

# Support Information of “Fluorescence and biological stabilization of phosphorous-functionalized mesoporous silica nanospheres modified with a bis(8-hydroxyquinoline) Zn complex”

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## 1. Materials and Methods

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**Figure S1:** N<sub>2</sub> adsorption (close circle) and desorption (open circle) isotherms of (a) 0.15Z/MPS, (b) 0.3Z/MPS, (c) 0.45Z/MPS, (d) 0.6Z/MPS, (e) 0.75Z/MPS, (f) 0.15Z/PMPS, (g) 0.3Z/PMPS, (h) 0.45Z/PMPS, (i) 0.6Z/PMPS and (j) 0.75Z/PMPS.

**Figure S2:** Low-angle PXRD patterns of (a) *n*Z/MPS and (b) *n*Z/PMPS. A broad diffraction peak observed in a range of  $2\theta = 1-4^\circ$  indicates presence of ordered porous structure with an interplanar  $d_{100}$  spacing.

**Figure S3:** (a) Variation in the molecular occupancy of Znq<sub>2</sub> for *n*Z/MPS and *n*Z/PMPS as a function of its equilibrium adsorption concentration. (b) Relation between the calculated molecular occupancy and BET surface area.

**Figure S4:** Fluorescence spectra of the Znq<sub>2</sub> solution and powder excited with  $\lambda_{\text{ex}} = 356$  nm.

**Figure S5:** N<sub>2</sub> adsorption (closed circle) and desorption (open circle) isotherms of (a) 0.75Z/MPS and (b) 0.75Z/PMPS, and (c) their  $S_{\text{BET}}$  values as a function of the SBF soaking time.

## 1. Materials and Methods

### 1.1 Preparation of the PMPS nanospheres

According to our previous report [1], the PMPS particles were synthesized. The copolymer comprising poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) with the formula of PEO<sub>20</sub>PPO<sub>70</sub>PEO<sub>20</sub> (43.1  $\mu$ mol), cetyltrimethylammonium bromide (670  $\mu$ mol), ethanol (19 mL), ultrapure water (40 mL) and 25 wt% aqueous ammonium solution (5.8 mL) were vigorously mixed at 40 °C. Tetraethyl orthosilicate (4.30  $\mu$ mol) and diethyl(2-bromoethyl)phosphonate of 0 or 25.8  $\mu$ mol were dissolved in the surfactant-dispersed solution. Here, the feed molar ratio of P to Si (P/Si) was 0 and 6, which were named as MPS and PMPS, respectively. The mixed solution was sealed in a stainless-steel hydrothermal synthesis reactor and hydrothermally treated at 100 °C with stirring. The white-colored precipitation was centrifuged, washed by ultrapure water, dried, and then calcined at 550 °C.

### 1.2 Chemisorption of Znq<sub>2</sub>

Adsorption of Znq<sub>2</sub> into the prepared mesoporous particles was conducted by admixture of them (dried at 393K for 2 h under dry air) with the ethanol solution of Znq<sub>2</sub> with different initial concentrations (0.15, 0.3, 0.45, 0.6, 0.75 mM: *n*) at room temperature for 3 h. The resulting particles were physically washed by ultrapure water and dried under reduced pressure for 1 day and were designated as *n*Z/MPS or *n*Z/PMPS. The adsorbed amount of Znq<sub>2</sub> on the particles was determined from the changes in the concentration of Znq<sub>2</sub> for the original complex solution before and after the adsorption experiment. The concentration of Znq<sub>2</sub> was determined from the absorbance spectra of Znq<sub>2</sub> in the ethanol solvent, recorded with a V-750 ultraviolet-visible (UV-vis) photospectrometer (JASCO, Japan). The adsorption amount at the equilibrium state (*W*) was

calculated using the equation (1) based on the adsorption isotherms. According to the Langmuir adsorption isotherm formula [2], the equation of state for the one-component adsorption can be represented as follows:

$$C / W = 1 / (K_{\text{eq}} \cdot W_{\text{max}}) + (1 / W_{\text{max}}) C \quad (1)$$

where  $C$ ,  $K_{\text{eq}}$  and  $W_{\text{max}}$  means the  $\text{Znq}_2$  concentration in the equilibrium state, the adsorption equilibrium constant and the maximum adsorption amount, respectively. The  $K_{\text{eq}}$  and  $W_{\text{max}}$  were determined from the slope of a  $C/W$  versus  $C$  plot. From the adsorbed amounts, the occupation molecular area of  $\text{Znq}_2$  in the mesopores was assumed and compared to the theoretical occupancy of the immobilized  $\text{Znq}_2$  evaluated from the gas-adsorption surface area analysis described below.

### 1.3 Stability tests in simulated body fluids

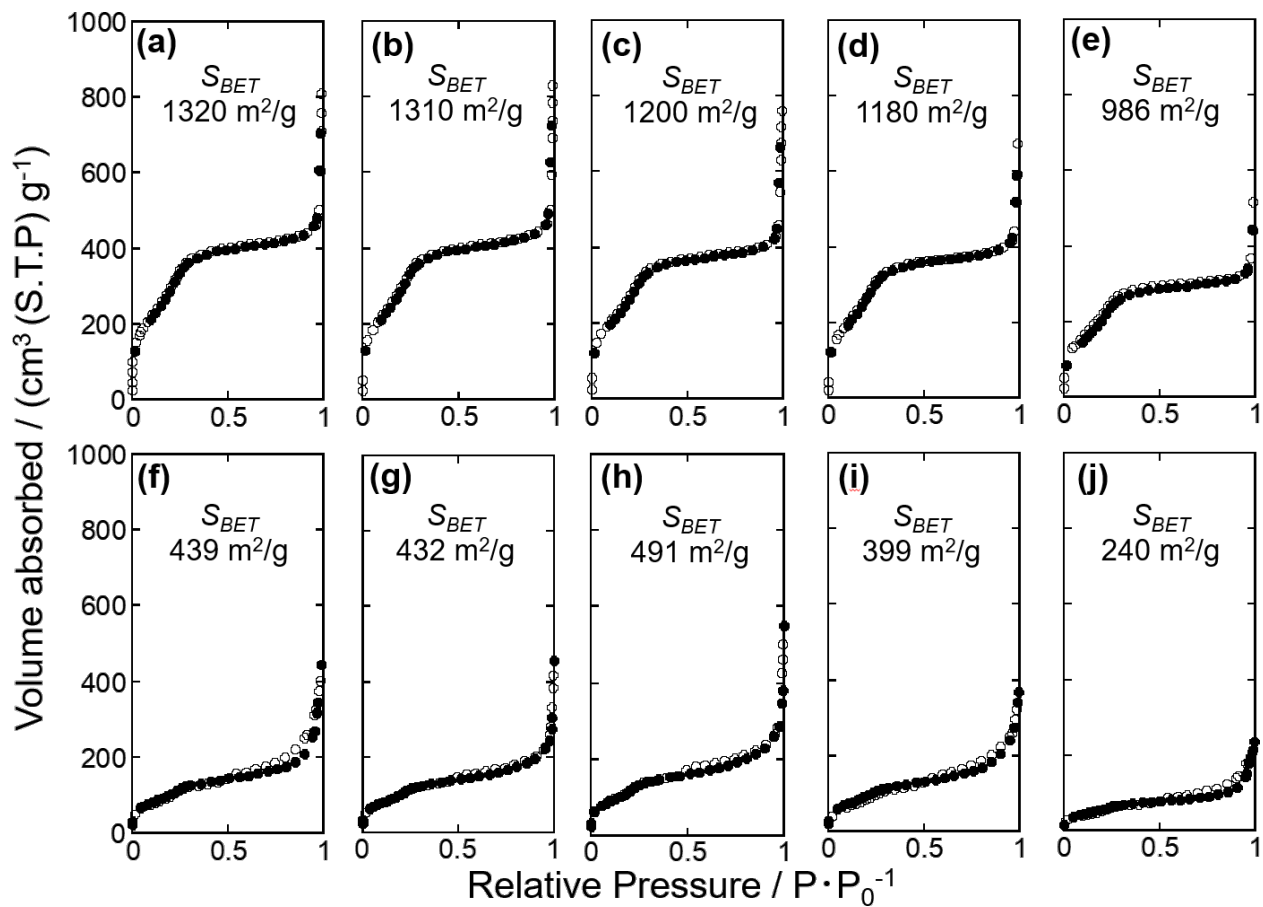
Chemical stability of the mesoporous particles was evaluated by immersing them into the body simulated fluid (SBF) solution. In this experiment, 0.1 g of the sample (0.75Z/MPS or 0.75Z/PMPS) was immersed in 3.75 mL of SBF containing 1.5 times ion concentrations (*i.e.*, 1.5 SBF) for 2, 6, 12, 24, 48 h at 37 °C. 1.5 SBF ( $\text{Na}^+$ , 213 mM;  $\text{K}^+$ , 7.5 mM;  $\text{Mg}^{2+}$ , 2.5 mM;  $\text{Ca}^{2+}$ , 3.8 mM;  $\text{Cl}^-$ , 222 mM;  $\text{HCO}_3^-$ , 6.3 mM;  $\text{HPO}_4^{2-}$ , 1.5 mM;  $\text{SO}_4^{2-}$ , 0.75 mM; Tris, 75 mM) was prepared according to the previous report [3], and the pH value was adjusted to be 7.4. The particles after the immersion times of  $Y$  h ( $Y = 0, 2, 6, 12, 24, 48$ ) were centrifuged and dried at 65 °C, and defined as 0.75Z/MPS- $Y$  for the 0.75Z/MPS particles, and as 0.75Z/PMPS- $Y$  for the 0.75Z/PMPS particles, respectively. For evaluating the eluted silicate ion concentration, the supernatant liquids were quantitatively analyzed using molybdenum-blue colorimetric method [4] using the UV-vis

photospectrometer. The calibration curve of the silicate ions dissolved in sodium carbonate solution at the absorbance at 590 nm were used for the standard data. The absorbance at no silicate ions in SBF was subtracted as the background from the resultant absorbance.

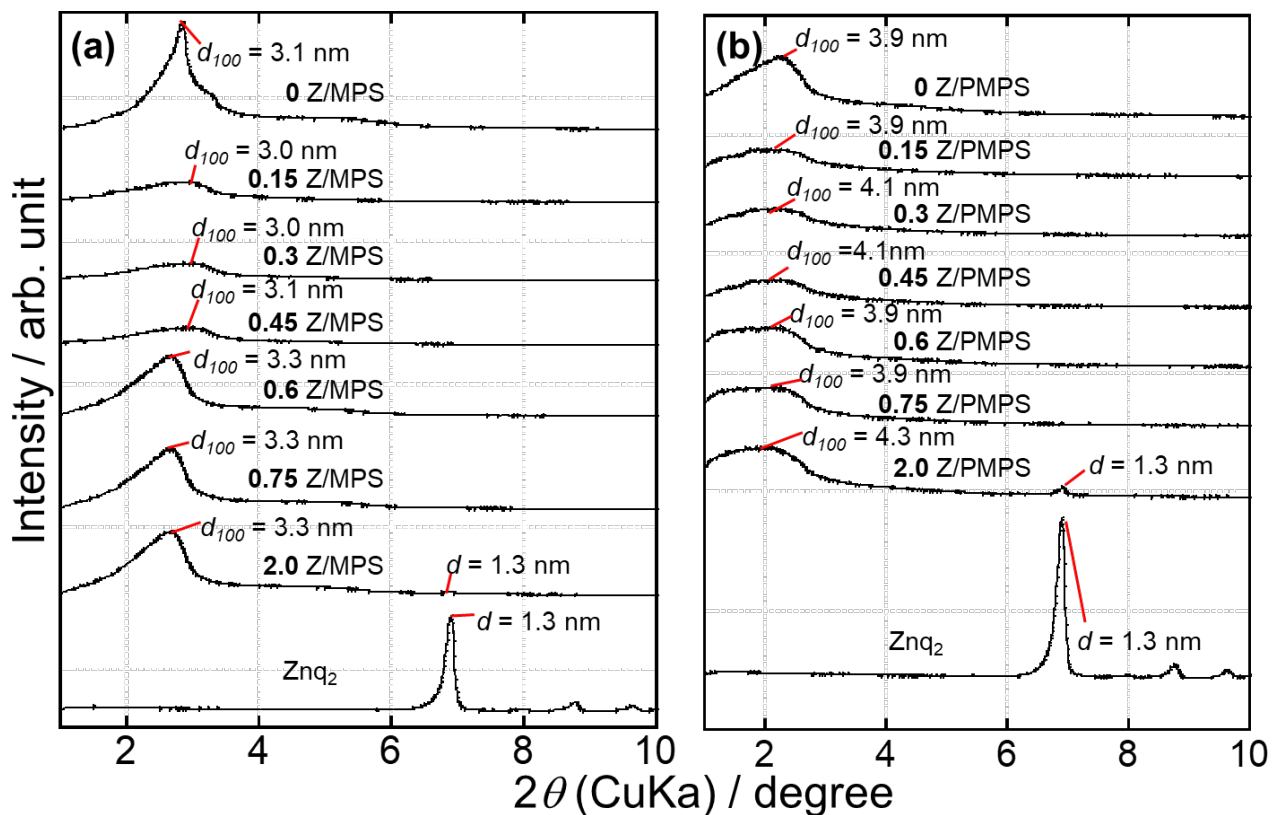
#### **1.4 Other characterization methods**

Characterization of the chemical bonding states was performed upon Fourier transform infrared (FT-IR) spectrometer FT/IR-4600ST (JASCO, Japan). For the analysis of the FT-IR spectra, the band peak due to siliceous bonding was deconvoluted by peak fitting with the Gaussian function using the SOLVER option in the software (Excel 2013). Then, center of wavenumber ( $x$ ) for each deconvoluted peak was optimized in the range of  $x \pm 5 \text{ cm}^{-1}$ , and full width at half maximum (FWHM) of each peak was also optimized under a restriction to unify them. Surface area of the prepared particles was determined from nitrogen ( $\text{N}_2$ ) adsorption and desorption instrument BELSORP-mini II (MicrotracBEL Corp., Japan). In the  $\text{N}_2$  adsorption and desorption experiments, Brunauer-Emmett-Teller (BET) [5] surface areas and Barrett-Joyner-Halenda (BJH) [6] pore sizes were calculated. The morphologies of the particles were observed using a FE-SEM SU8000 (Hitachi High-Technologies, Japan) and were defined as the averaged particle sizes and variation coefficients. The average size of the mesopores was characterized using an X-ray diffraction (XRD) spectrometer equipped with a  $\text{CuK}\alpha$  X-ray radiation source. Photoluminescence (PL) spectroscopy of the samples was recorded with a FP-8500 (JASCO, Japan) with an excitation wavelength at 356 nm.

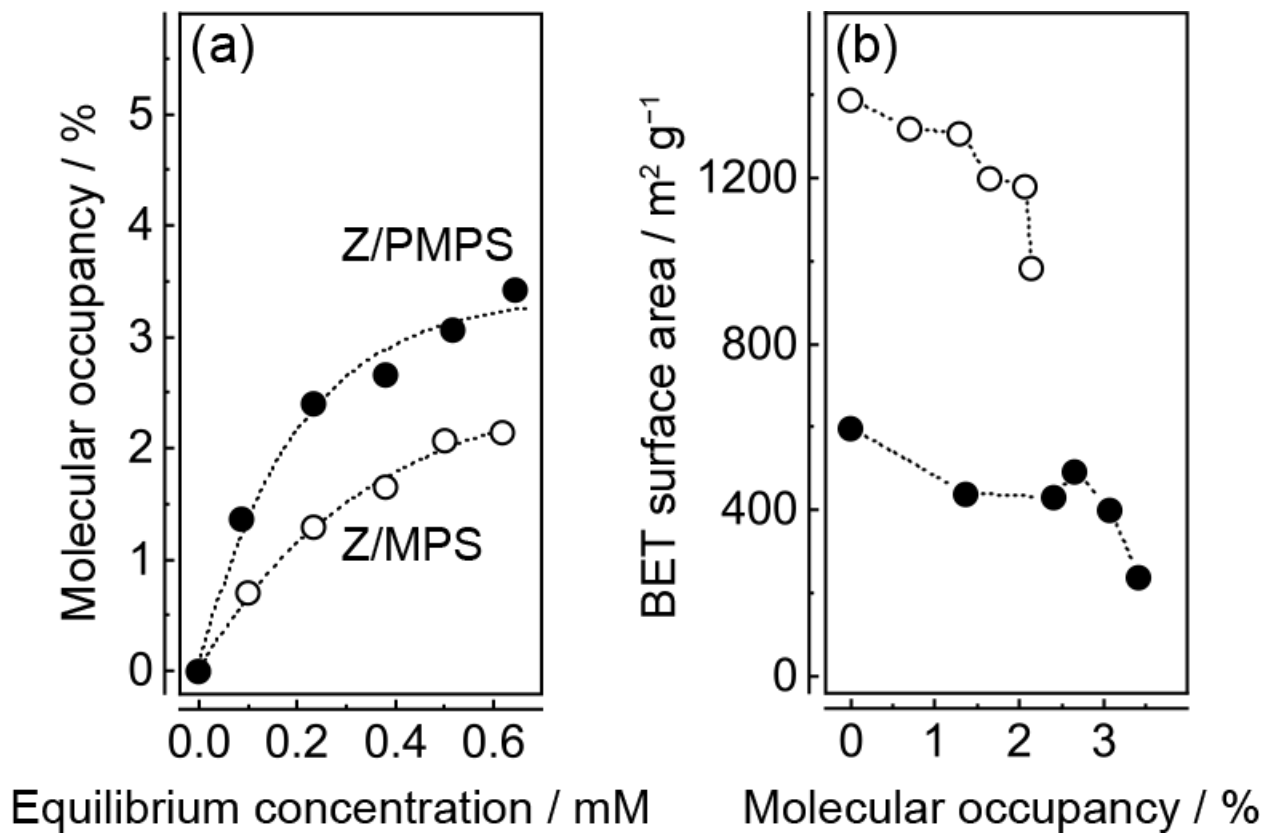
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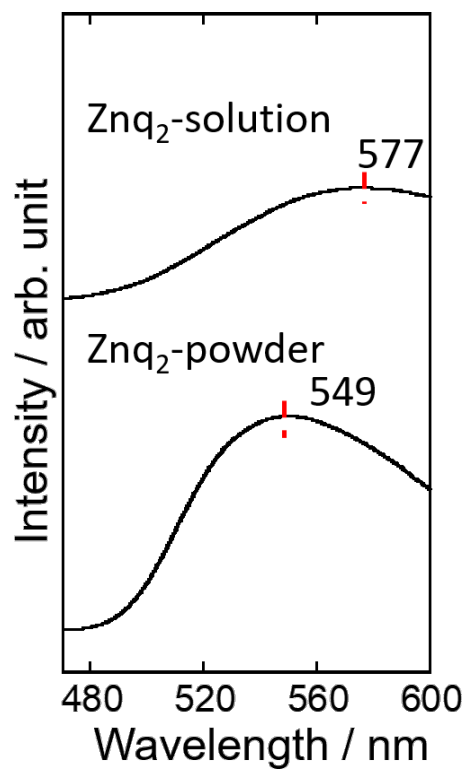


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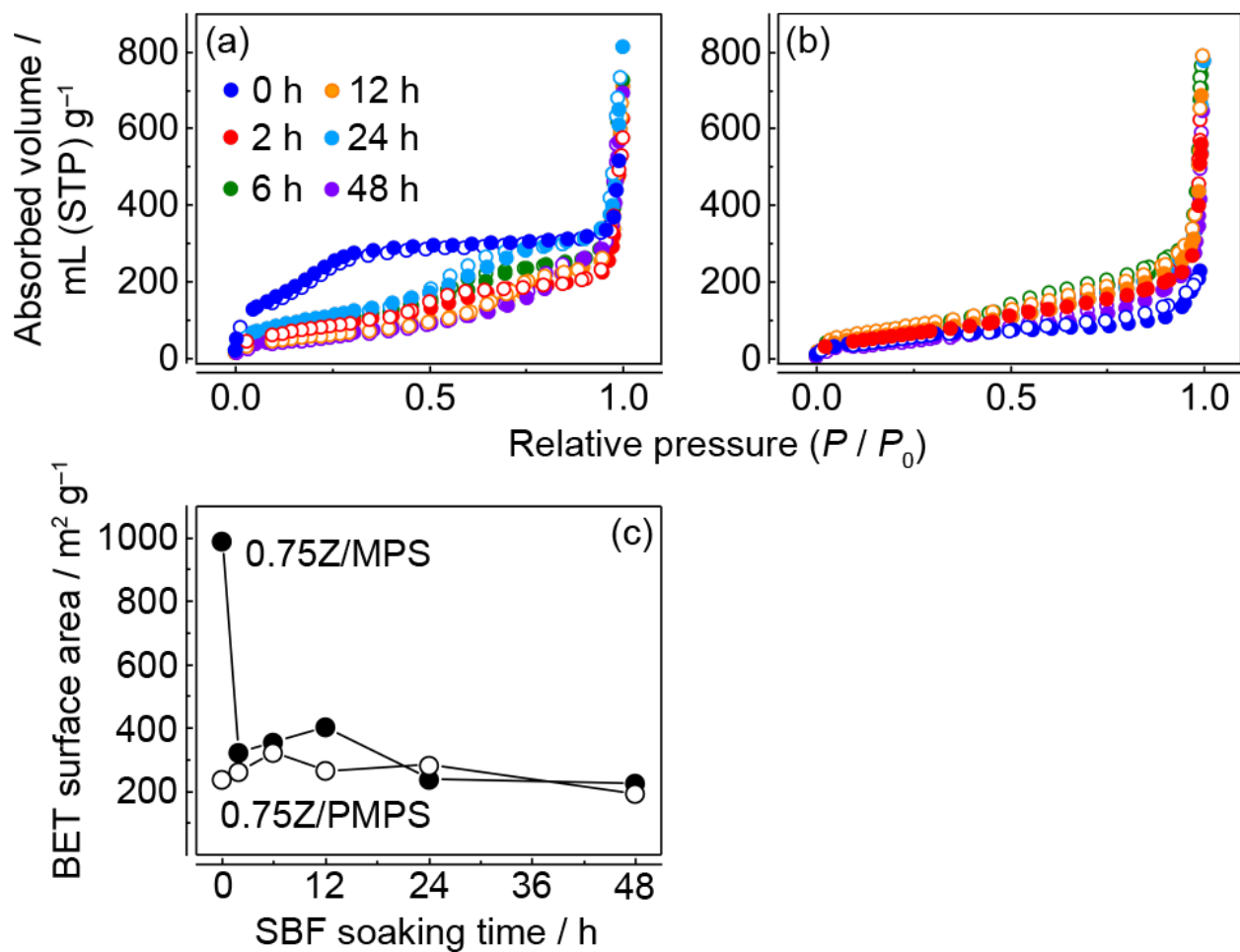


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## REFERENCES

- [1] S. Yamada, Y. Shang, I. Yamada, M. Tagaya, *Advanced Powder Technology*, 2019, **30**, 1116.
- [2] I. Abe, *Oleo Sci.*, 2002, **2**, 275.
- [3] T. Kokubo, H. Takadama, *Biomaterials*, 2006, **27**, 2907.
- [4] Y. Shang, S. Yamada, Y. Chai, M. Tagaya, *Key Eng. Mater.*, 2018, **782**, 59.
- [5] S. Brunauer, P.H. Emmett, E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, 309.
- [6] E.P. Barrett, L.G. Joyner, P.P. Halenda, *J. Am. Chem. Soc.*, 1951, **73**, 373.