

## Supplementary materials

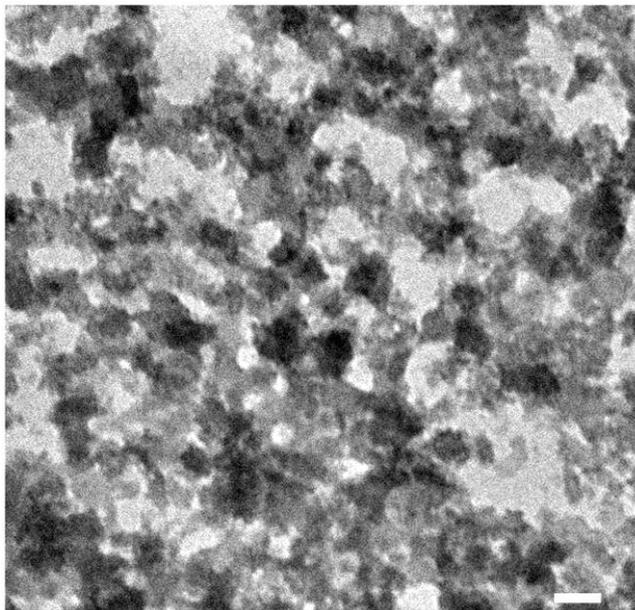
# Tumor Theranostics of Transition Metal Ions Loaded Polyaminopyrrole Nanoparticles

Shuyao Li<sup>1</sup>, Shuwei Liu<sup>1</sup>, Lu Wang<sup>2</sup>, Min Lin<sup>3</sup>✉, Rui Ge<sup>1</sup>, Xing Li<sup>2</sup>, Xue Zhang<sup>1</sup>, Yi Liu<sup>1</sup>, Lening Zhang<sup>4</sup>✉, Hongchen Sun<sup>1,2</sup>✉, Hao Zhang<sup>1</sup>✉ and Bai Yang<sup>1</sup>

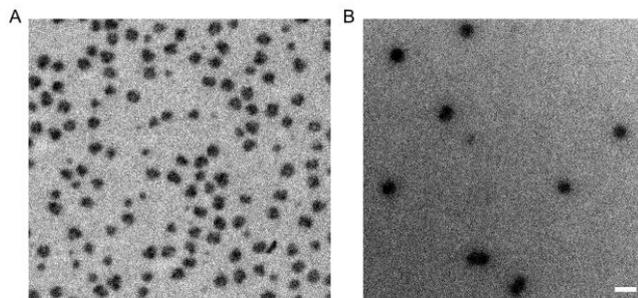
1. State Key Supramolecular Structure and Materials Laboratory, College of Chemistry, Jilin University, Changchun 130012, P. R. China;
2. The Oral Pathology Department, School and Hospital attached to Stomatology, Jilin University, Changchun 130021, P. R. China;
3. Collaborative Innovation Center attached to Marine Biomass Fibers, Shandong Province Materials and Textiles, Marine Biobased Materials Institute, Materials Science and Engineering School, Qingdao University, Qingdao 266071, P. R. China;
4. Department of Thoracic Surgery, China-Japan Union Hospital, Jilin University, Changchun 130033, P. R. China.

✉ Corresponding author: Hao Zhang, PhD, State Key Supramolecular Structure and Materials Laboratory, College of Chemistry, Jilin University, Changchun 130012, P. R. China. Tel: +86 431 85159205; Email: hao\_zhang@jlu.edu.cn. Hongchen Sun, PhD, The Oral Pathology Department, School and Hospital attached to Stomatology, Jilin University, Changchun 130021, P. R. China. Tel: +86 431 88796010; Email: hcsun@jlu.edu.cn. Min Lin, PhD, Collaborative Innovation Center attached to Marine Biomass Fibers, Shandong Province Materials and Textiles, Marine Biobased Materials Institute, Materials Science and Engineering School, Qingdao University, Qingdao 266071, P. R. China. Tel: +86 431 85159205; Email: linmin900401@126.com. Lening Zhang, PhD, Department of Thoracic Surgery, China-Japan Union Hospital, Jilin University, Changchun 130033, P. R. China. Tel: +86 431 85159205; Email: 951446482@qq.com.

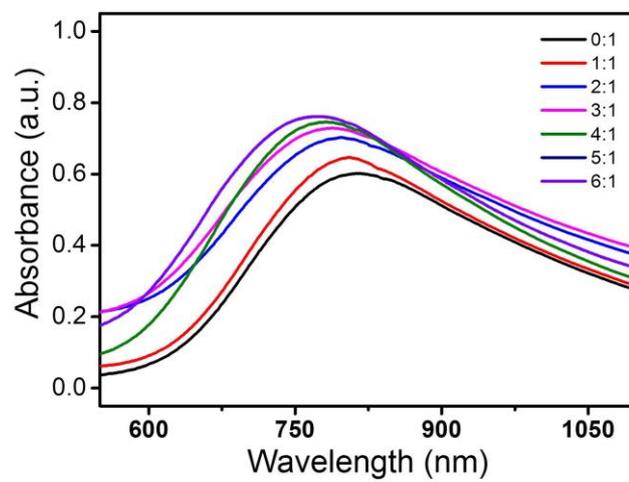
**Figure S1.** TEM image of CuPPy-NH<sub>2</sub> complexes as the dosage of Fe(III) is higher than 4.0 mmol. The scale bar represents 200 nm.



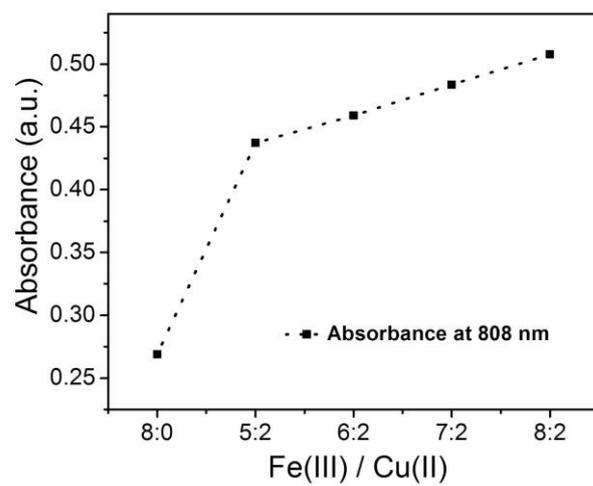
**Figure S2.** TEM image of the as-prepared PPy-NH<sub>2</sub> NPs (A) and CuPPy NPs (B). The scale bar represents 50 nm.



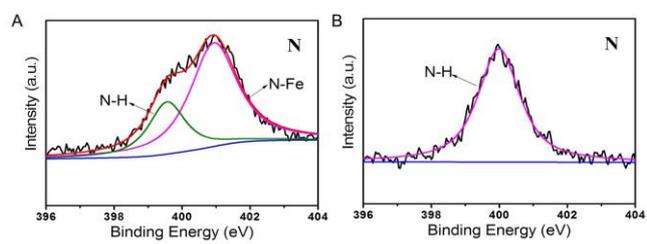
**Figure S3.** The UV-vis absorption spectra of the amino groups coordinate Cu(II). The ration of the amino to the Cu(II) is from 0:1 to 6:1.



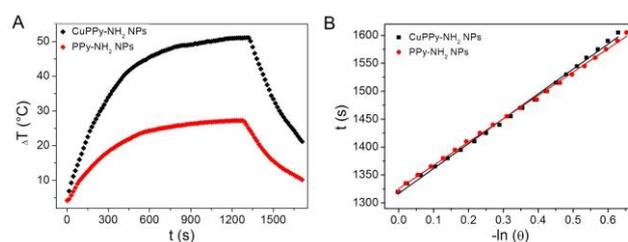
**Figure S4.** The UV-vis-NIR absorption spectra of PPy-NH<sub>2</sub> NPs at 808 nm.



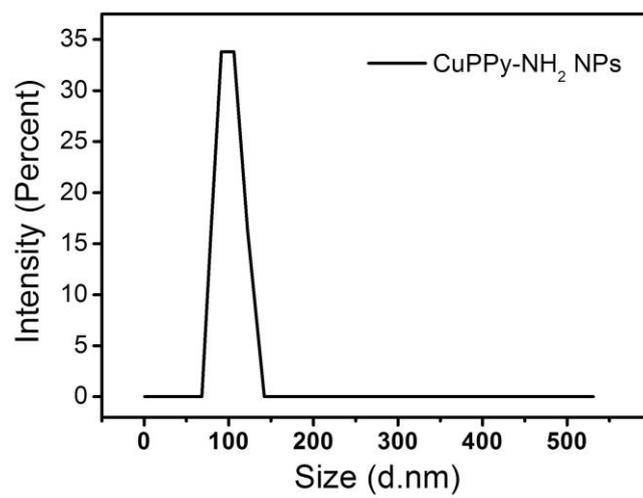
**Figure S5.** XPS N spectra of PPy-NH<sub>2</sub> NPs (A) and CuPPy NPs (B).



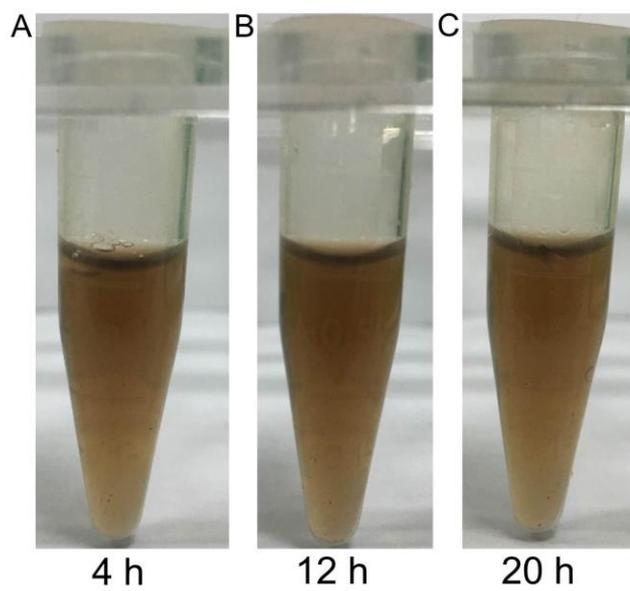
**Figure S6.** (A) Photothermal effect of 1 mg/mL aqueous solution of CuPPy-NH<sub>2</sub> NPs and PPy-NH<sub>2</sub> NPs. The solution is irradiated for 1320 s using a 3.5 w/cm<sup>2</sup> 808 nm laser and cooled to room temperature under ambient environment. (B) Time constant for heat transfer from the system is determined to be  $\tau_s = 455.6$  s (CuPPy-NH<sub>2</sub> NPs) and  $\tau_s = 445.7$  s (PPy-NH<sub>2</sub> NPs) by applying the linear time data from the cooling period (after 1320 s) *versus* negative natural logarithm of driving force temperature.



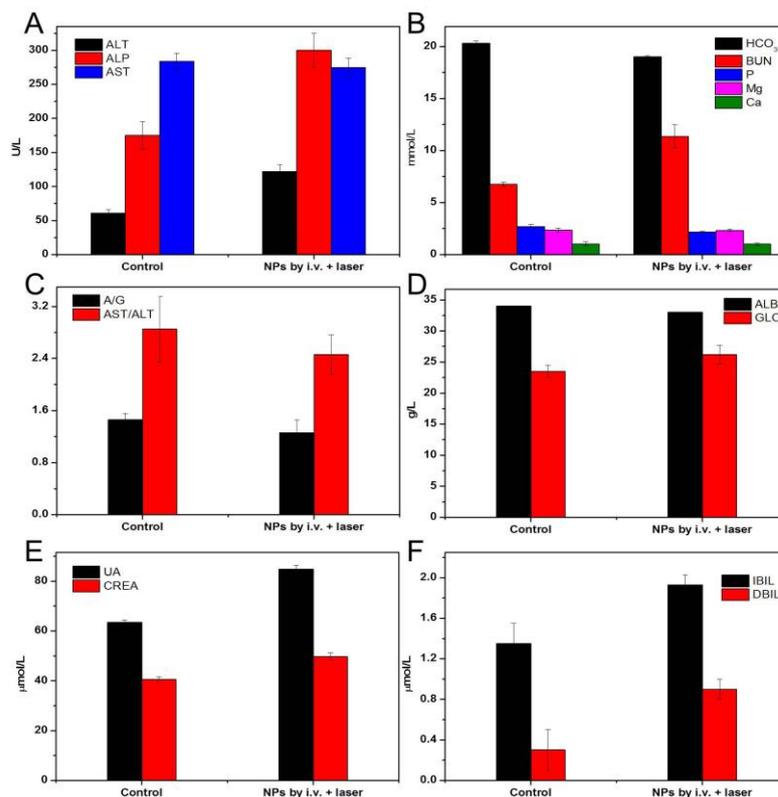
**Figure S7.** DLS size distribution of CuPPy-NH<sub>2</sub> NPs. The average diameter is 98.0 nm and the PDI is 0.357.



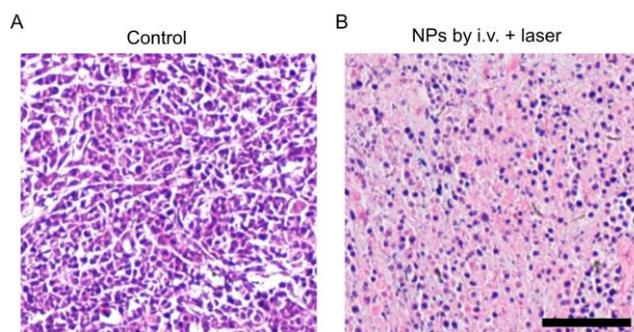
**Figure S8.** The photographs of precipitated CuPPy-NH<sub>2</sub> NPs in PBS after shaking for 4 (A), 12 (B), and 20 h (C).



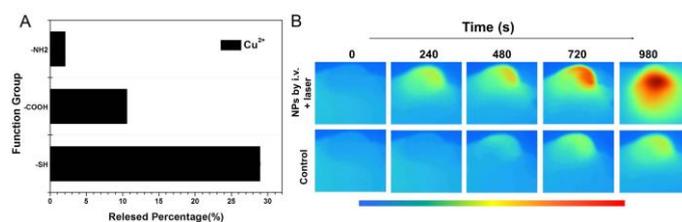
**Figure S9.** Liver and renal functions tested 24 h post i.v. injection of CuPPy-NH<sub>2</sub> NPs. All of the parameters are in normal scale comparing to the healthy control. (A) Alanine aminotransferase (ALT), alkaline phosphatase (ALP) and aspartate transaminase (AST). (B) Content of dicarbonate (HCO<sub>3</sub>), blood urea nitrogen (BUN), serum phosphorus (P), serum magnesium (Mg) and total calcium (Ca). (C) A/G represents the ratio of ALB to GLO, AST/ALT. (D) Albumin (ALB) and globulin (GLO). (E) Uric acid (UA) and creatinine (CREA). (F) Indirect bilirubin (IBIL) and direct bilirubin (DBIL).



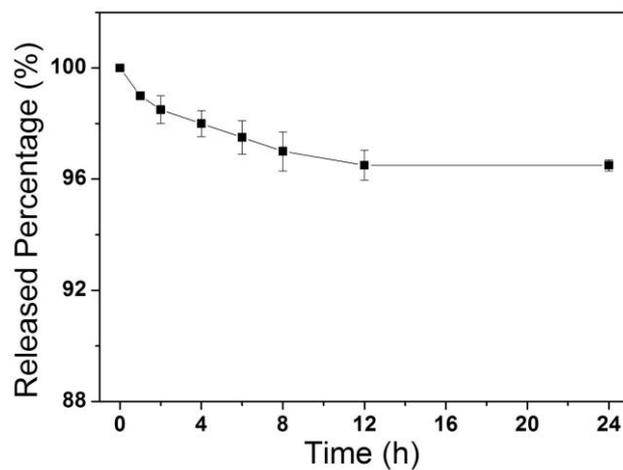
**Figure S10.** H&E stained tumor slices 30 days after the injection of CuPPy-NH<sub>2</sub> NPs. (A) The control group is age-matched healthy mice. (B) The NPs by i.v. + laser group is photothermal therapy group in our experiments. The scale bar is 50  $\mu$ m.



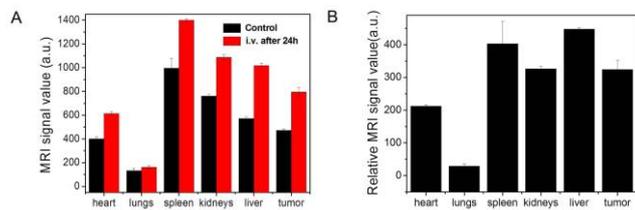
**Figure S11.** (A) The release percentage of Cu(II) from 1 mg/mL CuPPy-NH<sub>2</sub> NPs solution after 24 h incubation in the presence of 10 mM of -COOH, -NH<sub>2</sub> and -SH with the total volume of 10 mL. The -COOH, -NH<sub>2</sub>, and -SH are provided from citric acid, ammonia, and mercaptoglycerol. The Cu(II) concentration is determined by ICP. (B) IR thermal images of KB tumor-bearing mice recorded by an IR camera. Laser irradiation is conducted by using an 808 nm laser (0.33 W/cm<sup>2</sup>) for 980 s on the tumors. The inset color bar from blue to red represents the temperature from low to high.



**Figure S12.** The release of Cu(II) from the nanoparticles in serum. In the experiment, 400  $\mu\text{L}$  5 mg/mL CuPPy-NH<sub>2</sub> NPs is mixed with 2 mL serum. After 24 h, the leakage of Cu(II) from the nanoparticles in serum is 3.5%.



**Figure S13.** (A) MRI signal intensities in vital organs. (B) Biodistribution determined from MRI signal intensity.



**Figure S14.** H&E stained splanchnic slices 30 days after the injection of CuPPy-NH<sub>2</sub> NPs. The control group is age-matched healthy mice. The NPs by i.v. + laser group is photothermal therapy group in our experiments. The scale bar is 50 μm.

