

Electronic Supplementary Information

Oxygen-Powered Flower-like FeMo₆@CeO₂ Self-cascade Nanozyme: Turn-on Enhancement Fluorescence Sensor

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Section 1. Supporting Figures

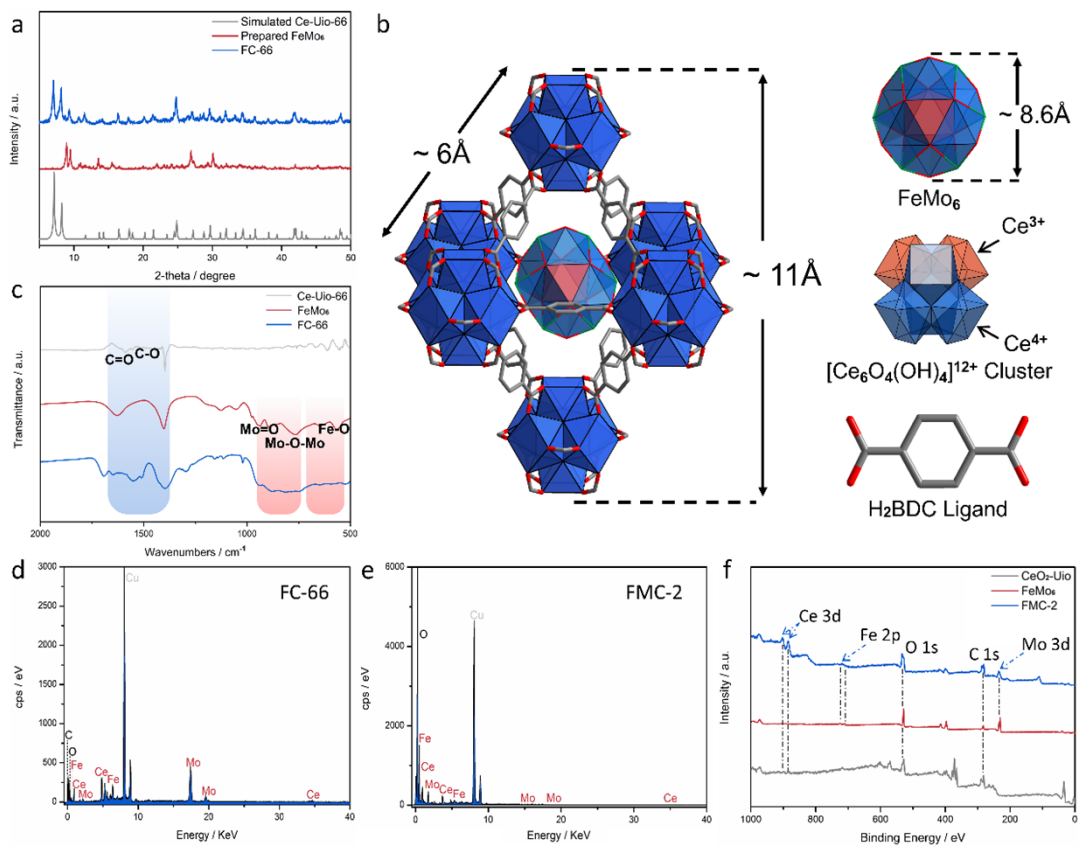


Figure S1. (a) XRD pattern observed for FC-66 in comparison with the prepared FeMo₆ as well as the simulated pattern of Ce-Uio-66; (b) combined wires/sticks/polyhedral representation of the asymmetric unit of FC-66; (c) the FT-IR spectra of Ce-Uio-66, FeMo₆ and FC-66; EDS spectrums of (d) FC-66 and (e) FMC-2; (f) full survey scan of XPS spectra for FMC-2, FeMo₆ and CeO₂-Uio, respectively.

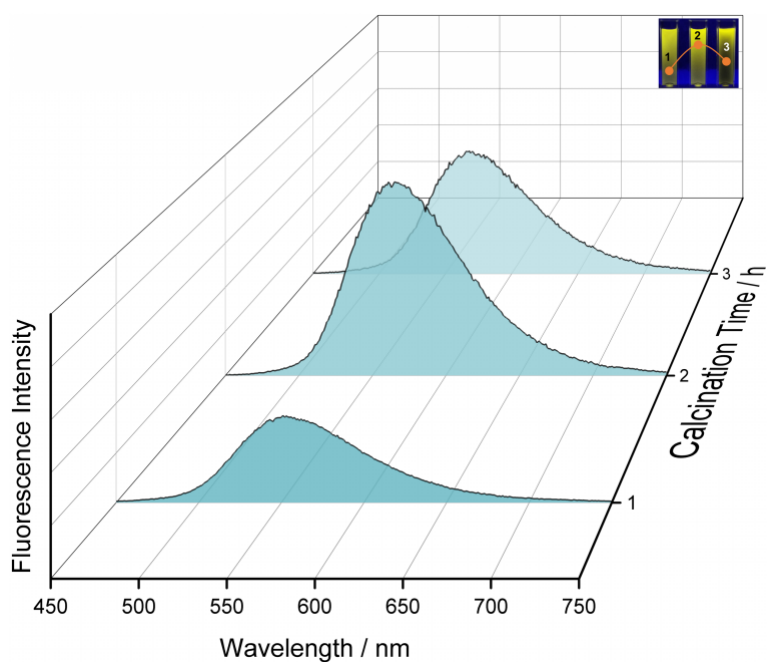


Figure S2 Fluorescence curves and optical photographs of FMC-n.

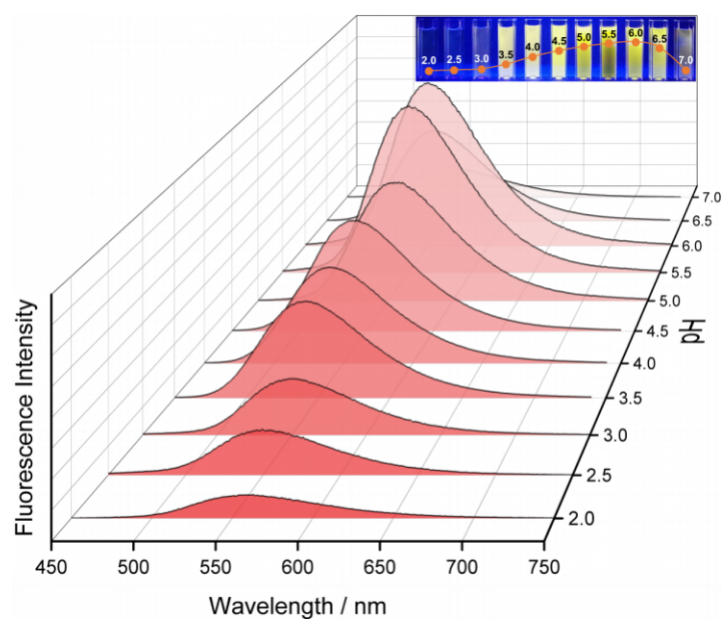


Figure S3 Fluorescence curves and optical photos of FMC-2 under different pH.

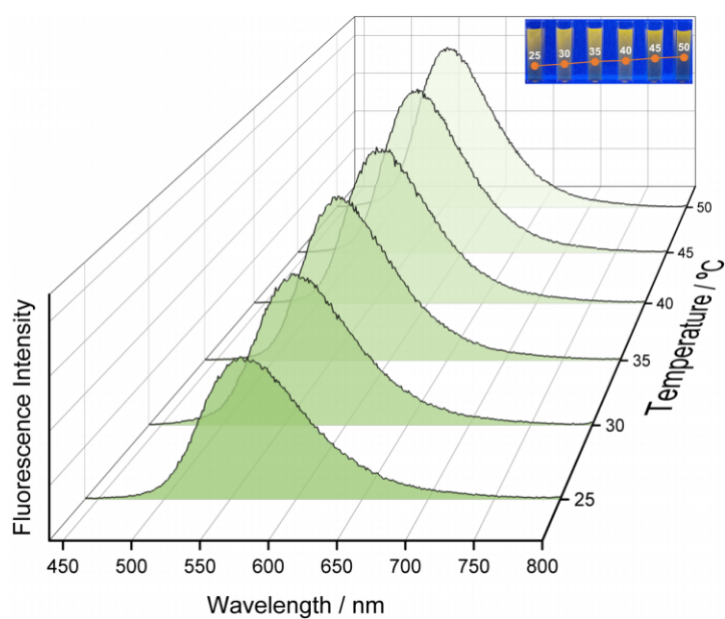


Figure S4 Fluorescence curves and optical photos of FMC-2 under different temperatures.

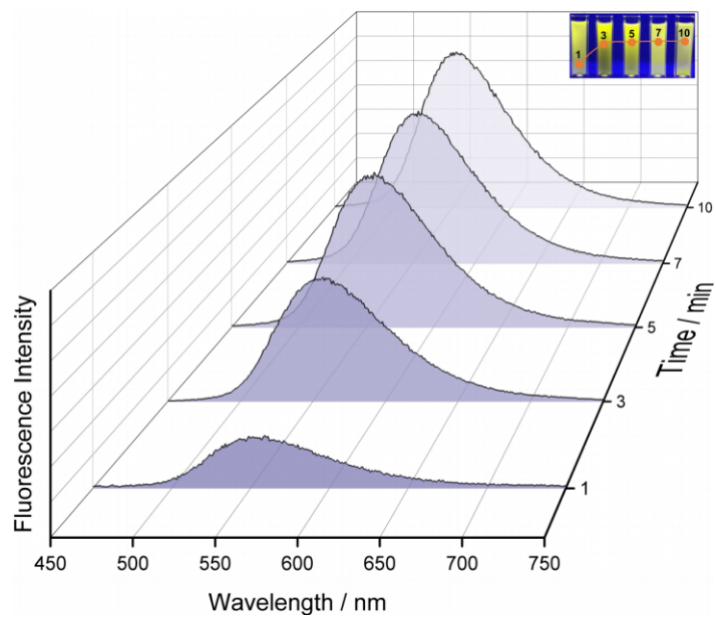


Figure S5 Fluorescence curves and optical photos of FMC-2 under different reaction times.

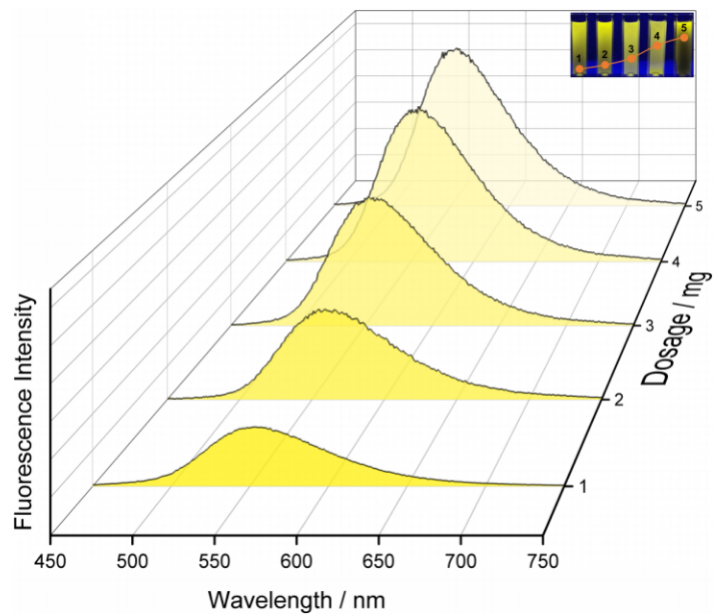


Figure S6 Fluorescence curves and optical photos of FMC-2 with different feeding dosage.

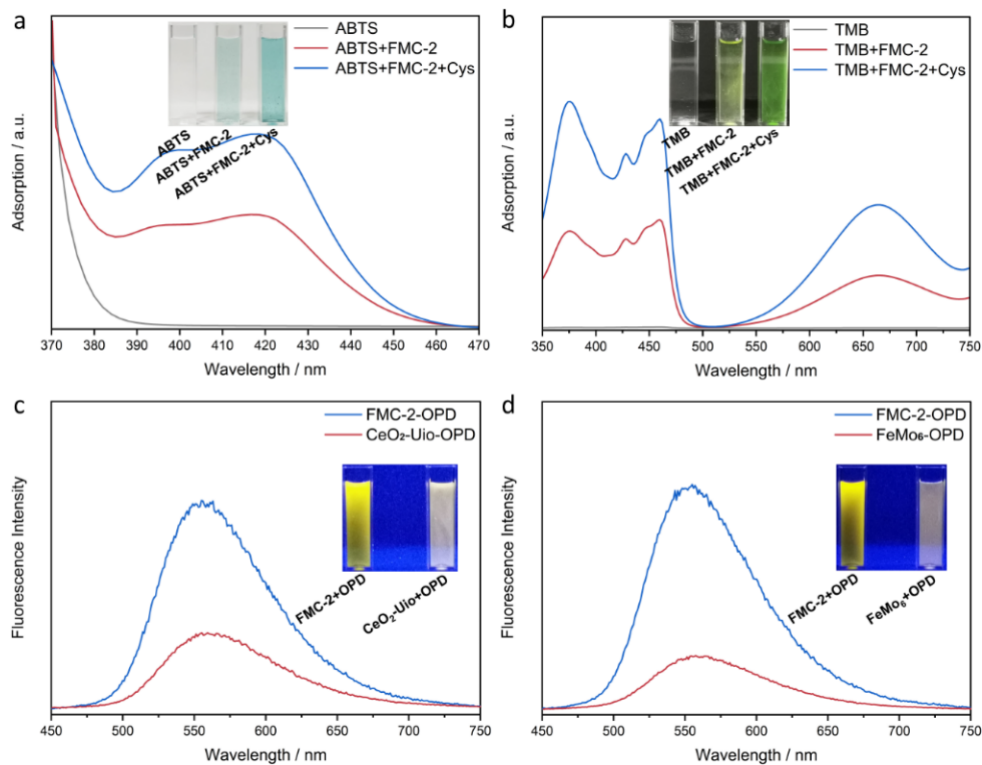


Figure S7. UV-vis spectra and the corresponding optical photographs of (a) ABTS, ABTS-FMC-2 and ABTS-FMC-2-Cys; (b) TMB, TMB-FMC-2 and TMB-FMC-2-Cys (pH=5.5, 5 min, 25 °C); fluorescence curves and corresponding optical photographs of (c) FMC-2-OPD and CeO₂-Uio-OPD; (d) FMC-2-OPD-H₂O₂ and FeMo₆-OPD-H₂O₂ (pH=5.5, 5 min, 25 °C).

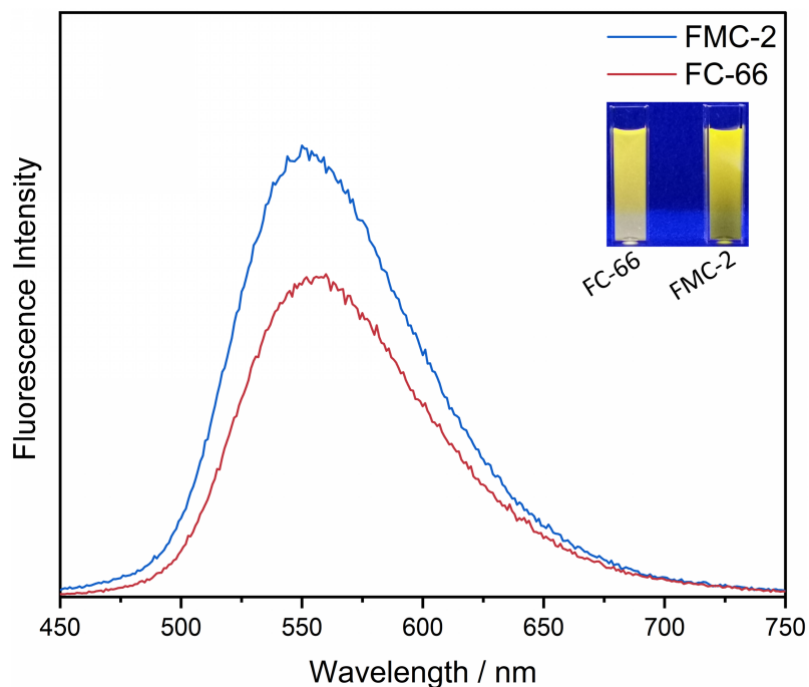


Figure S8. Fluorescence curves and corresponding optical photographs of FMC-2-OPD-O₂ and FC-66-OPD-O₂.

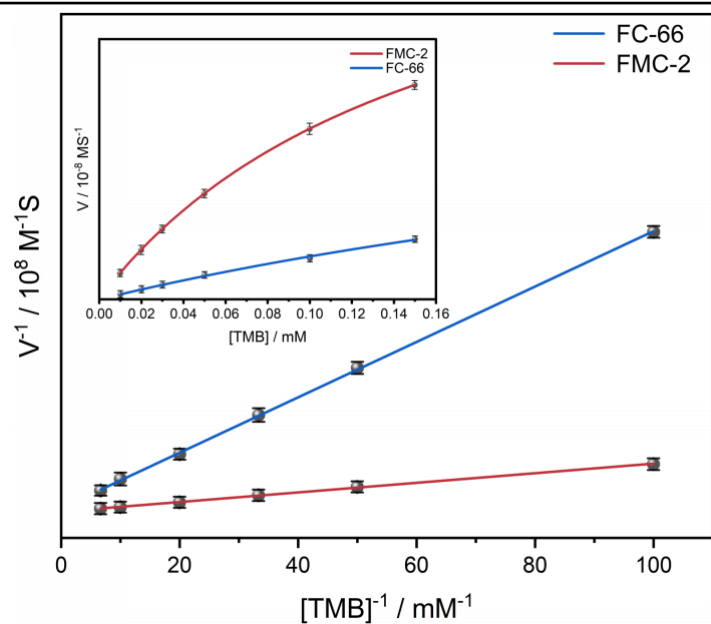


Figure S9. Steady-state kinetics curves of initial reaction rate (V) against varying TMB concentration for FC-66 and FMC-2, Lineweaver-Burk plot of $1/V$ against $1/C_{\text{TMB}}$ for FC-66 and FMC-2.

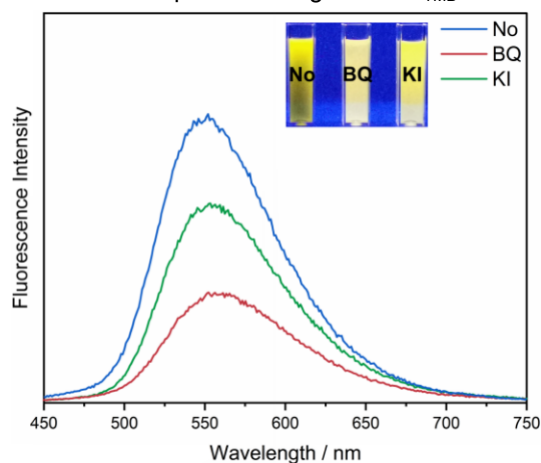


Figure S10 Fluorescence curves and corresponding optical photographs of FMC-2-OPD- O_2 under the effect of 1 mM *p*-benzoquinone (BQ) and potassium iodide (KI) quencher-spiked agent.

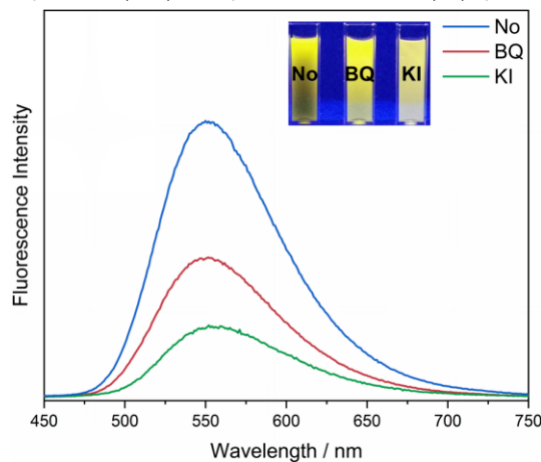


Figure S11 Fluorescence curves and corresponding optical photographs of FMC-2-OPD- O_2 -Cys under the effect of 1 mM *p*-benzoquinone (BQ) and potassium iodide (KI) quencher-spiked agent.



Figure S12 Optical photographs of FMC-2-TiOSO₄ over time.

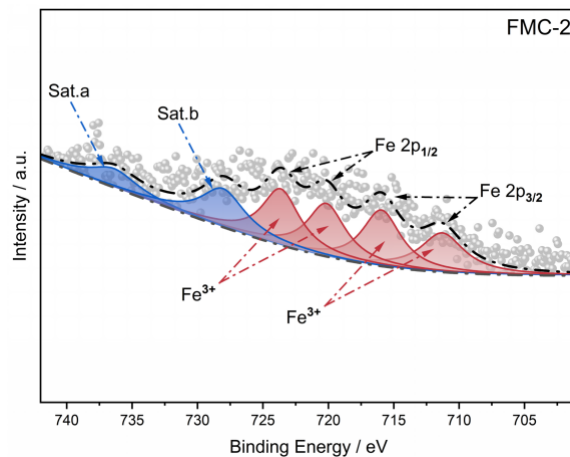


Figure S13. The high-resolution of Fe 2p XPS spectra for FMC-2.

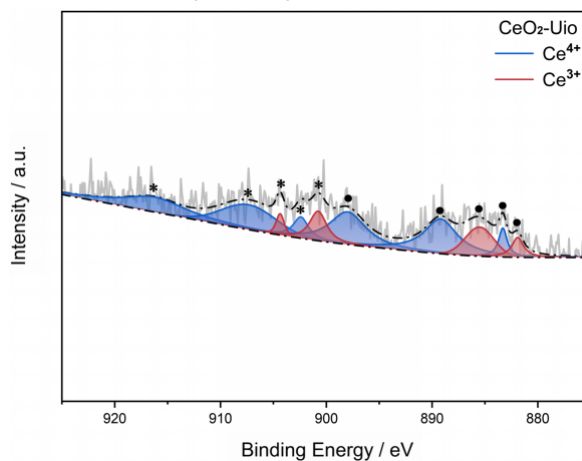


Figure S14. The high-resolution of Ce 3d XPS spectra for CeO₂-Uio, the asterisks assigned to the spin-orbit split 3d_{3/2} and circles for 3d_{5/2}.

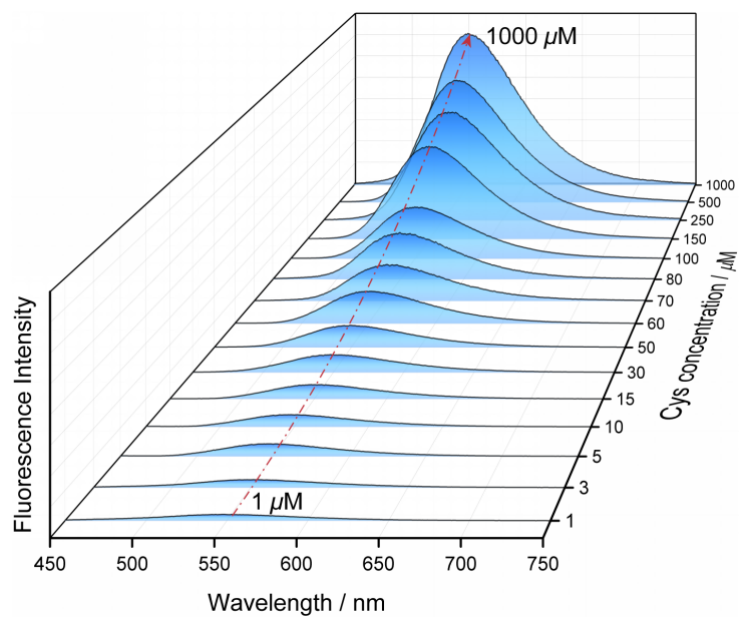


Figure S15 Fluorescence curves of FMC-2 catalyzed oxidation of OPD under the enhancement of different concentrations of Cys.

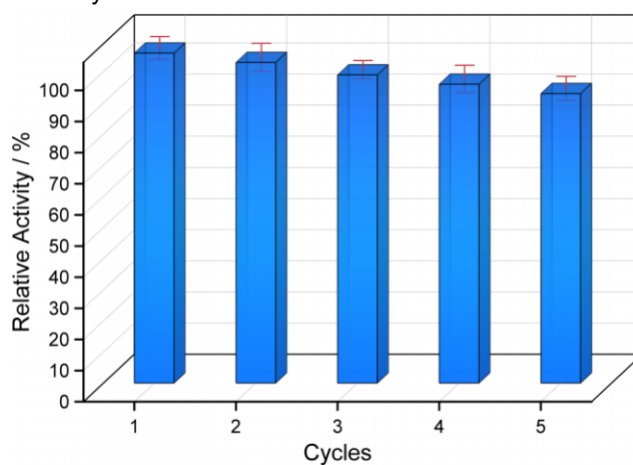


Figure S16 The reproducibility of FMC-2 after repeated cycles.

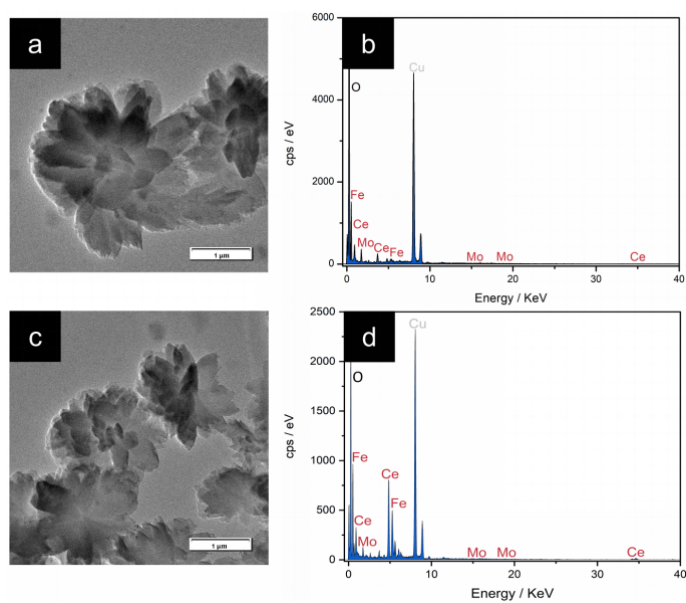


Figure S17 (a) and (b) TEM image and EDS spectrum of FMC-2 before evaluation of self-cascading multienzyme mimic activity, respectively; (c) and (d) TEM image and EDS spectrum of FMC-2 after the reaction, respectively.

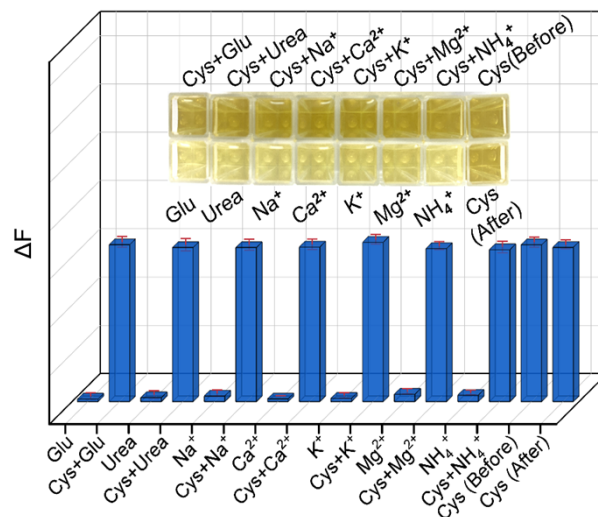


Figure S18 Optical photographs and ΔF of the developed self-cascading multienzyme sensing platform with different analytes. Analytes: 80 μM of K^+ , Na^+ , Mg^{2+} , Ca^{2+} , NH_4^+ , Glu and urea.

Section 2. Supporting Tables

Table S1. Summary of Physicochemical Properties of FC-66 and FMC-n

Sample	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)	Pore size (nm)	Pore volume ($\text{cm}^3\cdot\text{g}^{-1}$)
FC-66	11.61	9.59	0.0508
FMC-1	16.12	12.41	0.0527
FMC-2	35.06	12.10	0.2296
FMC-3	38.86	18.45	0.2345

Table S2. Ce $3d_{3/2}$ and Ce $3d_{5/2}$ components in XPS spectra of FMC-2.

Ionic state	Spin-orbit doublet	Components	BE (± 0.1 eV)	FWHM (± 0.1 eV)	Ce (III) ratio (%) ¹
Ce(IV)	$3d_{3/2}$	U	906.32	2.88	34 %
		U ^{II}	910.78	4.69	
		U ^{III}	918.43	8.87	
	$3d_{5/2}$	V	887.25	3.19	
		V ^{II}	892.07	4.79	
		V ^{III}	901.09	6.60	
Ce(III)	$3d_{3/2}$	U ⁰	903.94	3.08	
		U ^I	908.31	2.88	
	$3d_{5/2}$	V ⁰	884.67	4.25	
		V ^I	889.83	2.91	

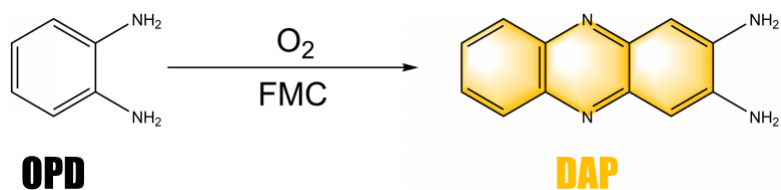
Table S3. Ce $3d_{3/2}$ and Ce $3d_{5/2}$ components in XPS spectra of CeO₂-Uio.

Ionic state	Spin-orbit doublet	Components	BE (± 0.1 eV)	FWHM (± 0.1 eV)	Ce (III) ratio (%) ¹
Ce(IV)	$3d_{3/2}$	U	901.94	2.47	29 %
		U ^{II}	908.09	3.42	
		U ^{III}	917.06	3.53	
	$3d_{5/2}$	V	883.68	1.91	
		V ^{II}	889.26	2.77	
		V ^{III}	897.71	2.68	
Ce(III)	$3d_{3/2}$	U ⁰	900.38	2.32	
		U ^I	904.56	2.44	
	$3d_{5/2}$	V ⁰	881.94	1.78	
		V ^I	886.13	2.36	

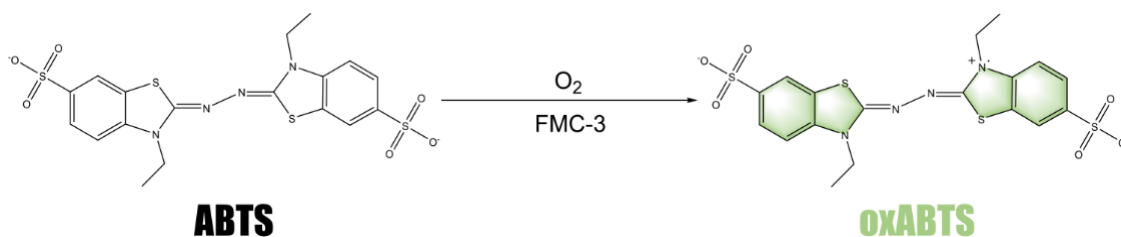
Table S4. Recoveries of the determination of Cys in human urine samples using the proposed self-cascading multienzyme sensing platform.

Sample	Added (μM)	Measured (μM)	Recovery (%)	RSD (% , n=3)
	0	9.97 ± 0.19	–	–
1	20	29.64 ± 0.13	98.2	1.92
	40	51.28 ± 0.18	102.6	2.03
	0	11.64 ± 0.16	–	–
2	20	30.96 ± 0.15	103.2	2.01
	40	50.56 ± 0.18	101.4	2.14

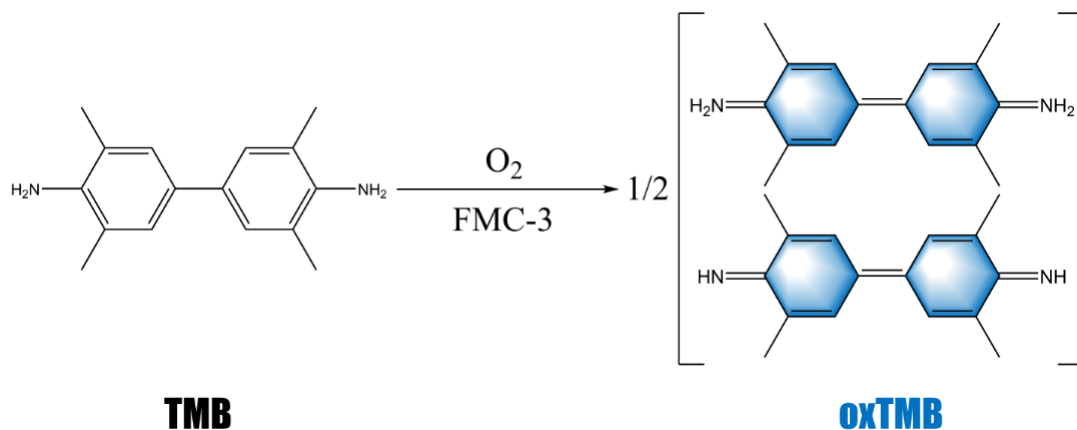
Section 3. Supporting Schemes



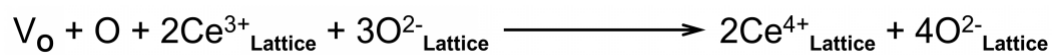
Scheme S1. Catalytic oxidation of OPD by flower-like FMC-3 in the presence of O₂.



Scheme S2. Catalytic oxidation of ABTS by flower-like FMC-3 in the presence of O₂.



Scheme S3. Catalytic oxidation of TMB by flower-like FMC-3 in the presence of O₂.



Scheme S4. The oxygen vacancy (V_o) action maintains the surface charge of FMC.

References

- (1) Beche E, Peraudeau G, Flaud V, et al. An XPS investigation of $(\text{La}_2\text{O}_3)_{1-x}(\text{CeO}_2)_x$ compounds[J]. Surface and interface analysis, 2012, 44(8): 1045-1050.