Electronic Supplementary Information

Zn^{2+}/Cd^{2+}-RNA-mediated intense white-light-emitting colloidal CdSe nanostructures in aqueous medium – enhanced photophysics and porous morphology induced by conformational change in RNA

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EXPERIMENTAL SECTION

Reagents

Ribonucleic acid derived from Torula yeast type VI, cadmium perchlorate, Se powder, fluorescein dye and rhodamine B dye (Sigma); sodium borohydride, zinc acetate, lead acetate (Merck); sodium hydroxide (BDH); perchloric acid (Qualigens); nitrogen gas (Grade 1, purity >99.99%), (Sigma, India); cobalt acetate, nickel acetate, copper acetate (Thomas Baker); manganese acetate (HiMedia). The RNA used was a heterogeneous mixture of varied molecular weight(s) and length(s) without any specific sequence.

Equipment

Optical absorption and steady state fluorescence measurements were carried out on Shimadzu UV2100S and FluoroMax-4 spectrofluorophotometer respectively. X-ray photoelectron spectroscopy was carried out on a PHI 5000 Versa Probe III supplied by ULVAC-PHI Inc., Japan equipped with a monochromatic Al Kα radiation source. X-Ray diffraction patterns were recorded on a Bruker AXS D8 Avance X-ray diffractometer (XRD) using the Cu-Kα line (1.5418 A˚) of the X-ray source. Transmission electron micrographs (TEM), high resolution transmission electron

micrographs (HRTEM) and selected area electron diffraction (SAED) measurements were performed on a FEI-Tecnai G2 20 STWIN equipped with a CCD camera. Morphological analysis was carried out by a QUANTA 200-FEG field emission scanning electron microscopes (FE-SEM). The surface morphology was analysed by recording the 2D and 3D images on an atomic force microscope (NTEGRE (NT-MDT)) equipped with NOVA software in semi-contact mode. Infrared (IR) spectra in the mid IR range (4000–400 cm^{-1}) were recorded with a spectral resolution of 1 cm^{-1} on a Thermo Nicolet Nexus Fourier Transform Infrared (FTIR) spectrophotometer in KBr medium. The ^{1}H and ^{31}P NMR were recorded on a Bruker Avance (500 MHz) and JEOL 400 MHz NMR (Model ECX 400 II) spectrometers, respectively. Circular dichroism (CD) spectra were recorded on a Chirascan spectropolarimeter supplied by M/s Applied Photophysics in 200 to 380 nm wavelength region in a 500μL cuvette. Current–voltage (I–V) measurements in the light and dark conditions were recorded by I-V – tracer auxiliary unit from Keithley equipped with a Keithley 2400 source meter at room temperature and solar simulator Model # CT50AAA from Photo Emission Tech. Inc., USA using the four probe method. Steady state anisotropic measurements were made on Edinburgh FLS-980 spectrometer equipped with a 450W continuous xenon arc lamp source and excitation and emission polarizers. Fluorescence lifetimes, time resolved emission spectra (TRES), and time resolved anisotropy in ns and μs time domains were analyzed by Horiba JobinYvon "FluoroCube Fluorescence Lifetime System" equipped with NanoLEDs and LDs as excitation source and automated polarization accessory. Zeta potential measurements were performed on a Malvern Zetasizer Nano ZS90 equipped with a He-Ne laser as the light source.

Fluorescence images were captured on a Nikon Eclipse LV100 microscope attached with UV-2A (Ex-330–380), B-2A (Ex-450–490) and G-2A (Ex-510–590) Filters.

Methodology

The as prepared colloidal sample(s) were used for the measurements of absorbance, steady-state fluorescence, fluorescence lifetime, CD, anisotropy, and zeta potential. For X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and infrared (IR) measurements solid material from the as-prepared colloidal solution were obtained by removing water on a rotary-evaporator supplied by IKA at 40°C, Samples for atomic force microscope (AFM) and FESEM were prepared by applying a small drop of the three times diluted as prepared sample on a glass plate, which was then dried in dark at

room temperature in a desiccator. AFM images were recorded in a semi-contact mode by varying the scanning frequency in the range of 1.5 to 3.13 Hz at room temperature. The FE-SEM images were recorded by applying an acceleration voltage of 15 kV. Samples for TEM analysis were prepared by applying a drop of the diluted colloidal sample on a carbon-coated copper grid G-200 (size 3.05 mm). The excess solution was removed with the help of a tissue paper. The coated grid was dried in dark at room temperature. The dried grid was scanned at different magnifications under the electron microscope at an accelerating voltage of 300 kV. Selected area electron diffraction (SAED) patterns of these colloidal samples were recorded to analyse the structure of inorganic core. Indexing of electron diffraction pattern was carried out using a ratio method, and Miller indices were then assigned corresponding to different rings.

Quantum yield (QY) of fluorescence has been measured by reference method using Fluorescein dye ($\phi_{fl} = 0.90$) as a reference as well as by absolute method using integrated sphere. The chromaticity diagram was plotted using Origin 2019 software. For NMR and I-V measurements the concentrated solution of these colloidal sample was employed. For NMR experiments, the deuterated sample was prepared in H_2O and D_2O media in the ratio of 9: 1. The ^{1}H and ^{31}P NMR spectra were analyzed by JEOL delta v 5.0.5 software. For I-V measurement(s), a drop of concentrated colloidal sample was applied on a transparent conducting indium titanium oxide (ITO) substrate which was dried overnight in desiccator at room temperature to form a thin film prior to measurements.

The surface area of different samples were measured by the adsorption studies using Rhodamine B dye as an adsorbate. For the calculation, the following equation was used:

$$S = \frac{q_m \times N \times A}{M}$$

Where S denotes the specific surface area, q_m - the maximum monolayer coverage in g/g adsorbent (adsorption capacity), A - the surface area of the dye molecule and M - the molecular weight of dye. The surface area of dye molecule was calculated by knowing the radius of dye using the following equation

$$r = \frac{kT}{6\,\pi\,\eta D}$$

Where k is Boltzmann constant (1.38×10^{-23} J K^{-1}), T is temperature in Kelvin, Ƞ is the viscosity of the medium and D is the diffusion constant of RhB. Surface area of RhB has been calculated from its diffusion constant (4.5×10^{6} cm^2 s^{-1}) and is found to be 2.79×10^{-18} m^2.

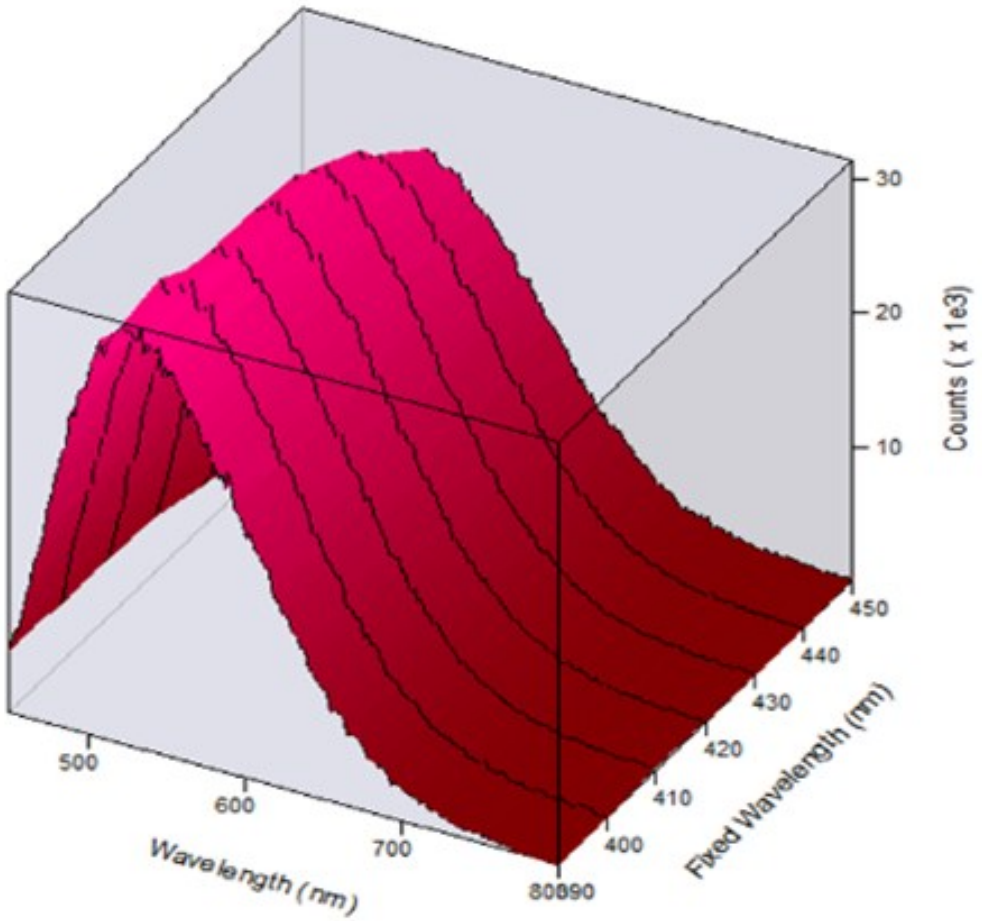


Fig. S1 3D excitation- emission spectra of ZnCS.

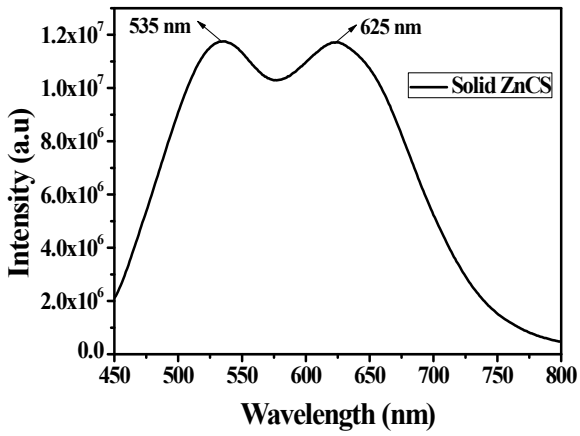


Fig. S2 Emission spectra for solid sample of ZnCS

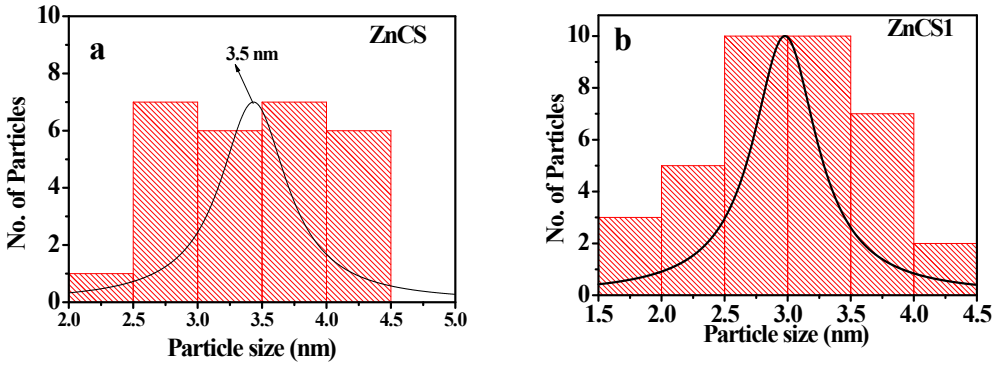


Fig. S3 Size histograms for average diameter of ZnCS (a), ZnCS1 (b).

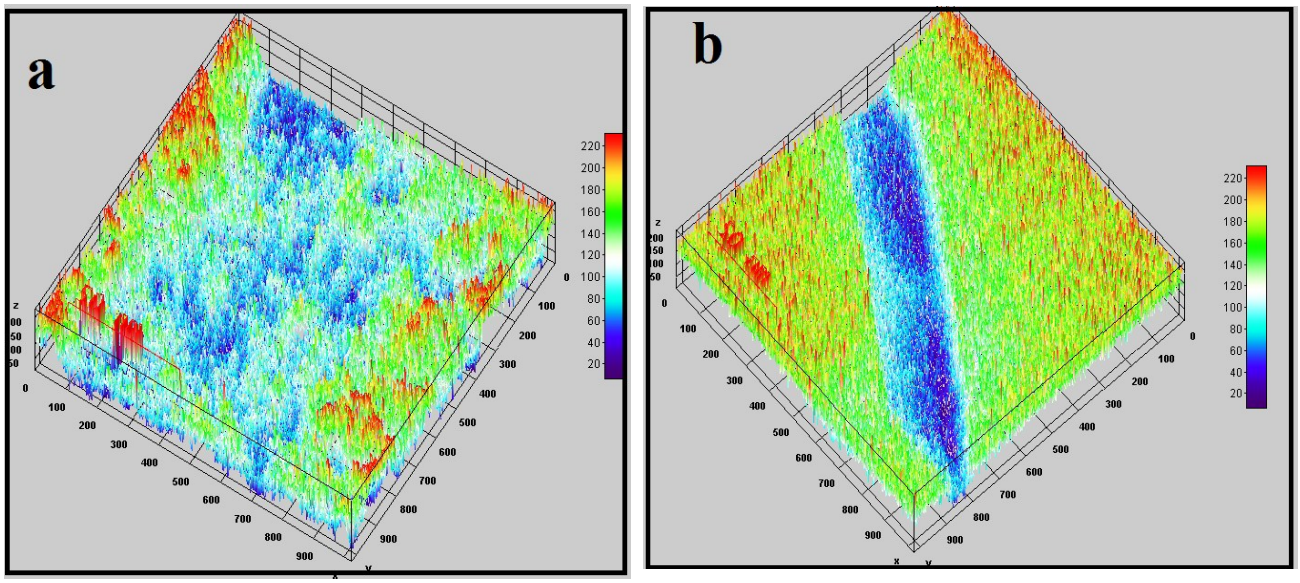


Fig. S4 3D surface recorded from TEM image of ZnCS1 (a) and ZnCS2 (b).

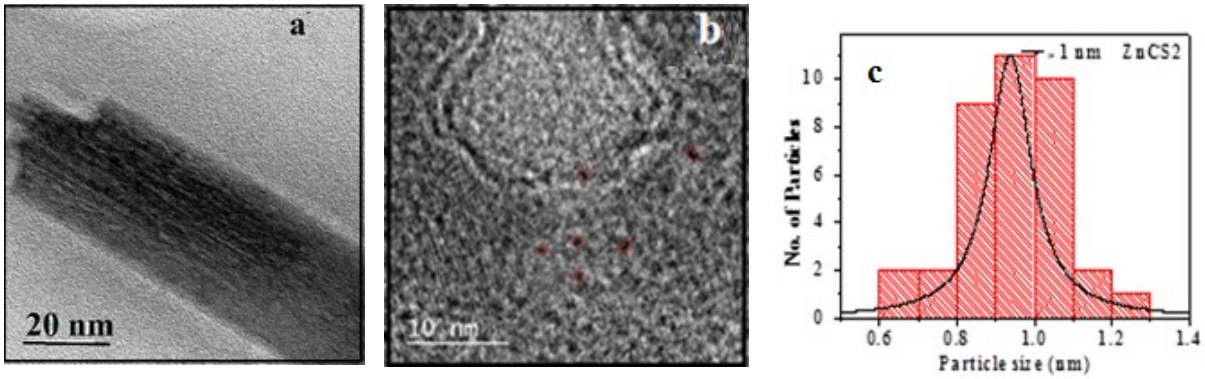


Fig. S5 TEM image of ZnCS2 at another locations (a and b) and size histogram of ZnCS2 (c).

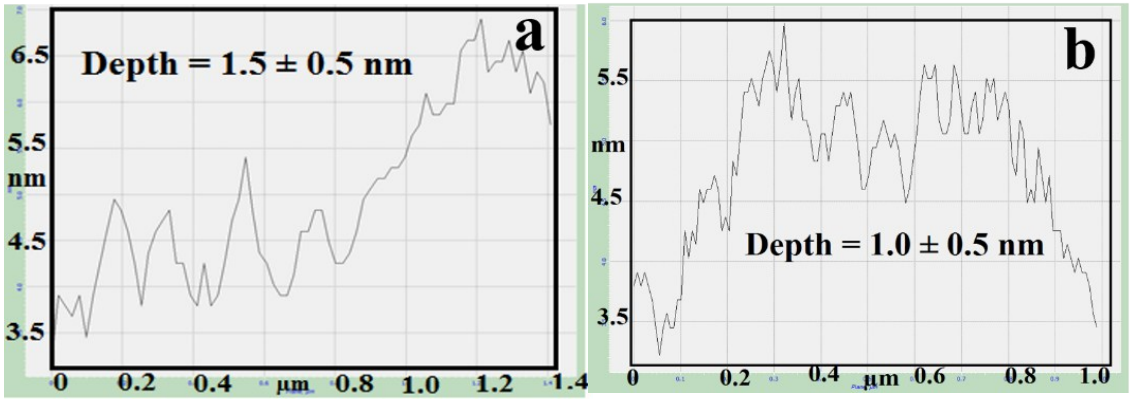


Fig. S6 Depth profile for ZnCS1 (a) and ZnCS2 (b).

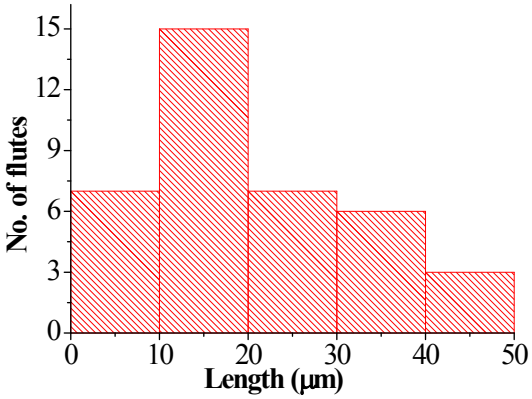


Fig. S7 Size histogram of flute-like morphology from different other FESEM images.

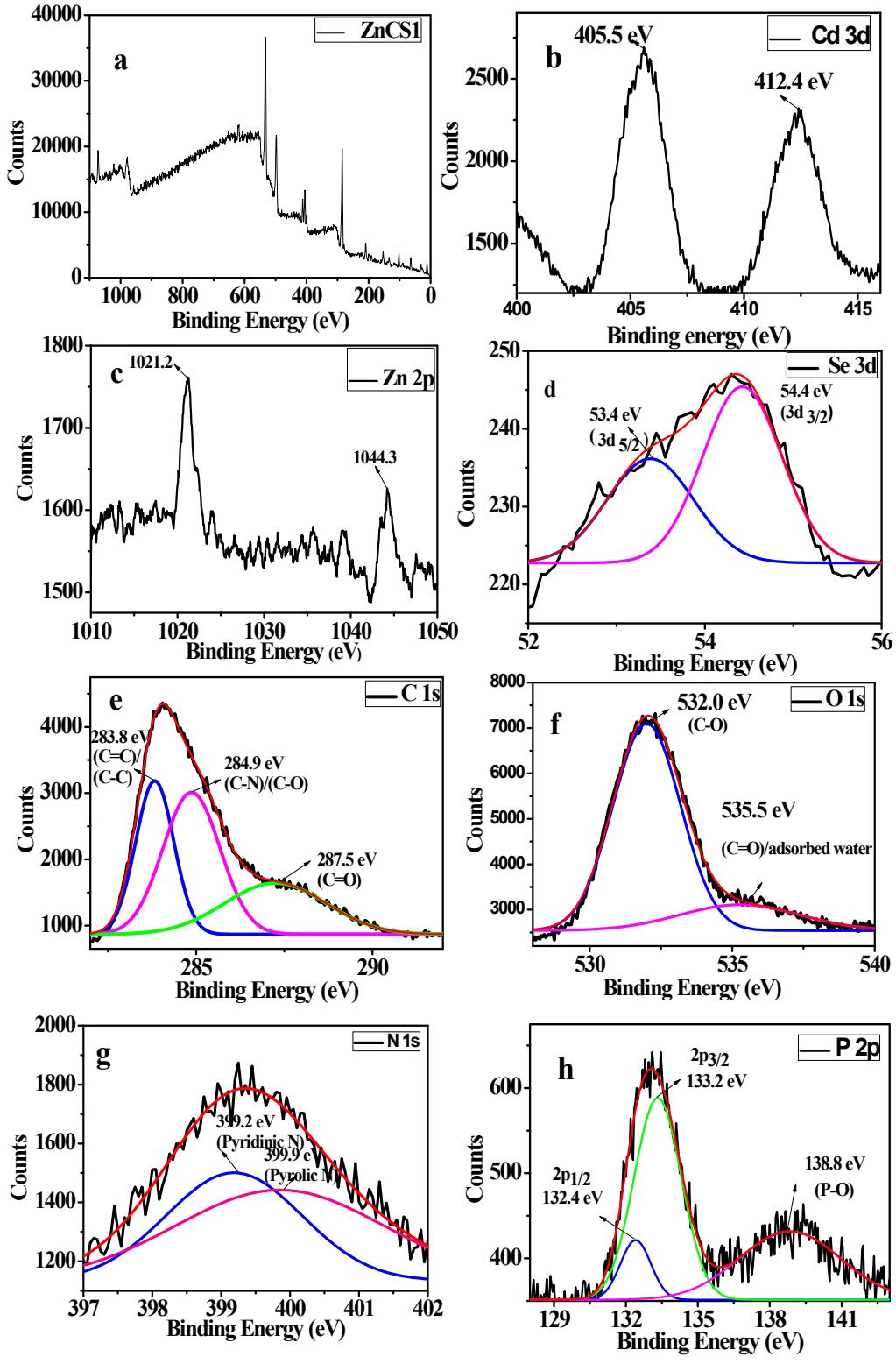


Fig. S8a XPS analysis of ZnCS1 – survey scan (a), high resolution spectra of its elements: Cd 3d (b); Zn 2p spectra (c); Se 3d spectra (d); C 1s spectra (e); O 1s spectra (f); N 1s (g); and P 2p spectra (h).

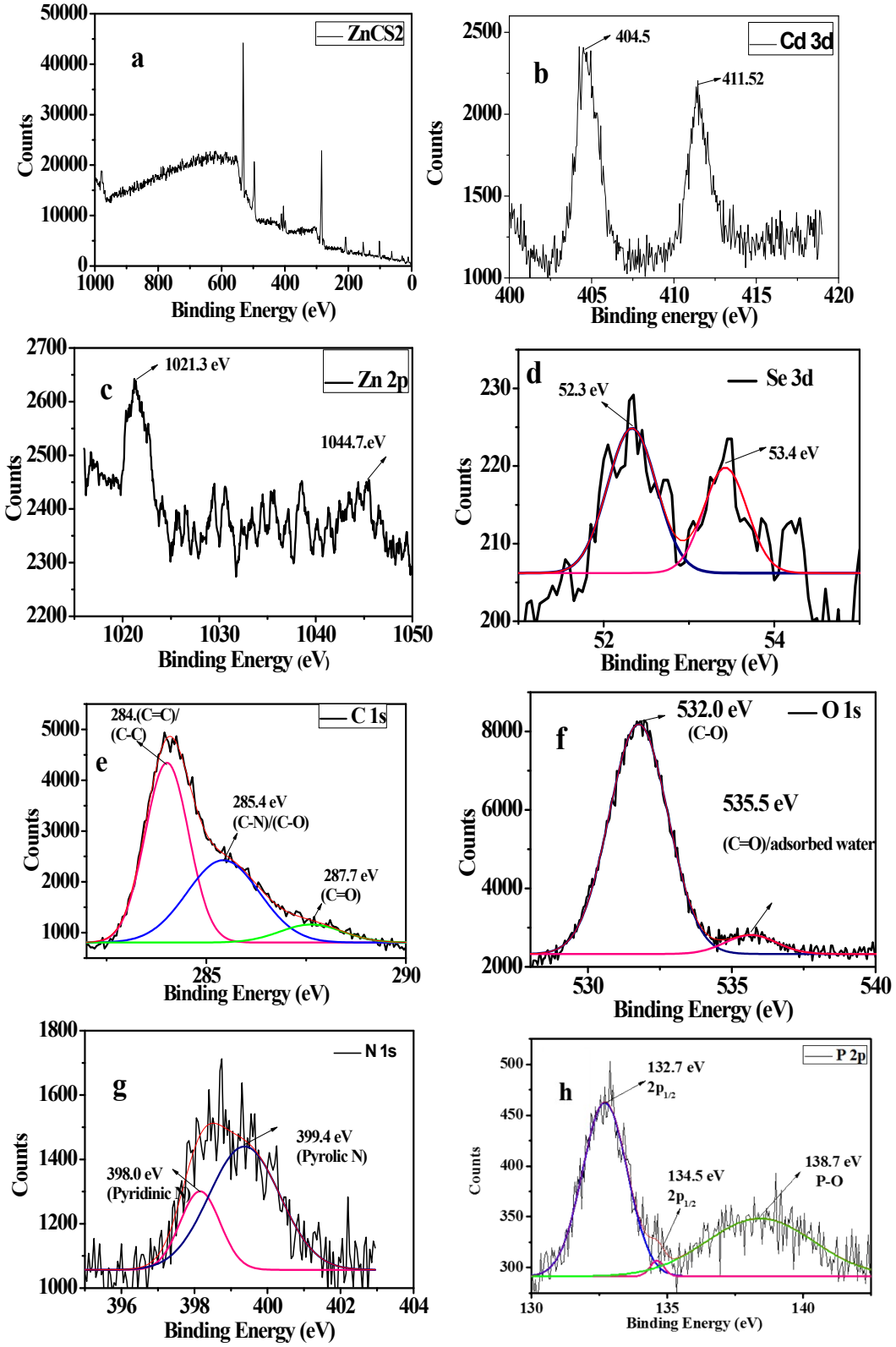
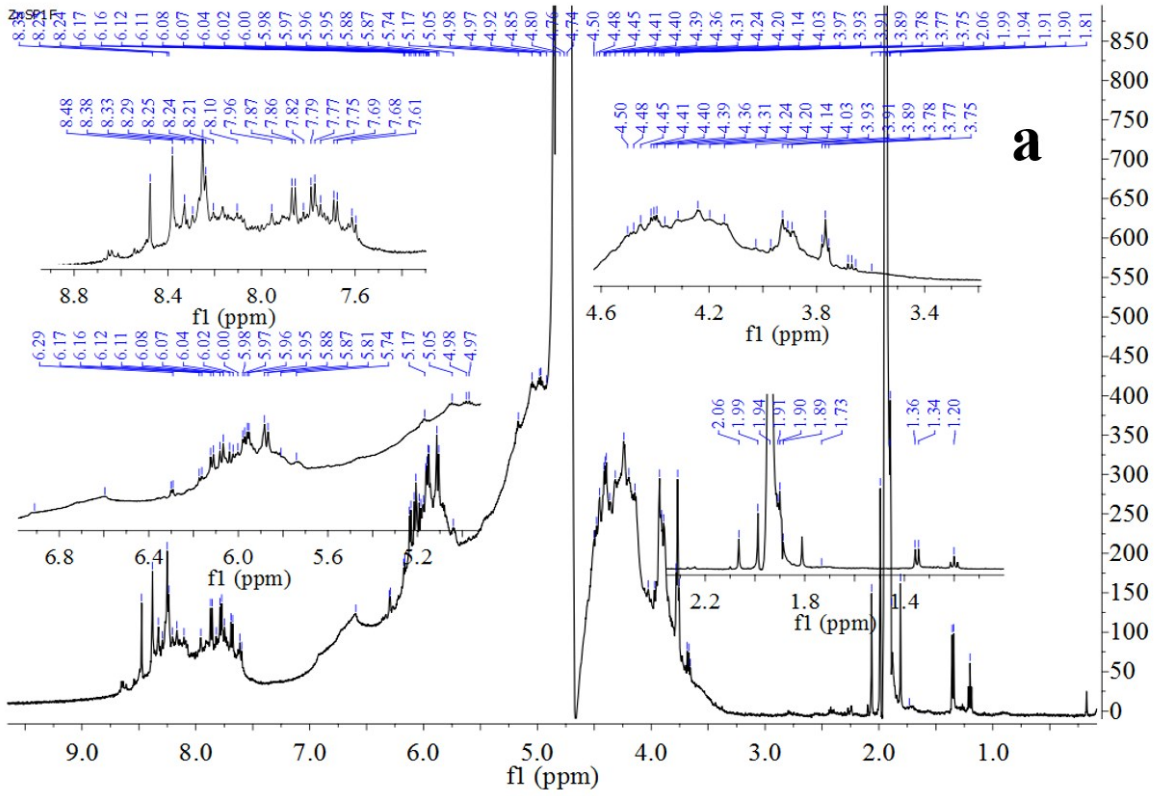
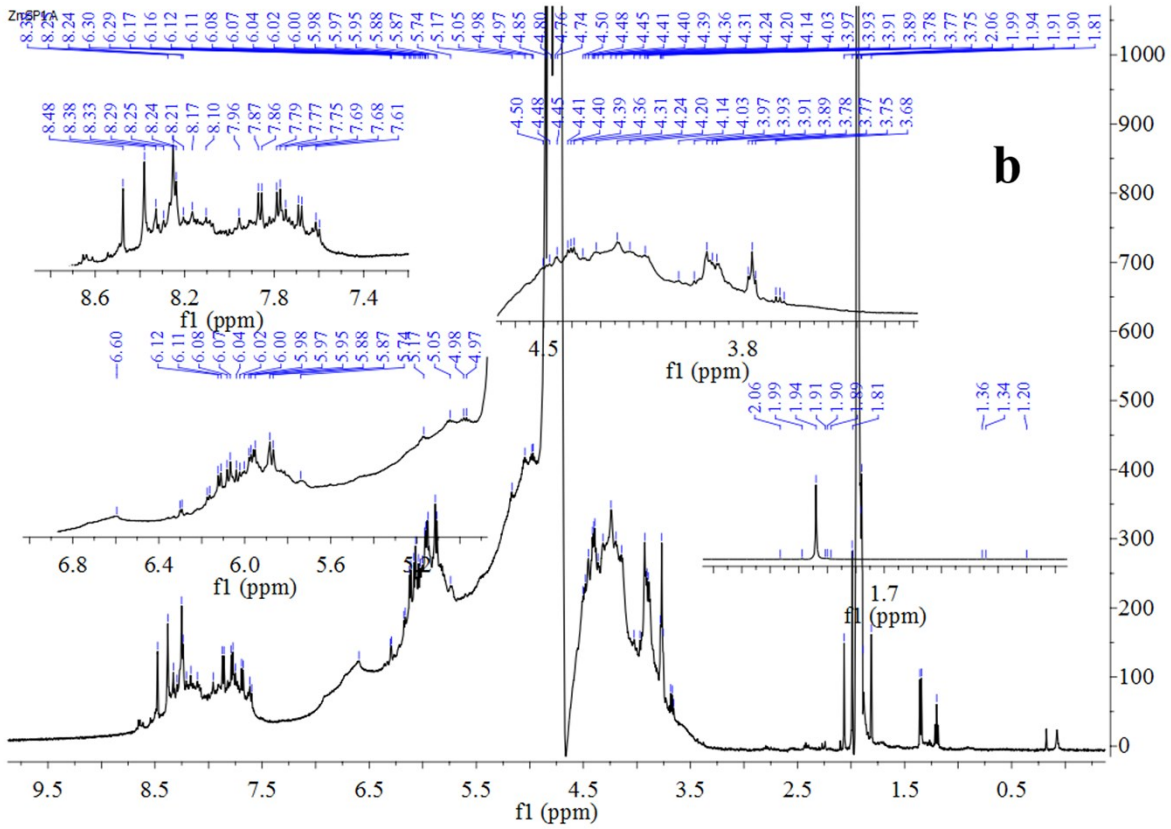


Fig. S8b XPS analysis of ZnCS2 – survey scan (a), high resolution spectra of its elements: Cd 3d (b); Zn 2p spectra (c); Se 3d spectra (d); C 1s spectra (e); O 1s spectra (f); N 1s (g); and P 2p spectra (h).


a
f1 (ppm)


b
f1 (ppm)

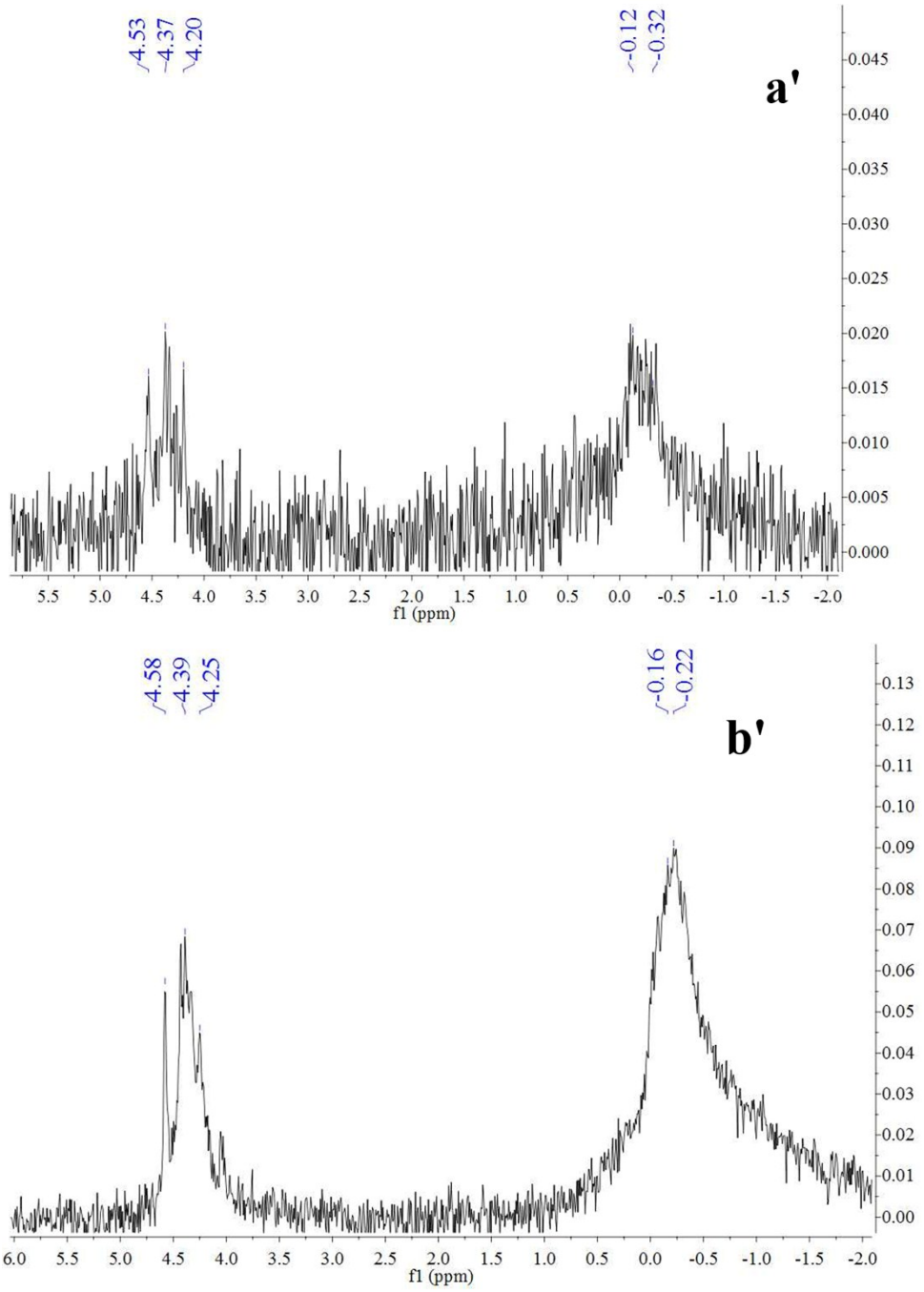


Fig. S9 ^{1}H and ^{31}P NMR spectra of ZnCS (a, a') and ZnCS1 (b and b').

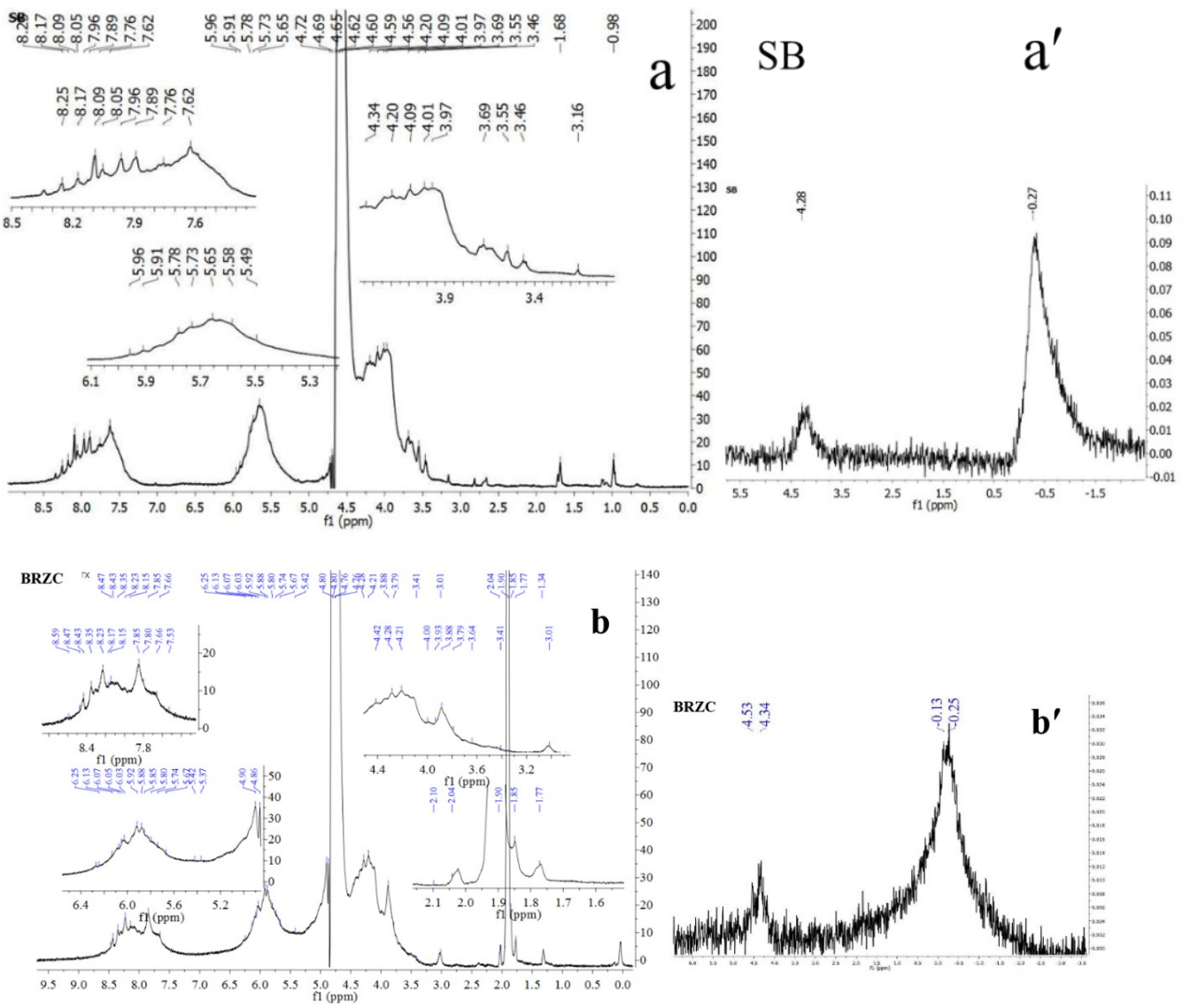


Fig. S10 ^{1}H and ^{31}P NMR spectra of RNA (denoted as BR) (a and a' taken from reference 52) and BRZC (b and b').

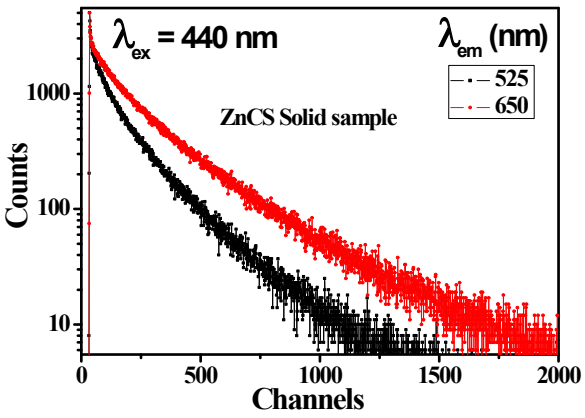


Fig. S11 Fluorescence decay curves for solid ZnCS at different emission wavelengths using λ_{ex} = 440 nm.

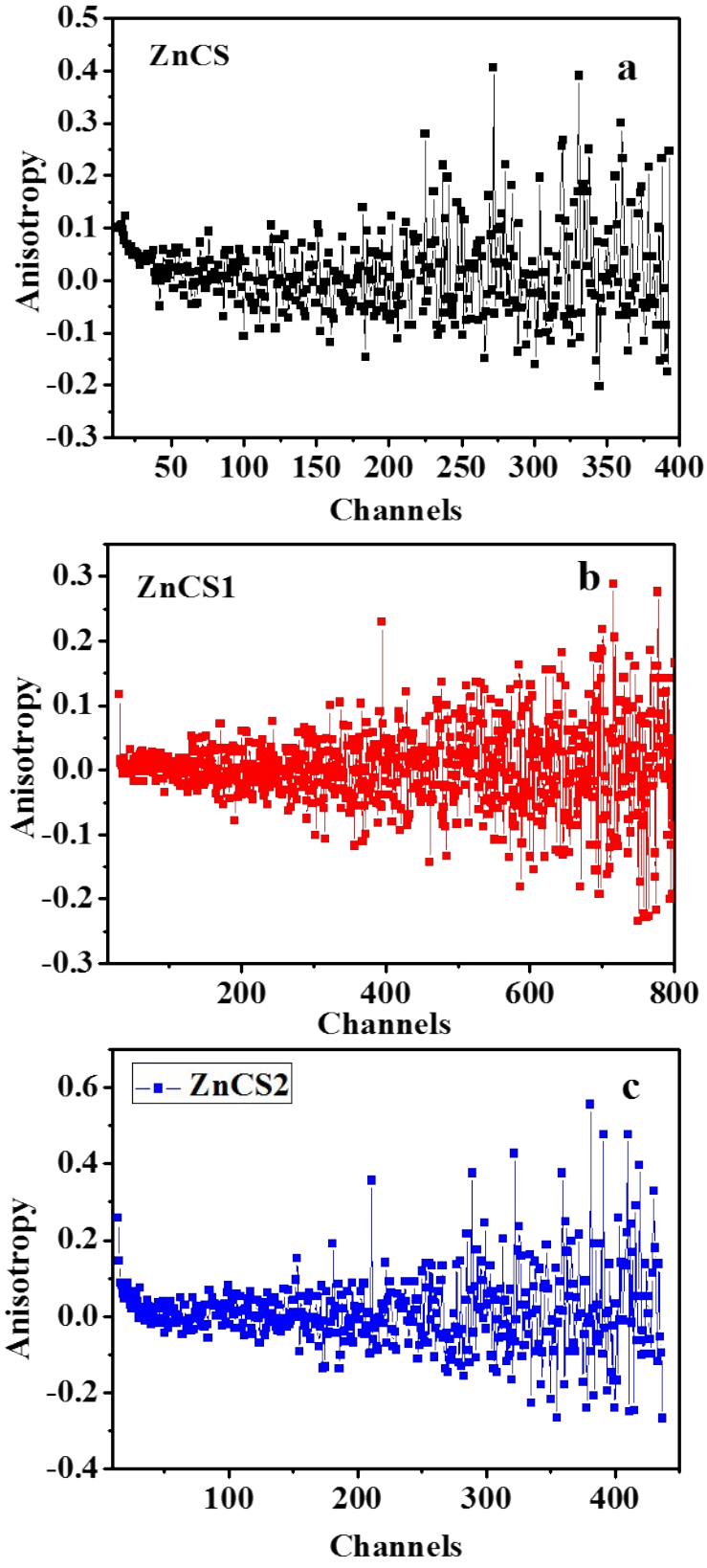


Fig. S12 Time-resolved anisotropy decay curves for ZnCS (a), ZnCS1 (b) and ZnCS2 (c).

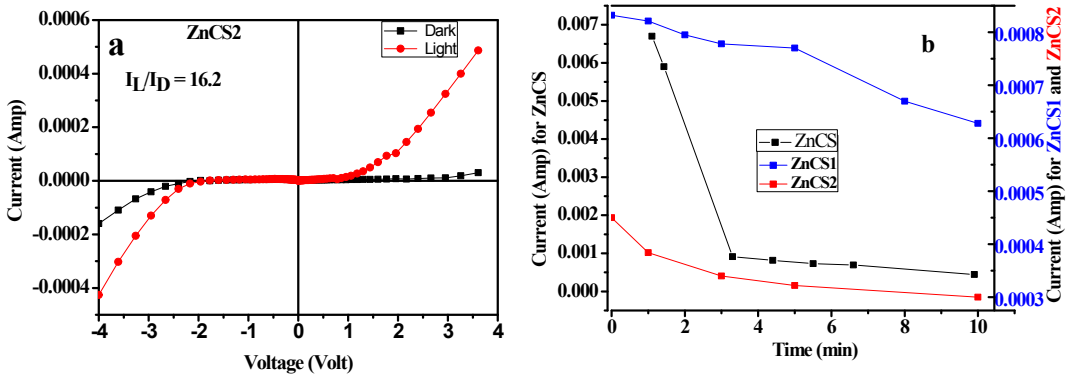


Fig. S13 I-V plot for ZnCS2 (a) and decay of current with time for ZnCS, ZnCS1 and ZnCS2.

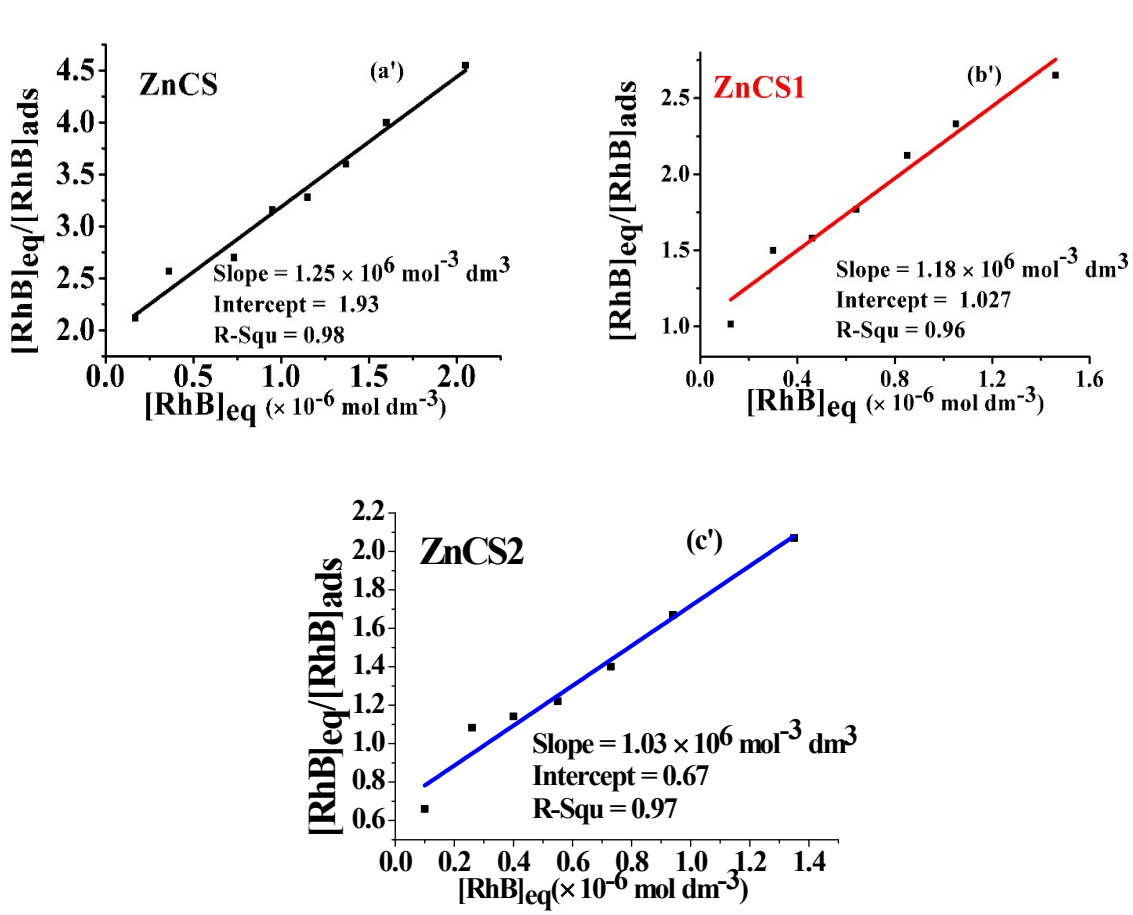


Fig. S14 Langmuir isotherms for the adsorption of RhB on ZnCS, ZnCS1 and ZnCS2 (a', b' and c').

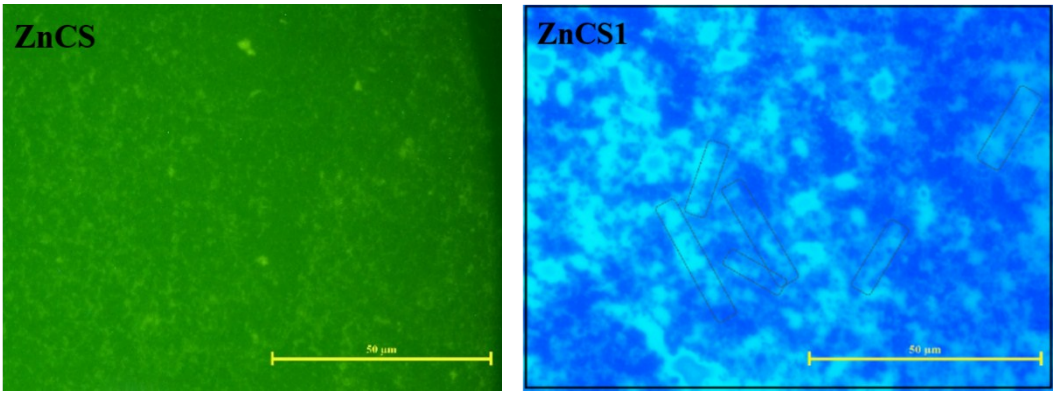


Fig. S15 Fluorescence images of ZnCS (using B-2A (Ex-450–490 filter) and ZnCS2 (using UV-2A (Ex-330–380) filter).

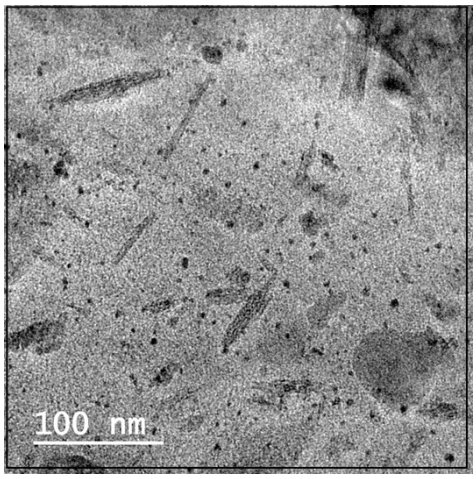


Fig. S16 TEM image of aged Cd^{2+} -CdSe nanohybrids showing the formation of needles like structure.

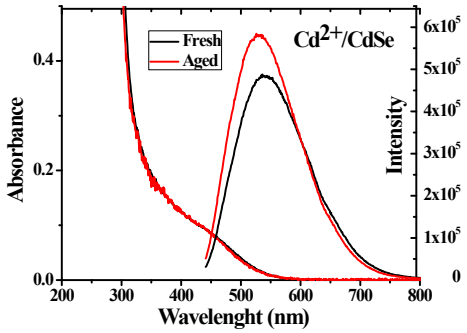


Fig. S17 Absorbance and emission spectra of Cd^{2+} /CdSe.

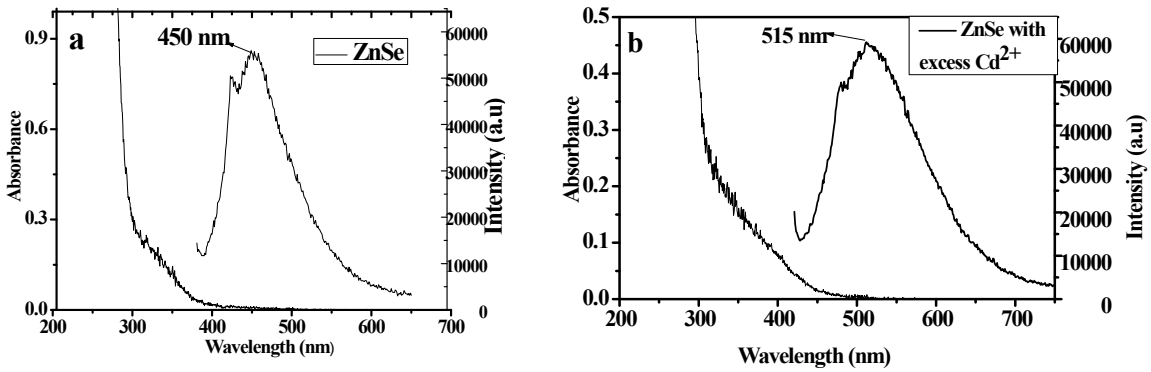


Fig. S18 Absorbance and fluorescence spectra of ZnSe (a) and ZnSe containing excess Cd^{2+} (b).

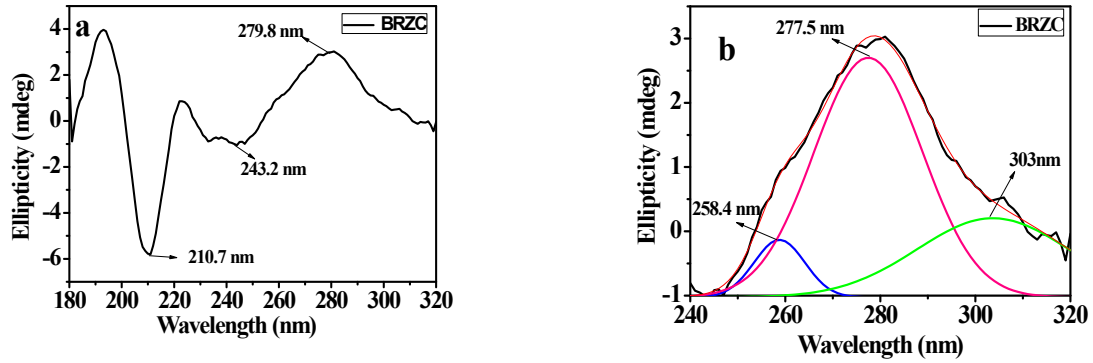


Fig. 19 CD spectra BRZC (a); deconvolution of the positive peaks (b).

Tables

Table S1a Effect of $[Zn^{2+}]$ on fluorescence lifetime of CdSe at λ_{em} = 545 nm.

$[Zn^{2+}]$ ($\times 10^{-3}$ mol dm^{-3}) λ_{em} = 545 nm	Lifetime (ns) at (λ_{em} = 545 nm)							
	τ_1 (ns)	Emission (%)	τ_2	Emission (%)	τ_3	Emission (%)	$<\tau>$	χ^2
0	2.86 (0.33)	8.64	33.4 (0.10) **(3.34)**	30.95	135 (0.049) **(6.62)**	60.43	92	1.3
1	2.23 (0.437)	5.23	31.9 (0.198) **(6.31)**	33.87	126 (0.09) **(11.34)**	60.90	87.6	1.3
1.5	2.92 (0.37)	5.11	36.4 (0.20) **(7.28)**	33.85	135 (0.097) **(13.1)**	61.04	**95**	1.3
2	2.01 (0.49)	5.97	31.35 (0.183) **(5.73)**	34.95	126 (0.076) **(9.57)**	59.08	85.92	**1.3**

Table S1b Effect of $[Zn^{2+}]$ on fluorescence lifetime of CdSe at λ_{em} = 650.

$[Zn^{2+}]$ ($\times 10^{-3}$ mol dm^{-3}) λ_{em} = 650 nm	Lifetime (ns) at (λ_{em} = 650 nm)							
	τ_1 (ns)	Emission (%)	τ_2	Emission (%)	τ_3	Emission (%)	$<\tau>$	χ^2
0	1.92 (0.46)	8.59	34.6 (0.08) (2.768)	27.58	156 (0.04) (6.24)	63.83	106	1.4
1	2.07 (0.42)	3.79	34.2 (0.20) (6.84)	29.34	148 (0.1051) (15.55 ns)	66.87	109	1.4
1.5	2.67 (0.37)	3.76	39.1 (0.20) (7.82)	29.43	157 (0.1127) (17.63)	66.81	**116**	1.4
2	2.06 (0.45)	4.39	34.1 (0.186) (6.34)	30.20	149 (0.09) (13.41)	65.41	**107**	**1.4**

Table S2 IR spectral data of different samples

Peak(s) assigned	IR peaks (cm^{-1})			
	BR	BRZC	ZnCS	ZnCS1
C=O str of G, C & U	(1689) 1715 – 1670	-	-	-
C=N and C=C ring of A, in plane vibration of C, *C=O str of U & C A&C*	(1642) 1650-1621	(1644) 1662-1620	(1644) 1660-1620	(1646) 1665-1622
in plane ring vib of C & U, C=N ring vib of G	(1610) 1617-1590	(1578) 1620-1560	(1578) 1615-1560	(1577) *1588-1544*
in plane vib of C	(1544) 1554-1510	(1535) 1557-1520	(1535) 1556-1518	*(1533) 1544-1522* (s)*
ring vib of A, G & U	(1470) 1485- 1450	(1494) 1455-1505	(1494) 1470-1508	(1490) 1470 -1508
In plane C2′-OH	1402	1402 (s)	1400	1400
Purine in anti confm.	1384	1385	1384	1385
Purine in syn confm.	1335	1344	1336	1337
C_4NH_2 str of C	1283	1294	-	1294
Assym. Stretch PO_2^-	1218 (s)	1242	1246	1246
Ribose C1' C2' OC3'	1139	1137 (s)	1143(s)	1143(s)
Ribose C1' C2' OC3'	1103	1112	1114	1114
Sugar backbone vib. (from sugar in C3'-endo confm.)	-	1193	1190	1190
CO stretch of backbone	1067 (br)*	1088	1088	1090(s)
Assigned to a vib involving the 2'-OH group (ref 27)	1000 (br)	Less intense	Less intense	Less intense
RNA backbone	966	980 (br)	981	981(s)
C3’-endo anti sugar marker	873 (br)	872 (br)	871 (s)	868(m)
Coupled furanose-phosphodiester chain vib.	818	825	825	824

Table S3 CD spectral data for different samples

Samples	Wavelength (nm) (ellipticity)			Deconvolution of positive peaks (ellipticity) {Peak Area}		
				Component I	Component II	Component III
ZnCS	210.5 (-5.66)	247.2 (-1.20)	278 (3.27)	260.8 (0.74) {3.86}	268.4 (1.44) {18.40}	281.0 (3.00) {74.98}
ZnCS1	209.0 (-4.62)	242.0 (-1.70)	276.4 (3.68)	261.4 (1.25) {9.72}	268.3 (1.85) {24.41}	279.2 (3.06) {70.36}
ZnCS2	208.7 (-4.34)	239.9 (-1.11)	274.0 (3.96)	261.8 (1.80) {29.82}	270.2 (1.68) {24.78}	280.1 (3.059) {66.46}

Table S4 Fluorescence lifetime for ZnCS, ZnCS1 and ZnCS2 at different emission wavelengths (λ_{ex} **= 440 nm)**.

Sample ($\lambda_{em\ in}$ nm)	**Lifetime (ns) by λ_{ex} = 440 nm**							
	τ_1 (ns)	**Emission (%)**	**τ_2**	**Emission (%)**	**τ_3**	**Emission (%)**	**< τ>**	**χ2**
ZnCS **(525)**	4.69 (0.29)	6.89	38.2 (0.20)	39.21	131 (0.082)	53.90	86	1.3
ZnCS1 **(525)**	3.13 (0.35)	4.82	36.65 (0.21)	33.57	133.5 (0.105)	61.62	95	1.3
ZnCS2 **(525)**	2.96 (4.05)	4.05	36.1 (33.15)	33.15	1.29 (0.119)	62.81	93	1.3
ZnCS **(650)**	3.60 (0.30)	3.81	42.0 (0.22)	31.56	164 (0.11)	64.63	118	1.3
ZnCS1 **(650)**	3.17 (0.34)	3.55	42.4 (0.193)	26.82	165 (0.13)	69.63	127	1.3
ZnCS2 **(650)**	2.01 (0.386)	2.38	40.0 (0.22)	27.32	162.7 (0.14)	70.30	125	1.3

Table S5 Fluorescence lifetime for solid ZnCS sample at different emission wavelengths (λ_{ex} **= 440 nm)**.

λ_{em} (nm)	**Lifetime (ns) at (λ_{ex} = 440 nm)**							
	τ_1 (ns)	**Emission (%)**	**τ_2**	**Emission (%)**	**τ_3**	**Emission (%)**	**< τ>**	**χ2**
525	0.95 (0.66)	3.82	30.8 (0.20)	37.51	107 (0.090)	58.67	74	1.4
650	1.10 (0.37)	1.70	46.3 (0.16)	30.18	150 (0.11)	68.12	117	1.4

Table S6 Surface characteristics for different samples**.**

Parameters	**ZnCS**	**ZnCS1**	**ZnCS2**
a (mol dm^{-3})	0.8×10^{-6}	0.85×10^{-6}	0.96×10^{-6}
b (mol^{-1} dm^3)	0.65×10^6	1.14×10^6	1.53×10^6
Surface area (m^2/g)	70	75	85

Table S7 Ratio of Cd/Zn obtained by XPS analysis

Sample	**Ratio Cd/Zn**
ZnCS	1
ZnCS1	0.700
ZnCS2	0.108

Table S8 CD spectral data for BRZC

Sample	**Wavelength (nm) (ellipticity)**			**Deconvolution of positive peaks (Peak Area)**		
				Component I	**Component II**	**Component III**
BRZC	210.7 (-5.89)	243.2 (-1.48)	279.8 (3.10)	258.4 (11.97)	277.5 (106.6)	303.0 (49.29)