

## Support Informating

# **Pd Nanoparticles Encapsulated in the Magnetic Carbon Nanocages: An Efficient Nanoenzyme for Selective Detection and Multicolor Imaging of Cancer Cells**

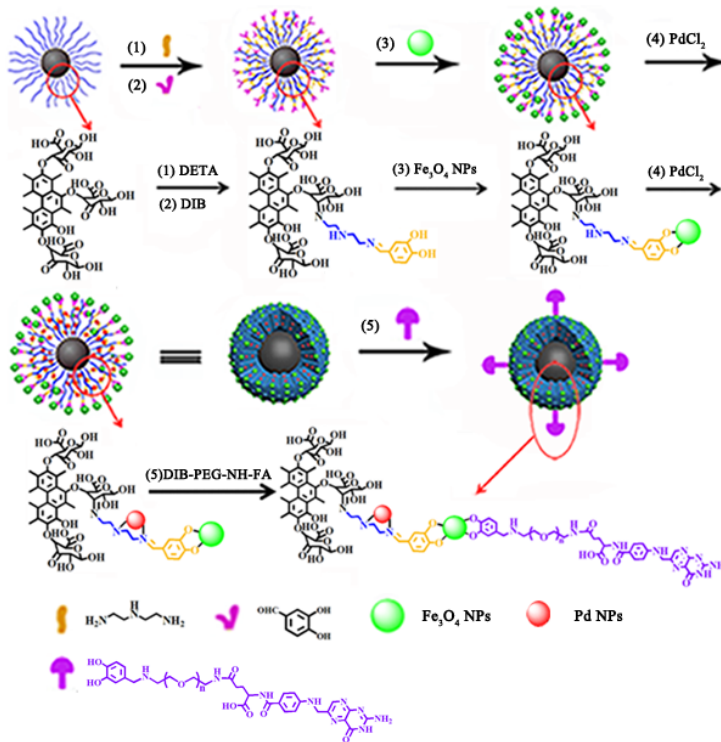
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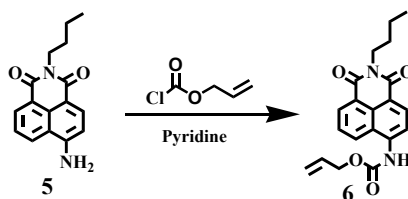
## **Experimental Section**

### **Experimental Procedures**



**Scheme S1. Preparation of FA-PdNPs/MCNC**

### 1.0 Synthesis of N-butyl-4-NHAlloc-1, 8-naphthalimide (6, NNPH)

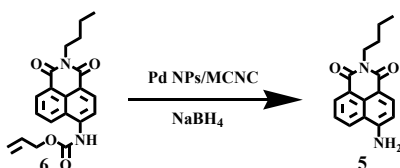


At 0 °C allyl chloroformate (0.5 mL, 5 mmol) was added to the solution of N-butyl-4-amido-1, 8-naphthalimide (0.27 g, 1 mmol) which was synthesized according to the literature.<sup>1</sup> The mixture was stirred at 0 °C for 2 h and then warmed to room temperature and maintained at this temperature for another 12 h. The reaction was quenched with diluted HCl and extracted three times with ether. The combined organic layers were dried, filtered, concentrated and purified by silica gel column chromatography (1/5, EtOAc/petroleum ether) to give 300 mg of compound 6 (yield: 85%) as a white solid. ESI-MS:  $m/z = 353.0112$  [M + H<sup>+</sup>].

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta = 8.60$  (d,  $J = 7.6$  Hz, 1H), 8.56 (d,  $J = 8.4$  Hz, 1H), 8.34 (d,  $J = 8.0$  Hz, 1H), 7.74 (dd,  $J = 8.4$  Hz, 7.6 Hz, 1H), 7.48 (s, 1H), 6.04-

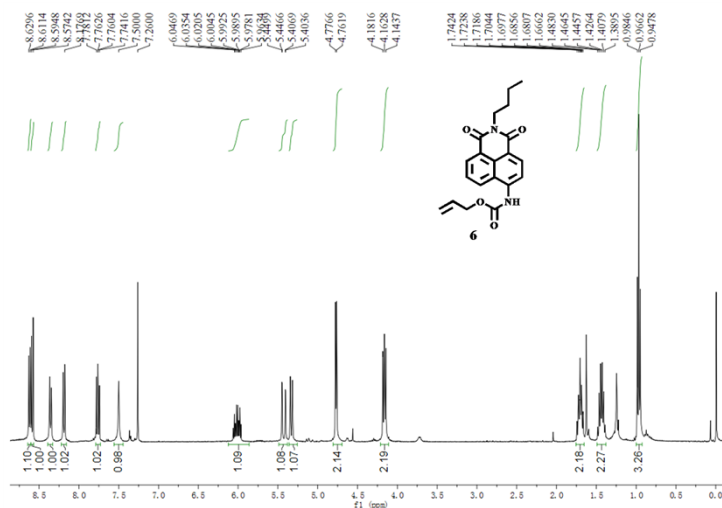
5.94 (m, 1H), 5.42 (dd,  $J = 17.2$  Hz, 1.2Hz, 1H), 5.31 (dd,  $J = 10.4$  Hz,  $J = 0.8$  Hz, 1H), 4.75 (d,  $J = 6.0$  Hz, 2H), 4.13 (t,  $J = 7.60$  Hz, 2H), 1.68 (m, 2H), 1.42 (m, 2H), 0.95 (t,  $J = 7.6$  Hz, 3H).

### 1.1 Formation of N-butyl-4-amido-1,8-naphthalimide (NPH) from N-butyl-4-NHAlloc-1,8-naphthalimide

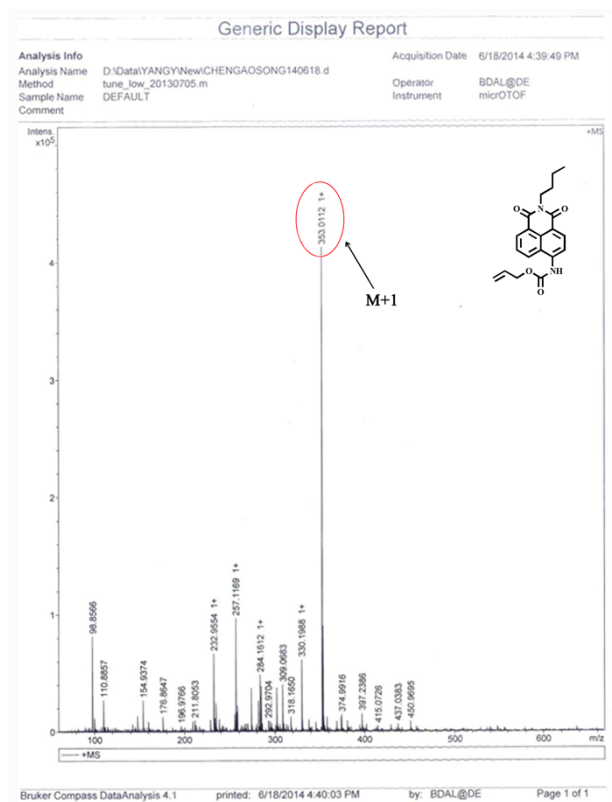


5 mg PdNPs/MCNC was added in a mixture of compound 6 (352 mg) with NaBH<sub>4</sub> (0.2 mg) in ethanol (20 mL) and stirred at room temperature. The process of reaction was monitored by thin layer chromatography TLC until completion. The solvent was removed in vacuo, and the crude product was purified by silica gel column chromatography to give 263 mg compound 5 (yield: 98%). ESI-MS:  $m/z = 269.1879$  [M + H<sup>+</sup>]

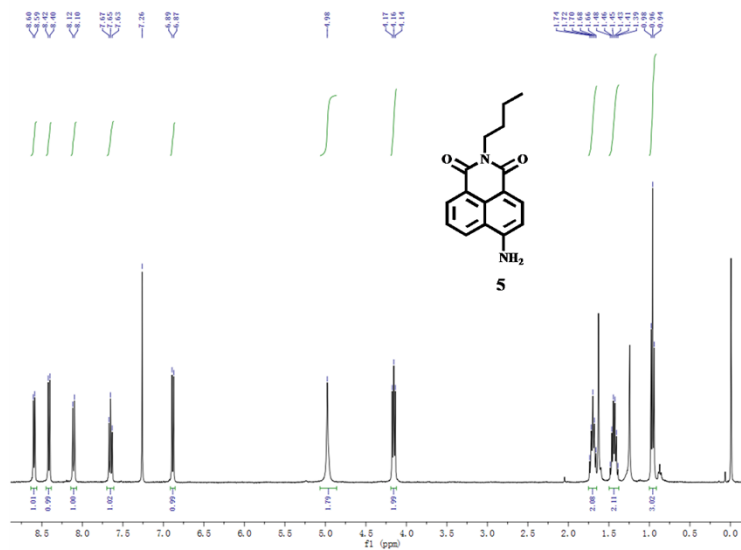
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta = 8.83$  (d,  $J = 8.8$  Hz, 1H), 8.74 (d,  $J = 7.6$  Hz, 1H), 8.69 (d,  $J = 8.0$  Hz, 1H), 7.98 (t,  $J = 7.6$  Hz, 1H), 4.18 (t,  $J = 7.6$  Hz, 1H), 1.72 (m, 2H), 1.45 (m, 2H), 0.98 (t,  $J = 7.6$  Hz, 3H).



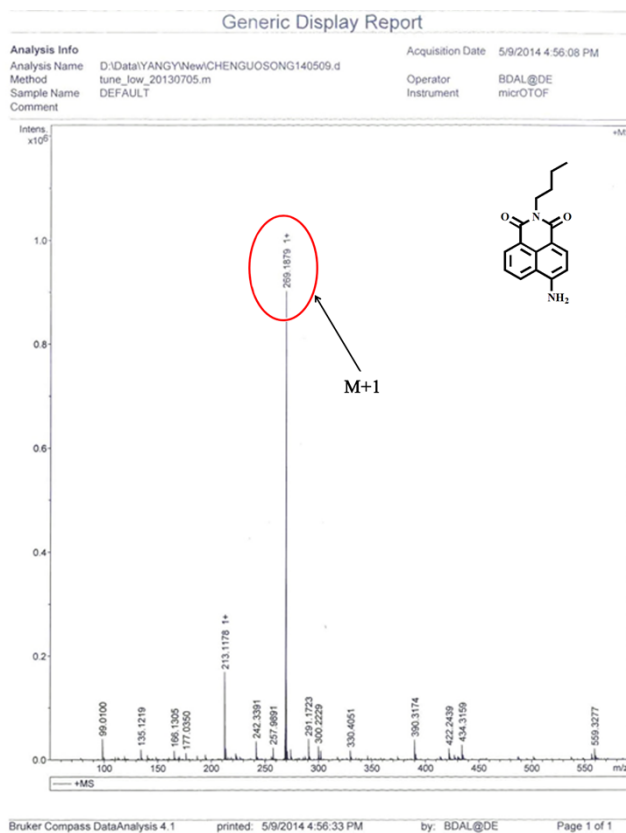
**Figure S1.** <sup>1</sup>H NMR spectrum of N-butyl-4-NHAlloc-1,8-naphthalimide (NNPH)



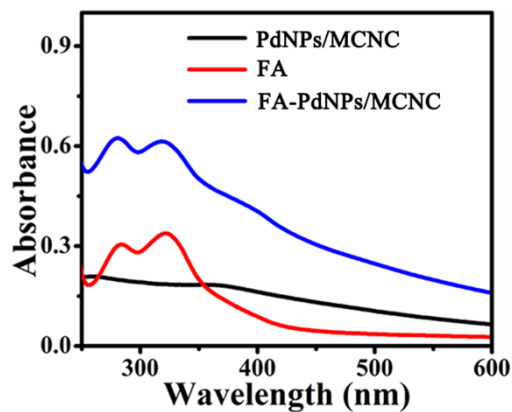
**Figure S2.** Mass spectrum of N-butyl-4-NHAlloc-1,8-naphthalimide (NNPH)



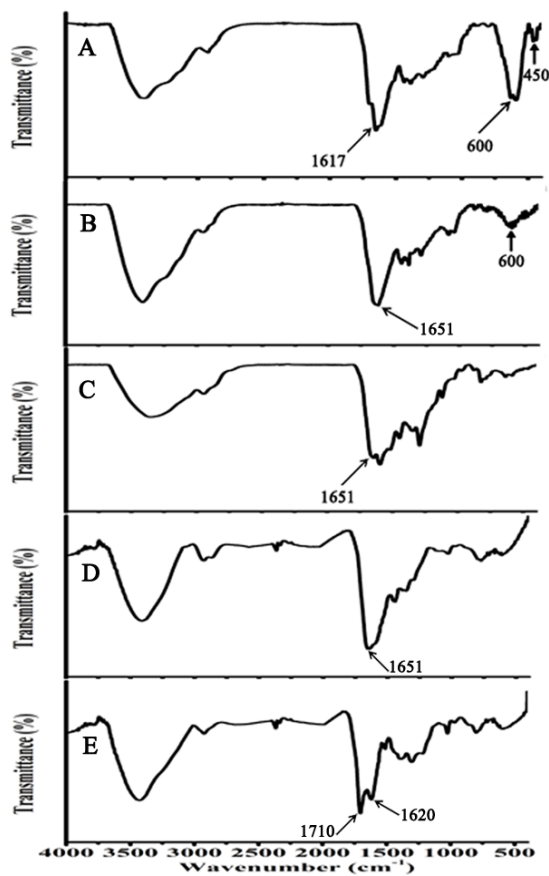
**Figure S3.** <sup>1</sup>H NMR spectrum of N-butyl-4-amido-1,8-naphthalimide (NPH)



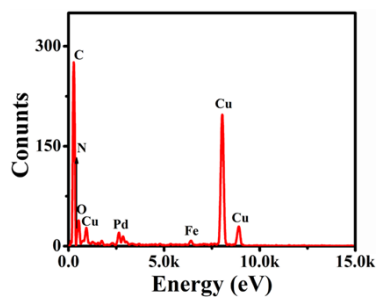
**Figure S4.** Mass spectrum of N-butyl-4-amido-1,8-naphthalimide (NPH)



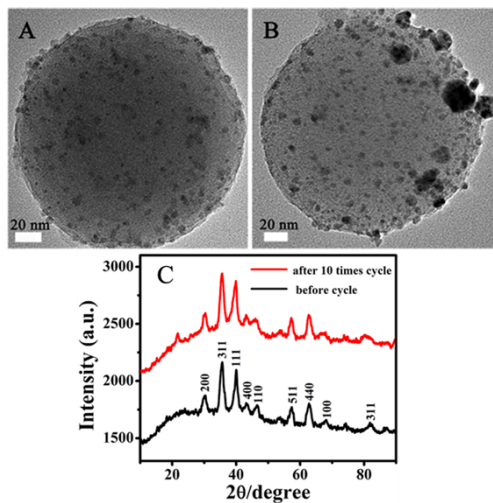
**Figure S5.** UV-vis detection of PdNPs/MCNC (black), folic acid (red), FA-PdNPs/MCNC (blue). In the UV-vis spectra, FA-PdNPs/MCNC shows two new absorbance peaks at 283 and 330 nm, respectively, which is from FA, indicating that FA has been grafted onto the surface of PdNPs/MCNC.



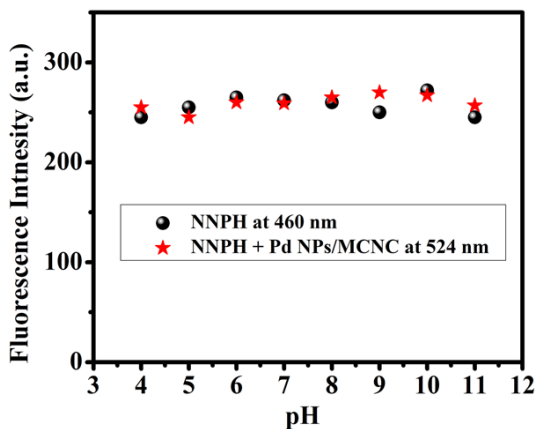
**Figure S6.** FT-IR spectra of CNSs (E), CNSs-DETA (D), CNSs-DETA-DIB (C), Fe<sub>3</sub>O<sub>4</sub> NPs/CNCs (B) and PdNPs/MCNC (A). The FT-IR spectrum of CNSs-DETA-DIB (C) showed strong absorption bands at 1651 cm<sup>-1</sup>, which attributed to C=N vibrations. After forming PdNPs/MCNC (A), bands at 1651 cm<sup>-1</sup> is red-shift to 1617 cm<sup>-1</sup>, and a new band at 450 cm<sup>-1</sup> is attributed to Pd-N absorption bands. In addition, the new peak at 600 cm<sup>-1</sup> is attributed to Fe-O absorption bands.



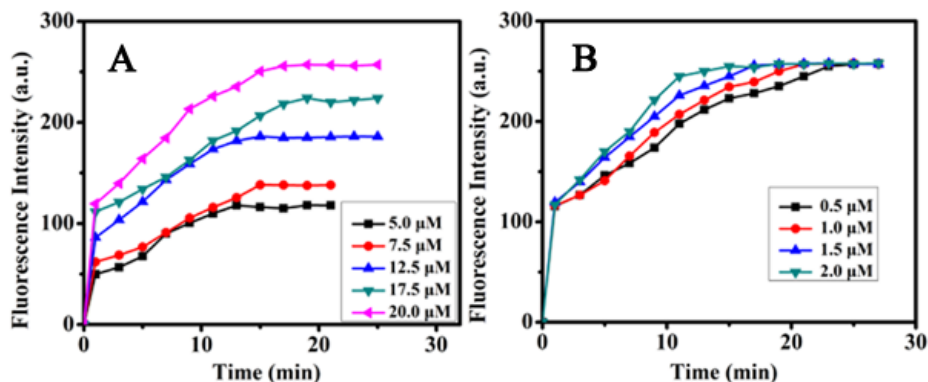
**Figure S7.** The typical EDX pattern of PdNPs/MCNC.



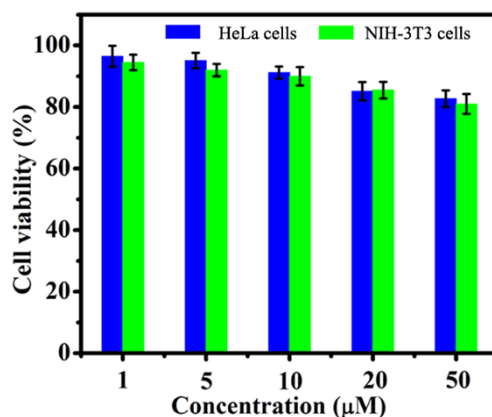
**Figure S8.** (A) The TEM image of PdNPs/MCNC before cycle. (B) The TEM image of PdNPs/MCNC after 10 times cycle. (C) XRD patterns of Pd NPs/MCNC before cycle (black) and PdNPs/MCNC after 10 times cycle (red).



**Figure S9.** The fluorescence intensity of NNPH (20  $\mu$ M) at 460 nm (black) as a function of pH under a series of buffer solution with various pH values. The fluorescence intensity of NNPH (20  $\mu$ M) in the presence of PdNPs/MCNC (the concentration of Pd is 2  $\mu$ M) at 524 nm (red) as a function of pH under a series of buffer solution incubated with various pH values for 15 minutes. Ex = 403 nm, Slit: 3.0 nm/1.5 nm.



**Figure S10.** (A) The evolution of fluorescence intensity of NNPH (5, 7.5, 12.5, 17.5 and 20 μM) in EtOH/H<sub>2</sub>O (v/v, 1/2) mixture solution catalyzed by 2 μM (Pd) PdNPs/MCNC with incubation time. It can be seen that the time of the conversions reaching near-completion increases with the increase of NNPH concentration. (B) The evolution of fluorescence intensity of NNPH (20 μM) in EtOH/H<sub>2</sub>O (v/v, 1/2) mixture solution catalyzed by different concentrations of PdNPs/MCNC (Pd: 0.5, 1, 1.5 and 2 μM) with incubation time. Ex = 403 nm. Slit = 3.0 nm/1.5 nm. It can be seen that the consume time of conversions reaching near-completion decreases with the increasing PdNPs/MCNC concentration.



**Figure 11.** In vitro cell viability tests by MTT assay for HeLa cells (blue) and NIH-3T3 cells (green) incubated with different concentrations (Pd: 1, 5, 10, 20 and 50 μM) PdNPs/MCNC for 48 h.