Electronic Supplementary Information

Photoresponsive Core-Shell-Corona Nanostructures Co-Assembled from Diblock Copolymers and Azobenzene-Containing Homopolymers

Si Wu,[†] Long Wang,[†] Anja Kröger,[†] Yeping Wu,[‡] Qijin Zhang,*[,‡] and Christoph Bubeck*[,†]

[†]Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

E-mail: bubeck@mpip-mainz.mpg.de (C. B.)

[‡]CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Key Laboratory of Optoelectronic Science and Technology in Anhui Province, Hefei, Anhui 230026 P.R. China

E-mail: zqjm@ustc.edu.cn (Q. Z.)

Synthesis

6-(methyl(4-((4-nitrophenyl)diazenyl)phenyl)amino)hexyl methacrylate (AzoN): It was synthesized according to Robello, D. R. *J. Polym. Sci. Part A: Polym. Chem.* **1990**, *28*, 1.

Poly(6-(methyl(4-((4-nitrophenyl)diazenyl)phenyl)amino)hexyl methacrylate (PAzoN): AzoN (1.5 g), 2,2'-azobisisobutyronitrile (75 mg) were dissolved in anhydrous tetrahydrofuran (20 mL). After 3 freeze-thaw cycles, the flask was sealed in vacuum. Polymerization was conducted at 60 °C for 72 hours. The obtained polymer was precipitated in methanol, and the purification was repeated three times in a THF/methanol system. The resulting polymeric solid was filtered off and thoroughly washed with methanol. Finally, the polymer was dried in an oven under vacuum.

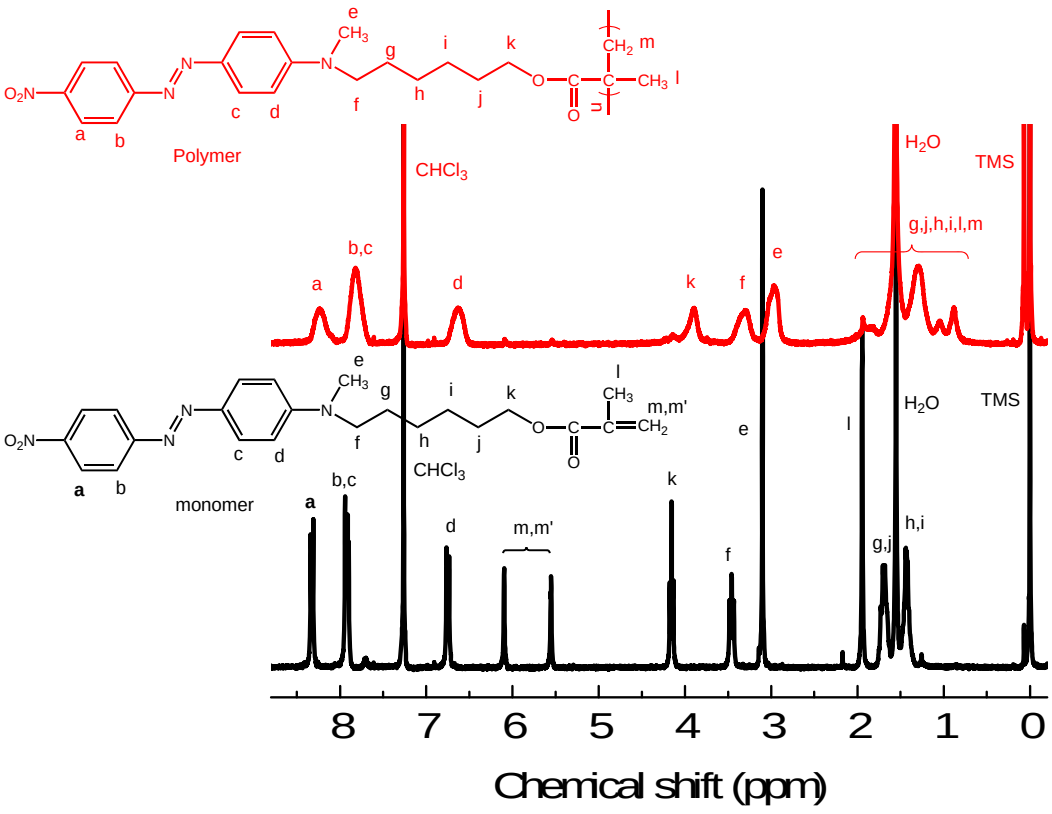

Figure S1. ^{1}H-NMR spectra of AzoN and PAzoN.

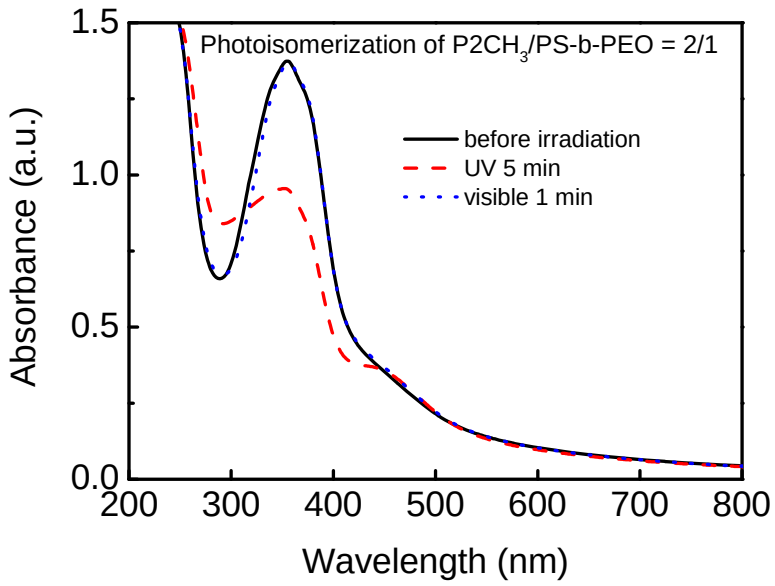

Figure S2. UV-vis absorption spectra of P2CH$_3$/PS-b-PEO = 2/1 before irradiation, after UV irradiation for 5 min and visible light irradiation for 1 min.

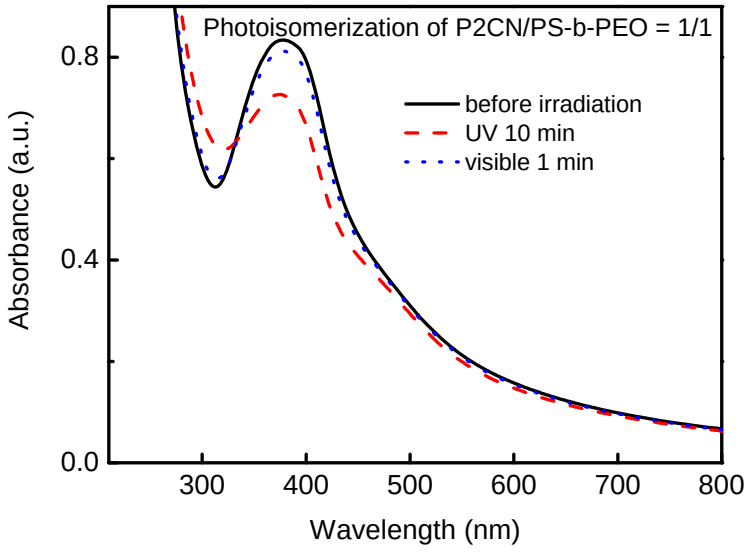

Figure S3. UV-vis absorption spectra of P2CN /PS-b-PEO = 1/1 before irradiation, after UV irradiation for 10 min and visible light irradiation for 1 min.

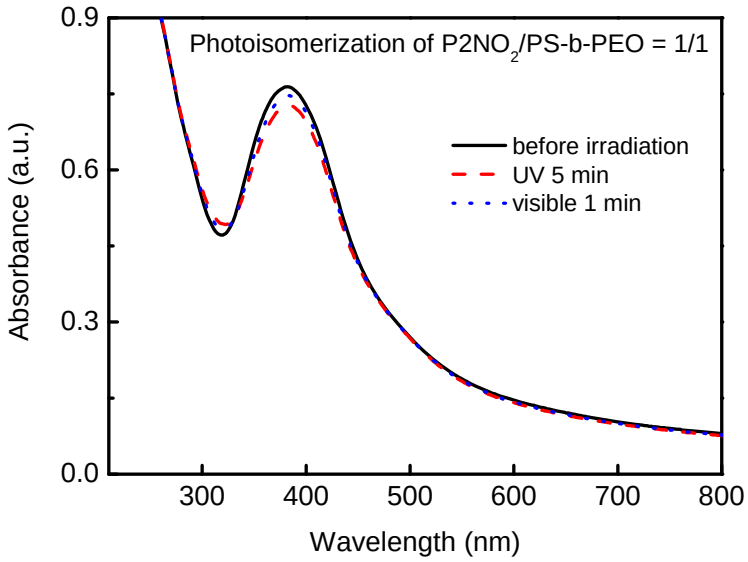

Figure S4. UV-vis absorption spectra of $P2NO_2$/PS-b-PEO = 1/1 before irradiation, after UV irradiation for 5 min and visible light irradiation for 1 min.

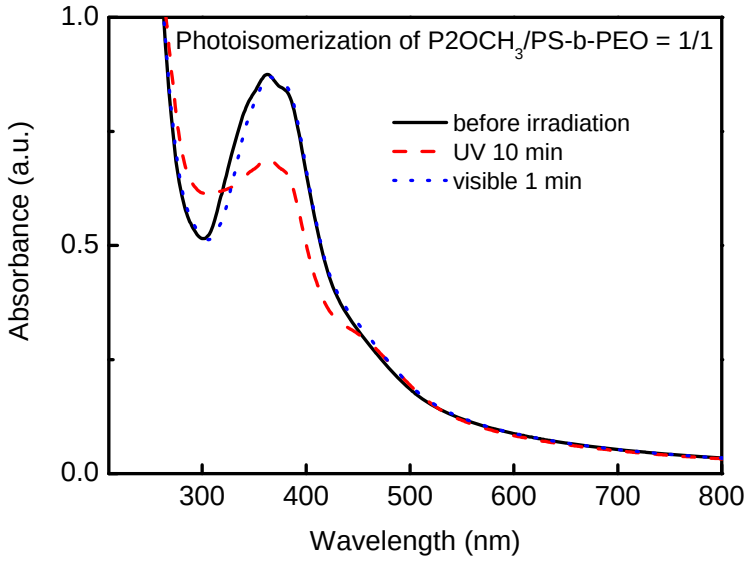

Figure S5. UV-vis absorption spectra of $P2OCH_3$/PS-b-PEO = 1/1 before irradiation, after UV irradiation for 10 min and visible light irradiation for 1 min.

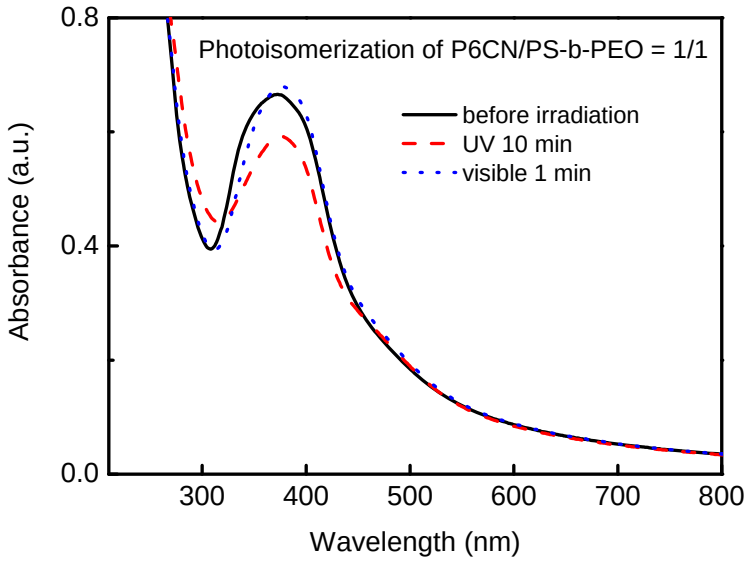

Figure S6. UV-vis absorption spectra of P6CN/PS-b-PEO = 1/1 before irradiation, after UV irradiation for 10 min and visible light irradiation for 1 min.

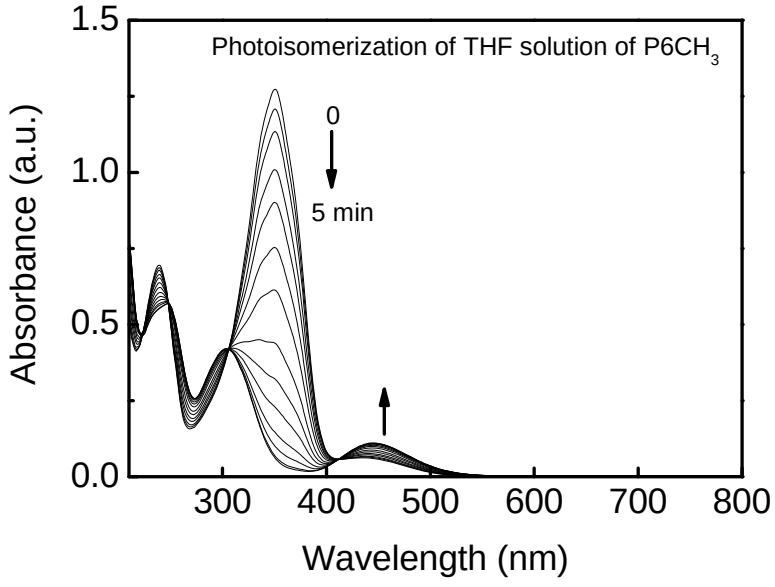

Figure S7. UV-vis absorption spectra of THF solution of $P6CH_3$ at different irradiation time of UV light.

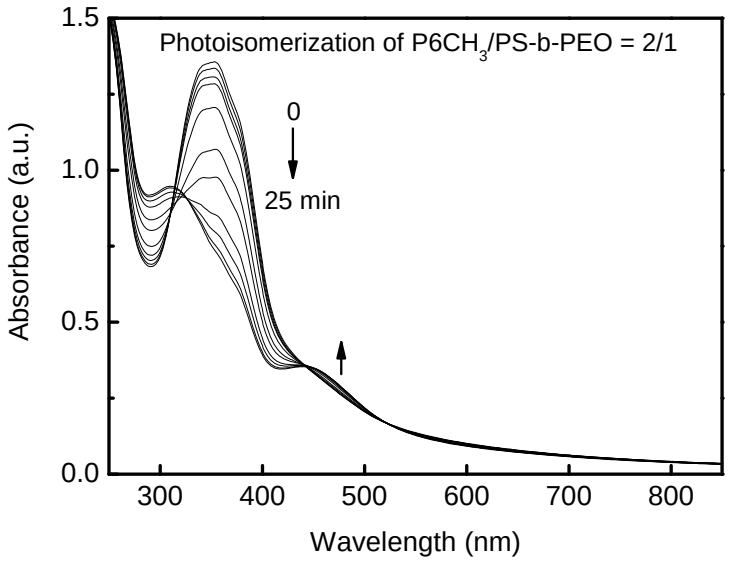

Figure S8. UV-vis absorption spectra of $P6CH_3$/PS-b-PEO = 2/1 at different irradiation time of UV light.

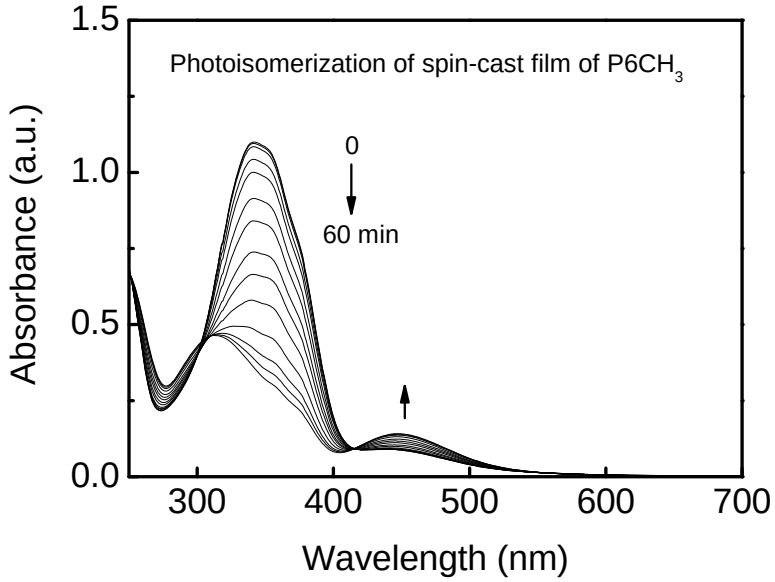

Figure S9. UV-vis absorption spectra of a spin-cast film of $P6CH_3$ at different irradiation time of UV light.

Figure S10. Photograph of dispersions. From left to right: P2CH_3/PS-b-PEO/ = 2/1, P6CH_3/PS-b-PEO = 2/1, P2OCH_3/PS-b-PEO = 1/1, P2CN/PS-b-PEO = 1/1, P6CN/PS-b-PEO/ = 1/1, P2NO_2/PS-b-PEO = 1/1, PS-b-PEO. All these dispersions are stable and without macroscopical precipitate.

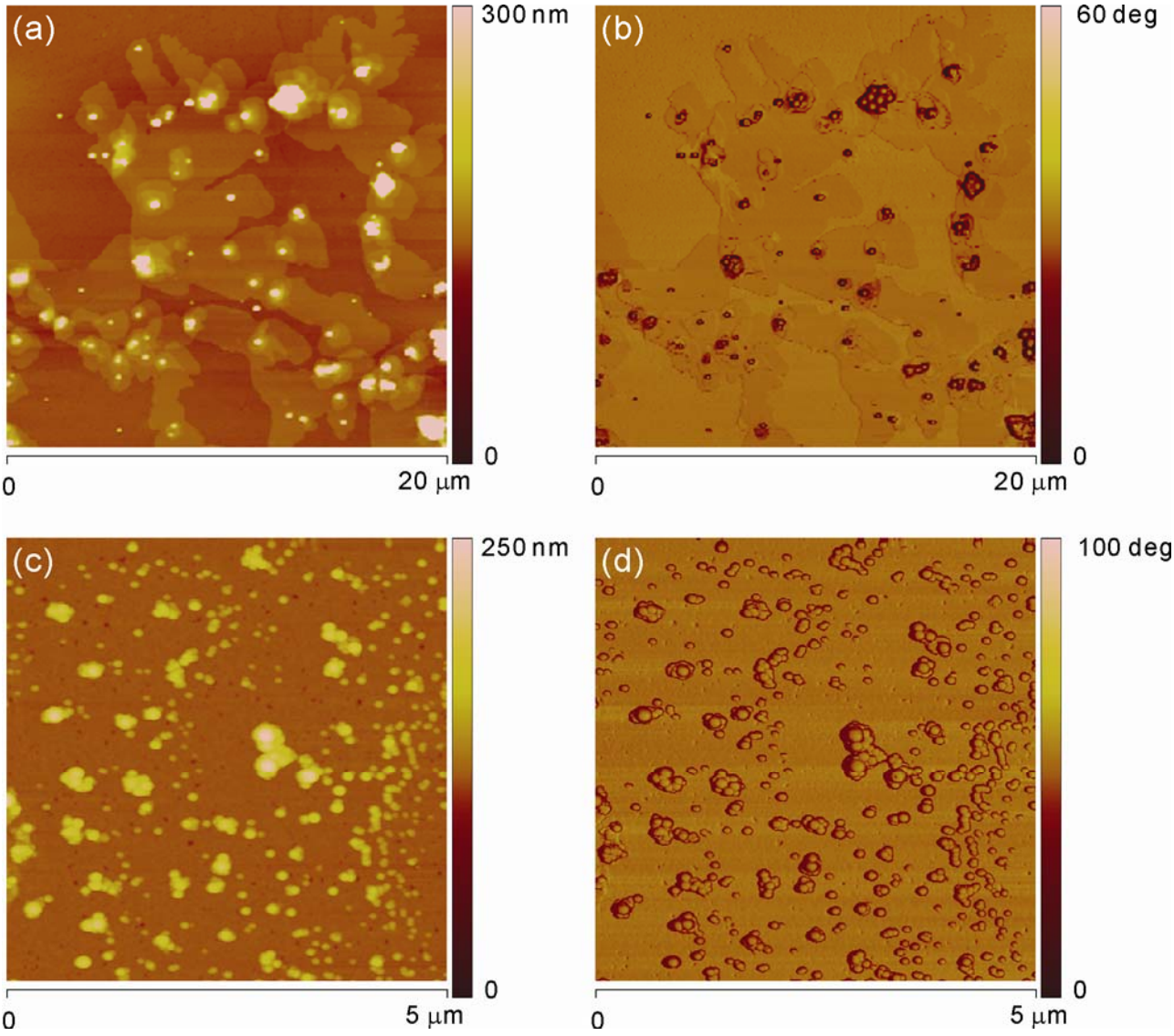

Figure S11. AFM height and phase images of PAzoN/PS-b-PEO = 0.1/1 prepared by adding water dropwise (the adding speed is in the order of ~1 μL/s) (a), (b), and adding water quickly (4.5 mL at once) to THF solution of PAzoN and PS-b-PEO (c) and (d). When water is added dropwise, not all PAzoN is co-assembled with PS-b-PEO, as film-like materials can be observed in both AFM height (a) and phase images (b), and macroscopical precipitate of PAzoN can be observed by naked eye. When water is added quickly, only nanoparticles but no film-like materials are observed by AFM (c) and (d), indicating that all PAzoN is successfully co-assembled with PS-b-PEO.