

Supporting information for:

Passivation, phase, and morphology control of CdS  
nanocrystals probed using fluorinated aromatic amines and  
solid-state NMR spectroscopy

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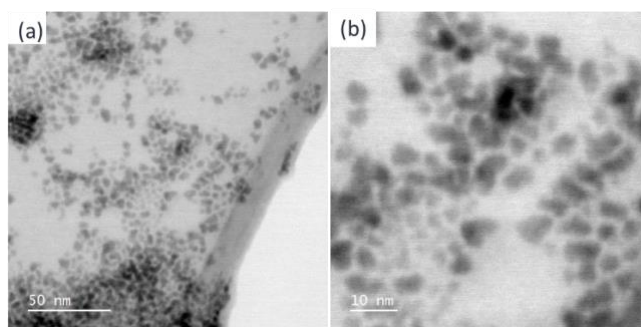
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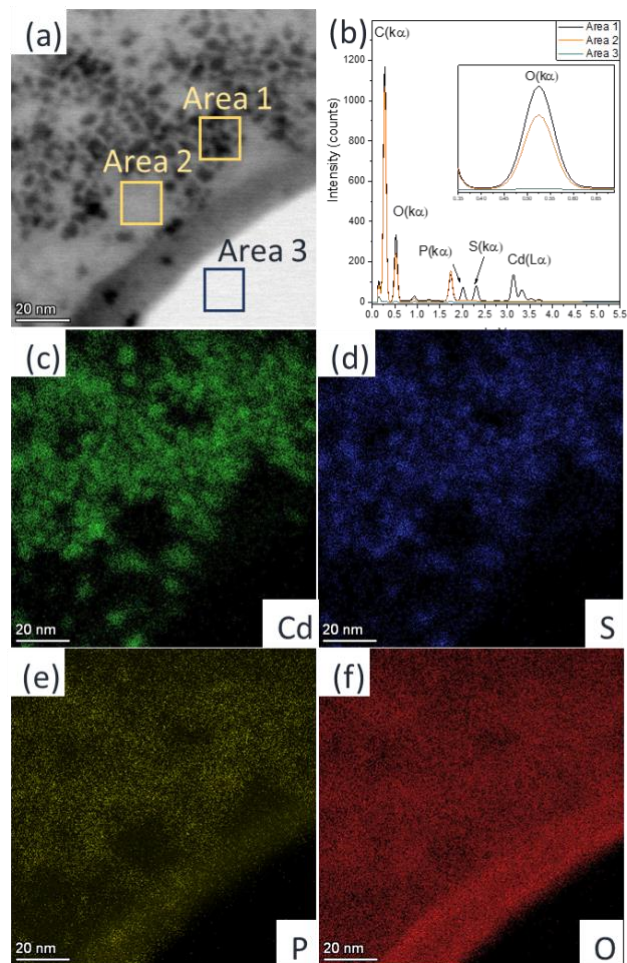
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## Transmission electron microscopy

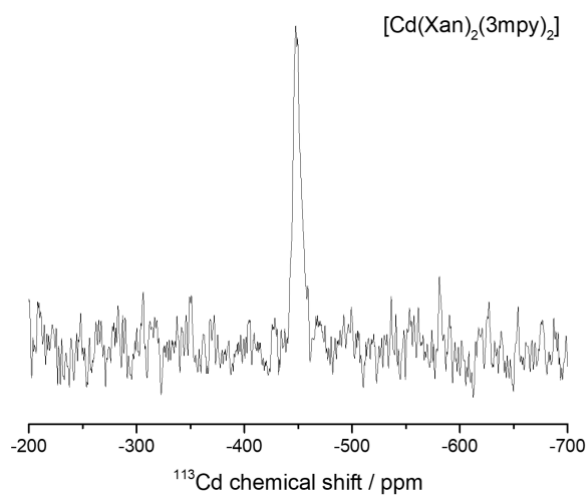


**Figure S1.** Scanning transmission electron microscope (STEM) bright field (BF) micrograph of CdS NCs synthesized in TOPO.

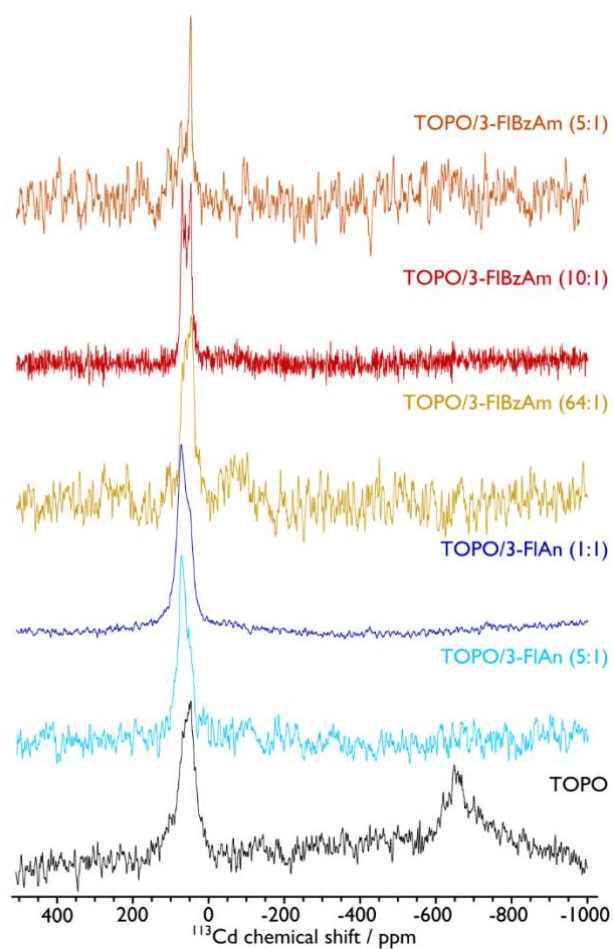


**Figure S2.** (a) Scanning transmission electron microscope (STEM) bright field (BF) micrograph of CdS NCs synthesized in TOPO (b) STEM-EDS spectra taken from area highlighted in a. Inset shows enlarged area of the O  $k\alpha$  lines. The difference in the EDS spectra between area 1 and area 2 suggest higher content of O in the vicinity of the CdS NC. Elemental mapping of the image shown in a. (c) Cadmium (d) Sulphur (e) Phosphorous (f) Oxygen

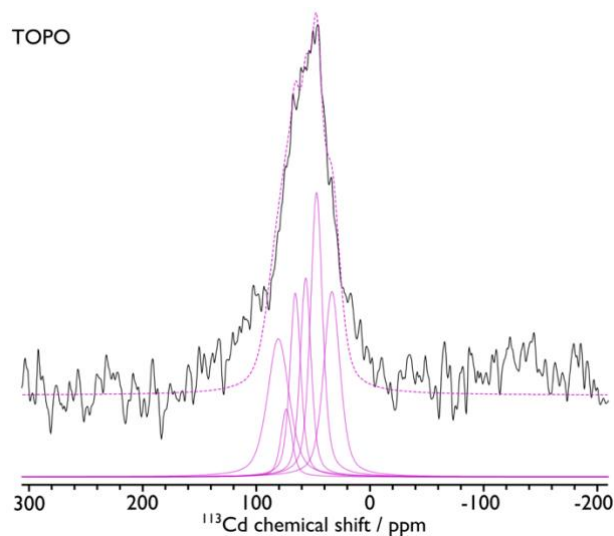
## Solid state NMR



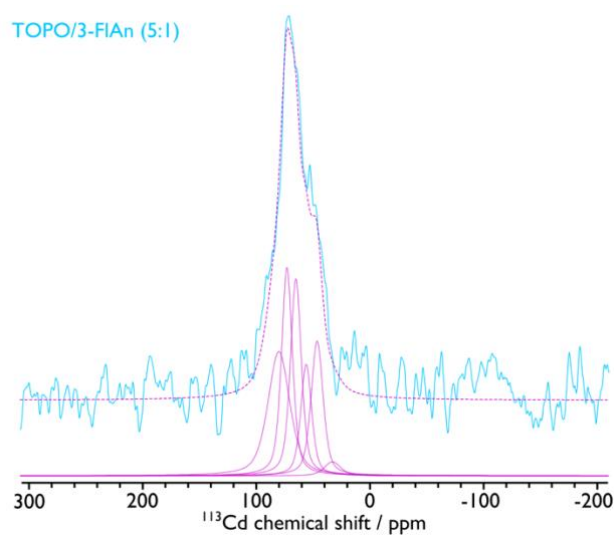
**Figure S3.**  $^{113}\text{Cd}$  MAS NMR spectrum of the molecular precursor  $[\text{Cd}(\text{Xan})_2(3\text{-mpy})_2]$ .



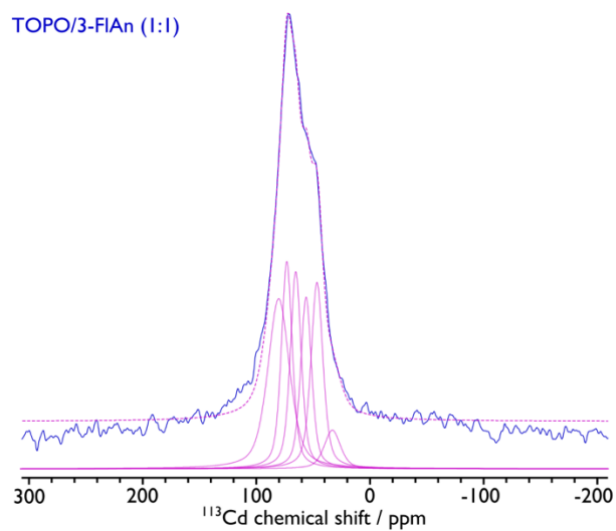
**Figure S4.**  $^{113}\text{Cd}$  MAS NMR spectra of CdS NCs with indicated ligands. An MAS frequency of 8 kHz was used for TOPO, 10 kHz was used for TOPO/3-FIAAn (1:1), and 12 kHz was used for TOPO/3-FIAAn (5:1), TOPO/3-FIBzAm (64:1), TOPO/3-FIBzAm (10:1), and TOPO/3-FIBzAm (5:1) CdS NCs.



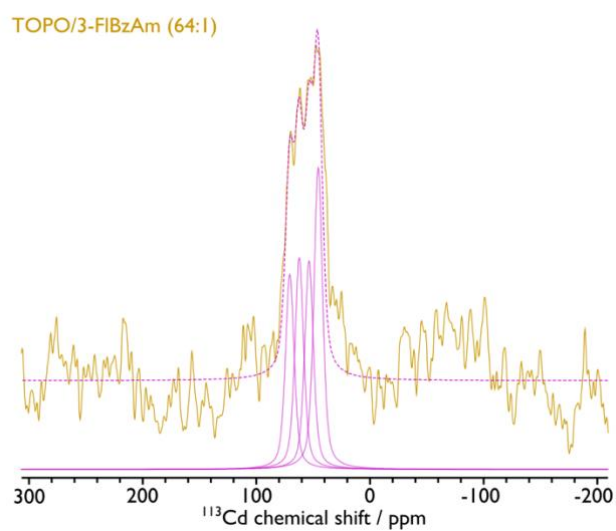
**Figure S5.**  $^{113}\text{Cd}$  MAS NMR spectrum of TOPO CdS NCs and associated fitting with deconvolution (pink) and summation (dashed pink).



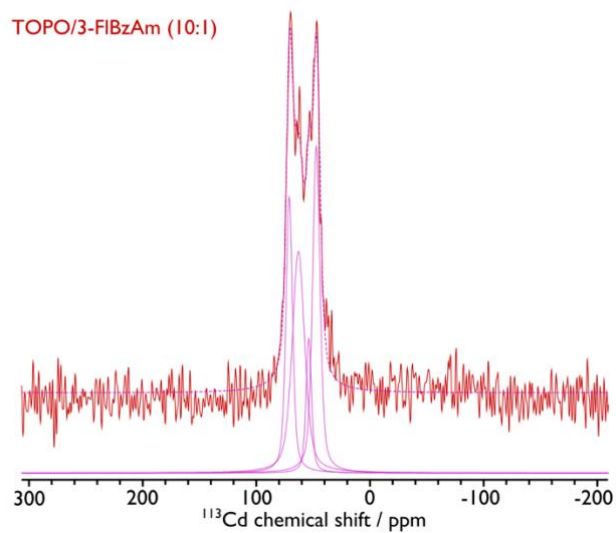
**Figure S6.**  $^{113}\text{Cd}$  MAS NMR spectrum of TOPO/3-FIAn (5:1) CdS NCs and associated fitting with deconvolution (pink) and summation (dashed pink).



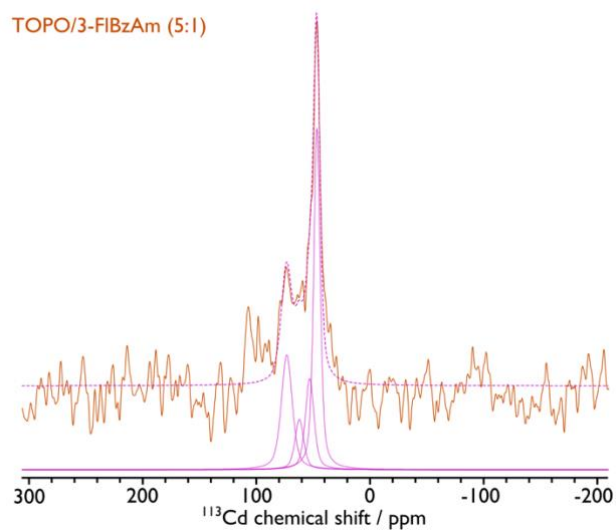
**Figure S7.**  $^{113}\text{Cd}$  MAS NMR spectrum of TOPO/3-FIAn (1:1) CdS NCs and associated fitting with deconvolution (pink) and summation (dashed pink).



**Figure S8.**  $^{113}\text{Cd}$  MAS NMR spectrum of TOPO/3-FIBzAm (64:1) CdS NCs and associated fitting with deconvolution (pink) and summation (dashed pink).



**Figure S9.**  $^{113}\text{Cd}$  MAS NMR spectrum of TOPO/3-FIBzAm (10:1) CdS NCs and associated fitting with deconvolution (pink) and summation (dashed pink).

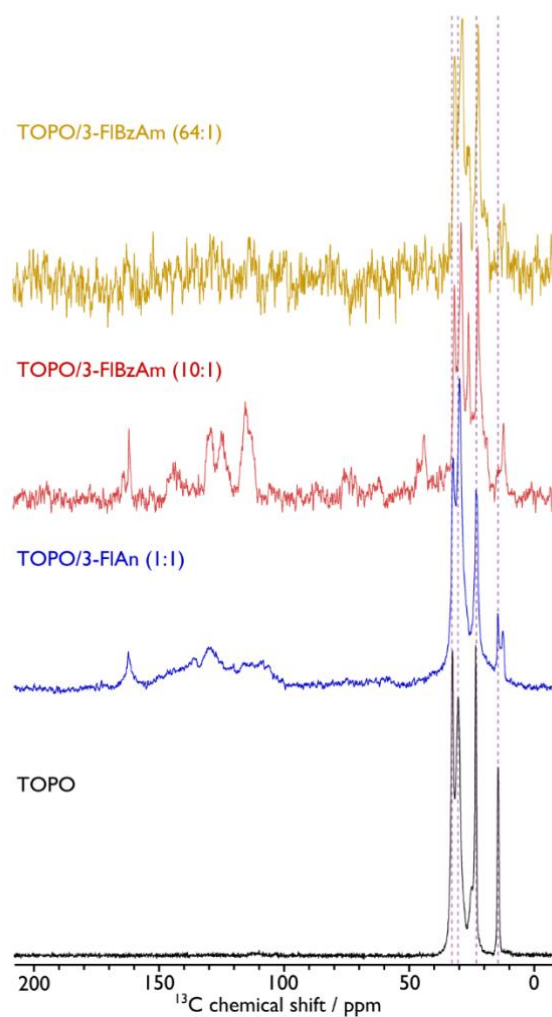


**Figure S10.**  $^{113}\text{Cd}$  MAS NMR spectrum of TOPO/3-FIBzAm (5:1) CdS NCs and associated fitting with deconvolution (pink) and summation (dashed pink).

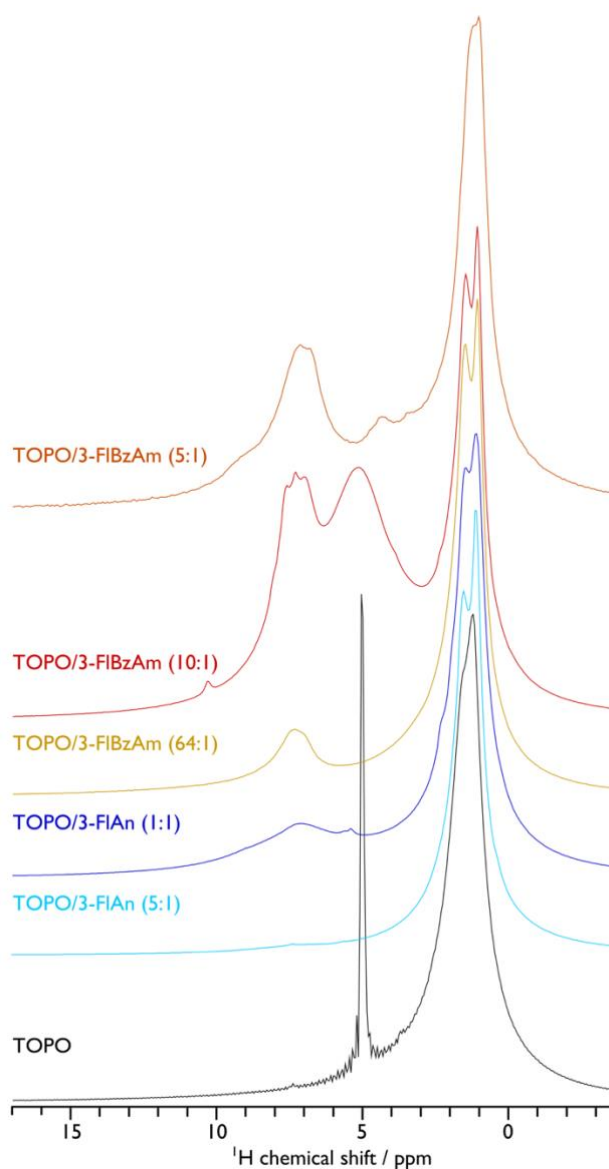


**Table S1.**  $^{113}\text{Cd}$  NMR parameters extracted from data fitting (see Figs. S2-S7). The fits are not definitive owing to the large associated errors and ambiguity.

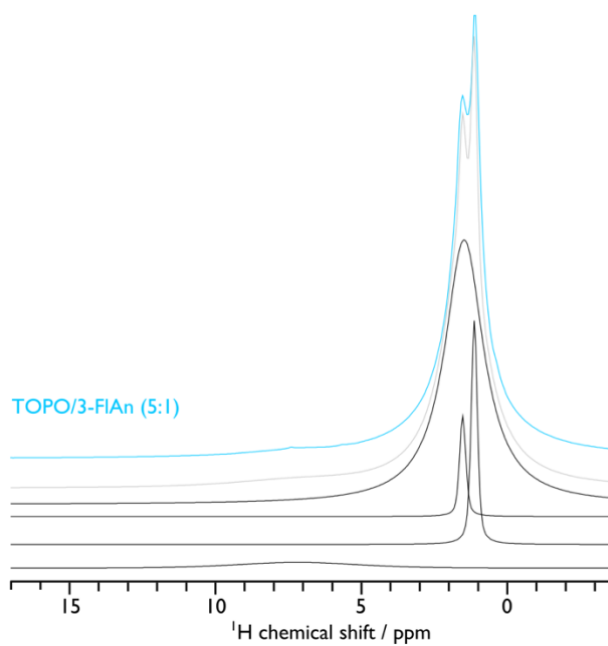
<b>CdS nanocrystal system</b>	<b><math>^{19}\text{F}</math> chemical shift (<math>\delta_{\text{iso}}</math>) / ppm</b>	<b><math>^{19}\text{F}</math> linewidth (FWHM) / Hz</b>	<b>Relative integral / %</b>
TOPO only	34	1500	21
	48	1100	24
	57	1000	15
	66	1000	14
	74	1000	5
	81	2000	21
TOPO:3-FlAn (5:1)	34	1500	2
	48	1100	16
	57	1000	12
	66	1000	21
	74	1000	22
	81	2000	27
TOPO:3-FlAn (1:1)	34	1500	5
	48	1100	17
	57	1000	15
	66	1000	17
	74	1000	17
	81	2000	29
TOPO:3-FIBzAm (64:1)	46	800	33
	54	800	23
	63	800	23
	71	800	21
TOPO:3-FIBzAm (10:1)	48	680	31
	54	505	9
	63	1150	36
	71	605	24
TOPO:3-FIBzAm (5:1)	48	600	47
	54	800	26
	63	800	17
	74	1000	10



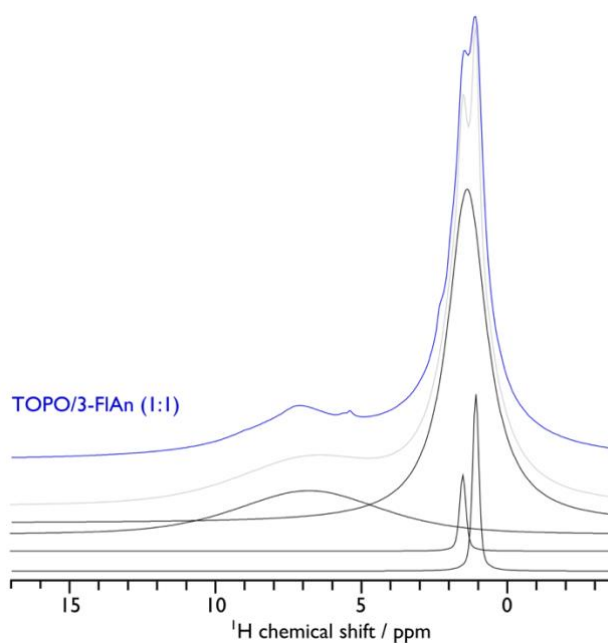
**Figure S11.**  $\{^1\text{H}\}\text{-}^{13}\text{C}$  CPMAS NMR spectra. An MAS frequency of 8 kHz was used for TOPO, 10 kHz was used for TOPO/3-FIAn (1:1) and TOPO/3-FIBzAm (10:1), and 12 kHz was used for TOPO/3-FIBzAm (64:1) CdS NCs. The dashed vertical lines are a guide for the eye.



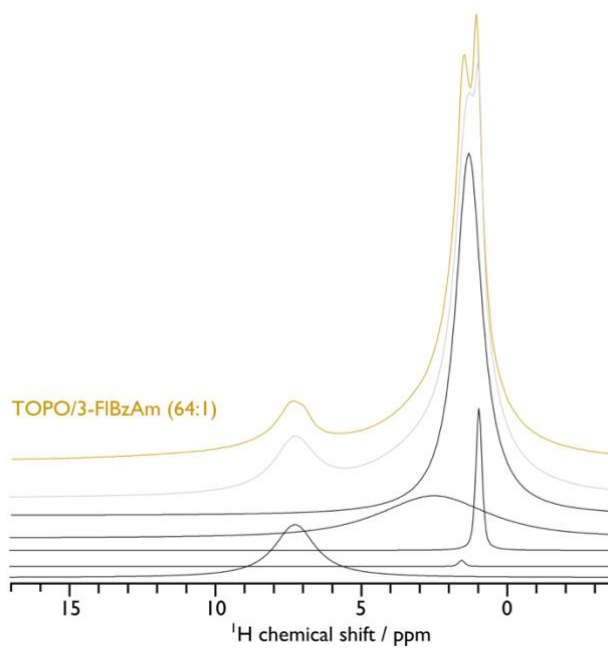
**Figure S12.**  $^1\text{H}$  MAS NMR spectra. An MAS frequency of 10 kHz was used for TOPO/3-FIAn (1:1), TOPO/3-FIBzAm (10:1), and TOPO/3-FIBzAm (5:1), and 12 kHz was used for TOPO, TOPO/3-FIAn (5:1), and TOPO/3-FIBzAm (64:1) CdS NCs.



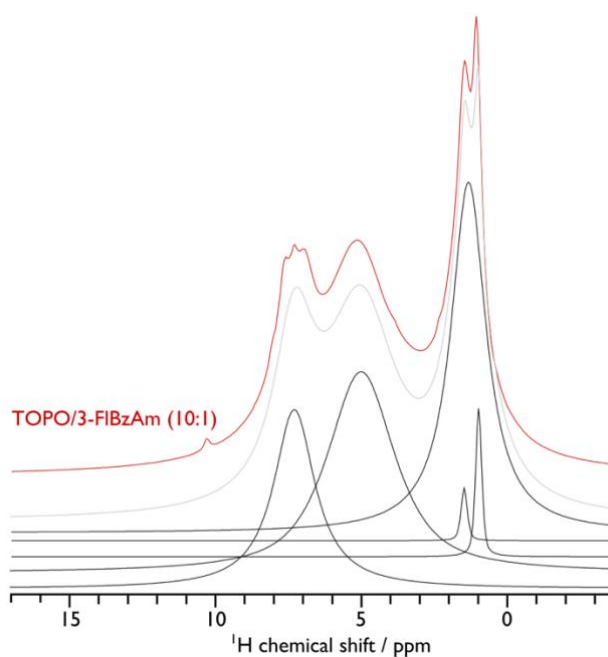
**Figure S13.**  $^1\text{H}$  MAS NMR spectrum of TOPO/3-FIAn (5:1) CdS NCs and associated fitting with deconvolution (black) and summation (grey).



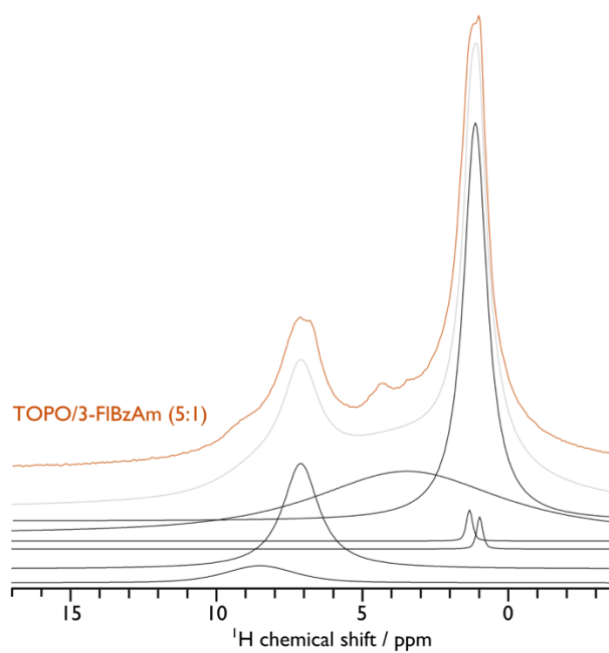
**Figure S14.**  $^1\text{H}$  MAS NMR spectrum of TOPO/3-FIAn (1:1) CdS NCs and associated fitting with deconvolution (black) and summation (grey).



**Figure S15.**  $^1\text{H}$  MAS NMR spectrum of TOPO/3-FIBzAm (64:1) CdS NCs and associated fitting with deconvolution (black) and summation (grey).



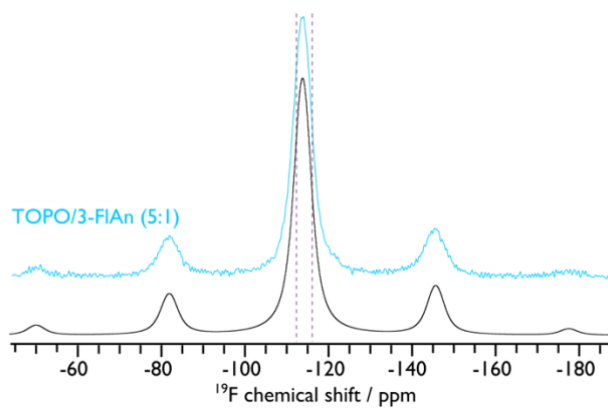
**Figure S16.**  $^1\text{H}$  MAS NMR spectrum of TOPO/3-FIBzAm (10:1) CdS NCs and associated fitting with deconvolution (black) and summation (grey).



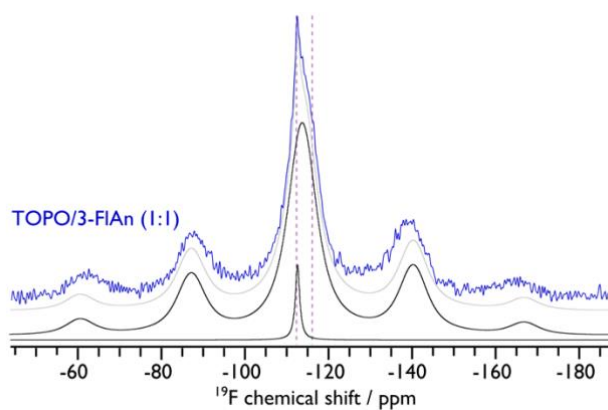
**Figure S17.**  $^1\text{H}$  MAS NMR spectrum of TOPO/3-FIBzAm (5:1) CdS NCs and associated fitting with deconvolution (black) and summation (grey).

**Table S2.**  $^1\text{H}$  NMR parameters extracted from data fitting (see Figs. S10-S14). The fits are not definitive owing to the large associated errors and ambiguity.

<b>CdS nanocrystal system</b>	<b><math>^1\text{H}</math> chemical shift (<math>\delta_{\text{iso}}</math>) / ppm</b>	<b><math>^1\text{H}</math> linewidth (FWHM) / Hz</b>	<b>Relative integral / %</b>	<b>TOPO:ligand molar ratio (from <math>^1\text{H}</math> integral)</b>	<b>Expected TOPO:ligand molar ratio</b>
TOPO only	N/A	N/A	N/A	N/A	N/A
TOPO:3-FlAn (5:1)	1	100	9	1.6:1	1.5:1
	1.4	650	82		
	1.5	100	4		
	7.4	2000	5		
TOPO:3-FlAn (1:1)	1	100	4	1:4.7	1:3.5
	1.4	650	67		
	1.5	100	2		
	7.4	2300	27		
TOPO:3-FlBzAm (64:1)	1	100	4	1:2.7	16:1
	1.4	440	57		
	1.5	100	0		
	2.6	1800	26		
	7.4	680	13		
TOPO:3-FlBzAm (10:1)	1	100	2	1:7.0	3:1
	1.4	580	37		
	1.5	100	1		
	5.1	1100	38		
	7.4	680	22		
TOPO:3-FlBzAm (5:1)	1	100	1	1:6.3	1.5:1
	1.4	390	37		
	1.5	100	1		
	3.2	3000	42		
	7.4	600	15		
	8.6	1120	4		

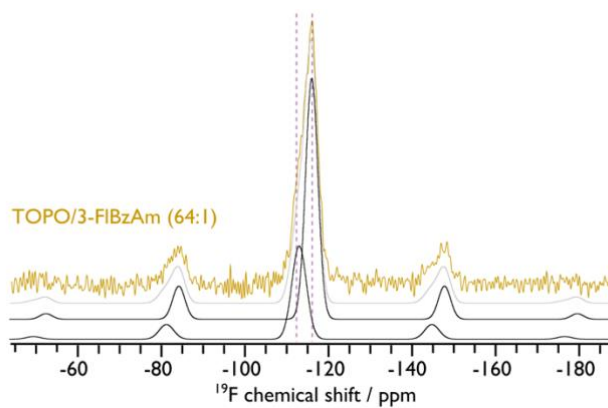


**Figure S18.**  $\{^1\text{H}\}\text{-}^{19}\text{F}$  CP MAS NMR spectrum of TOPO/3-FIAn (5:1) CdS NCs and associated fit (black). The positions indicated with the vertical dashed lines are the same as those given in Figure 5 of the main text.

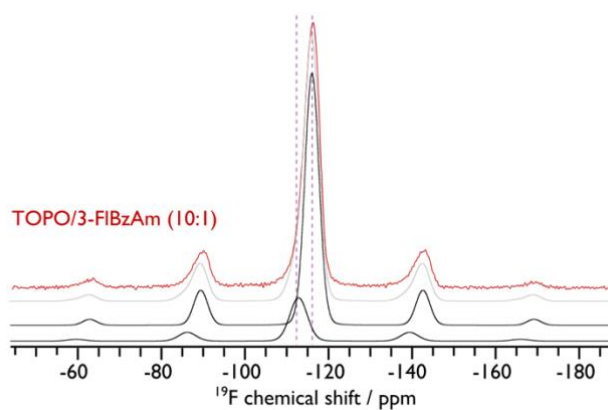


**Figure S19.**  $\{^1\text{H}\}\text{-}^{19}\text{F}$  CP MAS NMR spectrum of TOPO/3-FIAn (1:1) CdS NCs and associated fitting with deconvolution (black) and summation (grey). The positions indicated with the vertical dashed lines are the same as those given in Figure 5 of the main text.

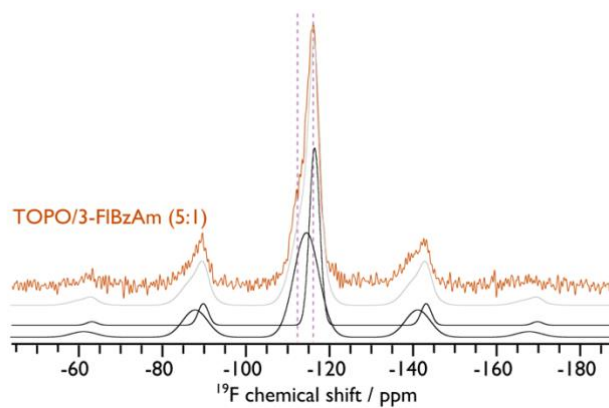




**Figure S20.**  $\{^1\text{H}\}\text{-}^{19}\text{F}$  CP MAS NMR spectrum of TOPO/3-FIBzAm (64:1) CdS NCs and associated fitting with deconvolution (black) and summation (grey). The positions indicated with the vertical dashed lines are the same as those given in Figure 5 of the main text.



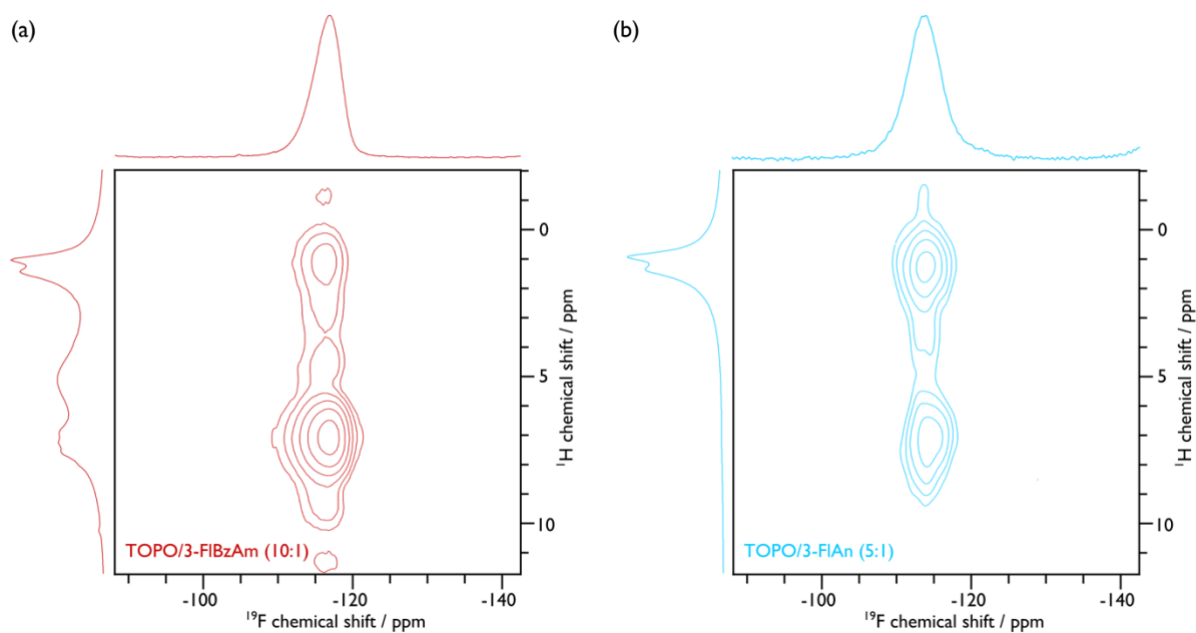
**Figure S21.**  $\{^1\text{H}\}\text{-}^{19}\text{F}$  CP MAS NMR spectrum of TOPO/3-FIBzAm (10:1) CdS NCs and associated fitting with deconvolution (black) and summation (grey). The positions indicated with the vertical dashed lines are the same as those given in Figure 5 of the main text.



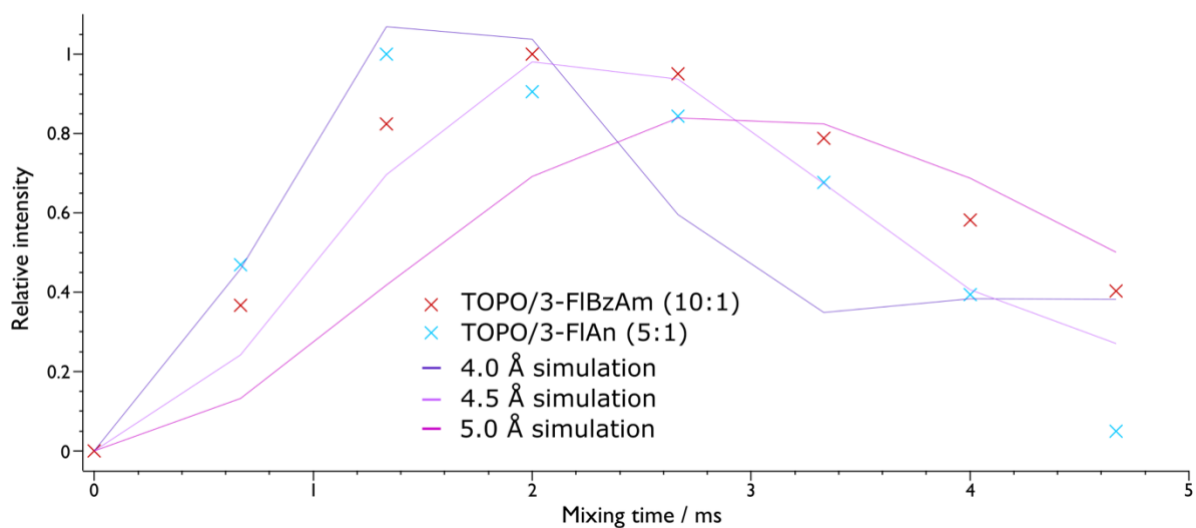
**Figure S22.**  $\{^1\text{H}-\}^{19}\text{F}$  CP MAS NMR spectrum of TOPO/3-FIBzAm (5:1) CdS NCs and associated fitting with deconvolution (black) and summation (grey). The positions indicated with the vertical dashed lines are the same as those given in Figure 5 of the main text.

**Table S3.**  $^{19}\text{F}$  NMR parameters extracted from data fitting (see Figs. S15-S19). The values given for the span ( $\Omega = \delta_{11} - \delta_{33}$ ) and skew ( $\kappa = 3(\delta_{22} - \delta_{iso})/\Omega$ ) are not definitive owing to the large errors with the fitting.

<b>CdS nanocrystal system</b>	<b><math>^{19}\text{F}</math> chemical shift (<math>\delta_{iso}</math>) / ppm</b>	<b><math>^{19}\text{F}</math> chemical shift span (<math>\Omega</math>) / ppm</b>	<b><math>^{19}\text{F}</math> chemical shift skew (<math>\kappa</math>)</b>	<b>Relative integral / %</b>
TOPO only	N/A	N/A	N/A	N/A
TOPO:3-FIAn (5:1)	-113.7	83	-0.2	100
TOPO:3-FIAn (1:1)	-113.7 -112.6	87 0	-0.2 N/A	97 3
TOPO:3-FIBzAm (64:1)	-116.0 -113.0	76 80	0 0	68 32
TOPO:3-FIBzAm (10:1)	-116.1 -112.9	64 76	0 0	81 19
TOPO:3-FIBzAm (5:1)	-117.5 -115.5	60 84	0 0	35 65

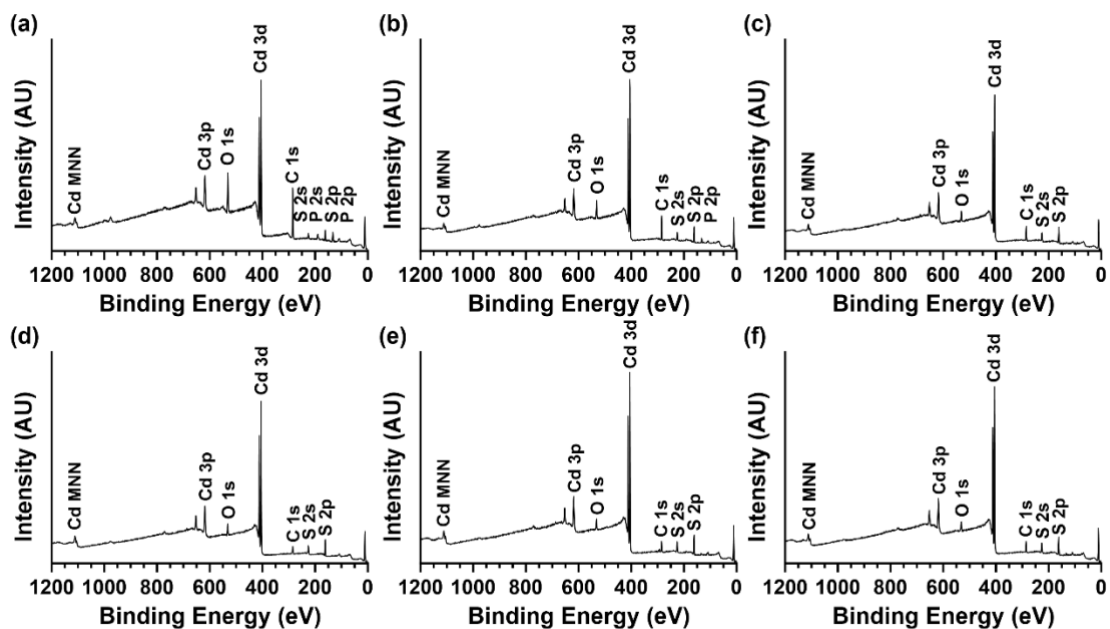


**Figure S23.**  ${}^1\text{H}$ - ${}^{19}\text{F}$  2D dipolar correlation MAS NMR spectra of indicated CdS NCs. An MAS frequency of 12 kHz was used for both. Corresponding  $\{{}^1\text{H}\}$ - ${}^{19}\text{F}$  CP (top) and  ${}^1\text{H}$  (left) MAS NMR spectra are provided for comparison.

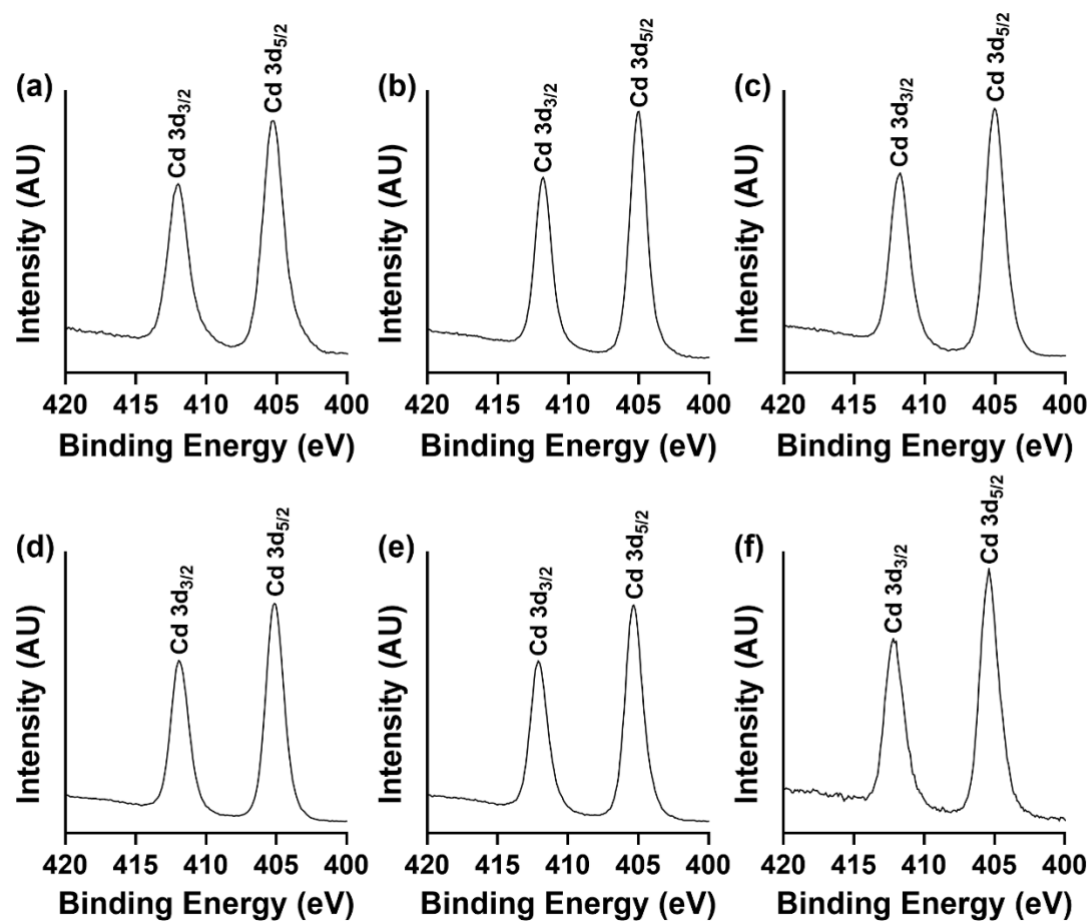


**Figure S24.** Plots of relative intensity of 1D  $^{19}\text{F}$  homonuclear double-quantum-filtered dipolar correlation NMR spectra as a function of SPC-5<sup>1</sup> mixing time for (a) TOPO/3-FIBzAm (10:1) and (b) TOPO/3-FIAn (5:1) CdS NCs. An MAS frequency of 12 kHz was used for both datasets. Also shown are numerical simulations using SIMPSON<sup>2</sup> software for the corresponding intensity buildup curves for the indicated internuclear distances.

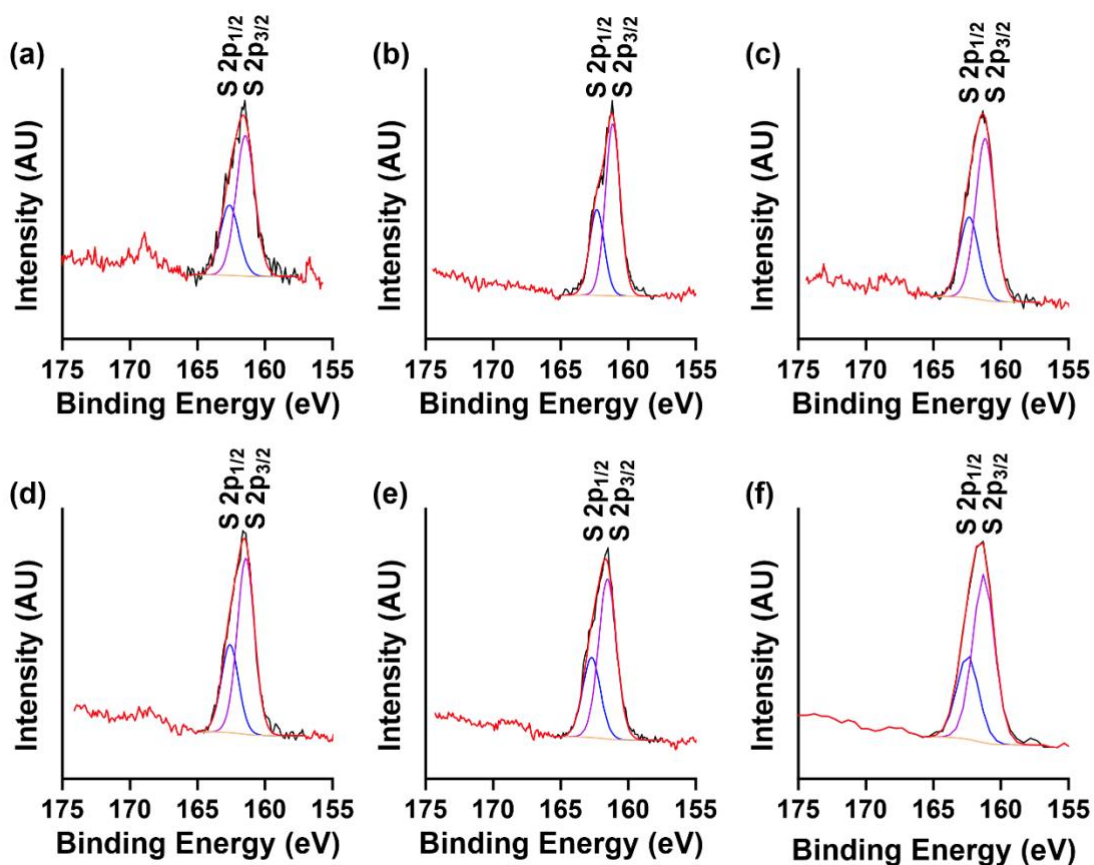
## X-ray photoelectron spectroscopy



**Figure S25.** XPS survey spectra where (a) TOPO only, (b) 5:1 TOPO:3-F1An, (c) 1:1 TOPO:3-F1An, (d) 5:1 TOPO:3-FIBzAm, (e) 10:1 TOPO:3-FIBzAm and (f) 64:1 TOPO:3-FIBzAm are all shown.



**Figure S26.** Cd3d of the XPS analysis where (a) TOPO only, (b) 5:1 TOPO:3-FIAn, (c) 1:1 TOPO:3-FIAn, (d) 5:1 TOPO:3-FIBzAm, (e) 10:1 TOPO:3-FIBzAm and (f) 64:1 TOPO:3-FIBzAm are all shown.



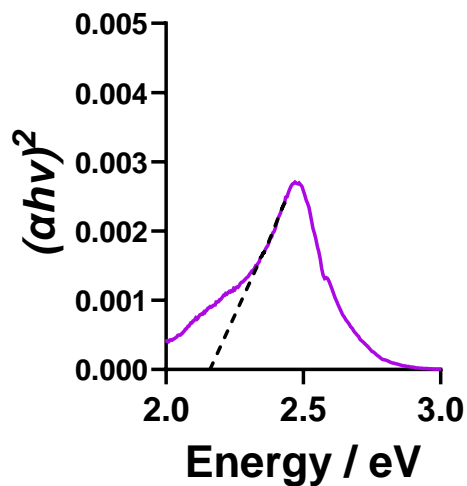
**Figure S27.** S2p of the XPS analysis where (a) TOPO only, (b) 5:1 TOPO:3-FIAn, (c) 1:1 TOPO:3-FIAn, (d) 5:1 TOPO:3-FIBzAm, (e) 10:1 TOPO:3-FIBzAm and (f) 64:1 TOPO:3-FIBzAm are all shown.

**Table S4.** Relative elemental amount from XPS quantification.

CdS NC system	C 1s %	Cd %	O 1s %	P 2p %	S 2p %
TOPO only	54.66	13.26	14.83	10.11	7.13
TOPO:3-FIAn (5:1)	40.02	21.20	12.66	7.77	18.35
TOPO:3-FIAn (1:1)	37.71	24.92	9.03	1.89	26.46
TOPO:3-FIBzAm (5:1)	25.62	30.98	12.06	0.93	30.41
TOPO:3-FIBzAm (10:1)	24.68	30.29	10.31	2.85	31.87
TOPO:3-FIBzAm (64:1)	27.14	28.47	10.41	4.37	29.61



## Band gap analysis



**Figure S28.** Calculated Tauc plot of the 64:1 TOPO:3-FIBzAm synthesised CdS nanocrystals suspended in toluene.

**Table S5.** Table of data for Scherrer analysis particle size and UV-Vis Tauc plot band gap energy of the synthesised CdS nanocrystals.

CdS nanocrystal system	Particle size (Scherrer) / nm	Band gap energy / eV
TOPO only	19	2.7
TOPO:3-FIAn (5:1)	37	2.2
TOPO:3-FIAn (1:1)	70	2.3, 3.7
TOPO:3-FIBzAm (64:1)	80	2.2, 4.2
TOPO:3-FIBzAm (10:1)	83	4.1
TOPO:3-FIBzAm (5:1)	200	4.0

## References

- 1 M. Hohwy, C. M. Rienstra, C. P. Jaroniec and R. G. Griffin, *The Journal of Chemical Physics*, 1999, **110**, 7983–7992.
- 2 M. Bak, J. T. Rasmussen and N. Chr. Nielsen, *Journal of Magnetic Resonance*, 2011, **213**, 366–400.