Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information for:

Coordination-driven Self-assembled Mn(II)-Metallostar Endowed with High Relaxivity and Synergistic Photothermal and Photodynamic Effects

Huiyu Wu,[1,2,§] Zhenghui Li,[1,4,§] Yao, Liu,[1,3] Xingchi Shi,[5] Yuan Xue,[1,3] Zuhua Zeng,[1,2] Fanglin, Mi,[4] Haiying Wang[1,*] and Jiang Zhu[1,*]

[1] Medical Imaging Key Laboratory of Sichuan province, Department of Oncology, Affiliated Hospital of North Sichuan Medical College, Maoyuan Road 1, Nanchong City, Sichuan, 637000, China.

[2] School of Pharmacy, North Sichuan Medical College, Fujiang Road 234, Nanchong City, Sichuan, 637000, China

[3] School of Basic Medical Sciences and Forensic Medicine, North Sichuan Medical College, Fujiang Road 234, Nanchong City, Sichuan, 637000, China

[4] Department of Stomatology, North Sichuan Medical College, Fujiang Road 234, Nanchong City, Sichuan, 637000, China

[5] Department of Cardiovascular disease, School of Clinical Medicine, Affiliated Hospital of North Sichuan Medical College, Maoyuan Road 1, Nanchong City, Sichuan, 637000, China.

[§] These authors contribute equally

* Corresponding Author(s): Haiying Wang, hywang@nsmc.edu.cn; Jiang Zhu, zhujiang@nsmc.edu.cn

Table of Contents

1. Photograph of aqueous solutions of three chelates.

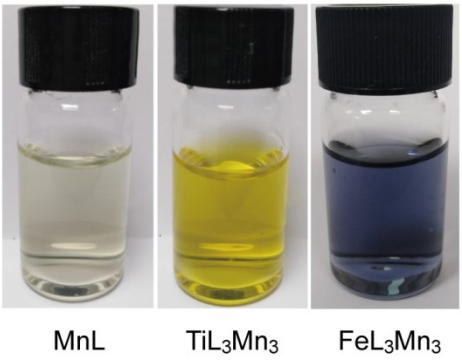

Figure S1 Photograph of aqueous solutions of MnL, TiL_3Mn_3 and FeL_3Mn_3 (pH = 7.4).

2. Photograph of FeL_3Mn_3 at different pH condition.

Figure S2 Photograph of FeL_3Mn_3 at pH = 7.4 and 9.0 (in Tris buffer, 0.1 M).

3. Stability of FeL_3Mn_3 in different mediums

4. Photothermal conversion efficiency measurement of FeL_3Mn_3.

To calculated the photothermal conversion efficiency (η) of FeL_3Mn_3, the FeL_3Mn_3 solution（0.25 mM, 0.3 ml, in HEPES buffer, pH = 7.4, 0.1 M）was irradiated by 808 nm laser (2.0 W cm^{-2}) for 10 min, and then the laser was shut off. The solution was naturally cooled to room temperature. The η was calculated according to a previously described method:

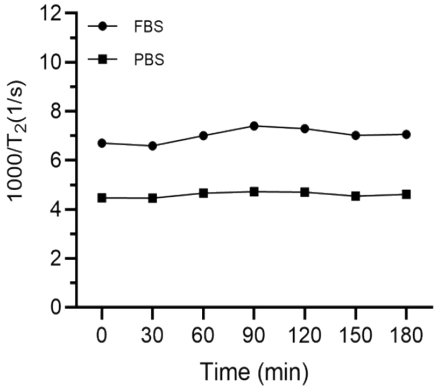

Figure S3 The stability of FeL_3Mn_3 (0.2 mM) in the presence of 10 % FBS (at 37 °C) and the PBS solution (pH = 7.4, 10 mM) of FeL_3Mn_3 was employed as the negative control.

$$\eta = \frac{hs(T_{Max} - T_{Surr}) - Q_{Dis}}{I\,(1 - 10^{-A808})} \quad \text{(A1)}$$

$$hs = \frac{mC}{\tau_s} \quad \text{(A2)}$$

$$t = -\tau_s ln(\theta) \quad \text{(A3)}$$

$$\theta = \frac{T - T_{Surr}}{T_{Max} - T_{Surr}} \quad \text{(A4)}$$

h represents the heat transfer coefficient,

s represents the surface area of the container,

$\mathbf{h_s}$ can be determined from the equation (A2),

T_{Max} represents the maximum steady state temperature,

T_{Surr} represents the ambient room temperature,

Q_{Dis} represents heat dissipated from the laser mediated by the solvent and container,

I represent the laser power and A is the absorbance at 808 nm.

m represents the mass of the solution (g) containing the photoactive material,

C approximate to the specific heat capacity of water,

τ_s represents the associated time constant, which can be determined from the equation (A3),

t represents the time required to cool to room temperature,

θ represents the driving force temperature, which be calculated from the equation (A4),

T represents instantaneous temperature during cooling.

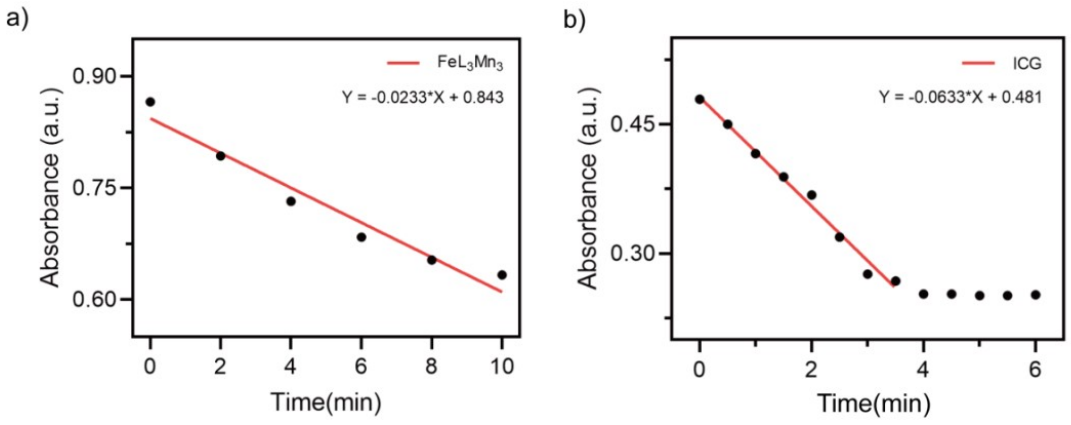

Figure S4 $^1O_2$ quantum yield measurement of FeL_3Mn_3. a) Decrease in absorbance intensity of DPBF recorded at 410 nm in the presence of FeL_3Mn_3 as a function of irradiation time. b) Decrease in absorbance intensity of DPBF recorded at 410 nm in the presence of indocyanine green (ICG) as a function of irradiation time.

5. $^1O_2$ quantum yield measurement of FeL_3Mn_3.

When indocyanine green was selected as the reference compound ($\Phi_{\Delta ICG}$ = 0.14 in water), the $^1O_2$ yield of FeL_3Mn_3 was calculated by the following equation: $\Phi_{\Delta S} = \Phi_{\Delta ICG} \cdot (k_S \cdot F_{ICG})/(k_{ICG} \cdot F_S)$, where superscript S and ICG represent the FeL_3Mn_3 and ICG respectively. k is the DPBF photobleaching rates (410nm). F is the absorption correction factor, which can be calculated from $F = 1\text{-}10^{-OD}$ (OD is the absorbance of samples at 808 nm).

6. Photothermal effect of FeL_3Mn_3 on BxPC-3 cells.

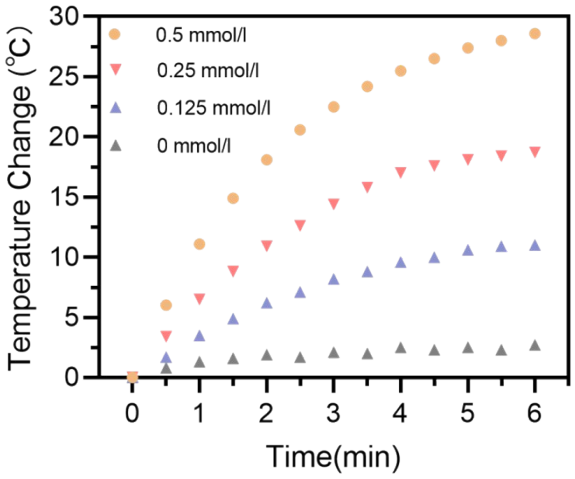

Figure S5 Hyperthermia heating curves of BxPC-3 cells media with FeL_3Mn_3 at various concentrations (0, 0.125, 0.25, 0.5 mM) under 808 nm laser (2 W cm^{-2}) irradiation for 6 min.

7. Shielding of the photodynamic effect of FeL_3Mn_3.

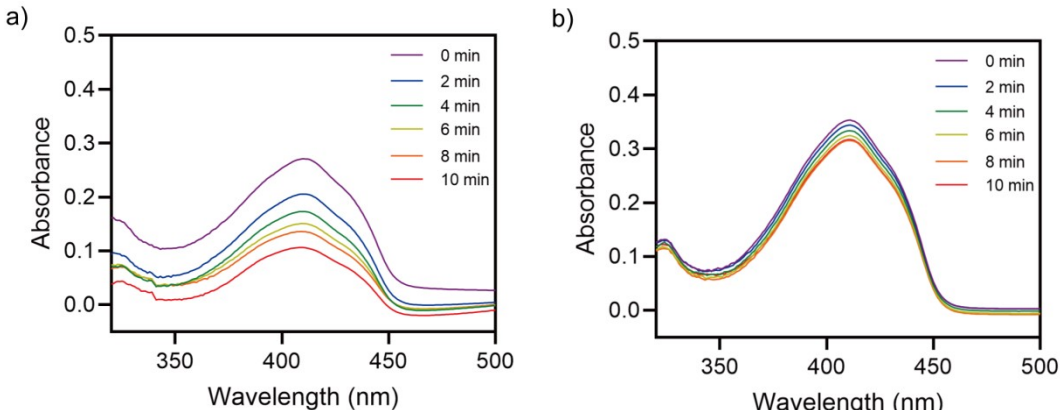

Figure S6 The change of absorption spectra of DPBF (20 μM) mixed with FeL_3Mn_3 (120 μM) over time without (a) / with (b) ascorbate sodium (1.0 mM) under 808 nm laser irritation (2.0 W cm^{-2})