

## IDENTIFICATION OF METALLOPORPHYRIN-CONTAINING COORDINATION POLYMER PARTICLES BY SURFACE-ENHANCED RAMAN SCATTERING THROUGH SURFACE METALLIZATION

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### Abstract

In this work, metalloporphyrin-containing coordination polymer particles (Z-CPPs) with 1D nanorod structures were synthesized by a surfactant-assisted self-assembly process. Furthermore, the identification of Z-CPPs in aqueous solution was achieved by surface-enhanced Raman scattering (SERS) through surface metallization. Our approach illustrates a novel method to detect coordination polymer particles in solution.

**Keywords:** Surface-enhanced Raman Scattering, Coordination Polymers, Surface Metallization, Metalloporphyrin

### 1. INTRODUCTION

Metal-organic interactions have been the focus of intense multidisciplinary research such as catalytic chemistry, materials science and molecular electronics. [1] Surface-enhanced Raman scattering (SERS) has been widely recognized as a powerful spectroscopic tool for studying molecular adsorbates on a metal surface due to its high surface sensitivity and accessibility to low wavenumber region, which gives direct information on metal-molecule interactions, even in IR-opaque media such as aqueous solutions. [2]

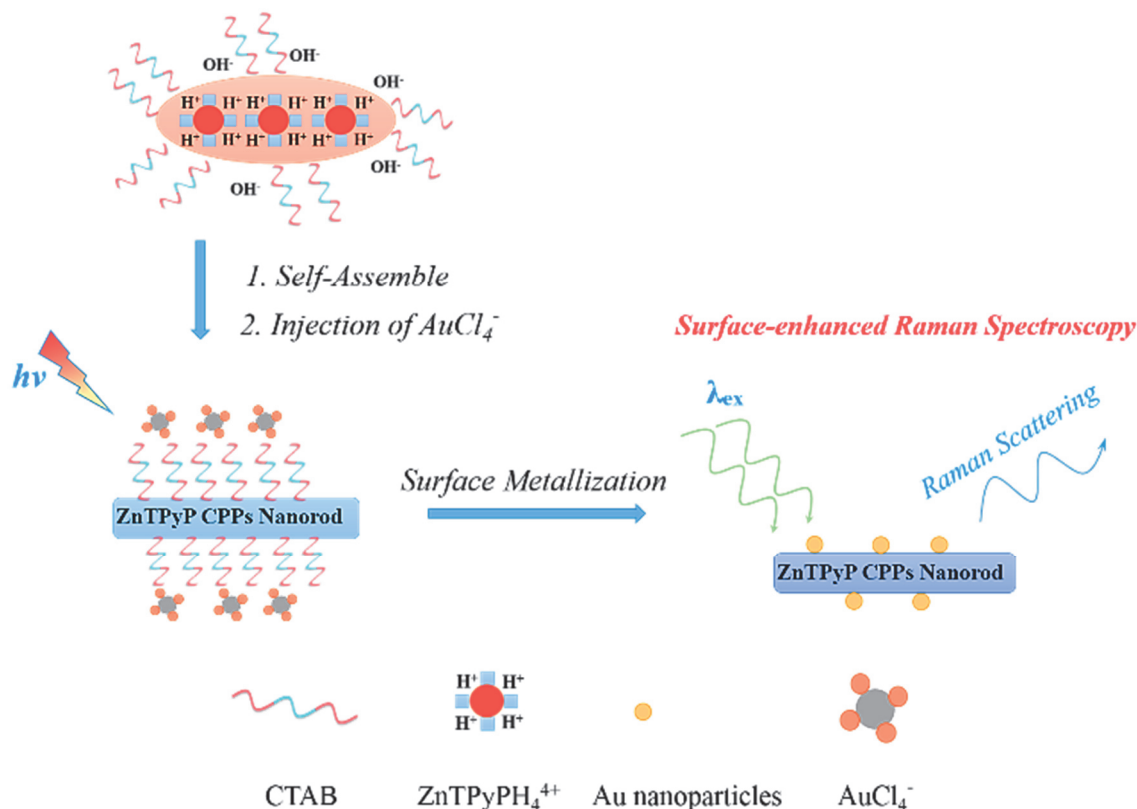


Fig. 1 Illustration of ZnTPyP-CPPs by surface-enhanced Raman scattering through surface metallization

The intensive research of metal-organic interactions by SERS detection has been focused on two different types: (1) molecular modification on substrates, including physical and chemical adsorption [3], and (2) molecular aggregation through self-assembly on substrates. [4]

On the other hand, metalloporphyrins are compounds formed by a combination of porphyrin and metal ions, playing an important role in catalysis, fluorescence, sensing, optical imaging, electronics, photochemistry and biological applications. [5]

Recently, many worldwide research groups reported that diverse metalloporphyrin-containing nano/micro-scale particles can be synthesized through a bottom-up self-assembly process assisted by surfactants, such as Pluronic F-127, SDS and CTAB. [6] However, less work has been dedicated to the identification of metalloporphyrin-containing CPPs in aqueous solution. In the present work, we chose a metalloporphyrin, zinc 5-, 10-, 15- and 20-tetra(4-pyridyl)-21H, 23H-porphyrin (abbreviated to ZnTPyP), to investigate the identification of metalloporphyrin-containing CPPs in aqueous solution by SERS methods (**Fig. 1**).

## 2. EXPERIMENTAL

### 2.1. MATERIALS

Zinc 5-, 10-, 15- and 20-tetra(4-pyridyl)-21H, 23H-porphine (ZnTPyP), Cetyltrimethylammonium bromide (CTAB), sodium tetrachloroaurate (III) dihydrate, ascorbic acid from Aldrich Chemical Co., Sodium hydroxide, hydrochloric acid from Wako Chemical were used without a further purification. All solvents were prepared by using Milli-Q water.

### 2.2. PREPARATION OF STOCK SOLUTIONS

As ZnTPyP does not readily dissolve in water, its homogeneous stock solution (0.01 M) was prepared by dissolving an appropriate amount of ZnTPyP in a HCl solution (0.2 M) to acidify the pyridyl groups, forming soluble tetrapyridium cations. The basic stock solution of surfactants was prepared by dissolving 0.01 M CTAB and 0.02 M sodium hydroxide in aqueous solution.

### 2.3. SYNTHESIS OF Z-CPPS AND Au-DECORATED Z-CPPS

An amount of 250  $\mu$ L of a ZnTPyP stock solution (0.01 M) was injected into 5 mL of basic stock solution with mild stirring for 12 h. Subsequently, 0.5 mL NaAuCl<sub>4</sub> (10 mM) and 1 mL ascorbic acid solution (0.1 M) were added into a as-prepared Z-CPPs solution. After continuous stirring for 30 min under visible light illumination, the mixed solution turned into dark red color, suggesting the formation of metal-decorated Z-CPPs.

### 2.4. CHARACTERIZATION

Powder X-ray diffraction data were collected by a Rigaku (D/MAX-2500/PC) diffractometer using Cu-K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) at room temperature. To prepare samples for the field-emission scanning electron microscopy (FE-SEM, TESCAN, MIRA3), the as-prepared ZnTPyP particles were first re-dispersed in pure water, then dropped onto silicon wafer substrate and finally dried at 50°C in the oven.

The procedures for TEM measurements were the same as that of the SEM measurement, except for dropping on Cu-grid. UV-vis absorption spectroscopy data (using Lambda 750 UV/VIS spectrometer, PerkinElmer) were also measured by re-dispersing particles in pure water. Raman measurements were performed using a Renishaw 2000 Raman microscope system (Renishaw, UK).

A Melles Griot He-Ne laser operating at  $\lambda = 785 \text{ nm}$  was used as excitation source, with a laser power of approximately 15 mW. The Rayleigh line was removed from the collected Raman scattering using a holographic notch filter located in the collection path. The Raman scattering was collected using a charge-coupled device (CCD) camera at a spectral resolution of 4  $\text{cm}^{-1}$ .

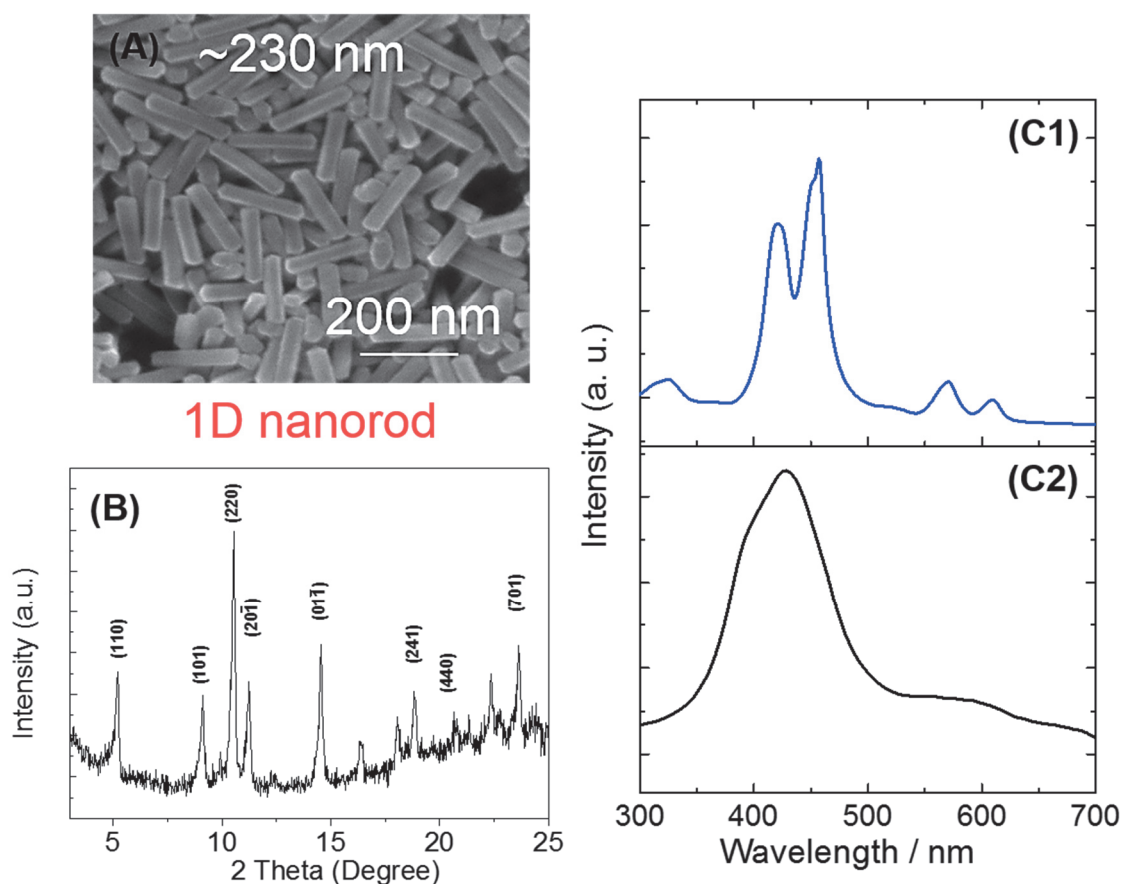
All spectra were calibrated to the 520 cm<sup>-1</sup> silicon line. An additional CCD camera was fitted to an optical microscope to obtain optical images. A 20× objective lens was used to focus a laser spot on the glass tube.

### 3. RESULTS AND DISCUSSION

The external morphology of the synthesized Z-CPPs was characterized by scanning electron microscopy (SEM). As shown in **Fig. 1(A)**, Z-CPPs nanorod structures with an average length of ~230 nm and width of ~60 nm were synthesized. The internal structures of the as-prepared Z-CPPs nanorods were investigated by X-ray diffraction (XRD) measurements (**Fig. 1(B)**), which are found to match well the simulated pattern based on the crystal structure of ZnTPyP compounds obtained by Goldberg and co-workers (CCDC ref. code YOVTOS). [7] This indicates that the crystal structure of the 1D nanorod structures have the *R3* space group.

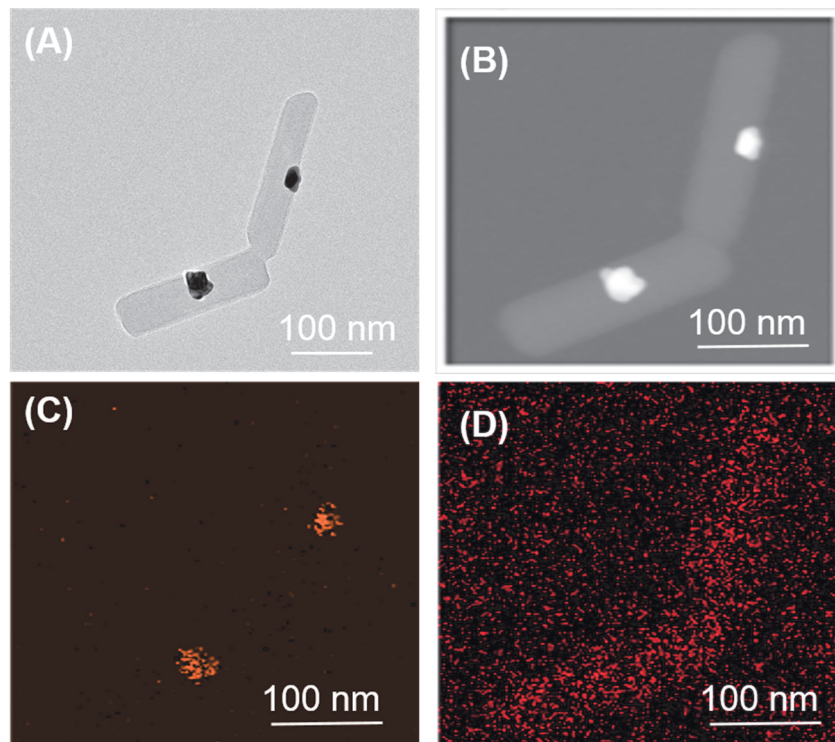
In these structures, the zinc atom at the center of ZnTPyP should be six-coordinated to four pyrrole nitrogens of the porphyrin core and to two pyridyl N-atoms of the other porphyrin molecules, which approach from both sides of the molecular frameworks. [8] As reported in our previous work [9], the electronic absorption properties of metalloporphyrins can be determined by UV-vis spectra due to their characteristic color derived from the highly conjugated  $\pi$ -electron systems.

As a reference, the electronic absorption spectrum of the ZnTPyP monomer was determined, showing a single Soret band at 426 nm and two weak Q-bands at 565 nm and 593 nm, respectively. The Soret band clearly splits into two bands with a relatively weak intensity appearing at 417 (blue-shifted) and one with a stronger intensity appearing at 447 nm (red-shifted). The former and latter Soret-band splits were ascribed to the transition moments parallel and perpendicular to the aggregate axis, respectively. We confirmed the aggregation type of ZnTPyP-CPPs synthesized in the presence of CATB is J-type aggregation. [9,10]

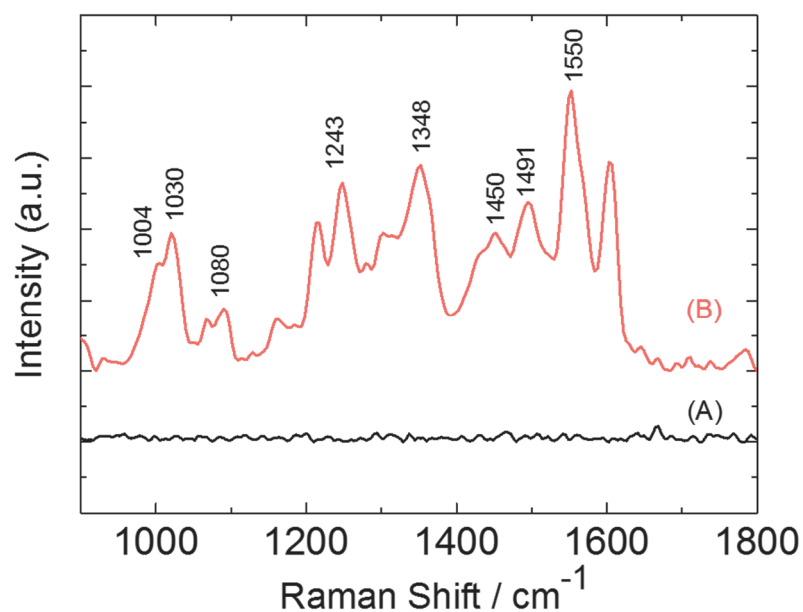


**Fig. 2** (A) SEM image and (B) XRD pattern of ZnTPyP-CPPs nanorod structures; UV-vis spectroscopy of (C1) ZnTPyP monomer and (C2) Z-CPPs nanorod structures

In order to synthesize metal-decorated Z-CPPs, ascorbic acid solution and  $\text{AuCl}_4^{2-}$  aqueous solution were added into Z-CPPs solutions. It is clearly shown that  $\text{AuCl}_4^{2-}$  complexes were reduced into Au nanoparticles on Z-CPPs nanorods under visible light illumination (**Figs. 2(A)** and **2(B)**). In our previous work, we confirmed that morphological transformation of Z-CPPs may occur by changing the solution pH, solution composition, temperature and so on. [9] The final experimental condition was fixed by a series experiments. As shown in **Figs. 2(C)** and **2(D)**, the mapping images for Au and carbon apparently revealed the gold nanoparticles formed on the surface of Z-CPPs nanorods.



**Fig. 3** (A) TEM image and (B) STEM image of Au-decorated Z-CPPs nanorod structures and elemental mapping data of (C) Au and (D) carbon



**Fig. 4** Raman spectra of (A) Z-CPPs and (B) Au-decorated Z-CPPs

Raman spectra of Z-CPPs and Au-decorated Z-CPPs are shown in **Figs. 4 (A)** and **(B)** respectively. It clearly revealed that no Raman spectra were detected for Z-CPPs in aqueous solution. However, after Au decoration on the surface of Z-CPPs nanorods, all characteristic group contributions (fingerprint) consistent with ZnTPyP structures were identified, including 1004 cm<sup>-1</sup> [ $\nu(\text{C}_\alpha\text{-C}_m)$ ], 1030 cm<sup>-1</sup> [pyrr  $\delta(\text{C-H})$ ], 1080 cm<sup>-1</sup> [ $\delta(\text{C}_\beta\text{-H})$ ], 1243 cm<sup>-1</sup> [ $\nu(\text{C}_m\text{-Pyrr})$ ] as well as the  $\phi$  stretch normal modes, 1384 cm<sup>-1</sup> [ $\nu(\text{C}_\alpha\text{-H})$ ], 1450 cm<sup>-1</sup> and 1491 cm<sup>-1</sup> [ $\nu(\text{C}_\alpha\text{-C}_\beta)$ ] and 1550 cm<sup>-1</sup> [ $\nu(\text{C}_\alpha\text{-C}_\beta)$  and ( $\text{C}_\beta\text{-C}_\beta$ ) stretch]. [4a]

#### 4. CONCLUSION

In this work, we introduced and described a novel method to identify CPPs in aqueous solution. Z-CPPs with 1D nanorod structures were synthesized through a bottom-up strategy assisted by CTAB as surfactants. UV-vis spectra confirmed that J-type aggregation exists in Z-CPPs nanorod structures. However, no Raman shift was observed for Z-CPPs nanorod structures.

After surface metallization by gold nanoparticles, identification of Z-CPPs nanorod structures was successfully achieved by Surface-enhanced Raman Spectroscopy (SERS). All characteristic group contributions (fingerprint) consistent with ZnTPyP structures were identified.

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#### REFERENCES

- [1] ULMAN A. Formation and Structure of Self-Assembled Monolayers. Chemical Review, Vol. 96, 1996, pp. 1533-1554. (b) WOLD D. J., FRISBIE C. D. Fabrication and Characterization of Metal-Molecule-Metal Junctions by Conducting Probe Atomic Force Microscopy. Journal of the American Chemical Society, Vol. 123, 2001, pp. 5549-5556. (c) XU B., TAO N. J. Measurement of Single-Molecule Resistance by Repeated Formation of Molecular Junctions. Science, Vol. 301, 2003, pp. 1221-1223.
- [2] HU J., TANABE M., SATO J., UOSAKI K., IKEDA K. Effects of Atomic Geometry and Electronic Structure of Platinum Surfaces on Molecular Adsorbates Studied by Gap-Mode SERS. Journal of the American Chemical Society, Vol. 136, 2014, pp. 10299-10307.
- [3] (a) IKEDA K, SATO J., UOSAKI K. Surface-enhanced Raman Scattering at Well-defined Single Crystalline Faces of Platinum-group Metals induced by Gap-mode Plasmon Excitation. Journal of photochemistry and photobiology A: Chemistry, Vol. 221, 2011, pp. 175-180; (b) IKEDA K, SATO J., FUJIMOTO N., HAYAZAWA N., KAWATA S, UOSAKI K. Plasmonic Enhancement of Raman Scattering on Non-SERS-Active Platinum Substrates. Journal of Physical Chemistry C, Vol. 113, 2009, pp. 11816-11821.
- [4] (a) CRISTESCU R., POPESCU C., POPESCU A. C., MIHAILESCU I. N., CIUCU A. A., ANDRONIE A., IORADACHE S., STAMATIN I., FAGADAR-COSMA E., CHRISEY, D. B. Functional Porphyrin Thin Films Deposited by Matrix Assisted Pulsed Laser Evaporation. Materials Science and Engineering B, Vol. 169, 2010, pp. 106-110; (b)
- [5] (a) KADISH K., SMITH K. M., GUILARD R. Porphyrin Handbook. Academic Press: New York, 1999; (b) CAMPBELL W. M., JOLLEY K. W., WAGNER P., WANGNER K., WALSH P. J., GORDON K. C., SCHMIDT-MENDE L., NAZEERUDDING M. K., WANG Q., GRATZEL M., OFFICER D. L. Highly Efficient Porphyrin Sensitizers for Dye-Sensitized Solar Cells. Journal of Physical Chemistry C, Vol. 111, 2007, pp. 11760-11762; (c) YAO C., YAN L., GUAN L., LIU C., SONG P., SU Z. Prediction of Second-order Optical Nonlinearity of Porphyrin-Metal-Polyoxometalate Sandwich Compounds, Dalton Transition, Vol. 39, 2010, pp. 7645-7649; (d) THUAGARIAJAN S., LEIDING T., ARSKOLD S. P., CHEPRAKOV A. V., and VINOGRADOV S. A., Highly Non-Planar Dendritic Porphyrin for pH Sensing: Observation of Porphyrin Monocation. Inorganic Chemistry, Vol. 49, 2010, pp. 9909-9920.
- [6] (a) ZHONG Y., WANG J. F., ZHANG R., WEI W. B., WANG H. M., Lu X. P., BAI F., WU. H. M., HADDAD. R., FAN. H. Y. Morphology-Controlled Self-Assembly and Synthesis of Photocatalytic Nanocrystals. Nano Letters, Vol. 14, 2014, pp. 7175-7179; (b) Bai F., WU H. M., HADDAD R. E., SUN Z. C., SAMANTHA K., SKOCYPEC V. R., Fan H. Y. Monodisperse Porous Nanodiscs with Fluorescent and Crystalline Wall Structure. Chemical Communication,

- Vol. 45, 2011, pp. 4941-4943; (c) QIU Y. F., CHEN P. L., LIU M. H., Evolution of Various Porphyrin Nanostructures via an Oil/Aqueous Medium: Controlled Self-Assembly, Further Organization, and Supramolecular Chirality. *Journal of the American Chemistry Society*, Vol. 132, 2010, pp. 9644-9652.
- [7] (a) IM S. H., JEONG U., XIA Y., Polymer Hollow Particles with Controllable Holes in their Surfaces. *Nature Materials*, Vol. 4, 2005, pp. 671-675; (b) KRUPITSKY H., STEIN Z., Goldberg I., STROUSE C. E. J. Crystalline Complexes, Coordination Polymers and Aggregation Modes of Tetra(4-pyridyl)porphyrin. *Journal of Inclusion Phenomena Molecular Recognition in Chemistry*, Vol. 18, 1994, pp. 177-192; (c) Lin K. J. SMTP-1: The First Functionalized Metalloporphyrin Molecular Sieves with Large Channels. *Angewandte Chemie International Edition*, Vol. 38, 1999, pp. 2730-2732.
- [8] SUN W., WANG H. L., QI D. D., WANG L., WANG K., KAN J. L., LI W. J., CHEN Y. L., JIANG J. Z. 5,10,15,20-tetra(4-pyridyl)porphyrinato Zinc Coordination Polymeric Particles with Different Shapes and Luminescent Properties. *CrystEngComm*, Vol. 14, 2012, pp. 7780-7786.
- [9] SUN Y., LI X. P., CARAVELLA A., GAO R. K. Controlled Formation of Fluorescent Metalloporphyrin-containing Coordination Polymer Particles from Seed Structures by Designed Shape-transformation Reactions. *Chemistry-A European Journal*, Vol. 21, 2015, pp. 6682-6685; (b) SUN. Y., YOO B. Y. Homogeneous Four-Petal Flower Structure Formation from Metalloporphyrin Self-assembly and its Reversible Transformation into an Octahedron Structures. *CrystEngComm*, Vol. 16, 2014, pp. 8950-8953; (c) SUN. Y., YOO B. Y. Designed Two-step Morphological Transformation: A New Strategy to Synthesize Uniform Metalloporphyrin-containing Coordination Polymer Particles. *New journal of Chemistry*, Vol. 39, 2015, pp. 3366-3370; (d) SUN. Y., YOO B. Y. Monitoring the Length-controlled Synthesis of One-dimensional Metalloporphyrin-containing Coordination Polymer Particles and their Photocatalytic Properties. *New journal of Chemistry*, Vol. 39, 2015, pp. 4218-4221; (e) SUN. Y., YOO B. Y. Morphological Transformation Reactions of Photocatalytic Metalloporphyrin-containing Coordination Polymer Particles from Seed Structures. *ChemistryOpen*, Vol. 4, 2015, pp. 438-442.