Supporting Information

Chelation-assisted assembly of multidentate colloidal nanoparticles into metal-organic nanoparticles

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Materials

All reagents used were purchased from Sigma-Aldrich, unless otherwise stated. Mn(III) meso-tetra (4-carboxyphenyl) porphine chloride (Mn-TCPP) was purchased from Frontier Scientific. Dimethylformamide (DMF) was purchased from Fisher. Sodium oleate was purchased from Tokyo Chemical Industry. Au nanoparticles (Au25, Au50, and AuNR) were purchased from Nanopartz. The water used was purified on a Milli-Q Biocel System.

METHODS

Synthesis of Au-15 nanoparticles

Au-15 nanoparticles were synthesized based on previously reported procedures.[32] All glassware used in this synthesis were rinsed with aqua regia and ultrapure water. In a typical synthesis, to a 250-mL flask, 100 mL of ultrapure water and 0.5 mL of $HAuCl_3$ solution (20 mg/mL) were added and heated to boiling with vigorous stirring. Four mL of freshly prepared sodium citrate (10 mg/mL) were added to the boiling solution. The solution was kept boiling for another 25 min and then cooled naturally.

Synthesis of iron oxide nanoparticles

Iron oleate precursor was synthesized using previously reported procedures with modification.[26] In a typical synthesis, iron chloride ($FeCl_3 \cdot 6H_2O$, 40 mmol) and sodium oleate (120 mmol) were dissolved in a solvent mixture composed of 60 mL of ultrapure water, 80 mL of ethanol, and 140 mL of hexane. The resulting solution was heated to 60 °C and refluxed for 4 h. Upon cooling to room temperature, the organic layer was washed three times with ultrapure water. After removing the hexane by rotary evaporation, the resulting iron oleate complex was in a waxy solid form. To synthesize iron oxide nanoparticles, iron oleate (0.9 g) and oleic acid (0.156 g) were added to a three-necked flask (25 mL) with 5 g of 1-octadecene. The resulting mixture was heated to 320 °C and maintained for 1 h before cooling. The resulting iron oxide nanoparticles were washed with hexane and ethanol and redispersed in tetrahydrofuran (THF) for future use.

Synthesis of upconversion nanoparticles

$NaYF_4$ (Yb 30%, Er 2%) (UCNP) was synthesized on the basis of reported procedures with modification.[26] In a typical synthesis, $Y(CH_3COO)_3$ (0.68 mmol), $Yb(CH_3COO)_3$ (0.3 mmol), and $Er(CH_3COO)_3$ were added to a 50 mL three-necked flask with 6 mL of oleic acid and 15 mL of 1-octadecene. The resulting solution was heated to 150 °C and maintained for 30 min. After cooling to room temperature, 6 mL of methanol solution with NaOH (2.5 mmol) and NH_4F (4 mmol) was added and stirred at 50 °C for another 30 min. Then, the reaction mixture was heated to 100 °C to remove the methanol. Finally, the reaction solution was heated to 290 °C and maintained for 2 h. The resulting hexagonal UCNP nanoparticles were washed with hexane and ethanol and redispersed in THF for future use.

Preparation of multidentate colloidal nanoparticles

Chelating ligand 3,4-dihydroxyhydrocinnamic acid (50 mg) was dissolved in 5 mL of THF, added to a 25 mL three-necked flask, and heated to 50 °C. Then 20 mg of iron oxide (or UCNP) nanoparticles in 2 mL of THF were added to the flask and incubated for 5 h. After cooling, aqueous NaOH (200 μL, 0.5 M) were added to the mixture. The precipitation was collected by centrifugation and redispersed in ultrapure water. Then 100 μL of HCl (0.5 M) were added to the aqueous colloidal nanoparticles to protonate the chelating ligands. Colloidal nanoparticles were recollected by centrifugation and redispersed in DMF.

Synthesis of ZnMONs

Solution 1: $Zn(NO_3)_2 \bullet xH_2O$ (8 mg), polyvinylpyrrolidone (PVP (20 mg)) and pyrazine (1.2 mg) were dissolved in a mixture solution of DMF (9 mL) and ethanol (3 mL) and sonicated for 15 min. Solution 2: Mn-TCPP (4.3 mg) was dissolved in another mixed solvent of DMF (3 mL) and ethanol (1 mL) and sonicated for 15 min. In a typical synthesis of ZnMONs, 300 µL of solution 1 Mn-TCPP (after centrifugation for 10 min at 14000 RPM/min) was added to 900 µL of solution 1 in a 5-mL vial dropwise. The resulting solution was sonicated for 5 min and then incubated in an oil bath for 24 h at 80 °C. The resulting ZnMONs were washed with ethanol and redispersed in ethanol for future characterization.

Synthesis of multidentate CN-assembled ZnMONs

First, aqueous Au nanoparticles, whether home-made or purchased from Nanopartz, were concentrated by centrifugation and redispersed in DMF (10 ml of 1.3 OD of Au15 nm were concentrated to 120 µL of DMF). In a typical synthesis of CN-assembled ZnMONs, a desired amount of coordination sites-modified CNs (Au, UCNP, and iron oxide nanoparticles) were added to 900 µL of solution 1. For example, Au15-ZnMON-1 was prepared with10 µL of concentrated Au15, and Au15-ZnMON-2 was prepared with 60 µL of concentrated Au15. Iron oxide11-ZnMON-1 was prepared with 5 µL of coordination sites functionalized iron oxide nanoparticles (2 mg/mL). Similarly, Iron oxide11-ZnMON-2 and Iron oxide11-ZnMON-3 were prepared with 30 and 60 µL of coordination sites-functionalized iron oxide nanoparticles, respectively. UCNP-assembled ZnMONs were prepared with 50 µL of coordination sites-functionalized UCNPs. Then 300 µL of solution 2 were added dropwise to solution 1. Finally, the resulting solution was incubated in an oil bath for 24 h at 80 °C. The resulting multidentate

CNs-assembled ZnMONs were washed with ethanol and redispersed in ethanol for future characterization.

Characterization and instruments

Transmission Electron Microscopy (TEM) was performed using a Hitachi H-7000 transmission electron microscope at 100 kV. Twenty microliters of multidentate CNs-assembled ZnMONs in DMF were dropped onto a carbon-coated copper grid and then dried for TEM.

The X-ray diffraction measurements were performed on a Bruker D8 ADVANCE diffractometer, employing the standard setup in reflection geometry.

EDS line scans. Energy-Dispersive-X-ray spectroscopy was performed with an Oxford Instruments EDS X-ray Microanalysis System coupled to the high-resolution TEM.

FT-IR Spectra. Spectra were recorded with a near- and mid-IR spectrometer (a Nicolet Nexus 670) in KBr pellets.

Optical Absorption Spectroscopy. UV−vis absorption spectra were recorded using a Shimadzu UV-1800. Nanoparticles were dissolved in DMF for measurement.

Dynamic light scattering (DLS) measurements were recorded on a Zetasizer Nano ZS (Malvern Instrument Ltd., U.K.) equipped with a He−Ne laser beam operating at 633 nm at 25 °C.

The diameter and shell thickness in Table 1 were characterized with MacBiophonics Imagej.

Detecting singlet oxygen generation: To detect the singlet oxygen generation, singlet oxygen sensor green (SOSG) was introduced into UCNP/MON core/shell nanoparticle solution using D_2O as solvent, followed by irradiation using 980 nm laser (600 mW/cm2) for different periods of time. The fluorescence of SOSG was obtained with excitation at 494 nm after irradiation at different periods of time.

Magnetic measurements were performed using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S) at 300K.

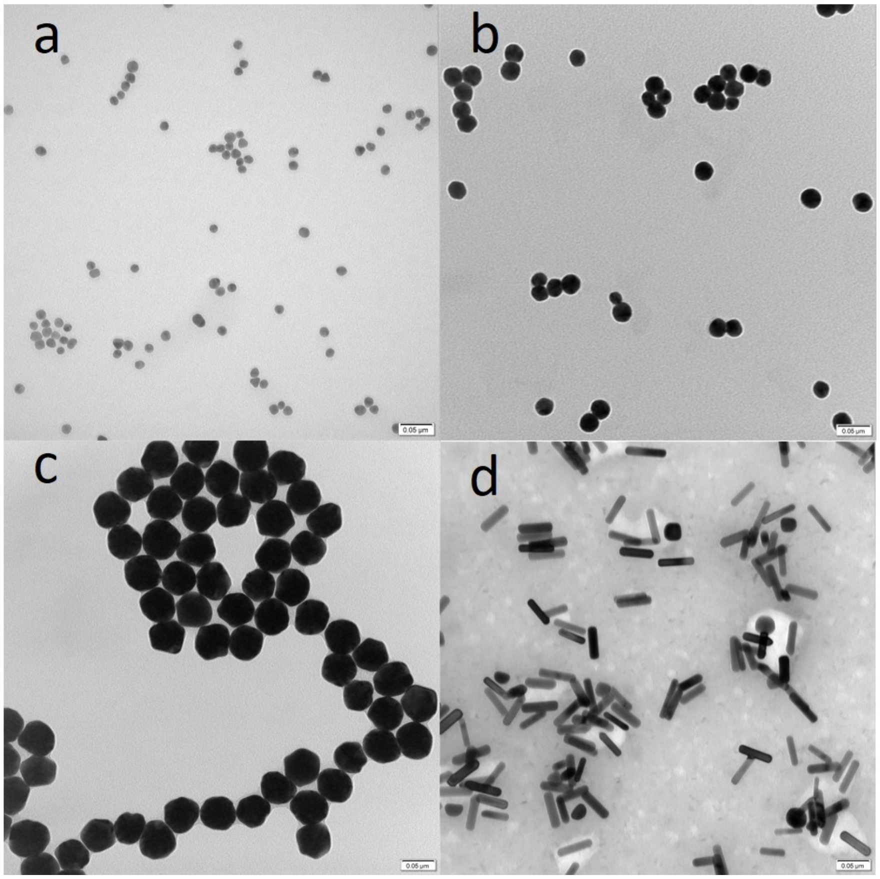

Fig. S1. TEM pictures of Au nanoparticles. a) Au-15, b) Au-25, c) Au-50, d) Au-NR (10 × 41 nm). Scale bar 50 nm.

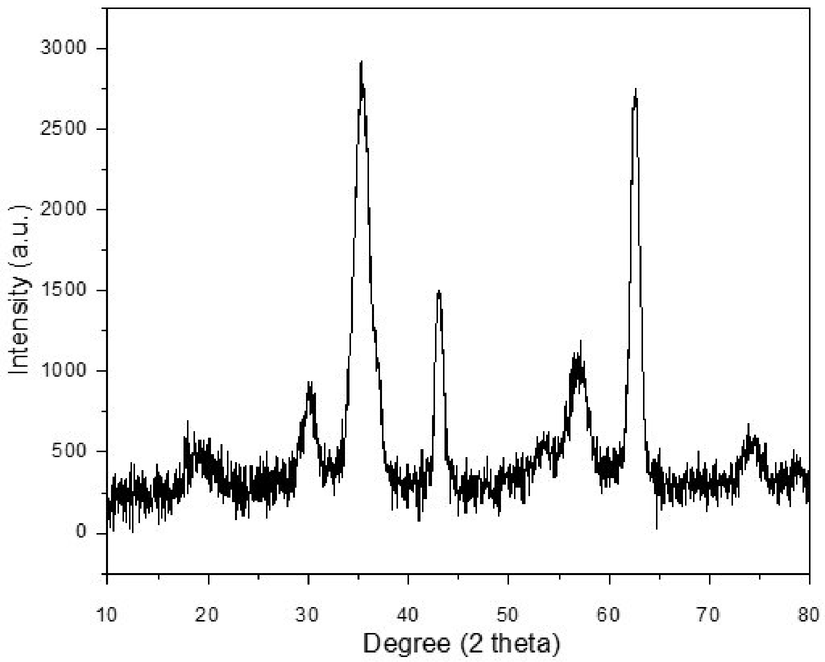

Fig. S2. Powder X-ray diffraction of iron oxide.

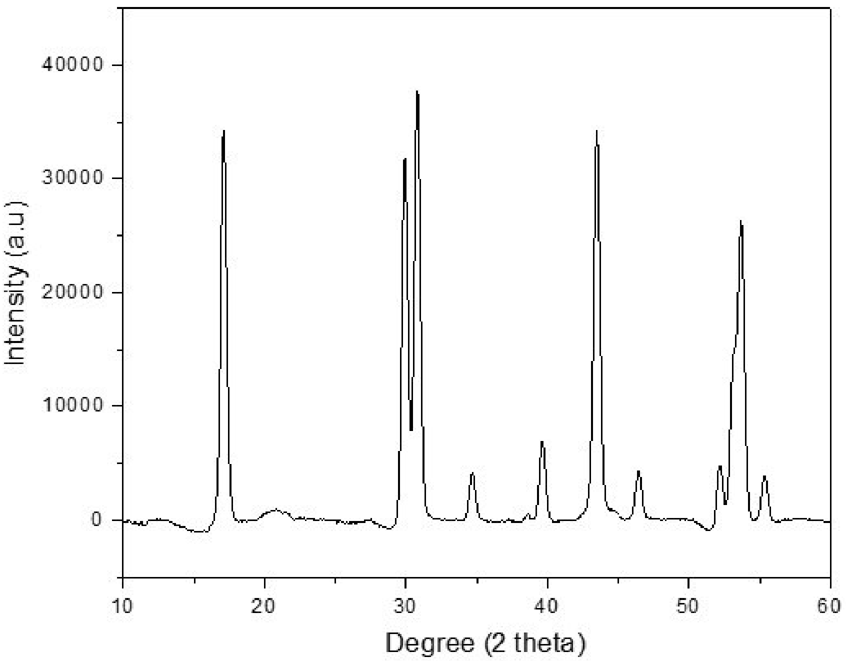

Fig. S3. Powder X-ray diffraction of UCNP.

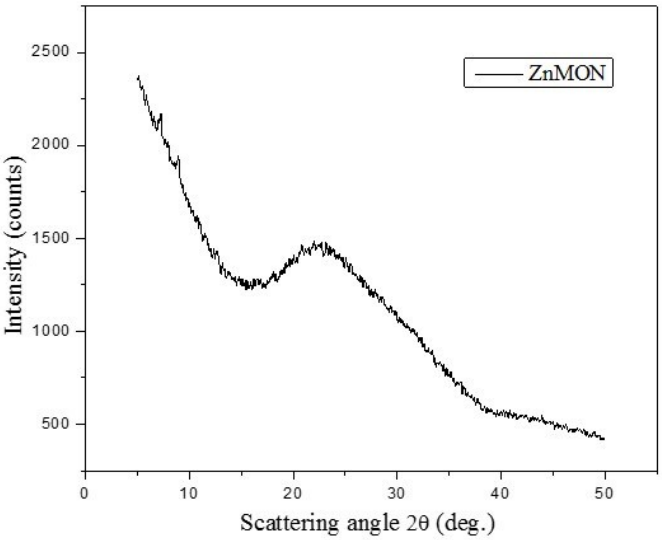

Fig. S4. Powder X-ray diffraction of ZnMON.

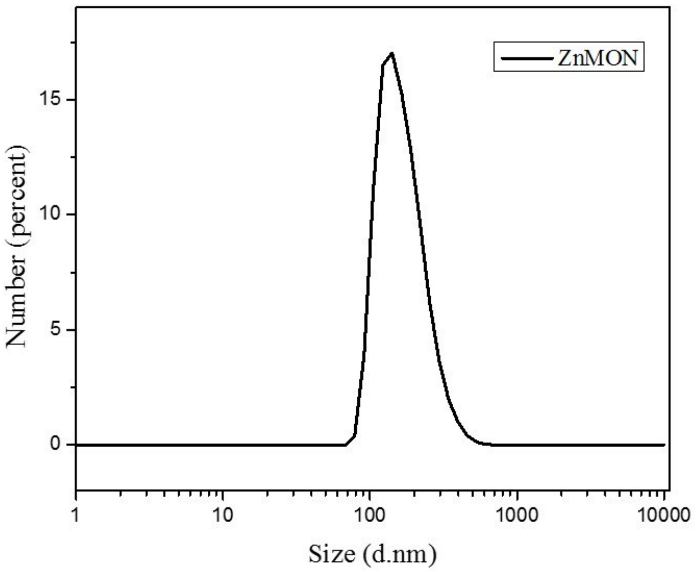

Fig. S5. Particle size analysis of ZnMON by DLS.

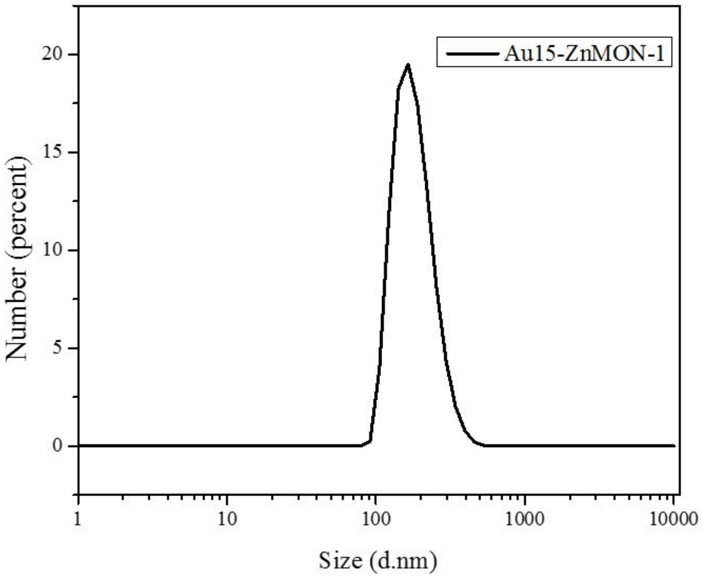

Fig. S6. Particle size analysis of Au15-ZnMON-1 by DLS.

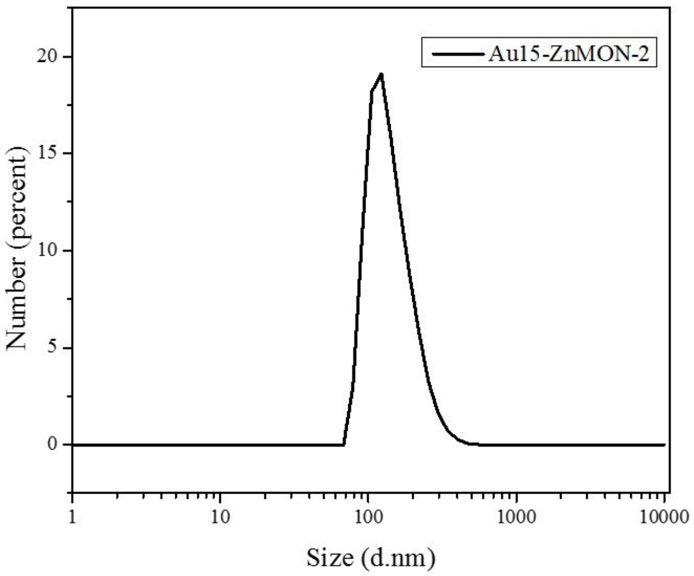

Fig. S7. Particle size analysis of Au15-ZnMON-2 by DLS.

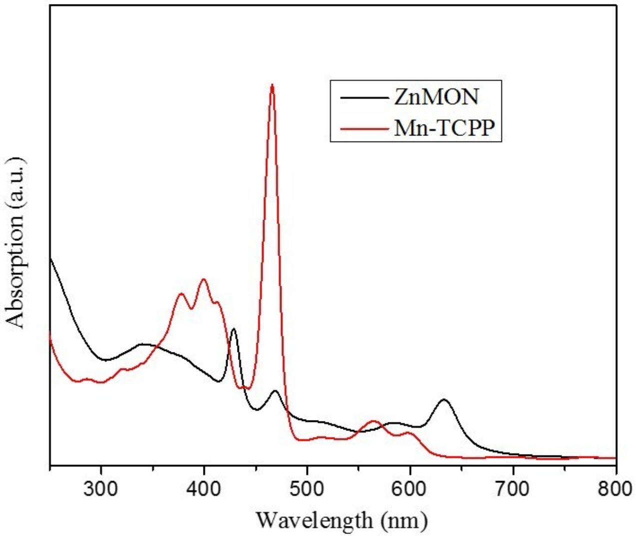

Fig. S8. UV-vis of Mn-TCPP and ZnMON.

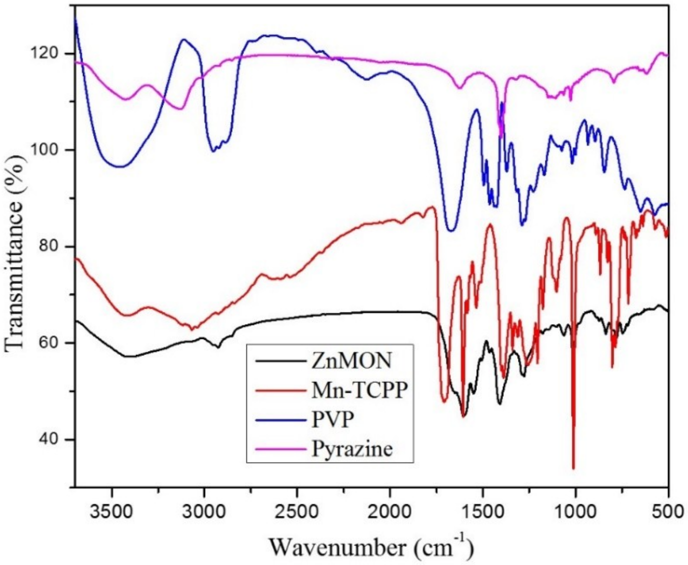

Fig. S9. IR spectroscopy of Mn-TCPP, PVP, pyrazine, and ZnMON.

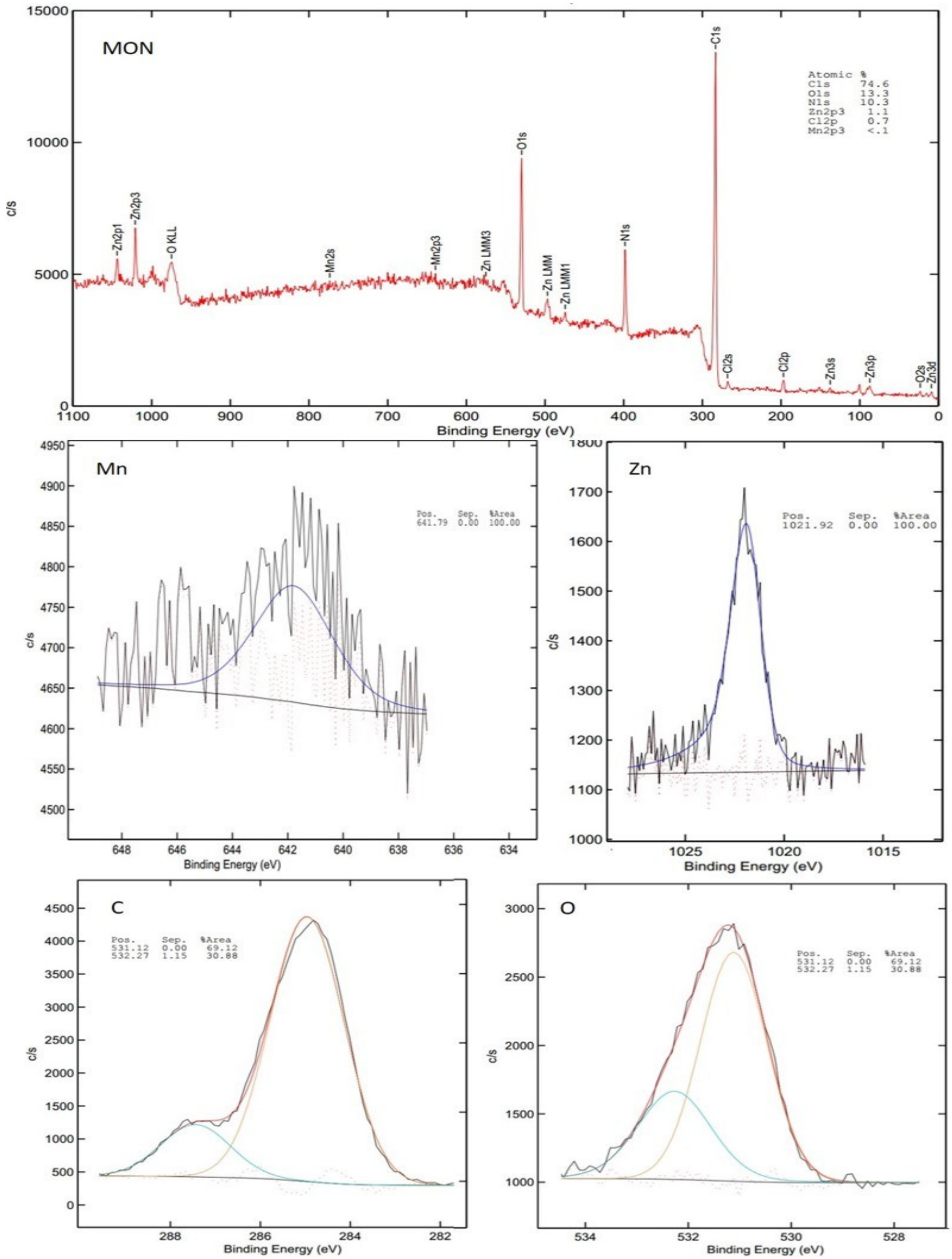

Fig. S10. XPS of metal organic nanoparticles.

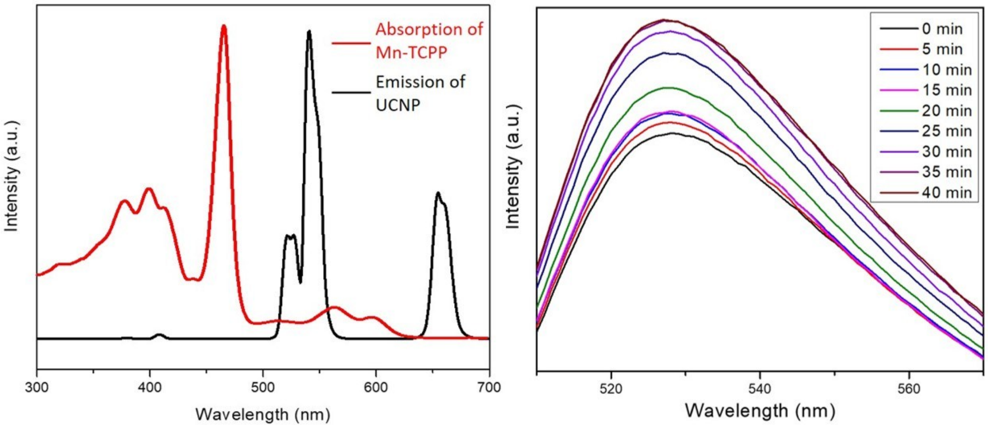

Fig. S11. The spectra overlap of the emission of UCNP and absorption of Mn-TCPP (left); Singlet oxygen generation monitoring of UCNP/MON core/shell nanoparticles (right).

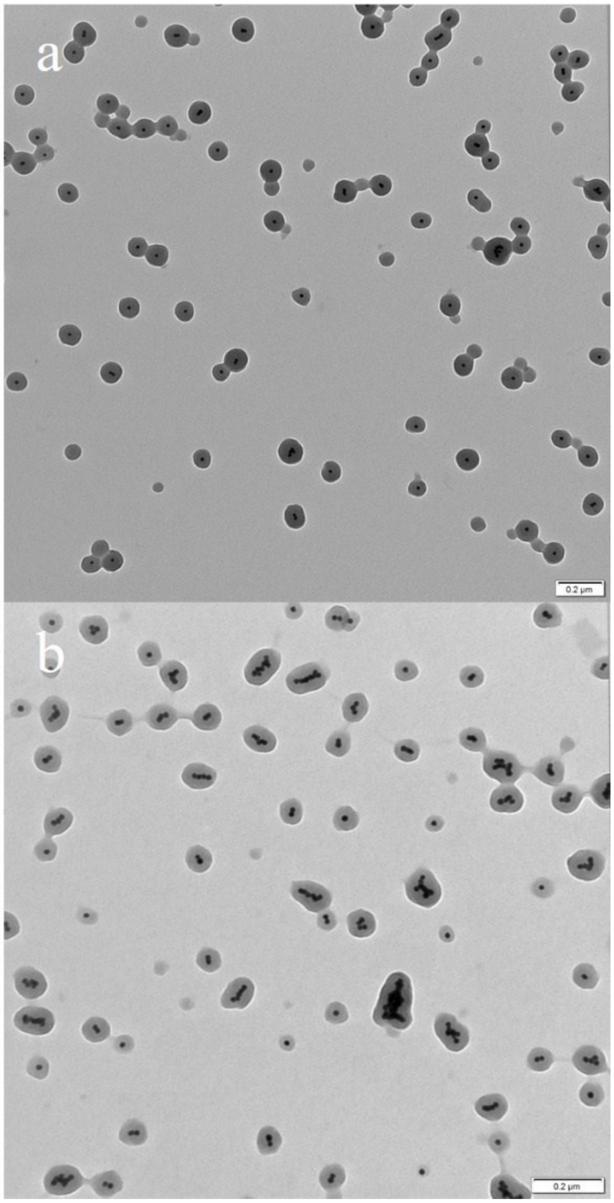

Fig. S12. TEM images of Au15-ZnMON-1 and Au15-ZnMON-2. Scale bar: 200 nm.

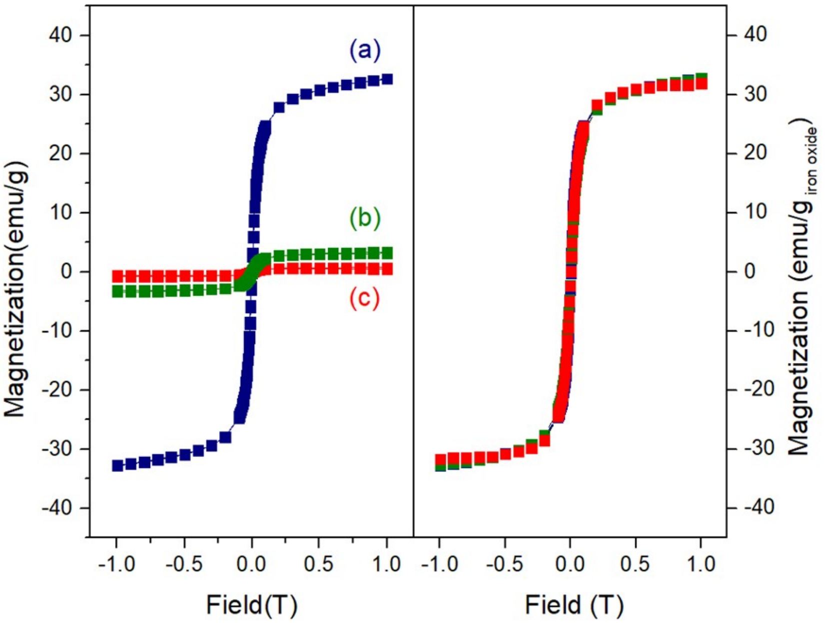

Fig. S13. Magnetic property of iron oxide: Left panel: Magnetic hysteresis loops of iron oxide nanoparticles (a), Iron oxide11-ZnMON-1 (b) and Iron oxide11-ZnMON-2 (c). All three samples demonstrated the typical superparamagnetic behavior, since neither remanent magnetization nor coercivity was detected. The corresponding mass saturation magnetization values were found to be 32.03, 3.25 and 0.644 emu/g, respectively. The suppressed magnetizations of those core-shell samples (b) & (c) are in consistency with the reduced concentration of magnetic iron oxide nanoparticles due to the introduction of non-magnetic ZnMON. While the mass magnetizations of iron oxide nanoparticles before and after assembly remain almost invariant as shown in the right panel.