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Electronic Supporting Information (ESI)

for

Smart Nanoprobe Based on Gadolinium Complex Encapsulated by ZIF-8 with Enhanced Room Temperature Phosphorescence for Synchronous Oxygen Sensing and Photodynamic Therapy

Zhongli Zhao,[a] Jiaxi Ru,[b] Panpan Zhou,[a] Yunsheng Wang,[a] Changfu Shan,[a] Xiaoxi Yang,[a] Jing Cao,*[a] Weisheng Liu,[a] Huichen Guo,*[b] and Yu Tang*[a]

[a] State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China

[b] State Key Laboratory of Veterinary Etiological Biology, Lanzhou Veterinary Research Institute, Chinese Academy of Agricultural Sciences, Lanzhou 730046, P. R. China

*E-mail: tangyu@lzu.edu.cn; caoj@lzu.edu.cn; guohuichen@caas.cn. Fax: +86 931-891-2582.

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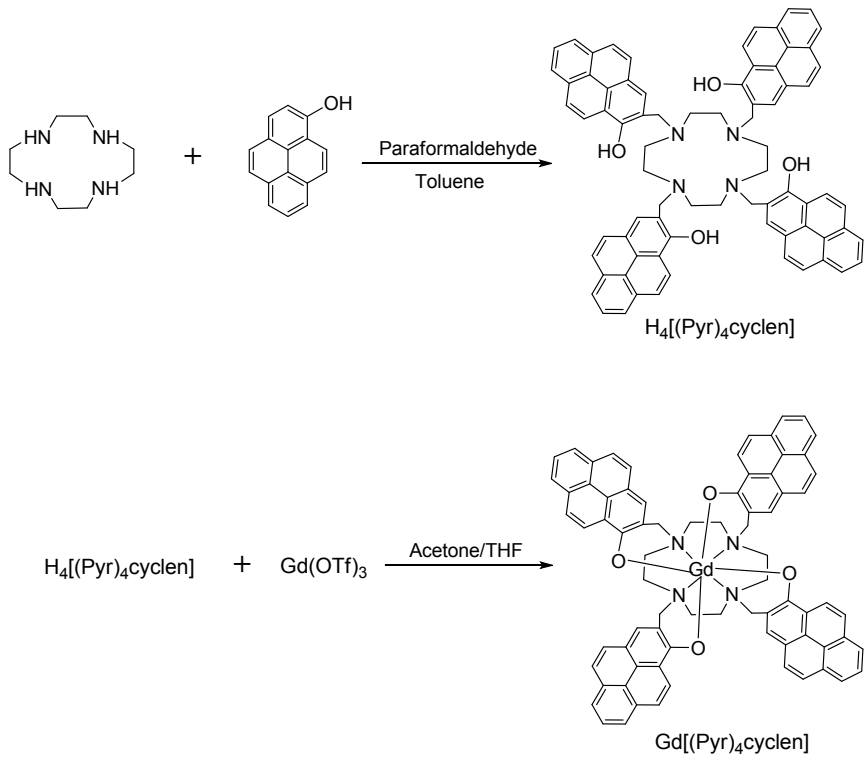

Scheme S1 Preparation of H_4[(Pyr)$_4$cyclen] and Gd[(Pyr)$_4$cyclen]

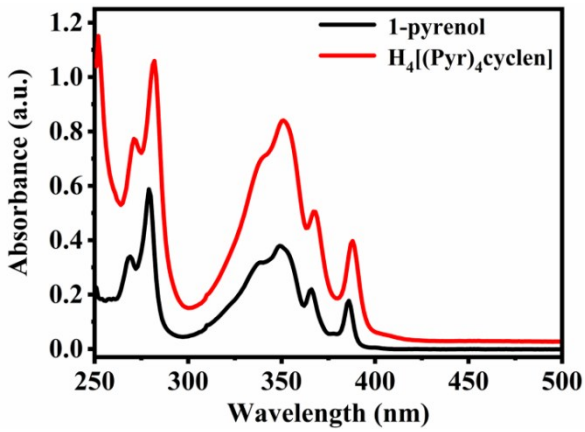

Fig. S1 UV-Vis absorption spectra of the 1-pyrenol (2.0×10^{-5} mol·L^{-1}) and H_4[(Pyr)$_4$cyclen] (1.1×10^{-5} mol·L^{-1})

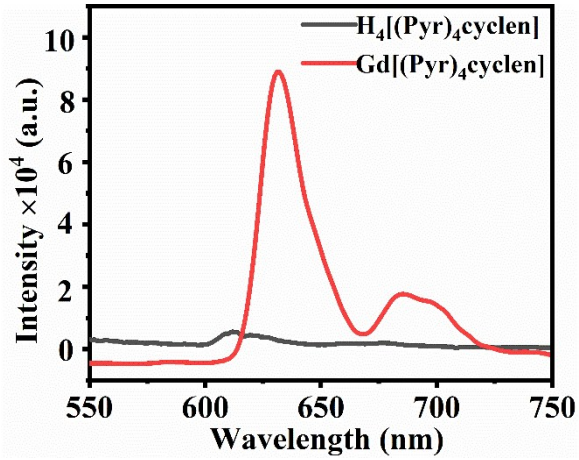

Fig. S2 The luminescence spectra of H_4[(Pyr)$_4$cyclen] (2.0×10^{-6} mol·L^{-1}) and Gd[(Pyr)$_4$cyclen] (2.0×10^{-6} mol·L^{-1}) in THF in air at low temperature (77 K, gate 100 μs).

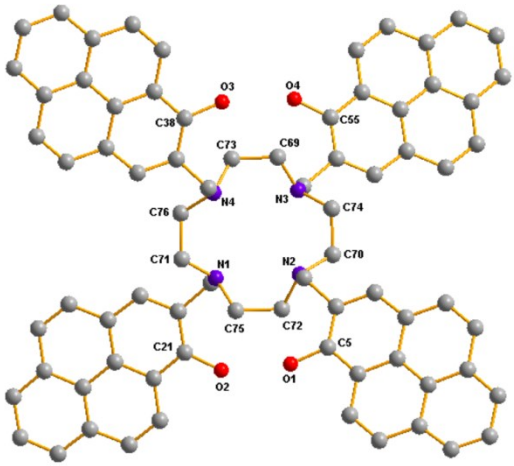

Fig. S3 An ORTEP drawing of H_4[(Pyr)$_4$cyclen]. Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [º].

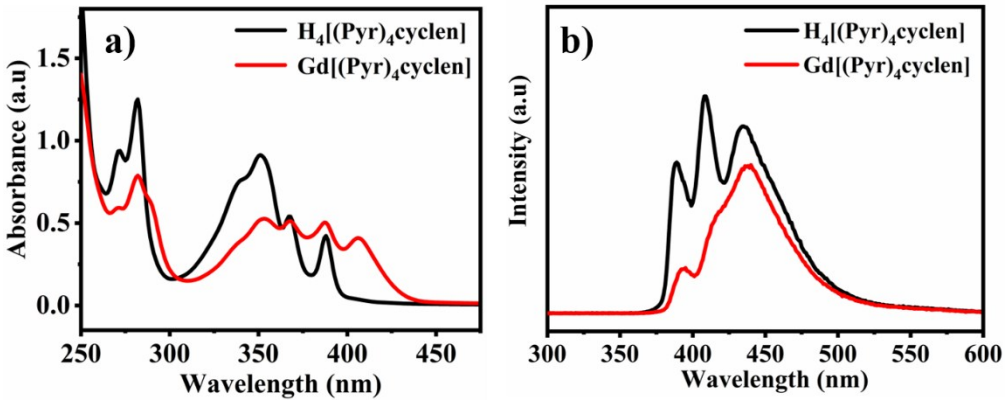

Fig. S4 a) UV-Vis absorption spectra and b) Emission spectra (λ_{ex} = 351 nm) of H_4[(Pyr)$_4$cyclen] (1.0×10^{-5} mol·L^{-1}) and Gd[(Pyr)$_4$cyclen] (9.5×10^{-6} mol·L^{-1}) in no degassed THF at room temperature.

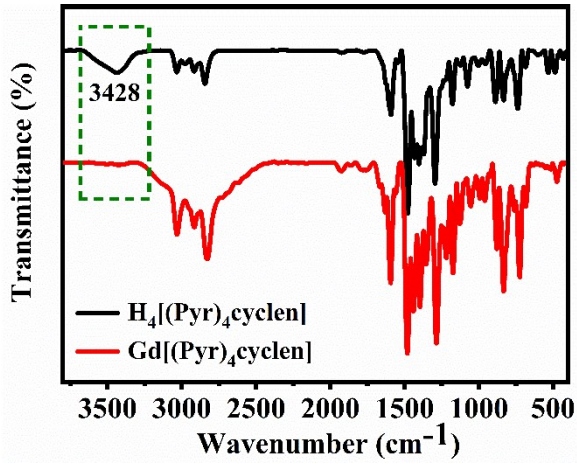

Fig. S5 FTIR spectra of H_4[(Pyr)$_4$cyclen] and Gd[(Pyr)$_4$cyclen]·

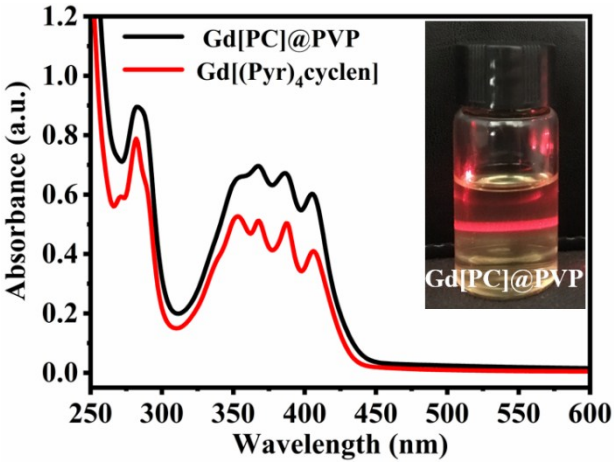

Fig. S6 UV-Vis absorption spectra of the Gd[(Pyr)$_4$cyclen] (9.5×10^{-6} mol·L^{-1}) and Gd[PC]@PVP (1.0 mg·mL^{-1}).

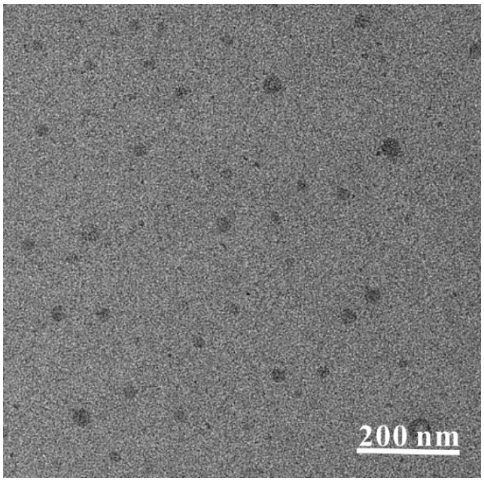

Fig. S7 TEM images of Gd[PC]@PVP nanoparticles.

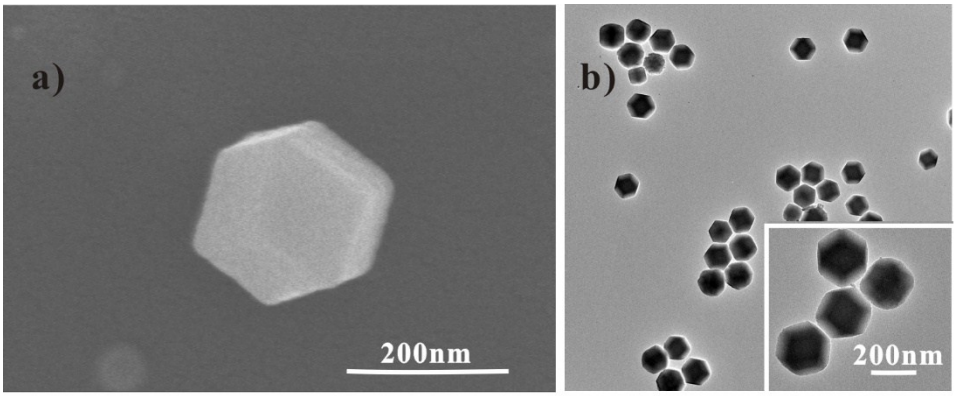

Fig. S8 a) SEM) image and b) TEM images of ZIF-8.

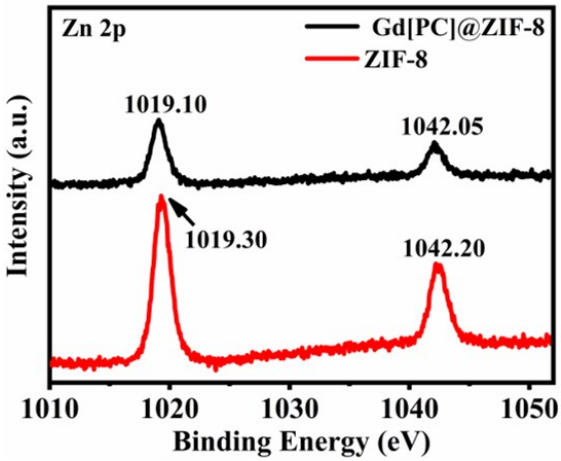

Fig. S9 The high resolution XPS spectra of Zn 2p in di□erent materials.

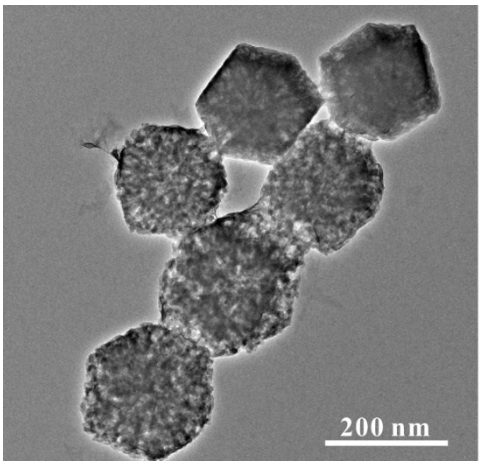

Fig. S10 TEM image of Gd[PC]@ZIF-8@PLL

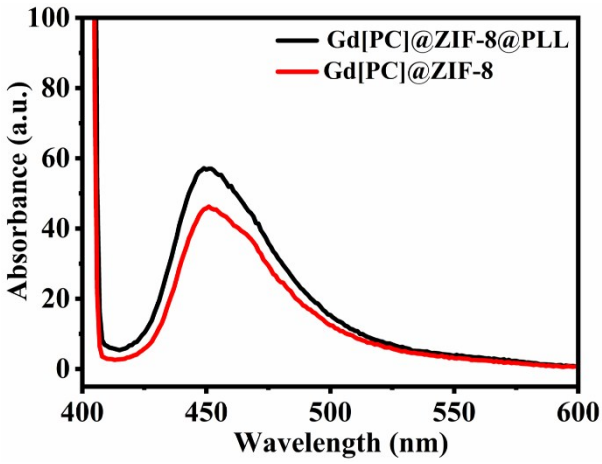

Fig. S11 Emission spectrum of Gd[PC]@ZIF-8 (1.0 mg·mL^{-1}) and Gd[PC]@ZIF-8@PLL (1.0 mg·mL^{-1}) in no degassed PBS at room temperature. λ_{ex} = 397 nm

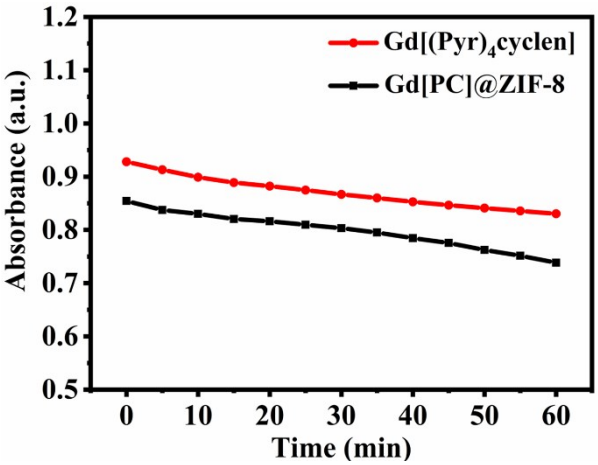

Fig. S12 The photostability curves of Gd[(Pyr)$_4$cyclen] (THF, 1.6 x 10^{-5} mol·L^{-1}) and Gd[PC]@ZIF-8 (H_2O, 0.5 mg·mL^{-1}) under radiation at 365 nm LED irradiation.

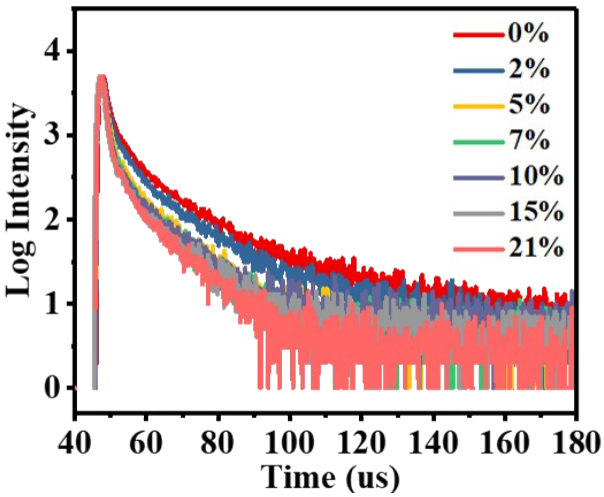

Fig. S13 Lifetime spectrum of Gd[PC]@ZIF-8 at different oxygen concentration under room temperature. λ_{ex} = 328 nm

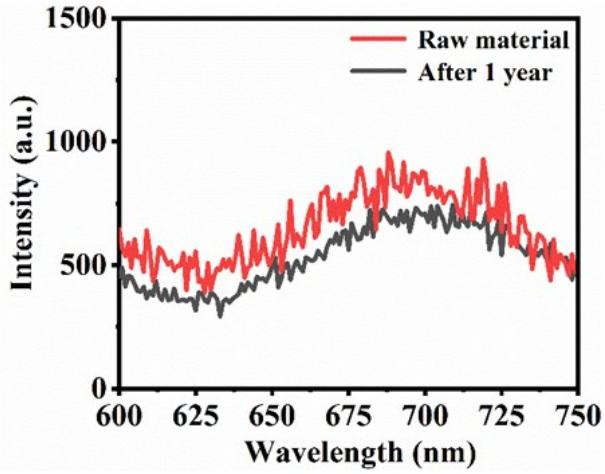

Fig. S14 The luminescence spectra Gd[PC]@ZIF-8 raw material and after 1year in H_2O (1.0 mg·mL^{-1}, of which c(Gd[(Pyr)$_4$cyclen]) = 2.2 ×10^{-5} mol·L^{-1}) at room temperature in air (gate 100 μs)

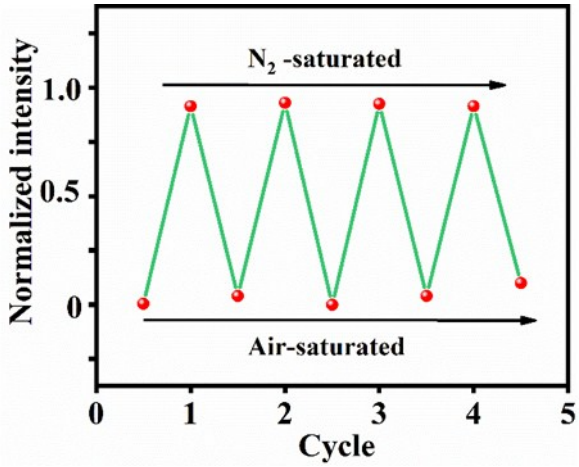

Fig. S15 Reversible luminescence response of Gd[PC]@ZIF-8 under alternating exposure N_2-saturated and air-saturated H_2O suspension.

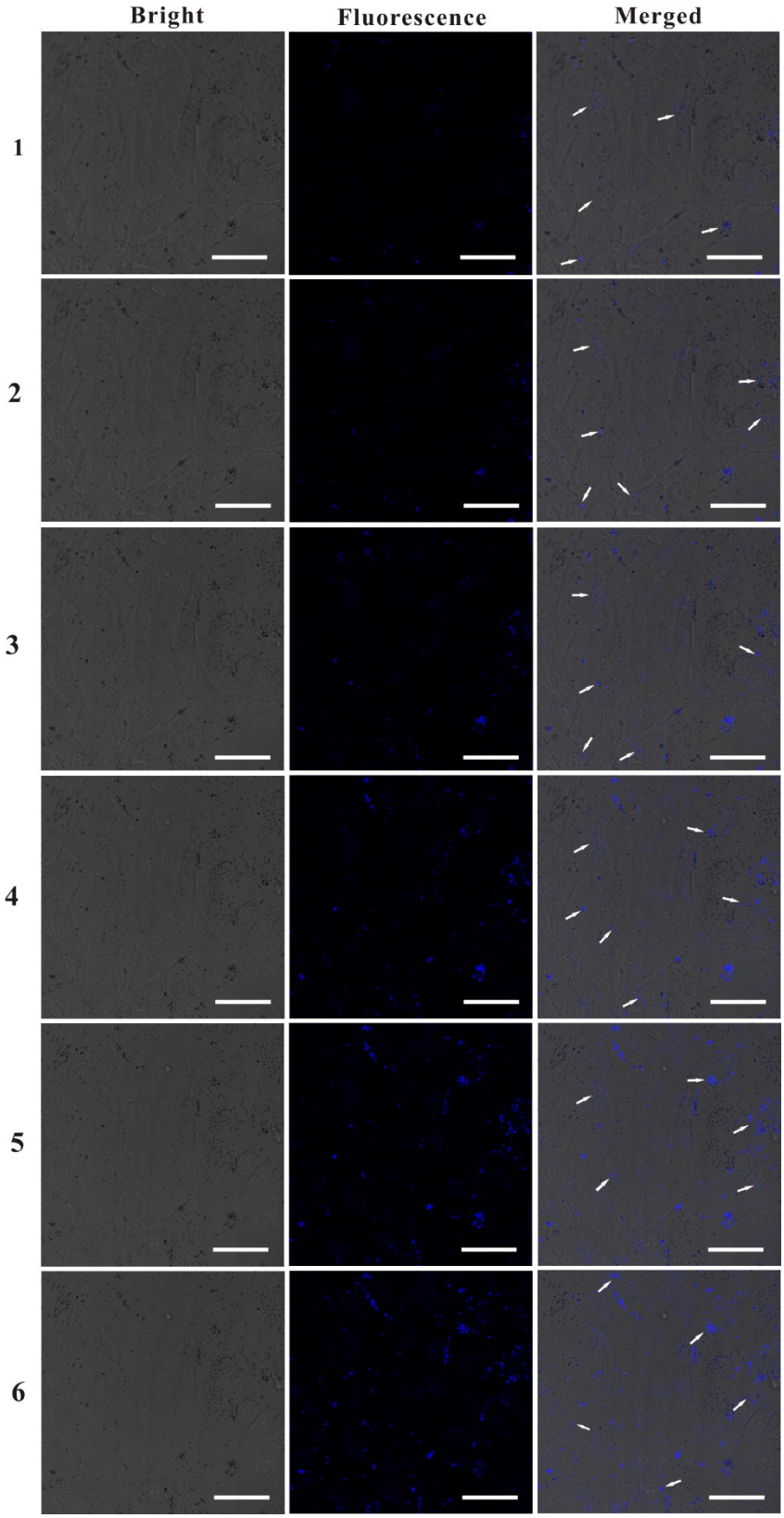

Fig. S16 Confocal microscopic tomography images of HeLa cells incubated with Gd[PC]@ZIF-8@PLL for 6 h. a) Bright, b) Fluorescence, c) Merged. Tomography was performed along the z-axis from the top to the bottom of the cell 1.0 μm per layer. The nanoprobe in Hela cell was partly marked by white arrows.

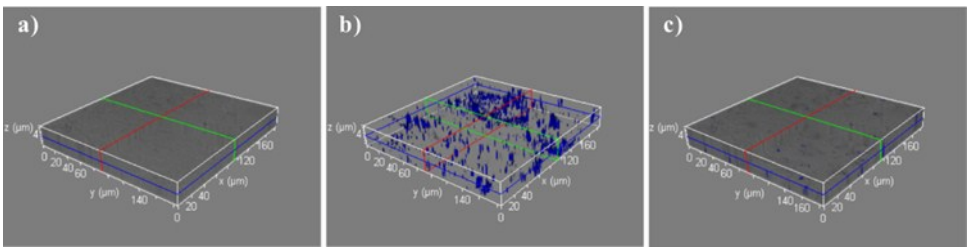

Fig. S17 The 3D reconstruction fluorescence images of HeLa cells incubated with Gd[PC]@ZIF-8@PLL for 6 h. a) Bright, b) Fluorescence, c) Merged.

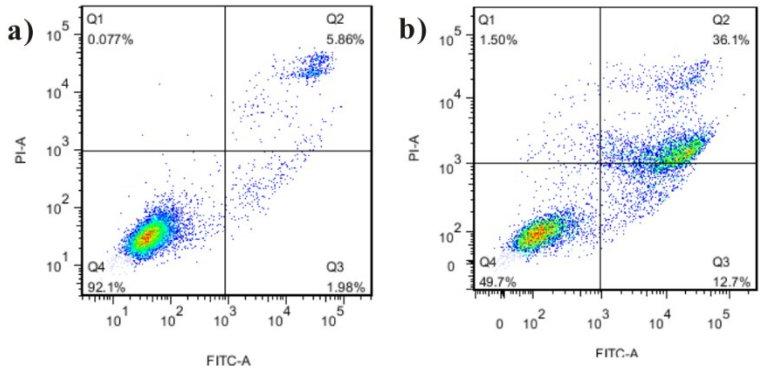

Fig. S18 The flow cytometry quantification of annexin V-FITC- and PI-labeled HeLa cells after irradiated by 365 nm LED lamp for 20 min: a) control, b) treated with the Gd[PC]@ZIF-8@PLL (32.0 μmol· L-1) at 37 ^{o}C for 24 h.

Table S1 Selected band distances and angles for H_4[(Pyr)$_4$cyclen] and Gd[(Pyr)$_4$cyclen]

Sample	Band distance (Å)	Angles (º)
H_4[(Pyr)$_4$cyclen]	C5–O1 = 1.371	C71-N1-C75 = 117.428
	C21–O2 = 1.371	C70-N2-C72 = 117.123
	C38–O3 = 1.371	C69-N3-C74 = 117.436
	C55–O4 = 1.371	C73-N4-C76 =117.079
Gd[(Pyr)$_4$cyclen]	Gd-N1= 2.351	N1-Gd-N3 = 142.367
	Gd-N2 = 2.340	N1-Gd-N4 = 95.650
	Gd-N3 = 2.353	N2-Gd-N3 = 95.138
	Gd-N4 = 2.337	N2-Gd-N4 = 147.684
	Gd-O1 = 2.475	O1-Gd-O2 = 131.345
	Gd-O2 = 2.582	O1-Gd-O3 = 65.188
	Gd-O3 = 2.504	O2-Gd-O4 = 62.016
	Gd-O4 = 2.558	O3-Gd-O4 = 130.765

Table S2 The molar extinction coefficiencies (ε) of the H_4[(Pyr)$_4$cyclen] and the Gd[(Pyr)$_4$cyclen] complex at various UV-Vis absorption peaks.

Compounds	Molar extinction coefficiency (ε) $mol^{-1}\cdot L\cdot cm^{-1}$				
	282 nm	351 nm	367 nm	388 nm	405 nm
H_4[(Pyr)$_4$cyclen]	8.74×10^4	7.02×10^4	4.14×10^4	3.24×10^4	-----
Gd[(Pyr)$_4$cyclen]	4.72×10^4	3.17×10^4	3.40×10^4	3.48×10^4	3.11×10^4

Table S3 Zeta potential of ZIF-8, Gd[PC]@PVP, Gd[PC]@ZIF-8 and Gd[PC]@ZIF-8@PLL.

	ZIF-8	Gd[PC]@PVP	Gd[PC]@ZIF-8	Gd[PC]@ZIF-8@PLL
ζ potential (mV)	+ 44.69	- 4.69	+ 2.53	+ 1.89

Table S4 Summarized surface area and pore propertyof ZIF-8 and Gd[PC]@ZIF-8

	ZIF-8	Gd[PC]@ZIF-8
BET Surface Area ($m^2 \cdot g^{-1}$)	1053.1207	806.1200
Langmuir Surface Area ($m^2 \cdot g^{-1}$)	1432.4139	1082.4739
t-Plot micropore volume ($cm^3 \cdot g^{-1}$)	0.4951	0.3614

Table S5 Phosphorescence lifetime (τ) of Gd[$(Pyr)_4$cyclen], Gd[PC]@PVP and Gd[PC]@ZIF-8 in N_2 at room temperature at 700 nm

	Gd[$(Pyr)_4$cyclen][a]	Gd[PC]@PVP[b]	Gd[PC]@ZIF-8[c]
τ(us)	< 1.0	4.06	36.95

a. In THF (5.0×10^{-5} mol·L^{-1})

b. In THF (1.3 mg·mL^{-1}, *c*(Gd[$(Pyr)_4$cyclen]) = 5.0×10^{-5} mol·L^{-1})

c. In H_2O (1.0 mg·mL^{-1}, *c*(Gd[$(Pyr)_4$cyclen]) = 2.2×10^{-5} mol·L^{-1})

Table S6 The luminescent quantum efficiencies of Gd[$(Pyr)_4$cyclen] and Gd[PC]@ZIF-8 in air

	Gd[$(Pyr)_4$cyclen][a]	Gd[PC]@ZIF-8[b]
Luminescent quantum efficiencies	0.044	0.13

a. In THF

b. In H_2O

2. Notes and references

(S1) Wang, X. H.; Peng, H. S.; Yang, L.; You, F. T.; Teng, F.; Hou, L. L.; Wolfbeis, O. S. *Angew. Chem. Int. Ed.* **2014**, *53*, 12471–12475.

(S2) Nakai, H.; Kitagawa, K.; Nakamori, H.; Tokunaga, T.; Matsumoto, T.; Nozaki, K.; Ogo, S. *Angew. Chem. Int. Ed.* **2013**, *52*, 8722–8725.