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Electronic Supplementary Information

of

Self-assembly of berberine and boron cluster for antibacterial regulation

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Experimental Section

Materials: Berberine chloride and amantadine hydrochloride was purchased from Beijing InnoChem Science & Technology Co. Ltd (Shanghai, China). Phosphate buffer saline (PBS), NaOH, and ethanol were obtained from Aladdin Industrial Co. Ltd (Shanghai, China). Yeast extract, tryptone and agar were obtained from BioFrox.

Instruments: Transmission electron microscopy (TEM) images were obtained using a HITACHI H-7000FA high-resolution transmission electron microscope operating at 200 kV. Ultraviolet−visible (UV−vis) spectroscopy was determined by a SP-756P UV−vis spectrometer. The fluorescence images were obtained with an inverted scanning microscopy (Olympus, FV1000) under ambient conditions. Fluorescence spectra were collected on a PerkinElmer LS-55 machine.

Syntheses of $B_{12}H_{12}^{2-}$

Cesium *closo*-dodecaborate was prepared according to the corresponding literature procedures.[1] First synthesize the triethylamine salt of $B_{12}H_{12}^{2-}$, and then exchange it for the cesium salt.

Synthesis of $(Et_3NH)_2B_{12}H_{12}$

$NaBH_4$ (49.18 g, 1.3 mol) was suspended in 200 mL of diglyme in a 500 mL three-necked flask. Iodine (101.52 g, 0.4 mol) was dissolved in diglyme to get a saturated solution and then was transferred to a dropping funnel. The whole device was vented with nitrogen for more than 10 min, and then the temperature rose to 100 ºC. After that, the iodine saturated solution was added dropwise over a period of 6 h. And the reaction mixture was continuously stirred overnight at 100 ºC under an atmosphere of nitrogen. During the reaction, the solution gradually turned yellow and became clear. On the next day, the temperature was increased to reflux for additional 24 h under an atmosphere of nitrogen. Then the reaction was cooled down and the solvent was removed under vacuum to obtain a large amount of white solid. The white solid was dissolved in 300 mL of water, and 140 mL of concentrated hydrochloric acid were added carefully. The acidified clear solution was stored at 4 ºC over night. Then the precipitated boric acid crystals were removed by filtration. The filtrate was treated with 200 mL of Et_3N and stirred overnight to get a large amount of white precipitates. The precipitates were collected by filtration. Then the solid was resuspended in water, and filtered at 60 ºC to wash off excess boric acid impurity. After vacuum drying for 24 h, the product

$(Et_3NH)_2B_{12}H_{12}$ (13.88 g, 0.04 mol, 50.1%) remained as a white solid.

Synthesis of $Cs_2B_{12}H_{12}$

$(Et_3NH)_2B_{12}H_{12}$ (6.92 g, 20 mmol) was suspended in 70 mL of boiling water, and then CsOH (7.50 g 50 mmol) was added. After that, the reaction mixture was cooled to room temperature, and a large amount of methanol was added to precipitate $Cs_2B_{12}H_{12}\cdot CH_3OH$ crystals. The obtained solid was collected by filtration and then dissolved in hot water. The water and methanol were removed by rotary evaporation to give the product $Cs_2B_{12}H_{12}$ (7.33 g, 89.97%) as a white solid.

References

1. V. Geis, K. Guttsche, C. Knapp, H. Scherer and R. Uzun, *Dalton Trans.*, 2009, **15**, 2687-2694.

Synthesis of the Supramolecular Complex

To prepare the supramolecular complex, the $Cs_2[B_{12}H_{12}]$ solution and the BBR solution were mixed in a 50 mL centrifuge tube. By simply stirring the mixture, the turbid solution of the supramolecular complex was obtained. After concentration, the resulting solid was washed with H_2O and ethanol alternately to give the supramolecular complex as a yellow powder.

Quantum Computation

All the DFT calculations were performed at the B3LYP/6-31g(d) level, with Gaussian 09 software. The DFT structures were initially optimized in the ground state as singlets then reoptimized as the triplets. Diagrams of the electrostatic potential and triplet spin density were modified by the Multiwfn software and visualized by the VMD software.

Antibacterial Study Measurement

The antibacterial activities of BBR and the supramolecular complex against *E. coli* and *S. aureus* were studied by colony counting method. The concentration of BBR and the supramolecular complex solution were set at 1 mM. The plates were incubated at 37 ºC for 24 h, the number of bacteris was counted.

Photodynamic Antibacterial Activity Measurement

The concentration of the supramolecular complex solution was set at 400 μM, taking water as a blank control. The three experimental groups mentioned above were irradiated with a 435 nm light at a power of 40 mW/ cm^2 for 10 min, 20 min, 30 min.

Figures and Tables

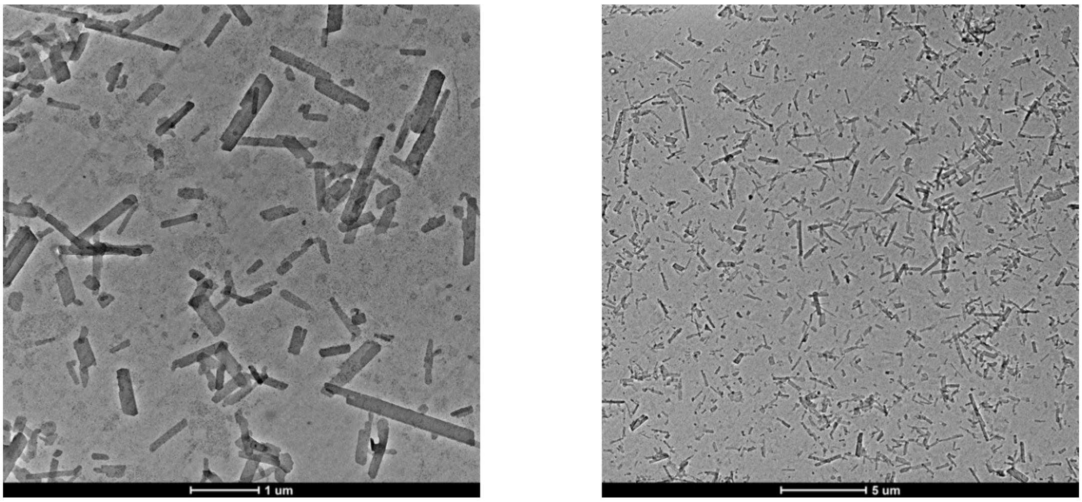

Fig. S1. TEM images of the supramolecular complex.

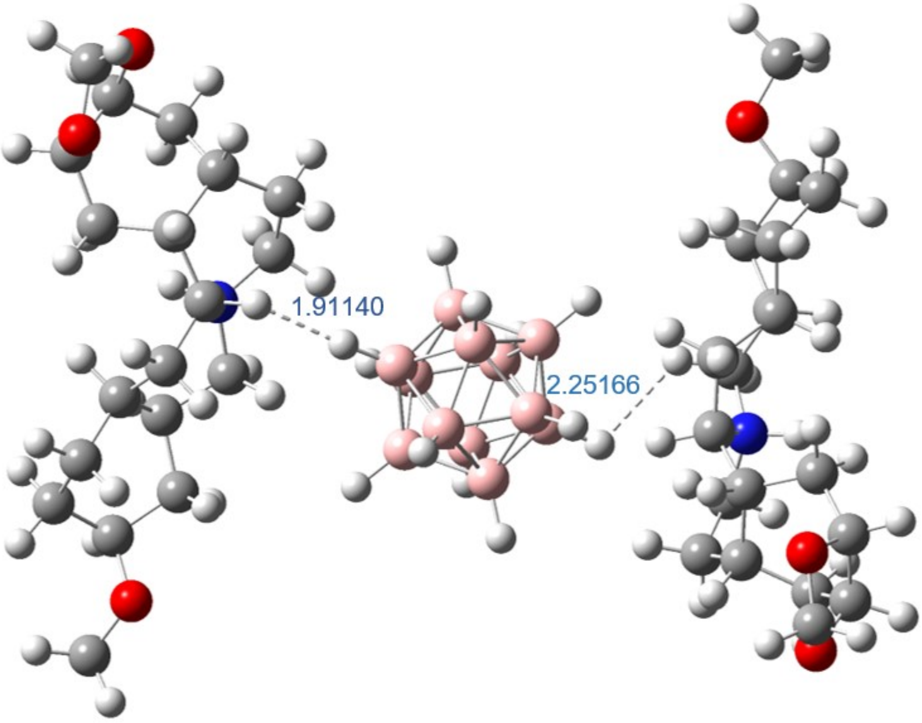

Fig. S2. The energy-optimized structure of the supramolecular complex based on BBR-$B_{12}H_{12}^{2-}$, and the interaction between $B_{12}H_{12}^{2-}$ and BBR.

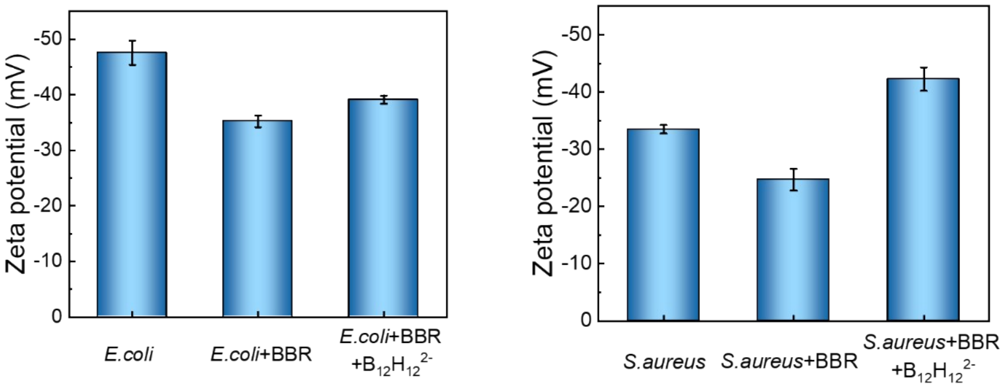

Fig. S3. Surface zeta potential of *E. coli* and *S. aureus* after co-culture with BBR and the supramolecular complex for 24 h, respectively.

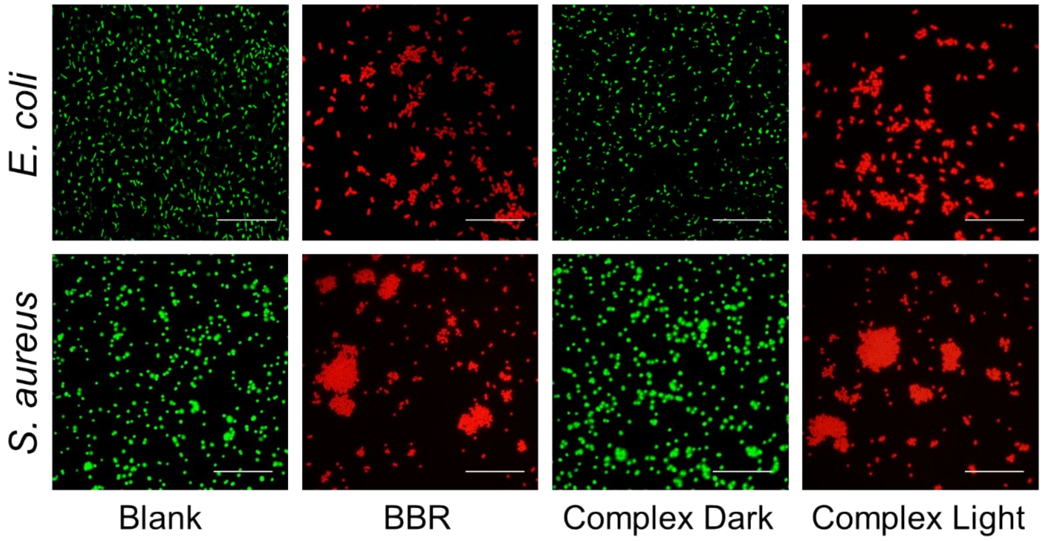

Fig. S4. LIVE/DEAD stain images of *E. coli* and *S. aureus* by various treatments.

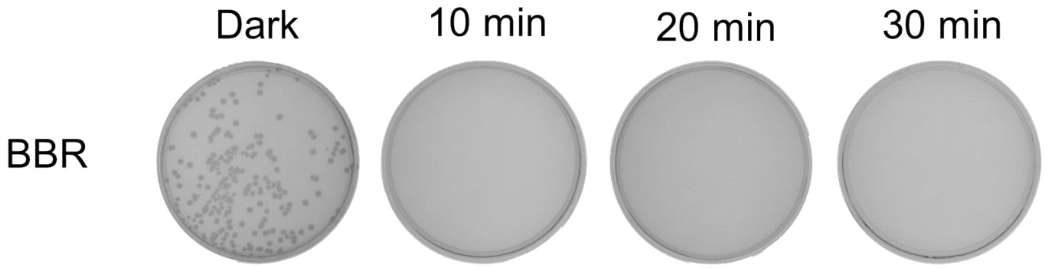

Fig. S5. Photographs of *E. coli* agar plates treated by BBR under different light time. λ_{ex} = 435 nm.

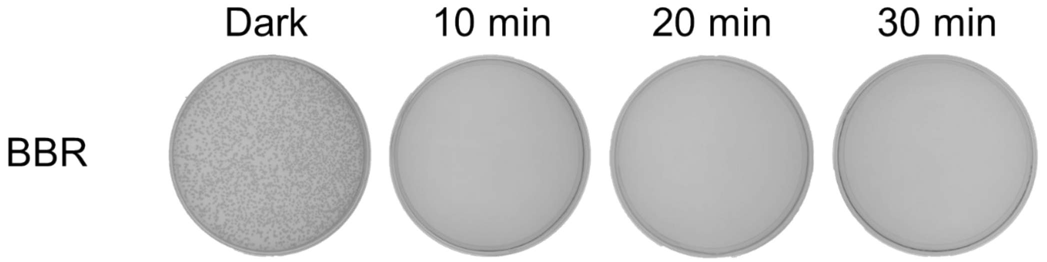

Fig. S6. Photographs of *S. aureus* agar plates treated by BBR under different light time. λ_{ex} = 435 nm.