Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Material

Imidazole derivative-functionalized carbon dots: Using as a fluorescent probe for detecting water and imaging of live cells

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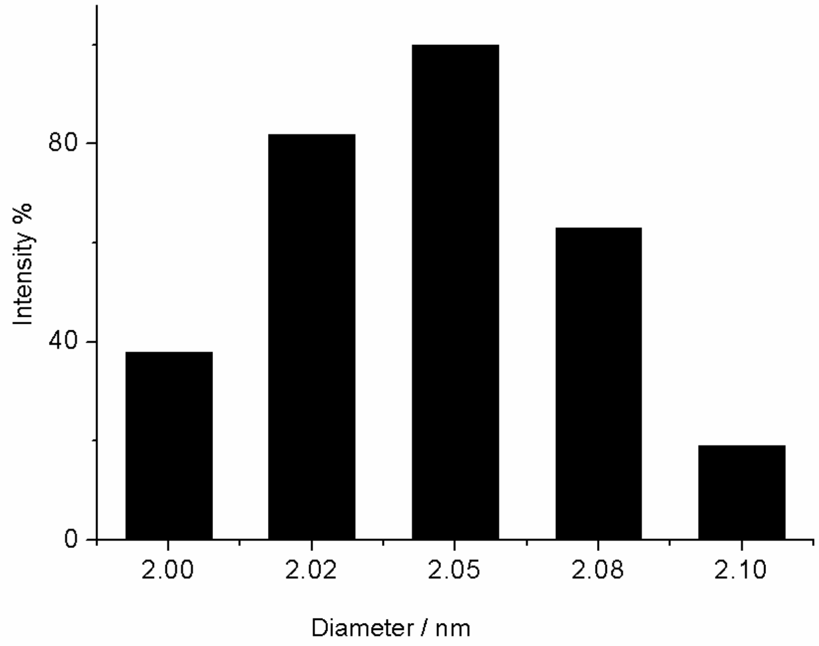


Fig. S1 DLS of CDs.

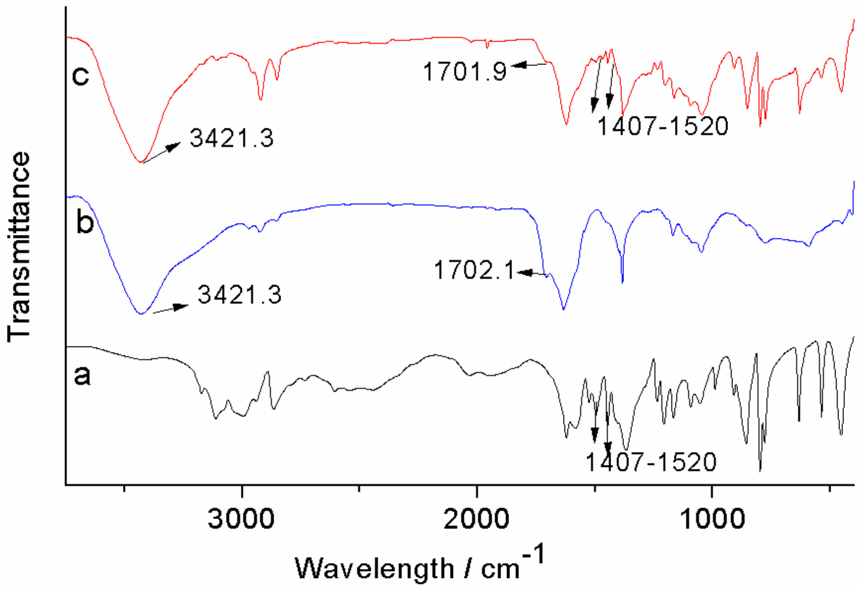


Fig. S2 FTIR spectra of 1H-Imidazole-4-carboxylic acid (a), CDs (b) and CDs-imidazole (c)

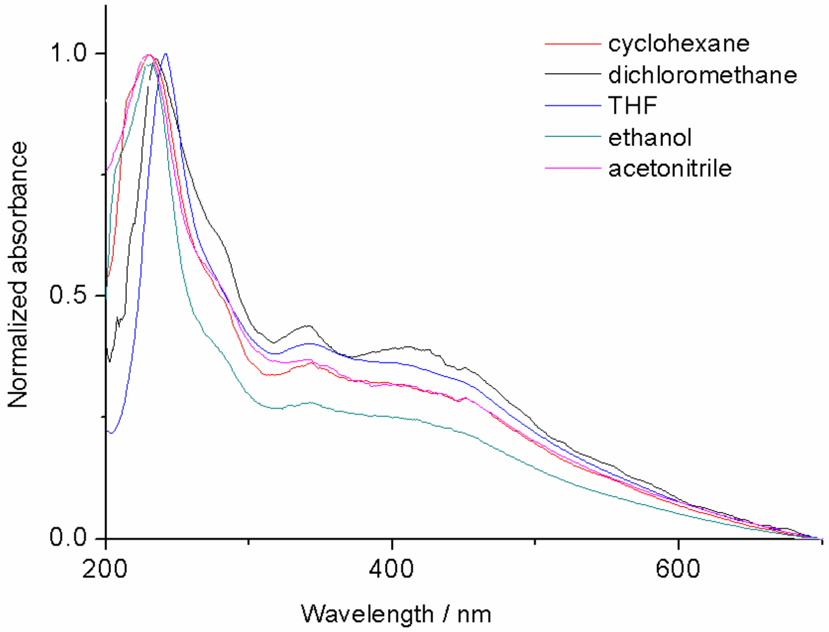


Fig. S3 Normalized UV-Vis spectra of the CDs-imidazole in different solvents.

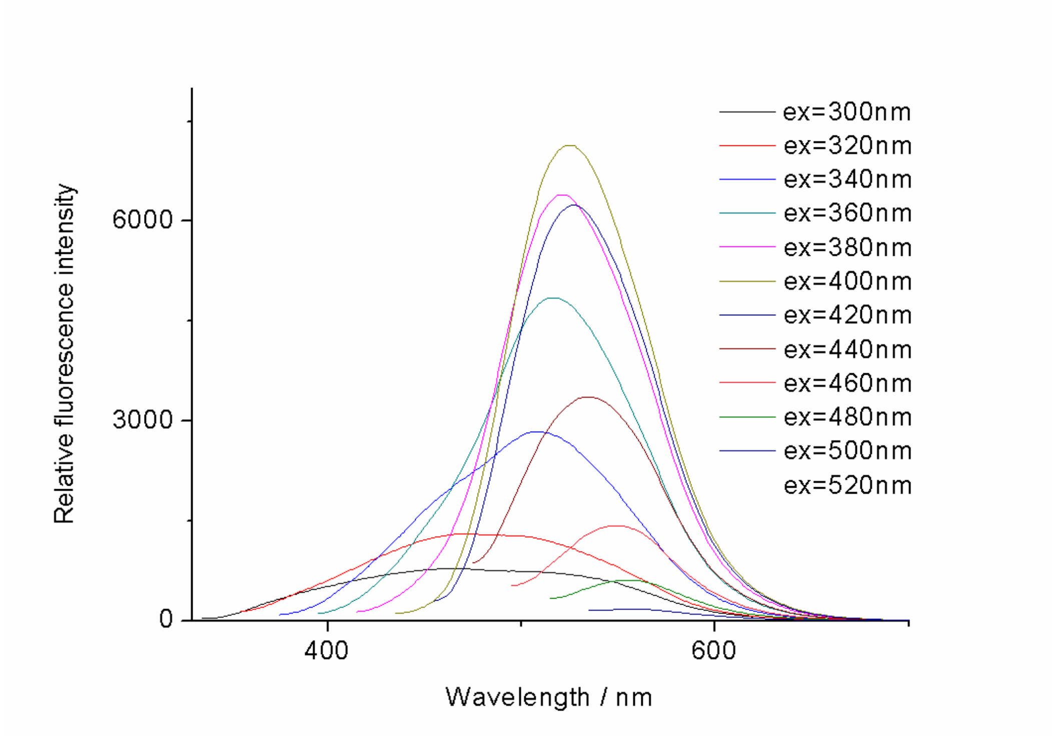


Fig. S4 Fluorescence spectra of CDs in water under different excitation wavelength.

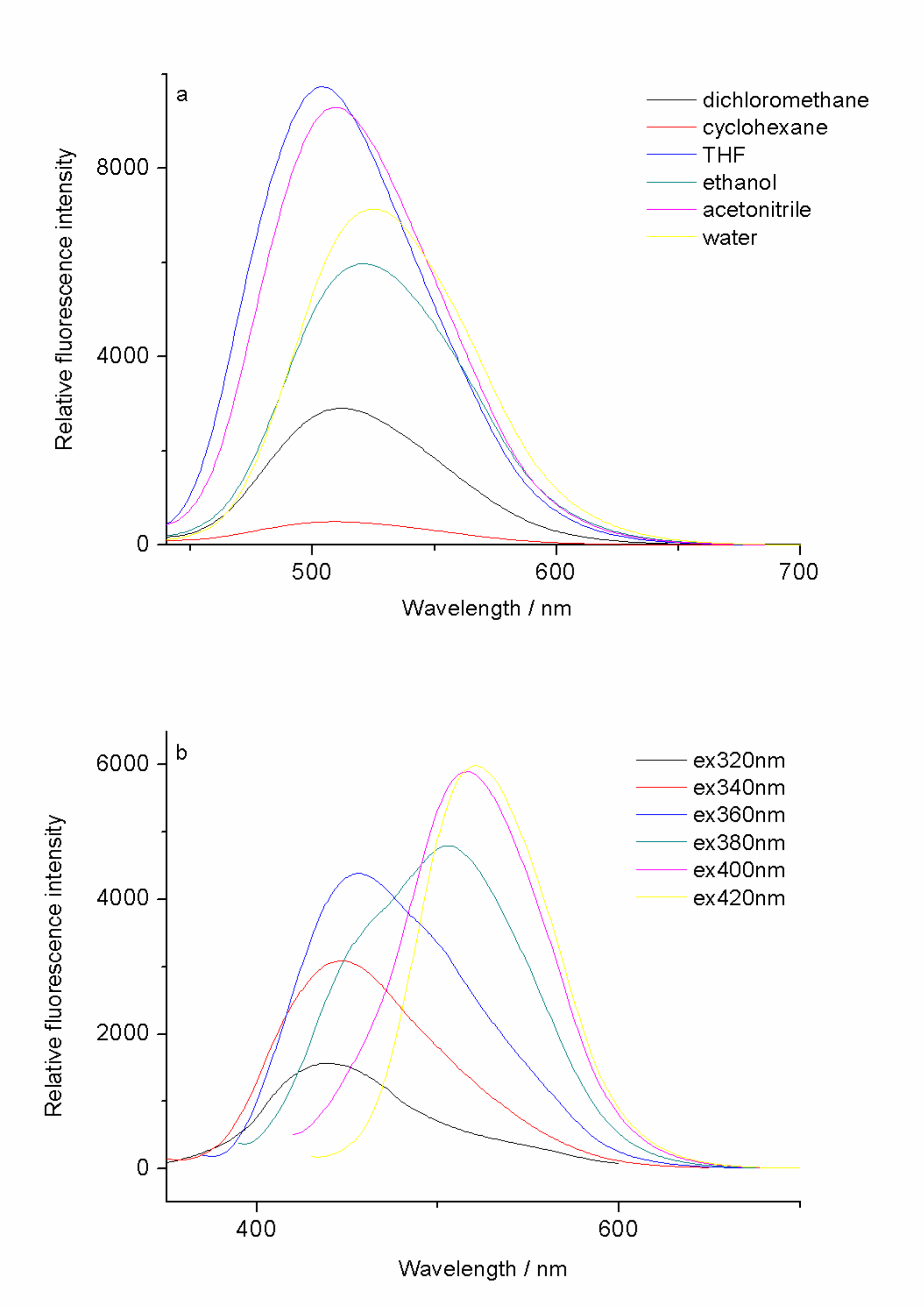
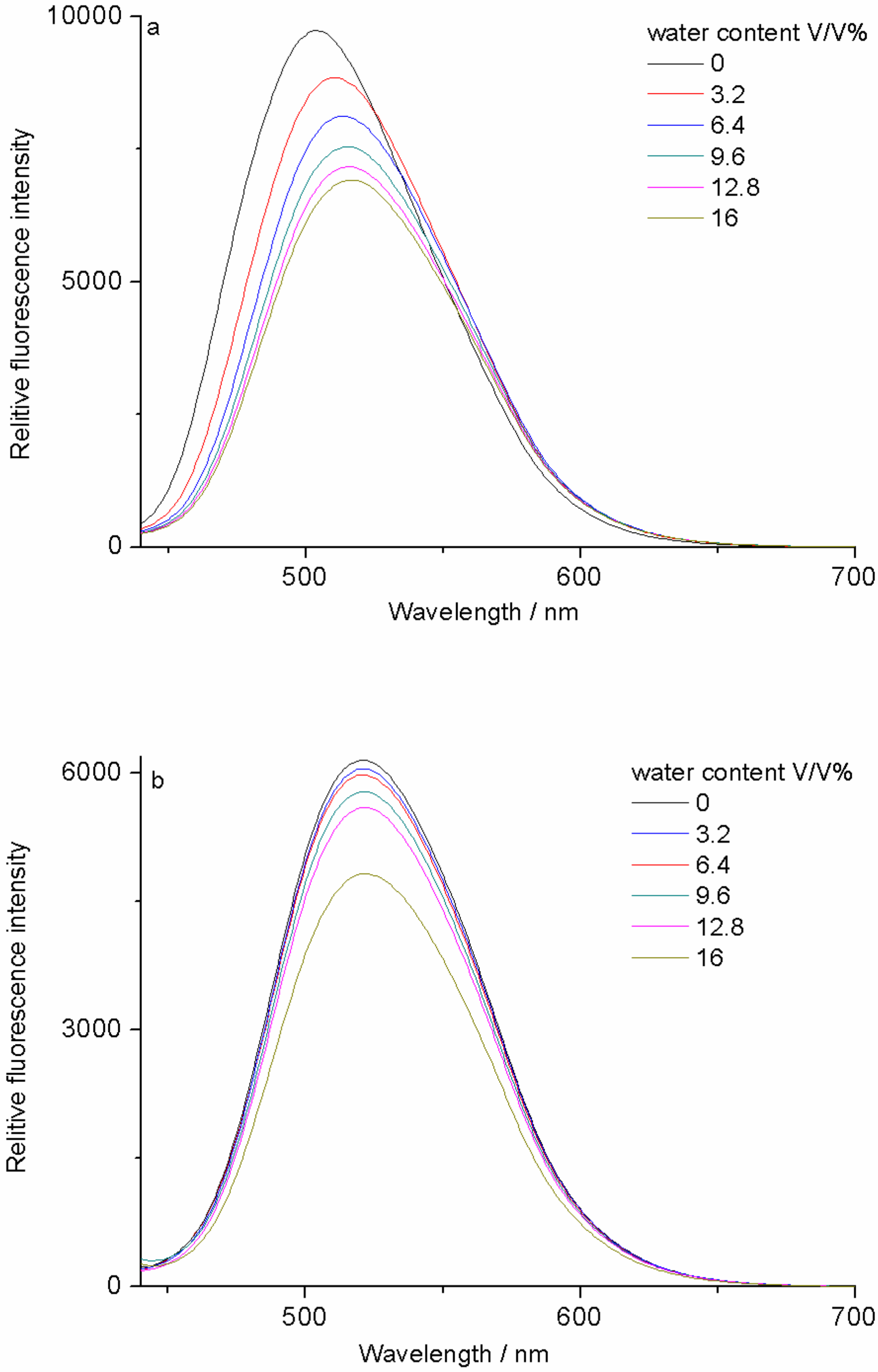


Fig. S5 (a) Fluorescence emission spectra （λ_{ex}=420 nm） of the CDs in different solvents and water. (b) Fluorescence emission spectra of the CDs in ethanol when excited at different wavelength.


10000
a
water content V/V%
0
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6.4
9.6
12.8
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Relitive fluorescence intensity
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Wavelength / nm
6000
b
water content V/V%
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Relitive fluorescence intensity
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Wavelength / nm

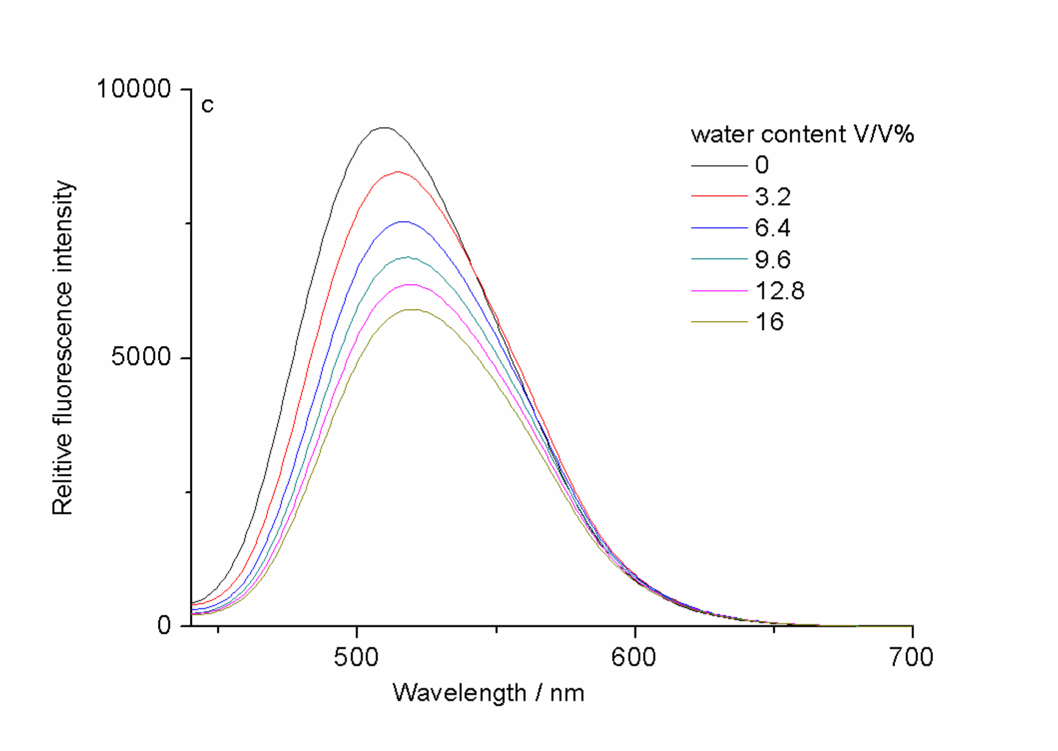


Fig. S6 Fluorescence emission spectra (λ_{ex}=420 nm) of CDs in THF (a), ethanol (b), acetonitrile (c) with increasing water content.

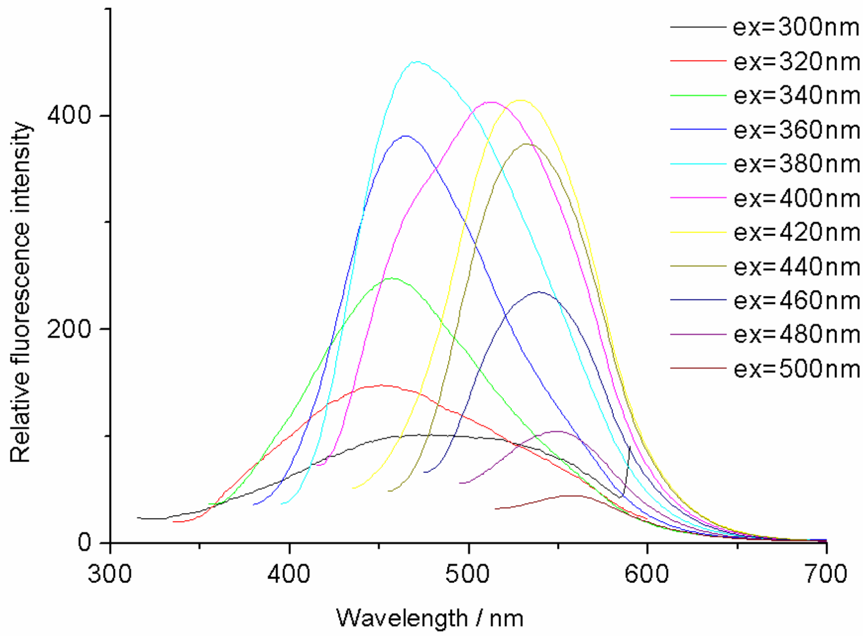


Fig. S7 Fluorescence spectra of CDs-imidazole in water under different excitation wavelength.

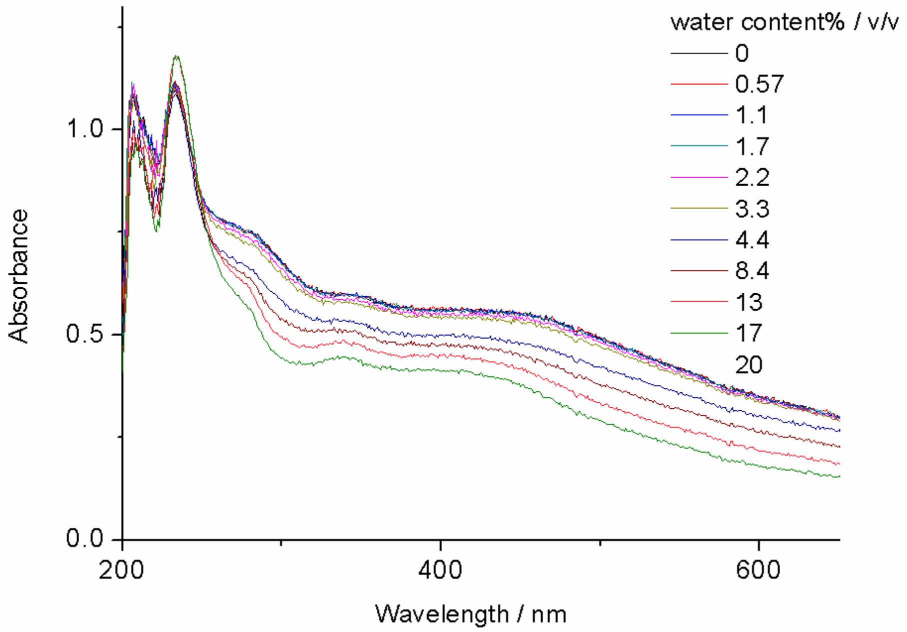
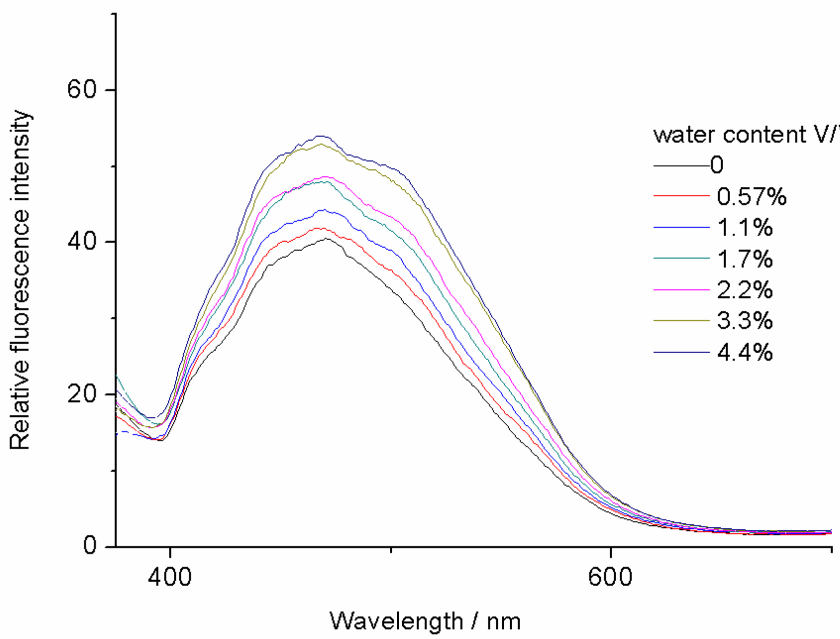


Fig. S8UV-Vis spectra of CDs-imidazole in ethanol with increasing water content (v/v).



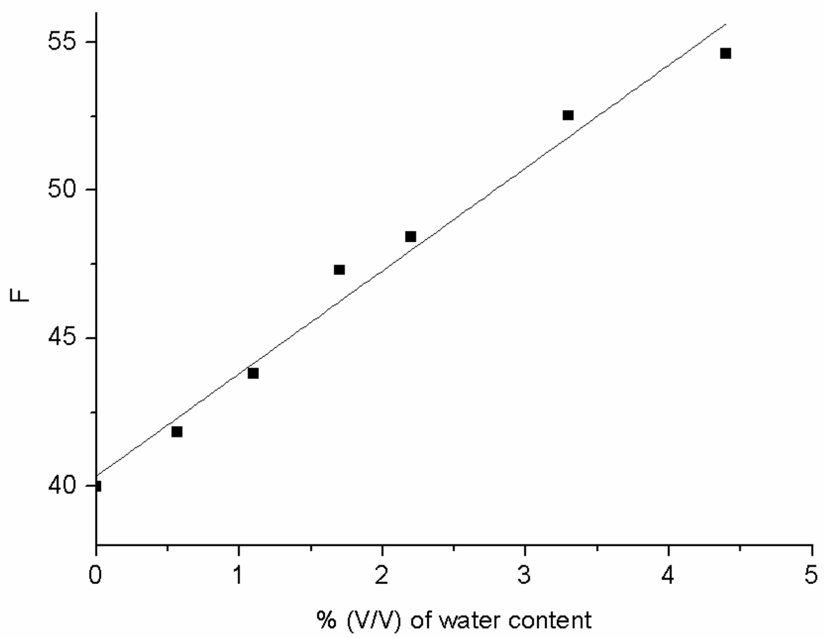


Fig. S9. Fluorescence emission spectra (λ_{ex}=360 nm) of CDs-imidazole in ethanol with increasing water content (0-5 %, v/v) (a); and calibration curves as a function of water content (0-5 %, v/v) in ethanol (b).

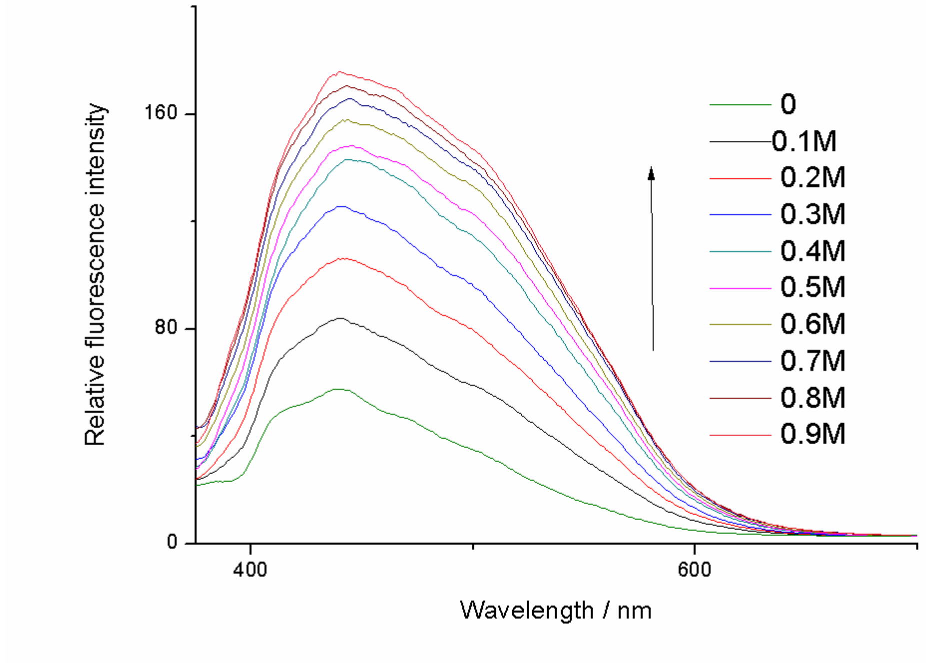


Fig. S10 Fluorescence emission spectra (λ_{ex}=360 nm) of CDs-imidazole upon addition of *p*TsOH in ethanol.

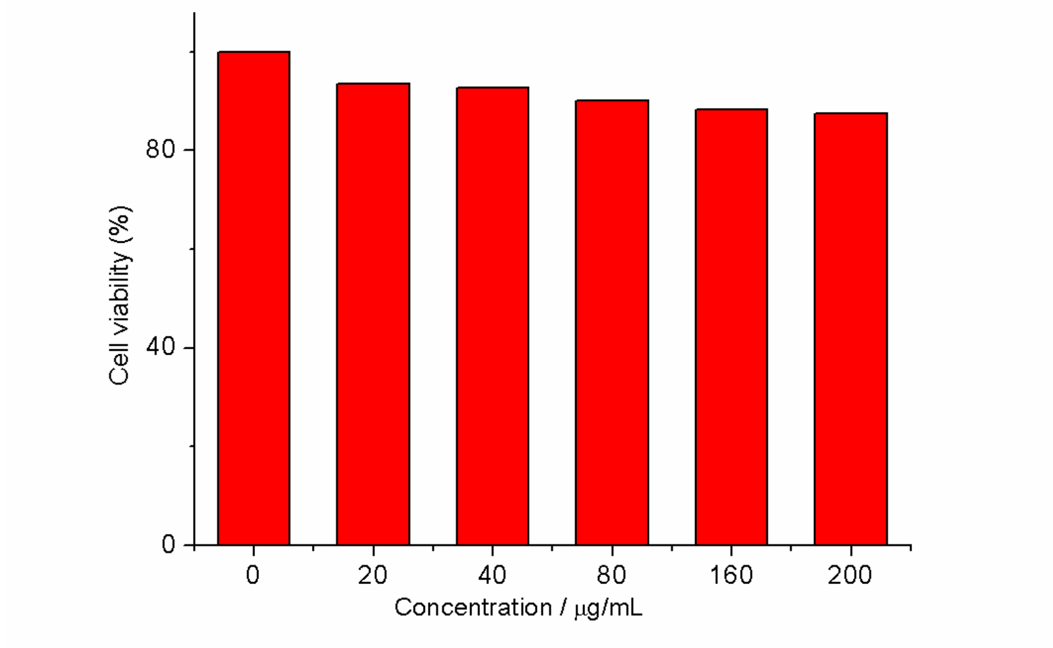


Fig. S11. Effects of CDs-imidazole at varied concentrations on the viability of BHK cells

To investigate the fluorescence dynamics of CDs and CDs-imidazole, fluorescence decay traces of CDs and CDs-imidazole in solvents were collected as a function of emission wavelength λ_{em} by the single-photon timing technique. Each fluorescence decay trace, was analyzed individually as a sum of three exponential function in terms of decay times τ_i and associated preexponential factors α_i (i = 1-3). Mono- or bi-exponential decay functions fail to describe the observed decay as evidenced by the large χ^2 and high non-random residuals. Table S2 summarizes the time resolved fluorescence data of CDs and CDs-imidazole in different solvents.

Before an attempt is made to analyze the results, it is worth recapitulating the literature data on CDs. For CDs in ethanol, a tri-exponential function (~1.0 ns, ~5.0 ns and ~13.0 ns) was used to fit the decay at all three emission wavelengths.[1] The fluorescence decay of CDs in the present work at λ_{ex}=360 nm also displays tri-exponential behavior in water and enthanol. In water, a tri-exponential function (~1.2 ns, ~5.5 ns and ~12.0 ns) was used to fit the decay at all three emission wavelengths (Fig. S10). The fast component (τ_1 ~ 1.2 ns) has the amplitude of about ~ 3 %, whereas the contributions of the τ_2 (~5.5 ns) and τ_3 (~12.0 ns) components are about ~ 30 % and ~ 67 %, respectively. The decay times are similar to those reported in the literature.[1,2] Change solvent from water to ethanol (Fig. S11) does not induce a clear change in the fluorescence decay, which is still a tri-exponential function (~1.2 ns, ~6.5 ns and ~12.0 ns) in ethanol. The multiexponential nature of the lifetime suggests that the components of CDs and their analogues in water are complicated, probably due to the involvement of different particle sizes and emissive trap sites.

The fluorescence lifetimes of CDs-imidazole in organic solvents were too short and could not be determined. So fluorescence decay traces of CDs-imidazole in different aqueous–organic (water–ethanol, water–THF and water–MeCN) media (1:1, v/v) were collected as a function of emission wavelength (Fig. S12). A tri-exponential function (~1.0 ns, ~5.0 ns and ~12.0 ns) was used to fit the decay at all three emission wavelengths for CDs-imidazole in water–ethanol media (1:1, v/v). The decay times are similar to the values of CDs in water (~1.2 ns, ~5.5 ns and ~12.0 ns). But the decays τ_1 and τ_2 become slightly shorter (Fig. S13a).

The decay times of CDs-imidazole in different aqueous–organic solvents are similar to each other. The fluorescence decay was fitted to the tri-exponential profile with the decay times of ~1.0 ns, ~5.0 ns and ~12.0 ns. From fig. 12 one could see that the fluorescence decay traces in different aqueous–organic solvents are almost completely overlapped. In pure water, analogously to the CDs-imidazole in aqueous–organic, tri-exponential function (~1.0 ns, ~5.0 ns and ~12.0 ns) was used to fit the decay in water.

On the other hand, the fluorescence decays of CDs-imidazole upon addition of 0.9 M *p*TsOH in acidic ethanol conditions was also invested with three lifetimes ~0.8 ns, ~3.5 ns and ~14.0 ns. The decays t_1 and t_2 become shorter which were compared to that of CDs-imidazole in water–ethanol media (1:1, v/v) (~1.0 ns, ~5.0 ns and ~12.0 ns) (Fig. S13b). The longest decay time becomes longer but its contribution decreases (from ~60% decreases to ~20%).

The fluorescence quantum yield (FLQY) of CDs in ethanol is 15.9% with the excitation wavelength at 360 nm. The FLQY of CDs-imidazole in ethanol which contains 50%water is 6.29%. The FLQY of CDs-imidazole in acidic ethanol (0.9 M *p*TsOH) is 3.0%. The FLQY of CDs-imidazole in ethanol is 0.2%. The results of steady–state fluorescent are corresponding to that of the time-resolved fluorescence spectroscopy.

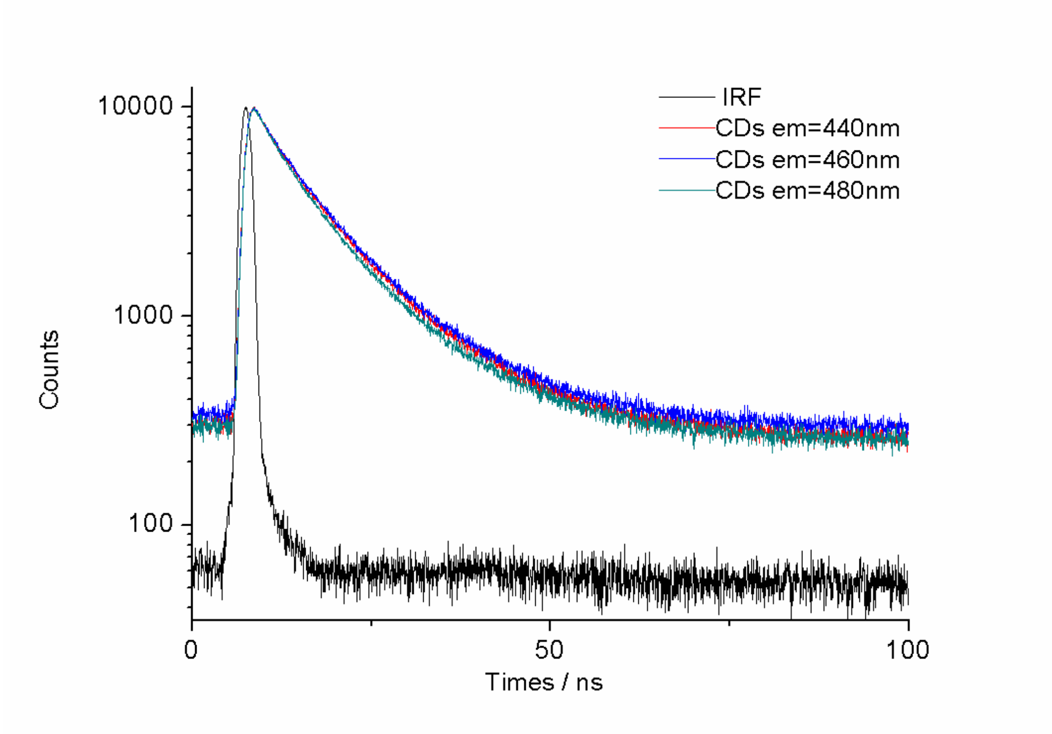


Fig. S12 The decay curves of CDs in water collected at different wavelengths when excited at 360 nm.

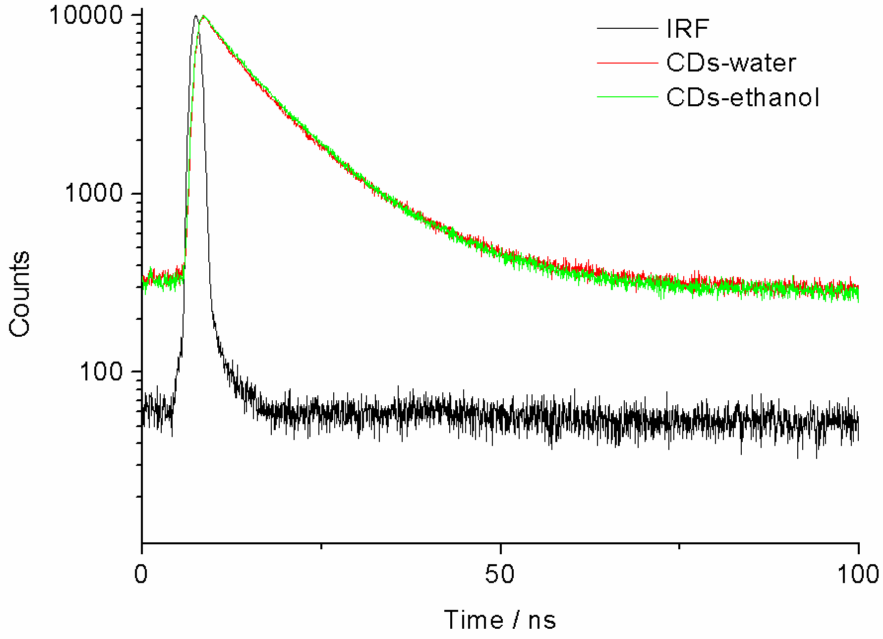


Fig. S13 The decay curves of CDs in water and ethanol collected at 460 nm when excited at 360 nm.

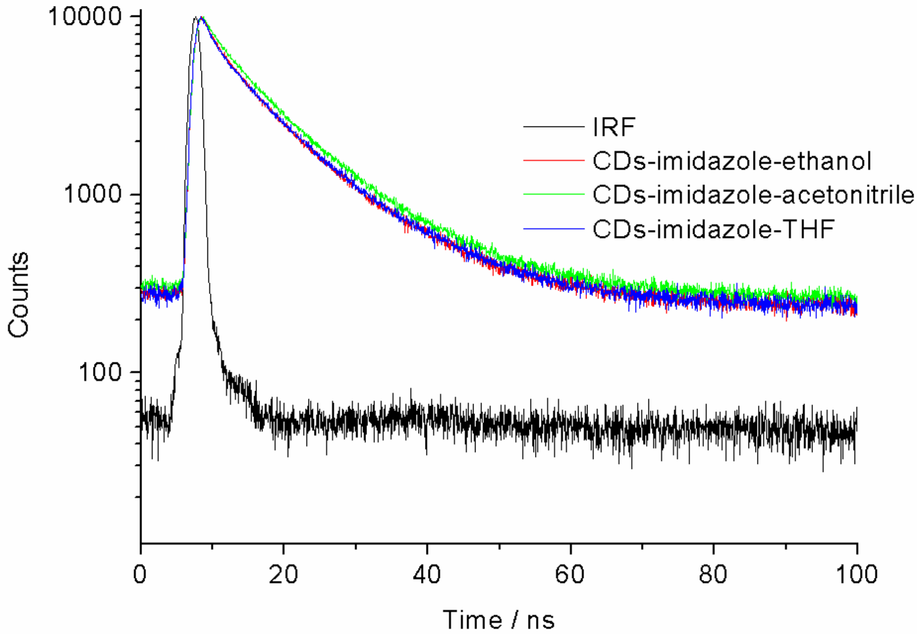


Fig. S14 Fluorescence lifetime decay of CDs-imidazole in different organic solvents.

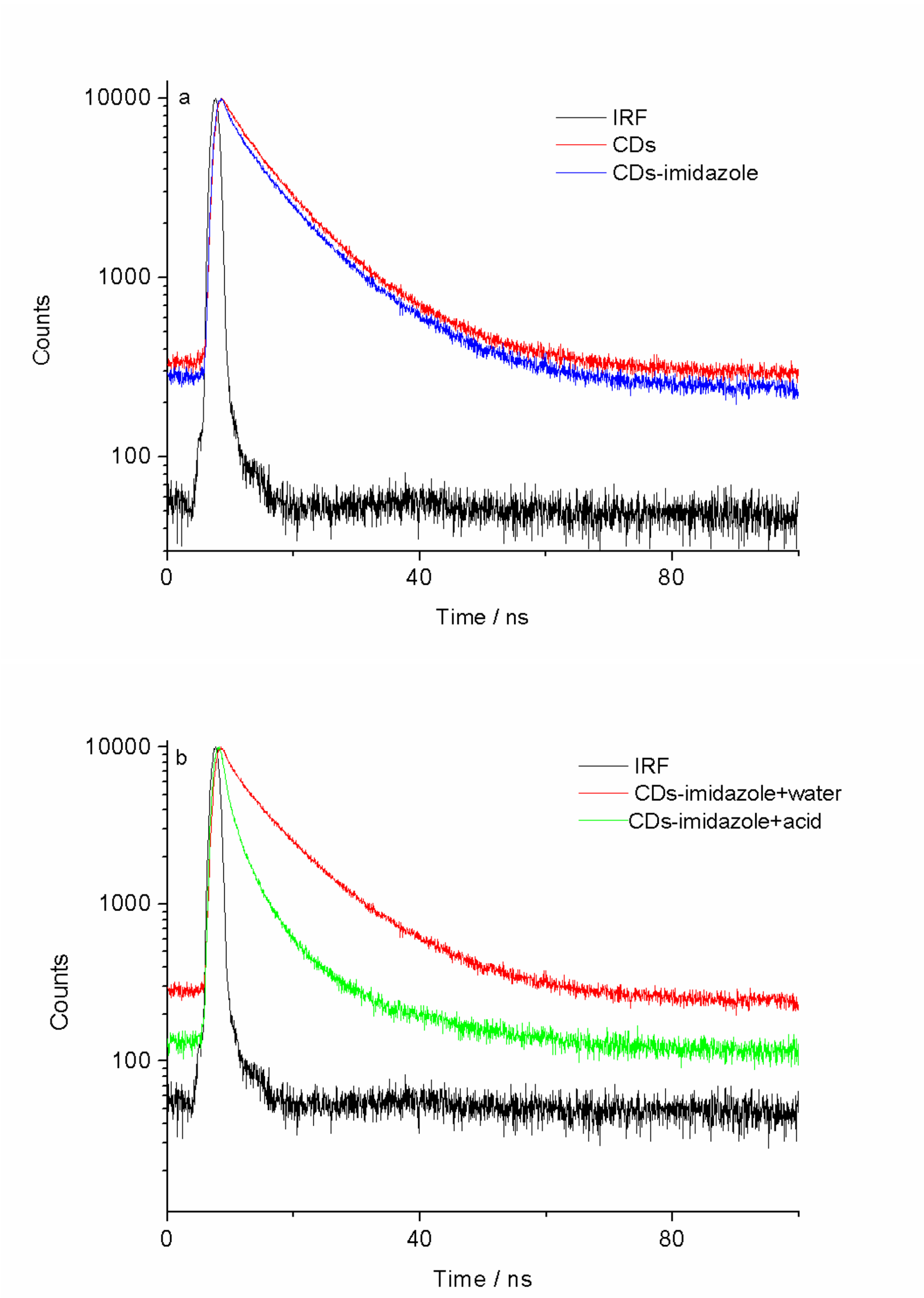


Fig. S15 Fluorescence lifetime decay of (a) CDs in water and CDs-imidazole in water–ethanol media (1:1, v/v) (b) CDs-imidazole in water–ethanol media (1:1, v/v) and CDs-imidazole upon addition 0.9 M *p*TsOH in ethanol collected at 460 nm when excited at 360 nm.

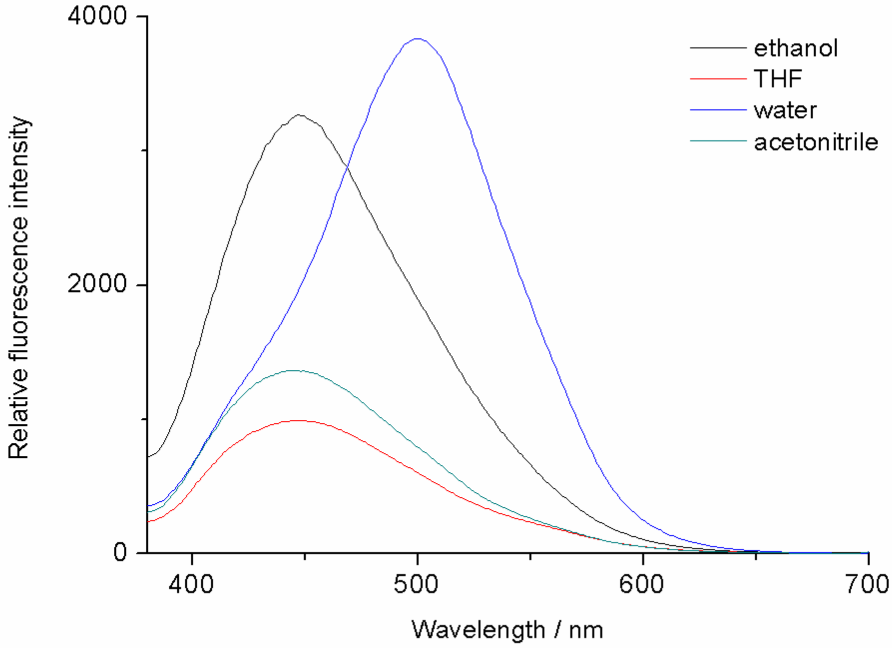


Fig. S16 Fluorescence emission spectra (λ_{ex}=360 nm) of CDs （CD-COOH ） in ethanol, THF, water, acetonitrile.

Table S1 Elemental analysis results of CDs and CDs-imidazole.

samples	N%	C%	H%	O%
CDs	20.79	37.32	4.70	37.19
	20.99	37.23	4.81	36.97
CDs-imidazole	18.26	40.19	4.10	37.46
	18.27	40.05	4.07	37.61

Table S2 Photophysical Properties of CDs and CDs-imidazole. Decay times τ_1, τ_2 and τ_3 and the relative amplitude (%).

Samples	solution	Emission Wavelength /nm	τ_1/ns	τ_2/ns	τ_3/ns
CDs	H_2O	440	1.18(3.13%)	5.46(29.64%)	12.11(67.23%)
		460	1.23(3.07%)	6.01(35.16%)	12.66(61.77%)
		480	1.77(4.63%)	6.26(45.82%)	13.31(49.55%)
	EtOH	440	1.22(3.40%)	6.52(44.56%)	12.06(52.04%)
		460	1.18(2.49%)	7.02(44.20%)	12.69(53.31%)
		480	1.32(1.75%)	7.91(39.13%)	13.20(59.12%)
CDs-imidazole	EtOH+H_2O (V/V,1:1)	440	1.16(8.52%)	5.06(28.81%)	12.11(62.67%)
		460	1.03(5.73%)	5.09(25.77%)	12.01(68.49%)
		480	1.09(3.53%)	5.00(20.73%)	11.78(75.74%)
	MeCN+H_2O (V/V,1:1)	440	0.88(4.41%)	5.17(26.62%)	12.02(68.97%)
		460	1.05(3.91%)	5.51(25.22%)	12.33(70.87%)
		480	1.05(4.43%)	6.12(24.55%)	12.93(71.03%)
	THF+H_2O (V/V,1:1)	440	1.06(7.50%)	6.03(34.60%)	12.50(57.90%)
		460	0.99(6.80%)	5.69(26.82%)	12.38(66.38%)
		480	1.04(4.45%)	6.18(25.26%)	13.00(70.29%)
CDs-imidazole	EtOH+0.9 M *p*TsOH	440	0.74(35.31%)	3.59(43.18%)	14.08(21.51%)
		460	0.83(32.01%)	3.76(45.29%)	14.90(22.70%)
		480	0.99(29.65%)	3.72(46.13%)	14.53(24.21%)

Reference

1 S. N. Baker and G. A. Baker, *Angew. Chem., Int. Ed.,* 2010, **49**, 6726-6744.

2 D. Wang, Y. Guo, W. Liu and W. Qin, *RSC Adv.*, 2014, **4**, 7435-7439.