Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information (ESI)

Temperature-induced Oriented Growth of Large area, Few-layer 2D Metal-Organic Framework Nanosheets

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Experimental Section:

Chemicals

$Zn(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, Pyrazine, *p*-xylene and Polyvinylpyrrolidone (PVP, average Mw 40,000) were purchased from Sigma Aldrich. Tetrakis(4-carboxyphenyl)porphyrin (H_2TCPP, 97%) was purchased from Tokyo Chemical Industry Co. Ltd. N,N-Dimethylformamide (DMF, 99.8%) and ethanol were purchased from Merck. All chemicals were of analytical grade and used as received without further purification.

Material Synthesis

The PPF-1 NS were prepared following a slightly modified method in the reported literature.[1]

Preparation of stock solution A:

Dissolving $Zn(NO_3)_2 \cdot 6H_2O$ (150 mg, 0.5 mmol), pyrazine (27 mg), PVP (667 mg) in the mixture solution of DMF (300 mL) and ethanol (100 mL).

Preparation of stock solution B:

Dissolving H_2TCPP (160 mg) in the suspension containing a mixture of DMF (120 mL) and ethanol (40 mL).

PPF-1 NS was synthesized in a typical procedure by pipetting 12 mL of mother solution A and 4 mL of mother solution B in a 20 mL glass vial. The glass vial that is filled with the established microemulsions was then sealed and heated at the designed temperature for 16 h in the oil bath. Finally, the purple precipitate was collected by centrifugation and washed with absolute ethanol for several times.

The preparation procedures for PPF-1(Co) and PPF-1(Cu) NS are the same as that for the PPF-1 previously described, except that different metal precursors (0.5 mmol) used.

The bulk PPF-1 material was synthesized like PPF-1 NS but without adding the PVP surfactant.

For the further use for the necessary characterizations, powdered PPF-1 NS were obtained by freezing the colloidal suspension of PPF-1 NS in *p*-xylene instead and removing the *p*-xylene solvent *via* a freeze-drying process to ensure its high dispersibility after drying. The obtained dried PPF-1 NS were then further used for the XRD patterns, FTIR, TGA characterizations.

Characterizations

Power X-ray diffraction (XRD) patterns were recorded on a diffractometer (BrukerD8 Advance, Germany) with Cu source (40 kV, 40 mA, λ=1.54060 Å) and a position sensitive detector, Lynxeye XE, from 5° to 30° with a step size of 0.005°. Small-angle X-ray scattering (SAXS) was taken on Bruker N8 Horizon with Cu source (50 kV, 1.0 mA, λ=1.54060 Å). A Vantec-500 2D detector was used for data collection. The surface morphologies of products were examined by scanning electron microscopy (SEM) (FEI Magellan 400 XHR) operated at an acceleration voltage of 5 kV in a high resolution mode and Back scattering electron images were collected by using a concentric back scattering detector. The structures and morphologies of products were also examined by Transmission electron microscope (TEM) (FEI Tecnai G2 T20 TWIN) at 200 kV. SEM samples of PPF-1 NS were prepared by placing a 1 cm-diameter drop of dilute PPF-1 NS ethanol suspension on a 1×1 cm section of silicon wafer and allowing the solvent to evaporate. The wafer was then attached to an aluminium sample holder with conductive carbon tab. The samples were coated with iridium to eliminate any possible charging effect. The transmission electron microscopy (TEM) samples were prepared by dropping a small amount of diluted PPF-1 ethanol suspension on 230 mesh copper TEM grids covered with thin carbon films and allowing the solvent to evaporate. Atomic force microscope (AFM) (Bruker Dimension Icon) was used to characterize samples in tapping mode in air. Thermogravimetric Analysis (TGA) was performed on a Perkin Elmer STA 6000 Thermogravimetric Analyzer, heated from 25°C to 800°C at a rate of 10°C/min under N_2 atmosphere. UV/Vis spectra were recorded on a UV spectrophotometer (Shimadzu UV-2401PC). The functional groups of products were identified by Fourier transform infrared spectroscopy (FTIR) (Perkin-Elmer Frontier) in the transmission mode. Zetasizer (Malvern Nano ZS, UK) was used to determine the lateral size distribution *via* dynamic light scattering (DLS) method and zeta potential of samples. PPF-1 NS suspensions (5 mg/L) were bath-sonicated for 10 min and analysed immediately afterwards. Each DLS and zeta potential process were repeated at least 3 runs. The freeze-drying process was performed in a freeze dryer (Freezone 2.5 L, Labconco Corporation, USA) to avoid the samples from aggregation.

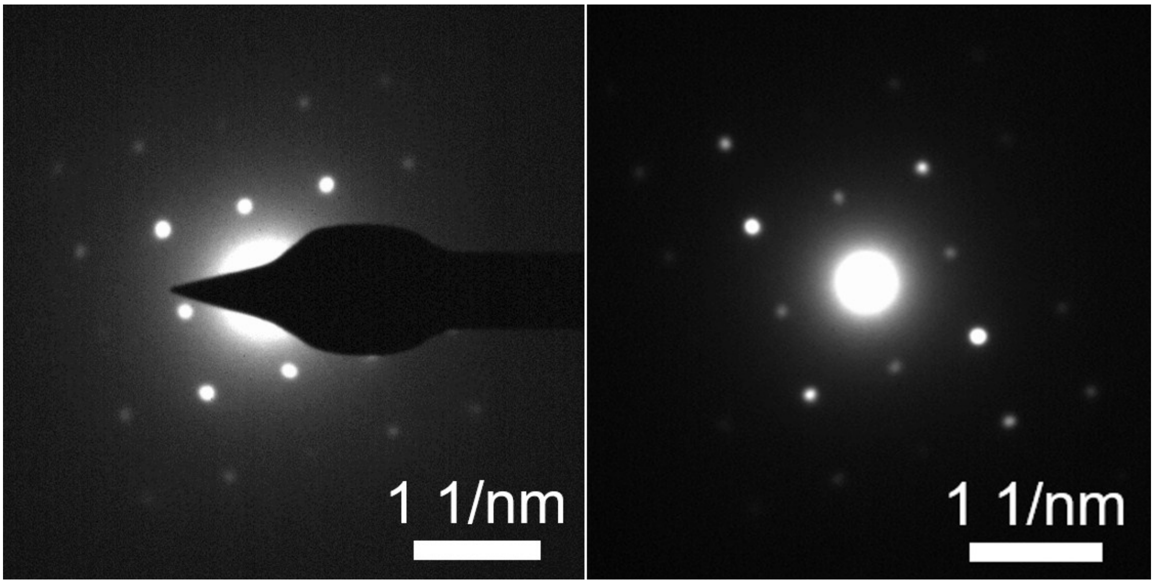
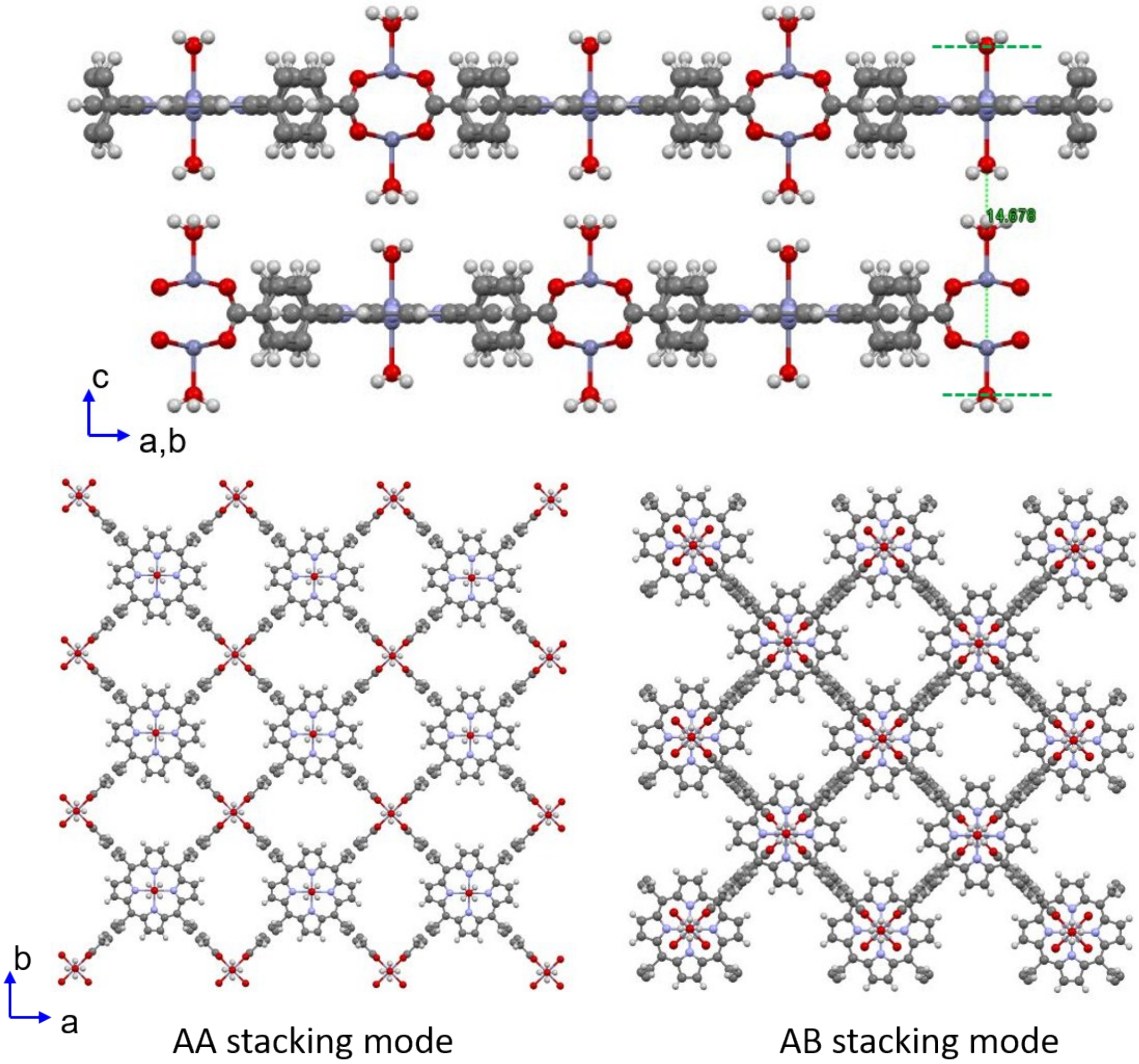


Figure S1. SAED patterns of the PPF-1 NS (left) and bulk-type PPF-1 (right).



AA stacking mode

AB stacking mode

Figure S2. Schematic diagrams of the crystalline structure of PPF-1. H atoms are shown in white, C in gray, N in light purple, O in red, and Zn in dark purple. Some H atoms have been omitted for clarity.

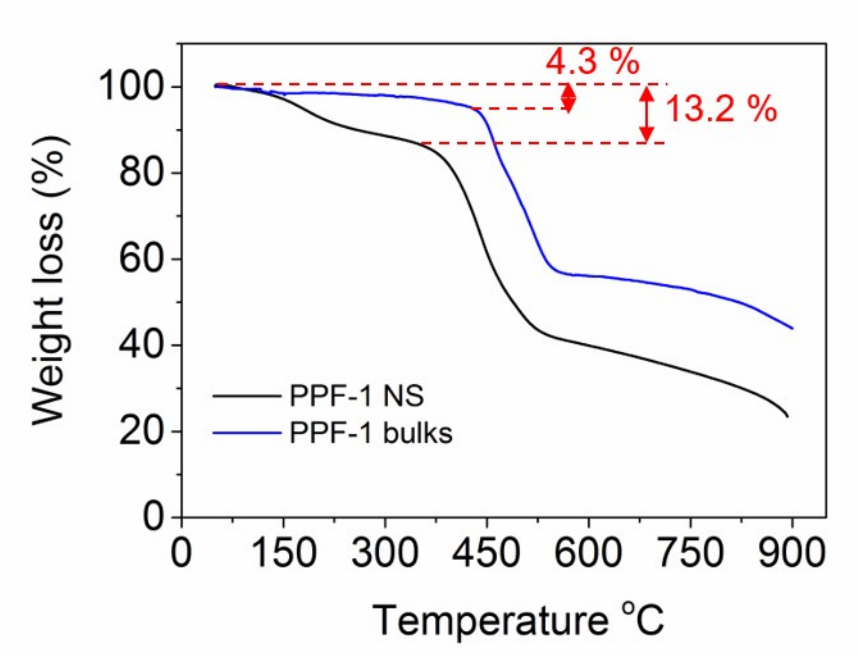


Figure S3. TGA curves of PPF-1 NS and PPF-1 bulks.

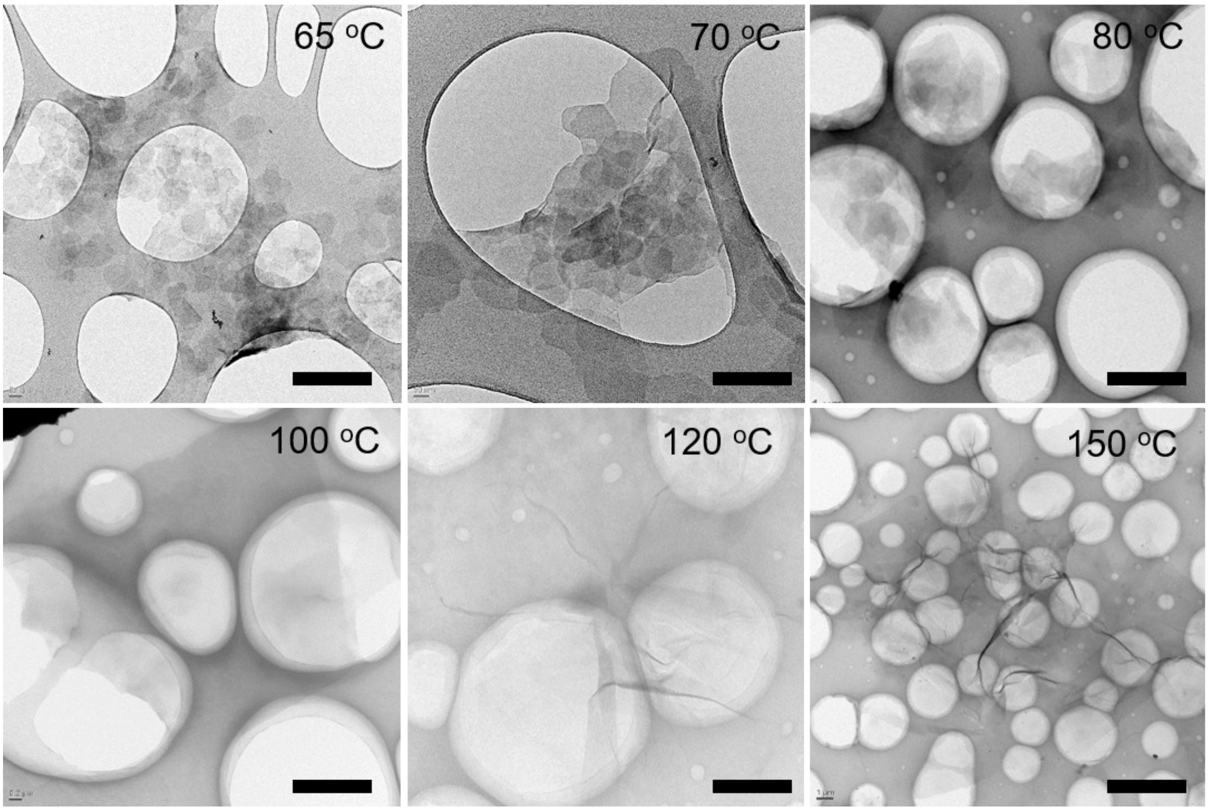


Figure S4. TEM images of the as-synthesized PPF-1 NS obtained at different temperatures. Scale bars: 2.0 um.

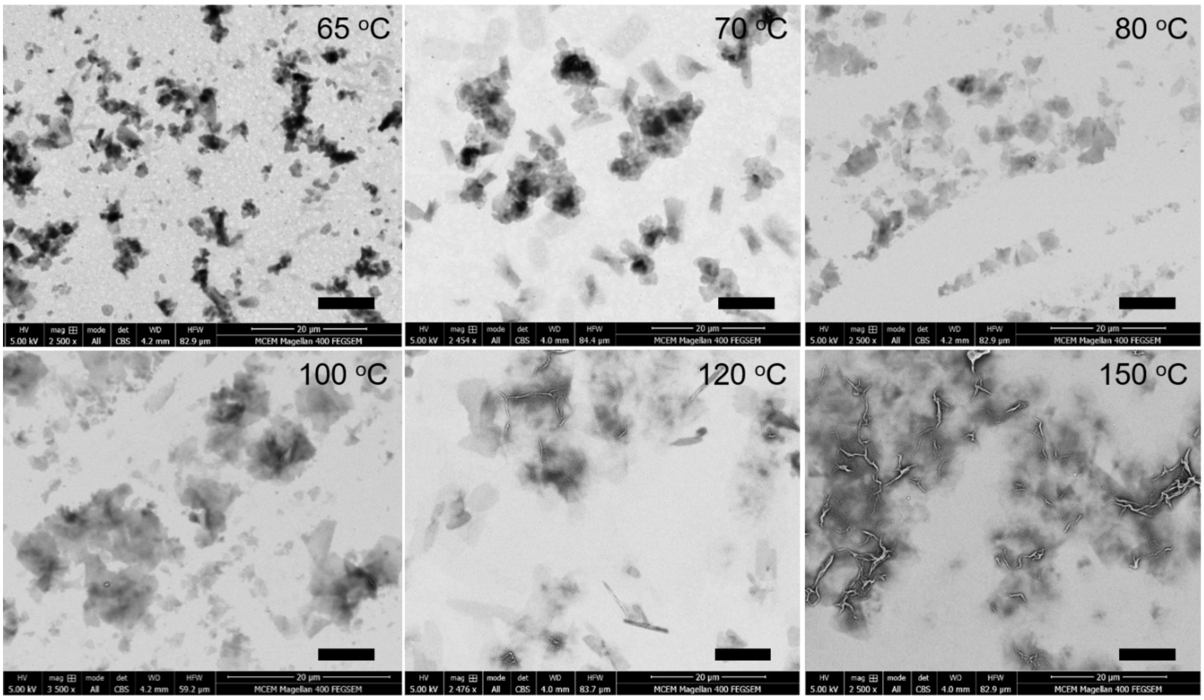


Figure S5. SEM images of the as-synthesized PPF-1 NS obtained at different temperatures. Scale bar: 10 um.

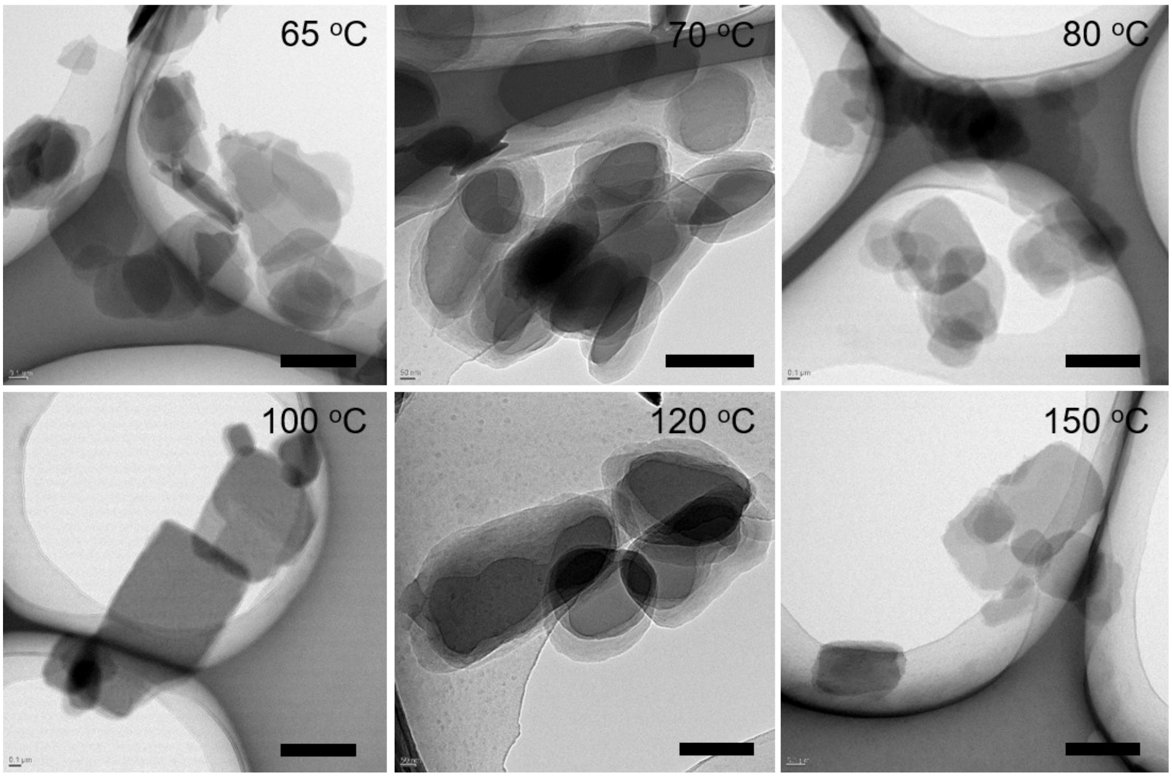


Figure S6. TEM images of the as-synthesized PPF-1 bulks obtained at different temperatures. Scale bars: 1.0 um.

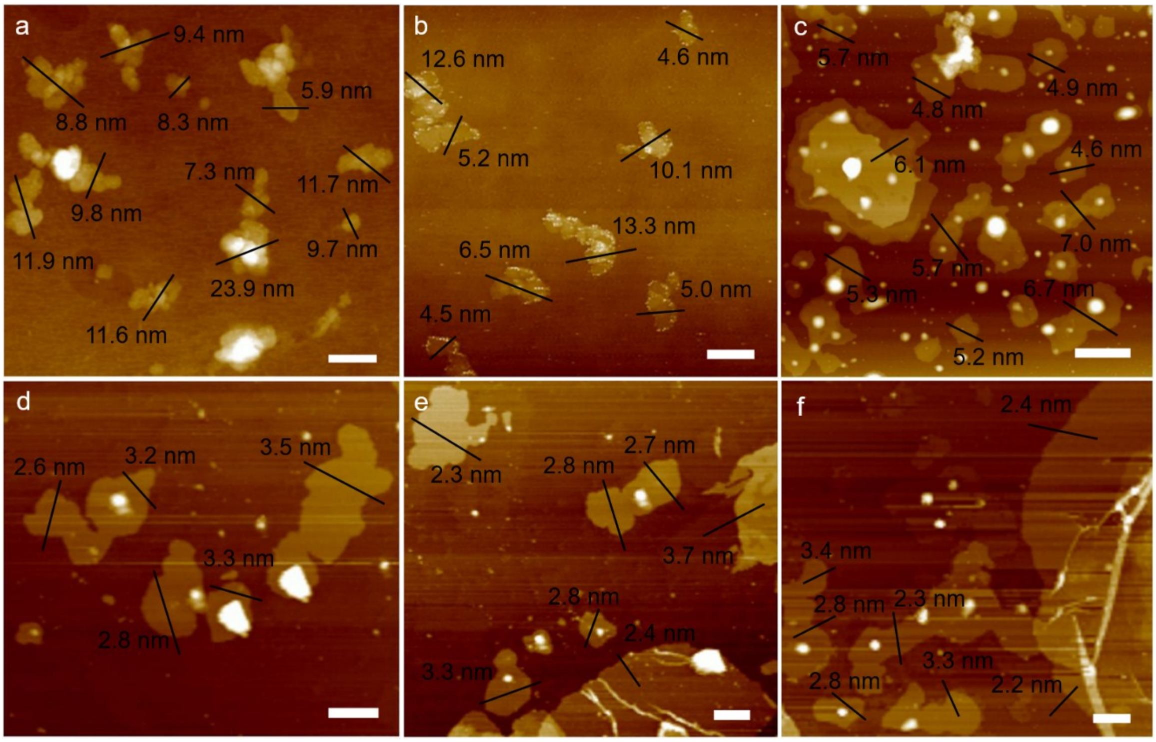


Figure S7. AFM images of the as-synthesized PPF-1 NS obtained at the temperature of (a) 65 ºC, (b) 70 ºC, (c) 80 ºC, (d) 100 ºC, (e) 120 ºC and (f) 150 ºC, repectively. Scale bar: 0.5 um.

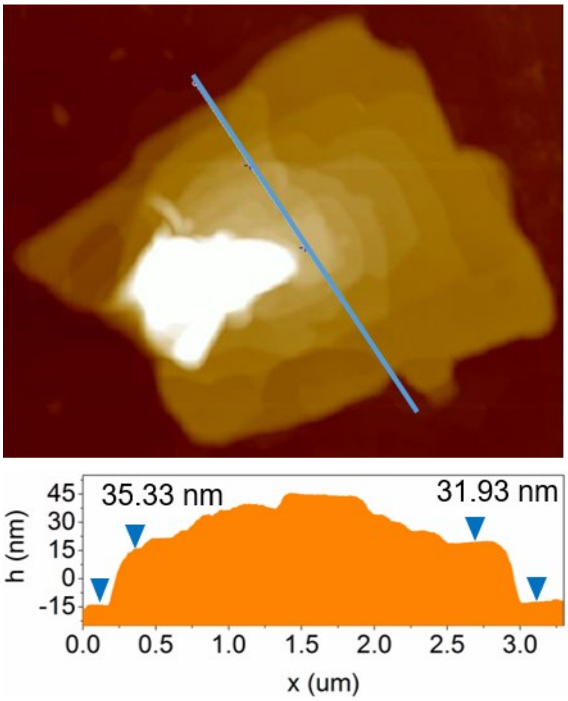


Figure S8. AFM image of bulk-type PPF-1 on the silicon wafer.

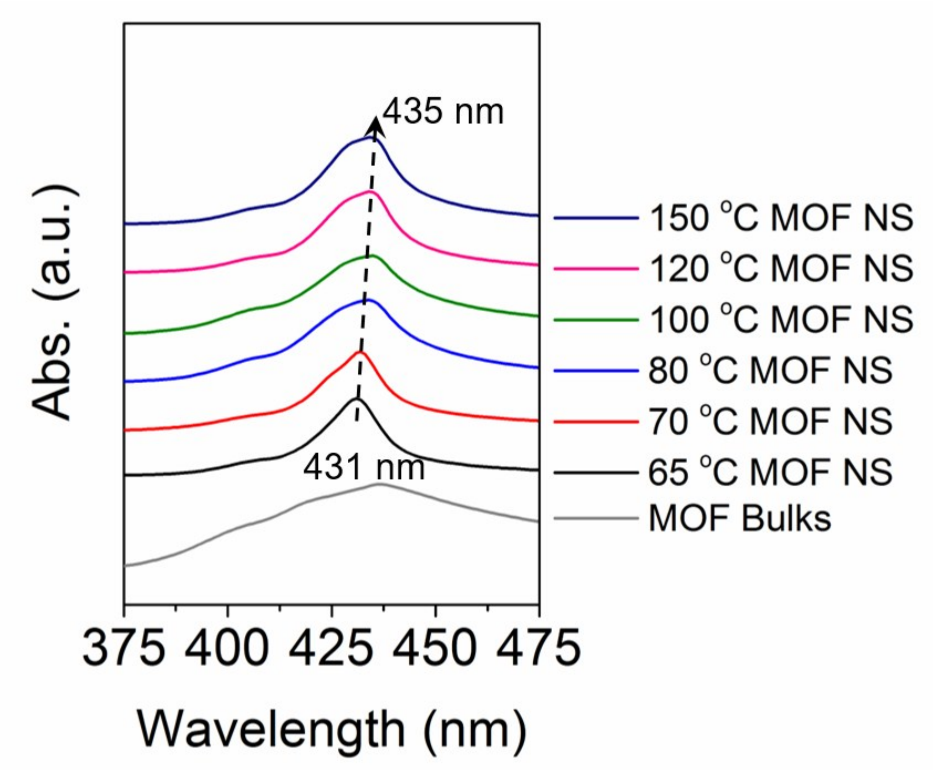


Figure S9. Comparison of the calculated absorbance in dependence of λ for the samples sizes difference.

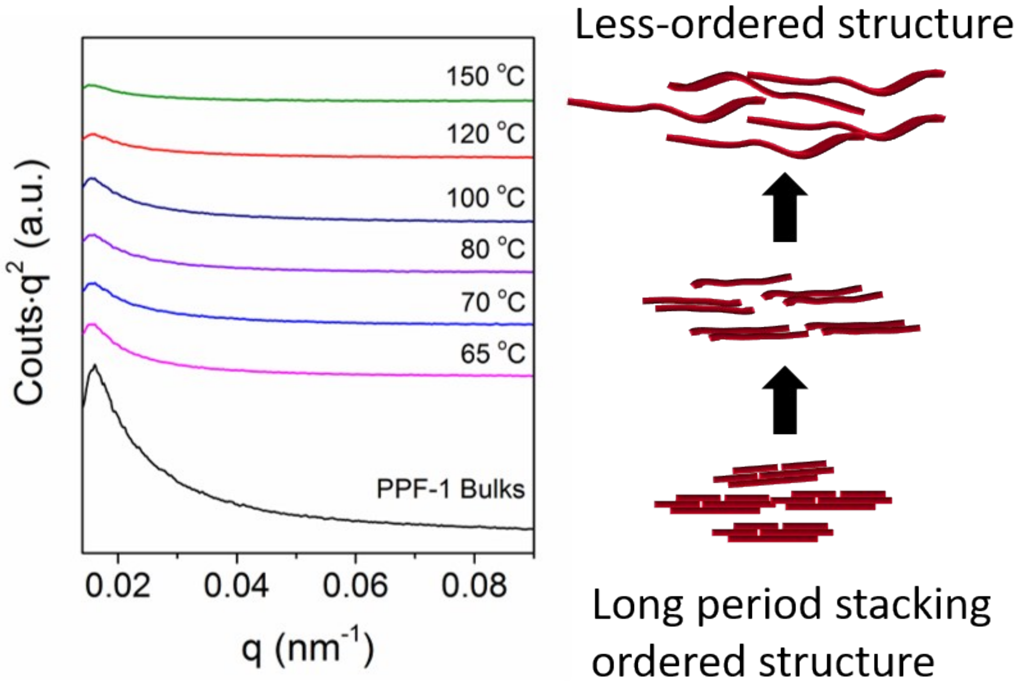


Figure S10. SAXS patterns comparison and schematic illustration of PPF-1 samples prepared at different temperatures.

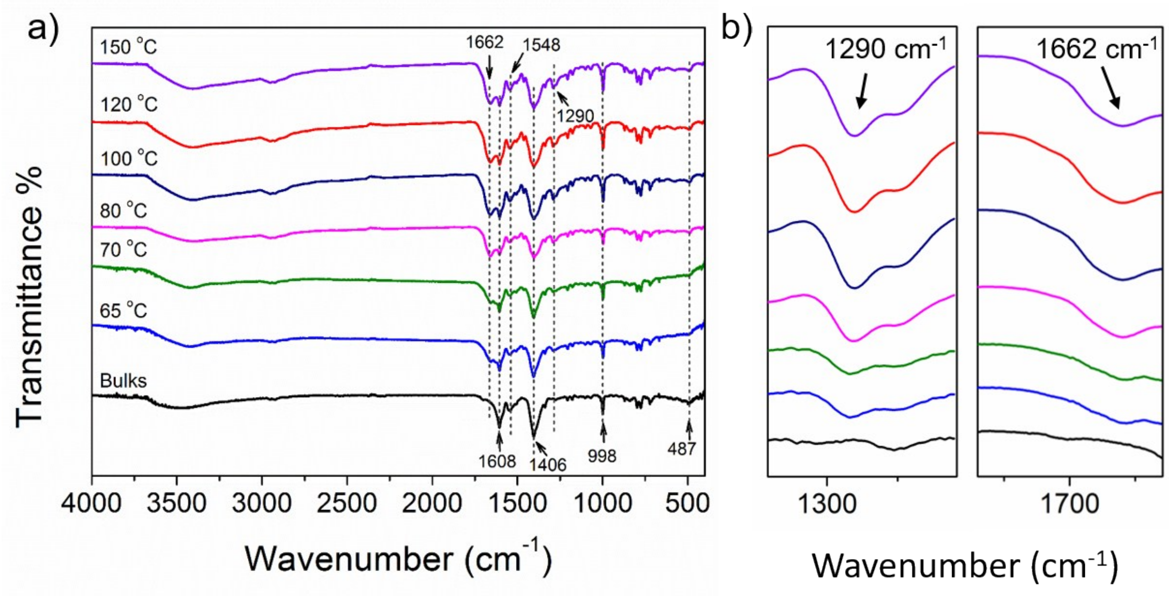


Figure S11. (a) FTIR spectra of PPF-1 NS at different temperatures and bulk-type PPF-1, respectively. (b) Partial enlarged profiles of PVP characteristic vibration bands at 1290 cm^{-1} and 1662 cm^{-1}, respectively.

To be more specific, the enlarged figures of the PVP characteristic peaks at 1290 cm^{-1} and 1662 cm^{-1} were compared. In the FTIR spectrum of PPF-1 bulks, no adsorption bands of PVP are observed. However, the PVP characteristic vibration bands at the both positions of PPF-1 NS that synthesised at high temperature is increasingly prominent. This indicates that the higher amount of PVP molecules covered on PPF-1 crystals at the elevated temperature.

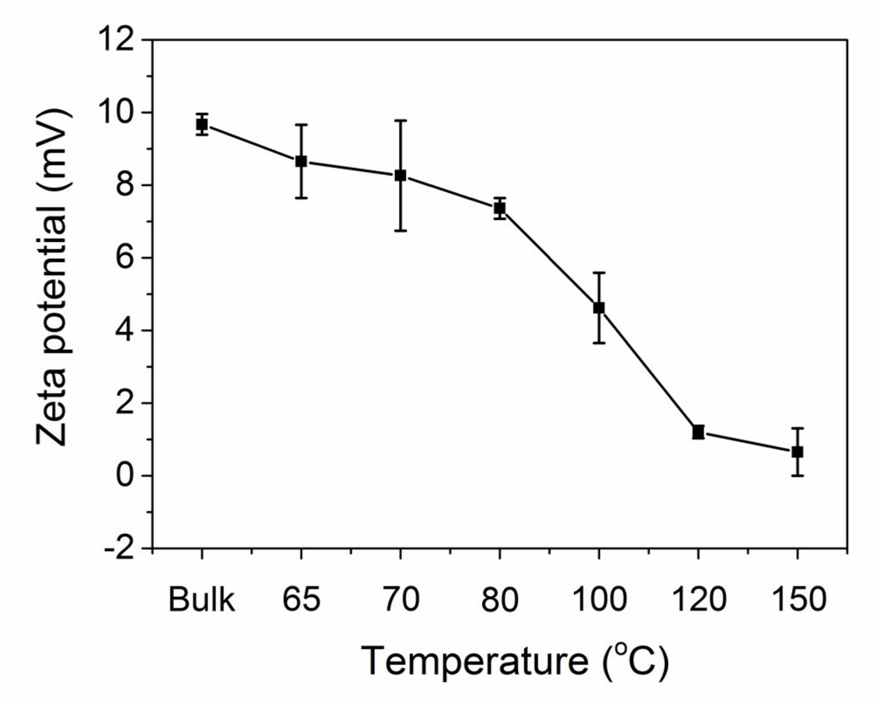


Figure S12. Zeta potential of PPF-1 samples prepared from different conditions.

Zeta potentials were measured to further confirm the presence of PVP on PPF-1 NS. The zeta potential of the bulk-type PPF-1 was 9.67 mV. When the reaction was involved with PVP, the surface charge declined because the low charged PVP took place onto the surface of positive charged PPF-1.[3] As the temperature increased, the zeta potential of the product gradually decreased and reached 0.65 mV at 150 °C, which further confirmed the increasing amount of PVP attached on the PPF-1 NS with temperature.

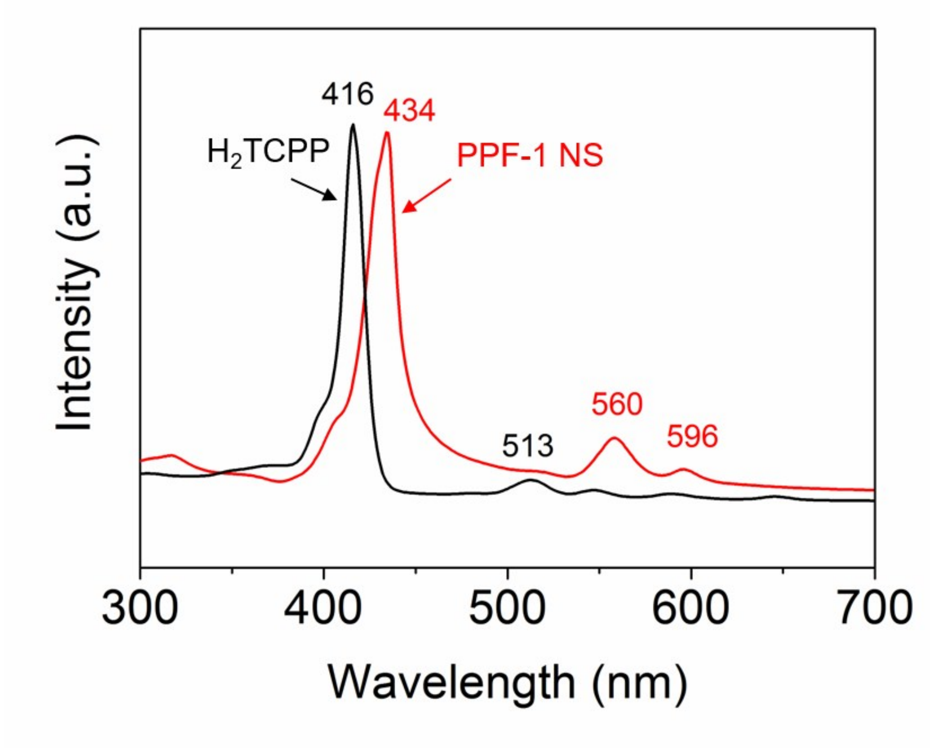


Figure S13. Comparison of UV-vis spectra of PPF-1 crystals and the H_2TCPP ligand.

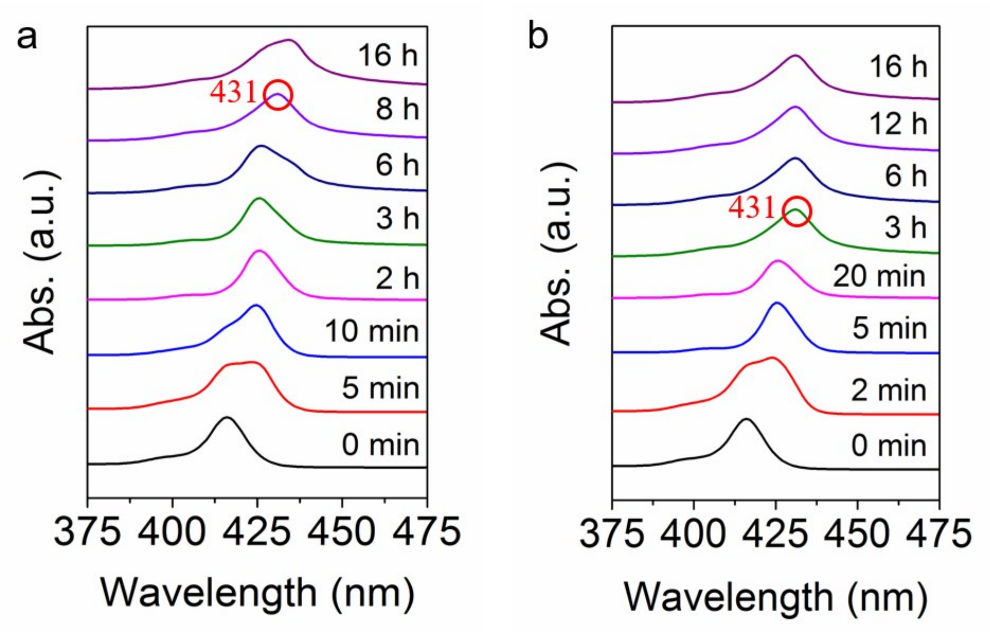


Figure S14. UV-Vis absorption spectra of PPF-1 NS reaction process at the temperature of (a) 80 ^{o}C and (b) 120 ^{o}C as a function of synthesis time.

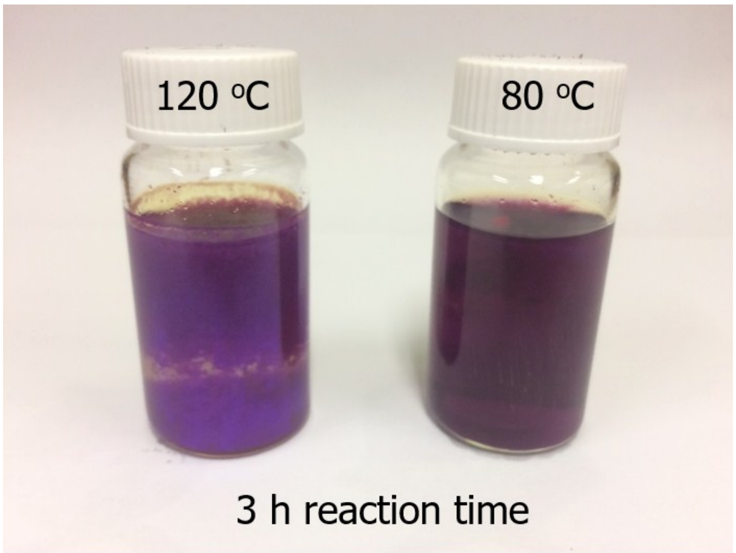


Figure S15. PPF-1 crystallization forming difference of the samples in two vials at the 3rd hour during the thermal reaction.

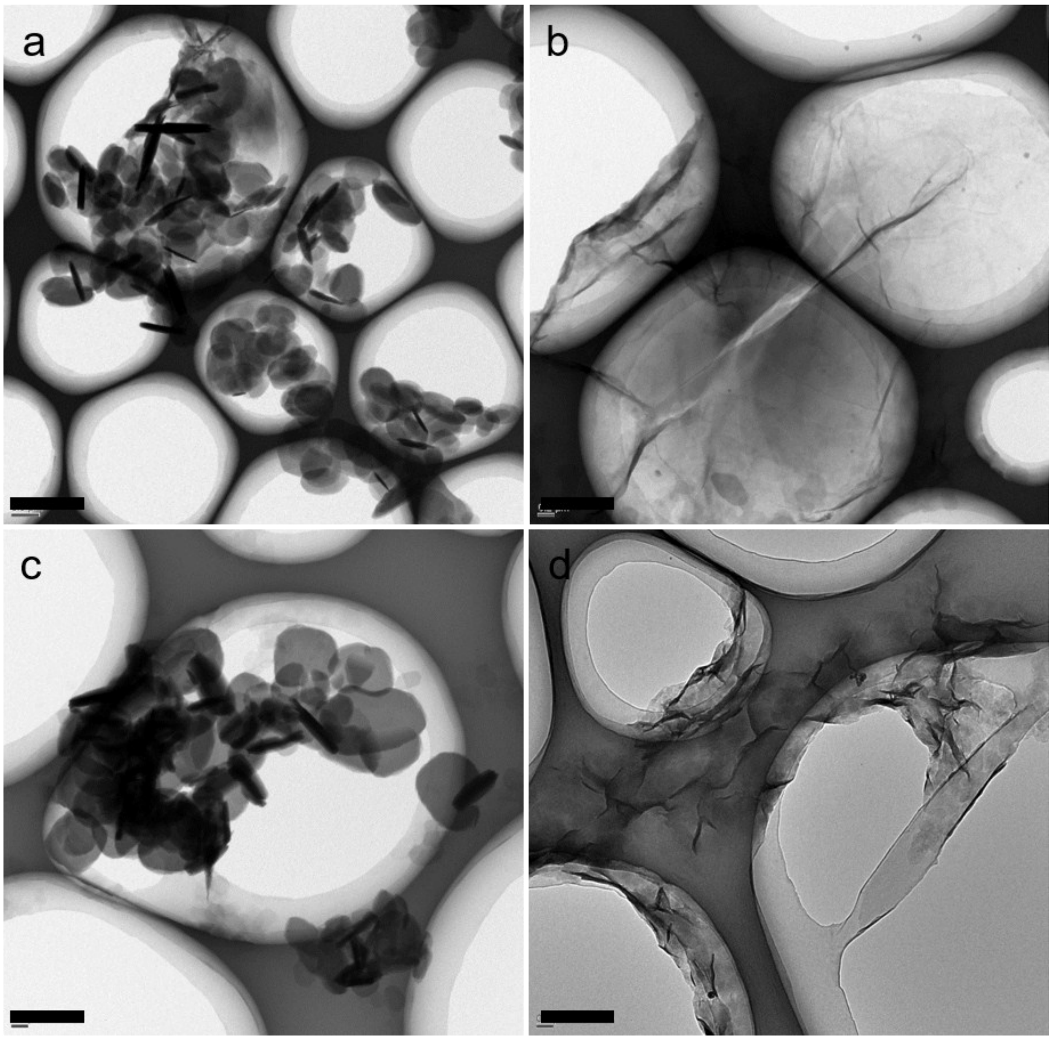


Figure S16. TEM images of the as-synthesized (a,b) PPF-1(Co) NS and (c,d) PPF-1(Cu) NS obtained at the temperature of (a,c) 80 ^{o}C and (b,d) 120 ^{o}C. Scale bars: 1.0 um.

References:

1. M. Zhao, Y. Wang, Q. Ma, Y. Huang, X. Zhang, J. Ping, Z. Zhang, Q. Lu, Y. Yu, H. Xu, Y. Zhao and H. Zhang, *Adv. Mater.*, 2015, 27, 7372-7378.
2. (a) H. Pan, C. Zhu, T. Lu, J. Lin, J. Ma, D. Zhang and S. Zhu, *Chem. Commun.*, 2017, 53, 1868-1871. (b) D. Yang, Z. Y. Lu, X. H. Rui, X. Huang, H. Li, J. X. Zhu, W. Y. Zhang, Y. M. Lam, H. H. Hng, H. Zhang and Q. Y. Yan, *Angew Chem Int Edit*, 2014, 53, 9352-9355.
3. N. Yan, Y.A. Yuan, P.J. Dyson, *Chem. Commun.*, 2011, 47, 2529-2531.