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Morpholinyl Dendrimer Phthalocyanine:Synthesis, Photophysical Properties and Photoinduce Intramolecular Electron Transfer

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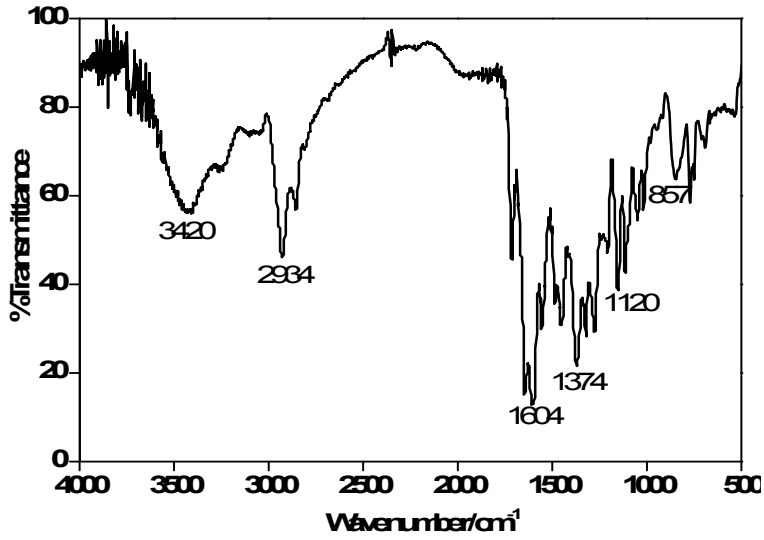

Fig. S1 The IR spectrum of **ME-ML-ZnPc**

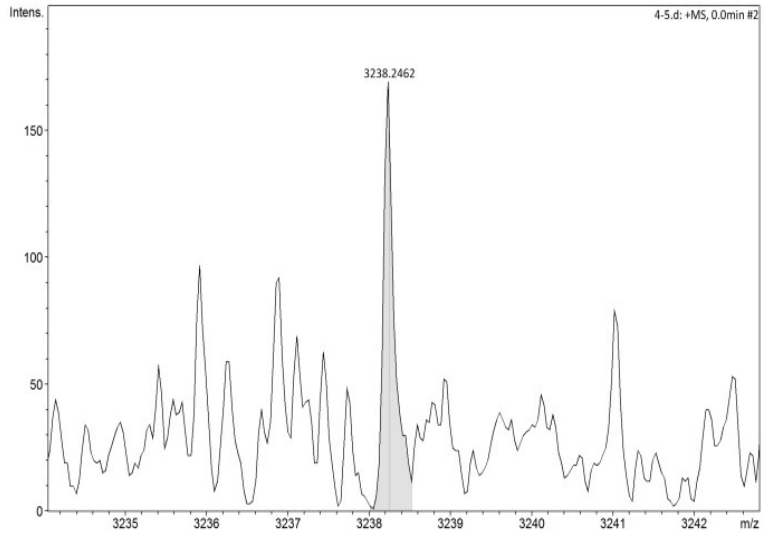

Fig. S2 The ESI-MS spectrum of **ME-ML-ZnPc**

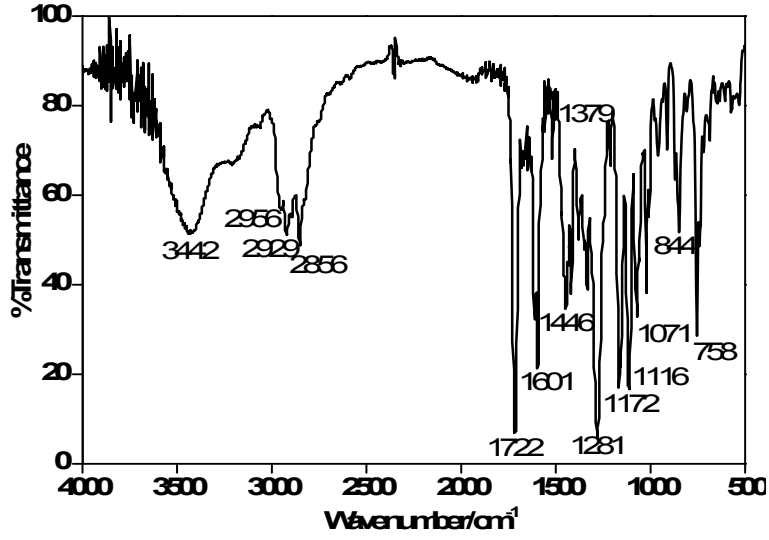

Fig. S3 The IR spectrum of **ME-ML-SiPc**

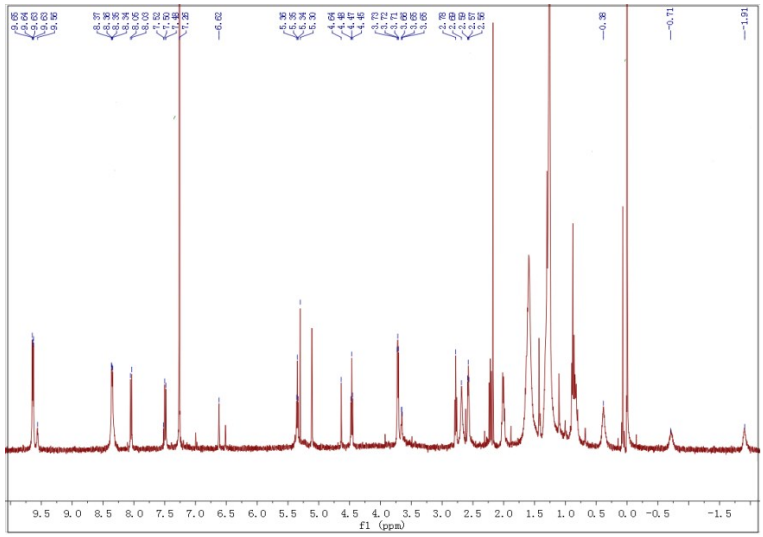

Fig. S4 The ^{1}H NMR spectrum of **ME-ML-SiPc** (400 MHz, $CDCl_3$)

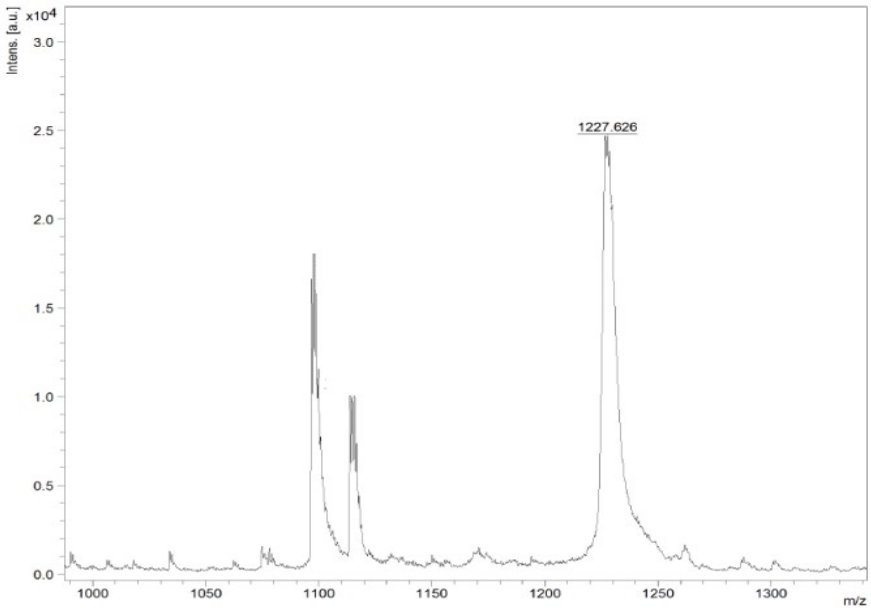

Fig. S5 The MALDI-TOF-MS spectrum of **ME-ML-SiPc**

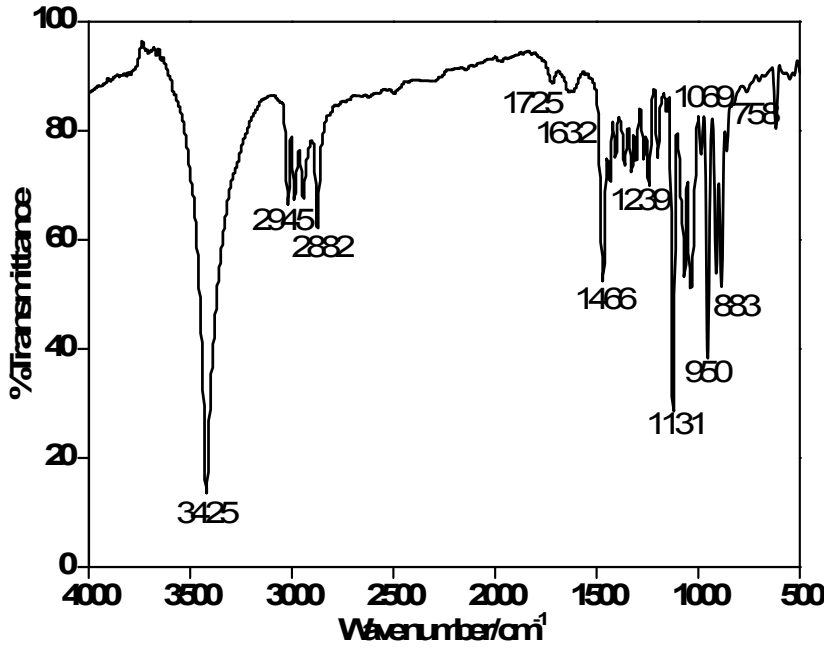

Fig.S6 The IR spectrum of **ME-MLI$_4$-SiPc**

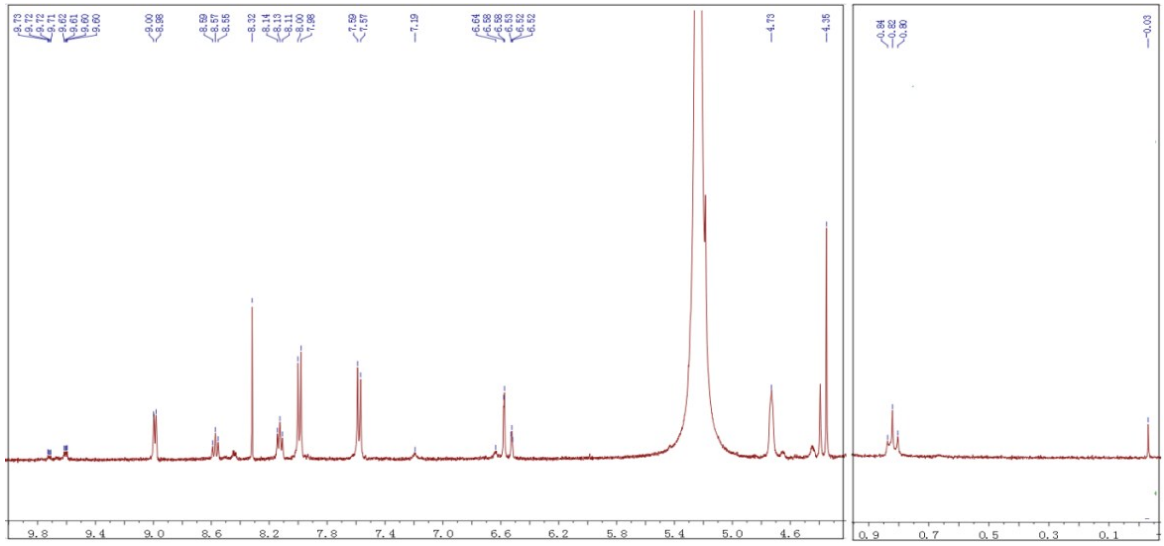

Fig.S7 The ^{1}H NMR spectrum of **ME-MLI$_4$-SiPc** (400 MHz, DMSO-*d6*)

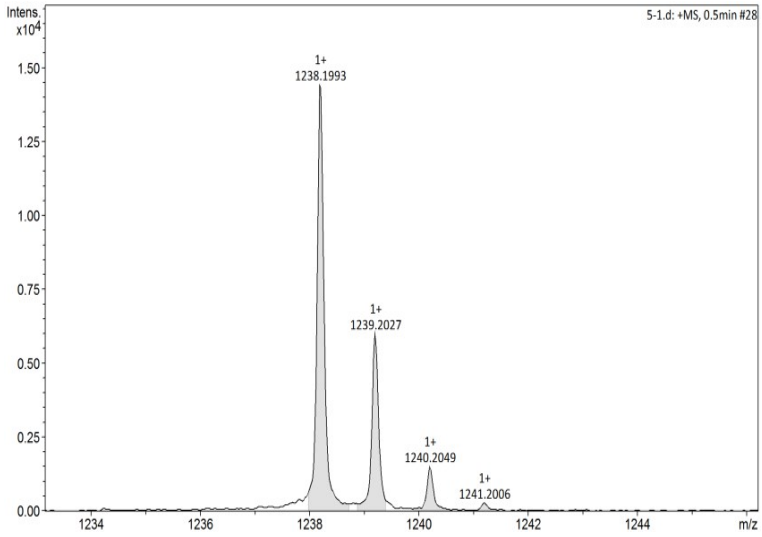

Fig.S8 The ESI-MS spectrum of **ME-MLI$_4$-SiPc**

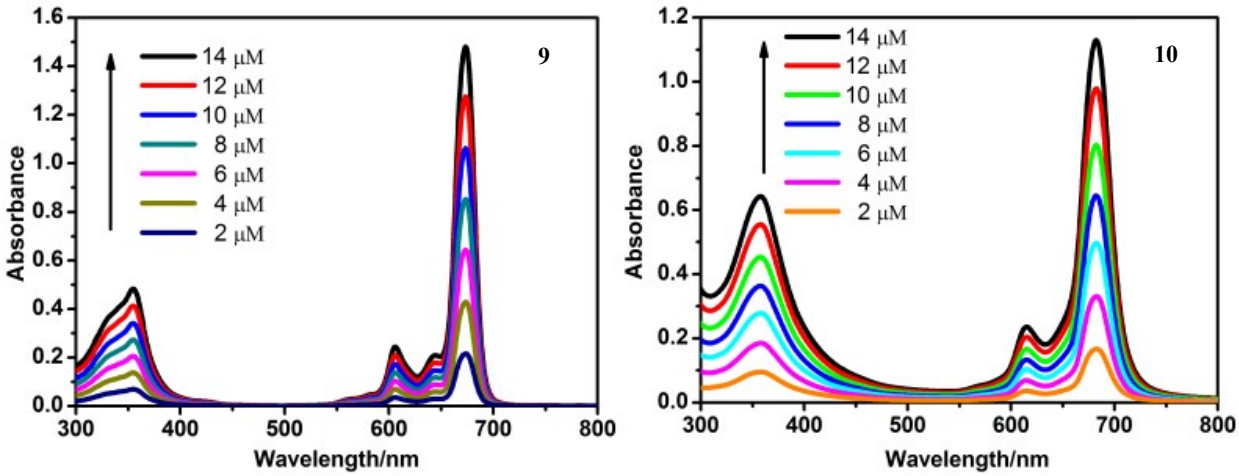

Fig.S9 UV-Vis spectra of **ME-ML-SiPc** in DMF (The inset shows the absorbance at 674 nm, 606 nm and 355 nm,as a function of its concentration)**; S10** UV-Vis spectra of **ME-ML-ZnPc** in DMF (The inset shows the absorbance at 683 nm, 614 nm and 358 nm, as a function of its concentration)

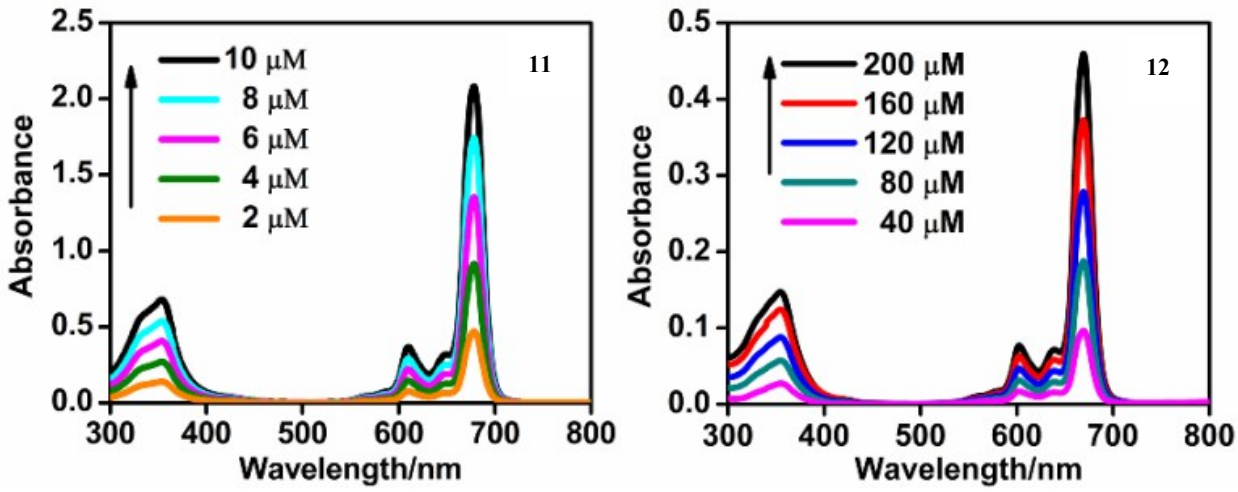

Fig.S11 UV-Vis spectra of **ME-SiPc** in DMF (The inset shows the absorbance at 678 nm, 610 nm and 354 nm, as a function of its concentration). **S12**. UV-Vis spectra of **ME-MLI$_4$-SiPc** in DMF (The inset shows the absorbance at 670 nm, 603 nm and 355 nm, as a function of its concentration)

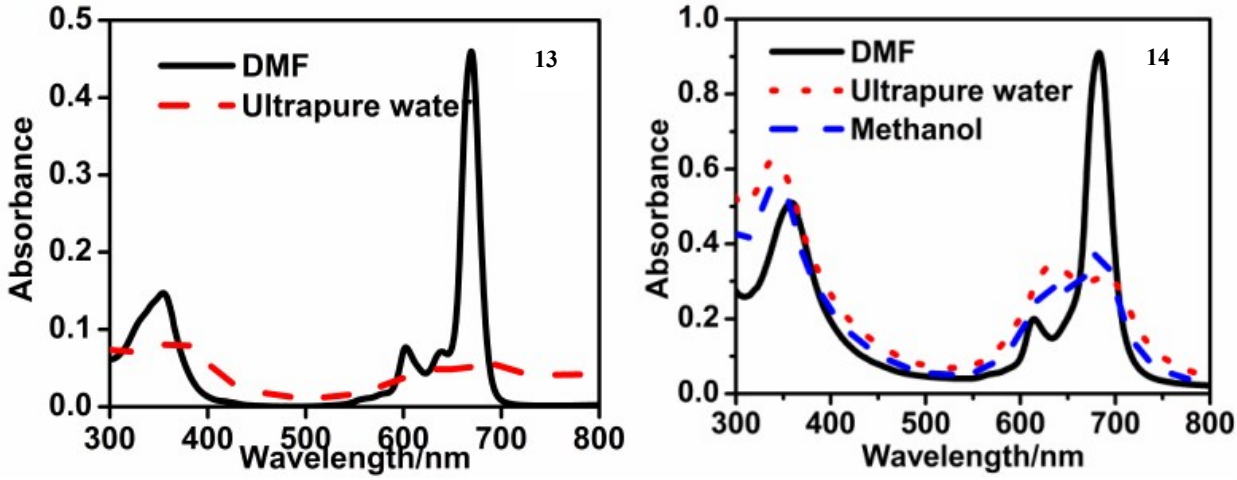

Fig.S13 UV-Vis spectra of phthalocyanine **ME-MLI$_4$-SiPc** in DMF and pure water（C=2×10^{-4} M）; **S14** UV-Vis spectra of **ME-ML-ZnPc** in DMF, pure water and methanol (C=1×10^{-5} M)

2.3 singlet oxygen quantum yield of dendrimer phthalocyanine

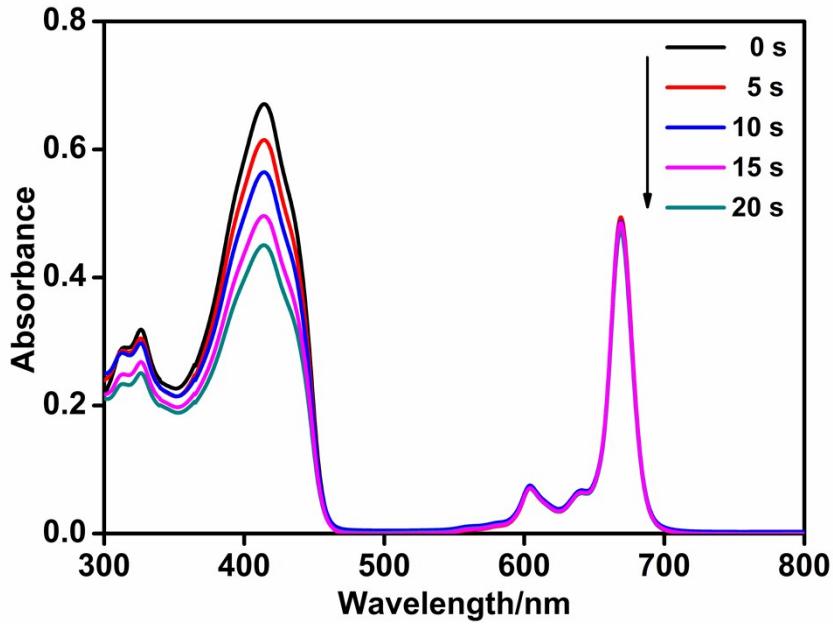

Fig.S15 The change of absorption spectra of DPBF test sample upon irradiation time in DMF containing n-ZnPc with irradiation at 670 nm

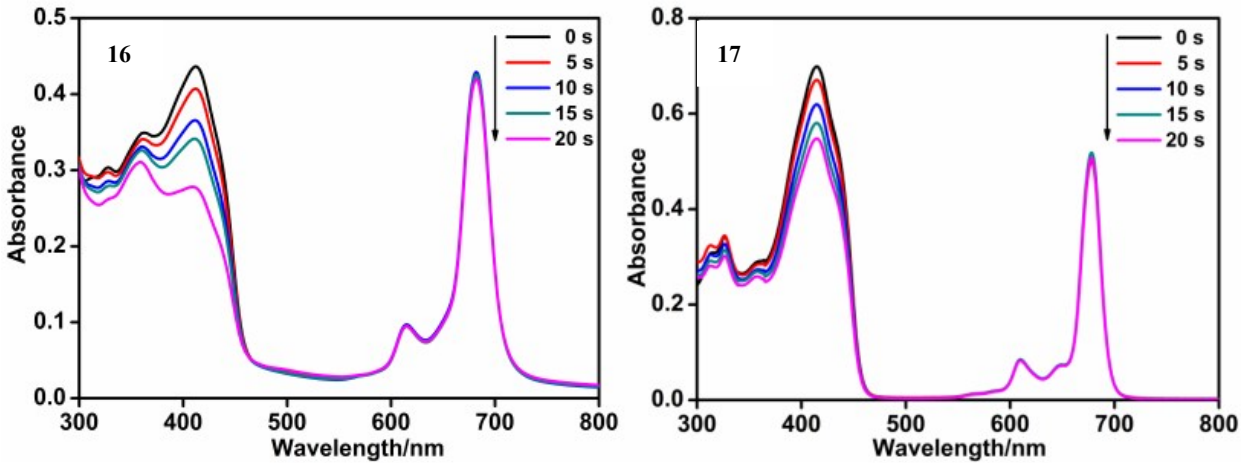

Fig.S16、S17 The absorption spectra of DPBF test sample upon irradiation time in DMF containing **ME-ML-ZnPc, ME-SiPc** with irradiation at 670 nm

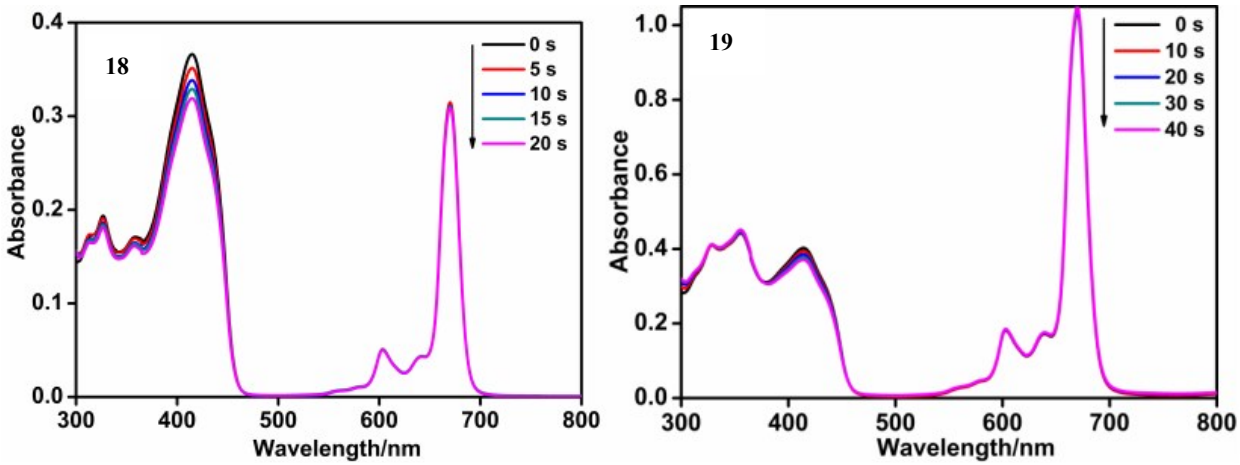

Fig.S18、S19 The absorption spectrum of DPBF test sample upon irradiation time in DMF containing **ME-ML-SiPc, ME-MLI$_4$-SiPc** with irradiation at 670 nm

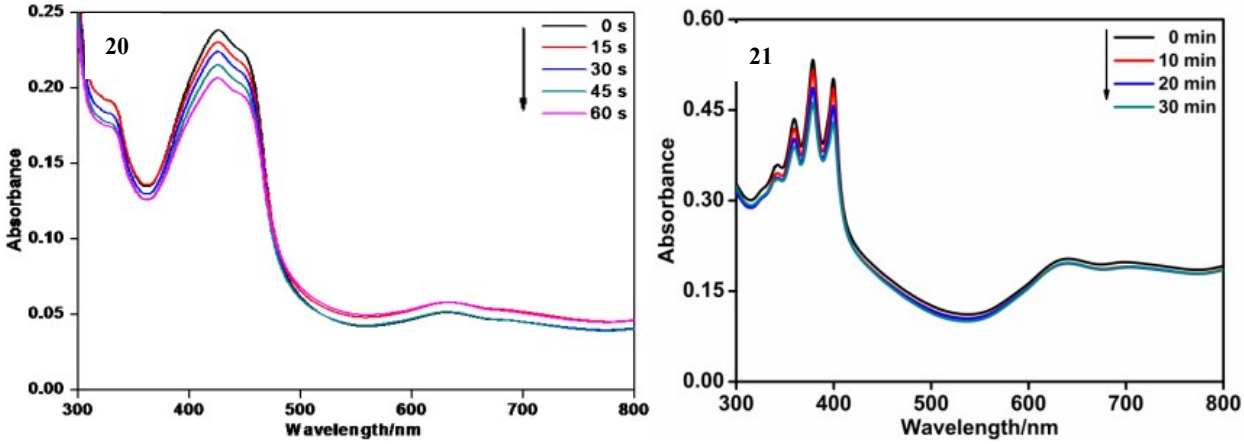

Fig.S20、S21 The absorption spectra of DPBF and 15 μM ABDA test sample upon irradiation time in water containing **ME-MLI$_4$-SiPc** with irradiation at 670 nm

2.4 The PDT efficacy and tumor specificity of the ME-ML-ZnPc

2.4.1 Intracellular localization of ME-ML-ZnPc

MCF-7 breast cells (2×10^4 cells/well) were incubated in a 96-well plate for overnight. The culture medium was then removed, and the serum-free medium and ME-ML-ZnPc mixture (1:1(*v*:*v*), 5 μM) were added. The cells were incubated at 37 ^{o}C for 6 h. The localization of ME-ML-ZnPc in cells was observed using Lysotracker as probes observed under confocal imaging.

After the cells were rinsed with phosphate buffered saline (PBS) for three times for removing the mixed medium, the cells were incubated with Lysotracker@Red DND-99 (50 nM in the medium) at 37 ^{o}C for 6 h, respectively. Then the cells were rinsed with phosphate buffered saline (PBS) for three times again after removed the mixed medium. Then the cells were imaging with a confocal microscope with Lysotracker excited at 577 nm and monitored at 590 nm.

2.4.2 In vitro PDT

MCF-7 breast cells cells (2×10^4 cells/well) were incubated in 96-well plate for overnight at 37 ^{o}C under 5% CO_2. The experimental group included ME-ML-ZnPc (5 μM) plus Laser (100 J/cm^2), and the control groups as follows: (a) ME-ML-ZnPc alone, the cells were incubated with ME-ML-ZnPc (5 μM) for 6 h; (b) laser light alone, using PBS to incubate for 6 h, the cells were irradiated with 100 J/cm^2 for 6 h; (c) ME-ML-ZnPc plus Laser plus FBS group without irradiation. After using FBS and 5 μM ME-ML-ZnPc was to the cells for incubation for 6 h, the cells were irradiated with 100 J/cm^2 for 6 h. Then glioma cells viability was determined by the colorimetric MTT assay.

2.4.3 The result of PDT efficacy and tumor specificity of the ME-ML-ZnPc

2.4.3.1 Sub-cellular localization of ME-ML-ZnPc in MCF-7 breast cells

To determine sublocalization of ME-ML-ZnPc in MCF-7 breast cells, the cells were incubated with ME-ML-ZnPc with Lysotracker@Red DND-99, a lysotracker-specific probe. The fluorescent images for ME-ML-ZnPc (green color) and Lysotracker@Red DND-99 (red color) were monitored by confocal laser scanning microscopy (CLSM), and the results were shown in Fig.S22. In comparison with their merged images, most of green-fluorescing ME-ML-ZnPc was

highly overlapped with the red fluorescing of Lysotracker@Red DND-99, as shown in yellow color. This suggested that ME-ML-ZnPc available localized at lysosomes in MCF-7 cells. This maybe due to the target effect of morpholinyl groups.

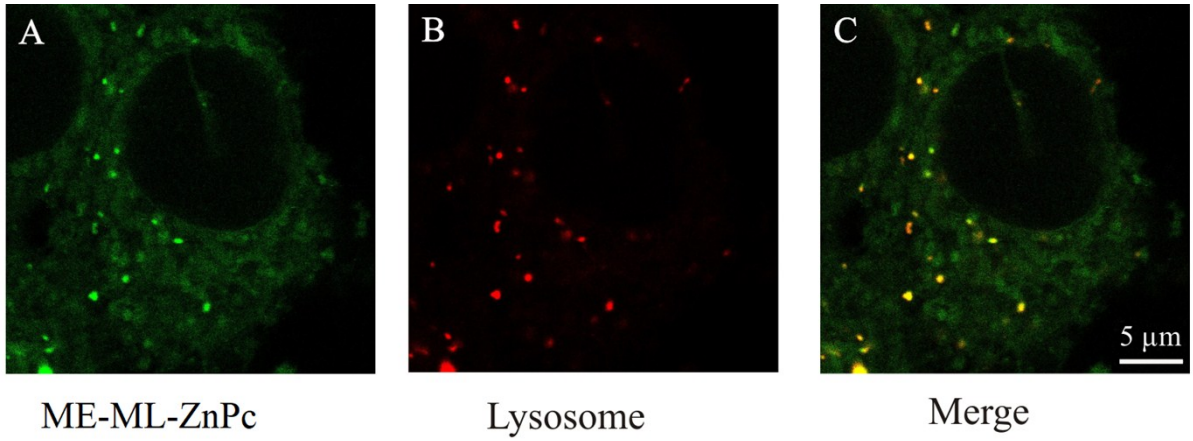

Fig. S22 Confocal imaging of ME-ML-ZnPc in MCF-7 breast cells for lysosomes positioning

2.4.3.2 Phototoxicity of ME-ML-ZnPc against MCF-7 breast cells

The photodynamic activities of ME-ML-ZnPc against MCF-7 breast cells were evaluated by MTT method. As shown in Fig.S23, ME-ML-ZnPc was essentially non-cytotoxicity in the absence of light, but exhibit very high photo-cytotoxicity toward MCF-7 breast cells under laser irradiation. The cell viability was found for ME-ML-ZnPc after PDT was only about 24%. Therefore, ME-ML-ZnPc is a potential photositizer for photodynamic therapy of cancer.

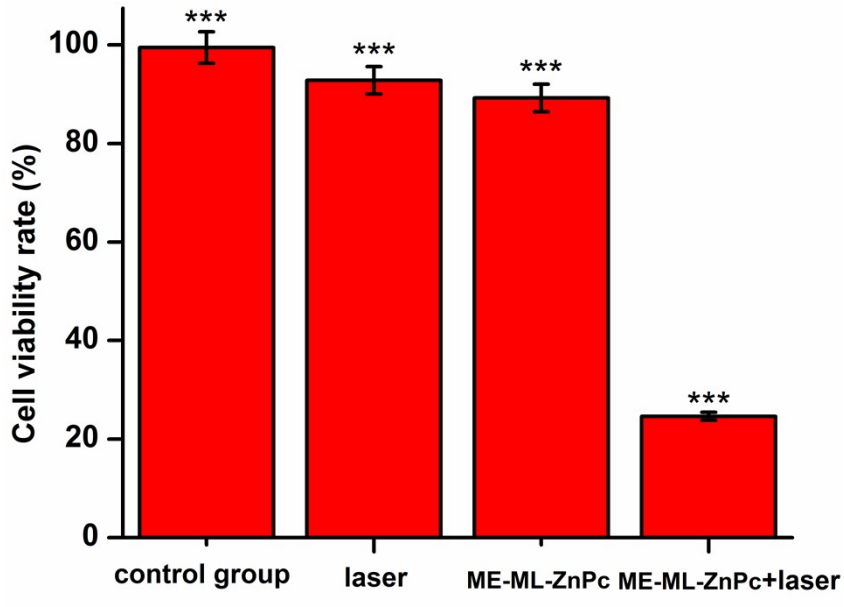

Fig. S23 Cells viability rate under different conditions: Control group, only ME-ML-ZnPc (5 μM), only Laser (100 J/cm^2), and ME-ML-ZnPc (5 μM) plus Laser (100 J/cm^2) (***p<0.001, the statistical analysis is performed in comparison to the ME-ML-ZnPc group)