Electronic Supplementary Material (ESI) for RSC Advances.

A novel assembling complex of hydrobobic phthalocyanine-cyclodextrin: Preparation, characterization, molecular modeling, and *in vitro* activity

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Tetra-1, 2-diethylamino substituted zinc (II) phthalocyanine (ZnPc) was synthesized according our previous reports using classic DBU catalyst method. The synthesizing process was listed as followed.

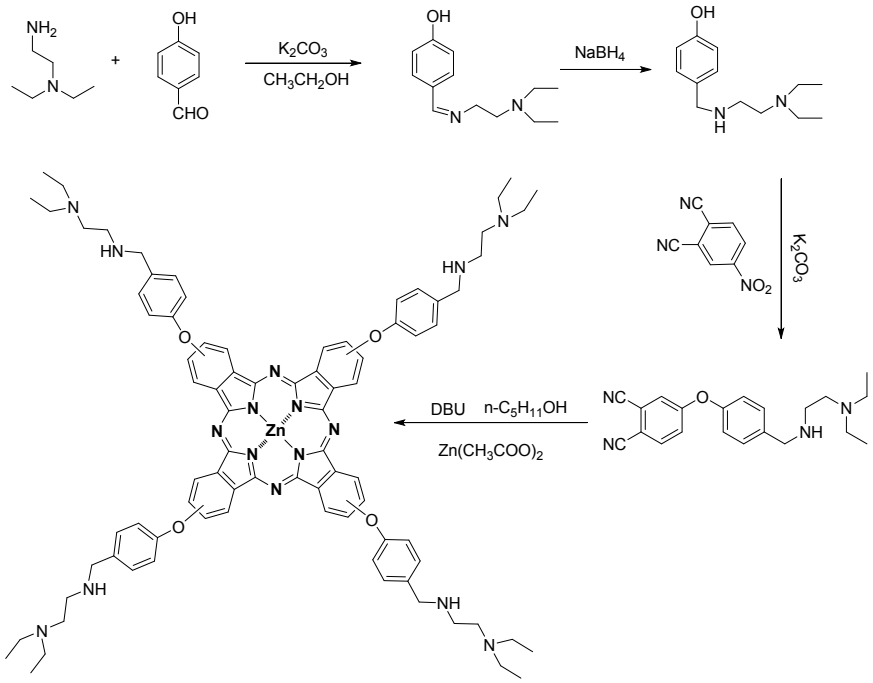
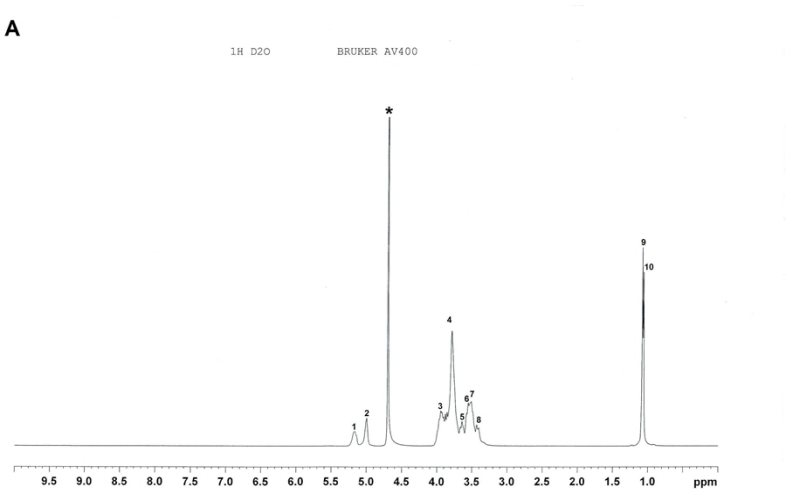


Fig. S1. Synthetic route to ZnPc.



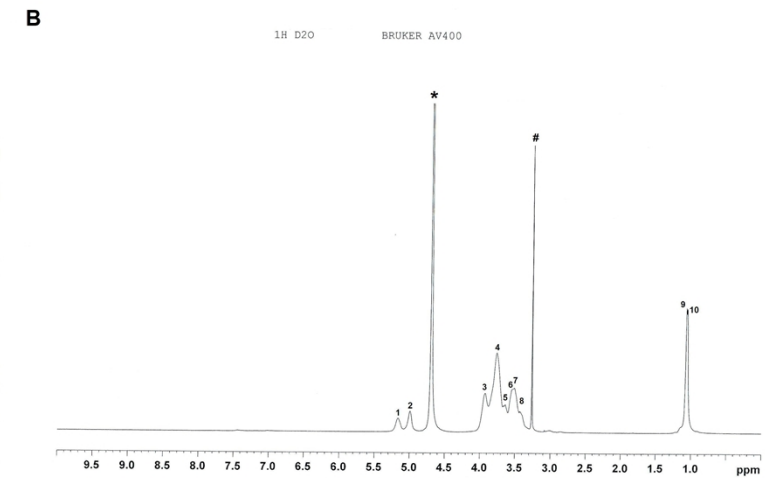


Fig. S2. ^{1}H NMR spectra of HP-β-CD in the absence (A) and presence (B) of ZnPc in D_2O at 25 ^{o}C (* marked signal is the D_2O peak, # marked signal is the residual methanol peak).

Table S1. The main chemical shifts of the HP-β-CD and $(HP\text{-}\beta\text{-}CD)_4$-ZnPc.

	δ(ppm)	
	HP-β-CD	$(HP\text{-}\beta\text{-}CD)_4$-ZnPc
H-1	5.165	5.165
H-2	5.005	4.994
H-3	3.946	3.929
H-4	3.790	3.765
H-5	3.642	3.640
H-6	3.552	3.546
H-7	3.513	3.512
H-8	3.433	3.429
H-9	1.078	1.071
H-10	1.062	1.060

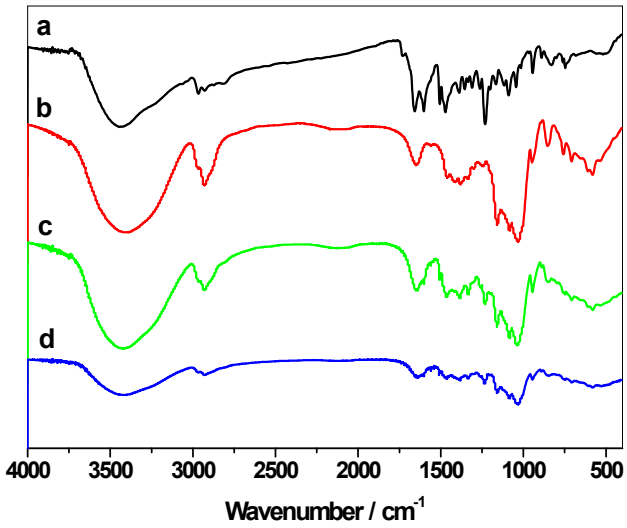


Fig. S3. FTIR spectra of ZnPc (a), HP-β-CD (b), physical mixture (c) and $(HP\text{-}\beta\text{-}CD)_4$-ZnPc (d).

Table S2. The detail of Decomposition temperature, Rate of weight loss at decomposition temperature and Total rate of weight loss from 20 to 800 ℃ for ZnPc, HP-β-CD, physical mixture and $(HP\text{-}\beta\text{-}CD)_4$-ZnPc.

	Decomposition temperature	Rate of weight loss at decomposition temperature	Total rate of weight loss from 20 to 800 ℃
HP-β-CD	324.9 ℃	11.3%	93.9%
ZnPc	306.8 ℃	2.2%	52.4%
Physical mixture	331.9 ℃	11.7%	88.9%
$(HP\text{-}\beta\text{-}CD)_4$-ZnPc	341.9 ℃	9.5%	77.2%

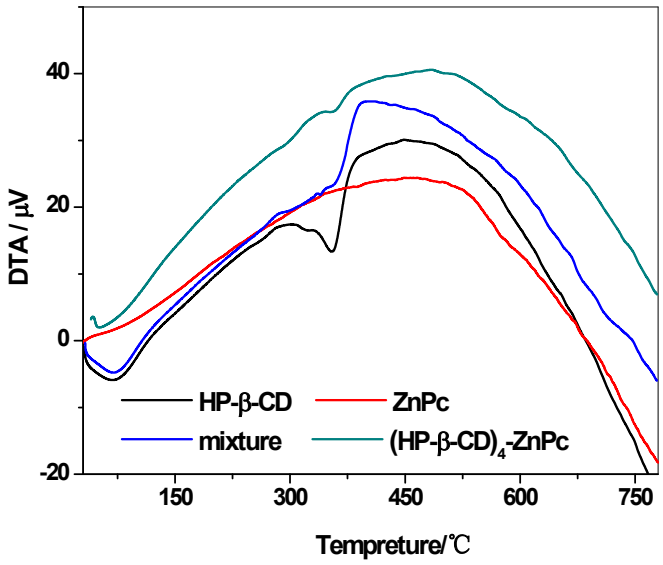


Fig. S4. DTV curves ZnPc, HP-β-CD, physical mixture and $(HP\text{-}\beta\text{-}CD)_4$-ZnPc.

Table S3. The Endothermic peak of ZnPc, HP-β-CD, physical mixture and $(HP\text{-}\beta\text{-}CD)_4$-ZnPc.

	Endothermic peak 1	Endothermic peak 2
ZnPc	-----	------
HP-β-CD	70.0 ℃	355.1℃
Physical mixture	71.3 ℃	356.2℃
$(HP\text{-}\beta\text{-}CD)_4$-ZnPc	49.7 ℃	359.2℃

Table S4. The value of pK_a and LogD for $(HP\text{-}\beta\text{-}CD)_4$-ZnPc at 25 °C.

Drugs	pKa	LogP
$(HP\text{-}\beta\text{-}CD)_4$-ZnPc	7.72	-0.033

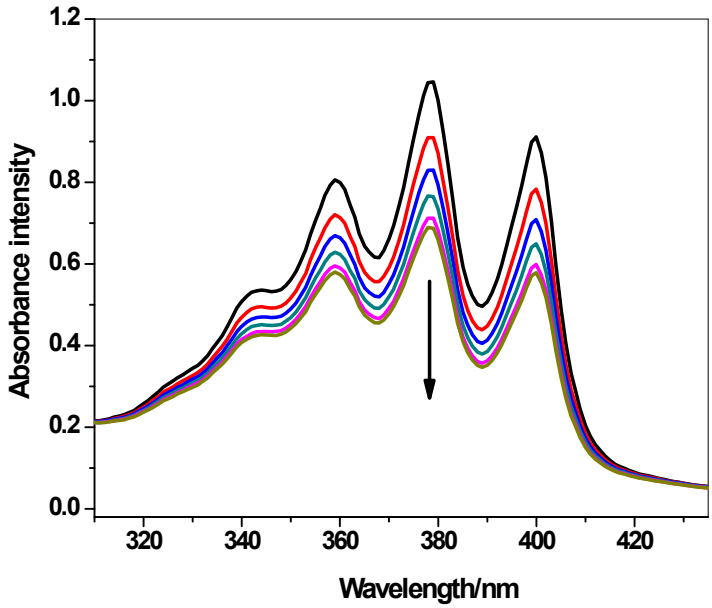


Fig. S5. Absorption spectra of ADPA in ZnPc system were irradiated for 0, 30, 60, 90, 120 and 150 s by 665 nm LED ([ZnPc]= 6 μM, [ADPA]= 55 μM).

The following equations are tailored specifically to the system we are dealing with, in which ADPA and sensitizer are irradiated together in a solution. Hypothetically, the following processes may take place:

$$ZnPc + Hv \rightarrow ZnPc^* \qquad I^{abs} \qquad (1)$$

$$ZnPc^* + {}^3O_2 \rightarrow ZnPc + {}^1O_2 \qquad k \qquad (2)$$

$$ADPA + {}^1O_2 \rightarrow ADPA\ endoperoxide \qquad k_c \qquad (3)$$

$${}^1O_2 \rightarrow {}^3O_2 \qquad k_d \qquad (4)$$

Here k is the rate constant for the quenching of excited HB by triplet oxygen to produce $^1O_2$; k_c is the rate constant of chemical quenching of $^1O_2$ in the presence of ADPA; however, the $^1O_2$ molecule also decays to the ground state by energy transfer to the solvent or to other species in solution, with a rate constant k_d. A rough estimation of the rate constant for the chemical quenching of ADPA by $^1O_2$ can be obtained using a simplification in which $[^1O_2]$ is independent of [ADPA]. According to Eq. (3), the loss of ADPA in reaction with $^1O_2$ is given by

$$-d[ADPA]/dt = k_c[ADPA][{}^1O_2] = k[ADPA]$$

Where

$$k = k_c[^1O_2] = \Phi^{^1O_2} I^{abs} k_c / k_d$$

Thus, the decay of [ADPA] follows first order kinetics.

$$[ADPA]_t = [ADPA]_0 \exp(-kt)$$

$$ln([ADPA]_t / [ADPA]_0) = -kt$$

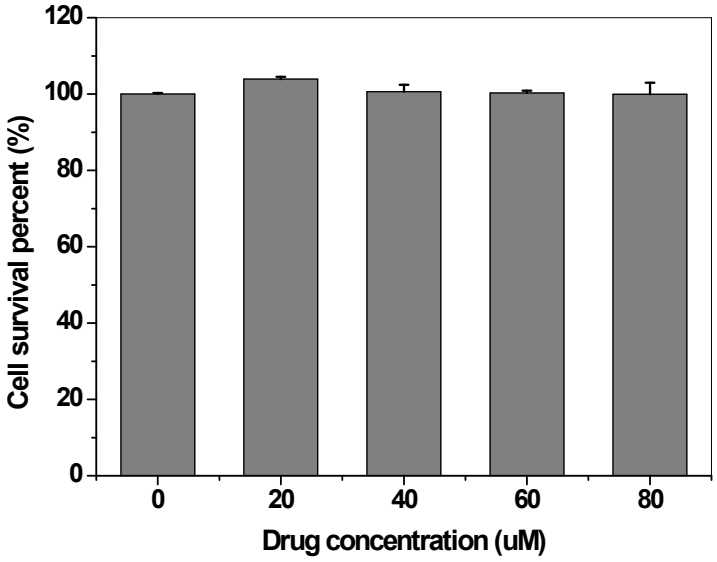
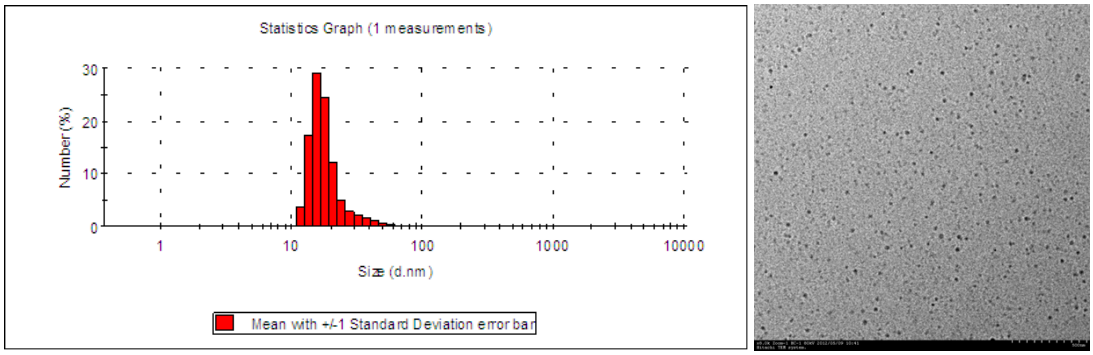


Fig. S6. The toxicity of HP-β-CD with increased concentration on HeLa cells.



A B

Fig. S7. (A) Size distribution of $(HP\text{-}\beta\text{-}CD)_4$-ZnPc in aqueous solution; (B) TEM image of $(HP\text{-}\beta\text{-}CD)_4$-ZnPc in aqueous solution.

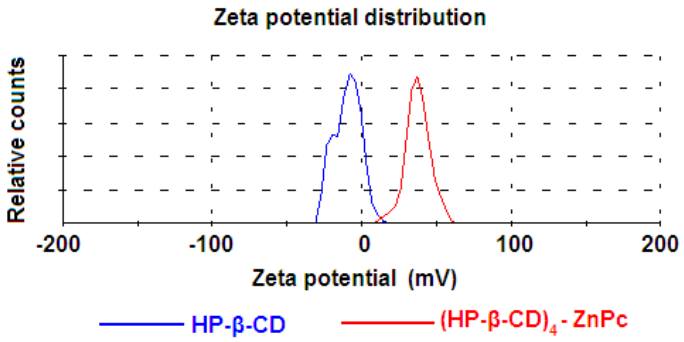


Fig. S8. Zeta potential of (HP-β-CD)$_4$-ZnPc and HP-β-CD in aqueous solution.