Supporting Information

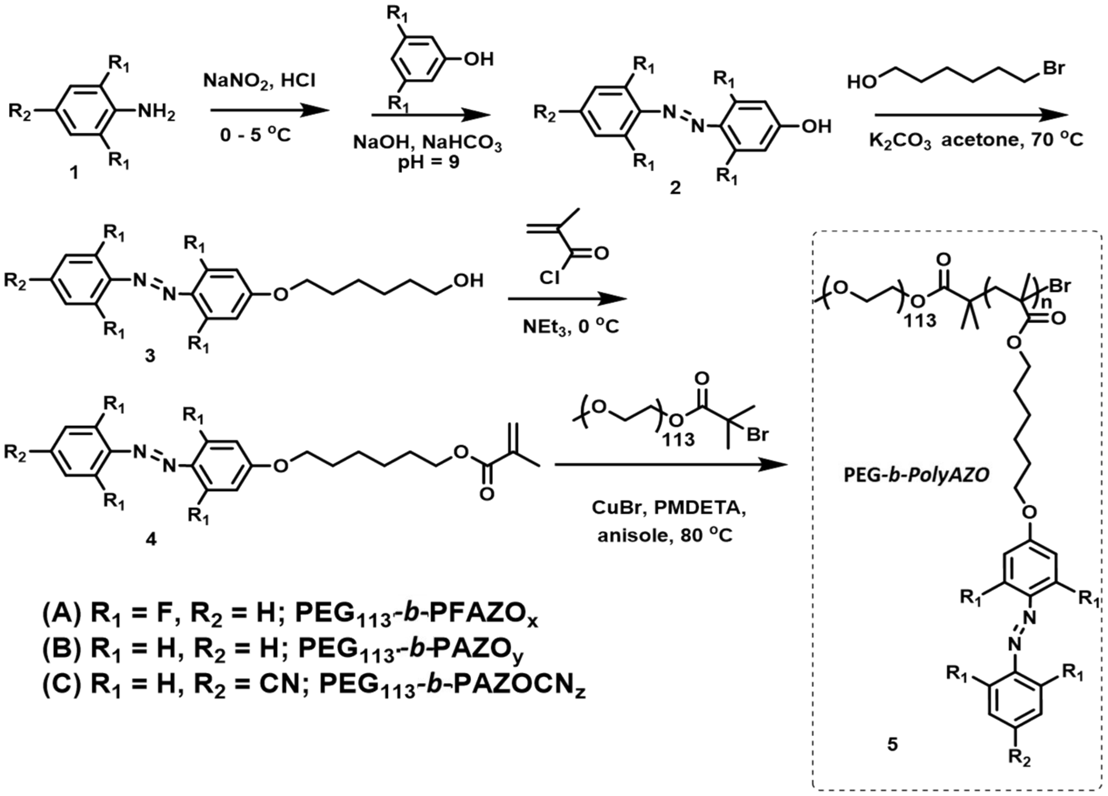
Morphological modulation of azobenzene-containing tubular polymersomes

Lishan Li, [1] *Yiwen Li,*[2] *Shuyuan Wang*[1], *Liandong Ye*[1]， *Wei Zhang,* *[,1] *Nianchen Zhou,* *[,1] *Zhengbiao Zhang* [1] *and Xiulin Zhu* [1]

1. State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123, P. R. China.

2. College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu, 610065, P. R. China.

*Email: nczhou@suda.edu.cn; weizhang@suda.edu.cn



Scheme S1. Synthetic route and chemical structures of PEG-*b*-PolyAZO: (A) PEG_{113}-*b*-$PFAZO_x$, (B) PEG_{113}-*b*-$PAZO_y$, (C) PEG_{113}-*b*-$PAZOCN_z$。.[1]

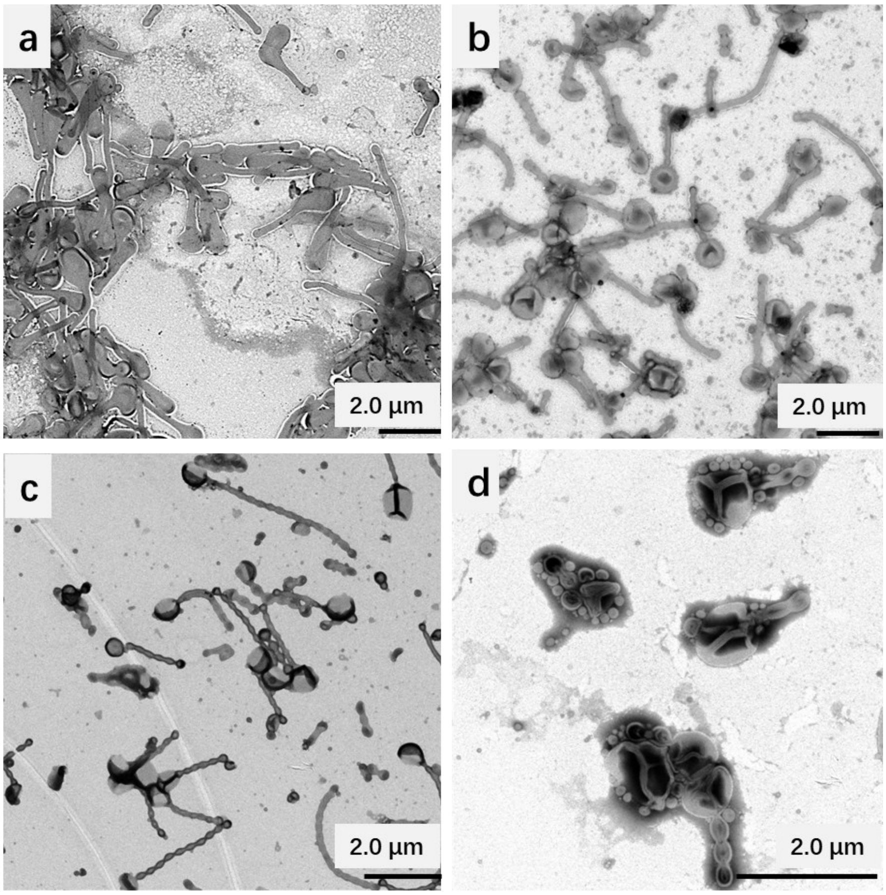


Figure S1. TEM images of the aggregates of the PEG_{113}-*b*-$PFAZO_{78}$ formed in the dioxane/water solvent at 25 ^oC with water adding rate of 0.1 mL/h in all cases. Initial concentrations: 2.0 mg/ mL in dioxane, with different water content (a) 37.5%; (b) 50%; (c) 60%; (d) initial concentrations: 5.0 mg/ mL in dioxane, 37.5 % water content.

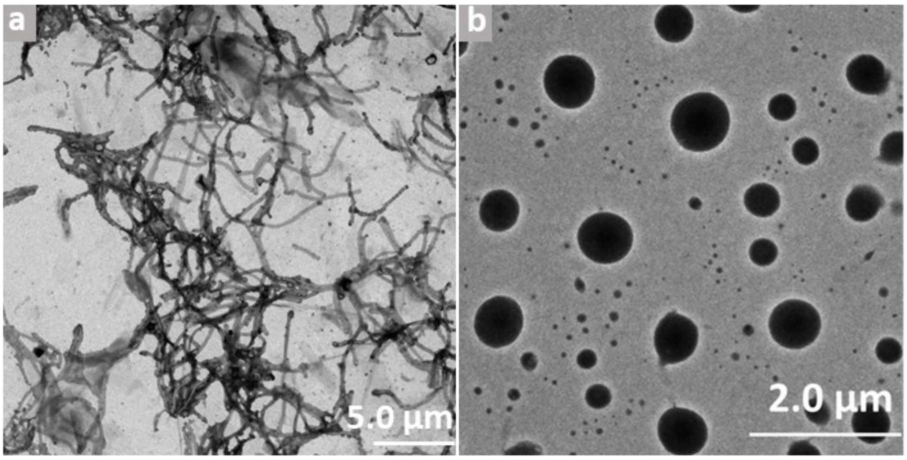


Figure S2. TEM images of the aggregates of the PEG_{113}-*b*-$PFAZO_{78}$ formed in the (a)1,4-dioxane/H_2O (0.6/1), (b) DMF/water (0.6/1). Temperature: 25 °C, water adding rate: 0.1 mL/h, initial concentrations: 1.0 mg/ mL.

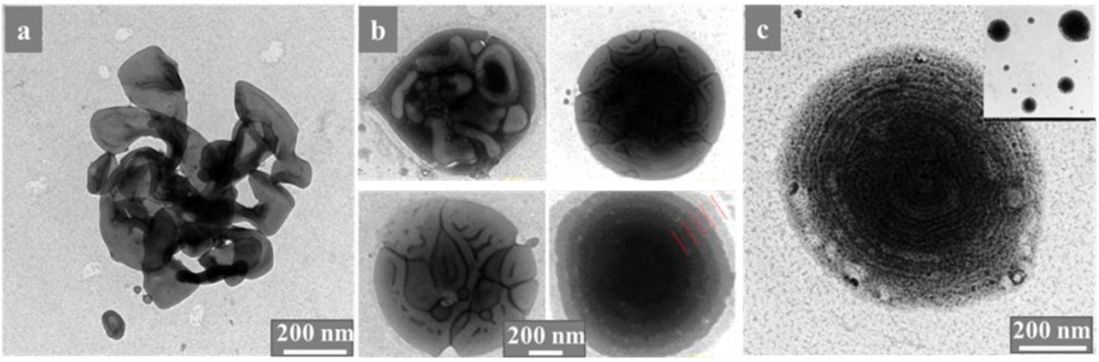


Figure S3. TEM images of the aggregates of the PEG_{113}-*b*-$PFAZO_{78}$ formed in the mixed solvent (dioxane and DMF)/water (0.6/1, v/v). Temperature: 25 °C, water adding rate: 0.1 mL/h, initial concentrations: 1.0 mg/ mL, common solvents: the mixed solvent of dioxane and DMF with different volume content of DMF (a) 30%; (b) 50%; (c) 70%.

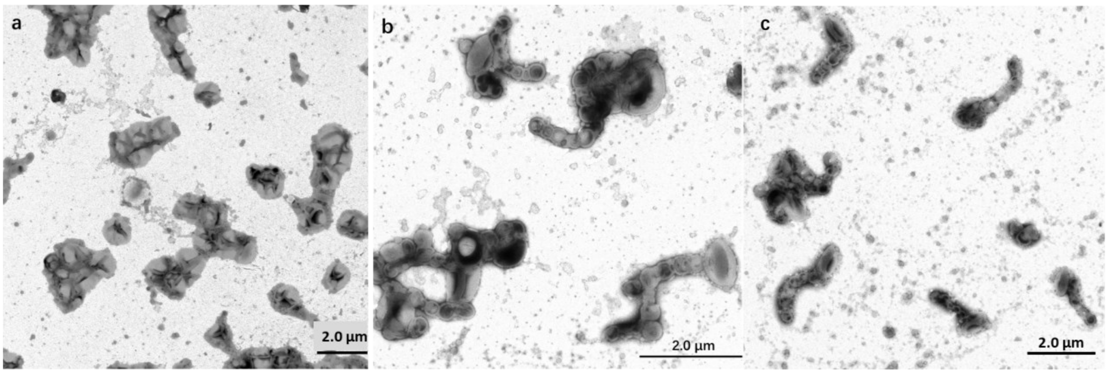


Figure S4. TEM images of PEG_{113}-*b*-$PFAZO_{78}$ aggregates. (a) self-assembly in 1,4-dioxane/water at 35 °C (b, c) first self-assemble in 1,4-dioxane/water at 25 °C, then heated up to 35 °C and hold for 1h (b), again cooling down to 25 °C overnight(c). The initial concentration was 1.0 mg/mL, water adding rate is 0.1 mL/h, and water content is 37.5% in all cases.

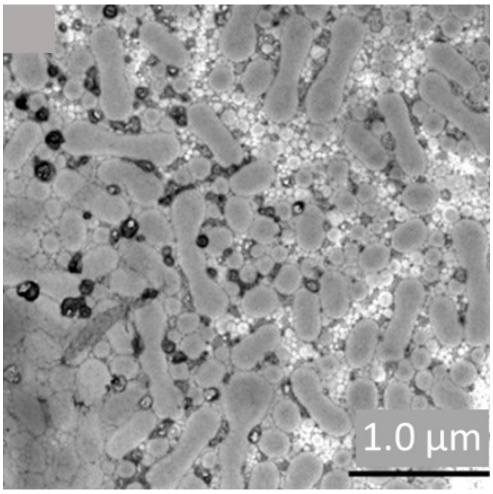


Figure S5. TEM images of aggregates formed by PEG_{113}-*b*-$PFAZO_{78}$ self-assembly in 1,4-dioxane/water (v/v) at 25 ^{o}C with 47.4% water content. The initial concentration was 1.0 mg/mL and water adding rate of 0.3 mL/h in all cases.

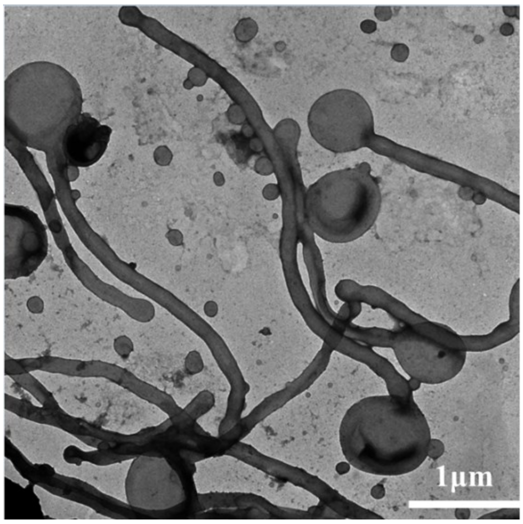


Figure S6. TEM image of PEG_{113}-*b*-$PFAZO_{78}$ aggregates formed by the self-assembly in 1,4-dioxane/water (water content 37.5%) under light irradiation of 532nm，with initial concentrations of 1.0 mg/ mL in 1,4-dioxane, and water adding rate of 0.1 mL/h at 25 ^{o}C.

As discussed in the previous articles, the PEG_{113}-*b*-$PFAZO_{78}$ formed soft tadpole-shaped tubular vesicles, the PEG_{113}-*b*-$PAZO_{64}$ formed smooth ones and PEG_{113}-*b*-$PAZOCN_{59}$ formed straight needle-like ones.[1] We speculate that this difference of surface morphology between these tubular vesicles with different azobenzene side-chain may be mainly due to the different arrangement of azobenzene molecules inside the vesicle wall. The differential scanning calorimetry (DSC) of copolymers and polarizing optical microscope (POM) of dried vesicles were used to support this viewpoint. Here, to further make clear this viewpoint, we further tested birefringence of copolymers in the bulk by differential scanning POM. By polarizing microscope, we found that in the process of cooling, for PEG_{113}-*b*-$PFAZO_{78}$, although the side chain fragment $FAZOC_6OH$ showed a slow phase transition from isotropy to anisotropy at 27.6 ^oC (Figure S7a), the copolymers showed always isotropic states in the whole cooling progress (Figure S7d). PEG_{113}-*b*-$PAZO_{64}$ and PEG_{113}-*b*-$PAZOCN_{59}$ displayed distinct phase transition from isotropy to anisotropy around 60 ^oC and 159^oC respectively (Figure S7e, f), just similar to their side chain fragments (Figure S7b, c), which was largely consistent with the DSC result reported previously. [1] The DSC and POM data indicated that in bulk state, the molecular order of the azobenzenes in the arrangement is enhanced as the side chain azobenzene group change from FAZO, AZO to AZOCN. The aggregation state of azobenzene molecular in the tubular polymersomes was also further researched. Through the observation of UV-vis spectra in Figure S8, compared with the absorption curve in THF solution, the maximum absorption wavelength of the aggregate in the aqueous solution of PEG_{113}-*b*-$PFAZO_{78}$ was significantly redshifted from 330 nm to 351 nm, indicating that the azobenzene molecules in the aggregate were mainly in J-aggregate style. The absorption peaks of PEG_{113}-*b*-$PAZO_{64}$ and PEG_{113}-*b*-$PAZOCN_{59}$ aggregates showed the redshift and blueshift, especially the PEG_{113}-*b*-$PAZOCN_{59}$ showed more obvious blueshift. The blueshift indicates the existence of higher-ordered face-to-face H-aggregates. Furthermore, through the observation of wide-angle X-ray scattering (WAXS) test (Figure S9), at about $2\theta = 20^o$, PEG_{113}-*b*-$PFAZO_{78}$ appeared a dispersed diffraction peak, which means that the azobenzene molecules in aggregates are in disordered arrangement. The sample of PEG_{113}-*b*-$PAZO_{64}$ tubular polymersomes showed sharp diffraction peaks at $2\theta = 20^o$, which means there existed ordered structure in vesicle walls. For PEG_{113}-*b*-$PAZOCN_{59,}$ from the green line in Figure S9, obvious diffraction peaks can be observed at angle 2θ equal to 9 °, 20 °, 27 °, and 38 °, which indicates that there is a periodic ordered arrangement within the PEG_{113}-b-$PAZOCN_{59}$ aggregates. So, the arrangement order of azobenzene molecules in soft tadpole-shaped tubular vesicles of PEG_{113}-*b*-$PFAZO_{78}$ was relatively disordered, and that in straight needle-like ones of PEG_{113}-*b*-$PAZOCN_{59}$ was well-ordered. From the data in previous article [1] and here, we confirm that the higher the arrangement order of the azobenzene molecules were, the straighter the morphology of tubular vesicle appeared.

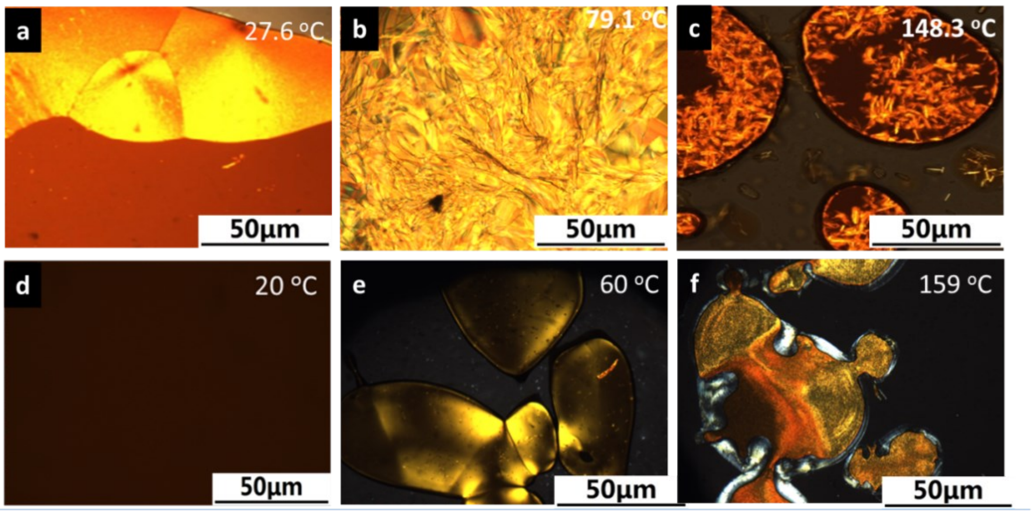


Figure S7. Polarizing optical micrographs (POM) of the small molecular side chains (a) FAZOC_6OH, (b)AZOC_6OH, (c) AZOCNC_6OH and the corresponding copolymers (d) PEG_{113}-*b*-$PFAZO_{78}$, (e) PEG_{113}-*b*-$PAZO_{64}$, (f) PEG_{113}-*b*-$PAZOCN_{59}$ recorded upon cooling from the isotropic phase.

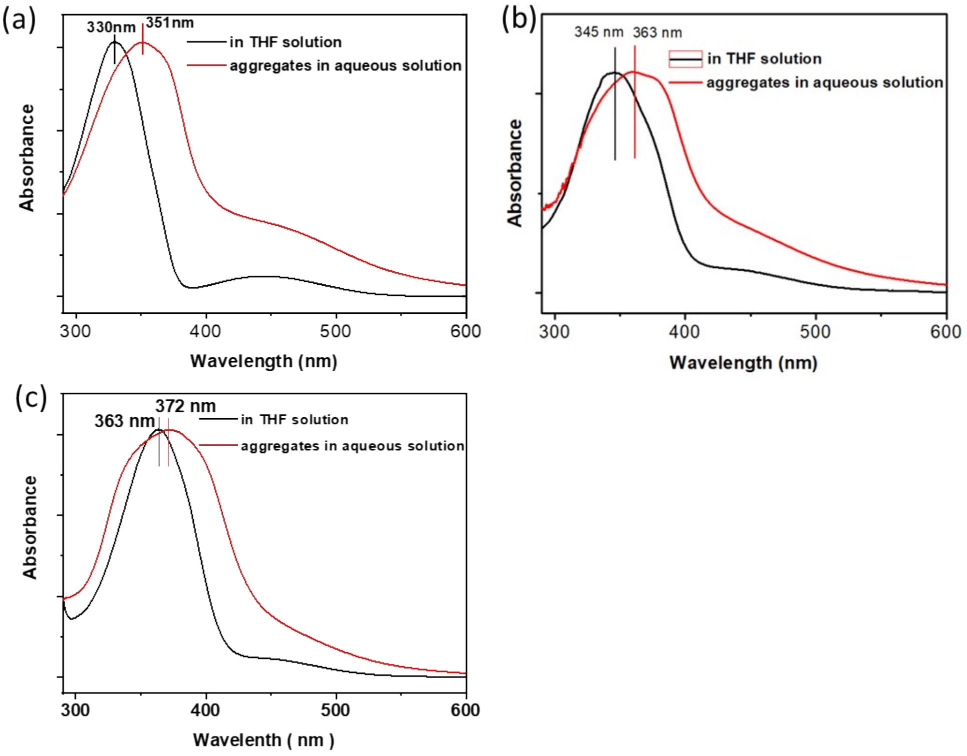


Figure S8. UV-vis spectra of (a)PEG_{113}-*b*-$PFAZO_{78}$, (b)PEG_{113}-*b*-$PAZO_{64}$, (c) PEG_{113}-*b*-$PAZOCN_{59}$ in THF solution (black curve) and their aggregates in aqueous solution obtained from the dialyzate of self-assembly solution with initial concentration of 1.0 mg/mL in dioxane, 37.5% water content, at 25°C (red curve).

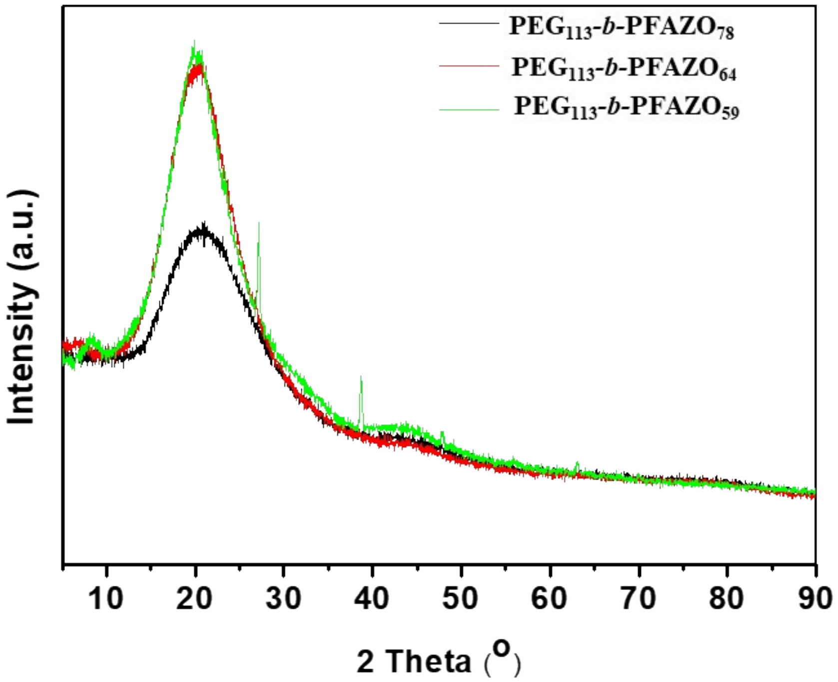


Figure S9. WXRD of the samples of PEG$_{113}$-*b*-PFAZO$_{78}$, PEG$_{113}$-*b*-PAZO$_{64}$, PEG$_{113}$-*b*-PAZOCN$_{59}$ at room temperature.

Reference:

1. L. Li, S. Cui, A. Hu, W. Zhang, Y. Li, N. Zhou, Z. Zhang and X. Zhu, *Chem. Commun.*, 2020, **56**, 6237-6240.