

Facile synthesis of size-tunable micro-octahedra *via* metal–organic coordination†

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Single-crystalline micro-octahedra of Zn(PyrPy)₂ with tunable sizes have been synthesized by manipulating the reaction kinetics of metal–organic coordination.

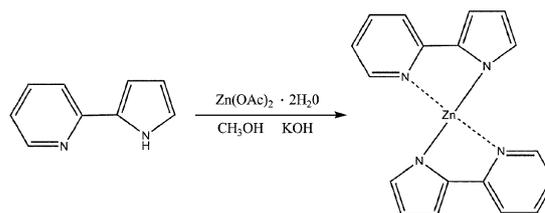
Micro- and nanosized particles of organic and inorganic materials have attracted tremendous interests in different areas, including optoelectronic,¹ catalysis,² biosensing,³ and so on. As a subset of these materials, organometallic compounds, consisting of polydentate organic ligands coordinated to metal ions, are being fabricated into nano- or microparticles due to their characteristic properties and wide-ranging potential applications.⁴ In addition, an appealing feature is that their chemical and physical properties can be manipulated through a combination of specific organic ligands and metal ions.

Recently, synthetic approaches have been developed for the preparation of amorphous particles from infinite metal–organic coordination polymers.⁵ Additionally, our group demonstrated the preparation of organic nanoparticles by employing a colloidal chemical reaction method.⁶ To the best of our knowledge, direct fabrication of size-tunable organometallic microparticles *via* a chemical reaction method remains a great challenge. Many chemical reaction syntheses are conducted in the solution phase in which the reactant precursors are well dissolved and the target product is generated as a precipitate. The homogeneous solution phase makes it possible to continuously tune the supersaturation during precipitation of the target product.⁷ We expect that the adjustment of the reaction conditions will pave the way for manipulating the precipitation process of the target product and thus the resultant microparticles. In this paper, by employing the metal–organic coordination reaction method, we demonstrate for the first time the direct fabrication of organometallic microparticles composed of the zinc complex (bis(2-(2′pyridyl)pyrrolyl)zinc, Zn(PyrPy)₂). The large-scale

synthesis of Zn(PyrPy)₂ ranging from 5 to 75 μm is achieved by simple addition of a basic solution to a precursor solution of metal ions and organic ligands. The particle size can be easily tuned by changing the concentration of the reaction solution.

2-(2′-Pyridyl)pyrrole (HPyrPy) was synthesized from 2-acetylpyridine and acetylene by the Trofimov reaction.⁸ This ligand is rarely reported in the literature. It has a mono-anionic, bidentate coordination mode and steric profile. Its structure was fully characterized by MS, ¹H NMR and ¹³C NMR spectroscopy (ESI† Fig. S1–S3). In 1927 and 1971, the zinc complex (bis(2-(2′pyridyl)pyrrolyl)zinc) was synthesized by a harsh low-yielding solvothermal method.⁹ Here in this paper, mild reaction conditions were utilized, which will hopefully lead to a wider exploration of PyrPy complexes. The zinc complex was prepared in yields of 82–90% by the reaction of PyrPy with zinc acetate (Zn(OAc)₂·2H₂O) in methanol under basic conditions (Scheme 1). In a typical experiment, a solution of Zn(OAc)₂·2H₂O in methanol was added to a solution of the ligand in methanol and the mixture was stirred for 1 h at room temperature. After a solution of KOH in methanol was added, the mixture was continuously stirred for several minutes. The newly generated Zn(PyrPy)₂ molecules undergo nucleation and growth, giving rise to microparticles, and yellow precipitates were obtained. The solid was filtered off, washed with methanol, and dried *in vacuo*. The resulting particles formed *via* metal–organic coordination of the PyrPy ligands with the Zn ions of the acetate salt. MALDI-TOF mass spectroscopy (ESI† Fig. S4) was found to be especially informative in identifying the above reaction products. A peak at *m/z* = 351 was assigned to the bidentate complex with a ligand–metal ratio of 2 : 1. The structure of the zinc complex was also characterized by ¹H and ¹³C NMR spectroscopy (ESI† Fig. S5 and S6).

Crystals suitable for an X-ray analysis were grown from CH₂Cl₂–CH₃OH solution and an ORTEP view of the zinc complex is shown in Fig. 1.† The crystallographic data and structure analysis for zinc complex is summarized



Scheme 1 The synthesis of Zn(PyrPy)₂.

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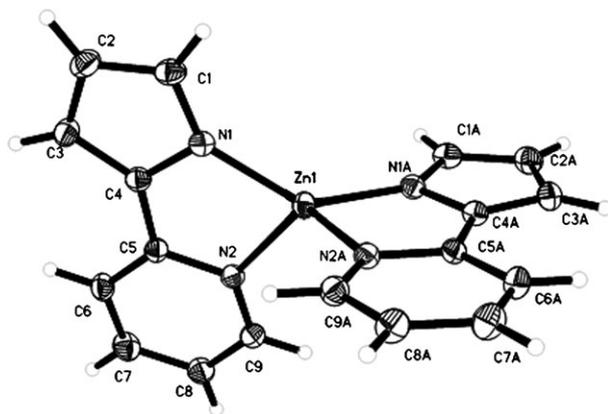


Fig. 1 ORTEP drawings of Zn(PyrrPy)_2 , as determined by X-ray diffraction.

in Table S1 (ESI,†). The coordination geometry around the metal center is distorted tetrahedral with two organic ligands in the asymmetric unit. The dihedral angles between N–Zn–N planes around the same metal center are 80.16° , indicating deviation from the ideal tetrahedral geometry. The ligand unit in the complex is planar, as expected through conjugation. The bite angle is found to be $84.40(7)^\circ$. The bond lengths are $1.9513(18) \text{ \AA}$ for the Zn–N(pyrrole) bond and $2.0444(18) \text{ \AA}$ for the Zn–N(pyridine) bond.

The Zn(PyrrPy)_2 microparticles were prepared as in aforementioned control experiments. By changing the concentration of the reaction solution, the particle size can be easily tuned. In our experiments large-scale synthesis of microparticles ranging from 5 to $75 \mu\text{m}$ has been achieved. The morphologies and sizes of the as-prepared Zn(PyrrPy)_2 microparticles were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4300). Typical FE-SEM images are shown in Fig. 2 in which the mean sizes are 5, 25 and $75 \mu\text{m}$, respectively (further FE-SEM images are shown in ESI,† Fig. S7–S9 with a mean size of 5, 25 and $75 \mu\text{m}$, respectively). It can be seen from Fig. 2 that the

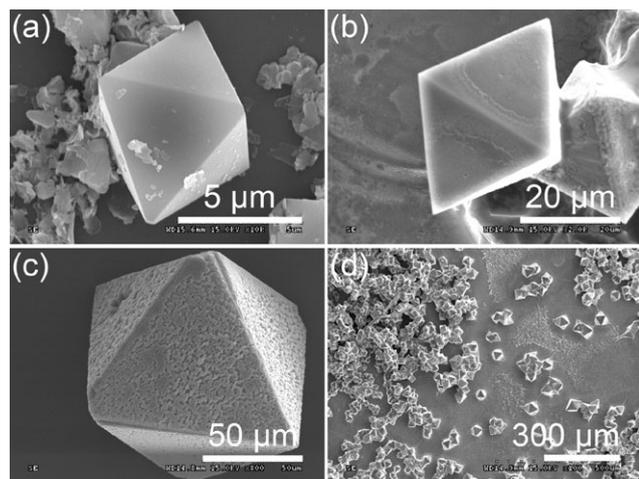


Fig. 2 Typical FE-SEM images of Zn(PyrrPy)_2 micro-octahedra with a size of (a) $\sim 5 \mu\text{m}$ at $C = 20 \text{ mM}$, (b) $\sim 25 \mu\text{m}$ at $C = 16 \text{ mM}$, (c) $\sim 75 \mu\text{m}$ at $C = 9 \text{ mM}$, and (d) low magnification FE-SEM image of (b).

microparticles obtained in all cases are octahedral, showing clear boundaries. The majority of the sample is disordered in Fig. 2(a), because the yield is very low in the case of $C = 20 \text{ mM}$. Fig. 2(d) shows a low-magnification SEM image of the sample synthesized at 16 mM . The micro-octahedra have a uniform side length of $\sim 25 \mu\text{m}$. The high-magnification SEM images (Fig. 2(a–c)) of some micro-octahedra indicate that they have highly regular octahedral geometric shape. Each micro-octahedron has eight regular facets. The energy dispersive X-ray (EDX) spectrum (ESI,† Fig. S10) of a micro-octahedron shows obvious peaks of the elements C, N and Zn which is consistent with the Zn(PyrrPy)_2 molecules ($\text{C}_{18}\text{H}_{14}\text{N}_4\text{Zn}$). Therefore, the result implies that the prepared micro-octahedra are composed of Zn(PyrrPy)_2 molecules.

XRD experiments were performed to further investigate the crystal structure of the Zn(PyrrPy)_2 micro-octahedra. The comparison among the XRD profiles of micro-octahedra of different sizes and simulated powder pattern in Fig. 3 provides a clue for us to understand the molecular packing at the microscale regime. The simulated powder pattern of Zn(PyrrPy)_2 is obtained by using the program MERCURY based on the single-crystal structure data. It can be seen that the diffraction peaks observed for micro-octahedra can be perfectly indexed to the single-crystal data, confirming the microstructures consisted of pure Zn(PyrrPy)_2 . Two distinct strong peaks corresponding to (102) and (113) planes are clearly observed in the diffraction profiles of micro-octahedra with three different sizes. With the size increasing, the peak corresponding to (113) plane becomes relatively weaker compared with the peak corresponding to the (102) plane. In addition, the area under the peak corresponding to the (113) plane changes as the particle size changes. It is likely due to preferred packing of (102) plane as the particle size increased and we believe that the micro-octahedra of $75 \mu\text{m}$ are most close to bulk crystals among the three.

The free ligand has absorbance maxima at 292 and 312 nm and an emission maximum at 396 nm in CH_2Cl_2 (ESI,† Fig. S11 and S12). It was reported previously by Perry

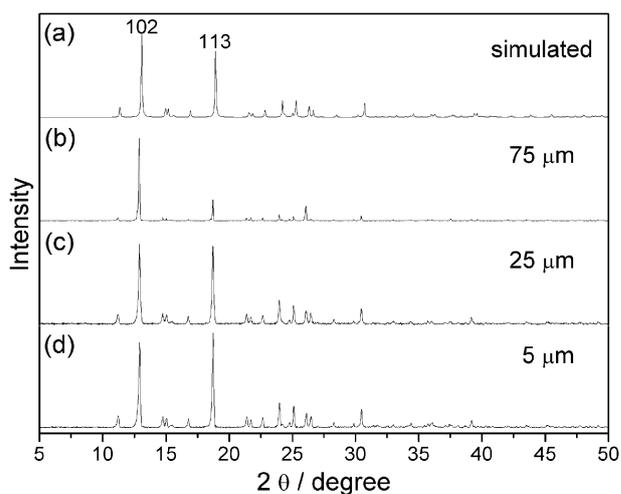


Fig. 3 XRD patterns of Zn(PyrrPy)_2 micro-octahedra with size of ~ 5 , ~ 25 and $\sim 75 \mu\text{m}$ and simulated powder pattern from crystal structure data of Zn(PyrrPy)_2 .

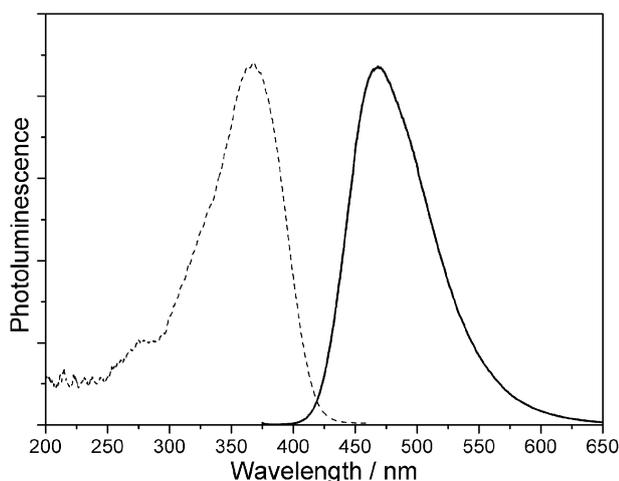


Fig. 4 Excitation (dashed line) and emission (solid line) spectra of Zn(PyPy)₂ in dichloromethane (10⁻⁵ M).

and Weber^{9b} that the Zn(PyPy)₂ has absorbance maxima at 325 and 378 nm, which is consistent with our findings. Comparing the electronic absorption of free ligand with that of zinc complex in CH₂Cl₂ (ESI,† Fig. S12), it is found that the enhancement of absorption at 366 nm indicates a strong interaction between the ligand and zinc center.

The zinc complex reveals one emitting band with a maximum at 468 nm (Fig. 4), which is consistent with emission from one excited state. The photoluminescence (PL) quantum yield (QY) was determined using 9,10-diphenylanthracene as a standard in cyclohexane ($\Phi = 1.00 \pm 0.05$ at an excitation wavelength of 366 nm).¹⁰ The QY of Zn(PyPy)₂ in CH₂Cl₂ is 0.66 ± 0.03 , while the substituted pyridylpyrrole zinc complexes show diminished QYs.¹¹ The origin of the higher QY for Zn(PyPy)₂ is presumably attributable to absence of steric bulk of the substituted group which leads to the higher degree of coplanarity. The crystal structure of Zn(PyPy)₂ shows that the angle between the ligand rings, as measured by the N–C–C–N torsion angle, is only 0.79°.

For Zn(PyPy)₂ micro-octahedra with a mean size of 75 μm and of a solution of 1×10^{-7} M, non-monoexponential PL decay is observed (ESI,† Fig. S13). The PL lifetimes are listed in Table S2 of ESI.† The PL decay for Zn(PyPy)₂ micro-octahedra with a mean size of 75 μm is a little faster than that of solution, with a fast-decay component of ~0.47 ns and a ~4.36 ns component with a relative amplitude of 0.65. A fast-decay component of ~0.88 ns is observed in the PL decay for Zn(PyPy)₂ solution of 1×10^{-7} M, along with a dominant ~4.03 ns component (with a relative amplitude of 0.82). We could roughly estimate the QY of micro-octahedra on the basis of $\Phi_{\text{octahedron}} = \Phi_{\text{solution}} \tau_{\text{octahedron}} / \tau_{\text{solution}}$. The close values of τ for micro-octahedra and solution suggests a high QY of micro-octahedra ($\Phi_{\text{octahedron}} \approx 0.57$), because the QY of Zn(PyPy)₂ solution is very high. High QY in the solid

state will enable Zn(PyPy)₂ to be used as a building block for future miniaturized photonic devices.

In summary, a facile chemical reaction method has been developed to synthesize Zn(PyPy)₂ micro-octahedra with regular shape and good crystallinity. Direct fabrication of size-tunable Zn(PyPy)₂ micro-octahedra is easily achieved by manipulating the reaction kinetics of metal–organic coordination. The crystallographic data and structure analysis for Zn(PyPy)₂ are reported for the first time. XRD experiments show that the prepared micro-octahedra have good crystallinity. We have roughly estimated a very high QY for micro-octahedra according to the close values of τ for micro-octahedra and solutions. The results presented in this paper will enable scientists to explore novel applications in the field of photonic devices.

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Notes and references

† Crystal data for Zn(PyPy)₂: C₁₈H₁₄N₄Zn, $M_r = 351.70$, tetragonal, space group $P4_12_12$, $a = 8.2425(12)$, $b = 8.2425(12)$, $c = 23.659(5)$ Å, $V = 1607.3(5)$ Å³, $T = 173(2)$ K, $Z = 4$, $\mu(\lambda) = 0.71073$ Å⁻¹ = 1.532 mm⁻¹, $D_c = 1.453$ g cm⁻³.

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