Supporting Information (ESI) for

Microwave-assisted fabrication of multicolor photoluminescent carbon dots as ratiometric fluorescence sensor for iron ions

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Experimental section

Preparation of M-CDs

Firstly, 0.55 g of three benzenediol isomers (*o*-benzenediol, *m*-benzenediol and *p*-benzenediol) was dissolved in 15 mL of ultrapure water, respectively. And then a certain amount of hydrazine hydrate was added into the solutions (Table S1). After sonication for 5 min, the mixture was heated in a household microwave oven with the power of 750 W. The products became deep-brown dry solids. The resultant three kinds of CDs (named *o*-M-CDs, *m*-M-CDs and *p*-M-CDs, respectively) were cooled to room temperature and dispersed in ethanol. The colors of *o*-M-CDs, *m*-M-CDs and *p*-M-CDs solutions were reddish-brown, yellowish-brown and brown, respectively. The solutions were further purified by filter and dialysis.

The effect of hydrazine hydrate on the product yield has been listed in Fig. S17. Different amounts of hydrazine hydrate used might be attributed to the differences in molecular structures and steric hindrance effect of three benzenediol isomers. In this experiment, *o*-benzenediol has larger steric hindrance effect, and the reaction seems more difficult. And the products from *o*-benzenediol show a relatively low product yield.

Controlled experiments

Synthesis of CDs-1: 0.55 g of *m*-benzenediol was firstly dissolved in 15 mL ultrapure water, and then 2 mL of ammonium hydroxide were inject. The mixture was sonicated for 5 min and heated in an ordinary household microwave oven at 750 W for 16 min. The products became brown dry solids. After cooling to room temperature, the products were dispersed in water and purified by filter and dialysis.

Synthesis of CDs-2: 0.55 g of *m*-benzenediol and 0.20 g of potassium borohydride were added into 15 mL ultrapure water. The mixture was also sonicated for 5 min and heated in an ordinary household microwave oven at 750 W for 16 min. The products became golden-yellow dry solids. After cooling to room temperature, the products were dispersed in water and purified by filter and dialysis.

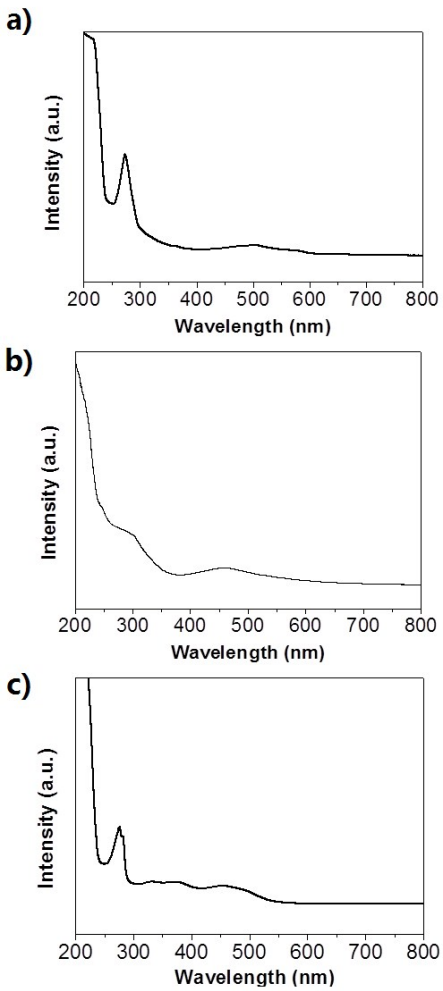


Fig. S1 UV-vis spectra of the *o*-M-CDs (a), *m*-M-CDs (b), and *p*-M-CDs (c), respectively.

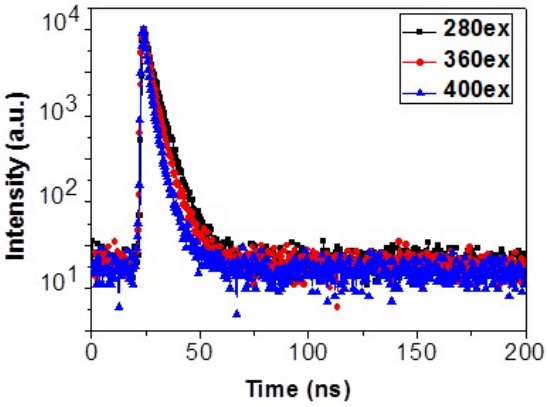


Fig. S2 FL decay curves of *m*-M-CDs at emissions of 340 nm, 430 nm and 550 nm detected at different excitation wavelengths as indicated.

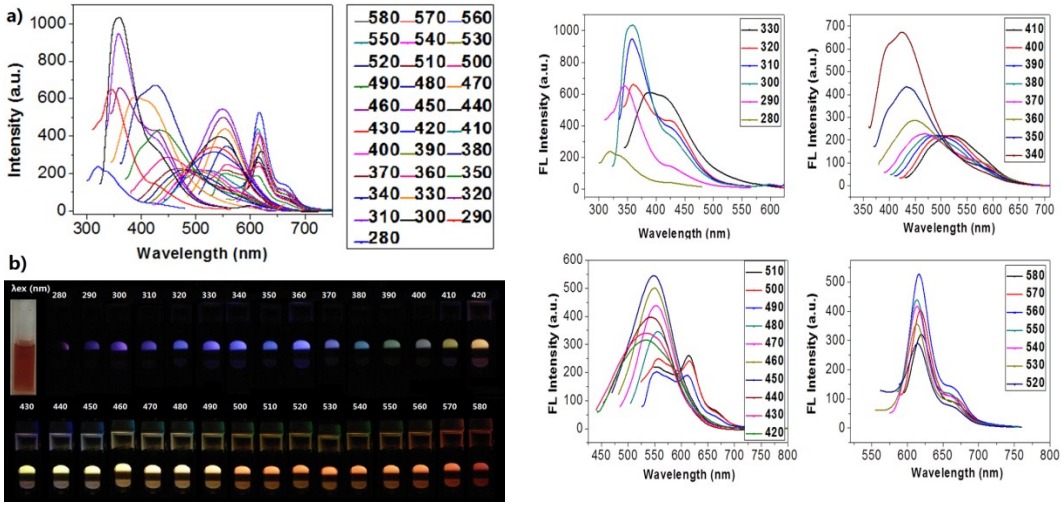


Fig. S3 (a) FL spectra of the *o*-M-CDs under different excitation wavelengths. (b) FL emission photographs of the *o*-M-CDs recorded from 280 to 580 nm in 10 nm increments. The spectra and photographs were obtained by the *o*-M-CDs dispersed in ethanol.

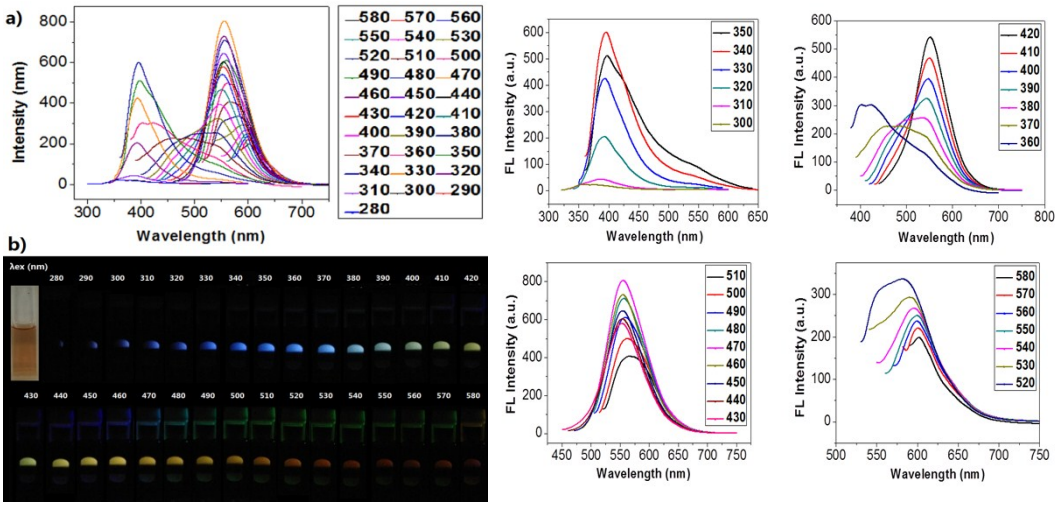


Fig. S4 (a) FL spectra of the *p*-M-CDs under different excitation wavelengths. (b) FL emission photographs of the *p*-M-CDs recorded from 280 to 580 nm in 10 nm increments. The spectra and photographs were obtained by the *p*-M-CDs dispersed in ethanol.

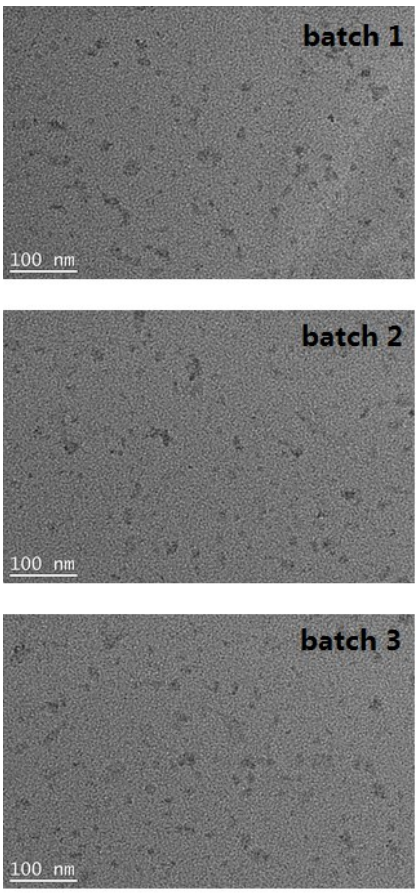


Fig. S5 TEM images of the *m*-M-CDs of three different batches under the same preparation conditions.

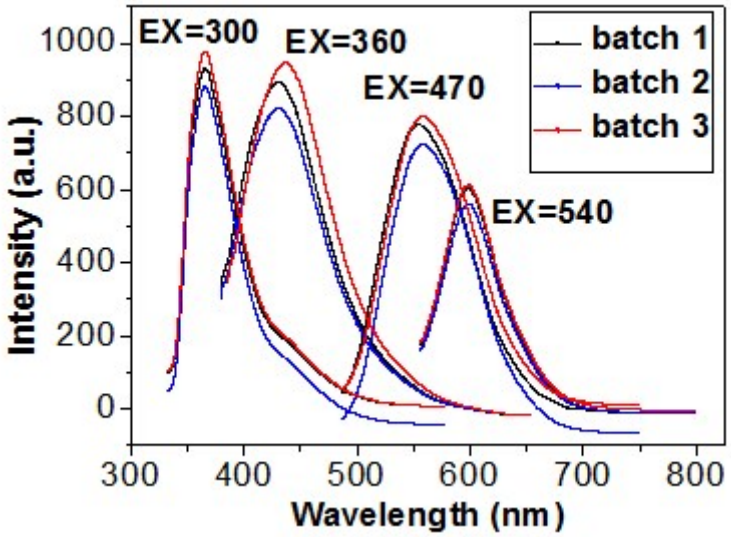


Fig. S6 FL spectra of the *m*-M-CDs from three different batches under the same preparation conditions.

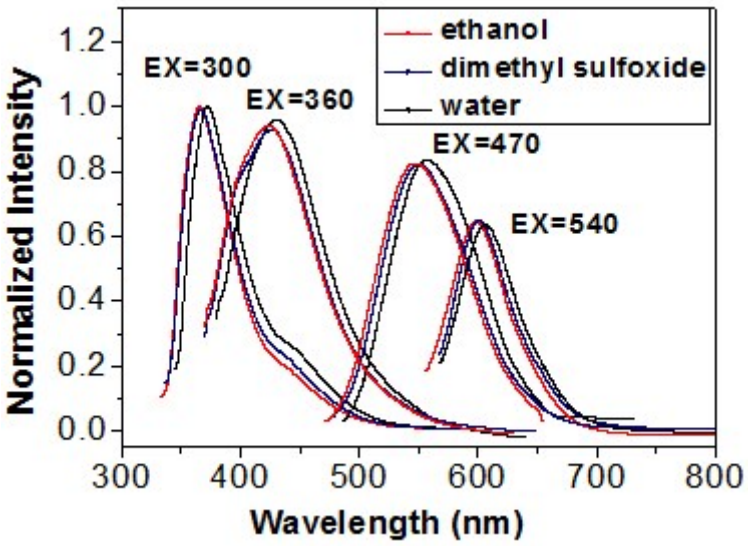


Fig. S7 FL spectra of the *m*-M-CDs dispersed in different solvents (ethanol, dimethyl sulfoxide and water).

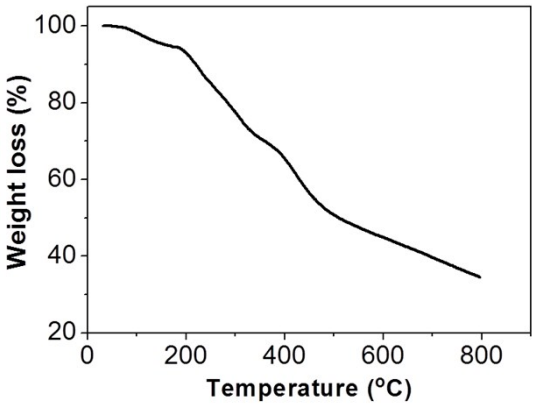


Fig. S8 TGA analysis of the *m*-M-CDs.

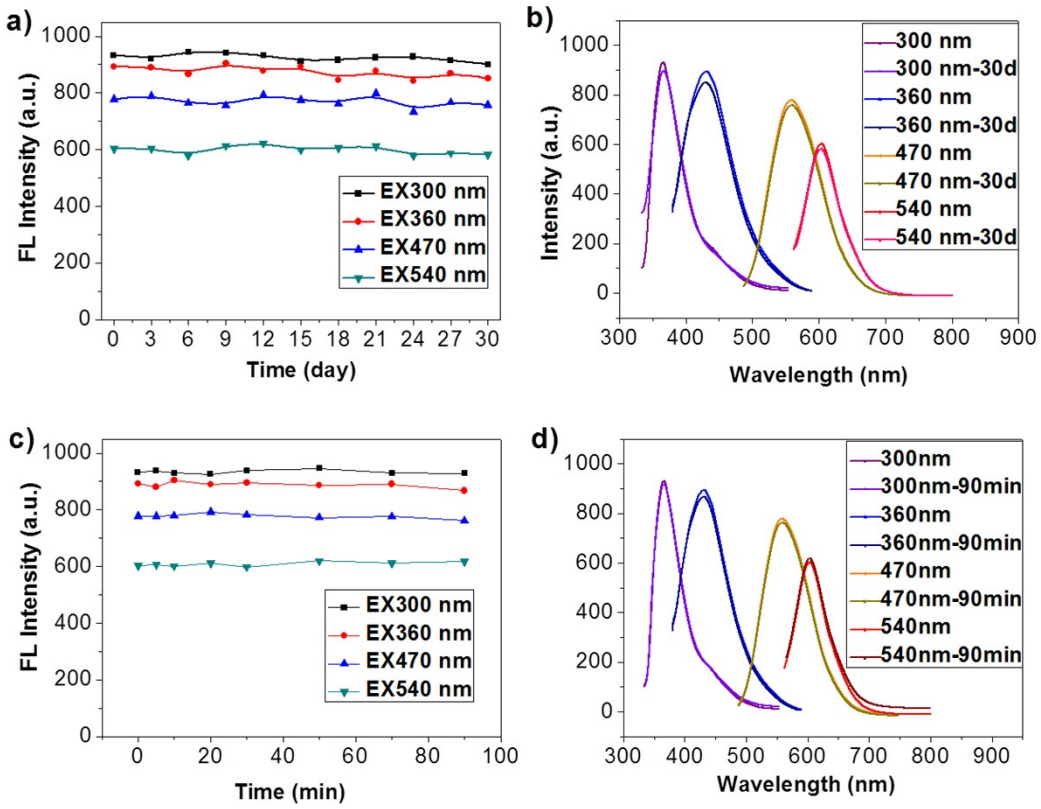


Fig. S9 (a-b) Effect of longtime storage (1 month) on the FL properties of the *m*-M-CDs; (c-d) effect of continuous UV irradiation (365 nm for 90 min) on the FL properties of the *m*-M-CDs.

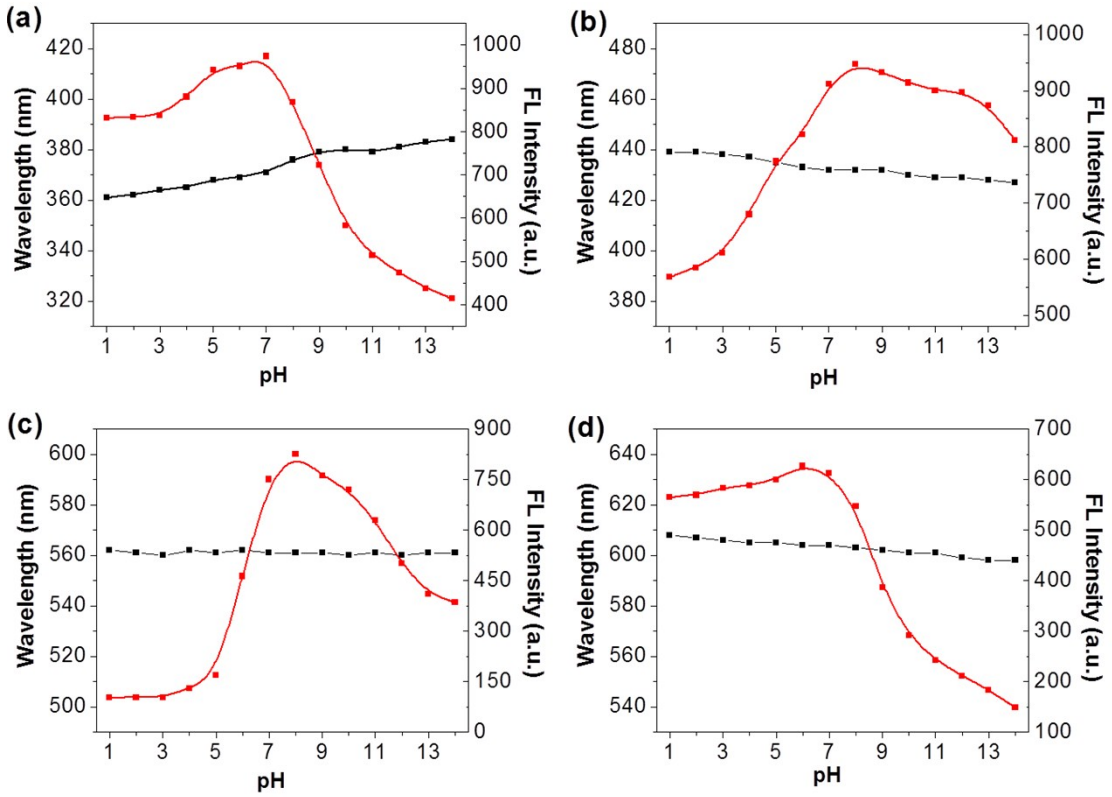


Fig. S10 The effect of pH on the emission wavelength and FL intensity of the *m*-M-CDs at various excitation wavelengths, (a) λ_{ex}=300 nm, (b) λ_{ex}=360 nm, (c) λ_{ex}=470 nm and (d) λ_{ex}=540 nm.

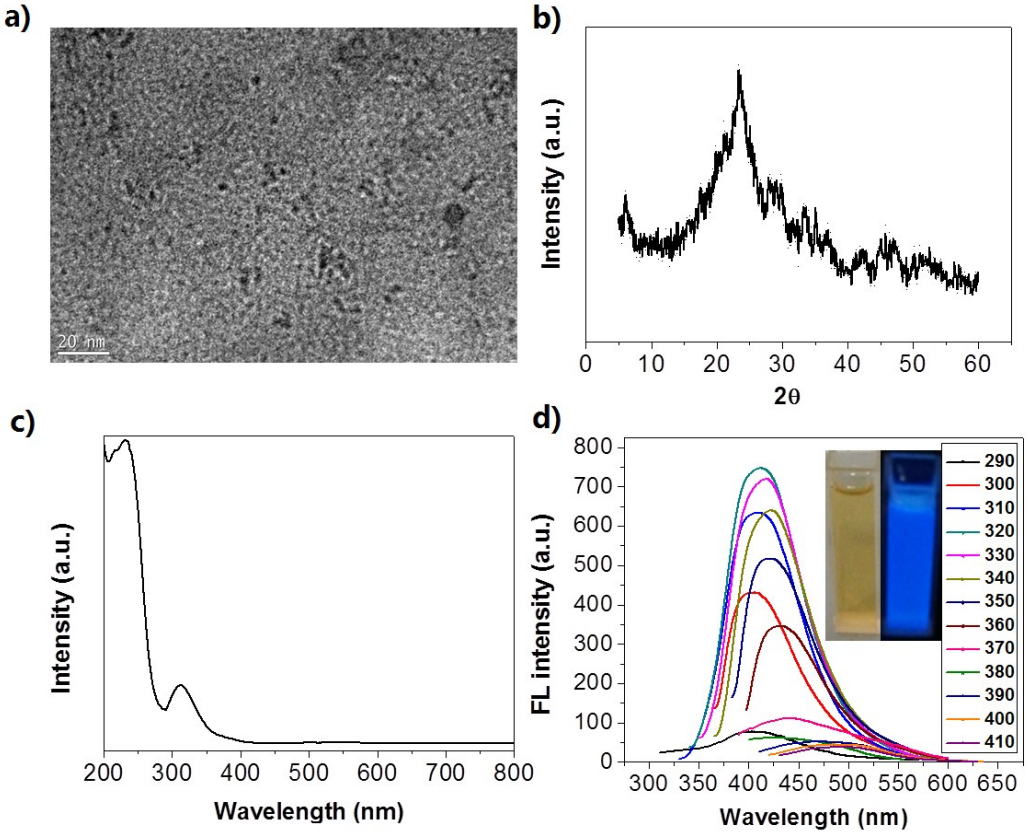


Fig. S11 (a) TEM image, (b) XRD pattern, (c) UV-vis spectrum and (d) FL emission spectra of the CDs-1 derived from microwave treatment of ammonium hydroxide and *m*-benzenediol.

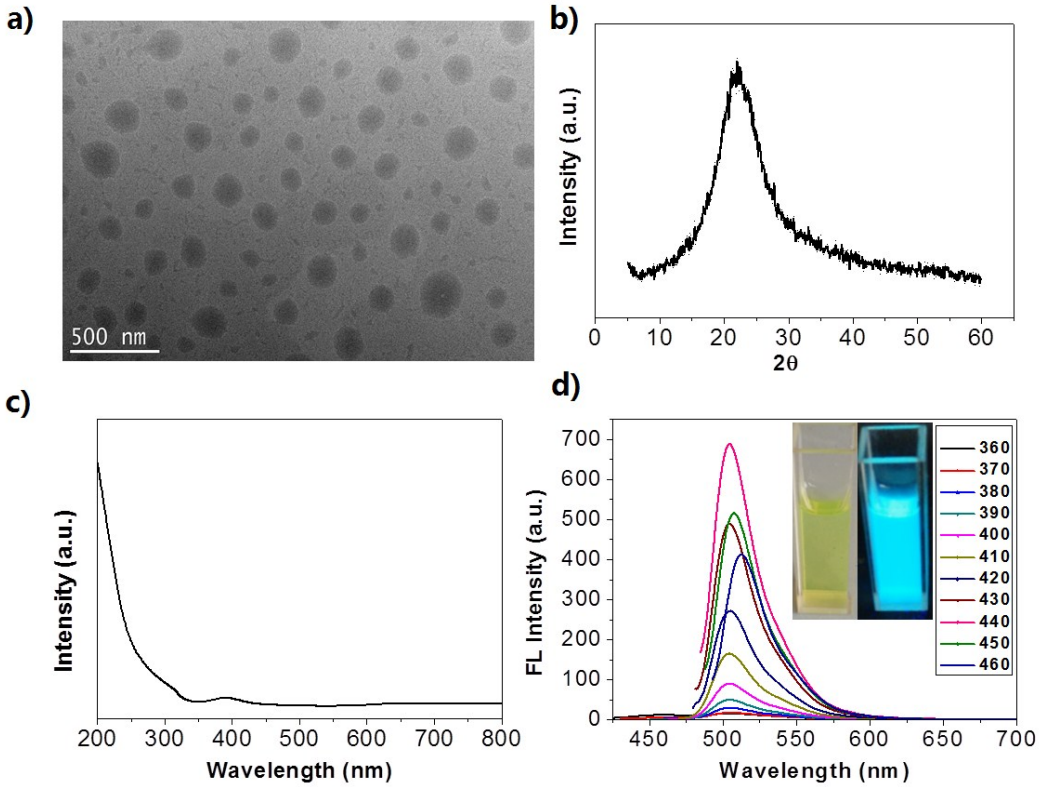


Fig. S12 (a) TEM image, (b) XRD pattern, (c) UV-vis spectrum and (d) FL emission spectra of the CDs-2 derived from microwave treatment of potassium borohydride and *m*-benzenediol.

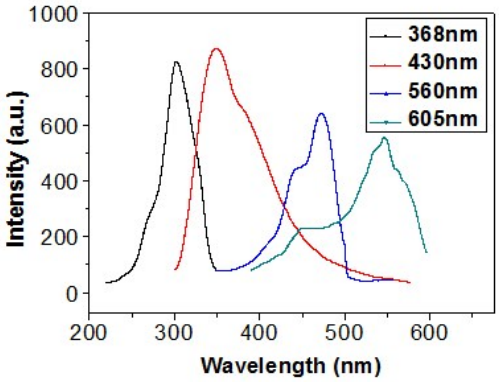
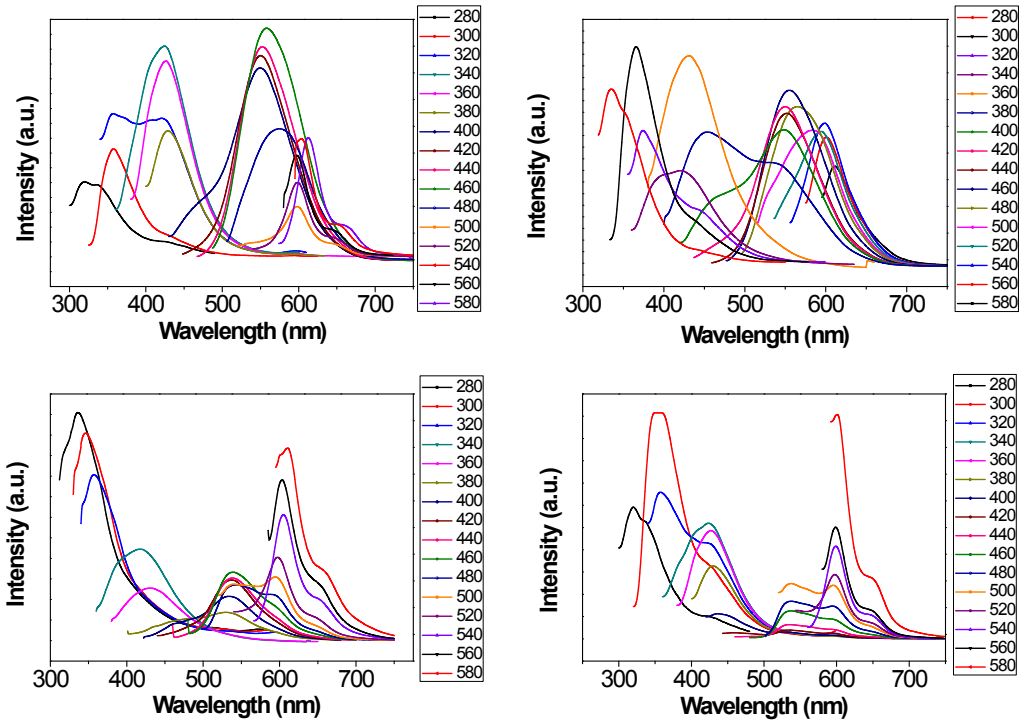


Fig. S13 FL excitation spectra of the as-prepared *m*-M-CDs at 368 nm, 430 nm, 560 nm and 605 nm, respectively.



Amount of hydrazine hydrate (mL)	C-C/C=C (%)	C-N/C-O (%)	C=N (%)
0.2	40.3	40.2	19.5
0.5	33.2	37.1	29.7
1	34.6	32.0	33.4
2	37.0	26.2	36.8

Fig. S14 The FL spectra of *m*-M-CDs with different amount of hydrazine hydrate used.

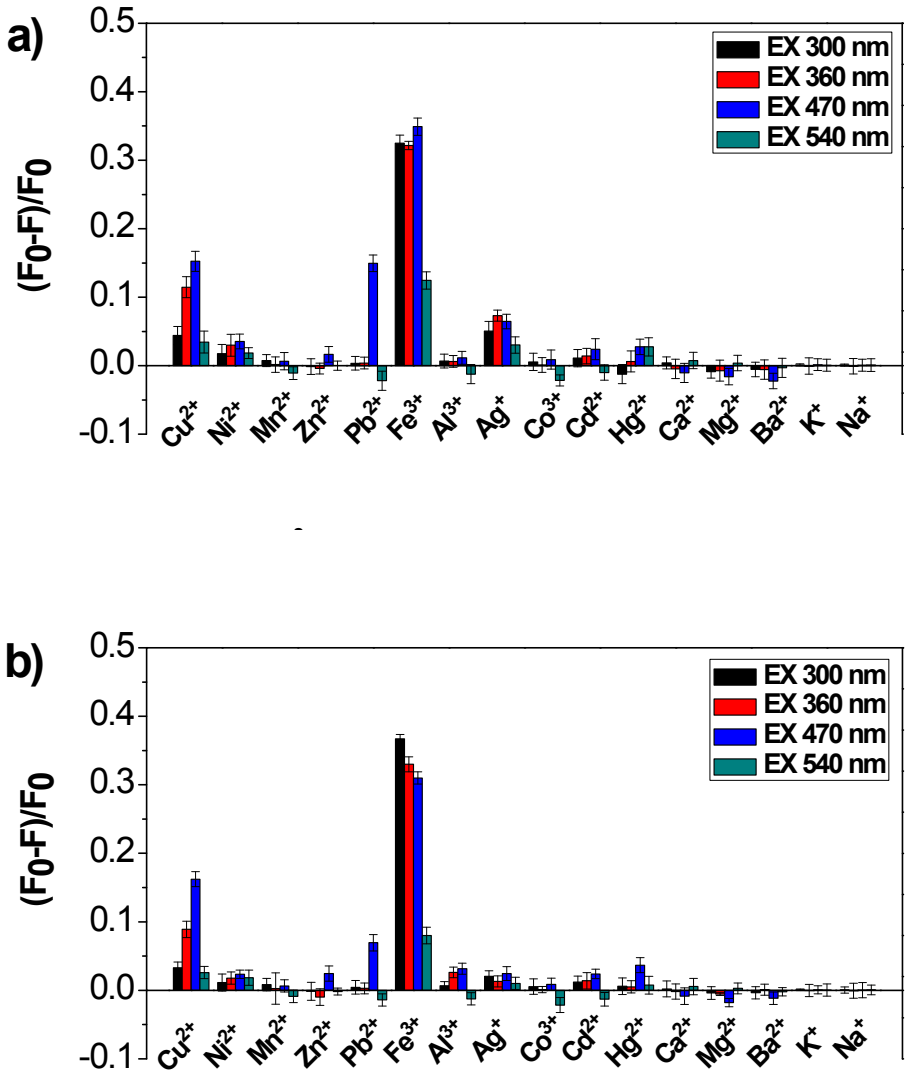


Fig. S15 The quenching efficiencies of a variety of metal ions (10 μM) with the same concentration to the four dominate emission maxima of the *m*-M-CDs, a) pH=7; b) pH=5.

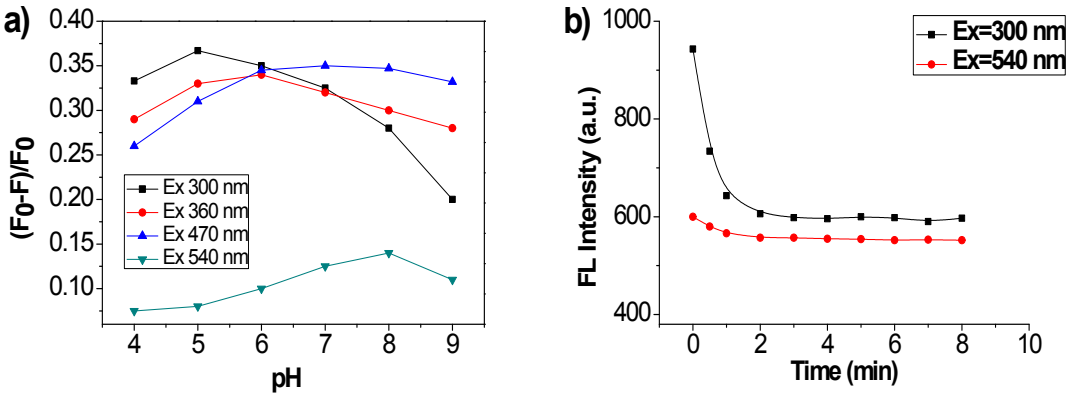


Fig. S16 Fluorescence quenching of Fe^{3+} on the *m*-M-CDs at different pH (a) and incubation times (b) (the concentration of Fe^{3+} is 10 μM).

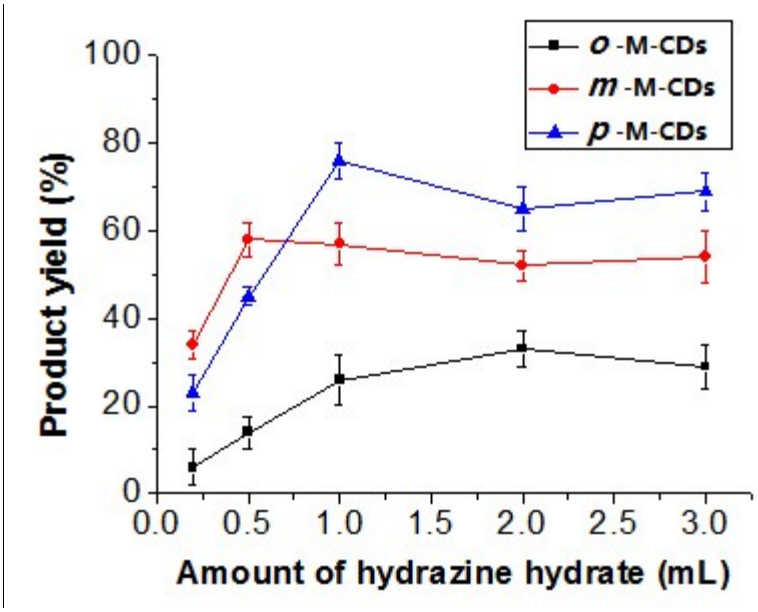


Fig. S17 The effect of amount of hydrazine hydrate on the product yield.

Table S1. Comparison of preparation conditions and fluorescence properties of the resultant M-CDs.

Nano materials	Reactant	Microwave power (W)	Amount of hydrazine hydrate (mL)	Reaction time (min)	Product yield of the M-CDs	Fluorescence property		FL quantum yield (%)
						λex(nm)	λem(nm)	
o-M-CDs	*o*-benzenediol	750	2	20	33%	300	360	26.2
						340	425	10.4
						450	545	9.3
						560	620	8.7
m-M-CDs	*m*-benzenediol	750	0.5	16	58%	300	370	13.8
						360	430	19.6
						470	560	17.4
						540	604	10.6
p-M-CDs	*p*-benzenediol	750	1	15	76%	340	394	12.5
						350	426	8.2
						470	558	21.5
						520	585	9.4

Table S2. FL properties of *m*-M-CDs

λex (nm)	λem (nm)	△λ (nm)	FHWM (nm)	Intensity
280	337	55	–	750
290	358	66	68	844
300	371	68	52	931
310	373	59	53	784
320	375	54	–	572
330	392	62	–	507
340	419	79	96	398
350	425	75	89	670
360	430	70	88	893
370	439	69	–	832
380	451	71	–	565
390	544	154	–	493
400	550	150	–	573
410	550	140	90	637
420	551	131	85	672
430	552	122	81	681
440	554	114	77	692
450	556	106	83	707
460	558	98	86	746
470	560	90	89	778
480	564	84	90	674
490	576	86	82	616
500	584	84	93	573
510	592	82	88	559
520	597	77	78	567
530	600	70	67	591
540	605	65	64	603
550	606	56	60	582
560	607	47	55	542
570	607	37	–	522
580	611	31	–	418

△λ (nm)= λem-λex; FWHM=full width at half maximum.

Table S3. Fitting parameters of the corresponding FL decay curves for *m*-M-CDs.

λ_{ex}/nm	τ_1/ns	B_1/%	τ_2/ns	B_2/%	τ_3/ns	B_3/%	τ_{avg}/ns	χ^2
280	1.26	35.4	2.94	55.0	7.31	9.6	2.76	1.008
360	1.72	27.0	3.57	62.0	7.89	11.0	3.55	1.020
400	1.65	33.2	4.24	58.2	8.44	8.6	3.74	1.112

Table S4. Comparison of three batches of the M-CDs under the same preparation conditions. The minor differences of the FL properties are due to their slight differences in concentrations.

		Product yield (%)	Average size (nm)	Fluorescence property	
				λex(nm)	λem(nm)
o-M-CDs	Batch 1	33	13.4	300	360
				340	425
				450	545
				560	620
	Batch 2	36	13.2	300	358
				340	422
				450	545
				560	617
	Batch 3	28	13.5	300	360
				340	425
				450	547
				560	622
m-M-CDs	Batch 1	58	9.7	300	370
				360	430
				470	560
				540	604
	Batch 2	56	9.7	300	371
				360	430
				470	562
				540	604
	Batch 3	52	9.9	300	369
				360	434
				470	562
				540	605
p-M-CDs	Batch 1	76	10.1	340	394
				350	426
				470	558
				520	585
	Batch 2	78	10.3	340	395
				350	425
				470	556
				520	584
	Batch 3	71	10.4	340	395
				350	428
				470	560
				520	586

Table S5. Analytical results for the determination of Fe^{3+} in the real water samples.

Tap samples	Spiked (μM)	Measured	Recovery (%)	RSD (n=3, %)
1	2.0	1.82	91	6
	10.0	9.86	99	3
2	2.0	1.92	96	4
	10.0	9.74	97	4
3	2.0	1.86	93	5
	10.0	9.83	98	3

Table S6 Comparison of analytical data with previous CDs-based sensors for Fe^{3+} detection.

CDs preparation method	Samples	Linear range	LOD (μM)	Recoveries (%)	RSD (%)	Ref.
Urea+diethylene glycol→Microwave-assisted method	Serum	1.6-333.3 μM	0.45	93-108	3.4	14
Citric acid+Tris→Hydrothermal method	Water	2-50 μM	1.3	97.4-108.1	Not given	15
Urea+EDTA→ Oil bath	—	0-2 mM	0.0136	Not given	Not given	16
Aspartic acid+NH_4HCO_3→ Microwave-assisted method	—	0-50 μM	0.26	Not given	Not given	S1
Citric acid+ethanediamine→ Hydrothermal method→ Bacterial cellulose assemble	—	0-600 μM	0.084	Not given	Not given	S2
Maminobenzoic acid→Hydrothermal method	Water	0-1.2 μM	0.05	Not given	Not given	S3
P. avium fruits+aqueous ammonia→Hydrothermal method	Water	0-100 μM	0.96	Not given	Not given	S4
PEG-diamine+citric acid→ Solid phase synthesis	Biological samples	0.01-500 μM	0.025	96.65-104.02	<2.32	S5
Benzenediol+hydrazine hydrate→Microwave-assisted method	Water	0.1 M-20 μM	0.01	91-99	<6	This work

References

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