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Supporting Information

for

Visual identification of $^1O_2$-induced crystal structure transformation of single Zr-MOF by dark-field microscopy

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Experimental Section

Materials and apparatus

Materials. Zirconyl chloride octahydrate ($ZrOCl_2$•$8H_2O$, 98%) was purchased from Macklin Biochemical Co., Ltd (Shanghai, China). Tetrakis (4-carboxyphenyl) porphyrin (H_2TCPP, 97%) was purchased from Frontier Scientific (Logan, Utah, USA). Benzoic Acid was purchased from Wuhan Organic Synthesis Chemical Plant (Wuhan, China).1,3-diphenylisobenzofuran (DPBF) (97%) was purchased from Aladdin Biochemical Technology Co., Ltd (Shanghai, China). Superoxide dismutase (SOD) was purchased from Shanghai Yuanye Bio-Technology Co., Ltd (Shanghai, China). All used reagents were commercially availablel and used without further purification. The Milli-Q water was used throughout all experiments.

Apparatus. Ultraviolet-visible absorption spectra were measured by a U-3010 spectrometer (Hitachi, Japan). The morphology of the ZrTCPP was imaged by S-4800 field-emission scanning electron microscope (Hitachi, Japan). Light scattering dark field microscope (DFM) images were captured by dark-field imaging system, which was equipped with optical microscope (BX51, Olympus, Japan), a DP72 single chip true-color charge-coupled device (CCD) camera (Olympus, Japan) and halogen light source (100 W, U-LH100-3). High numerical aperture dark-field condenser (U-DCW, NA=1.2−1.4) and 100 magnification oil immersion objective lens was used in the imaging. Scattering spectra of individual nanoparticles were obtained by a spectrometer (IsoPlane SCT-320, Princeton, USA) and a charge-coupled device (CCD) camera (PRO, Princeton, USA)

Preparation of ZrTCPP

ZrTCPP nanoparticles were synthesized as previous reported.[1] Briefly, 5, 10, 15, 20 -Tetrakis (4-carboxyphenyl) porphyrin (H_2TCPP) (10 mg, 0.013 mmol), zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) (30 mg, 0.093 mmol), and benzoic acid (BA) (300 mg, 2.4 mmol) in 10 mL of N, N -Dimethylformamide (DMF) were ultrasonically dissolved in a round bottom flask. The reaction mixture was heated at 90 ^oC oven for 5 h. After cooling

down to room temperature, dark purple crystals were collected by centrifugation (13500 rpm, 10 min), the following nan by washing with fresh DMF and ethanol three times, respectively. The obtained nanoparticles were dispersed in ethanol and stored at 4 ^{o}C for further study. The ZrTCPP particles with a spherical morphology had a size distribution from 100 to 200 nm from SEM images (Figure S1a). The Uv-visible spectrum (Figure S1b) shows that the strong absorption peak at 425nm and the weak absorption peak at 500-700nm correspond to the B-band and Q-band of porphyrins respectively. The successful synthesis of ZrTCPP was also confirmed by FITR-spectra (Figure S1c) and Powder XRD data (Figure S1d).

Preparation of *il*-ZrTCPP solution

The *il*-ZrTCPP is used to denote ZrTCPP after illumination. 100 μL of 0.1g/ml ZrTCPP stock solution was added to 1.5 mL EP tube, and diluted to 1ml with ultrapure water. The tube was illuminated by a Xenon lamp (300W, CEL-HXF300) for 3 hours. Repeat the preceding operations to collect a large amount of *il*-ZrTCPP solution. The change of scattering signal of ZrTCPP after Xe lamp illumination are same as the ZrTCPP under DFM illumination.

Real time monitoring in DFM

The ZrTCPP particles was monitored by light scattering dark field microscopy (DFM). Firstly, the flow reaction cell was made by using pre-cleaned glass microscope slide labeled and glass coverslip. After washed by ultrapure water and dried by N_2, 100 μL of 0.1 mg/mL ZrTCPP was deposited on the glass slide for 5 min which the residual liquid was washed with pure water. The reaction cell was placed on the DFM and added ultrapure water to the reaction cell that the ZrTCPP particles were exposed to ultrapure water. The appropriate area in the dark-field microscopy was selected for imaging. And the same area was monitored *in-situ* and in real time through color CCD and spectrograph with 15 min time interval.

DPBF degradation

To investigate the activity of ZrTCPP and *il*-ZrTCPP, the oxidation of DPBF catalyzed by ZrTCPP and *il*-ZrTCPP was performed by Ultraviolet spectrophotometry. The composition of each reaction solution was as follows, control experiment: 900 μL DPBF (100 μM) +100 μL H_2O, DPBF: 900 μL DPBF (100 μM) +100 μL ethanol, DPBF+ *il*-ZrTCPP: 900 μL DPBF (100 μM) +100 μL *il*-ZrTCPP (10 μg/mL), DPBF+ZrTCPP: 900 μL DPBF (100 μM) +100μL ZrTCPP (10 μg/mL). The control experiment was kept in the dark for 10 min, other group under white LED irradiation (37.3 mW/cm^2) for 10 min. Then the absorbance changes of these groups were measured respectively.

The antibacterial experiment

Photodynamic antibacterial ability has been used to assess the activity of ZrTCPP and *il*-ZrTCPP. Firstly, *E. coli* liquid culture medium with OD value of 0.8 was diluted 10^4 times to obtain *E. coli* suspension, then the following groups of solution were prepared.

E. coli group: the 50 μL *E. coli* suspensions were mixed with 450 μL H_2O. (Bacteria suspension without MOFs was set as the blank group).

E. coli + ZrTCPP: 50 μL *E. coli* suspensions were mixed with ZrTCPP (450 μL 10μg/mL).

E. coli +*il*-ZrTCPP: 50 μL *E. coli* suspensions were mixed with *il*-ZrTCPP (450μL 10μg/mL).

Take 50 μL from each of the above three sets of solutions. The solution was irradiated with a white LED light (37.3mW/cm^2) for 10 min. And then take 50μL from each of the above three sets of solutions again. After placed under dark for 10 min, the solution was added into Luria-Bertani (LB) solid medium by dilution plating procedures, then incubated with LB solid medium at 37 ^{o}C for 12 h (avoid illumination). Take photographs of the bacterial colony numbers on the LB plate, and the colonies number were counted by ImageJ software.

Additional figures

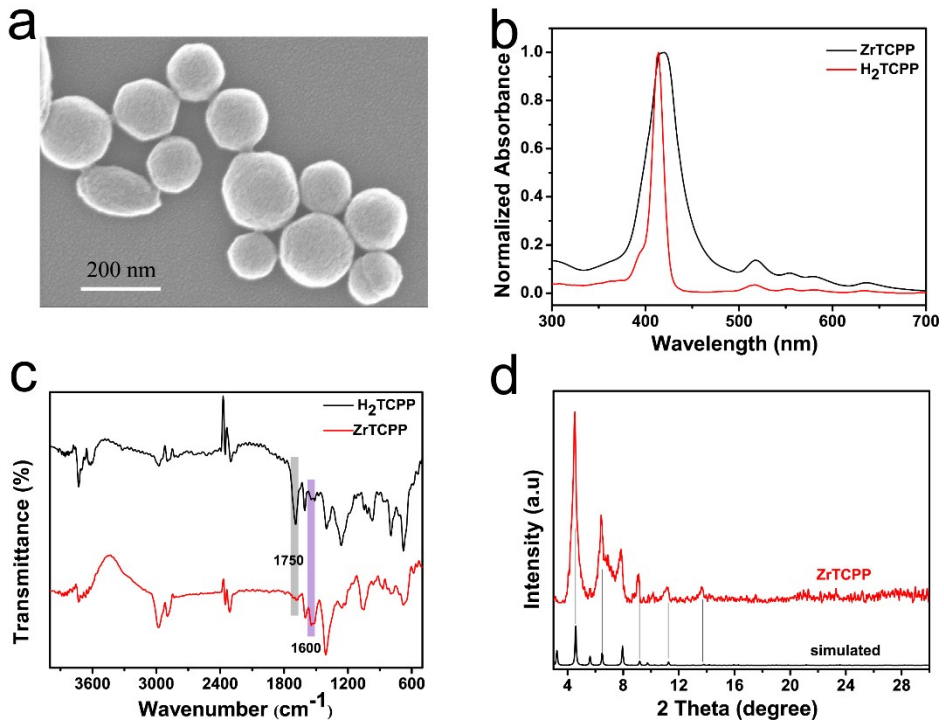

Fig. S1 Characterization of synthesized ZrTCPP. SEM image (a), UV–vis adsorption spectrum (b), FITR-spectra (c) and XRD spectra of ZrTCPP (d).

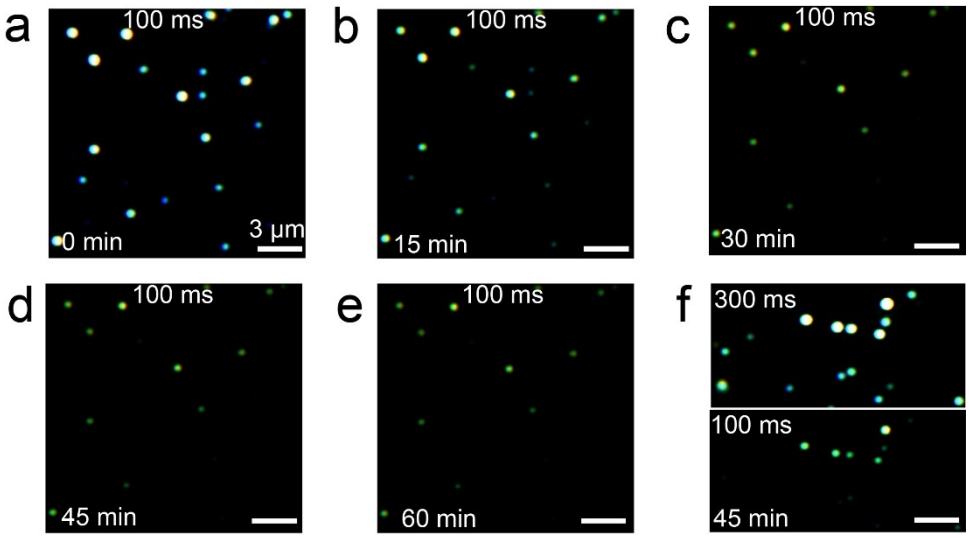

Fig. S2 DFM images of nano-sized ZrTCPP at different illumination time with different exposure time. (a)-(e) Dynamic DFM images of nanosized ZrTCPP particles in ultrapure water for 60 min continuous illumination with the exposure time of 100 ms. (f) DFM images for 45 min illumination with the exposure time of 100 ms and 300 ms, respectively.

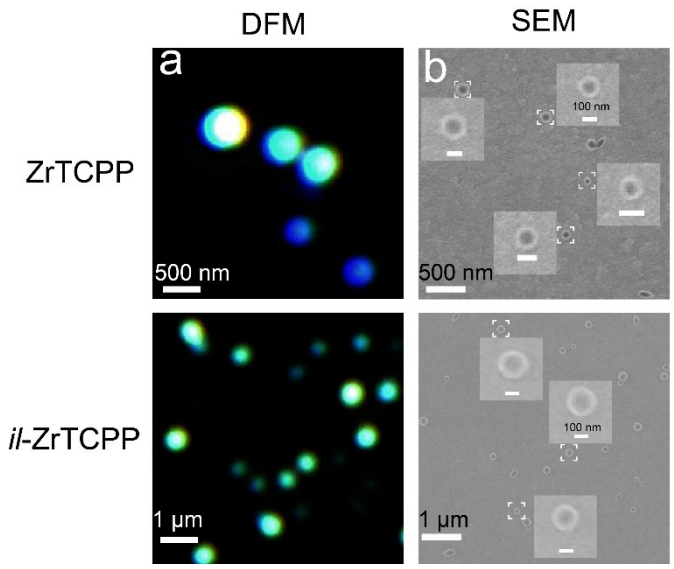

Fig. S3 Characterization of morphology. DFM (a) and SEM (b) images of ZrTCPP and *il*-ZrTCPP.

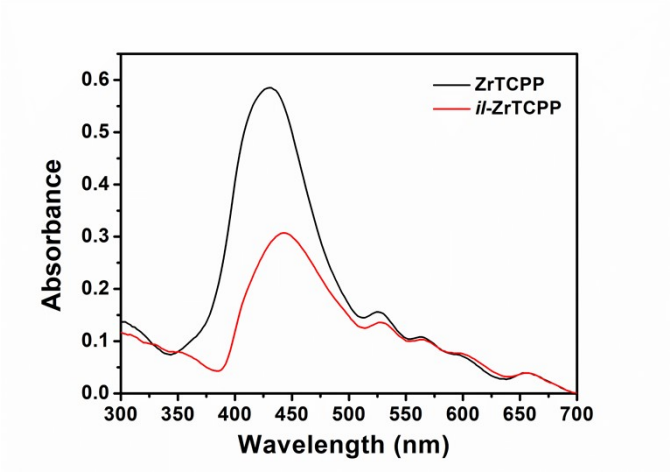

Fig. S4 UV-vis spectrum of ZrTCPP (black line) and *il*-ZrTCPP (red line).

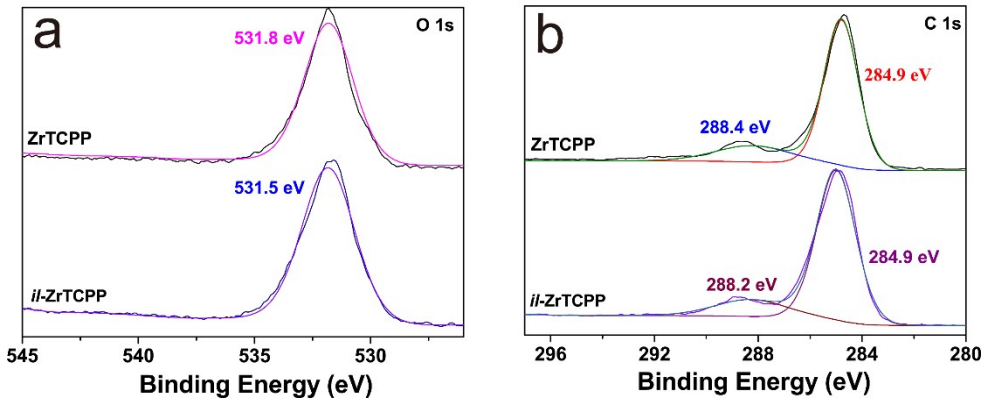

Fig. S5 XPS spectra of O1s (a) and C1s (b).

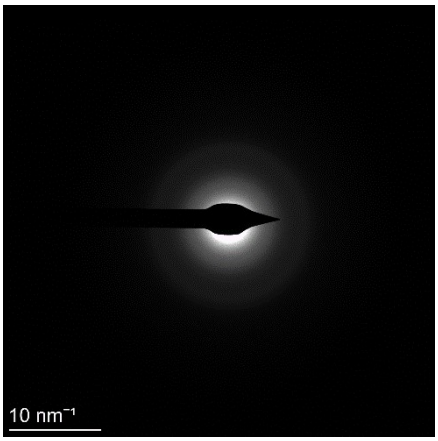

Fig. S6 SAED pattern of *il*-ZrTCPP.

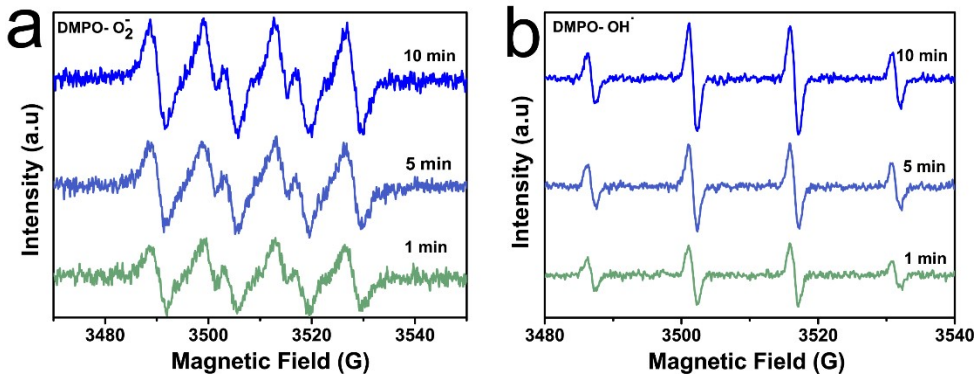

Fig. S7 The ESR spectra of DMPO-O_2^- (a) and DMPO-$OH^·$ (b) in the ZrTCPP-H_2O system under illumination.

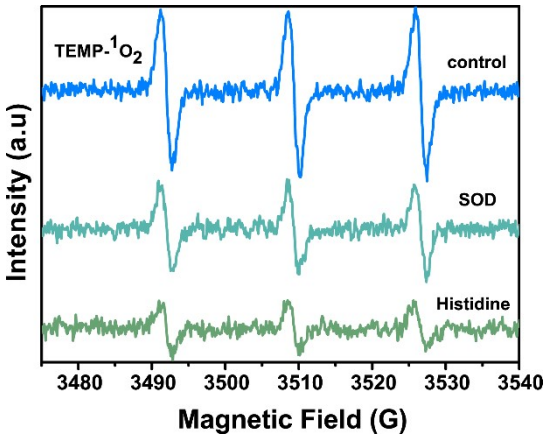

Fig. S8 The ESR spectra of $^1O_2$ with adding SOD and HIS.

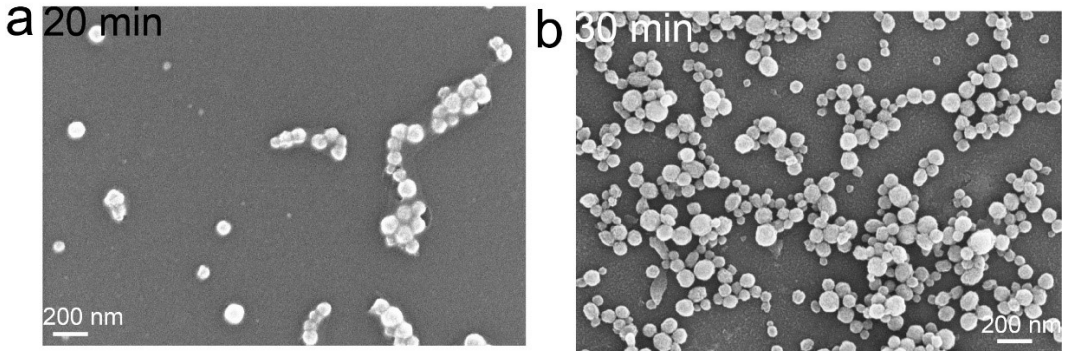

Fig. S9 SEM images of ZrTCPP after reacting 20 min (a) and 30 min (b).

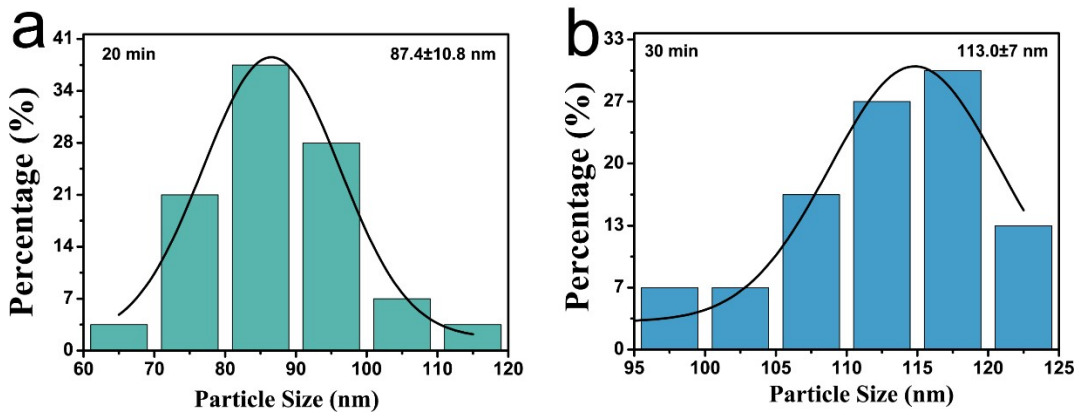

Fig. S10 Particle size of ZrTCPP at different reaction time.

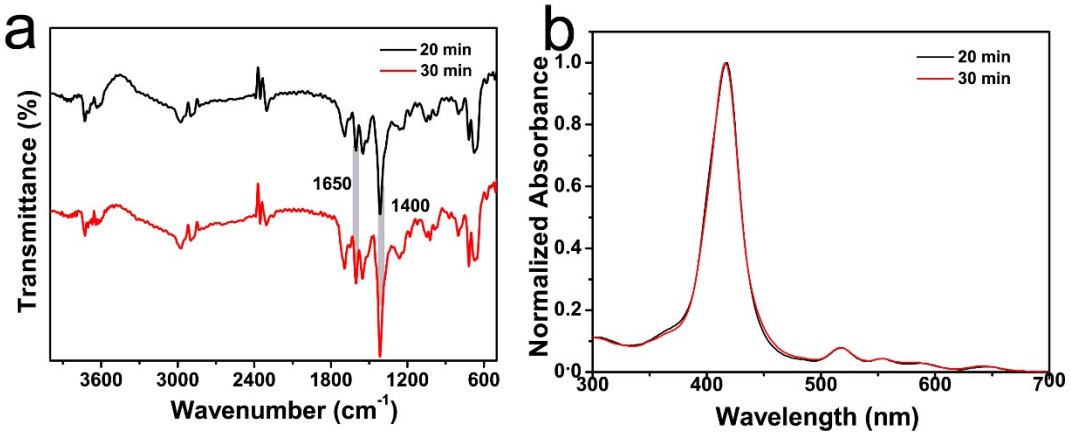

Fig. S11 FITR-spectra (a) and UV-spectra (b) characterization of ZrTCPP at 20 min (black line) and 30 min (red line).

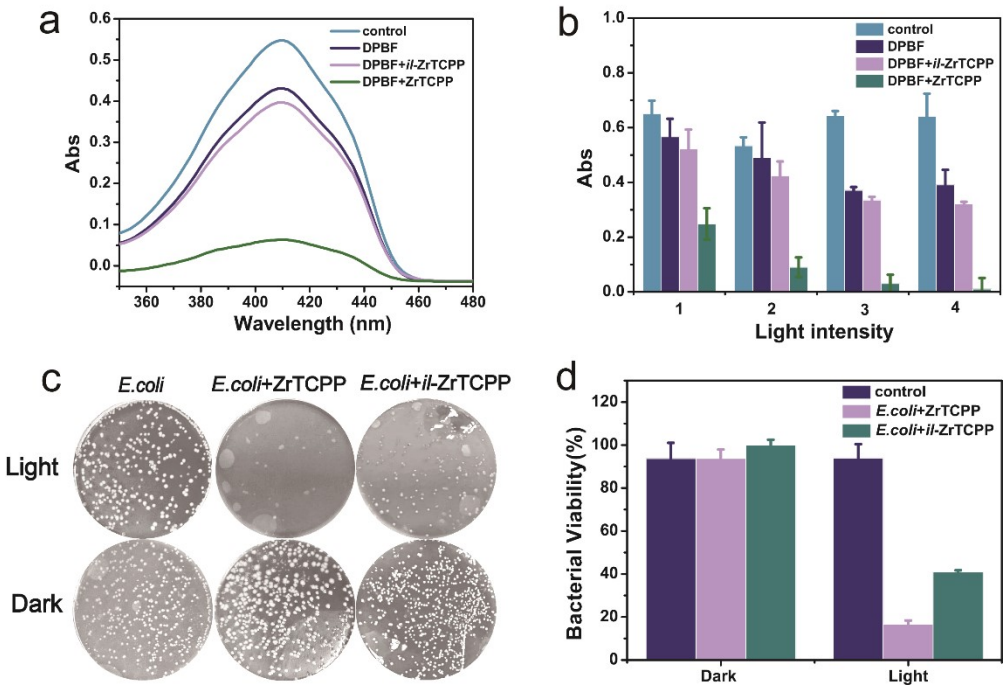

Fig. S12 Experiments of DPBF degradation and antibacterial. (a) UV-spectra of DPBF degradation with ZrTCPP and *il*-ZrTCPP. (b) Degradation of DPBF by ZrTCPP under different light intensities (1,2,3,4 represent different LED light intensities). Photograph (c) and bacterial viability (d) of *E. coli* incubated with ZrTCPP and *il*-ZrTCPP for 12 h.

Author contributions

Y. Xu: Investigation, Methodology, Experiment, Data Collection, Writing-Original Draft Preparation. **Q. Li:** Investigation, Methodology. **W. He:** Investigation, Methodology. **C. P. Yang:** Investigation, Methodology. **P. F. Gao:** Investigation, Methodology, Writing-Reviewing and Editing. **Y. F. Li:** Investigation, Methodology, Writing-Reviewing and Editing, Supervision. **C. Z. Huang:** Writing-Reviewing and Editing, Supervision.

References

1. J. Park, Q. Jiang, D. Feng, L. Mao and H.-C. Zhou, *J. Am. Chem. Soc.*, 2016, **138**, 3518-3525.