Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for:

Synthesis and characterisation of Ga- and In-doped CdS by solventless thermolysis of single source precursors

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Composition values of precursors for $M_xCd_{1-x}S_{1+0.5x}$

Table S1. Composition of $Ga_xCd_{1-x}S_{1+0.5x}$ ($0 \leq x \leq 0.1$).

Composition of [Ga]/([Ga]+[Cd])	[Ga(S_2CNEt_2)$_3$]	[Cd(S_2CNEt_2)$_2$]
0	0 mmol	0.3668 mmol
0.02	0.0972 mmol	4.3683 mmol
0.04	0.0972 mmol	2.1471 mmol
0.06	0.0972 mmol	1.4016 mmol
0.08	0.0972 mmol	1.0288 mmol
0.1	0.0972 mmol	0.8052 mmol

Table S2.

Composition of [In]/([In]+[Cd])	[In(S_2CNEt_2)$_3$]	[Cd(S_2CNEt_2)$_2$]
0	0 mmol	0.3668 mmol
0.02	0.0895 mmol	4.7618 mmol
0.04	0.0895 mmol	2.3323 mmol
0.06	0.0895 mmol	1.5225 mmol
0.08	0.0895 mmol	1.1117 mmol
0.1	0.0895 mmol	0.8746 mmol

Composition of $In_xCd_{1-x}S_{1+0.5x}$ ($0 \leq x \leq 0.1$).

pXRD of Ga_2S_3, CdS, and In_2S_3 synthesised *via* [Ga(DTC)$_3$], [Cd(DTC)$_2$] and [In(DTC)$_3$]

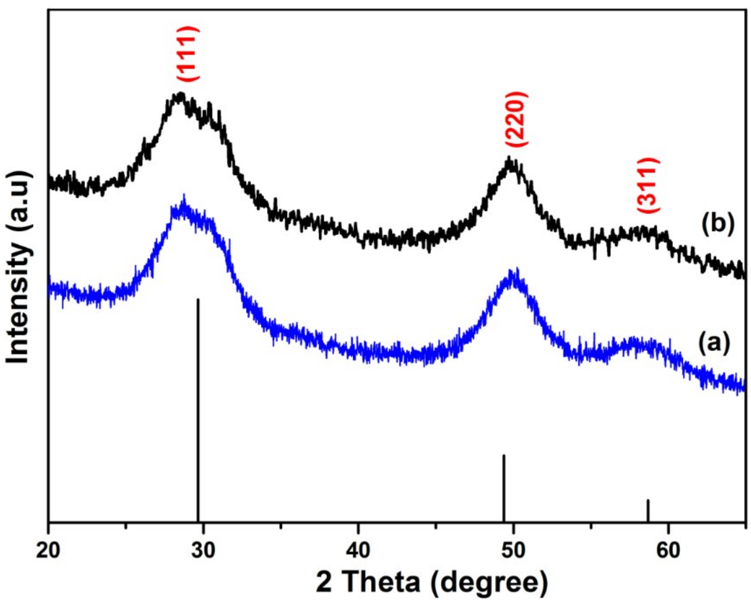

Figure S1. The powder XRD patterns of nanocrystals generated from the decomposition of [Ga(S$_2$CNEt$_2$)$_3$] complex (**1**) at 400 °C (a) and 450 °C (b) for 1 h. These patterns are corresponding to Ga_2S_3 (ICDD: 00-043-0916).

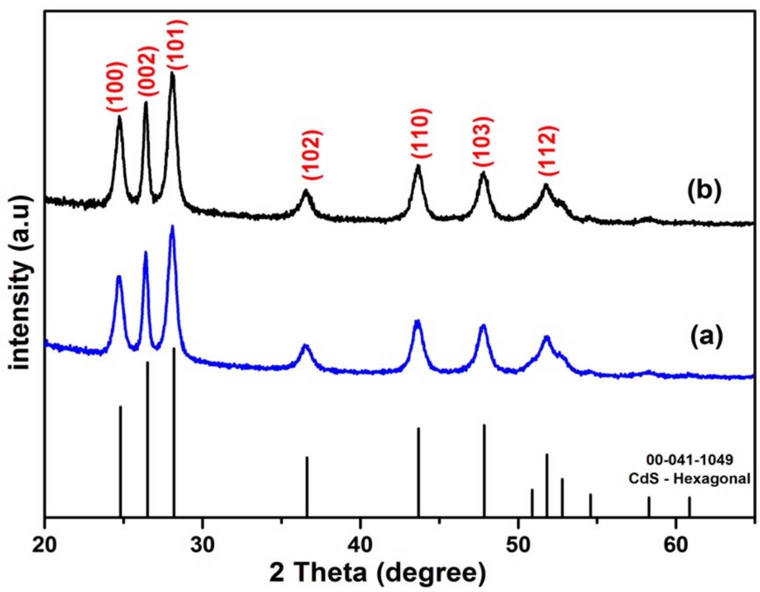

Figure S2. The powder XRD patterns of nanocrystals generated from the decomposition of [Cd(S$_2$CNEt$_2$)$_2$] complex (**2**) at 400 °C (a) and 450 °C (b) for 1 h. These patterns are corresponding to CdS (ICDD: 00-041-1049).

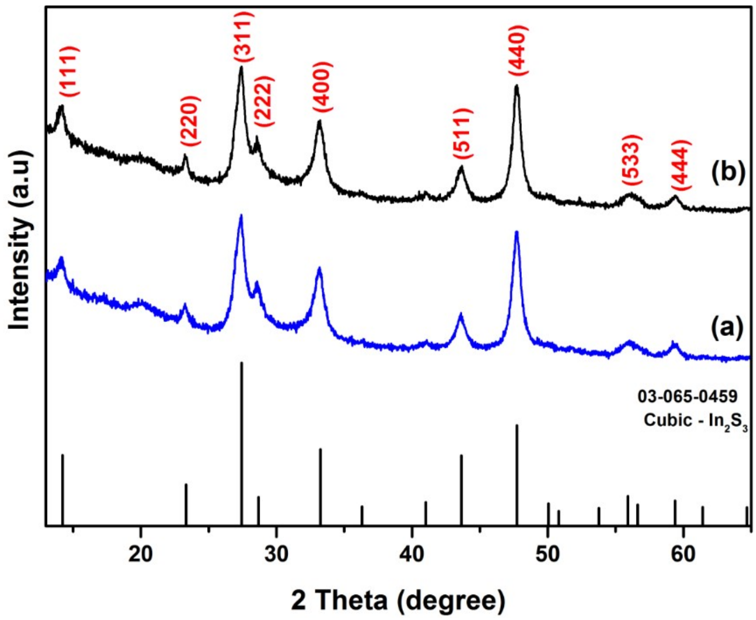

Figure S3. The powder XRD patterns of nanocrystals generated from the decomposition of $[In(S_2CNEt_2)_3]$ complex (3) at 400 ^oC (a) and 450 ^oC (b) for 1 h. These patterns are corresponding to In_2S_3 (ICDD: 03-065-0459).

Lattice constants and d(101) values with increasing Ga^{3+}-doping concentration

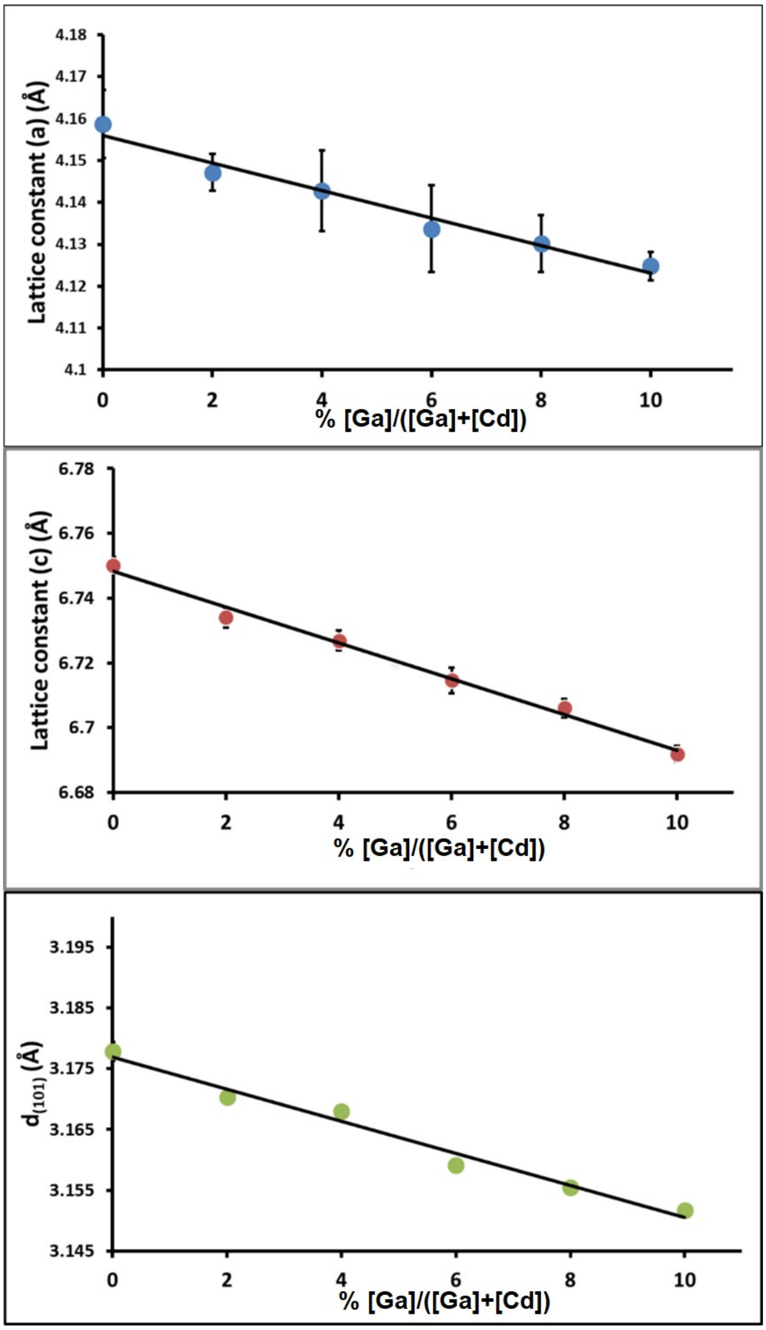

Figure S4. Lattice parameters a (Å) **(a)**, and c (Å) **(b)** and $d_{(101)}$ (Å) **(c)** of $Cd_{1-x}Ga_xS$ with the different mole % of composition [Ga]/([Ga]+[Cd]).

EDX and ICP-OES determined Ga^{3+} concentrations *vs* input Ga precursor

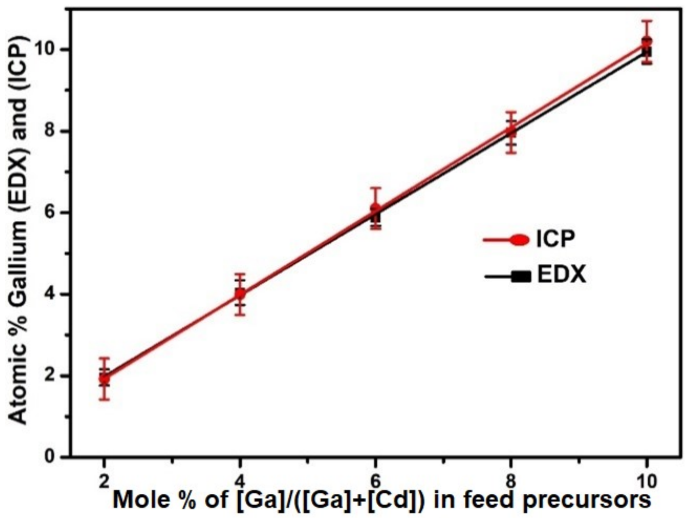

Figure S5. Linear correlation between mole % of [Ga]/([Ga]+[Cd]) in the precursor feedstock and atomic % of gallium found in $Ga_xCd_{1-x}S_{1+0.5x}$ ($0 \leq x \leq 0.1$) samples from ICP and EDX.

Table of data for EDX analysis for $Ga_xCd_{1-x}S_{1+0.5x}$

Table S3. The content of Cd, Ga, and S in $Ga_xCd_{1-x}S_{1+0.5x}$ ($0 \leq x \leq 0.1$) calculated from theoretical values, EDX and ICP-OES.

Mole fraction of [Ga]/[Ga]+[Cd]	Elements	Atomic % (Required composition)	Atomic % (Required composition by EDX)	Atomic % (Required composition by ICP-OES)
0	**Cd** **Ga** **S**	50 0 50	51.02 0 48.98	50.07 0 49.93
0.02	**Cd** **Ga** **S**	49 1 50	48.32 0.97 50.71	48.36 0.95 50.69
0.04	**Cd** **Ga** **S**	48 2 50	46.21 1.97 51.82	47.16 1.96 50.88
0.06	**Cd** **Ga** **S**	47 3 50	45.93 2.85 51.20	45.41 2.95 51.64
0.08	**Cd** **Ga** **S**	46 4 50	44.31 3.83 51.86	44.41 3.85 51.74
0.1	**Cd** **Ga** **S**	45 5 50	42.94 4.76 52.30	43.31 4.87 51.82

Lattice constants and d(101) values with increasing In^{3+}-doping concentration

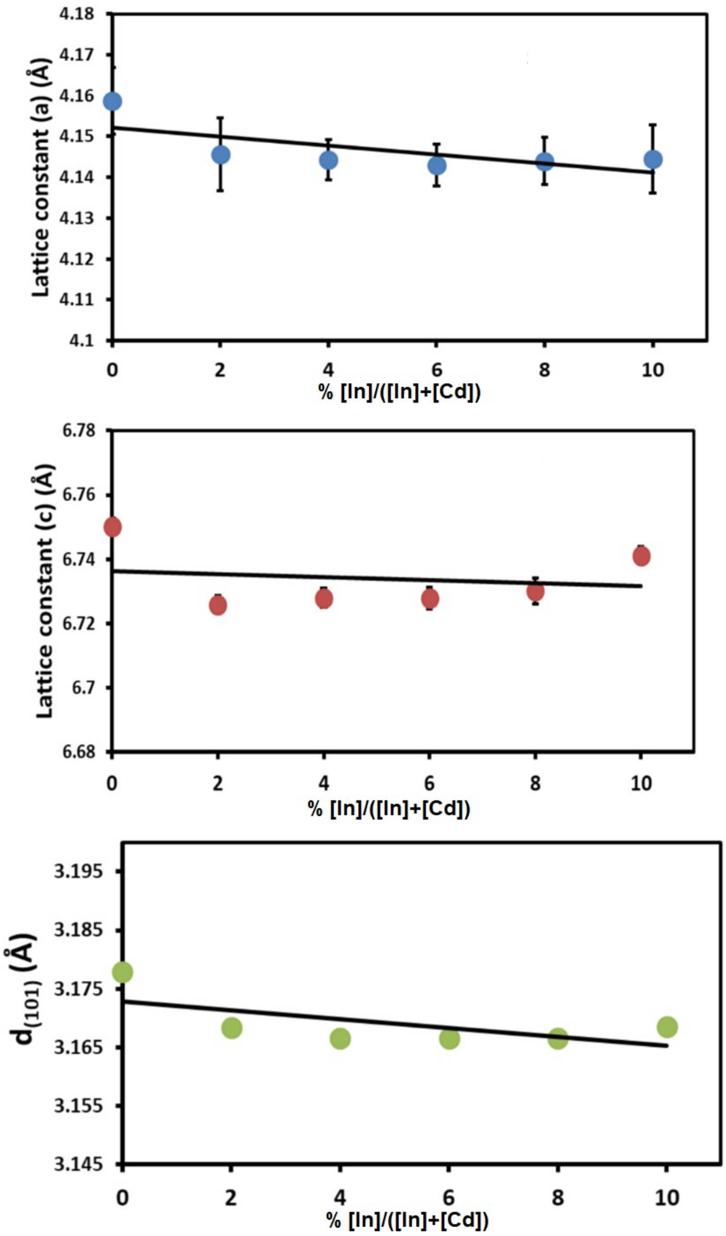

Figure S6. Lattice parameters a (Å) **(a)**, and c (Å) **(b)** and $d_{(101)}$ (Å) **(c)** of $In_xCd_{1-x}S_{1+0.5x}$ with the different mole % of composition [In]/([In+Cd]).

EDX and ICP-OES determined In^{3+} concentrations *vs* input Ga precursor

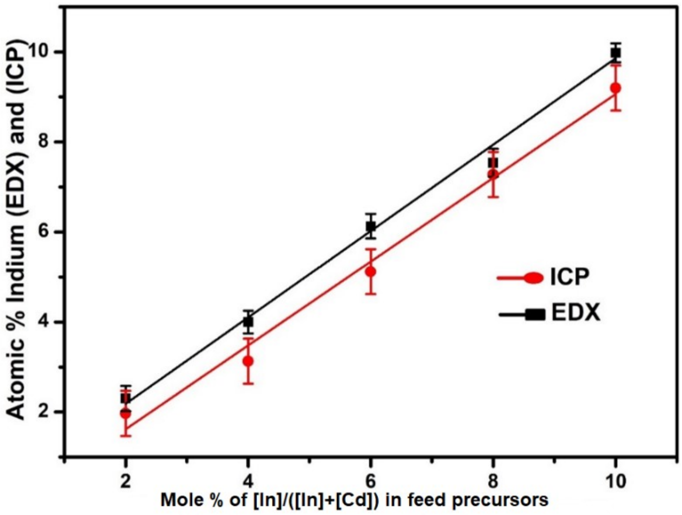

Figure S7: Approximately linear correlation between the mole % of [In]/([In]+[Cd]) in the precursor feedstock and atomic % of indium found in $Cd_{1-x}In_xS$ ($0 \leq x \leq 0.1$) samples from ICP and EDX.

Table of data for EDX analysis for $In_xCd_{1-x}S_{1+0.5x}$

Table S4. The content of Cd, In and S in $In_xCd_{1-x}S_{1+0.5x}$ ($0 \leq x \leq 0.1$) calculated from theoretical values, EDX and ICP-OES.

Mole fraction of [In]/([In]+[Cd])	Elements	Atomic % (Required composition)	Atomic % (Required composition by EDX)	Atomic % (Required composition by ICP-OES)
0	**Cd**	50	51.02	50.07
	In	0	0	0
	S	50	48.98	49.93
0.02	**Cd**	49	48.32	49.41
	In	1	0.97	0.97
	S	50	50.71	49.62
0.04	**Cd**	48	46.21	48.57
	In	2	1.97	1.57
	S	50	51.82	49.86
0.06	**Cd**	47	45.93	46.50
	In	3	2.85	2.50
	S	50	51.20	51.00
0.08	**Cd**	46	44.31	45.11
	In	4	3.83	3.54
	S	50	51.86	51.74
0.1	**Cd**	45	42.94	44.25
	In	5	4.76	4.42
	S	50	52.30	51.33

UV-Vis absorption spectra of $Ga_xCd_{1-x}S_{1+0.5x}$

i.e. plots of $(\alpha h\nu)^2$ versus hν with a straight line fitting to the linear region

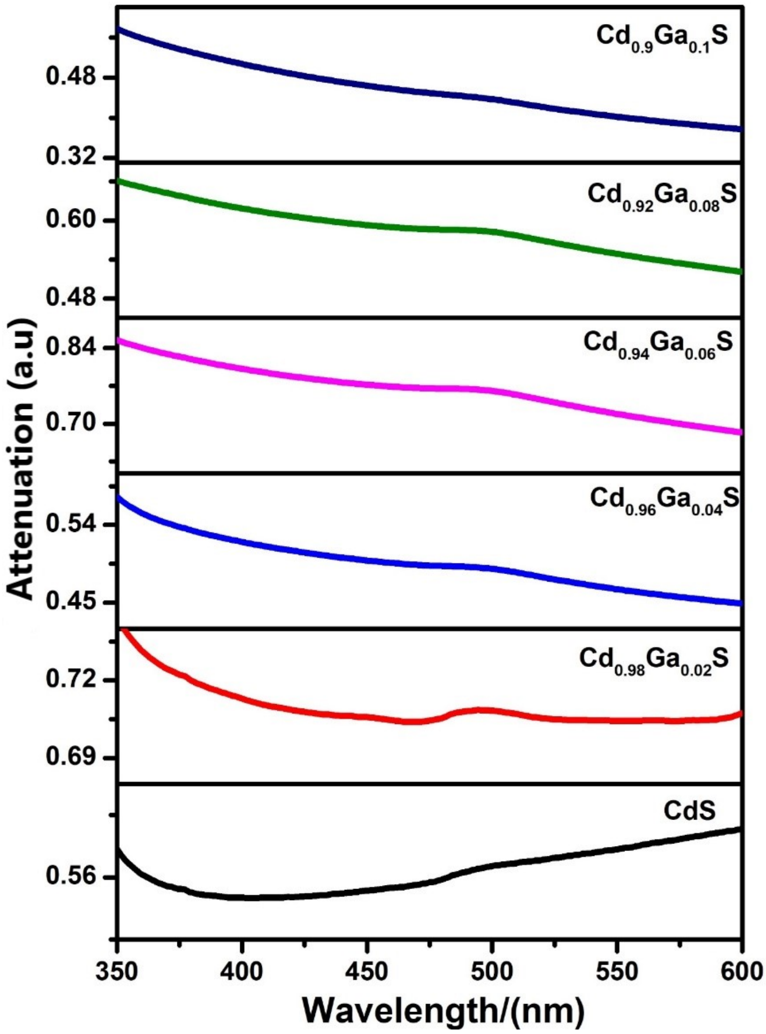

Figure S8. The UV-Vis-NIR absorbance spectra of $Ga_xCd_{1-x}S_{1+0.5x}$ powders x = 0 (black), x = 0.02 (red), x = 0.04 (blue), x = 0.06 (pink), x = 0.08 (green) and x=0.1 (navy).

UV-Vis absorption spectra of $In_xCd_{1-x}S_{1+0.5x}$

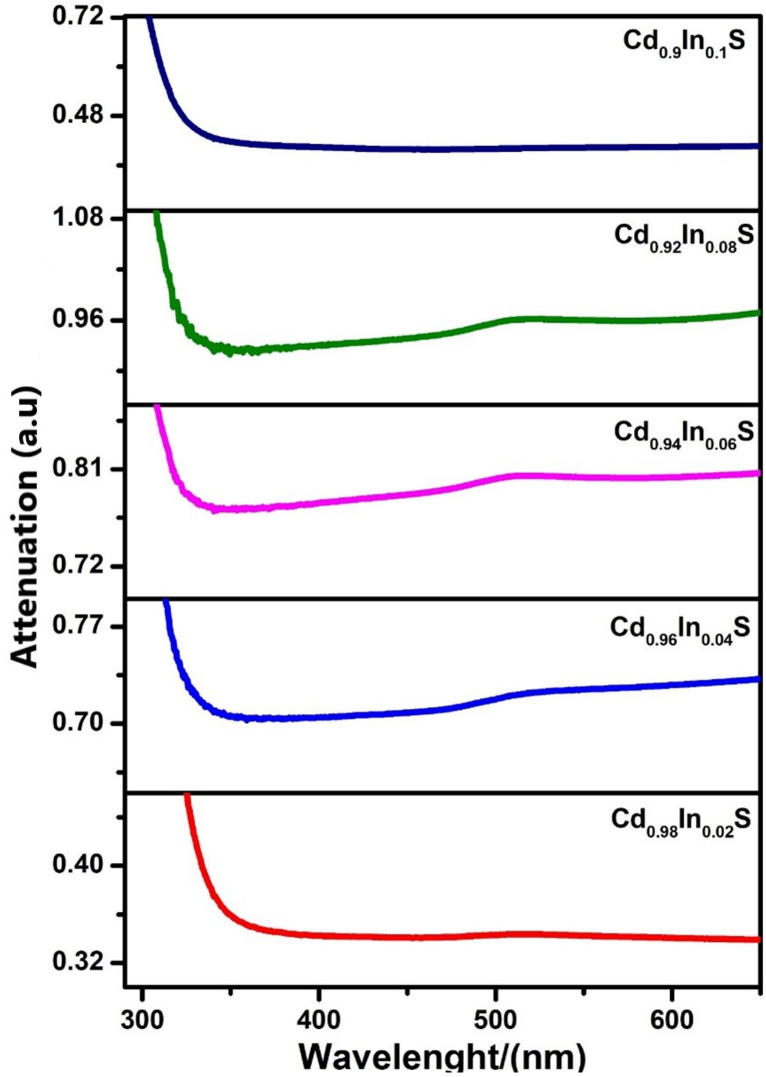

Figure S9. The UV-Vis-NIR absorbance spectra of $In_xCd_{1-x}S_{1+0.5x}$ powders x = 0 (black), x = 0.02 (red), x = 0.04 (blue), x = 0.06 (pink), x = 0.08 (green) and x=0.1 (navy).

Photoluminescence lifetime with doping concentration for both $Ga_xCd_{1-x}S_{1+0.5x}$ and $In_xCd_{1-x}S_{1+0.5x}$

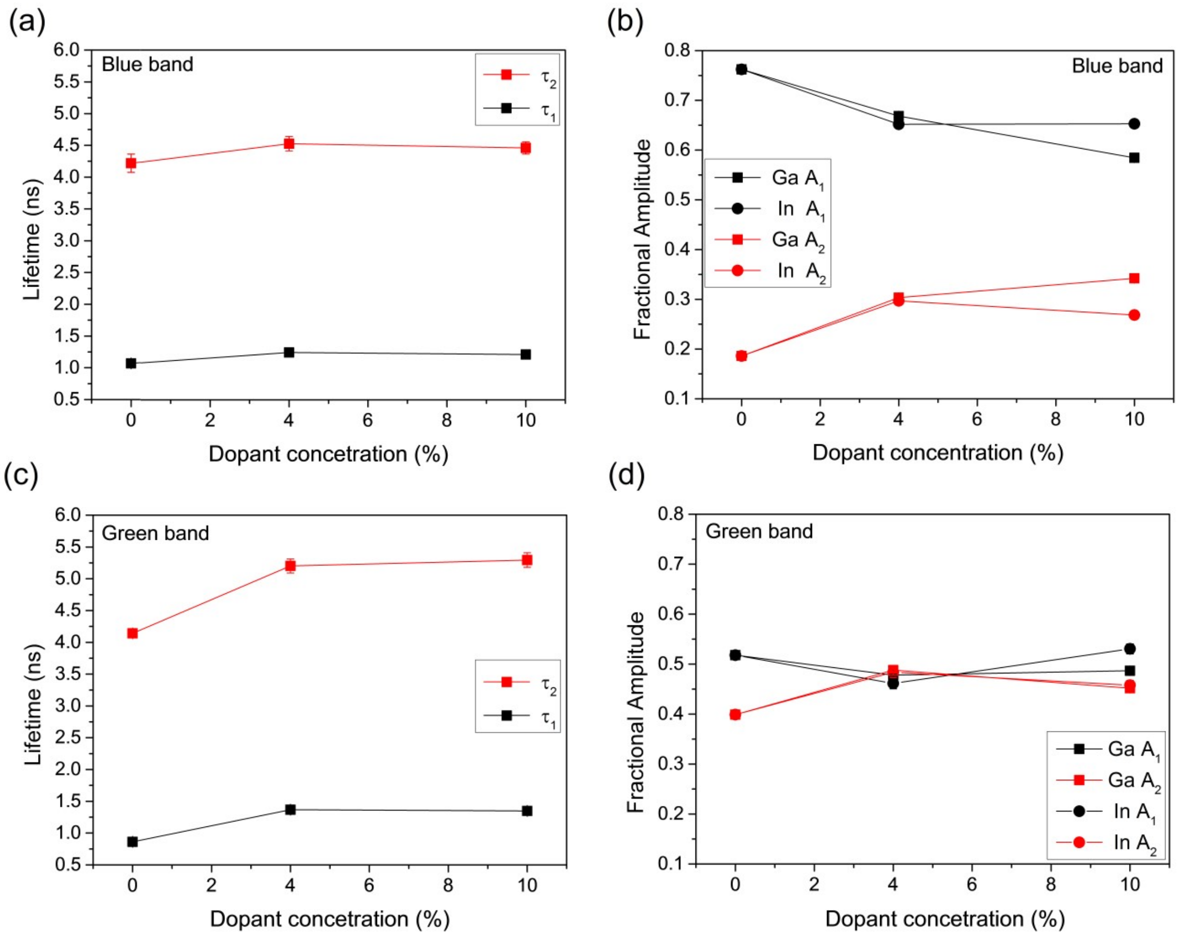

Figure S10. Lifetimes (a and c) and associated fractional amplitudes (b and d) as a function of dopant concentration for the blue and green emission bands, respectively.