Supplementary Information

Dual Functions of pH-sensitive Cation Zr-MOF for 5-Fu: Large Drug Loading Capacity and High Sensitivity Fluorescence Detection

Xi-yu Sun, [a] Hong-jing Zhang, [a] Xiao-yang Zhao, [a] Qian Sun, [a]* Yuan-yuan Wang, [a] and En-Qing Gao [b]

[a] Department of chemistry, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200241, P. R. China

[b] Shanghai key laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, P. R. China.

1. Experimental procedures

Synthesis of ligand 9H-carbazole-2,7 dicarboxylic acid (9H-2,7-CDC)

The ligand 9H-carbazole-2,7 dicarboxylic acid (9H-2,7-CDC) was synthesized according to a literature report.[i]. Summarily, dimethyl 4,4'-biphenyldicarboxylate (Me_2BPDC) (5.03g) and 45ml of 98% concentrated sulfuric acid was mixed and stirred mechanically at room temperature until to green solution. Reduce the temperature of the solution to 5° C and continue stirring for one hour. Then, 1.8ml 56% HNO_3 and 5ml 98% concentrated sulfuric acid was added dropwise. The reaction solution was poured onto crushed ice, and a milky white solid was precipitated immediately. The obtained solid dimethyl 2-nitro-4,4'-biphthalate ($Me_2BPDC\text{-}NO_2$) was mixed with triphenylphosphonium (DPh_3) (8.2782 g), adding 26 ml o-dichlorobenzene, heating at 180° C, and refluxing for 48h. The mixture was dissolved in tetrahydrofuran and reflux at 60° C for 19 hours. The reaction solution was evaporated under a vacuum rotary to obtain a solid powder, dissolved in water, and filtered to remove the insoluble Ph_3PO. The filtrate was adjusted to acid with dilute hydrochloric acid, filtered, and dried to obtain a brown powder (9H-carbazole-2 ,7 dicarboxylic acid, 9H-2,7-CDC) 1.105g (yield 23.26%).

2. Characterization

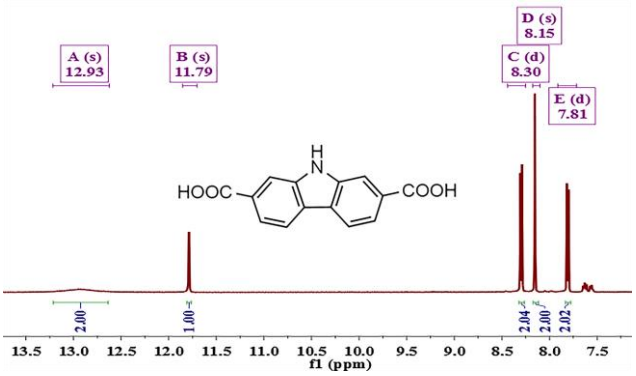

Figure S1 ^1H NMR spectrum of ligand 9H-carbazole-2,7 dicarboxylic acid (9H-2,7-CDC)

^1H NMR (500 MHz, DMSO) δ 12.93 (s, 1H), 11.79 (s, 1H), 8.30 (d, J = 8.2 Hz, 1H), 8.15 (s, 1H), 7.81 (d, J = 8.2 Hz, 1H).

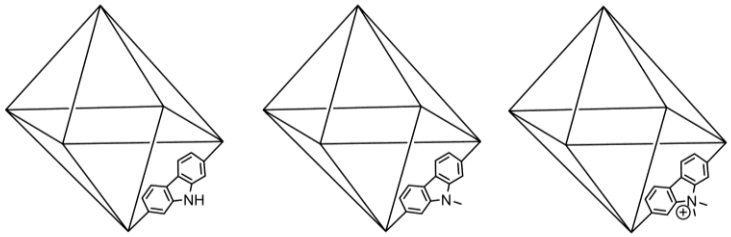

Figure S2 The three products after MeOTf methylation, from left to right, UiO-67-CDC，UiO-67-CDC-CH_3，UiO-67-CDC-$(CH_3)_2$

Table S1 The yield of the three products after methylation

product	UiO-67-CDC-$(CH_3)_2$	UiO-67-CDC-CH_3	UiO-67-CDC
Yield (%)	49.1	32.1	18.8

3. Standard curve of 5-Fu

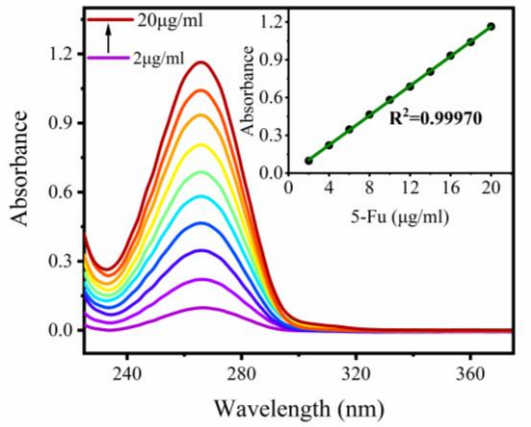

Figure S3 Standard curve of 5-Fu in ethanol

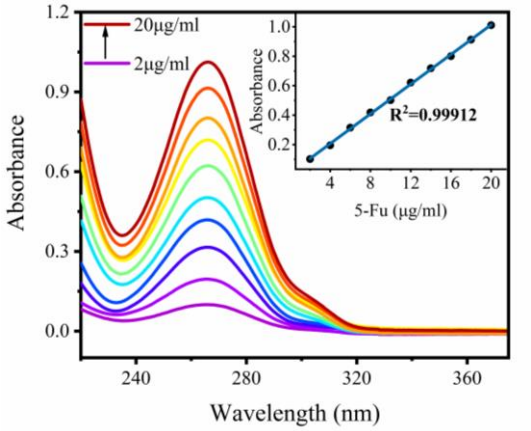

Figure S4 Standard curve of 5-Fu in PBS solution

4. Zeta potential

Table S2 Zeta potential of UiO-67-CDC, UiO-67-CDC-$(CH_3)_2$ and 5-Fu@UiO-67-CDC-$(CH_3)_2$

Sample	UiO-67-CDC	UiO-67-CDC-$(CH_3)_2$	5-Fu@UiO-67-CDC-$(CH_3)_2$
ζ (mV)	0.229	22.017	-0.106

5. The fitting of kinetic models

Table S3 Summary of four types of kinetic model fitting tables for drug sustained-release behavior under different pH conditions

PH	Model	Equation	Correlation coefficients (R^2)
PH=7.4	Korsmeyer-Peppas	$y=3297\times x^{5.32054E-5}-3297$	0.78103
	Higuchi	$y=0.14373\times x^{0.5}+0.2756$	0.60220
	Weibull	$y=0.87973\times(1-e^{-1.18077x})^{0.44827}$	0.99114
	First order	$y=0.87973\times(1-e^{-0.52931x})$	0.99213
PH=6.8	Korsmeyer-Peppas	$y=2397\times x^{6.71748E-5}-2397$	0.86138
	Higuchi	$y=0.13127\times x^{0.5}+0.20544$	0.68094
	Weibull	$y=0.76247\times(1-e^{-1.39451x})^{0.32206}$	0.98931
	First order	$y=0.76247\times(1-e^{-0.44911x})$	0.99050
PH=5	Korsmeyer-Peppas	$y=1803\times x^{7.15013E-5}-1803$	0.87101
	Higuchi	$y=0.09999\times x^{0.5}+0.09093$	0.70426
	Weibull	$y=0.5323\times(1-e^{-0.38331x})^{0.87146}$	0.97321
	First order	$y=0.5323\times(1-e^{-0.33404x})$	0.97618
PH=3	Korsmeyer-Peppas	$y=0.02064\times x^{0.32101}+0.00364$	0.55848
	Higuchi	$y=0.0103\times x^{0.5}+0.0121$	0.67984
	Weibull	$y=0.06253\times(1-e^{-0.32729x})^{0.64221}$	0.6323
	First order	$y=0.06253\times(1-e^{-0.21019x})$	0.67316

6. Scanning electron micrograph

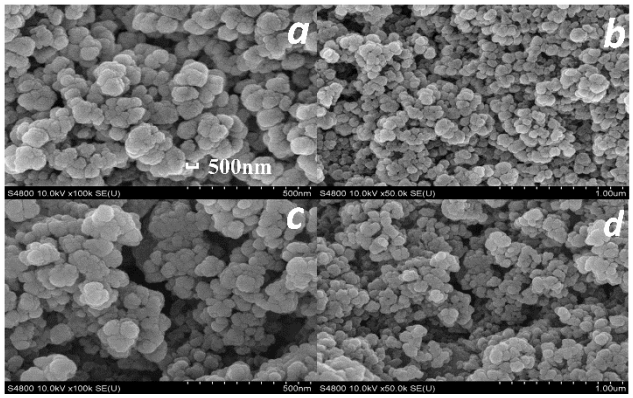

Figure S5 Scanning electron micrograph of UiO-67-CDC (a) (b), and UiO-67-CDC-$(CH_3)_2$ (c) (d).

7. Cell viability test

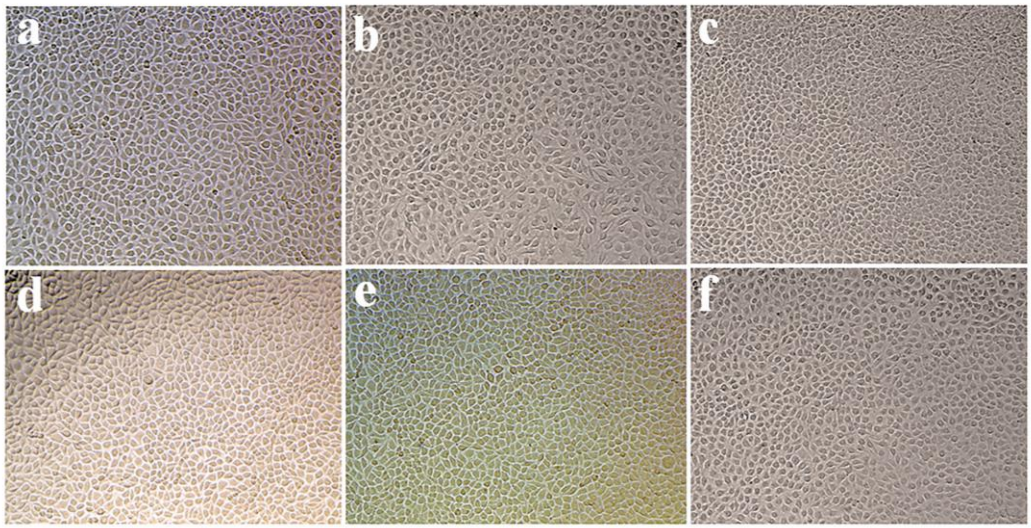

Figure S6 Morphology of L929 cells under microscope after treatment with different concentrations of UiO-67-CDC-$(CH_3)_2$, (a) control group, (b) 20 μg/ml, (c) 40μg/ml, (d) 60 μg/ml, (e) 80 μg/ml, (f) 100 μg/ml

[i] Xiu-Chun Yi, Fu-Gui Xi, Kun Wang, Zhao Su, En-Qing Gao, Synthesis, structure and properties of zinc(II) coordination polymers with 9H-carbazole-2,7-dicarboxylic acid, J. Solid State Chem, 206 (2013) 293–299.