Supplementary Information

Design of Experiment to obtain a systematic understanding of the effect of synthesis parameters on the properties of perovskite nanocrystals

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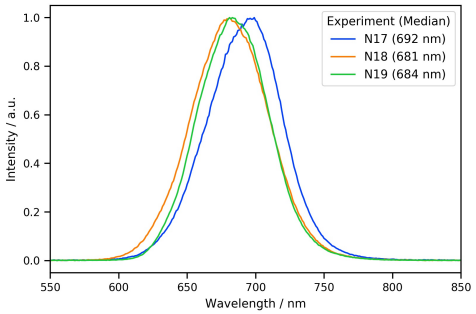
Broad Screening Design

Table S1: Reactant and purification solvents selected for broad screening design. For the reactant solvent, the polarity was fixed at 1 indicating a non-polar solvent, and the polarizability was varied from a low polarizability (-1) to a high polarizability (1). For the purification solvent, polarity and polarizability was varied which therefore covered a wider range of solvent properties. Polar solvents have a -1 value. 0 indicates the centre point, a moderately polar or polarizable solvent.

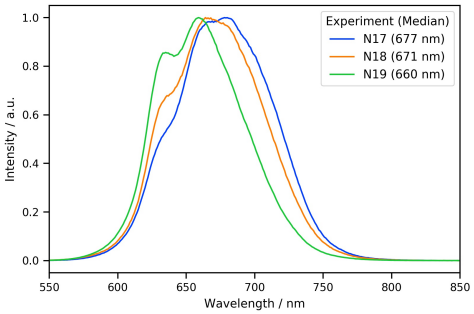
Solvent	Polarity	Polarizability	Solvent used
Reaction	1	-1	Hexane
Reaction	1	0	Dodecane
Reaction	1	1	1-octadecene
Purification	-1	-1	Ethyl acetate
Purification	-1	1	Dichloromethane
Purification	0	0	Ethyl butanoate
Purification	1	-1	Hexane
Purification	1	1	Mesitylene

Table S2: Broad screening median, interquartile range (IQR) and intensity results for the S1 and S2 supernatants.

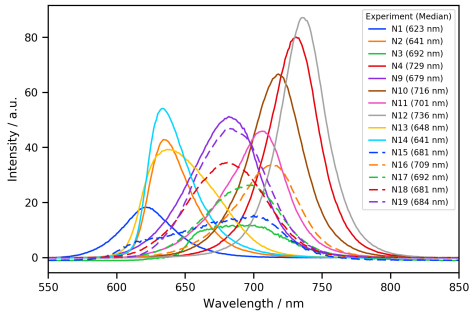
	S1			S2		
Exp no.	Median / nm	IQR / nm	Intensity / a.u.	Median / nm	IQR / nm	Intensity / a.u.
N1	622.9	28.0	18.5	670.0	80.1	1.2
N2	641.0	24.0	43.0	637.0	28.0	37.6
N3	692.0	40.0	1.0	726.0	30.0	370.9
N4	729.0	26.9	80.2	716.0	39.0	86.4
N5						
N6						
N7						
N8						
N9	679.0	35.0	51.3	641.0	64.0	169.2
N10	716.0	29.0	66.8	741.9	28.9	55.3
N11	701.0	33.1	46.0	750.0	26.0	49.8
N12	736.0	25.1	87.3	655.0	43.0	382.1
N13	648.0	35.0	39.4	700.0	65.0	22.5
N14	641.0	25.0	54.3	651.0	32.0	1.4
N15	681.0	51.9	0.5	726.0	38.0	4.6
N16	709.0	32.9	33.9	733.0	31.9	60.1
N17	692.0	37.0	26.4	677.0	48.0	131.1
N18	681.0	38.0	34.6	671.0	48.0	150.9
N19	683.9	34.0	47.0	660.0	45.0	171.3



(a) S1

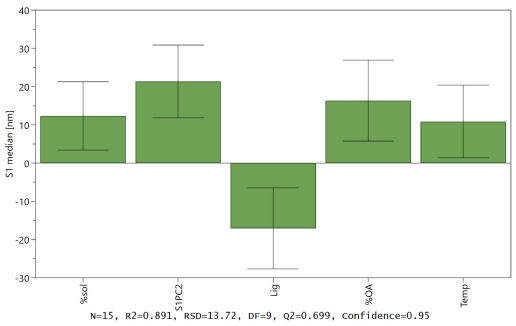


(b) S2

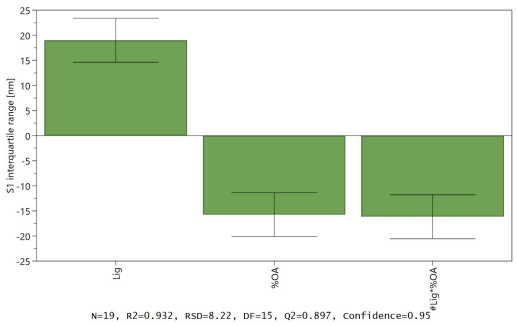


(c) S1 unnormalised

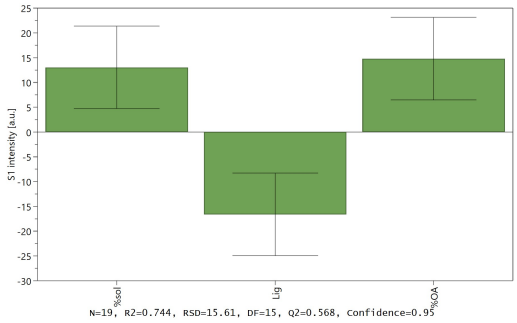
Figure S1: Normalised photoluminescence emission for the (a) unpurified S1 and (b) purified S2 supernatants in the broad screening design centre point experiments N17-N19, and (c) unnormalised PL emission for all the experiments in the broad screening design.



(a) Peak position



(b) Peak width



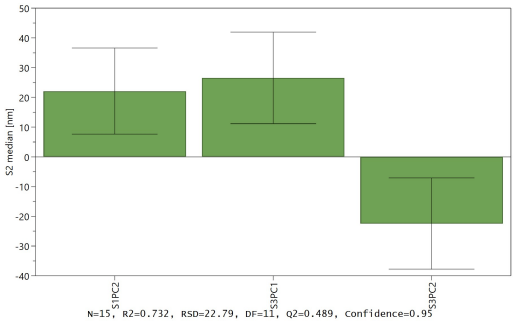
(c) Peak intensity

Figure S2: Broad screening design S1 coefficient plots for photoluminescence peak: (a) position (median), (b) width (IQR) and (c) intensity

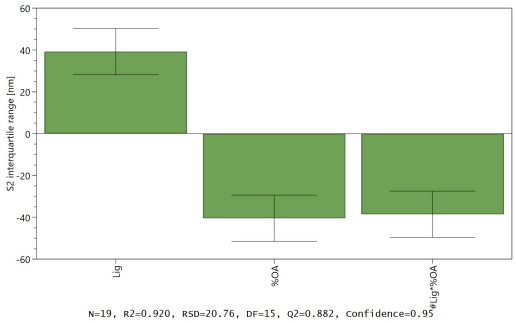
Coefficient plots were used to build the models by identifying significant and insignificant factors. In the centre is the average median, interquartile range or intensity for the entire dataset. Bars above (or below) the centre line indicate that the higher value of each factor, on average, increases (or decreases) the value of that response compared to the average of the entire dataset. For example in Figure S2 (a), the sol% (solvent ratio) bar indicates that increasing the amount of the reactant solvent in relation to 1-butanol (%sol = 65%) red shifts the PL median by 12.4 nm. Meanwhile increasing the ligand concentration (ligand:Pb = 18:1) blue shifts the PL median by 17.1 nm compared to the average of the dataset. Main terms and interactions where the error bars pass through 0 are immediately excluded from the model. Exceptions to this are when a main term is insignificant by itself but is involved with a significant interaction with another main term, as shown in Figure S5 (b).

Table S3: R^2, Q^2, model validity and reproducibility ranges for poor, satisfactory and good fit models.

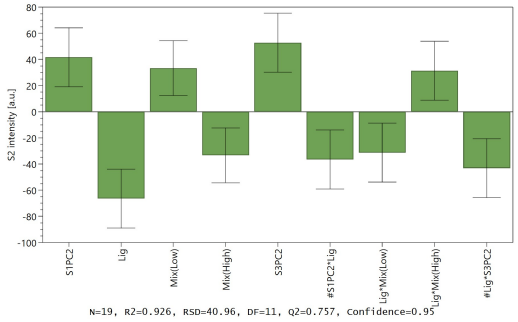
Model metric	Poor fit	Satisfactory fit	Good fit
R^2	< 0.50		0.50 - 1.00
Q^2	< 0.10	0.10 - 0.50	0.50 - 1.00
Model validity	< 0.25		0.25 - 1.00
Reproducibility	< 0.50		0.50 - 1.00



(a) Peak position



(b) Peak width



(c) Peak intensity

Figure S3: Broad screening design S2 coefficient plots for photoluminescence peak: (a) position (median), (b) width (IQR) and (c) intensity

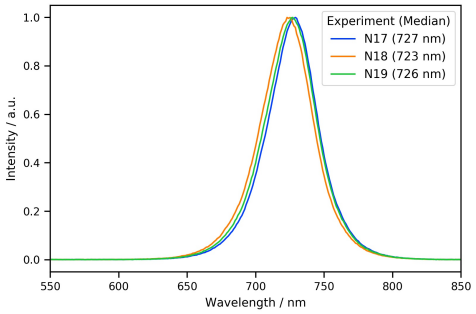
Table S4: Model results for the broad screening design

Supernatant	R^2	Q^2	Model validity	Reproducibility
S1 position	0.89	0.70	0.49	0.97
S2 position	0.73	0.49	0.45	0.95
S1 width	0.93	0.90	0.26	0.99
S2 width	0.92	0.88	−0.20	0.99
S1 intensity	0.74	0.57	0.72	0.86
S2 intensity	0.93	0.76	0.57	0.97

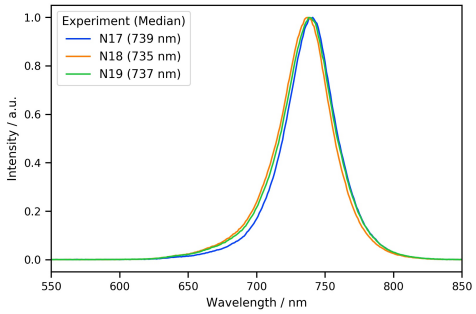
Refined Screening Design

Table S5: Reaction and purification solvents selected for refined screening design. For the reactant and purification solvent, the polarity was fixed at 1 indicating a non-polar solvent, and the polarizability was varied from a low polarizability −1 to high polarizability 1 with a moderately polarizability solvent as the centre point 0.

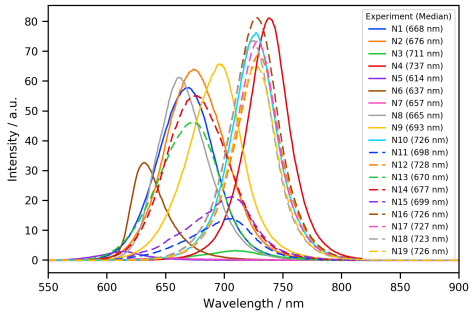
Solvent	Polarity	Polarizability	Solvent used
Reaction	1	−1	Hexane
Reaction	1	0	Dodecane
Reaction	1	1	1-octadecene
Purification	1	−1	Hexane
Purification	1	0	Toluene
Purification	1	1	Mesitylene



(a) S1



(b) S2



(c) S1 unnormalised

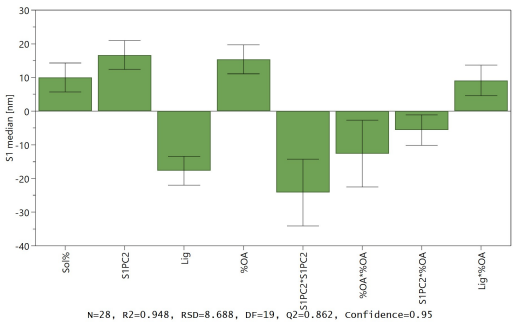
Figure S4: Normalised photoluminescence for the (a) unpurified S1 and (b) purified S2 supernatants in the refined screening design centre point experiments N17-N19, and (c) unnormalised PL emission for all the experiments in the refined screening design.

Table S6: Refined screening median, interquartile range and intensity results for the S1 and S2 supernatants.

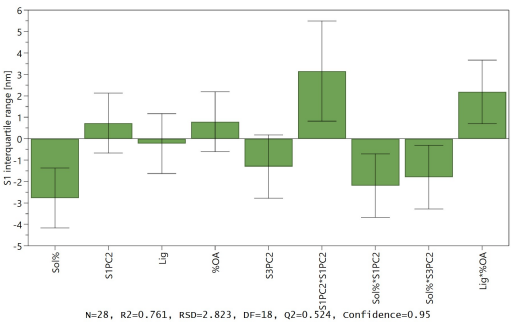
	S1			S2		
Exp no.	Median / nm	IQR / nm	Intensity / a.u.	Median / nm	IQR / nm	Intensity / a.u.
N1	668.0	32.9	57.8	708.0	40.0	58.6
N2	676.0	35.0	64.2	676.0	41.0	85.8
N3	711.0	41.0	3.4	746.9	28.0	65.2
N4	737.0	26.1	81.3	745.0	29.0	66.4
N5	614.1	26.0	2.8	645.1	25.0	40.3
N6	637.0	22.1	32.8	635.0	26.0	26.0
N7	657.0	35.0	5.4	638.0	33.0	718.1
N8	665.1	29.0	61.3	669.0	27.0	82.4
N9	693.0	32.0	65.9	741.9	30.9	57.8
N10	726.1	27.0	76.3	739.0	29.0	61.0
N11	698.0	39.1	14.0	744.0	26.9	57.5
N12	728.0	29.0	68.8	753.1	27.0	55.4
N13	670.0	35.0	46.5	732.0	30.9	63.6
N14	677.0	36.0	55.3	683.0	45.0	40.7
N15	699.0	39.1	21.5	745.0	28.0	59.2
N16	726.1	29.0	81.4	738.0	31.0	61.5
N17	727.0	27.1	73.7	739.0	26.9	68.7
N18	723.0	28.0	73.7	735.1	29.0	70.6
N19	726.1	28.0	65.6	737.0	29.0	65.3
N20	708.0	32.0	41.8	741.0	26.0	83.4
N21	726.1	29.0	73.0	701.0	52.1	37.9
N22	683.0	36.0	58.8	715.1	38.0	66.4
N23	723.0	28.0	59.5	741.9	26.0	78.3
N24	736.1	25.1	73.2	745.0	26.1	78.8
N25	709.0	31.9	62.3	711.0	44.9	52.0
N26	702.0	33.0	59.6	696.0	41.0	68.8
N27	727.0	28.0	63.0	743.1	26.0	71.1
N28	727.0	27.1	69.2	731.0	34.0	63.4
N29	727.0	27.1	69.2	730.0	37.0	58.2
N30	727.0	27.1	69.2	733.0	34.1	60.0

Table S7: Refined screening design models R^2, Q^2, model validity and reproducibility values

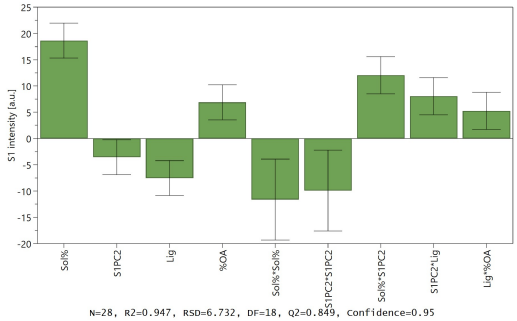
Supernatant	R^2	Q^2	Model validity	Reproducibility
S1 position	0.94	0.86	−0.11	1.00
S2 position	0.97	0.88	0.33	0.99
S1 width	0.63	0.24	−0.20	0.99
S2 width	0.24	−0.01	0.38	0.83
S1 intensity	0.95	0.85	0.56	0.97
S2 intensity	0.35	0.08	0.03	0.95



(a) Peak position

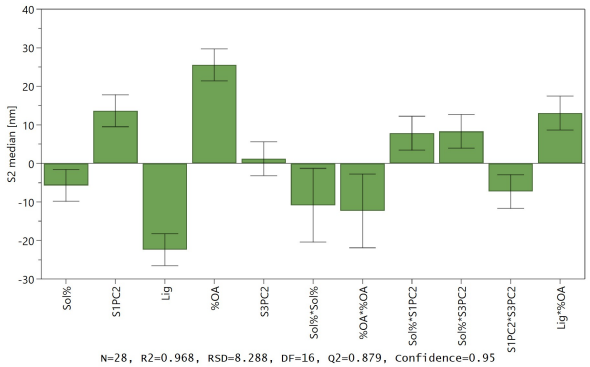


(b) Peak width

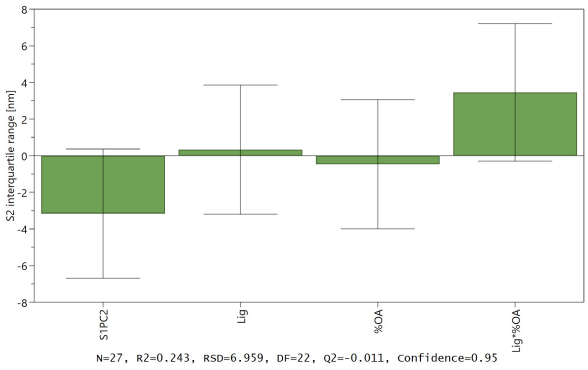


(c) Peak intensity

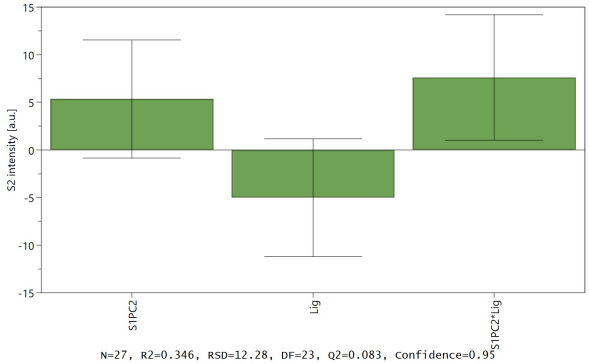
Figure S5: Refined screening design S1 coefficient plots for photoluminescence peak: (a) position (median), (b) width (IQR) and (c) intensity



(a) Peak position

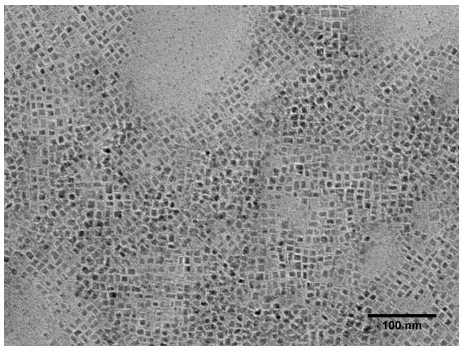


(b) Peak width

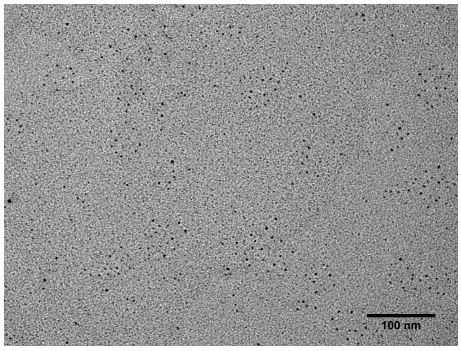


(c) Peak intensity

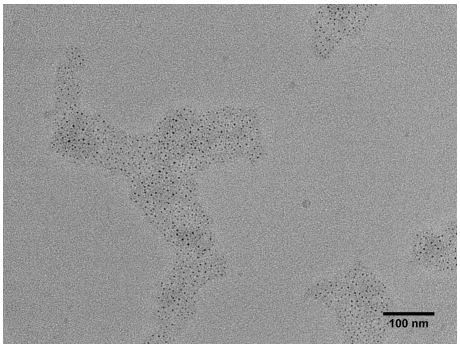
Figure S6: Refined screening design S2 coefficient plots for photoluminescence peak: (a) position (median), (b) width (IQR) and (c) intensity



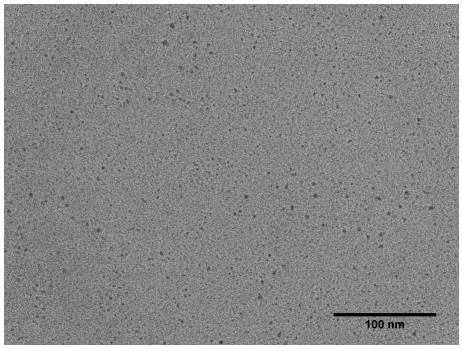
(a) N20 50% dodecane



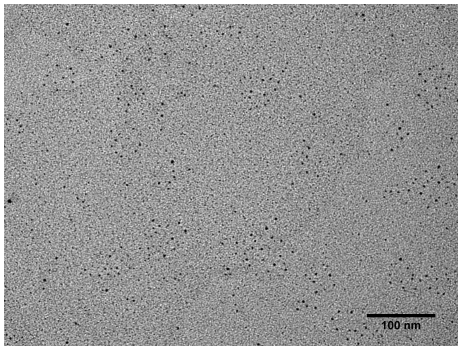
(b) N28 57.5% dodecane



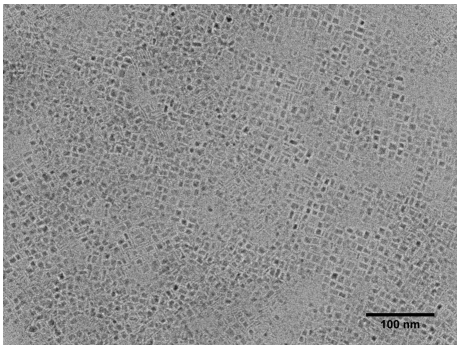
(c) N21 65% dodecane



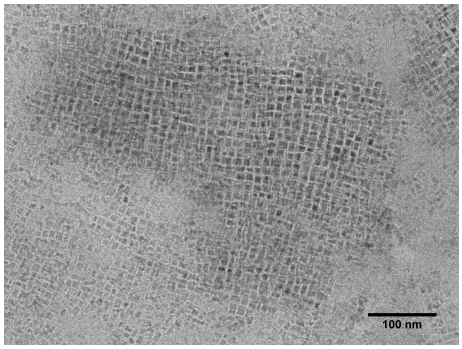
(d) N22 hexane



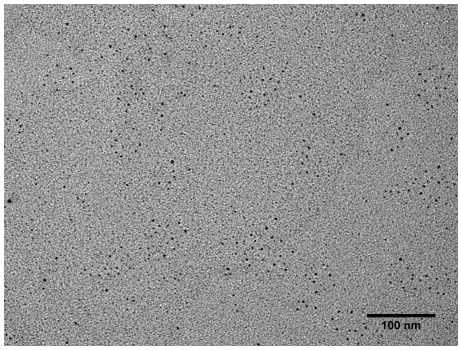
(e) N28 dodecane



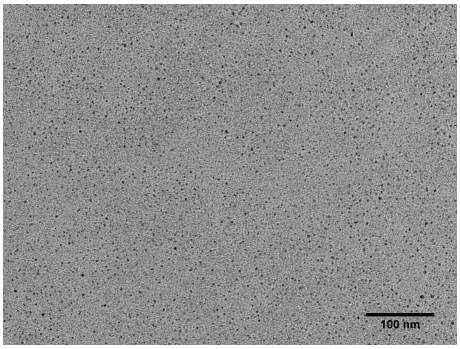
(f) N23 1-ODE



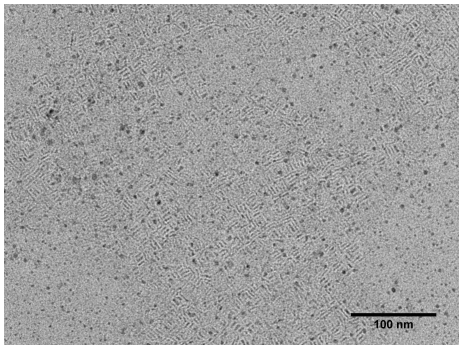
(g) N24 ligand:Pb = 6



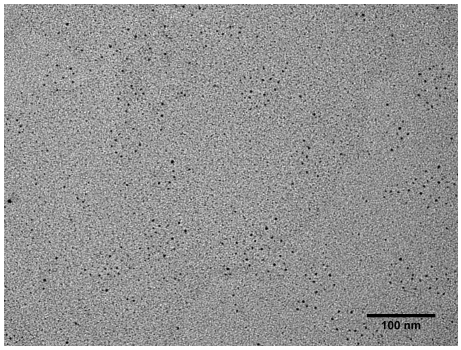
(h) N28 ligand:Pb = 8



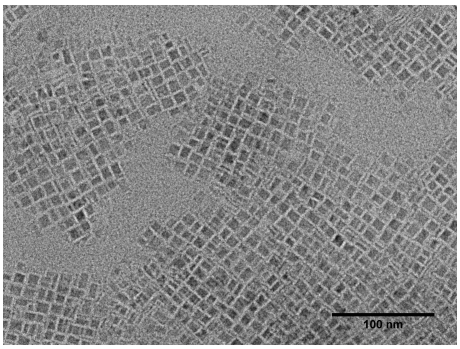
(i) N25 ligand:Pb = 10



(j) N26 50% OA

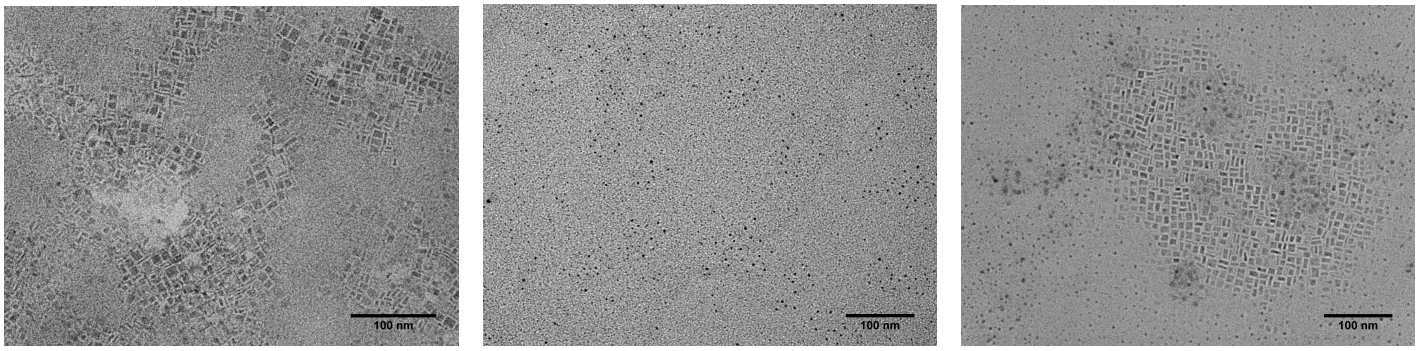


(k) N28 57.5% OA



(l) N27 65% OA

Figure S7: TEM images of N20-28 complementary experiments.



(a) N29 hexane (b) N28 toluene (c) N30 mesitylene

Figure S8: TEM images showing the effect of the purification solvents (a) hexane, (b) toluene and (c) mesitylene.

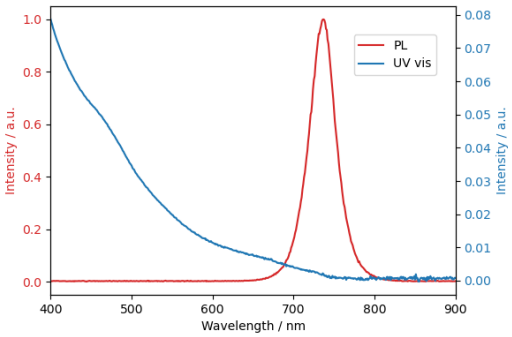
Design Validation

Table S8: Design validation target wavelengths and experimental conditions

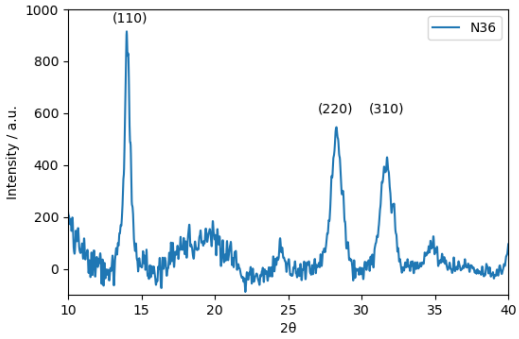
Exp no.	Target wavelength / nm	%S1	S1 solvent	Ligand:Pb	% OA	Wash solvent
N31	620	54.2	Hexane	10.0	50.2	Toluene
N32	640	64.8	Hexane	9.9	51.0	Toluene
N33	660	52.2	Hexane	9.9	57.7	Toluene
N34	680	51.6	Hexane	6.5	54.3	Toluene
N35	700	51.8	1-ODE	9.6	63.7	Toluene
N36	720	64.5	1-ODE	9.1	60.7	Toluene
N37	740	64.9	1-ODE	6.0	61.8	Toluene
N38		57.5	Dodecane	8.0	57.5	Toluene

Table S9: Design validation median, interquartile range and intensity results for the S1 and S2 supernatants.

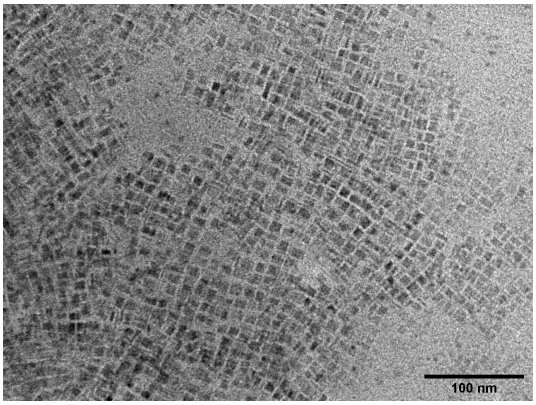
	S1			S2		
Exp no.	Median / nm	IQR / nm	Intensity / a.u.	Median / nm	IQR / nm	Intensity / a.u.
31	633.0	29.0	16.5	647.0	29.0	53.3
32	637.0	25.0	32.1	629.0	27.1	64.7
33	649.0	36.0	29.7	677.0	52.0	44.3
34	674.0	33.0	65.1	712.0	36.0	67.0
35	711.0	38.0	19.0	741.9	26.0	67.2
36	733.9	28.0	60.2	741.0	37.1	33.5
37	738.0	27.0	65.8	739.0	29.1	61.3
38	725.1	28.0	72.0	735.1	30.0	66.0



(a) PL and UV-vis



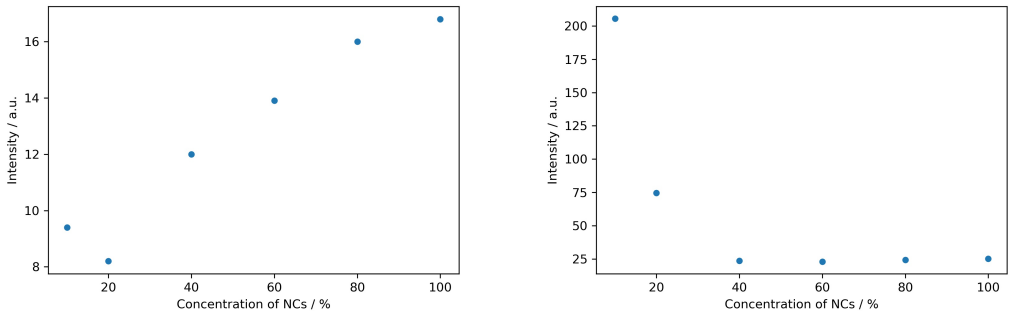
(b) XRD



(c) TEM

Figure S9: (a) Photoluminescence emission and UV-vis, (b) X-ray diffraction and (c) TEM image of N36 from the design validation.

Dilution of supernatants



(a) S1 (b) S2

Figure S10: Photoluminescence intensity vs the concentration colloidal solutions in the (a) unpurified S1 and (b) purified S2 supernatants.