

Supplementary Information

## **Quantum dots with photopolymerisable ligands for green-solvent direct photolithography**

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**Table S1** Boiling point, molar volume and HSPs for the OA-QDs and solvents.

	Materials	Boiling point °C	Molar volume mL/mol	$\delta_D$ MPa <sup>0.5</sup>	$\delta_P$ MPa <sup>0.5</sup>	$\delta_H$ MPa <sup>0.5</sup>	$R_a$ -	RED -
0	OA-QD			17.6	1.3	3.4	6.5	
1	Dichloromethane	39.6	171.2	18.2	6.3	6.1	5.813	0.888
2	Cyclohexanone	155.6	104.2	17.8	8.4	5.1	7.291	1.113
3	1,2,-dichlorobenzene	180.5	113	19.2	6.3	3.3	5.955	0.909
4	p-xylene	138.0	123.9	17.6	1	3.1	0.4359	0.067
5	tetrahydrofuran	66.0	81.9	16.8	5.7	8	6.544	0.999
6	nitromethane	100.0	54.3	15.8	18.8	5.1	17.898	2.733
7	diethylene glycol	245.0	94.9	16.6	12	20.7	20.443	3.122
8	ethanolamine	170.0	59.8	17	15.5	21.2	22.803	3.482
9	toluene	110.6	106.6	18	1.4	2	1.628	0.249
11	chloroform	61.2	80.5	17.8	3.1	5.7	2.968	0.453
12	chlorobenzene	132.0	102.1	19	4.3	2	4.357	0.665
13	hexane	68.7	131.4	14.9	0	0	6.428	0.982
14	n-octane	125.6	163.5	15.5	0	0	5.478	0.837
15	acetone	56.1	73.8	15.5	10.4	7	10.597	1.618
16	ethanol	78.2	58.5	15.8	8.8	19.4	18.0337	2.754
17	isopropyl alcohol	82.6	76.8	15.8	6.1	16.4	14.317	2.186
18	benzene	80.1	89.4	18.4	0	2	2.548	0.389
19	acetonitrile	81.6	52.6	15.3	18	6.1	17.480	2.669
20	diethyl ether	34.6	104.8	14.5	2.9	5.1	6.544	0.999
21	ethyl acetate	77.1	98.5	15.8	5.3	7.2	6.540	0.999
22	PGMEA	152.0	136.2	15.6	5.6	9.8	8.655	1.322
23	DGMEA	166.2	174.3	16.2	5.1	9.2	7.456	1.14
24	TGME	204.0	160.0	16.2	7.6	12.5	11.405	1.74
25	PGME	112.0	98.4	15.6	7.2	13.6	12.429	1.90
26	methyl benzoate	199.0	125.1	18.9	8.2	4.7	7.492	1.14

**Table S2** Boiling point, molar volume and HSPs for the MMES-QDs and solvents.

	Materials	Boiling point °C	Molar volume mL/mol	$\delta_D$ MPa <sup>0.5</sup>	$\delta_P$ MPa <sup>0.5</sup>	$\delta_H$ MPa <sup>0.5</sup>	$R_a$ -	RED -
0	MMES-QD			18.0	5.8	7.4	8.0	
1	Dichloromethane	39.6	171.2	18.2	6.3	6.1		
2	Cyclohexanone	155.6	104.2	17.8	8.4	5.1	3.530	0.442
3	1,2-dichlorobenzene	180.5	113	19.2	6.3	3.3	4.777	0.598
4	p-xylene	138.0	123.9	17.6	1	3.1	6.525	0.817
5	tetrahydrofuran	66.0	81.9	16.8	5.7	8	2.531	0.317
6	nitromethane	100.0	54.3	15.8	18.8	5.1	13.946	1.747
7	diethylene glycol	245.0	94.9	16.6	12	20.7	14.919	1.868
8	ethanolamine	170.0	59.8	17	15.5	21.2	16.965	2.125
9	toluene	110.6	106.6	18	1.4	2	6.993	0.876
11	chloroform	61.2	80.5	17.8	3.1	5.7	3.242	0.406
12	chlorobenzene	132.0	102.1	19	4.3	2	5.962	0.747
13	hexane	68.7	131.4	14.9	0	0	11.322	1.418
14	n-octane	125.6	163.5	15.5	0	0	10.704	1.341
15	acetone	56.1	73.8	15.5	10.4	7	6.859	0.859
16	ethanol	78.2	58.5	15.8	8.8	19.4	13.117	1.643
17	isopropyl alcohol	82.6	76.8	15.8	6.1	16.4	10.018	1.255
18	benzene	80.1	89.4	18.4	0	2	7.982	1.000
19	acetonitrile	81.6	52.6	15.3	18	6.1	13.438	1.683
20	diethyl ether	34.6	104.8	14.5	2.9	5.1	7.986	1.000
21	ethyl acetate	77.1	98.5	15.8	5.3	7.2	4.500	0.564
22	PGMEA	152.0	136.2	15.6	5.6	9.8	5.412	0.678
23	DGMEA	166.2	174.3	16.2	5.1	9.2	4.127	0.52
24	TGME	204.0	160.0	16.2	7.6	12.5	6.505	0.81
25	PGME	112.0	98.4	15.6	7.2	13.6	7.976	1.00
26	methyl benzoate	199.0	125.1	18.9	8.2	4.7	4.035	0.51

**Table S3** Boiling point, molar volume and HSPs for the N-BP ligand and solvents.

	Materials	Boiling point °C	Molar volume mL/mol	$\delta_D$ MPa <sup>0.5</sup>	$\delta_P$ MPa <sup>0.5</sup>	$\delta_H$ MPa <sup>0.5</sup>	$R_a$ -	RED -
0	N-BP			18.0	9.8	11.7	11.3	
1	Dichloromethane	39.6	171.2	18.2	6.3	6.1	6.592	0.584
2	Cyclohexanone	155.6	104.2	17.8	8.4	5.1	6.734	0.596
3	1,2-dichlorobenzene	180.5	113	19.2	6.3	3.3	9.365	0.829
4	p-xylene	138.0	123.9	17.6	1	3.1	12.326	1.091
5	tetrahydrofuran	66.0	81.9	16.8	5.7	8	6.049	0.536
6	nitromethane	100.0	54.3	15.8	18.8	5.1	11.995	1.062
7	diethylene glycol	245.0	94.9	16.6	12	20.7	9.733	0.862
8	ethanolamine	170.0	59.8	17	15.5	21.2	11.293	1.000
9	toluene	110.6	106.6	18	1.4	2	12.818	1.135
11	chloroform	61.2	80.5	17.8	3.1	5.7	8.998	0.797
12	chlorobenzene	132.0	102.1	19	4.3	2	11.293	1.000
13	hexane	68.7	131.4	14.9	0	0	16.493	1.460
14	n-octane	125.6	163.5	15.5	0	0	16.070	1.423
15	acetone	56.1	73.8	15.5	10.4	7	6.927	0.613
16	ethanol	78.2	58.5	15.8	8.8	19.4	9.000	0.797
17	isopropyl alcohol	82.6	76.8	15.8	6.1	16.4	7.509	0.665
18	benzene	80.1	89.4	18.4	0	2	13.797	1.222
19	acetonitrile	81.6	52.6	15.3	18	6.1	11.314	1.002
20	diethyl ether	34.6	104.8	14.5	2.9	5.1	11.883	1.052
21	ethyl acetate	77.1	98.5	15.8	5.3	7.2	7.778	0.689
22	PGMEA	152.0	136.2	15.6	5.6	9.8	6.721	0.595
23	DGMEA	166.2	174.3	16.2	5.1	9.2	6.477	0.57
24	TGME	204.0	160.0	16.2	7.6	12.5	4.384	0.39
25	PGME	112.0	98.4	15.6	7.2	13.6	5.873	0.52
26	methyl benzoate	199.0	125.1	18.9	8.2	4.7	7.353	0.65

**Table S4** Calculated RED values for PGMEA, DGMEA, TGME and PGME with respect to the OA-QDs, MMES-QDs and N-BP.

	$\delta_D$	$\delta_P$	$\delta_H$	$R_0$	RED
OA-QD	17.6	1.3	3.4	6.5	
PGMEA	15.6	5.6	9.8		1.34
DGMEA	16.2	5.1	9.2		1.15
TGME	16.2	7.6	12.5		1.76
PGME	15.6	7.2	13.6		1.91

	$\delta_D$	$\delta_P$	$\delta_H$	$R_0$	RED
MMES-QD	18	5.8	7.4	8	
PGMEA	15.6	5.6	9.8		0.67
DGMEA	16.2	5.1	9.2		0.51
TGME	16.2	7.6	12.5		0.81
PGME	15.6	7.2	13.6		1.00

	$\delta_D$	$\delta_P$	$\delta_H$	$R_0$	RED
N-BP	18	9.8	11.7	11.3	
PGMEA	15.6	5.6	9.8		0.83
DGMEA	16.2	5.1	9.2		0.80
TGME	16.2	7.6	12.5		0.54
PGME	15.6	7.2	13.6		0.72

**Table S5** Summary of QD patterning strategies using green solvents.

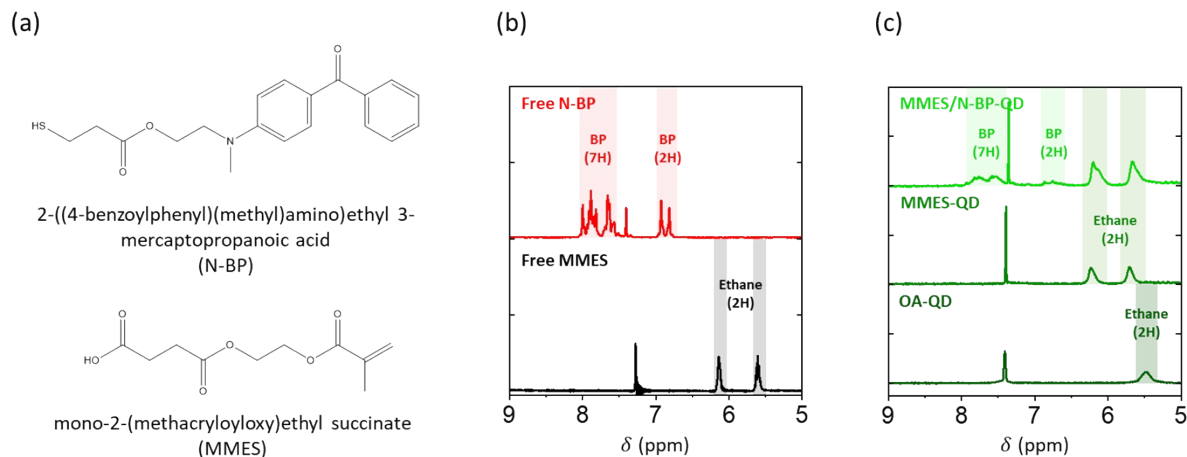
QD layer composition	Processing solvent	Applications	Ref
QD with monomeric dispersing ligand(N-BP) & photoinitiating ligand (MMES)	propylene glycol monomethyl ether acetate	QD light-emitting diode (electroluminescence)	<b>This work</b>
QD, PMMA, negative PR (SU-8)	$\gamma$ -butyrolactone	QD color conversion layer (photoluminescence)	1
QD, negative PR	N/A	QD color conversion layer (photoluminescence)	2
QD, negative PR	N/A	QD color conversion layer (photoluminescence)	3
QD, dispersant (DisperBYK), acrylate oligomer (PO94F)	propylene glycol monomethyl ether acetate	QD color conversion layer (photoluminescence)	4
Epoxy-silica coated QD, negative PR (SU-8)	$\gamma$ -butyrolactone, propylene glycol monomethyl ether acetate	QD color conversion layer (photoluminescence)	5
QD, acrylic oligomer (N/A), monomer (N/A), photoinitiator (N/A)	N/A	QD color conversion layer (photoluminescence)	6
SiO <sub>2</sub> -coated QD, dispersant (N/A), negative PR (SU-8)	propylene glycol monomethyl ether acetate, cyclopentanone, $\gamma$ -butyrolactone	QD color conversion layer (photoluminescence)	7
QD, acrylate, photoinitiator (1-hydroxycyclohexylphenyl ketone)	dipentaerythritol penta-acrylate, dipentaerythritol hexa-acrylate, pentaerythritol triacrylate, 4-acryl-oylmorpholine	QD color conversion layer (photoluminescence)	8
QD, acrylate, photoinitiator (1-hydroxycyclohexylphenyl ketone)	penta-acrylate, dipentaerythritol hexa-acrylate, pentaerythritol triacrylate, 4-acryl-oylmorpholine	QD color conversion layer (photoluminescence)	9
QD with dispersing ligand (MMES), negative PR	propylene glycol monomethyl ether acetate	QD color conversion layer (photoluminescence)	10
QD with dispersing ligand (MMES), acrylate resin (bisphenol A ethoxylated diacrylate, Irgacure Oxo-02)	propylene glycol monomethyl ether acetate	QD color conversion layer (photoluminescence) QD light-emitting diode (electroluminescence)	11
QD with photosensitizing ligands (MMPE or MEMA)	propylene glycol monomethyl ether acetate	QD light-emitting diode (electroluminescence)	12

**Table S6** Summary of previous QLEDs prepared using green solvents. The solvents in bold are non-green solvents that were used in preparing these devices.

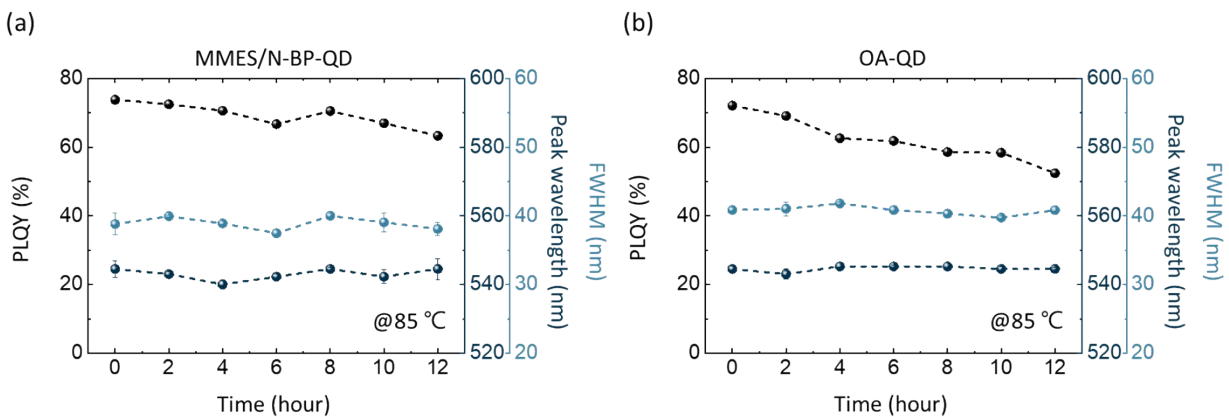
	Functional layers	Processing Solvents	Max EQE	Ref
HTL	TFB	cyclopentanone		
EML	In/ZnSe/ZnS	propylene glycol monomethyl ether acetate	1.5%	<b>This work</b>
ETL	ZnMgO NP	ethanol		
HTL	Poly-TPD	chlorobenzene		
EML	CdSe/ZnS QD (Green)	octane, cyclohexylbenzene	2.4%	13
ETL	ZnMgO NP	ethanol		
HTL	PVK	chlorobenzene		
EML	InP/ZnSe/ZnS QD (Red)	decane, cyclohexylbenzene	0.5%	14
ETL	ZnMgO NP	isopropanol		
HTL	TFB	chlorobenzene		
EML	CdSe/ZnS QD (Red)	decane, cyclohexylbenzene	9.32%	15
ETL	ZnO NP	ethanol		
HTL	TFB, PVK	chlorobenzene		
EML	InP/ZnSeS QD (Red)	octane, cyclohexylbenzene	0.02%	16
ETL	ZnMgO NP	ethanol		
HTL	TFB, PVK	chlorobenzene		
EML	InP/ZnSeS QD (Green)	octane, cyclohexylbenzene	0.14%	16
ETL	ZnMgO NP	ethanol		
HTL	TFB, PVK	chlorobenzene		
EML	ZnTeSe/ZnSeS/ZnS QD (Blue)	octane, cyclohexylbenzene	0.12%	16
ETL	ZnMgO NP	ethanol		
HTL	TFB	chlorobenzene		
EML	CdZnSe/ZnS QD (Red)	indane, cyclohexylbenzene	0.20%	17
ETL	ZnO NP	ethanol		
HTL	Poly-TPD	chlorobenzene		
EML	CdZnSe/ZnS QD (Red)	indane, cyclohexylbenzene	1.90%	17
ETL	ZnO NP	ethanol		
HTL	PVK	chlorobenzene		
EML	CdZnSe/ZnS QD (Red)	indane, cyclohexylbenzene	17.0%	17
ETL	ZnO NP	ethanol		
HTL	PF8CZ, FLCZ-V	chlorobenzene		
EML	CdSe/ZnS QD (Blue)	decahydronaphthalene, cyclohexylbenzene	9.2%	18
ETL	ZnMgO NP	ethanol		
HTL	TFB	chlorobenzene		
EML	CdSe/ZnS QD (Red)	octane, cyclohexylbenzene	N/A	19
ETL	ZnO NP	<i>n</i> -butanol, methanol, chloroform		
HTL	TFB	chlorobenzene		
EML	CdSe/ZnS QD (Green)	octane, cyclohexylbenzene	N/A	19
ETL	ZnO NP	<i>n</i> -butanol, methanol, chloroform		
HTL	TFB	N/A	16.6%	20

EML	CdSe/ZnSe QD (Red)	decane, cyclohexylbenzene		
ETL	ZnO NP	<i>n</i> -octanol, <i>n</i> -butanol		
HTL	PDA-FLCZ	chlorobenzene		
EML	CdSe/ZnS QD (Red)	cyclohexylbenzene, decahydronaphthalene	15.28	21
ETL	ZnMgO NP	N/A		
HTL	TFB	N/A		
EML	N/A (Red)	decane, cyclohexylbenzene	18.4%	22
ETL	ZnO NP	N/A		
HTL	TFB	N/A		
EML	N/A (Green)	decane, cyclohexylbenzene	13.3%	22
ETL	ZnO NP	N/A		
HTL	TFB	N/A		
EML	N/A (Blue)	decane, cyclohexylbenzene	5.6%	22
ETL	ZnO NP	N/A		
HTL	TFB	N/A		
EML	CdZnSe/ZnS QD (Red)	octane, 1-cyclohexyl-ethanol, <i>n</i> -butyl acetate	19.3%	23
ETL	ZnMgO NP	ethanol		
HTL	TFB	N/A		
EML	N/A (Green)	octane, 1-cyclohexyl-ethanol, <i>n</i> -butyl acetate	18.0%	23
ETL	ZnMgO NP	ethanol		
HTL	TFB	N/A		
EML	ZnCdSe/ZnS QD (Red)	octane, 1-cyclohexyl-ethanol, <i>n</i> -butyl acetate	4.4%	23
ETL	ZnMgO NP	ethanol		
HTL	TFB	N/A		
EML	N/A (Cd)	octane, 1-cyclohexyl-ethanol, <i>n</i> -butyl acetate	21.0%	24
ETL	ZnMgO NP	ethanol		
HTL	TFB	chlorobenzene		
EML	CdSe/ZnS QD (Red)	propylene glycol monomethyl ether acetate	22.0%	11
ETL	ZnMgO NP	ethanol		
HTL	TFB	chlorobenzene		
EML	CdSe/ZnS QD (Green)	propylene glycol monomethyl ether acetate	15.0%	11
ETL	ZnMgO NP	ethanol		
HTL	TFB	chlorobenzene		
EML	CdSe/ZnS QD (Blue)	propylene glycol monomethyl ether acetate	12.0%	11
ETL	ZnMgO NP	ethanol		
HTL	PVK	anisole		
EML	InP/ZnSe/ZnS QD (Green)	toluene	0.15%	25
ETL	ZnO NP	1-butanol		
HTL	PVK	cyclopentanone		
EML	InP/ZnSe/ZnS QD (Green)	toluene	1.0%	25
ETL	ZnO NP	1-butanol		
HTL	PVK:TCTA	anisole	1.0%	26
EML	CdSe/ZnS QD (Red)	toluene		

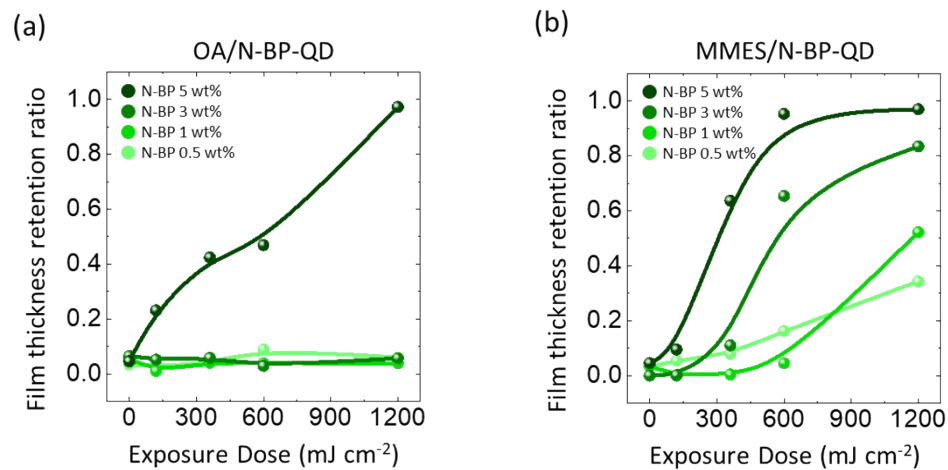
ETL	ZnO NP	N/A		
HTL	TCTA	physical vapor deposition		
EML	InP/ZnSe/ZnS QD (Green)	propylene glycol monomethyl ether acetate	2.0%	12
ETL	ZnO NP	ethanol		
HTL	TCTA	physical vapor deposition		
EML	InP/ZnSe/ZnS QD (Green)	diethylene glycol monobutyl ether acetate	2.88%	27
ETL	ZnO NP	N/A		
HTL	NPB	physical vapor deposition		
EML	CdSe/CdS/ZnS QD (Red)	nonane, cyclohexylbenzene	0.55%	28
ETL	ZnO	magnetron sputtering		



**Fig. S1** (a) Chemical structures of N-BP and MMES. (b)  $^1\text{H}$  NMR spectra of free MMES and N-BP acquired using  $\text{CDCl}_3$  as the NMR solvent.  $^1\text{H}$  NMR spectra of MMES ( $\delta$  6.23–6.05 (m, 1H), 5.73–5.55 (m, 1H), 4.43–4.16 (m, 4H), 2.69–2.53 (m, 4H), 2.06–1.79 (m, 3H)) and N-BP ( $\delta$  8.19–7.31 (m, 7H), 7.00–6.70 (m, 2H), 4.59–4.29 (t, 2H), 3.98–3.68 (t, 2H), 3.33–3.13 (s, 3H), 3.04–2.57 (m, 2H), 1.87–1.47 (m, 2H)), acquired at 298 K. (c)  $^1\text{H}$  NMR spectra of the OA-QDs, MMES-QDs and MMES/N-BP-QDs acquired using  $\text{CDCl}_3$  as the NMR solvent.  $^1\text{H}$  NMR data for the OA-QDs ( $\delta$  5.81–5.20 (2H, s), 2.75–1.98 (2H, d), 1.83–0.76 (25H, m)), MMES-QDs ( $\delta$  6.23–6.05 (m, 1H), 5.73–5.55 (m, 1H), 4.43–4.16 (m, 4H), 2.69–2.53 (m, 4H), 2.06–1.79 (m, 3H)) and N-BP ( $\delta$  8.19–7.31 (m, 7H), 7.00–6.70 (m, 2H), 4.59–4.29 (t, 2H), 3.98–3.68 (t, 2H), 3.33–3.13 (s, 3H), 3.04–2.57 (m, 2H), 1.87–1.47 (m, 2H)), measured at 298 K.

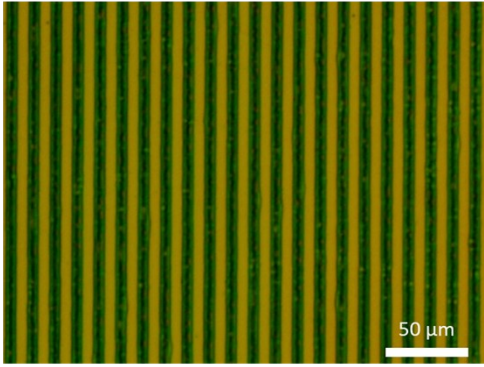


**Fig. S2** Luminescence characteristics retention (PLQY, peak wavelength and FWHM) of the (a) MMES/N-BP-QD and (b) OA-QD ink stored at 85 °C for 12 h. Error bar represents the standard deviation.

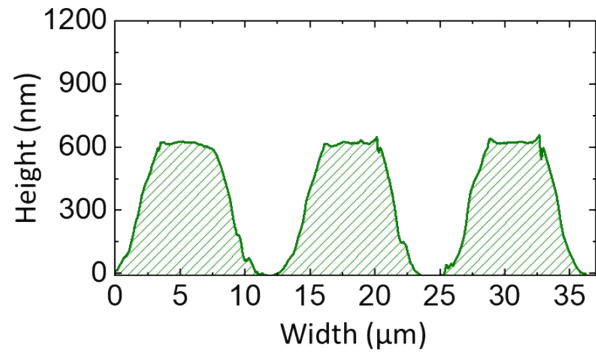


**Fig. S3** The film thickness retention ratio (FRR) graph of (a) OA/N-BP QD and (b) MMES/N-BP QD cases after irradiation under the ambient condition.

(a)



(b)



**Fig. S4** (a) OM image and (b) AFM height profile of the 600 nm line patterns

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