

Supporting information

**Pore Engineering of Biomolecule-Based Metal–Organic Framework
Nanocarriers for Improving Loading and Release of Paclitaxel**

Linh Ho Thuy Nguyen,^{1,2,3,†} Y Thi Dang,^{1,2,†} Trang Thi Thu Nguyen,^{1,2} Bao Quang Gia
Le^{1,2,4}, Ngoc Xuan Dat Mai,^{1,2} Ha Van Nguyen,^{2,5} Tri Minh Le,^{2,5} Thang Bach Phan,^{1,2} Tan
Le Hoang Doan,^{1,2,*}

¹*Center for Innovative Materials and Architectures (INOMAR), Ho Chi Minh City, Viet Nam*

²*Viet Nam National University, Ho Chi Minh City, Viet Nam*

³*Faculty of Chemistry, University of Science, Ho Chi Minh City, Viet Nam*

⁴*Department of Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts,
United States*

⁵*School of Medicine, Ho Chi Minh, Vietnam*

[†]These authors contributed equally to this work.

*Email: dlhtan@inomar.edu.vn

Section S1: Materials and General Methods

Materials

Zinc acetate dihydrate ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, $\geq 98\%$), polyvinylpyrrolidone (PVP, average mol wt 40000) were obtained from Sigma-Aldrich company. 4-nitrobenzoic acid (99%), adenine (99%), 4,4'-biphenyldicarboxylic acid (H_2BPDC , 98%), paclitaxel (PTX, 99%) were obtained from Acros Chemical company. NaOH ($\geq 97\%$), d-glucose anhydrous, hydrochloric acid (HCl, 37%), *N,N*-dimethylformamide (DMF, $\geq 99.8\%$), ethanol (99%), methanol (99%) were supplied by Fisher. All the chemicals were used in the experiments without further purification. Organic linker, azobenzene-4,4'-dicarboxylic acid ($\text{H}_2\text{azo-BDC}$), was synthesized following the reported procedure.¹

General methods

Powder X-ray diffraction (PXRD) patterns were recorded using a Bruker D8 Advance with a Cu $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) source. The synthesized material was examined by Fourier transform infrared (FT-IR) spectra in the range of 4000–400 cm^{-1} on a Bruker Vertex 70 system. Nitrogen adsorption isotherms at 77 K were measured on a Quantachrome Autosorb iQ2. The microscope images were obtained on Olympus BX53 and Nikon SMZ1000. Field Emission Scanning Electron Microscopy analysis (FE-SEM) was conducted on SU8010, Hitachi, Japan. The residual content of PTX was analyzed by high-performance liquid chromatography (HPLC), equipped with a UV detector. HPLC analyses were recorded on Agilent Technologies 1200 Series with ZORBAX SB-C18 (Agilent, 5 μm , 4.6 \times 250 mm) column. The mobile phase was water: acetonitrile (50:50 v/v). The separation was carried out at 30 °C. The detection wavelength was 227 nm, and a flow rate of 1.0 mL min^{-1} was employed. A sample volume of 20 μL was injected.

Section 2. Synthesis of b-MOFs

b-Zn-BPDC was solvothermal synthesized through a solvothermal reaction containing zinc acetate dihydrate (54.88 mg, 0.25 mmol), adenine (16.89 mg, 0.125 mmol), H₂BPDC (60.56 mg, 0.25 mmol) respectively, in 4.5 mL *N,N*-dimethylformamide (DMF) with polyvinylpyrrolidone (PVP, average mol wt 40000) added as a modulator. We studied the effect of the molar ratio of PVP on b-Zn-BPDC crystal formation. The mixture was then sonicated for 20 minutes with 1.8 mL methanol and 0.45 mL DI water. The suspension was heated at 85 °C for 24 h. Powder X-ray diffraction (PXRD) measurements were used to monitor the crystallinity of samples.

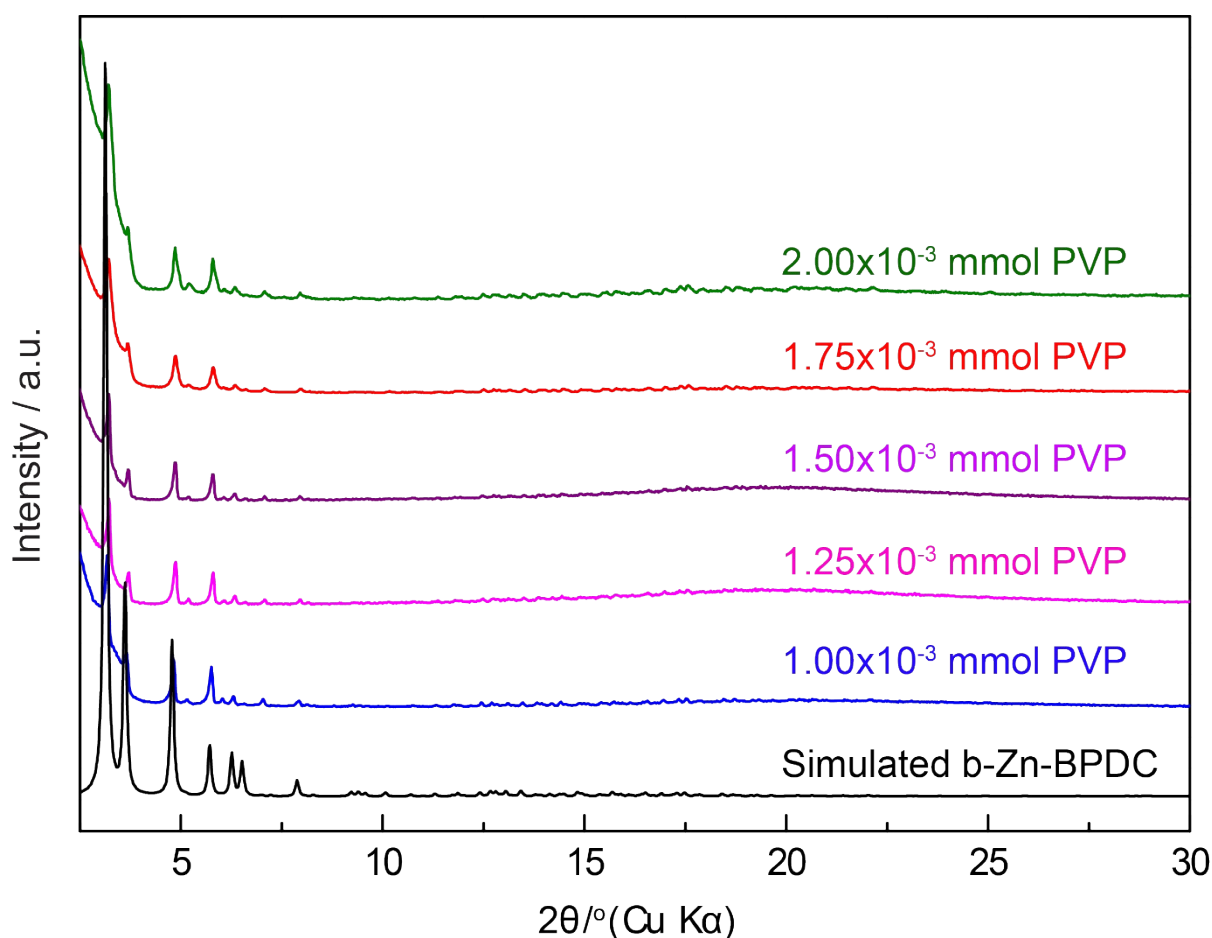


Figure S1. PXRD patterns of Zn-BPDC samples with the effect of the amount of PVP

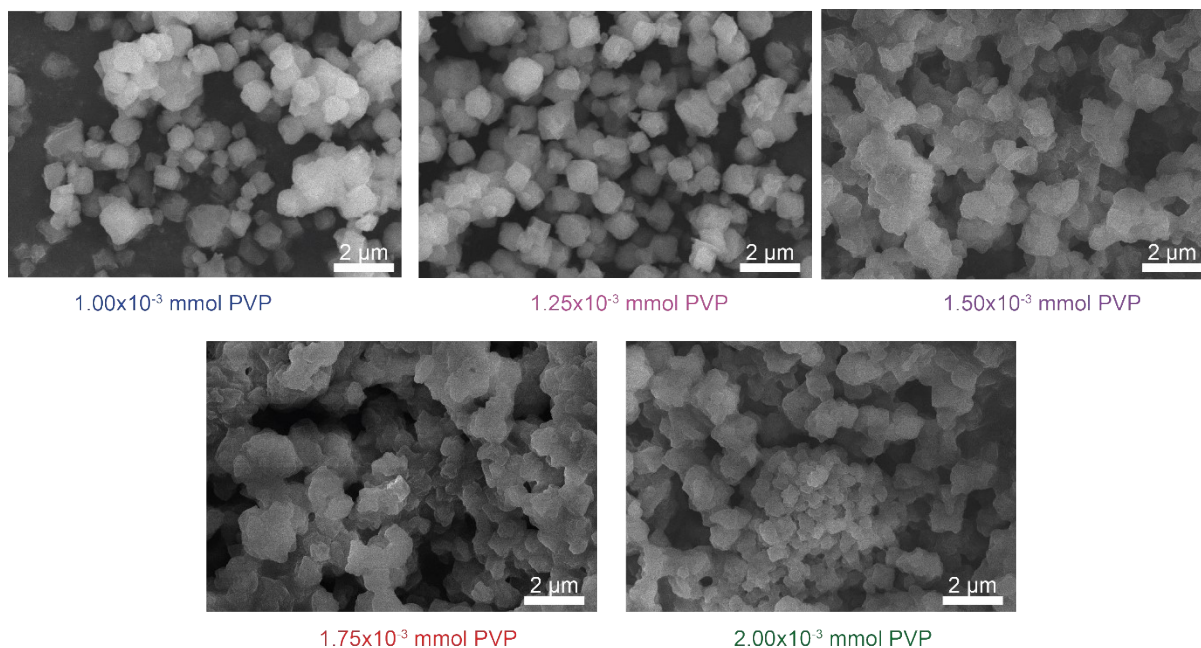


Figure S2. SEM images of b-Zn-BPDC nanoparticles at PVP screening.

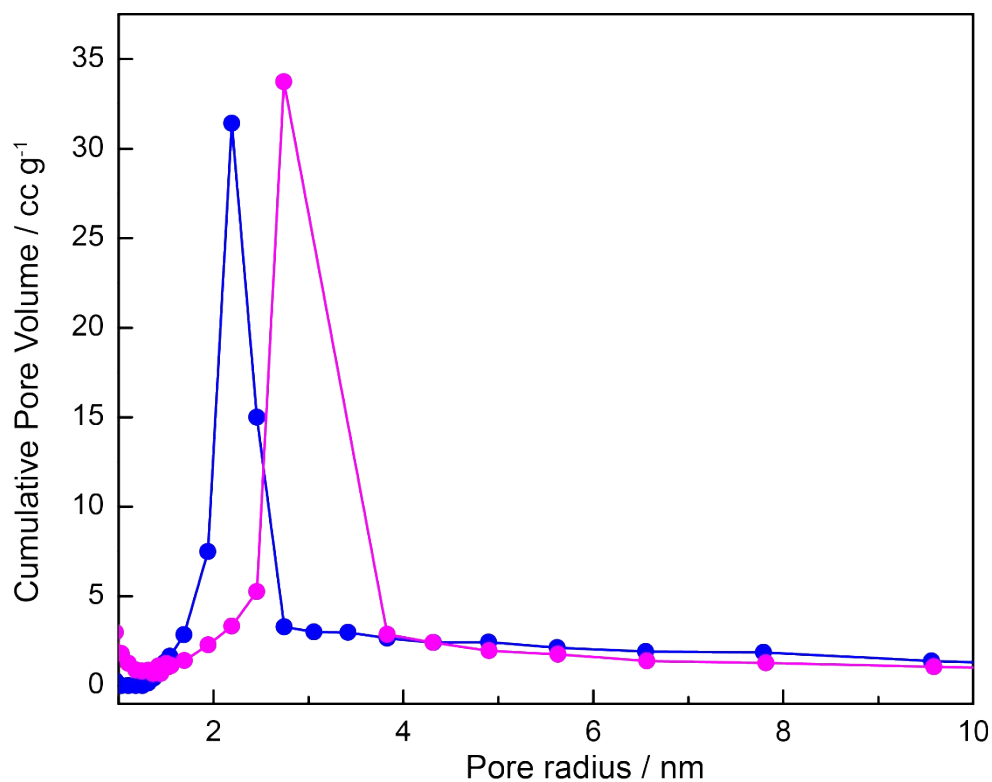


Figure S3. Pore size distribution of nano b-Zn-BPDC (blue), and nano b-Zn-azoBDC (magenta) from the Barrett-Joyner-Halenda (BJH) desorption isotherm analysis.

Section 3. Dynamic light scattering (DLS) measurements

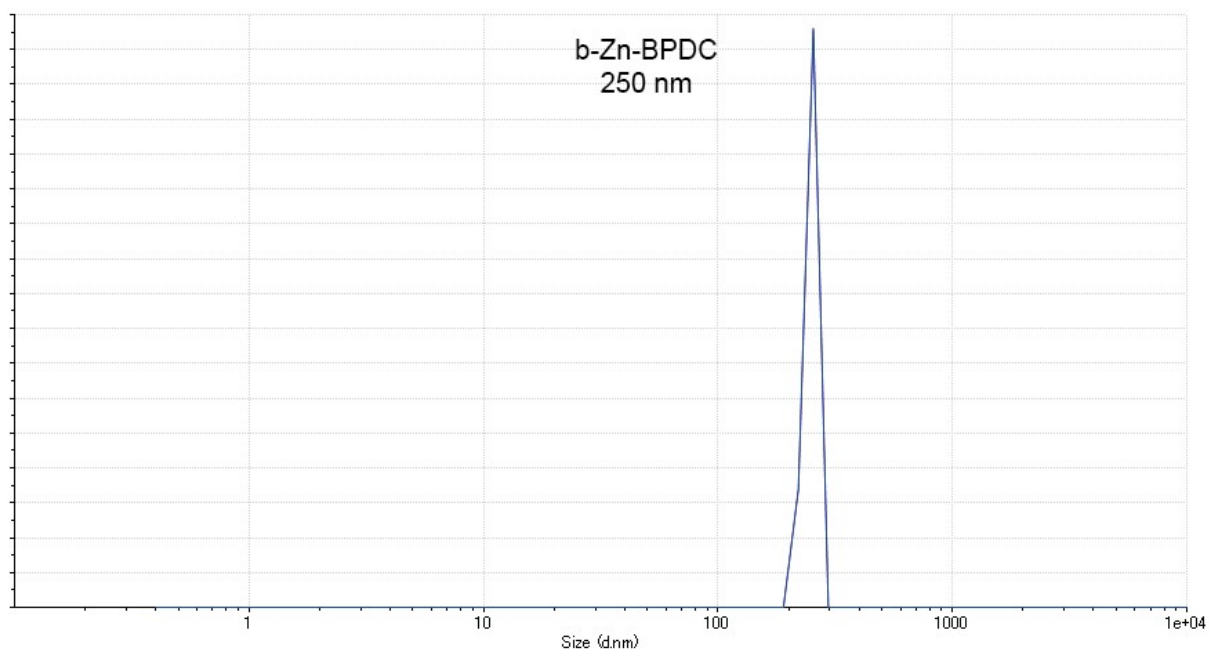


Figure S4. DLS of b-Zn-BPDC was analyzed by Zetasizer μ V Malvern apparatus.

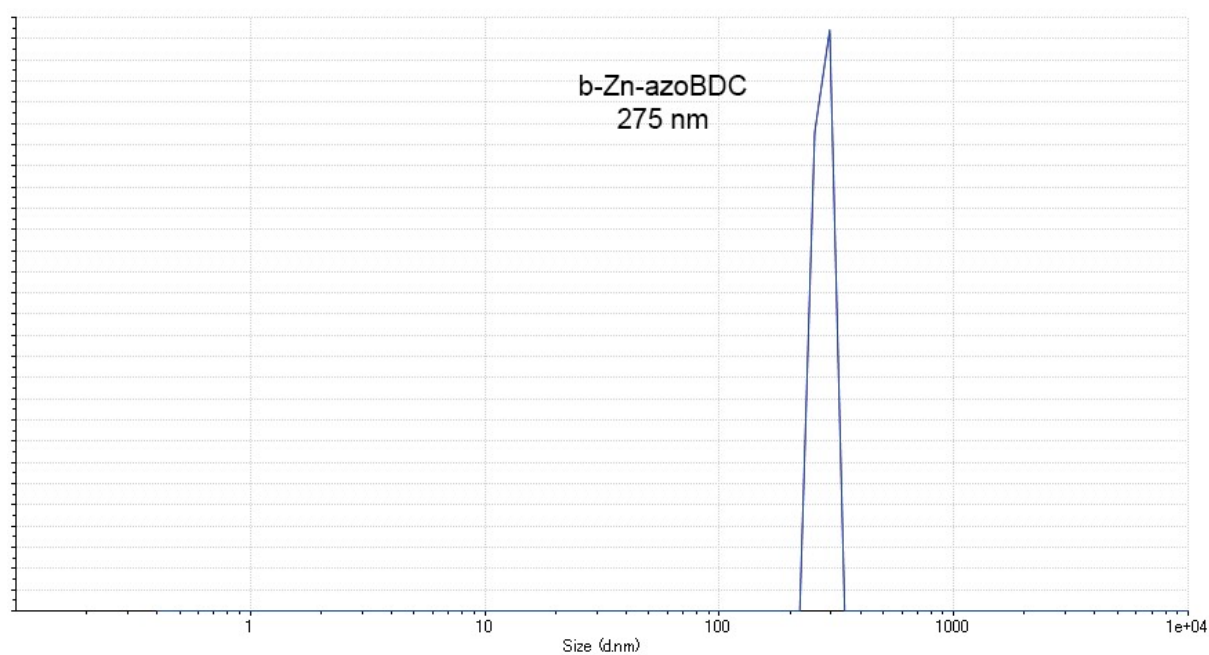


Figure S5. DLS of b-Zn-azoBDC was analyzed by Zetasizer μ V Malvern apparatus.

1. Hoang, L. T. M.; Ngo, L. H.; Nguyen, H. L.; Nguyen, H. T. H.; Nguyen, C. K.; Nguyen, B. T.; Ton, Q. T.; Nguyen, H. K. D.; Cordova, K. E.; Truong, T., An azobenzene-containing metal–organic framework as an efficient heterogeneous catalyst for direct amidation of benzoic acids: synthesis of bioactive compounds. *Chemical Communications* **2015**, *51* (96), 17132-17135.