, X. Wang, X. He, J. Lin, L. Li and S. Lin, Directional Photomanipulation of Breath Figure Arrays, *Angew. Chem. Int. Ed.*, 2014, **53**, 12116-12119.
2. D. Stewart and c. T. Imrie, Synthesis and characterization of spin-labelled and spin-probed side-chain liquid crystal polymers, *Polymer*, 1996, **37**, 3419-3425.
3. Y. Que, C. Feng, S. Zhang and X. Huang, Stability and Catalytic Activity of PEG-b-PS-Capped Gold Nanoparticles: A Matter of PS Chain Length, *J. Phys. Chem. C*, 2015, **119**, 1960-1970.