Supporting Information

A versatile and multifunctional metal–organic framework nanocomposite toward chemo-photodynamic therapy

Experimental section:

1. The calibration curve of 5-FAM

Weigh accurately 5 mg FAM dissolved in 50 mLdeionized water in a beaker and used 0.01 mol/L NaOH to adjust pH =9. Then, the solution is removed to a 100mL volumetric flask and addsdeionized water to obtain the 50 mg/L FAM standardsolution. The solutions were diluted to 1, 2, 3, 4, 5 mg/L and determinedthe absorbency at λ=492 nm using UV-vis spectrophotometer.The obtained data were used to draw the standard curve.

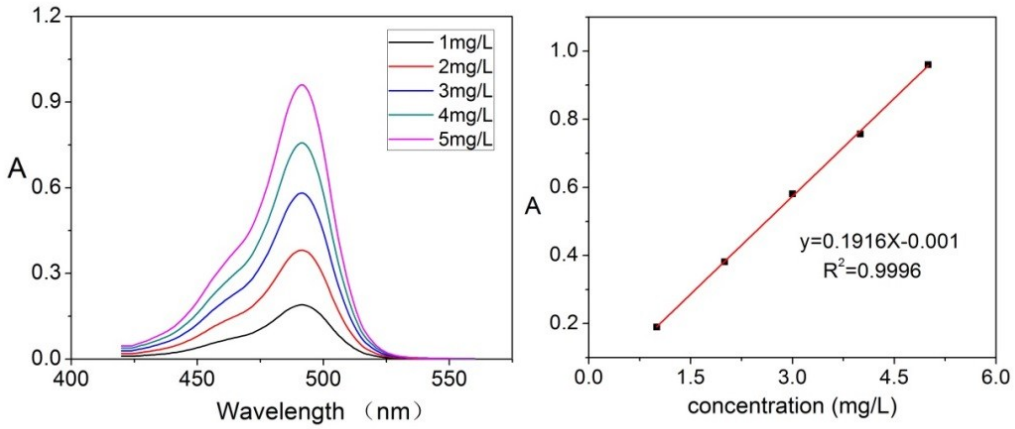


Fig. S1 Theabsorption spectrum and calibration curve of 5-FAM.

2 .The calibration curve of FA

Folic acid and sodium hydroxide at the molar ratio of 1 to 2 is dissolved deionized water to prepare the 200 mg/L standard solution. And then, the solutions were diluted to 4, 8, 12, 16, 20, 24 mg/L by water and determined absorbency at λ=279 nm using UV-vis spectrophotometer.The obtained data were used to draw the standard curve.

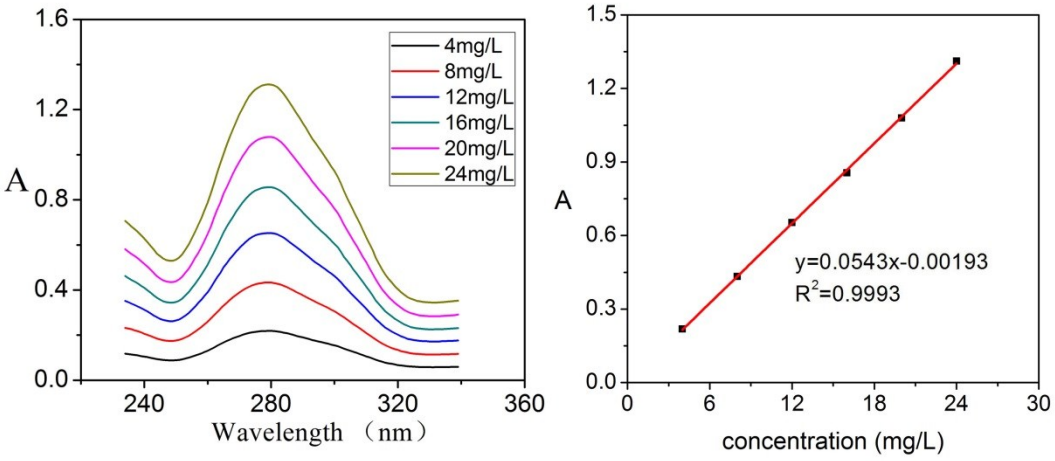


Fig. S2 The absorption spectrum and calibration curve of FA.

3. The calibration curve of ALA

Preparation of chromogenic agent: 1g 4-dimethylaminobenzaldehyde, 30mL acetic acid,5mL 70% perchloric acid and 5mL deionized water were added into a 50mL volumetric flask to dissolved and add acetic acid to the constant volume, mix uniformity and put them in the fridge.

Weigh accurately 10 mg ALA dissolvedin a 100mL volumetric flaskto prepare the standardsolution and the solutions are diluted to 4, 8, 12, 16 and 20 mg/L.2 mL different concentrate standard solution, 2 mL pH=4.6 acetate solution and 0.4 mL ethyl acetoacetate is added to colorimetric tubemixing uniformityand colorimetric tube isheated for 10 minutes in a 100℃ water bath. When colorimetric tube cooled down to room temperature,4 mL ethyl acetateisadded and shock for 50 minutes. Finally, the mixed solution iscentrifuge to separation and take 2 mL of ethyl acetate extract (supernatant fluid) is placed in another colorimetric tubeand add 2 mL of chromogenic agentmixinguniformity, then the absorbency is determined at λ=553 nm.Ethyl acetate was used as blank control group.The obtained data were used to draw the standard curve.

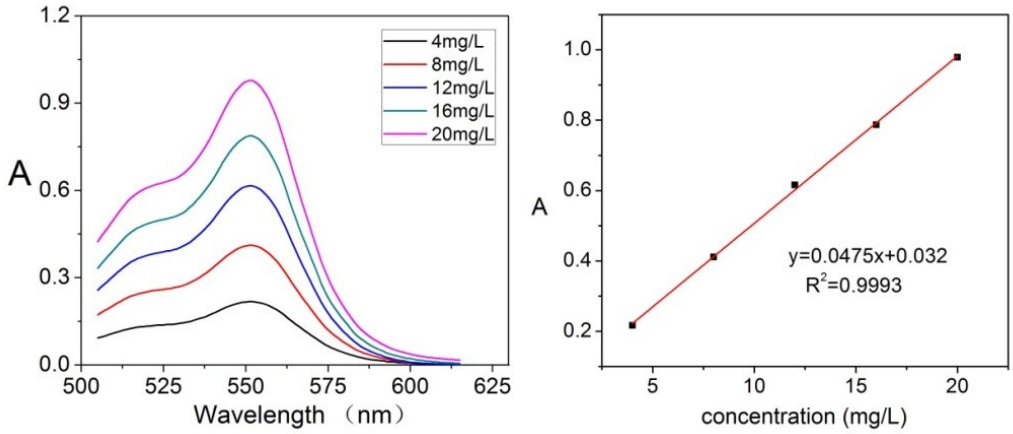


Fig. S3 The absorption spectrum and calibration curve of ALA.

4. The calibration curve of MTA

Weigh accurately 10 mg $MTANa_2$ dissolved in a 100-mL volumetric flask to prepare the standard solution. Then, the solutions are diluted to 4, 8, 12, 16, 20, 24 mg/L and determined absorbency at λ = 224 nm using UV-vis spectrophotometer. The obtained data were used to draw the standard curve.

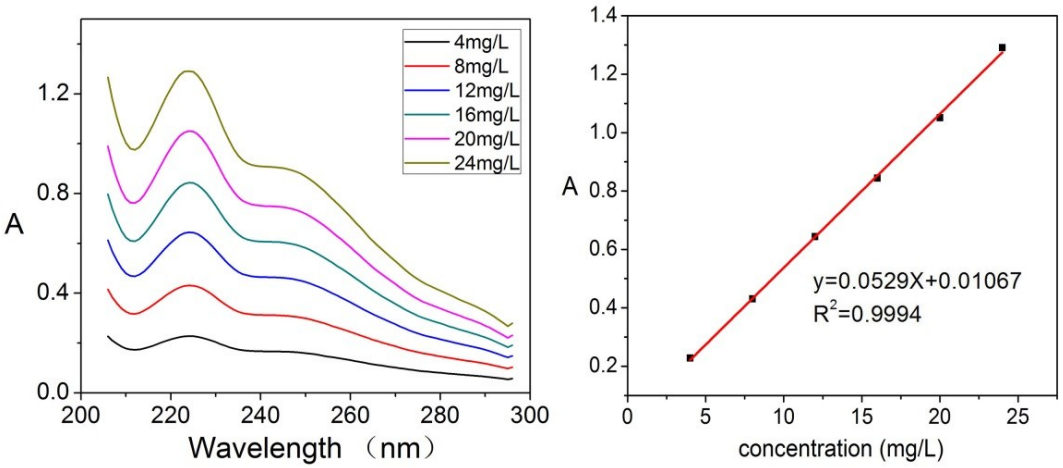


Fig. S4 The absorption spectrum and calibration curve of MTA.

Cellsthawing

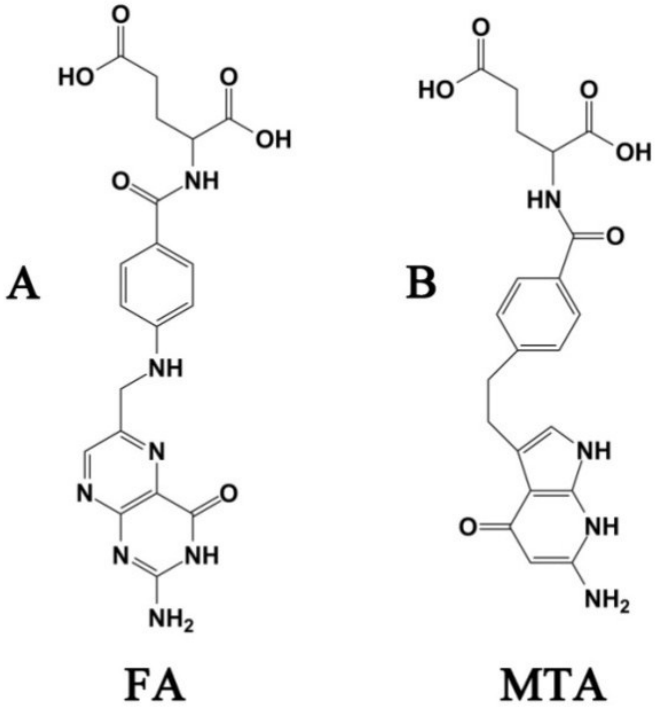
Cells cryopreserved tubes of A549 cells, Hela cells, KB cells and LO2 is placed in 37 ℃ water bath with gently shakingto melt freezing liquid.The cell suspension is moved to centrifuge tube and add equal amount of RPMI1640 medium (containing 79% RPMI1640 medium, 10% FBS and 1% of Penicillin-Streptomycin), then centrifuge 3 min900 r/min,discarded supernatant liquor and add 1 mL RPMI1640 medium with

lightly dissociatingcells. Cells are moved to a Petri dish and place in 37 ^{o}C incubator (5% CO_2)to incubate24 h. When cells fully adherentPetri dish, remove the medium and add fresh medium.

Cell subculture

Whencells grow to 80%,the subcultureexperiment can be performed.First, the original medium are removed and washing cellswith PBS buffer3 times,then add 1 mL of trypsin digestive juice to digest for 2 minutes,add equal amount of RPMI1640 medium to terminate digestionand gently dissociate adherent cells,the cells suspension moved to the centrifugal tube for centrifuging 900 r/min3min,add 1 mlRPMI1640 medium anddissociatinglightly.Cells are moved to a petri dish and place in 37 ^{o}C incubator (5% CO_2) to incubate 24 h. After cells fully adherent petri dish, remove the medium and add fresh medium.

SupplementaryFigure



Scheme S1 Chemical structures of FA (A) and MTA (B).

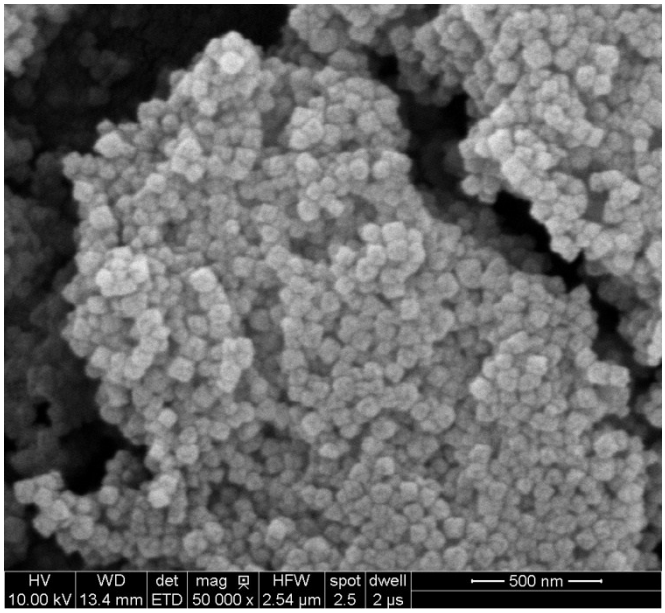


Fig. S5 SEM image of UIO-66-NH_2.

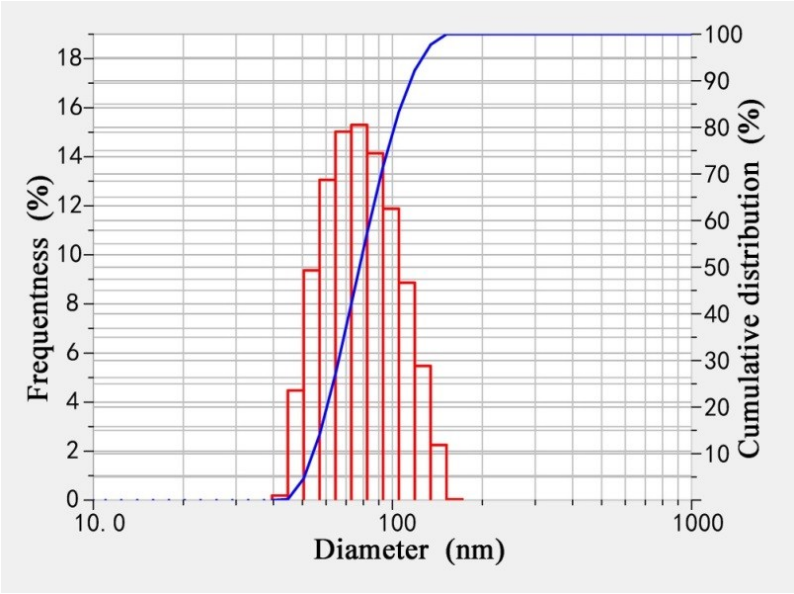


Fig. S6 The DLS result of UIO-66-NH_2.

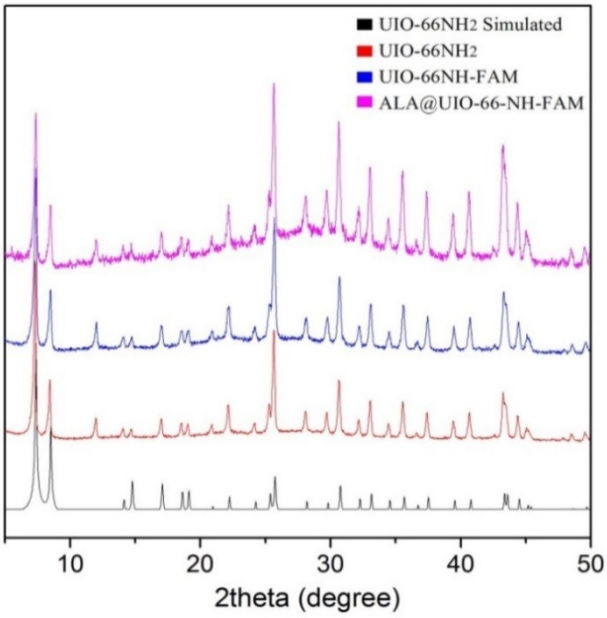


Fig. S7 PXRD patterns of UIO-66-NH_2 (simulated); as-synthesized UIO-66-NH_2 (red), UIO-66-NH-FAM (blue) and ALA@UIO-NH-FAM (pink).

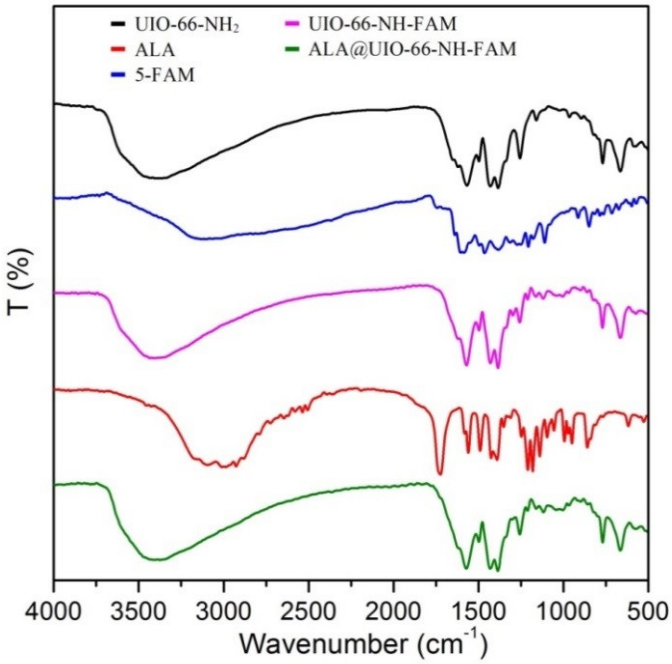


Fig. S8 IR spectrums ofUIO-66-NH_2, ALA, 5-FAM, UIO-66-NH-FAM and ALA@UIO-NH-FAM.

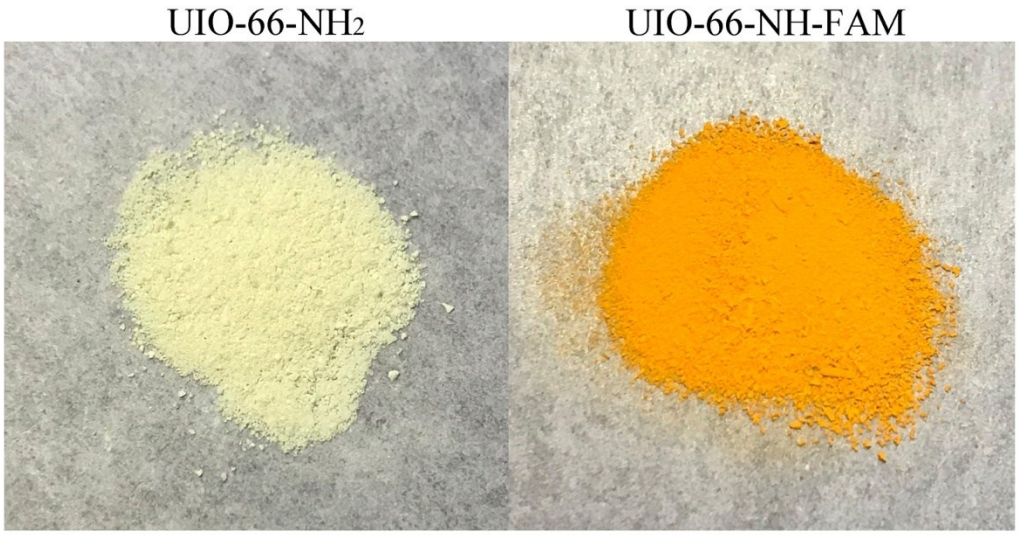


Fig. S9 The optical photosof UIO-66-NH_2 and UIO-66-NH-FAM.

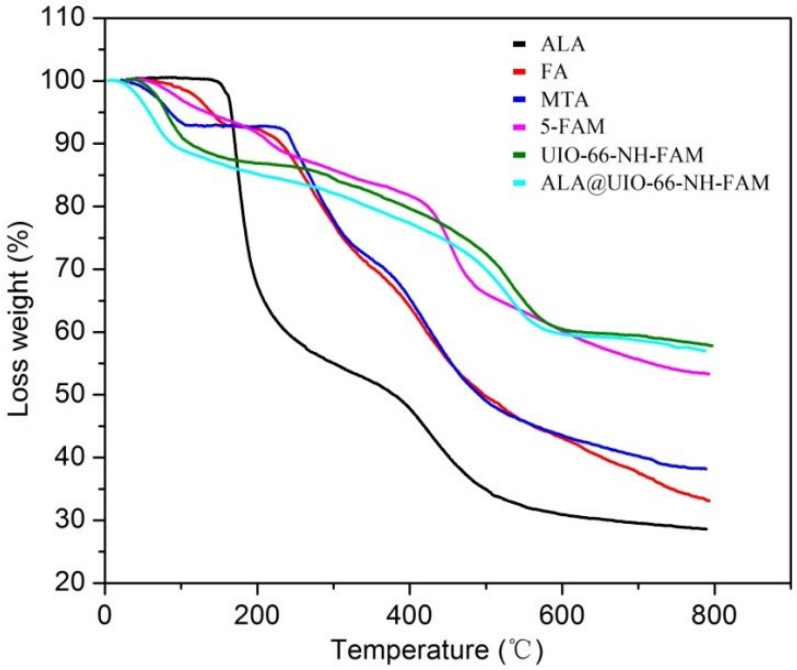


Fig. S10 TG curves of ALA, FA, MTA, 5-FAM, UIO-66-NH-FAM and ALA@UIO-NH-FAM.

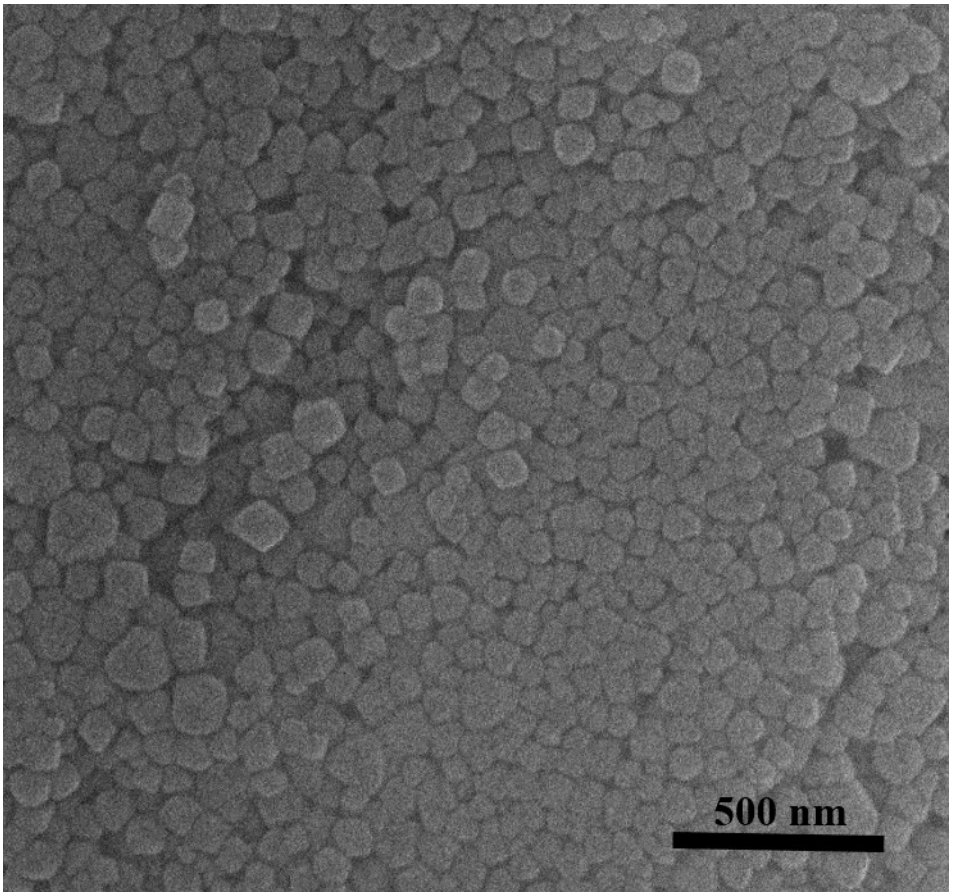


Fig. S11 SEM image of UIO-66-NH-FAM.

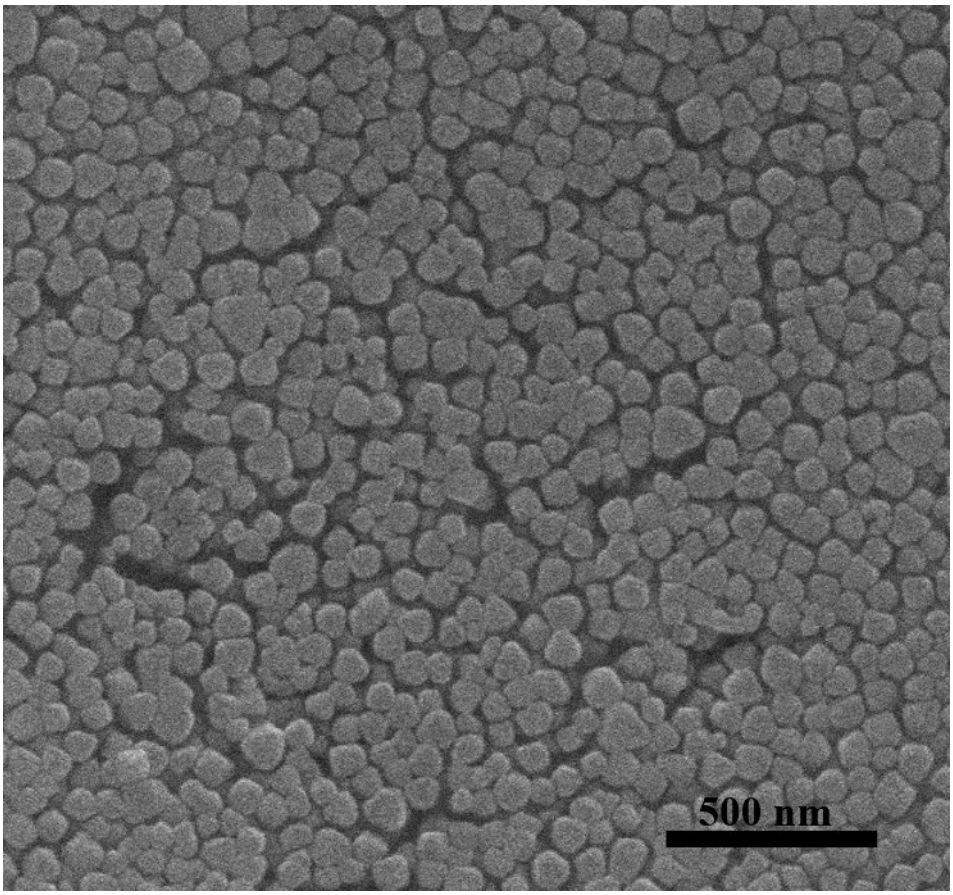


Fig. S12 SEM image of ALA@UIO-66-NH-FAM.

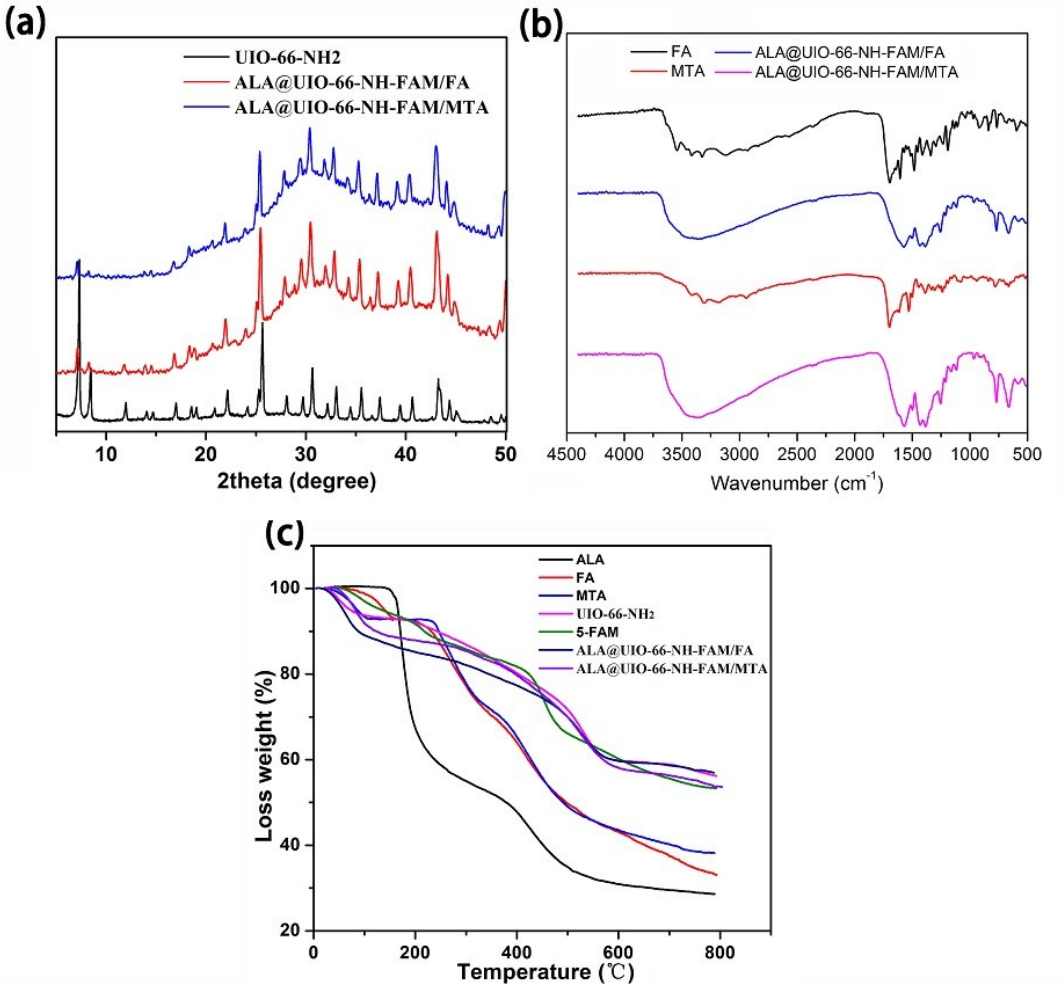


Fig. S13 (a) The PXRD spectrum of different compositions; (b) IR spectrum of FA, MTA, and UIO-66-based series of materials; (c) TGA curves of UIO-66-based series of materials.

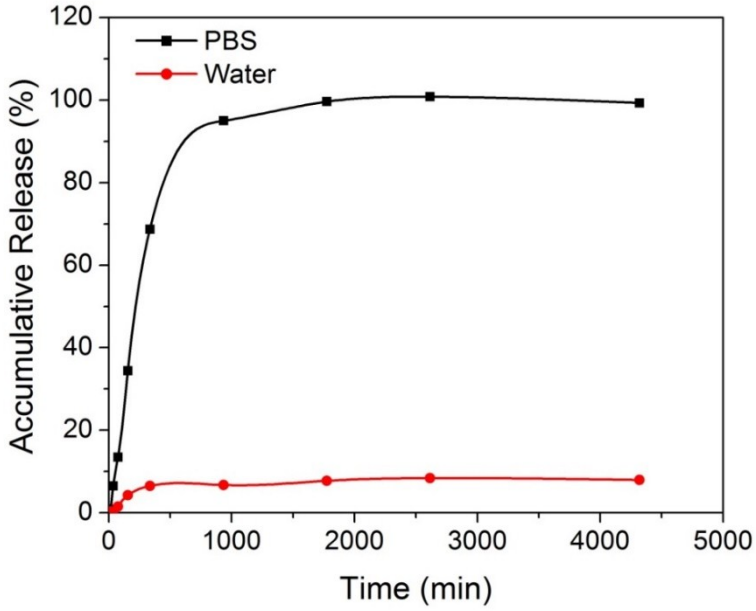


Fig. S14 The profile of MTA releasing behavior at PBS and water medium.

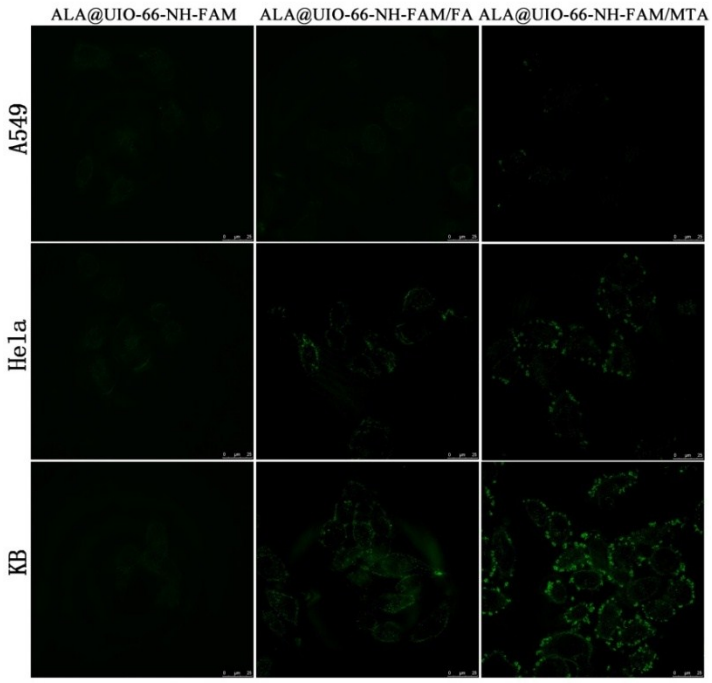


Fig. S15 The fluorescent imaging of UIO-66-NH-FAM, UIO-66-NH-FAM/FA andUIO-66-NH-FAM/MTA in KB cells, Hela cells and A549 cells after incubating 30 min.

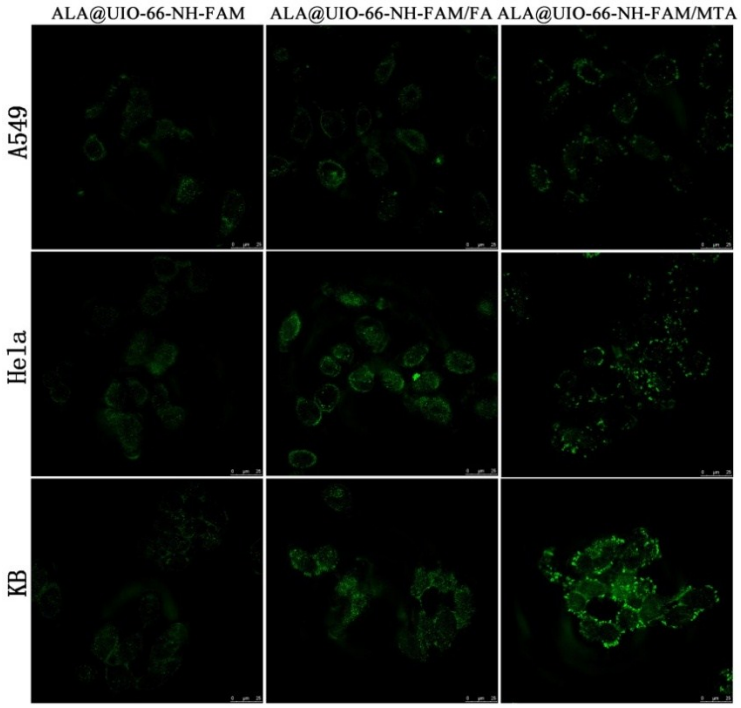


Fig. S16 The fluorescent imaging of UIO-66-NH-FAM, UIO-66-NH-FAM/FA and UIO-66-NH-FAM/MTA in KB cells, Hela cells and A549 cells after incubating 60 min.

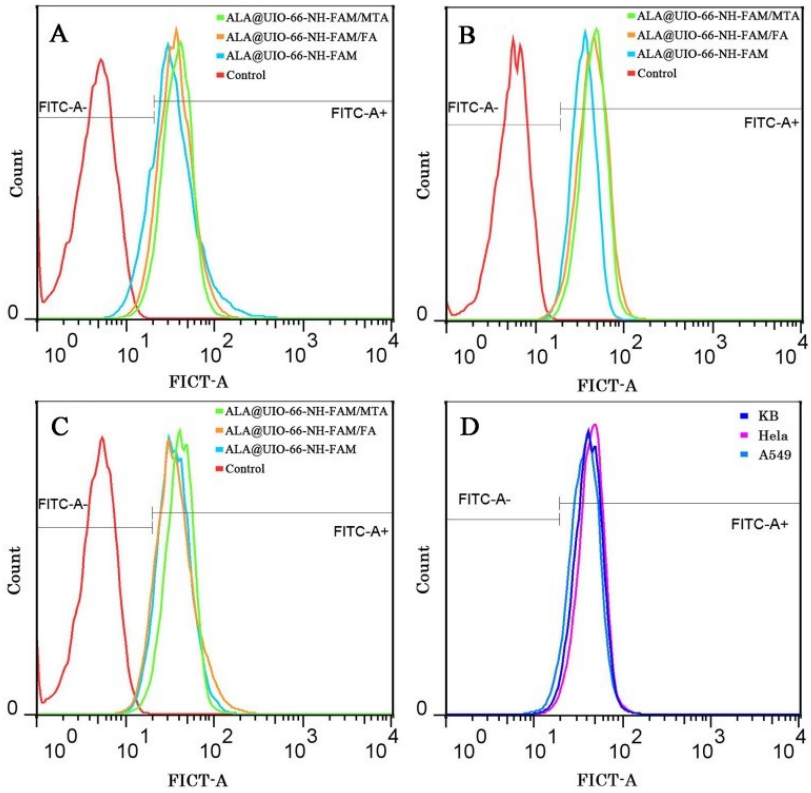


Fig. S17 The flow cytometry data of A549 cells (A)Hela cells (B) KB cells (C) incubating inUIO-66-NH-FAM-MTA, UIO-66-NH-FAM-FA ，UIO-66-NH-FAM for 30min, (D) is the comparing of the three kinds of cellsincubating inUIO-66-NH-FAM.

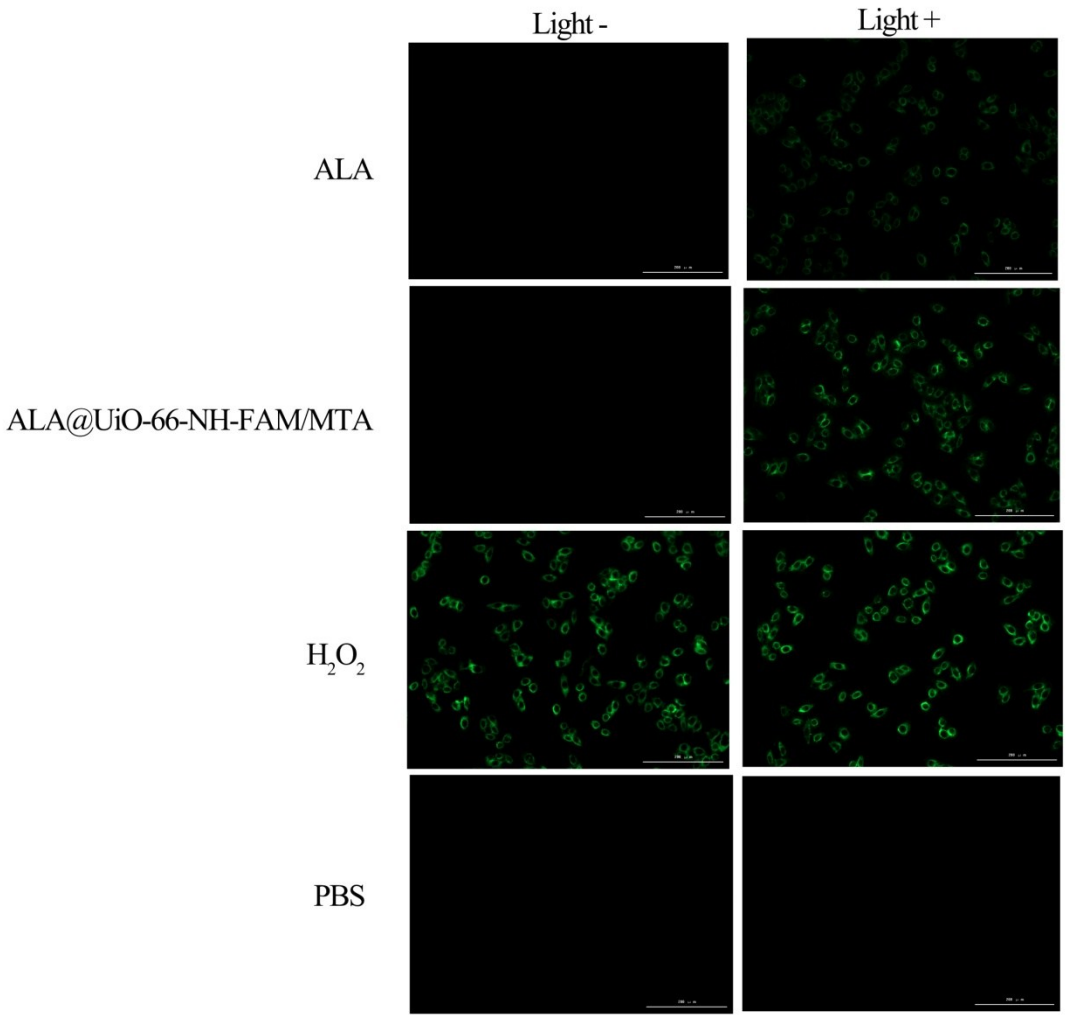


Fig. S18 Detection and quantification of ROS levels induced by H_2O_2 and ALA@UIO-NH-FAM/MTA on Hela cells before irradiation using cell-permeable oxidation sensitive fluorescent probe

Table S1. Textural properties of the as-synthesized samples.

Sample	S_{BET}[a] $m^2\ g^{-1}$	V_{total}[b] $cm^3\ g^{-1}$
UIO-66-NH_2	1299	0.77
UIO-66-NH-FAM	1137	0.64
ALA@UIO-66-NH-FAM	896	0.58
ALA@ UIO-66-NH-FAM/FA	703	0.49
ALA@ UIO-66-NH-FAM/MTA	720	0.49

[a] S_{BET} was calculated in the partial pressure (P/P_0) range of 0.05 to 0.20 which gives the best linearity;[b] Total pore volume at relative pressure P/P_0 = 0.98

Table S2 The loading rate of MTA and FA at different concentrate.

FA concentrate(mg/ml)	Loading rate (%)	MTA concentrate(mg/mL)	Loading rate (%)
0.2	11.02	0.2	18.69
0.5	15.53	0.5	19.92
1	23.91	1	22.25
1.5	23.61	1.5	22.18
2	22.19	2	20.83

Table S3 The mean value of FITC-A after incubating 30min.

	A549 cells	Hela cells	KB cells
Control	4.94	5.84	5.23
UIO-66-NH-FAM	42.3	36.3	38.6
UIO-66-NH-FAM/FA	39.6	46.9	41.9
UIO-66-NH-	40.5	47.4	42.9

FAM/MTA			

Table S4 The mean value of FITC-A after incubating 120min.

	A549 cells	Hela cells	KB cells
Control	2.15	7.28	7.41
UIO-66-NH-FAM	53.2	57.4	85.7
UIO-66-NH-FAM/FA	50.9	74.5	84.1
UIO-66-NH-FAM/MTA	49.8	95.5	99.1