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Electronic Supplementary Information (ESI)

Facile synthesis of size-tunable micro-octahedrons via metal-organic coordination

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Experimental section

A. Materials

All starting materials were purchased from Aldrich Co., Germany and used without further purification. The solvents methanol, dichloromethane were purchased from Beijing Chemical Co., China.

B. Measurements

The ESI-MS measurements were carried out with a Brucker APEX II instrument. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance dpx 300 MHz instrument using TMS as internal standard. The morphologies and sizes of the as-prepared $Zn(PyrPy)_2$ micro-octahedrons were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4300) at an accelerating voltage of 15 kV. To minimize sample charging, a thin layer of Pt was deposited onto the samples before SEM examination. Energy-dispersive X-ray analysis (EDX) were carried out by using a Hitachi, S-4300 equipped with an energy-dispersive X-ray detector. X-ray diffraction (XRD) measurements were performed by using a Rigaku X-Ray Diffractometer (D/max-2400) with an X-ray source of Cu Kα (l = 1.5406 Å) at 40 kV and 120 mA, at a scan rate of 0.028 (2θ) per 0.12 s.

The stationary UV-visible absorption spectra of the $Zn(PyrPy)_2$ solution was measured on a Perkin-Elmer Lambda 35 spectrometer with a scanning speed of 480 nm/min and a slit width of 1 nm. The stationary fluorescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer using a right angle configuration. Slits were set to provide widths of 5 nm for both the excitation and the emission monochromators. Cuvettes with a 1 cm path length were used. All the spectroscopic measurements were carried out at room temperature.

Photoluminescence (PL) kinetics were measured using the time-resolved fluorescence spectrometer. Briefly, PL collected with the 90-degree-geometry was dispersed by a polychromator (250is, Chromex) and collected with a photon-counting type streak camera (C5680, Hamamatsu Photonics). Streak camera used a Ti:Sapphire femtosecond laser system running at 1 KHz. The system's output wavelength was set to the desired excitation at 360 nm by using an optical parameter amplifier (OPA800-CF,

Spectra-Physics). The time-resolved spectra were recorded with a temporal resolution of about 100 ps and a spectral resolution of 2 nm. The excitation pulse energy was about 100 nJ/pulse which was focused onto a spot 0.5 mm in diameter. To optimize the signal-to-noise ratio, 4000 photon counts were collected. The data detected by digital camera (C4742-95, Hamamatsu) was rountinely transferred to PC for analysis with HPDTA software. All the spectroscopic measurements were carried out at room temperature.

Crystals suitable for X-ray diffraction studies were grown from CH_2Cl_2–CH_3OH solution. Accurate unit cell parameters were determined by a least-squares fit of 2θ values, measured for 200 strong reflections, and intensity data sets were measured on a Bruker Smart 1000 CCD or Rigaku R-AXIS Rapid IP diffractometer with Mo Kα radiation (λ = 0.71073 Å) at room temperature. The intensities were corrected for Lorentz and polarization effects, but no corrections for extinction were made. Crystal structure was solved by direct methods. Crystallographic data and experimental details for structure analyses are summarized in Table S1.

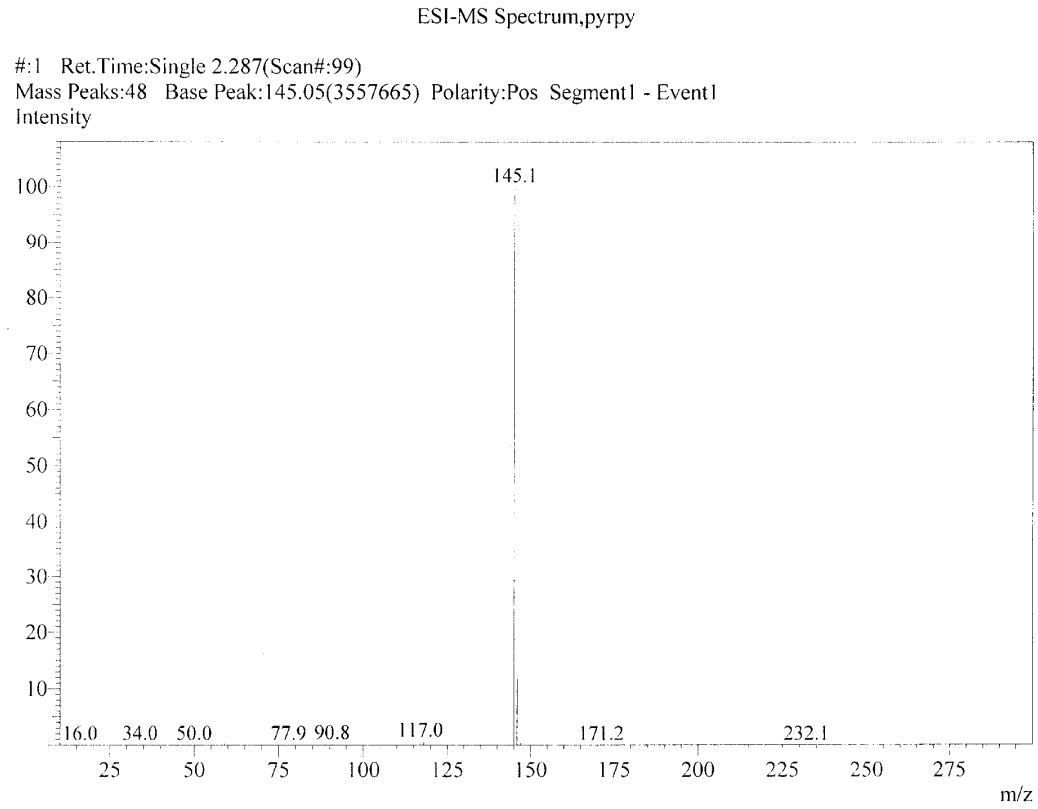

Fig. S1 Mass spectrum of PyrPy.

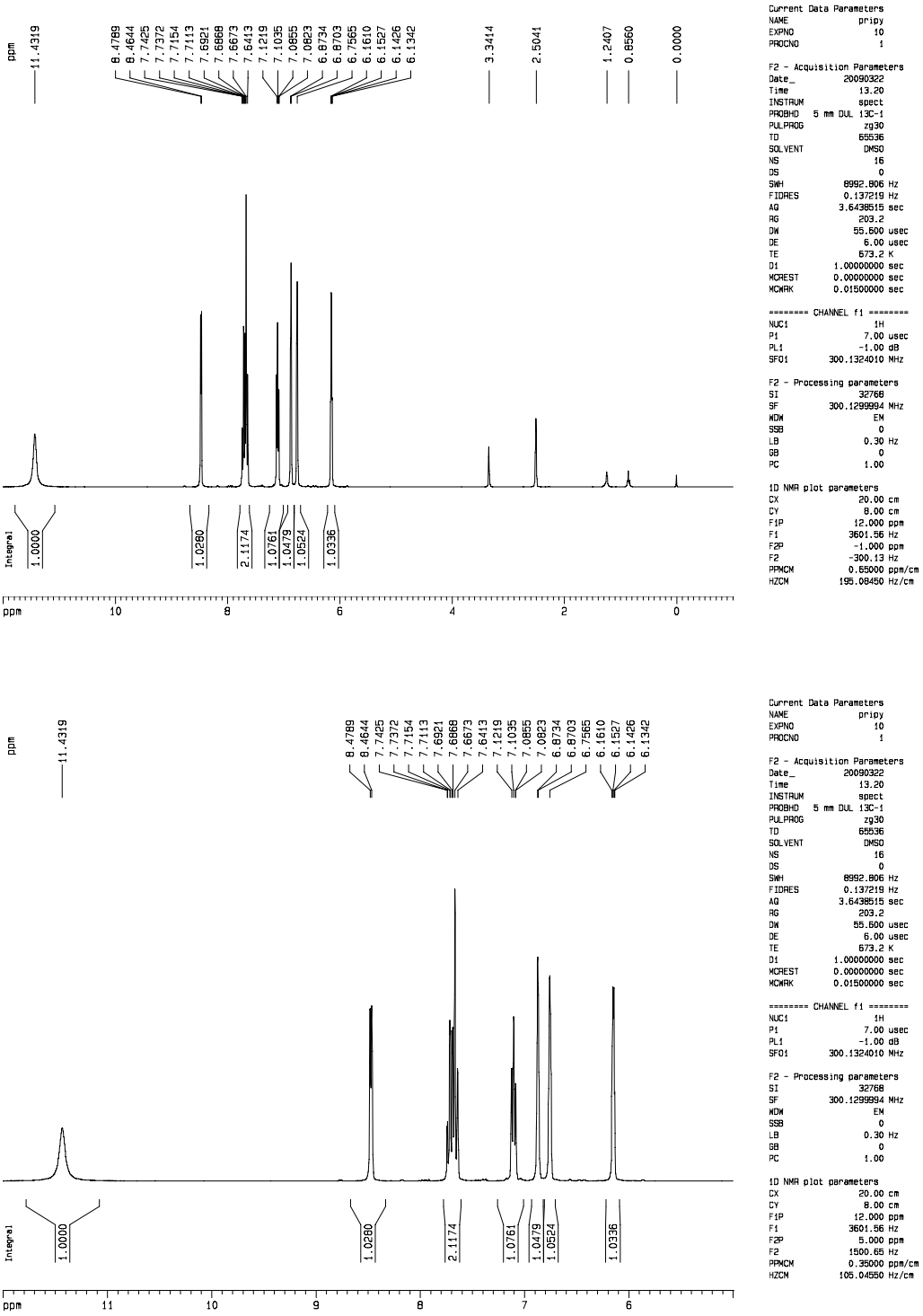

Fig. S2 ^{1}H NMR spectrum of PyrPy.

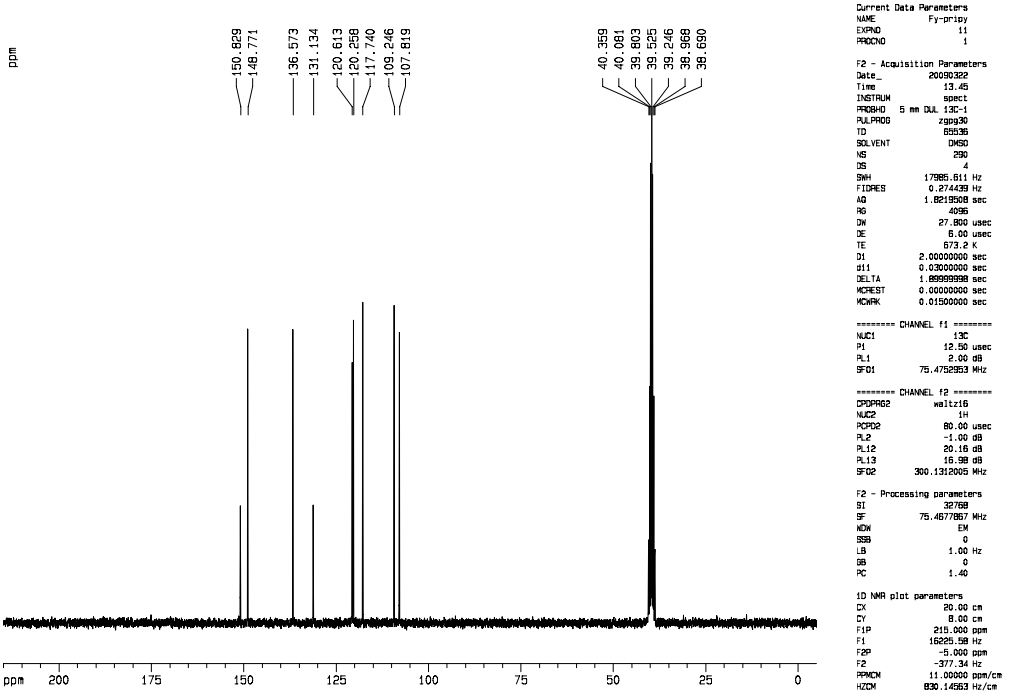

Fig. S3 ^{13}C NMR spectrum of PyrPy.

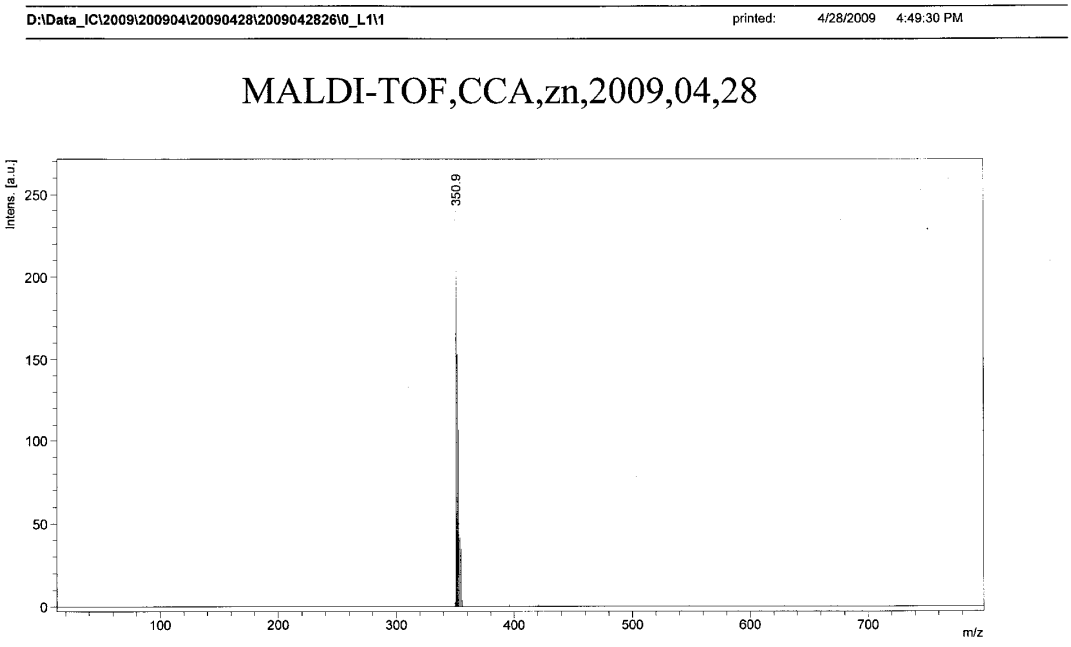

Fig. S4 Mass spectrum of $Zn(PyrPy)_2$.

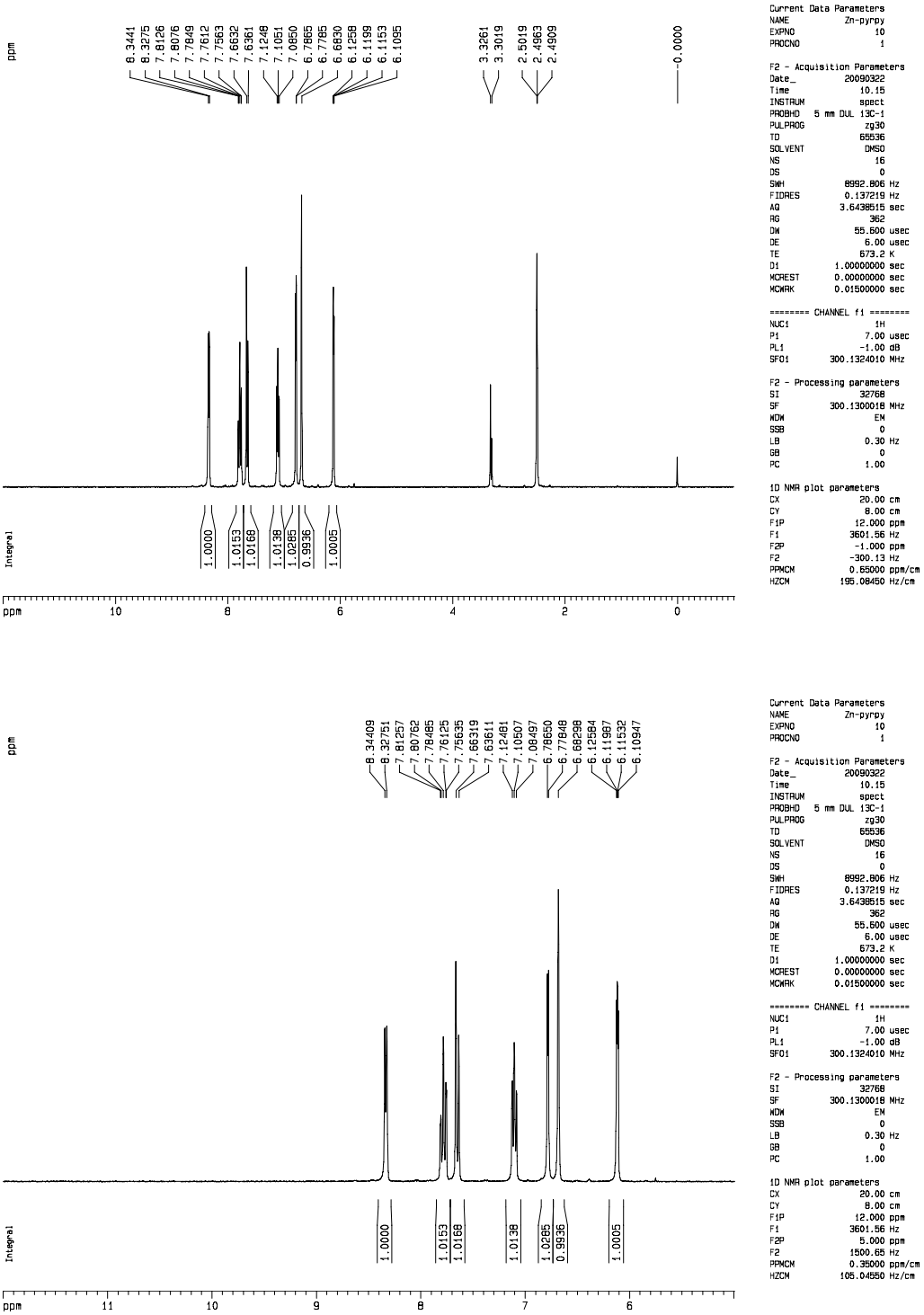

Fig. S5 ^{1}H NMR spectrum of $Zn(PyrPy)_2$.

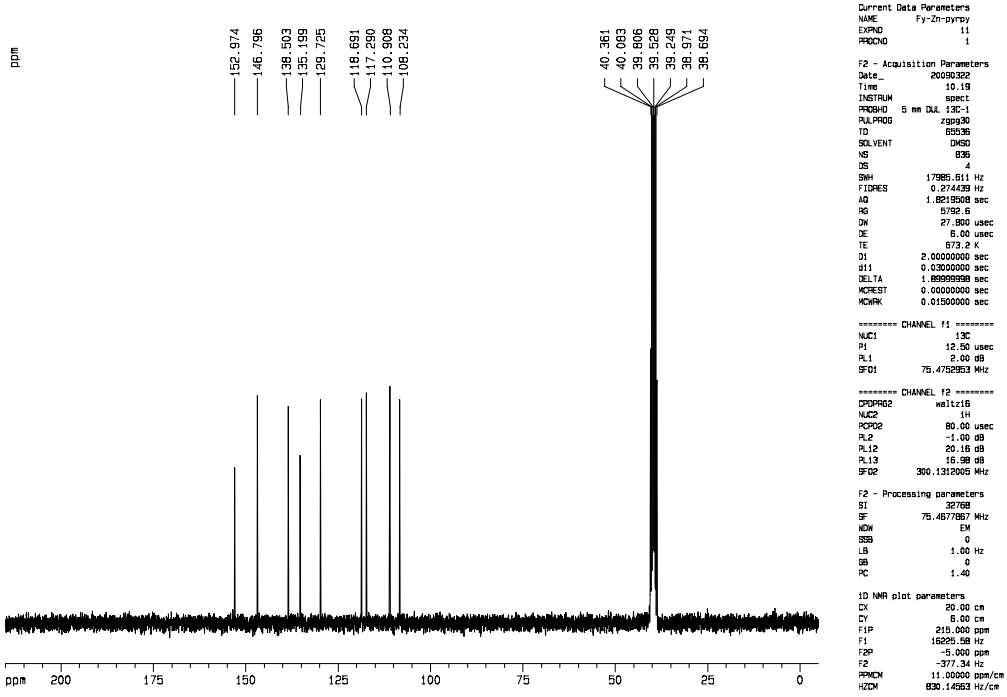

Fig. S6 ^{13}C NMR spectrum of $Zn(PyrPy)_2$.

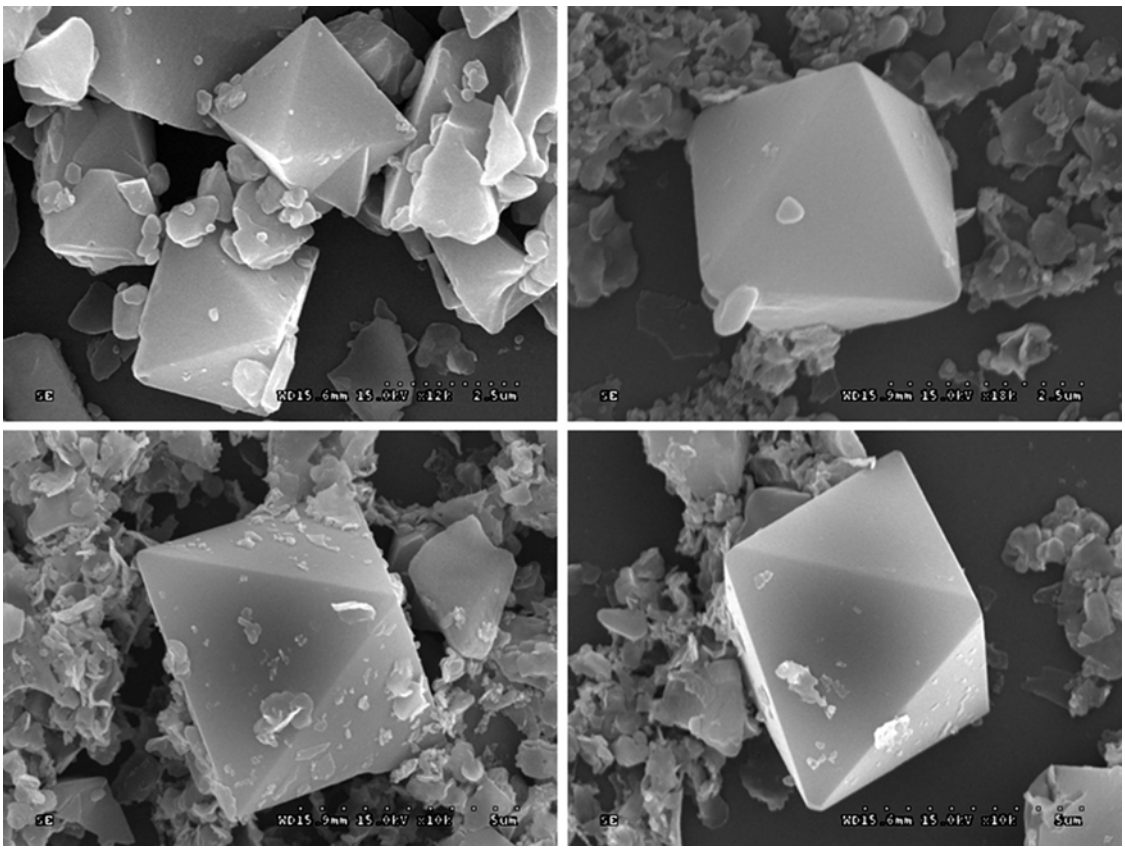

Fig. S7 Typical FE-SEM images of $Zn(PyrPy)_2$ micro-octahedrons with a size of ~5 um at C=20 mM.

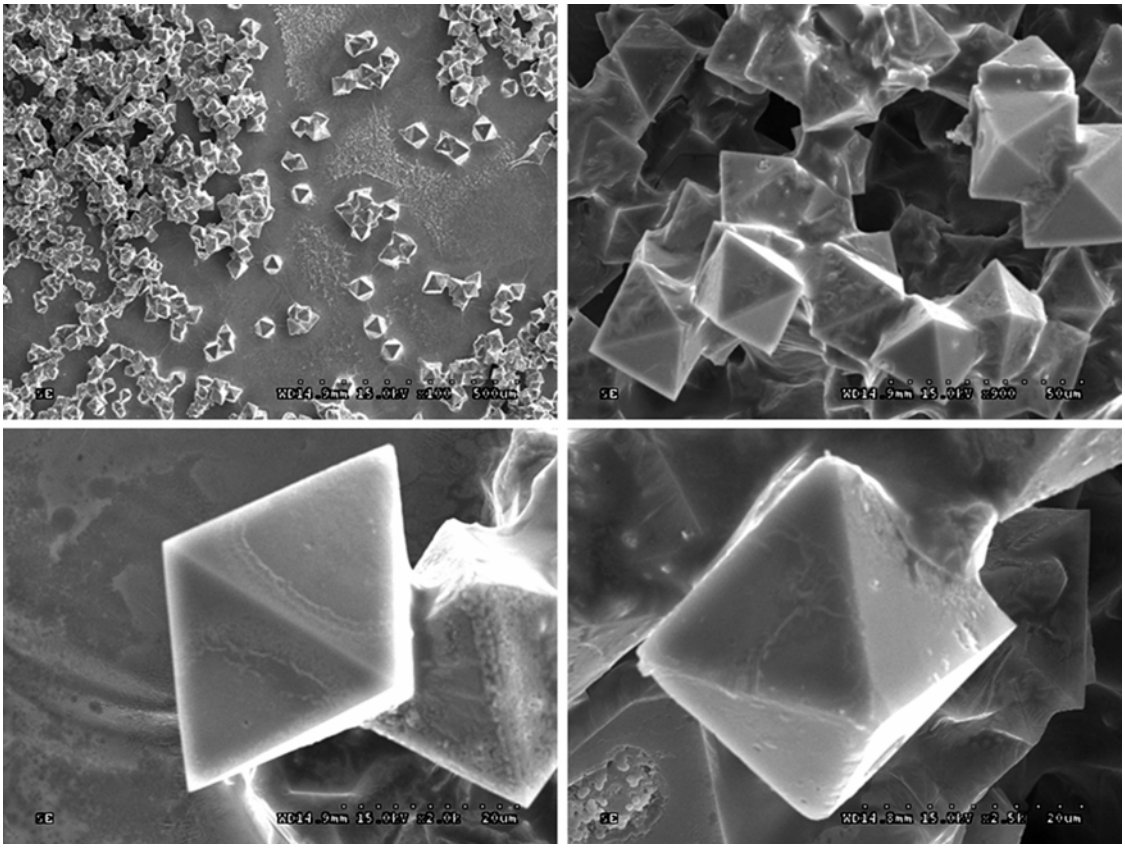

Fig. S8 Typical FE-SEM images of $Zn(PyrPy)_2$ micro-octahedrons with a size of ~25 um at C=16 mM.

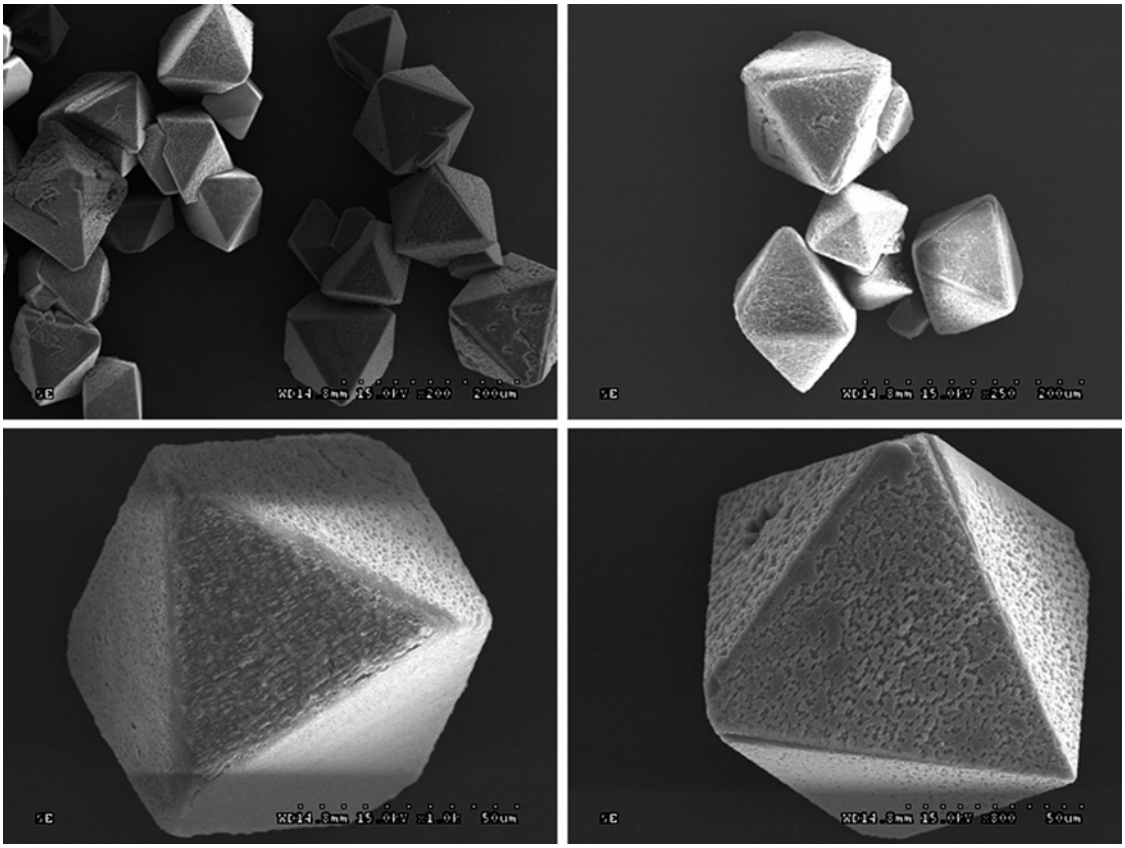

Fig. S9 Typical FE-SEM images of $Zn(PyrPy)_2$ micro-octahedrons with a size of ~75 um at C=9 mM.

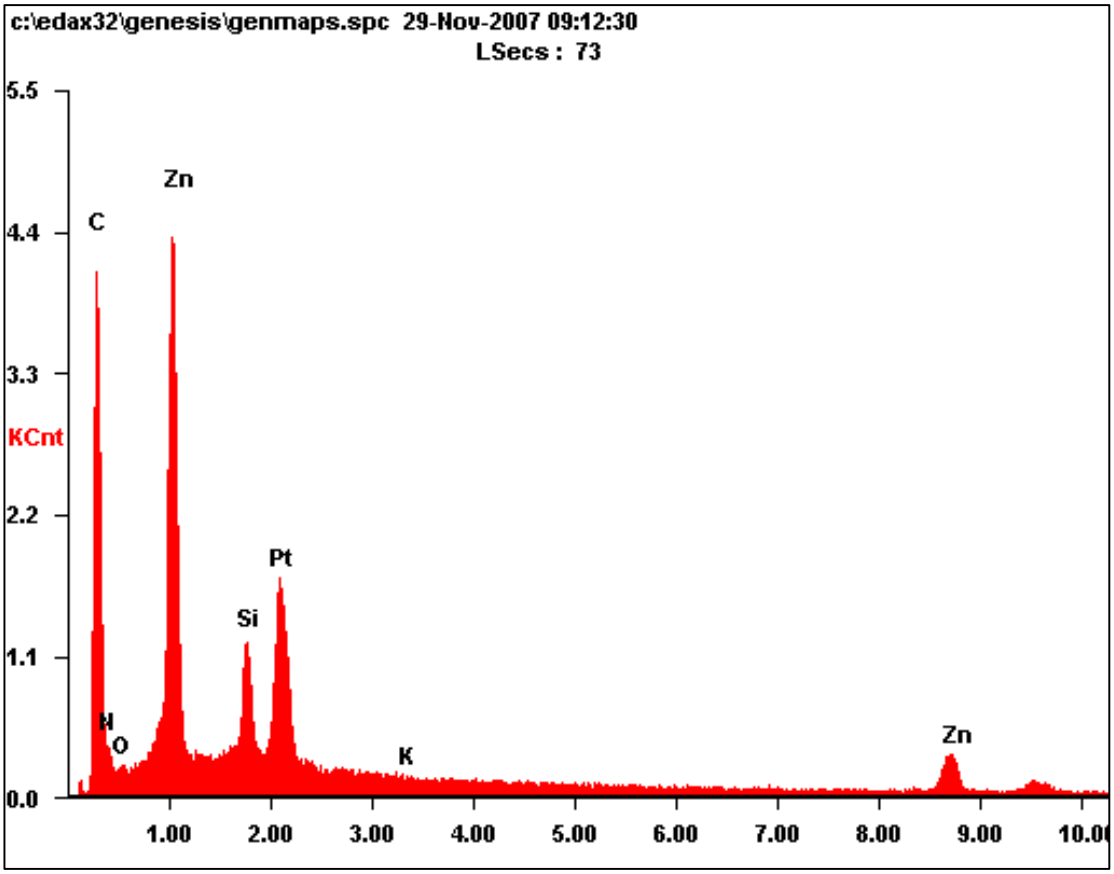

Fig. S10 The energy dispersive X-ray (EDX) spectrum of the micro-octahedrons. The peak of Si arises from the Si grid for SEM characterization. The presence of O comes mainly from atmospheric contamination due to exposure of the sample to air. The peak of Pt arises from the pre-deposited Pt layer for SEM characterization.

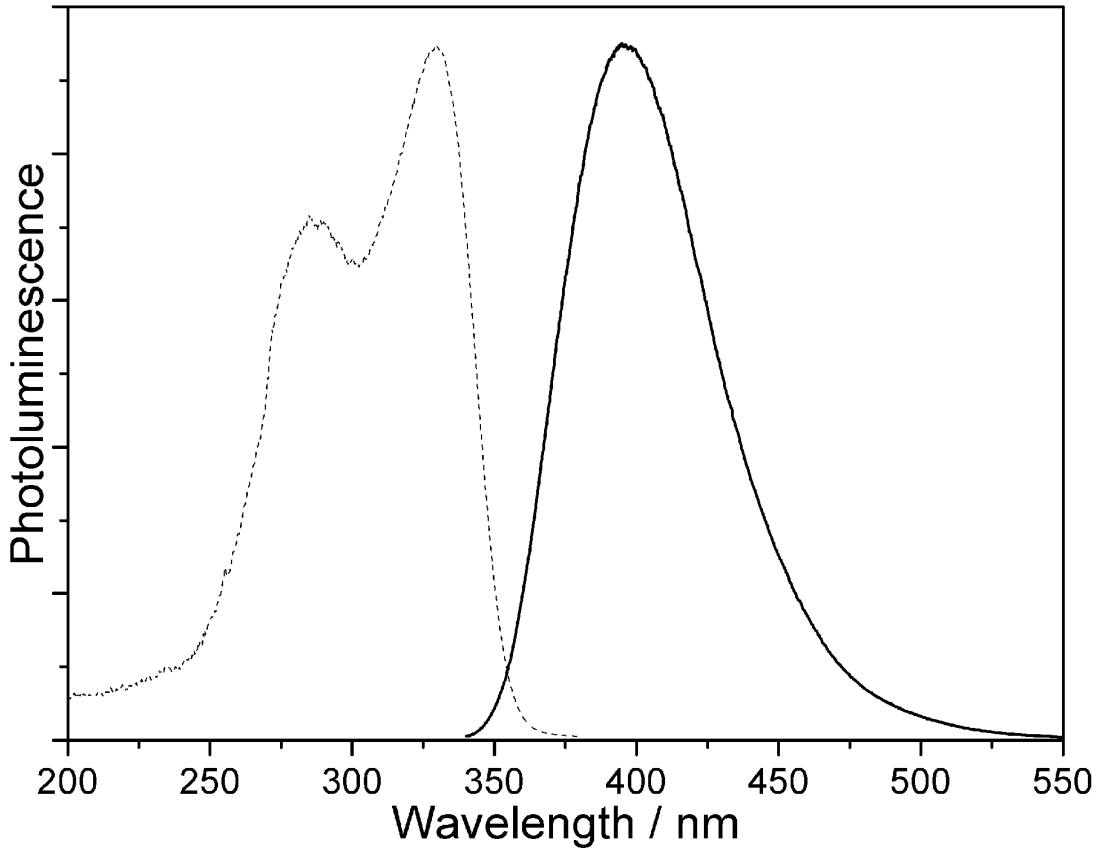

Fig. S11 Excition (dashed line) and emission (solid line) spectra of PyrPy dissolved in dichloromethane (10^{-5} *M*).

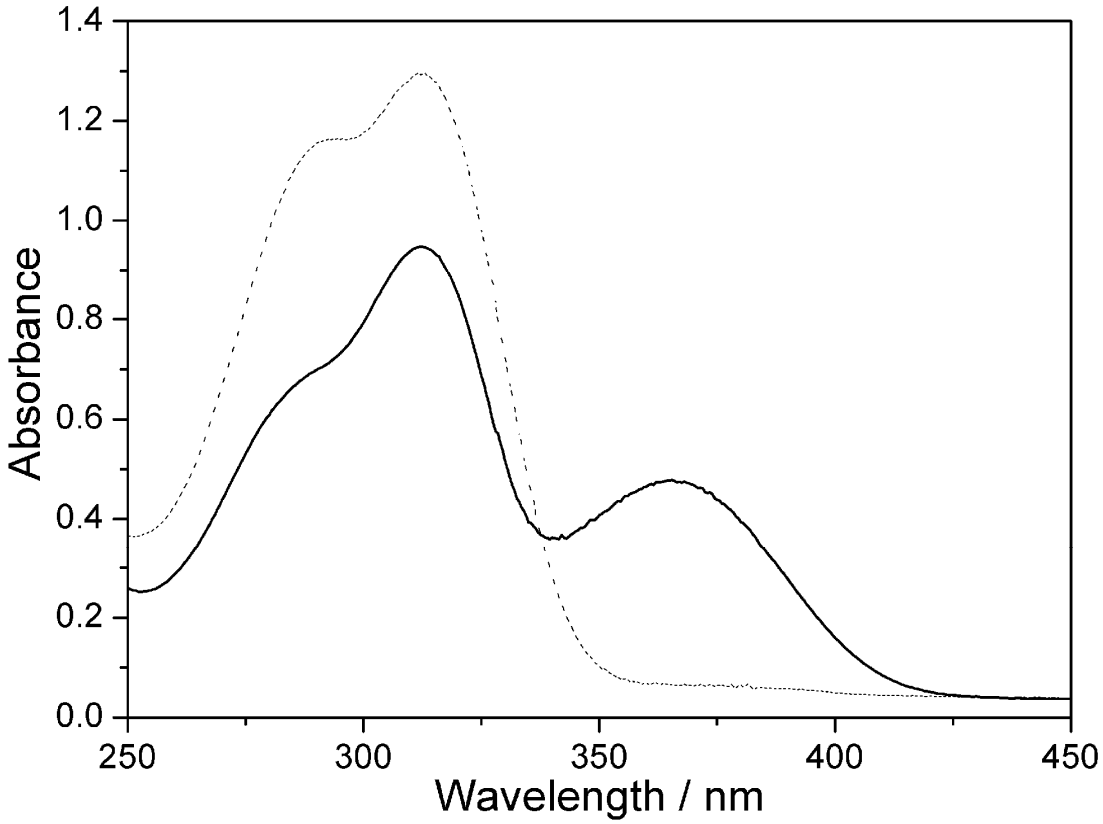

Fig. S12 Absorbance spectra of PyrPy (dashed line) and $Zn(PyrPy)_2$ (solid line) dissolved in dichloromethane (10^{-5} *M*).

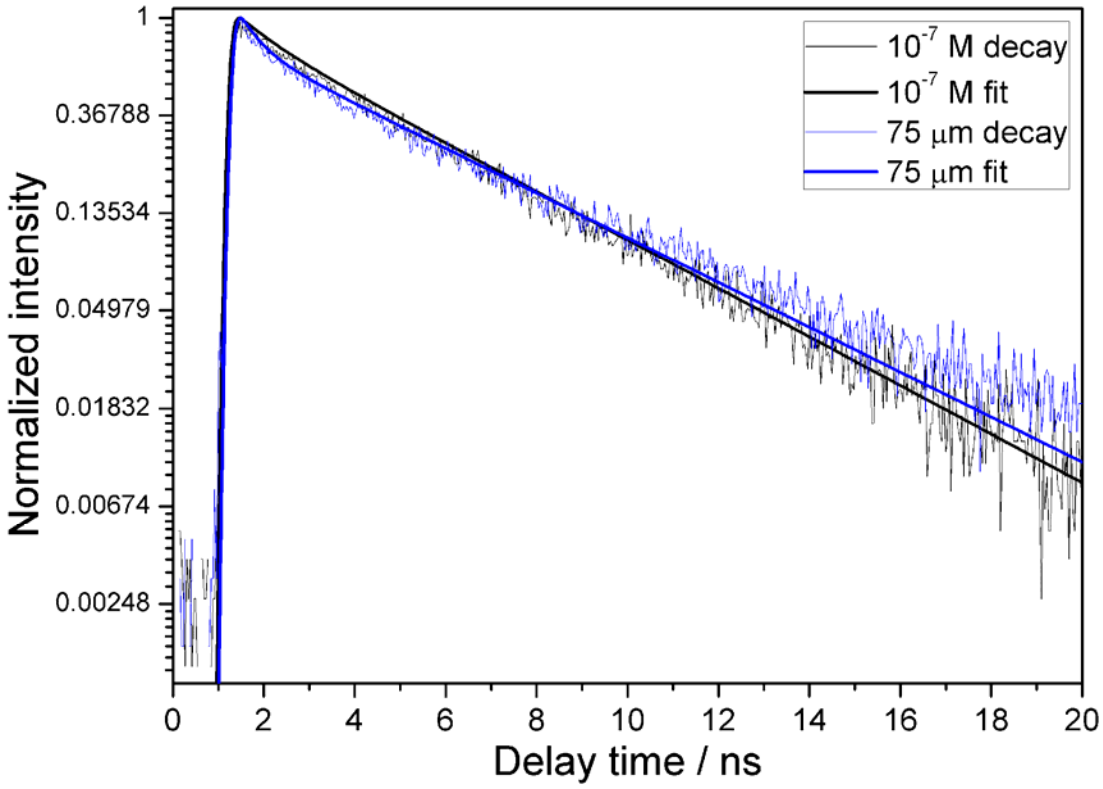

Fig. S13 The PL signal decay curves for $Zn(pyrpy)_2$ micro-octahedrons with a mean size of 75 μm and solution of 1×10^{-7} *M*.

Table S1 Crystal data and structure refinement for $Zn(PyrPy)_2$.

Empirical formula	$C_{18}H_{14}N_4Zn$
Formula weight	351.70
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Tetragonal
Space group	$P\,4_1\,2_1\,2$
a (Å)	8.2425(12)
b (Å)	8.2425(12)
c (Å)	23.659(5)
Alpha (deg.)	90.00
Beta (deg.)	90.00
Gamma (deg.)	90.00
Volume ($Å^3$)	1607.3(5)
Z	4
Calculated density (Mg/m^3)	1.453
Absorption coefficient (mm^{-1})	1.532
F(000)	720
Crystal size (mm)	0.48 x 0.40 x 0.36
Theta range for data collection (deg.)	2.62 to 27.48
Limiting indices	-10<=h<=8, -10<=k<=9, -30<=l<=30
Reflections collected / unique	12088 / 1848 [R(int) = 0.0387]
Completeness to theta = 27.48	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6086 and 0.5268
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1848 / 0 / 105
Goodness-of-fit on F^2	1.161
Final R indices [I>2sigma(I)]	R1 = 0.0288, wR2 = 0.0778
R indices (all data)	R1 = 0.0292, wR2 = 0.0780
Absolute structure parameter	0.000(18)
Largest diff. peak and hole (e. $Å^{-3}$)	0.382 and -0.283

Table S2 The PL lifetimes for $Zn(PyrPy)_2$ micro-octahedrons and solutions.

Samples	τ_1 (ns) [a]	A_1 [a]	τ_2 (ns) [a]	A_2 [a]	τ (ns) [a]
75 μm	0.47	0.35	4.36	0.65	3.00
1×10^{-7} M	0.88	0.18	4.03	0.82	3.46

[a] The decay kinetics were fitted by a sum of exponential functions: $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where the A and τ terms represent the pre-exponential factors and time constants, respectively; $\tau = \tau_1A_1 + \tau_2A_2$.