Electronic Supplementary Information (ESI)

Aggregation-Induced Red Shift in N, S-doped Chiral Carbon Dot Emission for Moisture Sensing

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Quantum Yield Calculation:

Quantum yields (QY) of Cdots in different solvents were calculated using the below mentioned formula with respect to quinine sulphate (QS) in 0.1 M H_2SO_4.[1,2]

$$Q_S = Q_R \times \frac{I_S}{I_R} \times \frac{A_R}{A_S} \times \frac{\eta_S^2}{\eta_R^2}$$

Where Q_S= QY of Cdots; Q_R= QY of reference; I_S= area under PL curve of Cdots; I_R= area under PL curve of QS; A_R= absorbance of the QS; A_S= absorbance of the Cdots; η_S= refractive index of Cdots; η_R= refractive index of QS.

QY of quinine sulphate = 0.54.

(The optical densities of Cdots in different solvents and quinine sulphate were 0.1 ± 0.006 at the excitation wavelength)

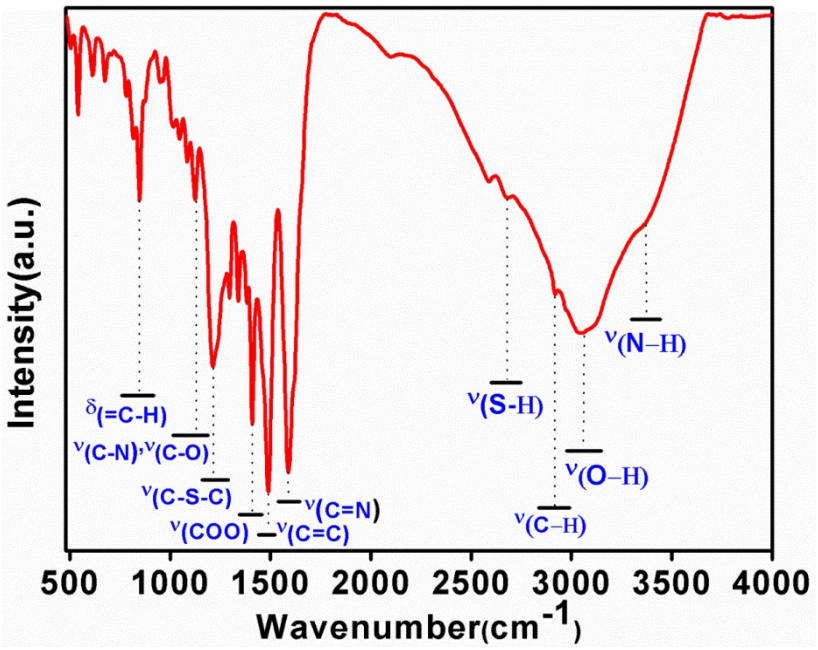

Fig. S1 FT-IR spectrum of Cdots.

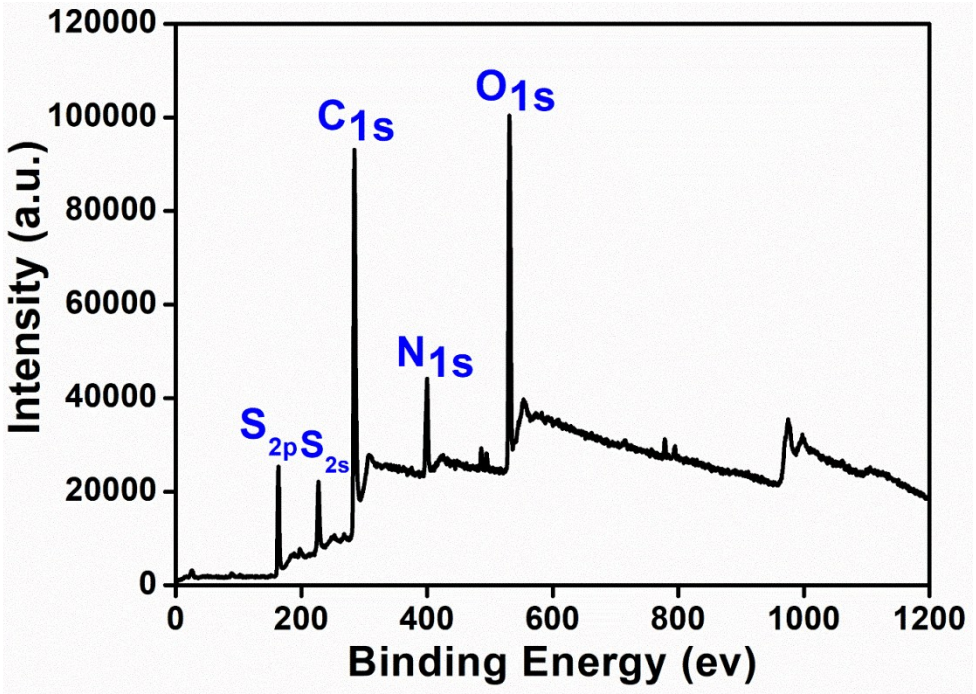

Fig. S2 Full XPS spectrum of Cdots.

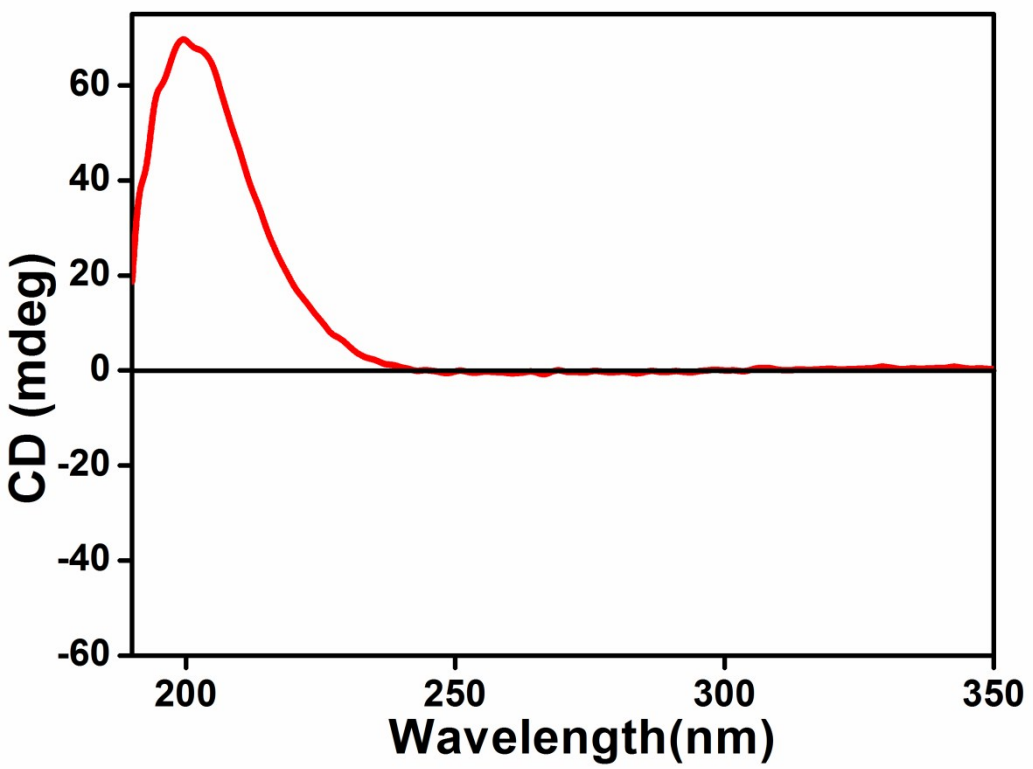

Fig. S3 Circular dichroism spectrum of pure L-Cysteine.

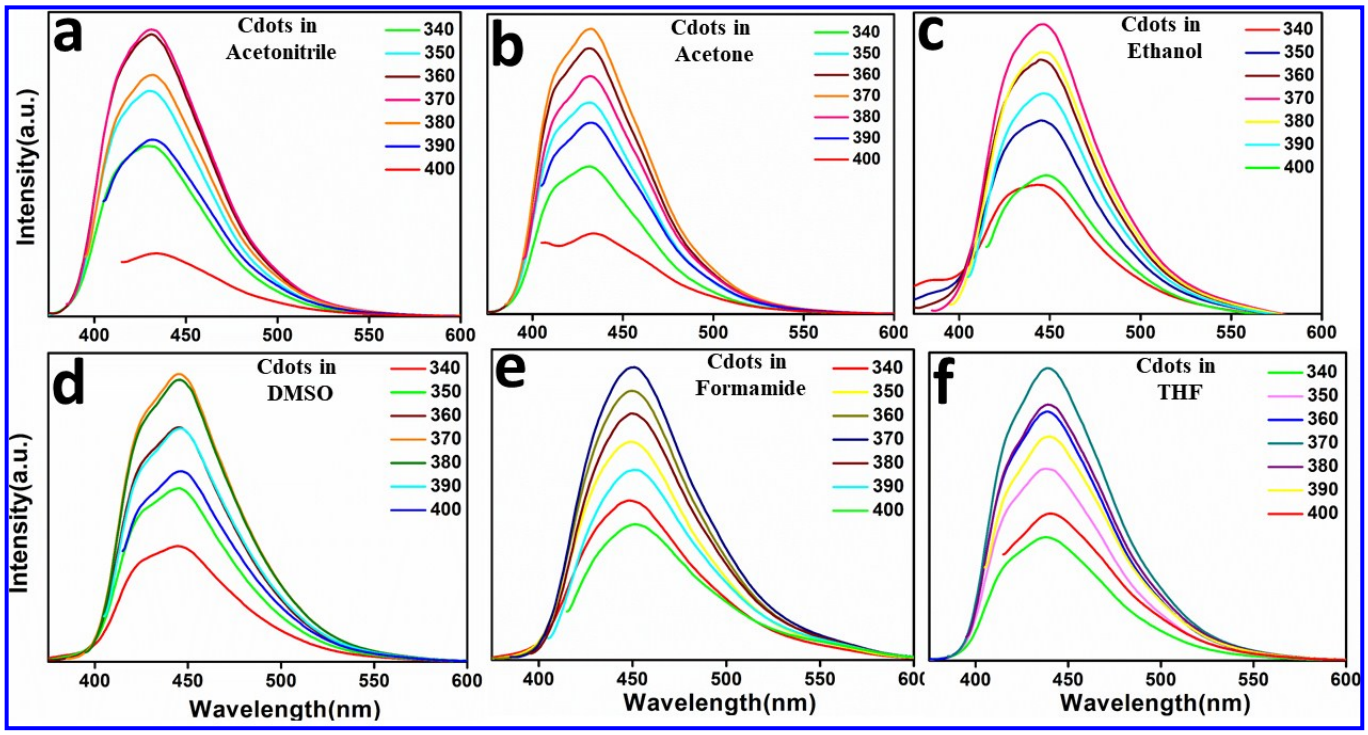

Fig. S4 Photoluminescence spectra (PL) of the Cdots dispersed in (a) acetonitrile, (b) acetone, (c) ethanol, (d) DMSO, (e) formamide, and (f) THF.

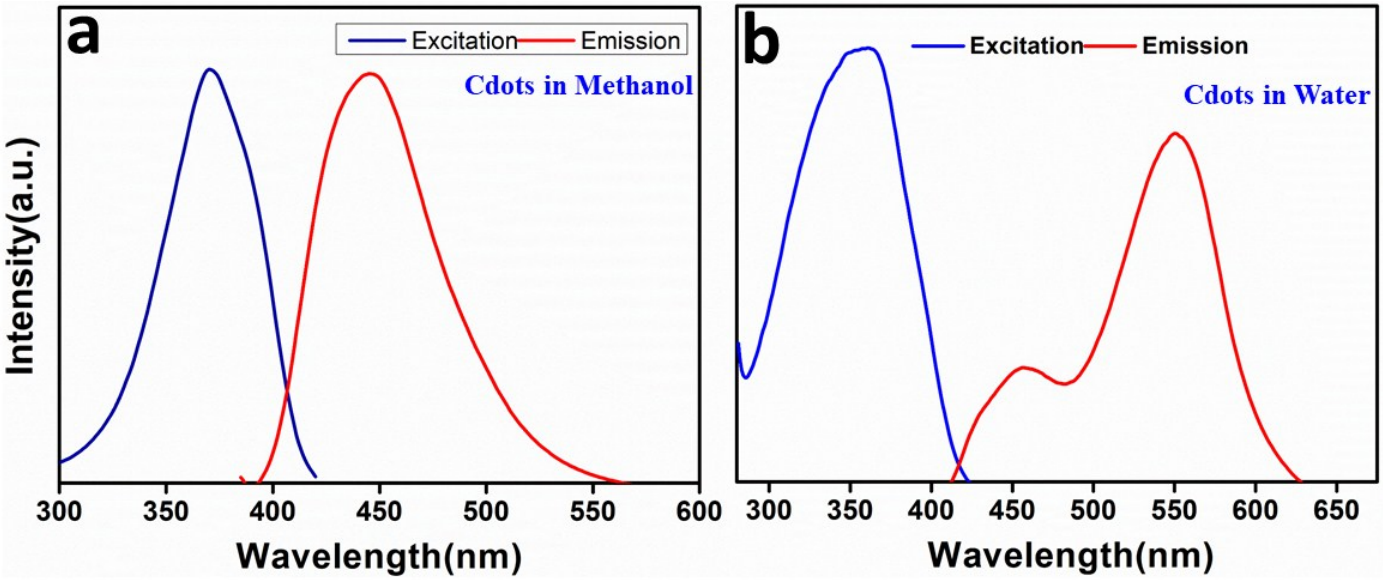

Fig. S5 Excitation spectra of the Cdots dispersed in (a) methanol at an emission wavelength of 443 nm with an absorption maximum at 370 nm, and (b) water at an emission wavelength of 546 nm with an absorption maximum at 358 nm.

Table S1. Quantum yield of Cdots in different solvents.

Cdots medium	Quantum yield (%)
Ethanol	36
Acetone	32
Methanol	23
DMSO	21
THF	20
Formamide	20
Acetonitrile	16
Water	7

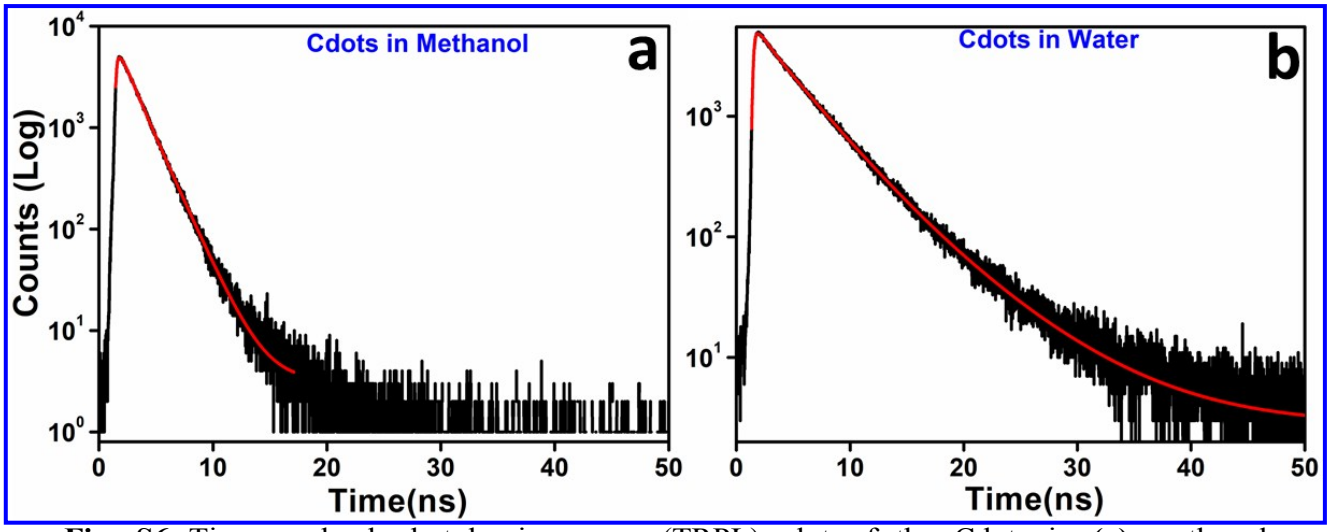

Fig. S6 Time-resolved photoluminescence (TRPL) plot of the Cdots in **(a)** methanol (emission at 443 nm), and **(b)** H_2O (emission at 546 nm). Excited using a 375 nm pulsed diode laser source.

Table S2. Time-resolved photoluminescence (TRPL) and calculated parameters.

Cdots Medium	λ^2	Fraction of the first component (α_1)	First component lifetime (τ_1) (ns)	Fraction of the second component (α_2)	Second component lifetime (τ_2) (ns)	Average lifetime (τ_{av}) (ns)
Methanol	1.139	0.26	0.67	0.74	1.73	1.6
Water	1.161	0.37	1.64	0.63	4.53	4.02

Table S3. Calculated radiative and non-radiative decay rate constants of the Cdots dispersed in water and methanol.

Cdots Medium	Measured quantum yield (QY) (%)	Radiative decay rate constant (K_r) (sec^{-1})	Non radiative decay rate constant (K_{nr}) (sec^{-1})
Cdots in Water	7 (emission at 546 nm)	17.41×10^6	23.13×10^7
Cdots in Methanol	23 (emission at 443 nm)	14.37×10^7	48.12×10^7

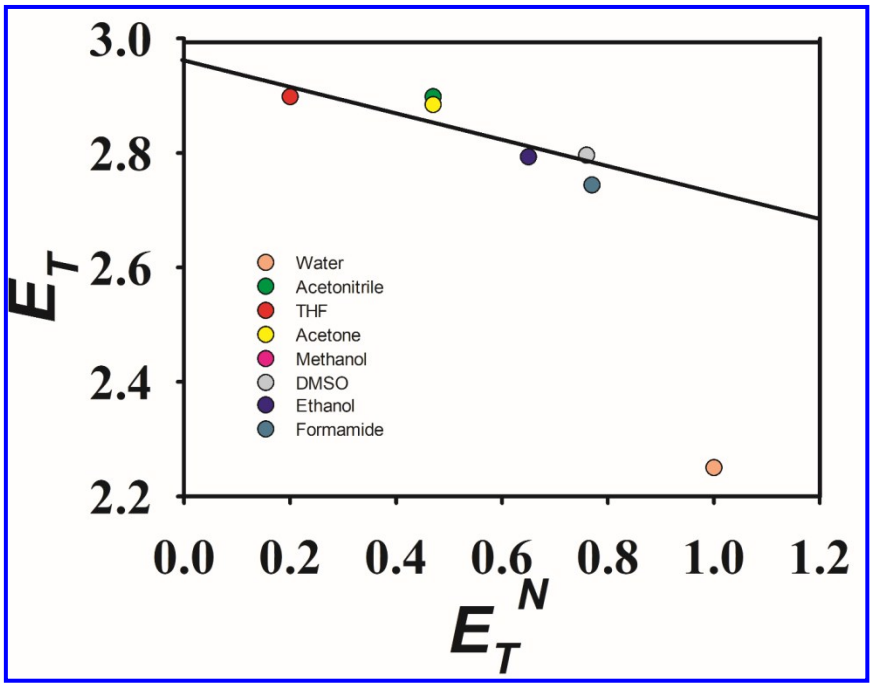

Fig. S7 Plot of emission maxima E_T against E_T^N.

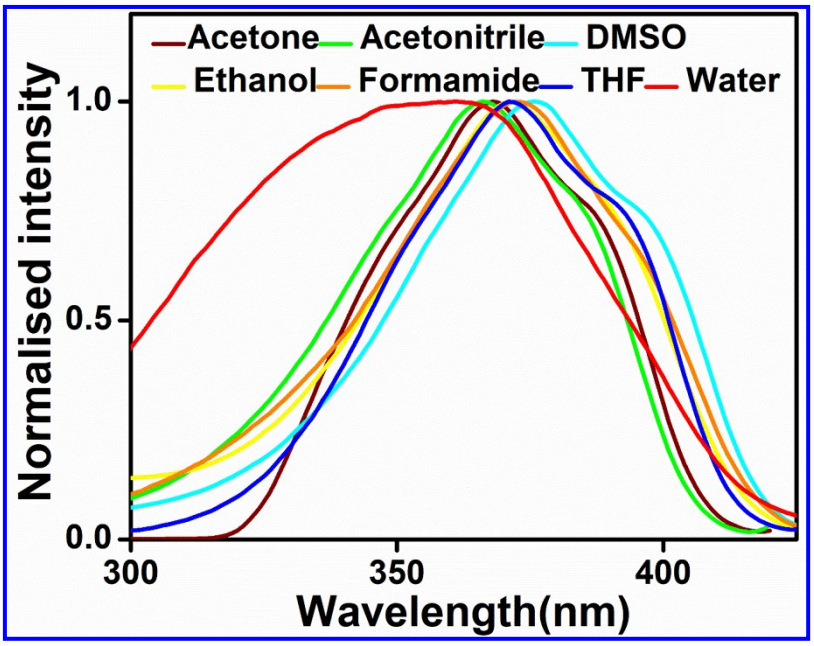

Fig. S8 Normalized excitation spectra of Cdots in different solvents corresponding to their emission wavelength.

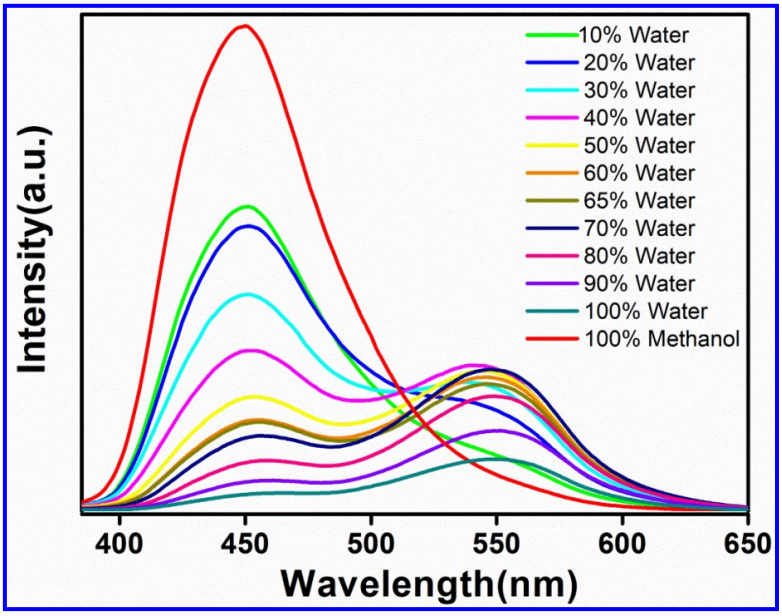

Fig. S9 PL spectra of Cdots in methanol with water (0-100%) at an excitation wavelength of 360 nm.

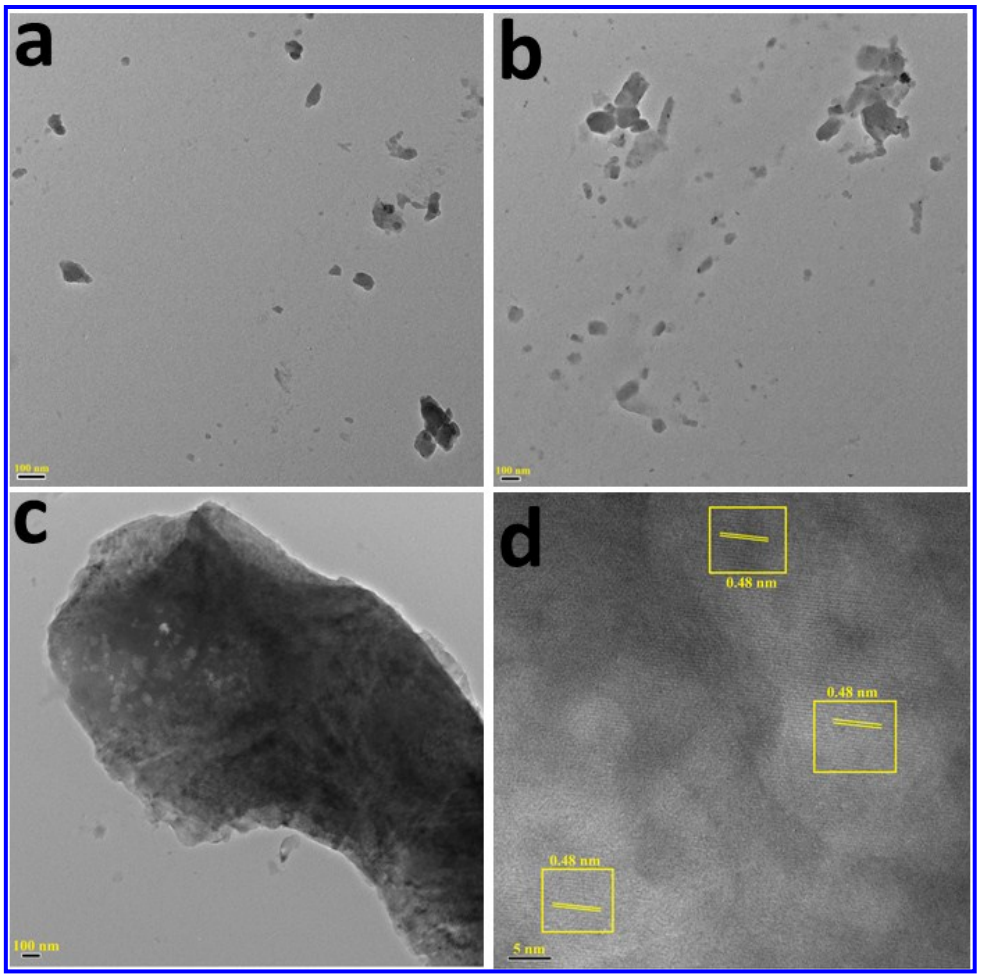

Fig. S10 (a-c) Representative additional TEM images of aggregated Cdots in the aqueous medium of 25% acetonitrile. (d) HRTEM Analysis of image c.

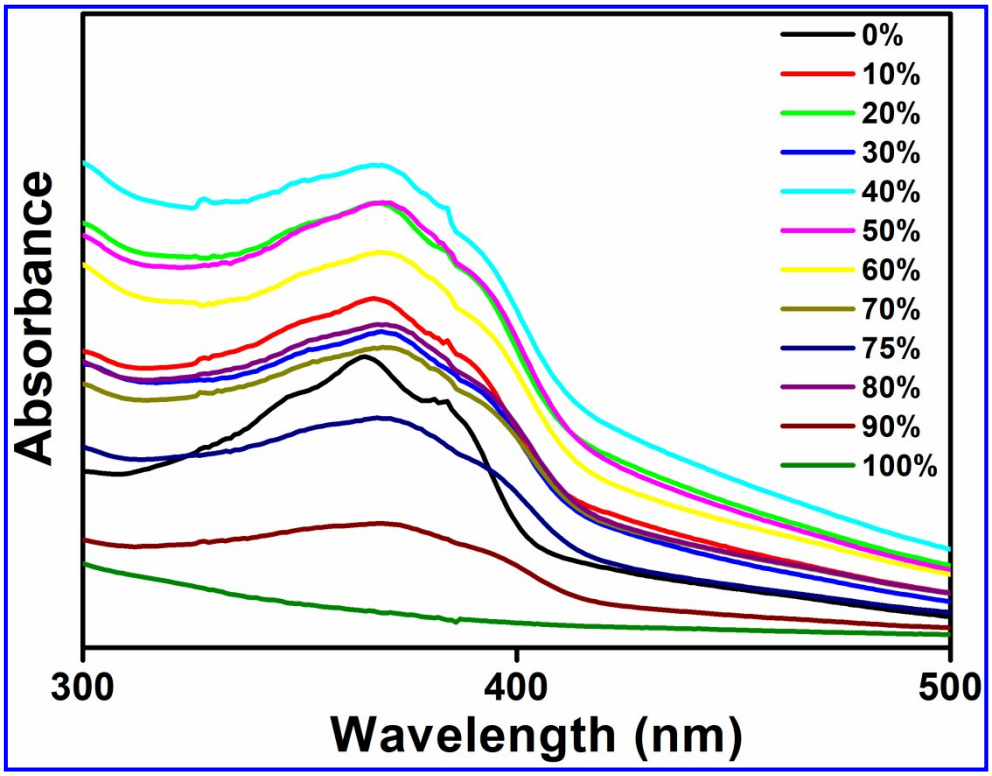

Fig. S11 UV-Vis absorption spectra of the Cdots dispersed in acetonitrile with different ratios of water.

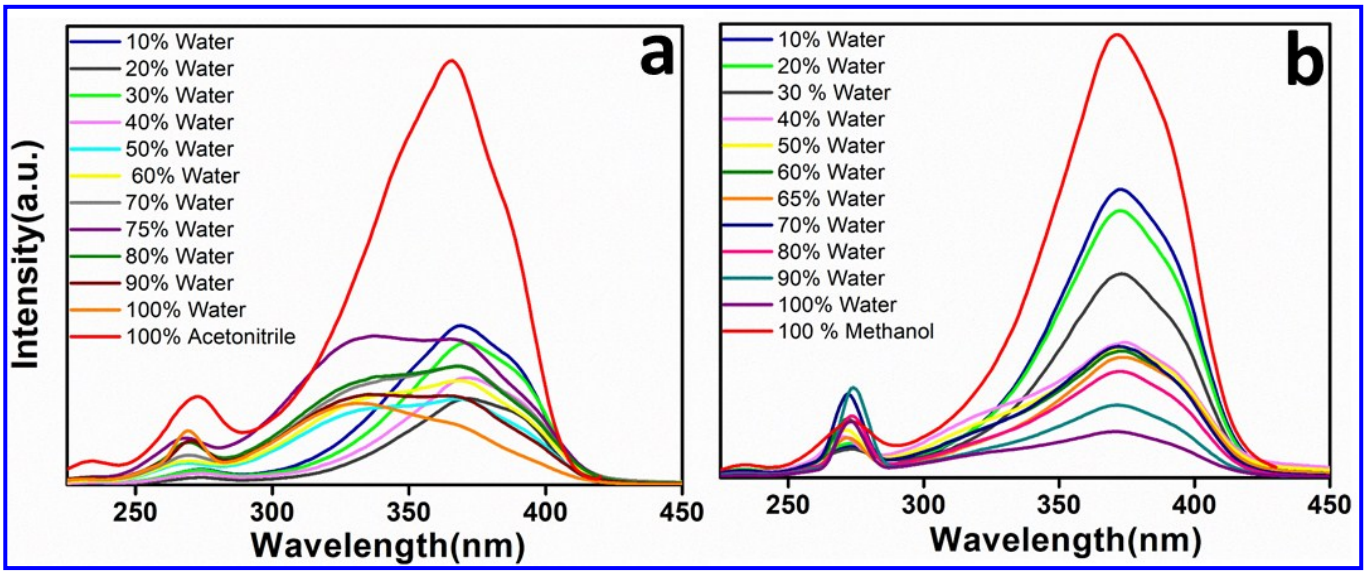

Fig. S12 Excitation spectra of Cdots in **(a)** acetonitrile and **(b)** methanol, with water (0-100%) corresponding to the 550nm emission wavelength.

Table S4. Tabulated Form of Chromaticity Color Coordinates (x, y).

S.N	Water Fraction in Acetonitrile	(x, y)	Water Fraction in Methanol	(x, y)
1	0%	(0.15, 0.06)	0%	(0.15, 0.11)
2	10%	(0.15, 0.10)	10%	(0.17, 0.15)
3	20%	(0.17, 0.15)	20%	(0.19, 0.21)
4	30%	(0.18, 0.19)	30%	(0.21, 0.26)
5	40%	(0.20, 0.25)	40%	(0.23, 0.32)
6	50%	(0.22, 0.30)	50%	(0.24, 0.36)
7	60%	(0.24, 0.36)	60%	(0.26, 0.39)
8	65%	(0.26,0.42)	65%	(0.26, 0.39)
9	70%	(0.26, 0.44)	70%	(0.27, 0.42)
10	80%	(0.27, 0.45)	80%	(0.28, 0.45)
11	90%	(0.28, 0.49)	90%	(0.29, 0.46)
12	100%	(0.28, 0.50)	100%	(0.29, 0.48)

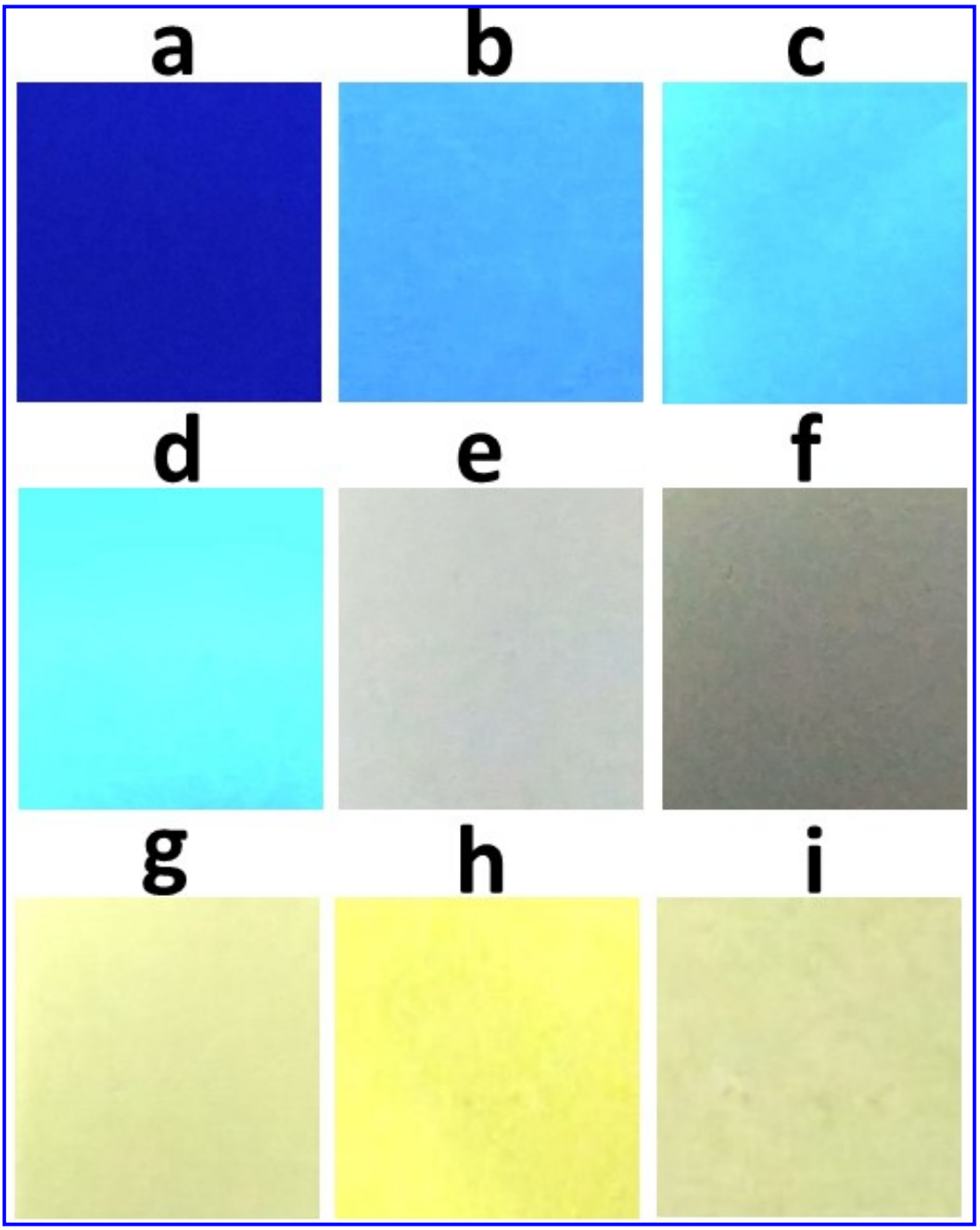

Fig. S13 Sample colour of Cdots in acetonitrile with **(a)** 0% water, **(b)** 10% water, **(c)** 20% water, **(d)** 30% water, **(e)** 40% water, **(f)** 50% water, **(g)** 60% water, **(h)** 75% water and **(i)** 100% water (Pure). All these fluorescence images were captured using a smartphone at 90^0 angles to the Cdots solution under the UV light of excitation of 365 nm.

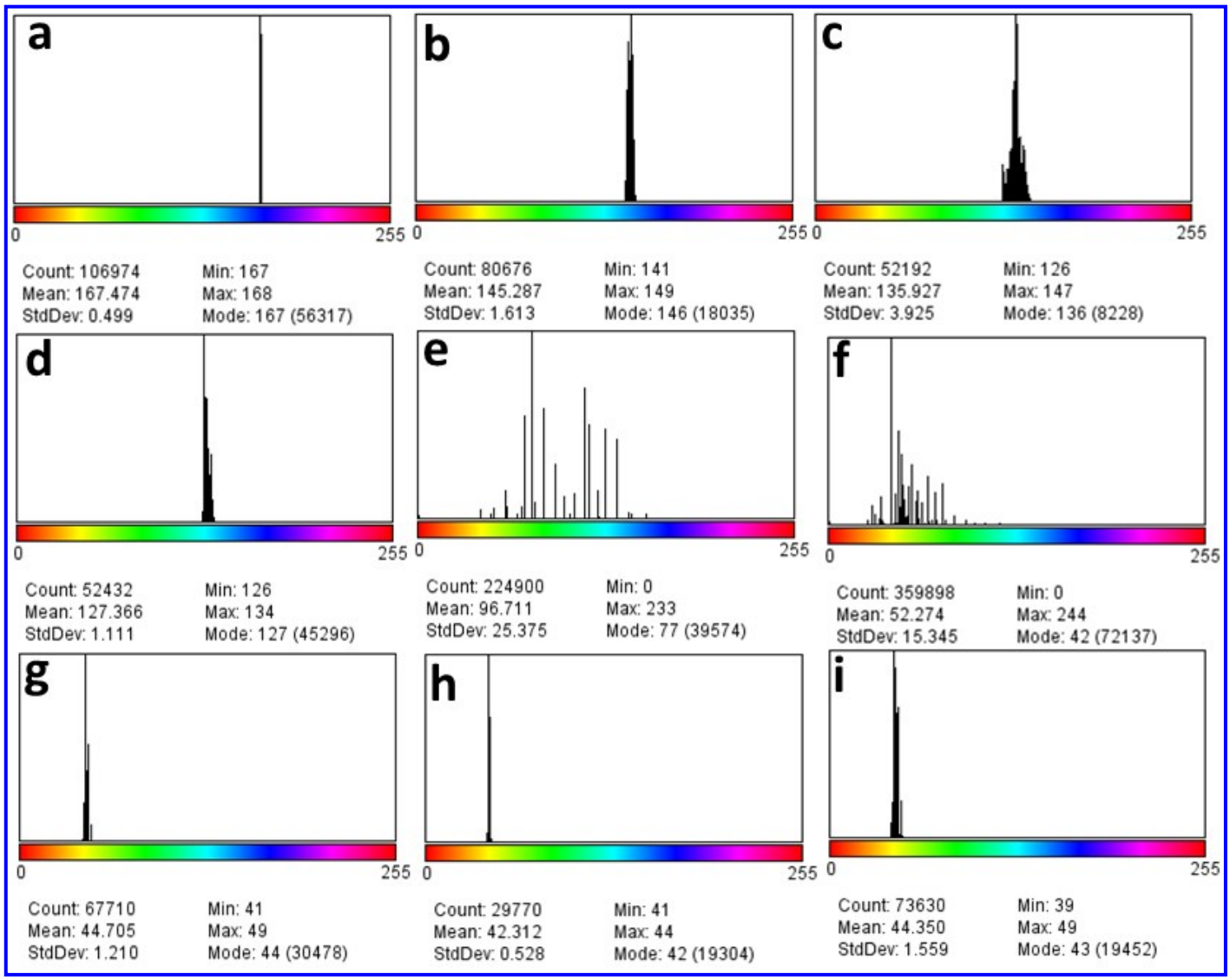

Fig. S14 Hue spectrum/histograms of Cdots in acetonitrile with **(a)** 0% water (hue value-167.47), **(b)** 10% water (hue value-145.28), **(c)** 20% water (hue value-135.92), **(d)** 30% water (hue value-127.36), **(e)** 40% water (hue value-96.71), **(f)** 50% water (hue value-52.27), **(g)** 60% water (hue value- 44.70), **(h)** 75% water (hue value- 42.31) and **(i)** 100% pure water (hue value-44.35). The hue parameter/histograms of Cdots were calculated using image-J software.

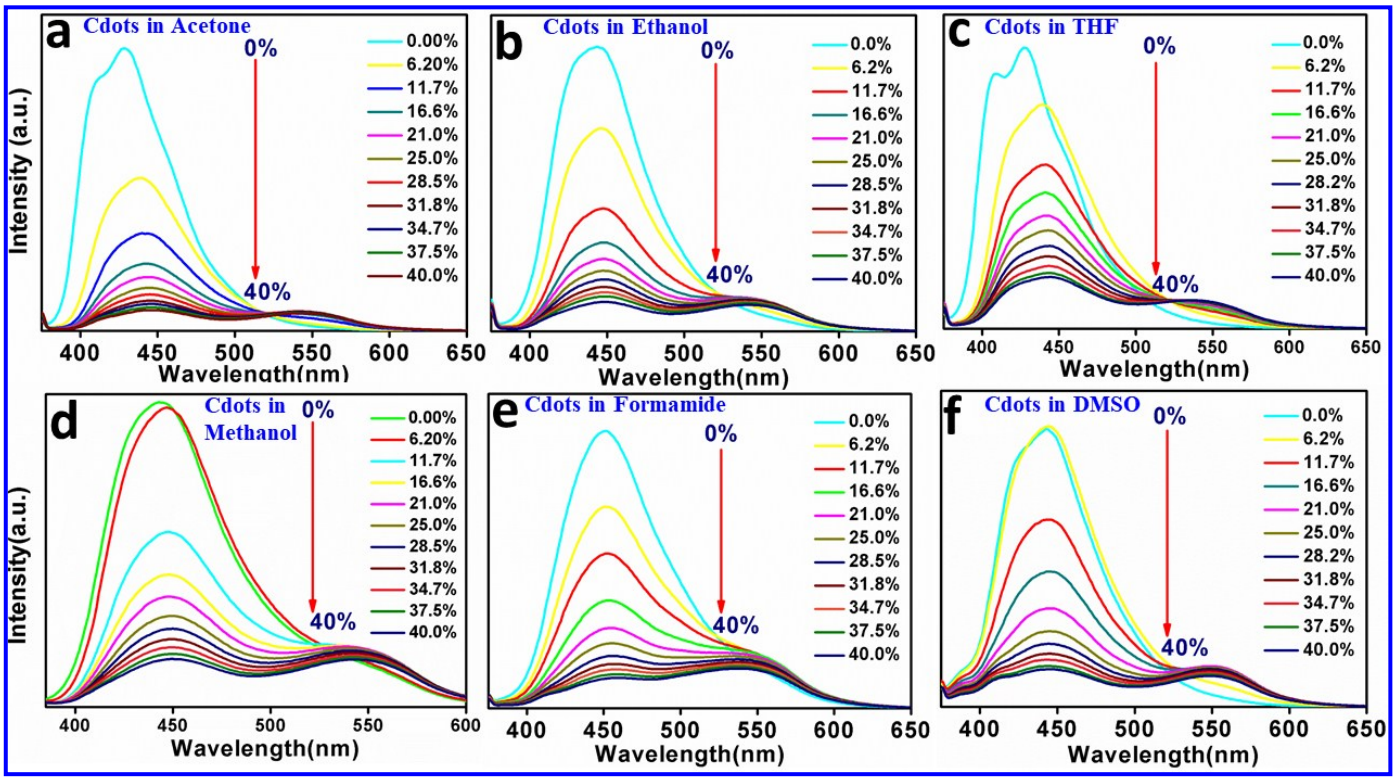

Fig. S15 PL response of the Cdots dispersed in (a) acetone, (b) ethanol, (c) THF, (d) methanol, (e) formamide, and (f) DMSO, with increasing water content (0-40%) at an excitation wavelength of 360nm.

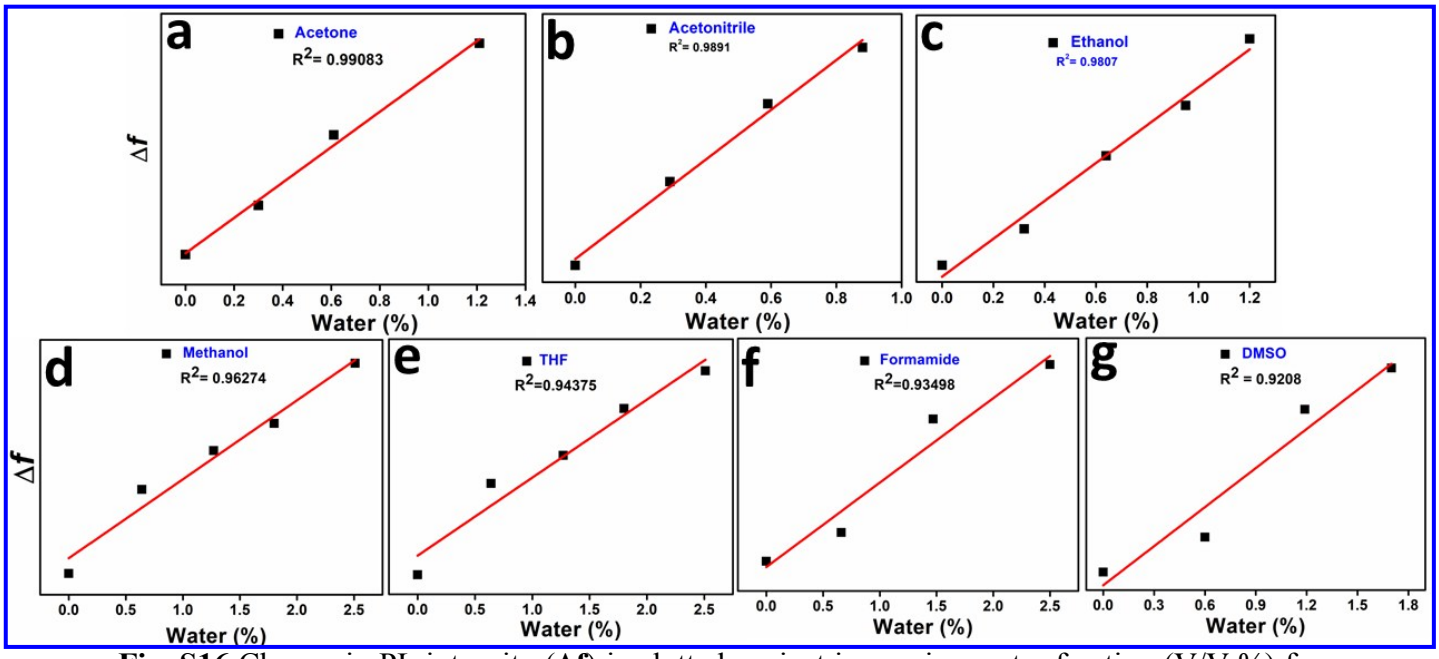

Fig. S16 Change in PL intensity (**Δf**) is plotted against increasing water fraction (V/V %) for all the solvents (a) acetone, (b) acetonitrile, (c) ethanol, (d) methanol, (e) THF, (f) formamide, and (g) DMSO. In the particular case of methanol and DMSO, **Δf** (or calibration) plots are achieved after spiking of 6 % (V/V) water.

Table S5. Slope of calibration plot and limit of detection (LOD) of Cdots dispersed in different solvents

S No	Cdots in Solvent	Slope	LOD (ppm)	LOD (V/V %)	LOD (wt%)
1	Acetone	2937.20	8.47±0.370	0.000847±0.000037	0.00107±0.00004
2	Acetonitrile	742.24	33.57±0.371	0.003357±0.0000371	0.00427±0.00004
3	Ethanol	1136.90	95.03±1.610	0.009503±0.000161	0.01204±0.00020
4	THF	397.21	230.35±1.527	0.023035±0.0001527	0.02591±0.00017
5	Methanol	371.85	231.72±1.436	0.023172±0.0001436	0.02925±0.00018
6	DMSO	361.65	247.69±1.490	0.024769±0.000149	0.02251±0.00013
7	Formamide	568.25	253.44±2.375	0.025344±0.0002375	0.02242±0.00021

Table S6. Previously reported limit of detection (LOD) for the detection of water content using various probes.

SN	Type of Sensor	Sensing Mechanism	LOD	Reference
1	Fluorescent	Excited state intramolecular proton transfer (ESIPT)	<0.05% (v/v)	Chen et al. *Nature Communications* 2017, 8, 15985.
2	Fluorescent	Chemodosimeter	0.18 V/V %	Kim et al. *Chem. Commun.,* 2016,52, 8675-8678
3	Fluorescence	Aggregation induced emission (AIE) and electron donation	11 ppm	Chen et al. *Mater. Chem. Front.,* 2017, 1, 1841-1846.
4	Fluorescence	Intra molecular charge transfer	0.0022% (25 ppm) & 0.0032% (36 ppm)	Ding et al. *Chem.Commun.,* 2013,49, 7319-7321.
5	Colorimetric	Protonation of 1F. and 2F.	0.0042% & 0.0058 wt %.	Kumar et al. *ACS Appl. Mater.Interfaces* 2017, 9, 30, 25600-25605.
6	Fluorescent	Twisted Intra Molecular Charge Transfer (TICT)	0.003 wt %	Kumar et al. *Anal. Chem.* 2016,88,23,11314-11318
7	Colorimetric and ratiometric fluorescent sensor	Intra molecular charge transfer	0.25 wt %	Enoki et. al. *Dalton Trans.,* 2019, 48, 2086-2092.
8	Fluorescent	Fluorescence quenching	0.04%	Xua et al. *J. Mater. Chem. C,* 2016,4, 9651-9655.

9	Fluorescence	Dynamic Quenching	0.01(V/V) %	Wei et al. *New J. Chem.,* 2018,42, 18787-18793.
10	Fluorescence		0.014 wt %	Song et al. *Dyes and Pigments* 2019, 162, 160-167.
11	Fluorescence	fluorescent donor-acceptor	0.001% (v/v) or 14 mg/L (20 ppm)	Citterio et al *Anal. Chem.* 2001, 73, 21, 5339-5345.
12	Graphene flexibility	flexible humidity sensors	< 12% RH	Hosseini et al. *J. Mater. Chem. C*, 2017, 5, 8966-8973.
13	Fluorescence	Solvatochromism	0.019%	Niu et al. *Analytical sciences* 2010, 26 (6), 671-674.
14	Fluorescent	Chemodosimeter	22 ppm	Men et al. Analyst, 2013,138, 2847-2857
15	Fluorescence	Photoinduced electron transfer	0.28% (0-5%, v/v) and 0.1% (5-20%, v/v)	Wang et al. *Dalton Trans.* 2015, 44 (12), 5547-54.
16	Colorimetric	Aggregation	0.33% (DMF) and 0.25% (Cyclopropane)	Wu et al. *Dalton Trans.* 2017, 46, 7098-7105.

Determination of Water Content in Commercial Samples

The commercially available raw sample was dried in an incubator at 60 ^{0}C for 24 hours before performing the calibration plot experiment. The calibration plots were obtained after spiking 50 µl water with dried commercially available samples and then we added small aliquots of water to it for recording emission of Cdots. For the determination of the moisture in the commercial samples (manufacture date less than a month), emission of Cdots (at the excitation 360 nm) was recorded without samples ($\mathbf{I_0}$) and with samples (**I**). The $\mathbf{I_0/I}$ values are marked on the corresponding calibration curve of aspirin, salt and sugar. Acetone solvent was used in all the experiments of calibration plot.

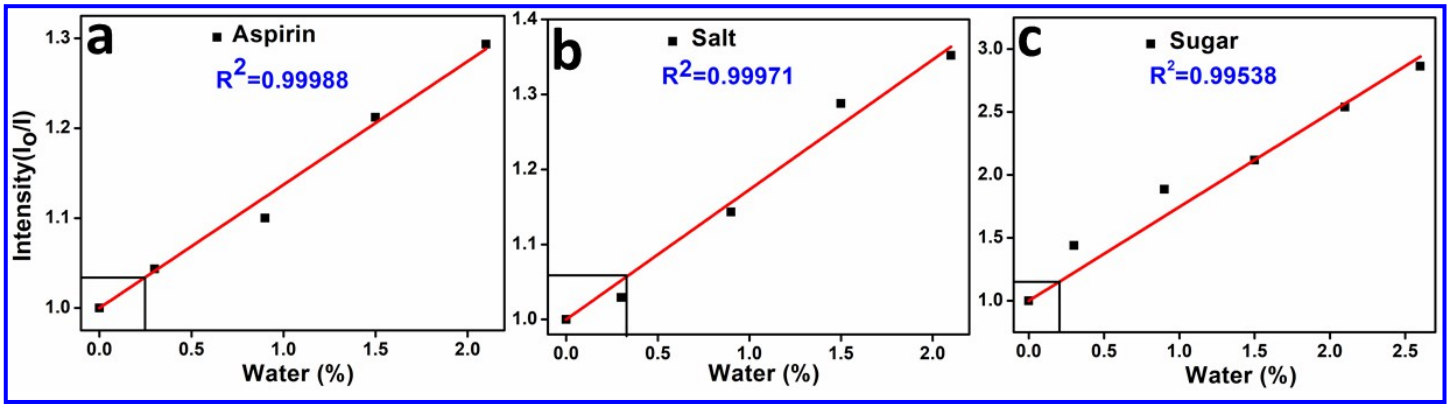

Fig. S17 Calibration plot (V/V %) for the commercially available raw samples such as (a) Aspirin, (b) Salt and, (c) Sugar.

Table S7. Moisture content of apirin, salt and sugar, calulated from their calibration plot.

SN	Samples	Water content (V/V %)	Water content in samples (weight %)
1	Aspirin	0.248 %	1.49 %
2	Salt	0.320 %	1.92 %
3	Sugar	0.201 %	1.21%

References:

(1) J. E. Murphy, M. C. Beard, A. G. Norman, S. P. Ahrenkiel, J. C. Johnson, P. Yu, O. I. Micic, R. J. Ellingson and A. J. Nozik, *J. Am. Chem. Soc*. 2006, **128,** 3241.

(2) M. P. Sk, A. Chattopadhyay, *RSC Adv.* 2014, **4**, 31994-31999.