Supplementary Information

Enhanced Properties of Metal-Organic Framework Thin-Films Fabricated via a Coordination Modulation-controlled Layer-by-Layer processes

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Experimental

Materials

The starting materials (Table S1) were prepared using procedures described in our previous publications. Basic zinc acetate ($Zn_4O(OAc)_6$), a product of the sublimation of zinc acetate dihydrate at 280 ℃ under vacuum, was used as the pre-formed secondary building unit (SBU) metal precursor. The purity of basic zinc acetate was characterized by powder X-ray diffraction (PXRD) prior to using for MOF syntheses. Three different 3,5-alkyl-substituted-4-carboxypyrazole molecules i.e. 3,5-dimethyl-4-carboxypyrazole (H_2DM), 3-methyl-5-ethyl-4-carboxypyrazole (H_2ME) and 3,5-diethyl-4-carboxypyrazole (H_2DE) were used as the organic linkers. The purity of organic linkers was proved by ^{1}H nuclear magnetic resonance (NMR) spectroscopy. Acetic acid was used as a coordination modulator in these experiments.

Syntheses of MOF powders by ligand replacement approach and integration of coordination modulation with the ligand replacement approach

The preliminary studies involved the syntheses of three different analogues of Zn_4O(carboxypyrazolate)$_3$ MOFs (*i.e.* **Zn-DM, Zn-ME** and **Zn-DE**, Table S1) as bulk powders by direct mixing of the pre-formed metal secondary building unit (SBU) solution with the organic linker solution within a screw-capped jar, so-called ligand replacement approach. The 1.6 mM of $Zn_4O(OAc)_6$ solution in ethanol and the 4.8 mM of organic linker solution (H_2DM and H_2ME in 4:1 v/v ethanol/water mixture and H_2DE in 5:1 v/v ethanol/water mixture) were used as precursor solutions. In order to study the influences of coordination modulation, acetic acid was selected as a coordination modulator and added to the reaction. Specifically, acetic acid was firstly mixed with the $Zn_4O(OAc)_6$ solution. Subsequently, the organic linker solution was slowly added to the reaction mixture. The modulator-to-linker molar ratio (r_L) was varied from 1 to 5 for the syntheses of the three analogue MOFs and furthermore increased up to 30 in the case of **Zn-DM**. After mixing the precursor solutions at room temperature, the reaction mixtures were left in the oven at 50℃ for 24 h in order to achieve complete crystallization under this equilibrium condition. The products were collected by centrifugation and repeatedly washed with ethanol for 3 times. The activation of as-synthesized MOF powders was conducted at 120℃ under vacuum for 3 days prior to the adsorption measurements.

Fabrication of MOF films by integration of coordination modulation with LPE process

Herein, Au-coated quartz crystal microbalance sensors (QCM, commercially available by Q-Sense, AT cut type of quartz crystal, Au electrode, diameter 14 mm, thickness 0.3 mm and fundamental frequency ca. 4.95 MHz) were used as the substrates. Prior to the fabrication of MOF thin-films, the substrates were immersed in 20 μM solution of 16-mercaptohexadecanoic acid (MHDA) in ethanol and 5% v/v acetic acid for 24 h in order to functionalize the substrate surface. Self-assembled monolayer (SAM) formed by thiol bonding of MHDA molecules on the Au surface provides the -COOH terminated functionality at the substrate surface; consequently, were used for fabrication of MOF films. For each experiment, the precursor solutions were freshly prepared as follow: $Zn_4O(OAc)_6$ solution (0.5 mM) in ethanol, H_2DM and H_2ME solution (0.5 mM) in 4:1 v/v ethanol/water mixture and H_2DE in 5:1 v/v ethanol/water mixture. Acetic acid (used as the coordination modulator) was mixed in the $Zn_4O(OAc)_6$ solution. Three different MOF films (**Zn-DM**, **Zn-ME** and **Zn-DE**) were fabricated by integrating coordination modulation with the LPE process for 45 cycles at controlled temperature of 40℃ using the automated QCM instrument (Q-Sense E4 Auto) operated in the continuous flow mode with a flow rate of 100 μL min^{-1}. In each deposition cycle, the functionalized QCM substrate was alternatingly exposed to the precursor solutions as follow: $Zn_4O(OAc)_6$ mixed with acetic acid 10 min, ethanol (as a solvent) 5 min, organic linker 10 min and finally ethanol 5 min.

In order to investigate the influences of the modulator, the modulator-to-metal molar ratio (r_M) were varied ranging from 1 to 5. Three main sets of experiments were performed: (A) MOF films grown for total 45 cycles without self-seeding layer (in other words, the $Zn_4O(OAc)_6$ solution mixed with acetic acid was used from the first deposition cycle), (B) MOF films grown for 40 cycles on top of the pre-deposited MOF films of the same type grown by typical LPE method without using modulator for 5 cycles as a self-seeding layer (here, the $Zn_4O(OAc)_6$ solution mixed with acetic acid was used from the sixth deposition cycle), and (C) MOF films grown for total 45 cycles without self-seeding layer, however mixing acetic acid with the linker solution instead of the $Zn_4O(OAc)_6$ solution. Moreover, the MOF films grown by typical stepwise LPE method were grown as a control experiment. The change of QCM frequency was recorded *in situ* during the MOF film fabrication to study the MOF film growth.

Characterization of MOF powders

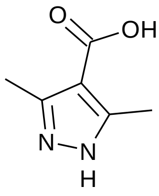
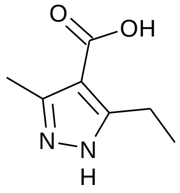
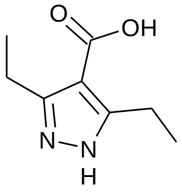
Crystalline phase and purity of the obtained MOF powders were characterized by powder X-ray diffraction (XRD) patterns collected on an X'Pert PanAnalytical instrument (Bragg-Bentano geometry with automatic divergent slits, Cu K_α radiation, 2θ range from 5° to 35°, scan step size 0.02°, position sensitive detector, operated at ambient atmosphere). Morphology of the synthesized MOFs was determined by scanning electron microscopic (SEM) images collected on a JEOL JSM-7500F electron microscope using an emission voltage of 15 kV. The samples were activated to remove the residue solvent molecules, then attached to the sample holder using double-side carbon tape, and were coated with osmium nanoparticles to increase the conductivity before loading into the SEM instrument. To investigate the adsorption properties of the MOF powders, nitrogen sorption measurements at 77 K were performed on a BELSORP-max adsorption analyzer (BEL Japan, Inc.). The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) model.

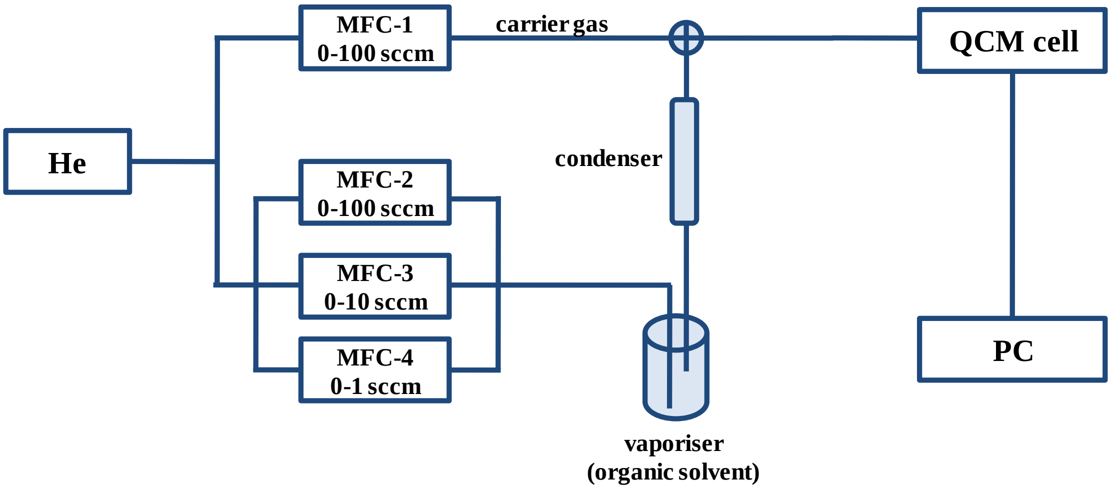
Characterization of MOF films

The fabricated MOF films were identified the crystalline phase by powder XRD using an X'Pert PanAnalytical instrument (Bragg-Bentano geometry, Cu K_α radiation, 2θ range from 5° to 20° with scan step size of 0.01°). Two-dimensional grazing incidence X-ray diffraction (2D-GIXRD) were performed at Beamline 9, DELTA Synchrotron facility, Germany (using X-ray wavelength of 1.0013 Å, incidence angle of 0.6° and refined sample-to-detector distance of 440.0 mm) to characterize the crystal orientation of the fabricated MOF films. Top view and cross section SEM images were taken by an environmental scanning electron microscope (ESEM, FEI ESEM Dual Beam^{TM} Quanta 3D FEG) in order to investigate surface morphology and surface coverage of the MOF films. Here, the samples were sputtered with carbon before loading to the SEM instrument. Infrared reflection adsorption spectra of the activated MOF films were measured inside a glovebox by a Bruker Alpha-P FTIR instrument operated with the external reflection module.

Sorption properties of the MOF films were carried out on an environmental-controlled quartz crystal microbalance (BEL-QCM-4 instrument, BEL Japan), of which the schematic setup is illustrated in Scheme S1. All the adsorption experiments were measured at controlled temperature of 25℃ and methanol was used as probe molecules. To activate the MOF films, the samples were firstly immersed in dichloromethane for 24 h to exchange the residue solvent molecules within the MOF pore with highly volatile dichloromethane molecules. Finally, the films were activated *in-situ* within the BEL-QCM instrument by heating at 80℃ together with a dry He purging with a flow rate of 100 sccm for total 2 h. After activation, the samples were cooled down to 25℃. When the change of QCM frequency was stable within the range of ±5Hz in 20 min, the masses of the MOF films (as a conversion according to Sauerbrey's equation of the difference between the QCM frequency at the final activation and the fundamental frequency of the QCM substrates) were recorded. After that, methanol adsorption isotherms were collected by varying the relative vapor pressure (P/P_0) of saturated methanol vapor in He gas flow at 25℃ from 0.0 to 95.0%. The adsorption amounts were calculated according to the Sauerbrey's equation.

Table S1 Starting materials for Zn_4O(3,5-dialkyl-4-carboxypyrazolate)$_3$ (**Zn-L**) MOF powder syntheses by coordination-modulation assisted ligand replacement approach and for fabrication of MOF thin films by employing coordination modulation method in conjunction with stepwise liquid phase epitaxial process, reported in this study

MOF films	Metal precursor	Organic linkers	Modulator
1. Zn_4O(3,5-dimethyl-4-carboxypyrazolate)$_3$ (**Zn-DM**)	$Zn_4O(CH_3COO)_6$	 (H_2DM)	CH_3COOH
2. Zn_4O(3-methyl-5-ethyl-4-carboxypyrazolate)$_3$ (**Zn-ME**)	$Zn_4O(CH_3COO)_6$	 (H_2ME)	CH_3COOH
3. Zn_4O(3,5-diethyl-4-carboxypyrazolate)$_3$ (**Zn-DE**)	$Zn_4O(CH_3COO)_6$	 (H_2DE)	CH_3COOH



Scheme S1 Schematic experimental setup of an environmental controlled quartz crystal microbalance (BEL-QCM) used for organic vapor adsorption experiments of MOF thin films

1. Preparation of Zn_4O(3,5-dialkyl-4-carboxypyrazolate)$_3$ powders by integrating coordination modulation with ligand replacement approach

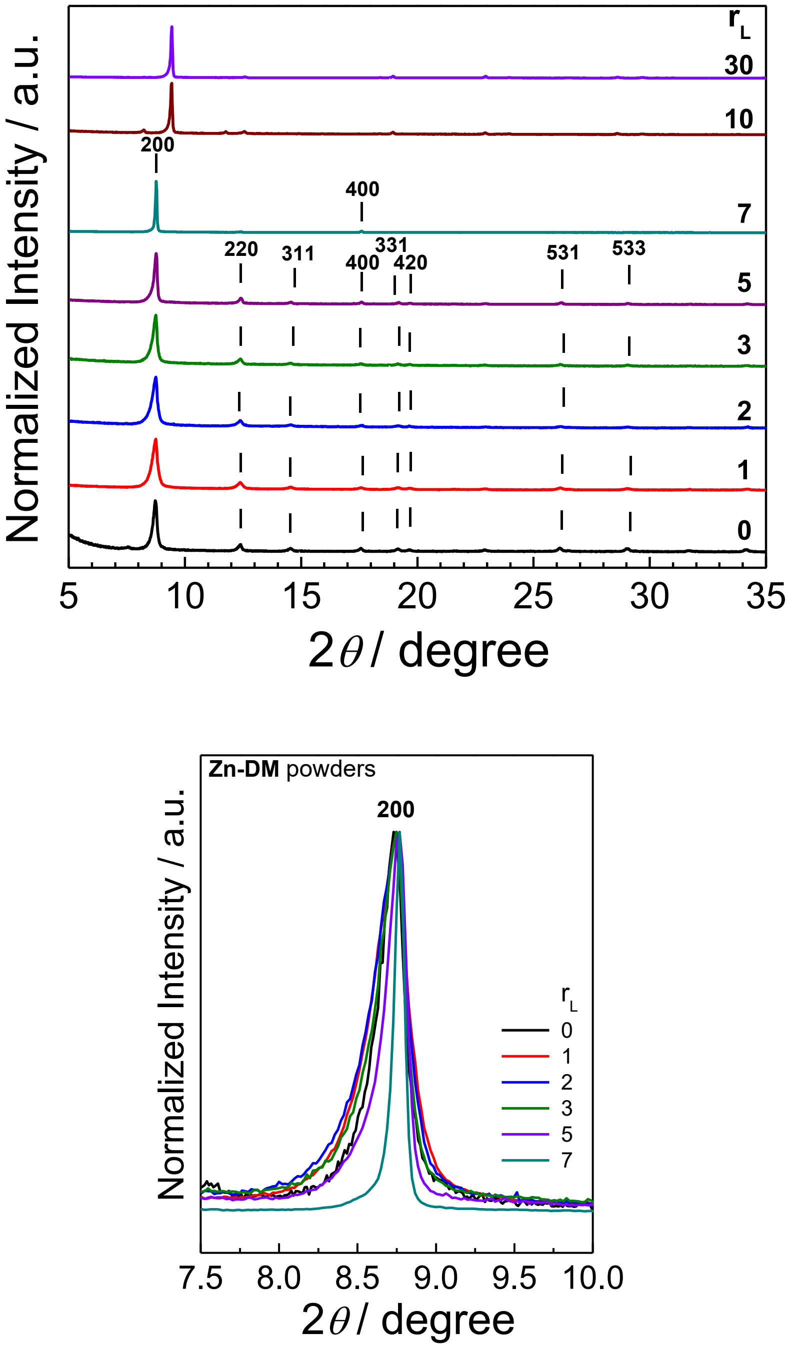


Figure S1 Powder X-ray diffraction patterns for **Zn-DM** powders synthesized by combining coordination modulation with ligand replacement approach at 50 °C using acetic acid as the modulator with various modulator-to-linker molar ratio (r_L) ranging from 1 to 30 comparing with the **Zn-DM** powder synthesized by ligand replacement approach without using the modulator. The numbers in the figure indicate the Miller indices of the diffractions.

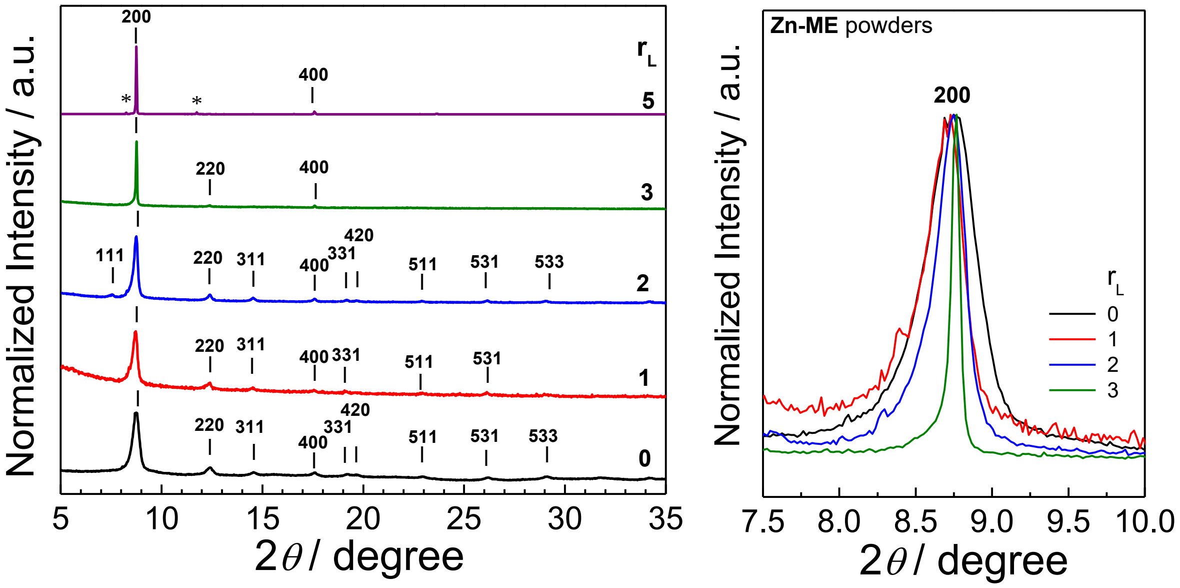


Figure S2 Powder X-ray diffraction patterns for **Zn-ME** powders synthesized by combining coordination modulation with ligand replacement approach at 50 °C using acetic acid as the modulator with r_L = 0 - 5. The numbers in the figure indicate the Miller indices of the diffractions.

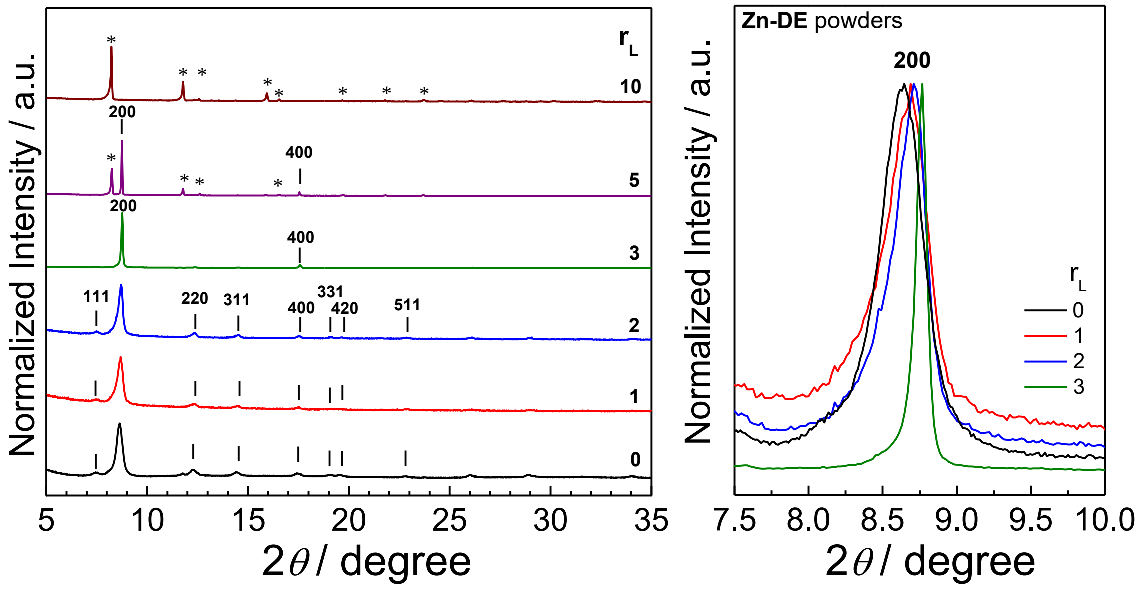


Figure S3 Powder X-ray diffraction patterns for **Zn-DE** powders synthesized by combining coordination modulation with ligand replacement approach at 50 °C using acetic acid as the modulator with r_L = 0 - 10. The numbers in the figure indicate the Miller indices of the diffractions.

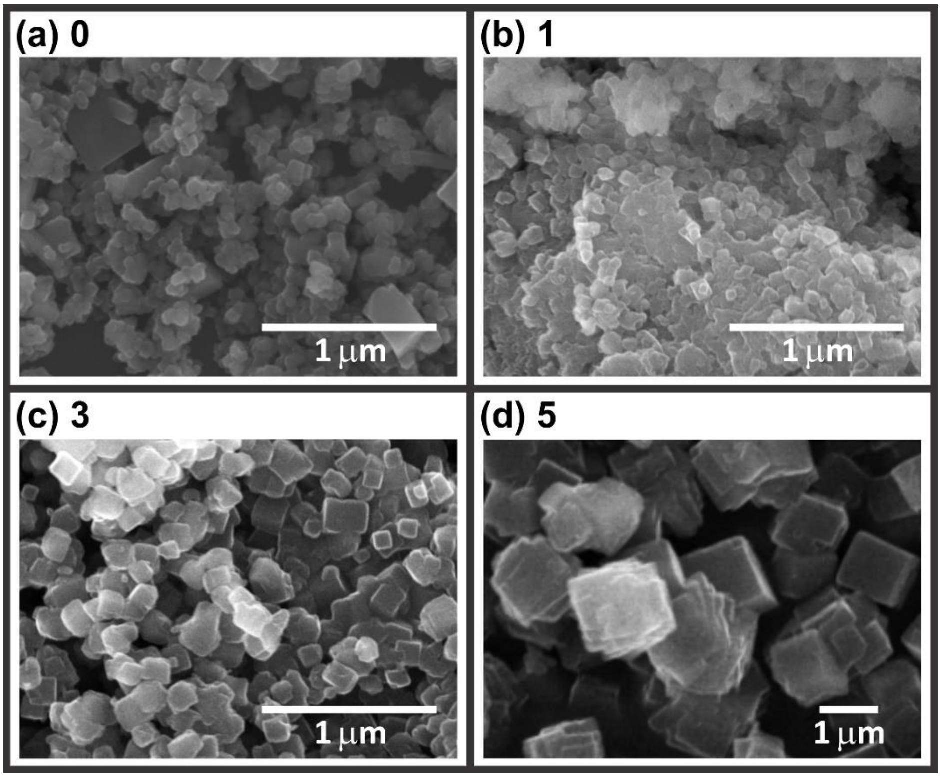


Figure S4 Scanning electron microscopy (SEM) images of **Zn-DM** powders synthesized at 50°C by (a) ligand replacement approach without using the modulator ($r_L = 0$) comparing with **Zn-DM** powders synthesized by integrating coordination modulation into the procedure using acetic acid as the modulator with r_L of (b) 1, (c) 3 and (d) 5.

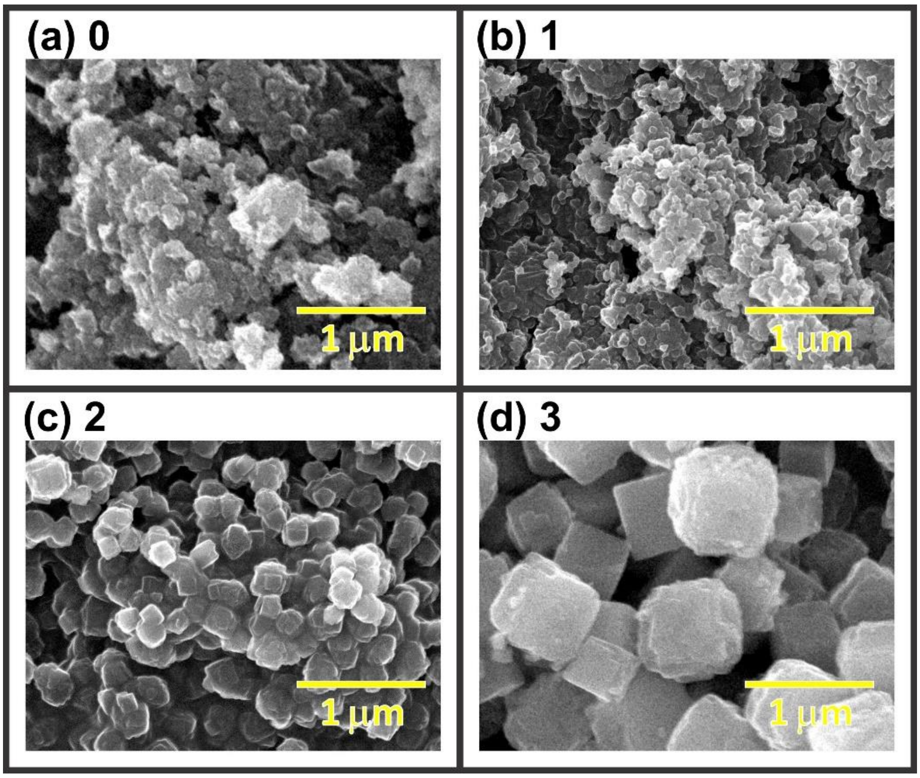


Figure S5 Scanning electron microscopy (SEM) images of **Zn-ME** powders synthesized at 50°C by (a) ligand replacement approach without using the modulator ($r_L = 0$) comparing with **Zn-ME** powders synthesized by integrating coordination modulation into the procedure using acetic acid as the modulator with r_L of (b) 1, (c) 2 and (d) 3.

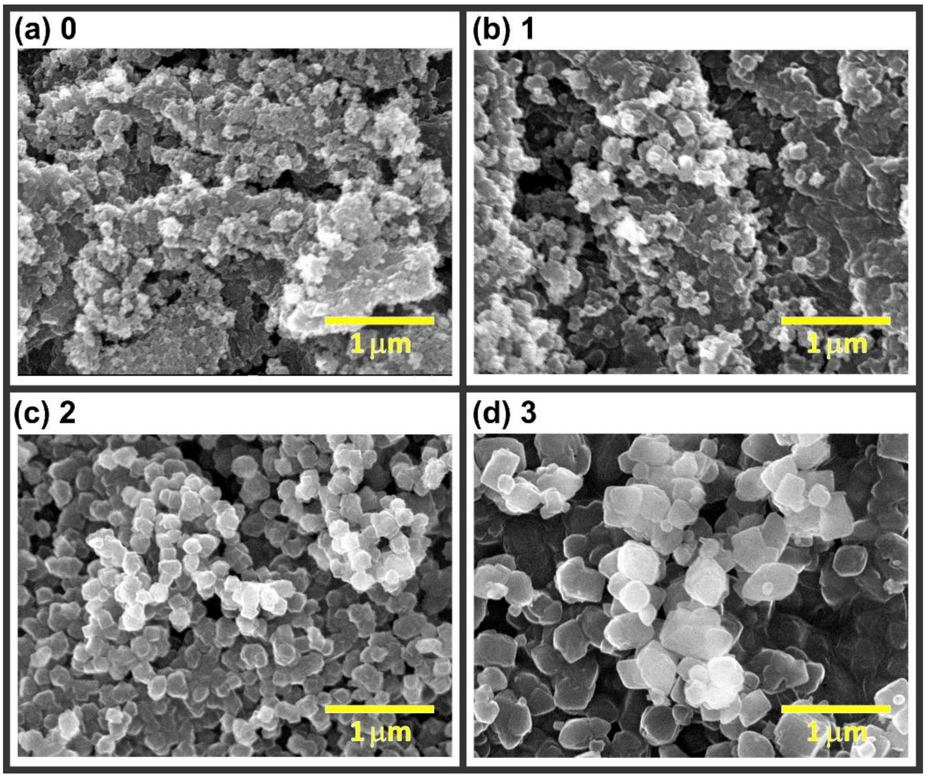


Figure S6 Scanning electron microscopy (SEM) images of **Zn-DE** powders synthesized at 50°C by (a) ligand replacement approach without using the modulator ($r_L = 0$) comparing with **Zn-DE** powders synthesized by integrating coordination modulation into the procedure using acetic acid as the modulator with r_L of (b) 1, (c) 2 and (d) 3.

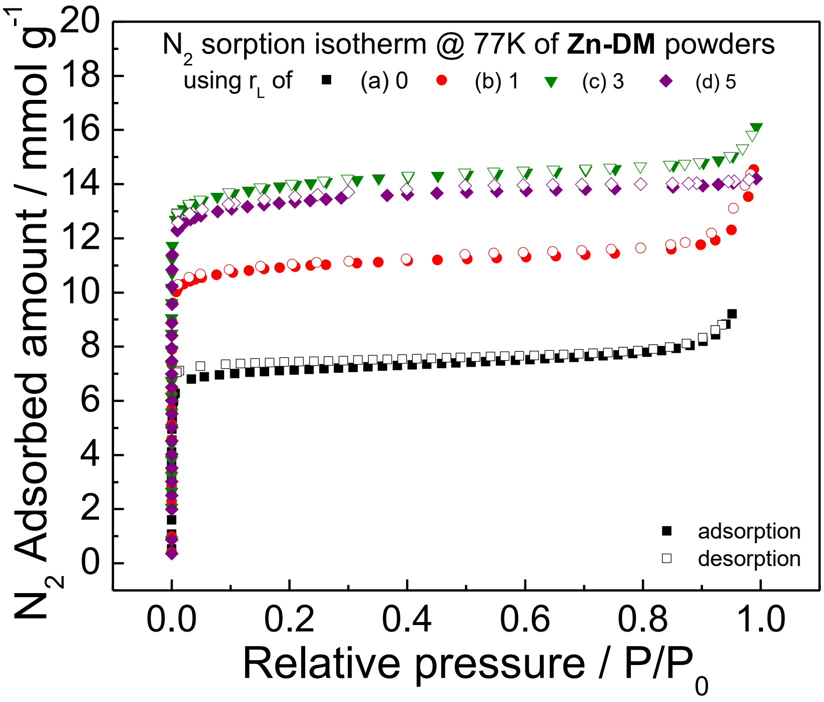


Figure S7 N_2 sorption isotherm at 77 K of the **Zn-DM** powders synthesized at 50°C by integrating coordination modulation with the ligand replacement approach using r_L ratio of (a) 0, (b) 1, (c) 3 and (d) 5.

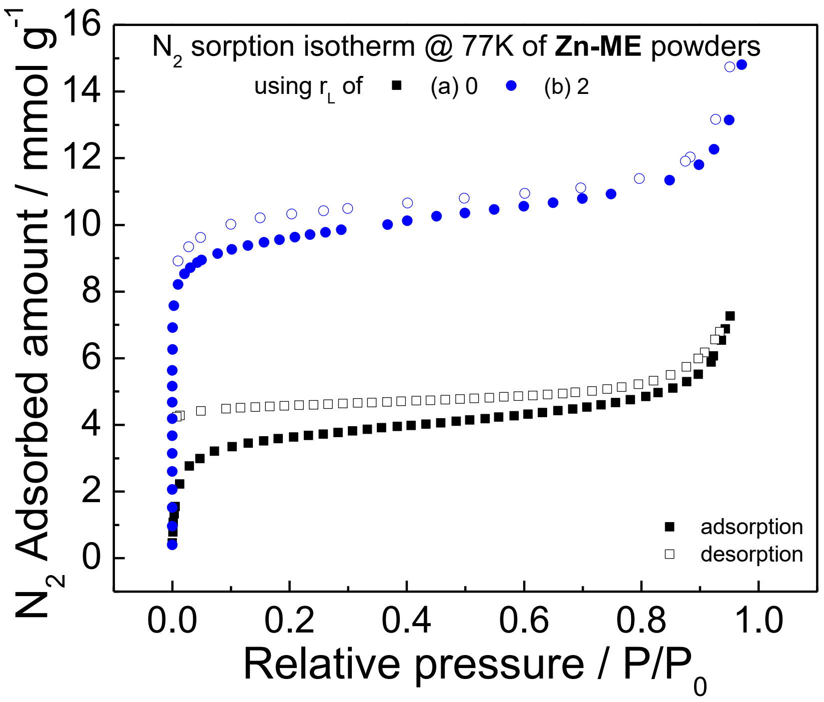


Figure S8 N_2 sorption isotherm at 77 K of the **Zn-ME** powders synthesized at 50°C by integrating coordination modulation with the ligand replacement approach using r_L ratio of (a) 0 and (b) 2.

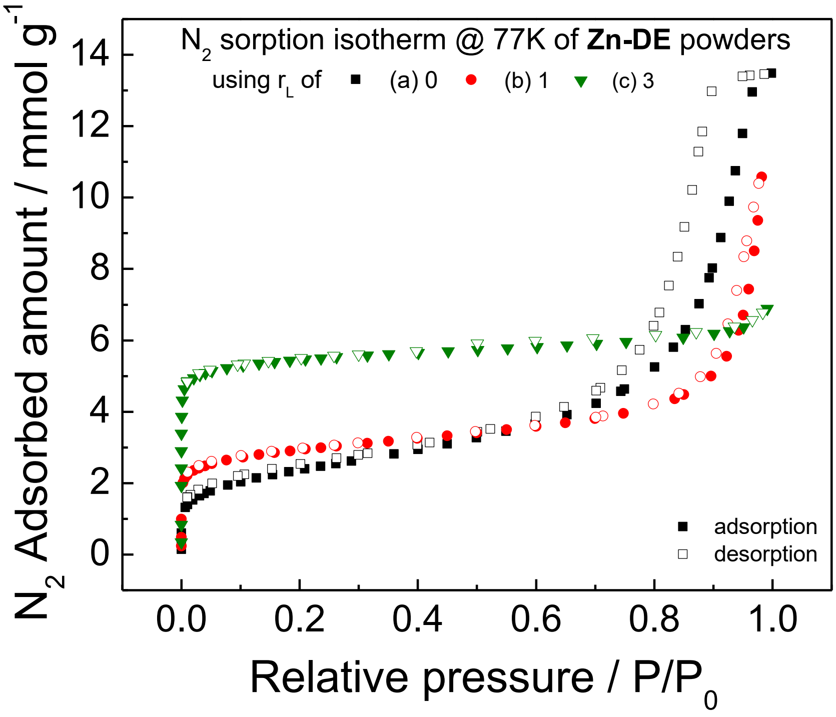


Figure S9 N_2 sorption isotherm at 77 K of the **Zn-DE** powders synthesized at 50°C by integrating coordination modulation with the ligand replacement approach using r_L ratio of (a) 0, (b) 1 and (c) 3.

2. Integration of coordination modulation in the LPE-based fabrication of Zn-L thin-films on quartz crystal microbalance (QCM) substrates

A. Zn-DM films

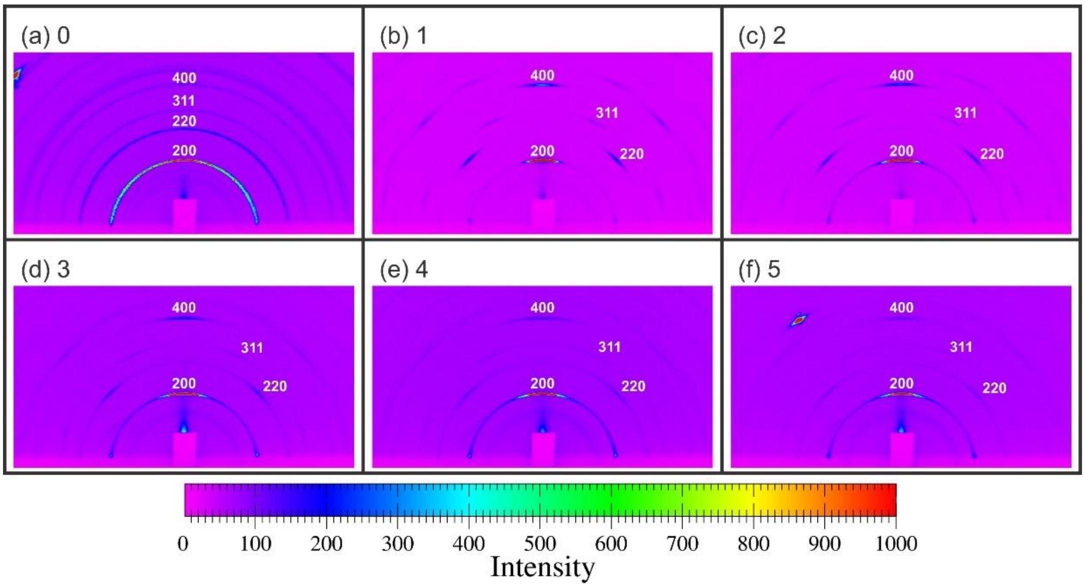


Figure S10 Two-dimensional grazing incidence X-ray diffraction patterns (2D-GIXRD) of **Zn-DM** films fabricated at 40 °C via integration of coordination modulation with LPE fabrication process; using $Zn_4O(OAc)_6$ 0.5 mM, H_2DM 0.5 mM as precursor solutions and acetic acid as coordination modulator by mixing it with the $Zn_4O(OAc)_6$ solutions with various modulator-to-metal ratio (r_M) from 0 to 5). The synchrotron parameters are X-ray wavelength 1.0013 Å, incidence angle 0.6° and refined sample-to-detector distance 440.0 mm.

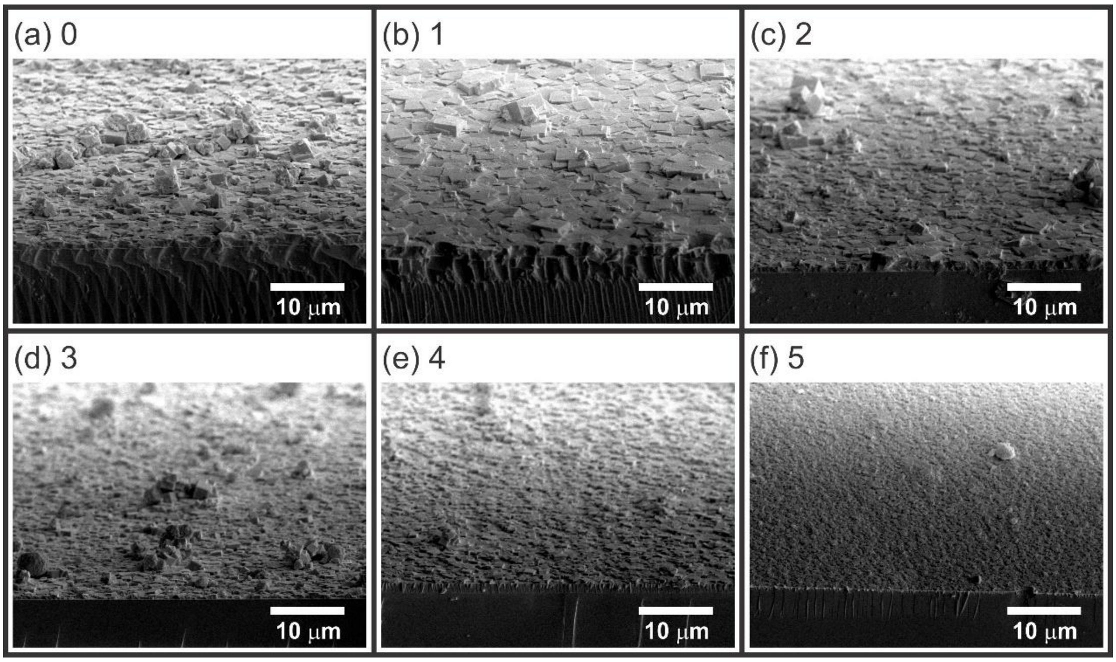


Figure S11 Cross-sectional view SEM images of **Zn-DM** films fabricated at 40 °C via integration of coordination modulation with LPE fabrication process; using $Zn_4O(OAc)_6$ 0.5 mM, H_2DM 0.5 mM as precursor solutions and acetic acid as coordination modulator by mixing it with the $Zn_4O(OAc)_6$ solutions with $r_M = 0 - 5$.

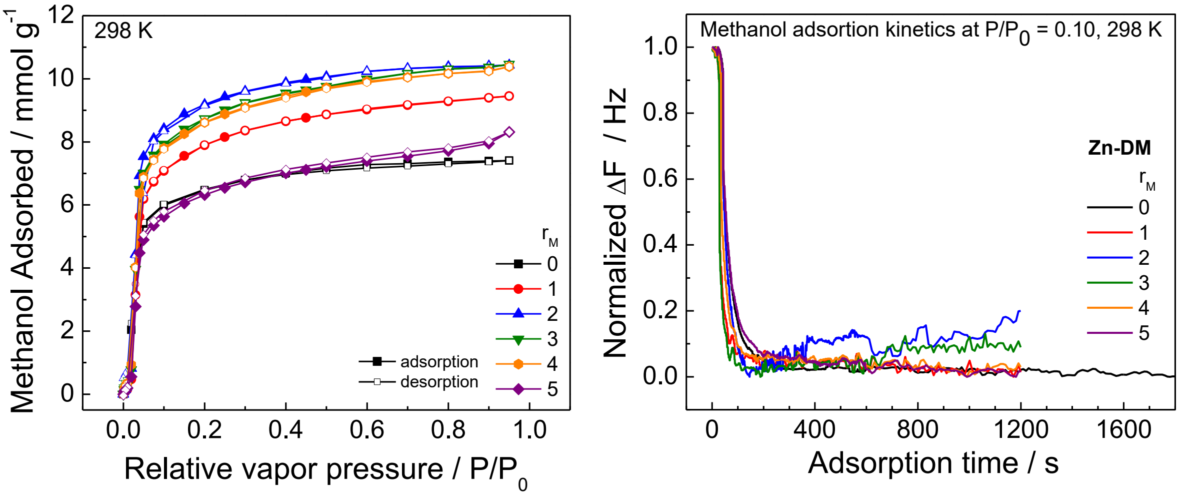


Figure S12 Methanol sorption isotherms at 25 °C and adsorption kinetics at $P/P_0 = 0.10$ measured using the environmentally controlled quartz crystal microbalance (QCM) of **Zn-DM** films fabricated at 40 °C via integration of coordination modulation with LPE fabrication process; using $Zn_4O(OAc)_6$ 0.5 mM, H_2DM 0.5 mM as precursor solutions and acetic acid as coordination modulator by mixing it with the $Zn_4O(OAc)_6$ solutions with $r_M = 0 – 5$.

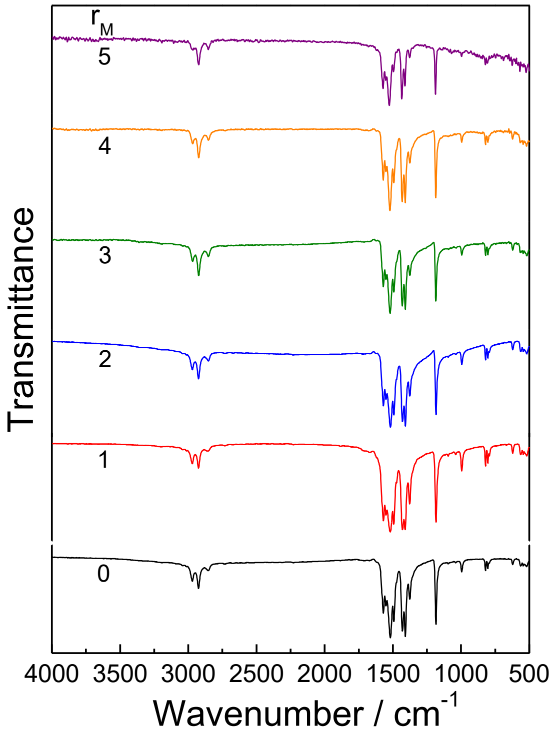


Figure S13 Infrared reflection absorption spectra (IRRAS) of **Zn-DM** films fabricated at 40 °C via integration of coordination modulation with LPE fabrication process; using $Zn_4O(OAc)_6$ 0.5 mM, H_2DM 0.5 mM as precursor solutions and acetic acid as modulator by mixing it with the $Zn_4O(OAc)_6$ solutions with $r_M = 0 - 5$.

B. Zn-ME films

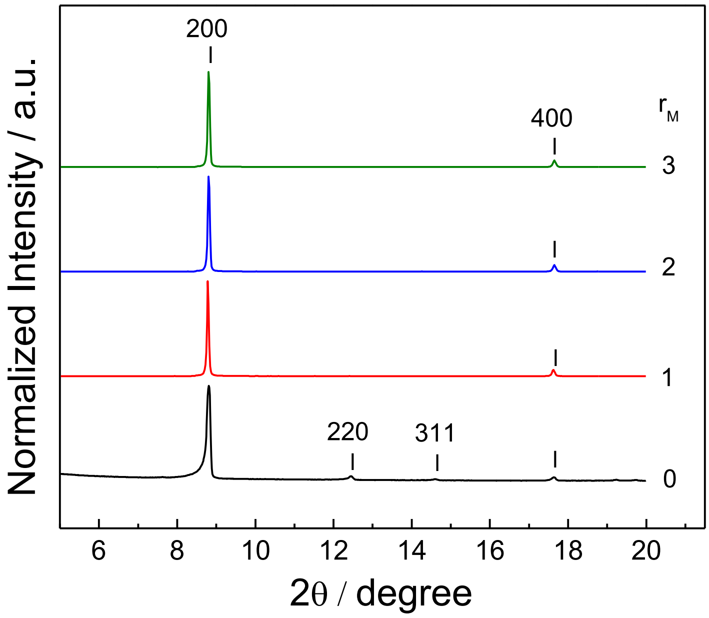


Figure S14 Powder X-ray diffraction patterns (XRD) of **Zn-ME** films fabricated at 40 °C via integration of coordination modulation with LPE fabrication process; using $Zn_4O(OAc)_6$ of (a) 0.5 mM and (b) 1.0 mM, H_2ME 0.5 mM as precursor solutions and acetic acid as coordination modulator by mixing it with the $Zn_4O(OAc)_6$ solutions with $r_M = 0 – 3$.

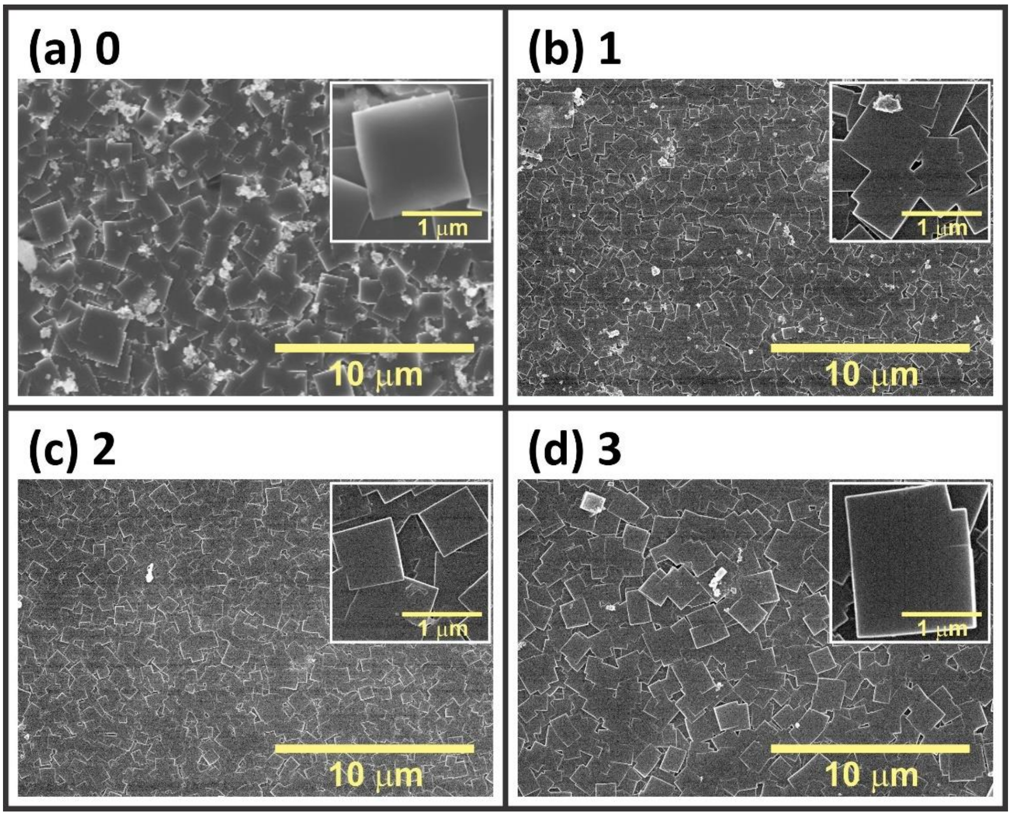


Figure S15 SEM images of the surfaces of **Zn-ME** films fabricated at 40 °C via integration of coordination modulation with LPE fabrication process; using $Zn_4O(OAc)_6$ 0.5 mM, H_2ME 0.5 mM and acetic acid as coordination modulator by mixing it with the $Zn_4O(OAc)_6$ solutions with $r_M = 0 – 3$.

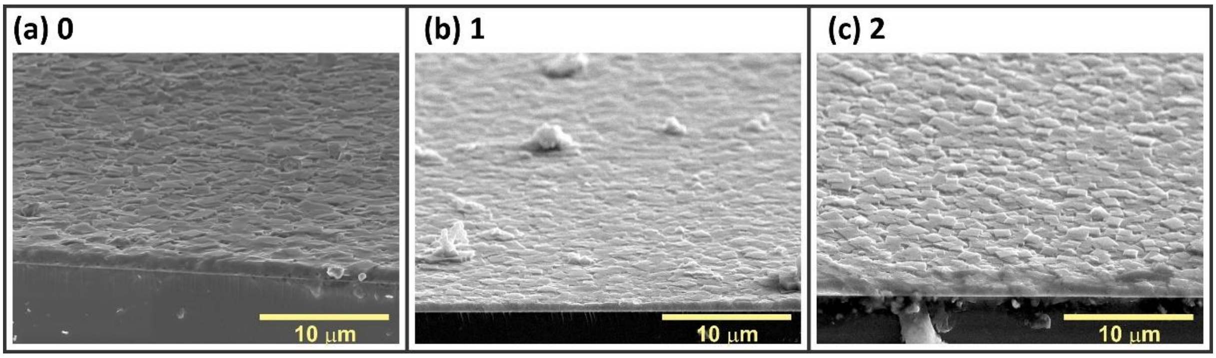


Figure S16 Cross-sectional view SEM images of **Zn-ME** films fabricated at 40 °C via integration of coordination modulation with LPE fabrication process using $r_M = 0 - 3$.

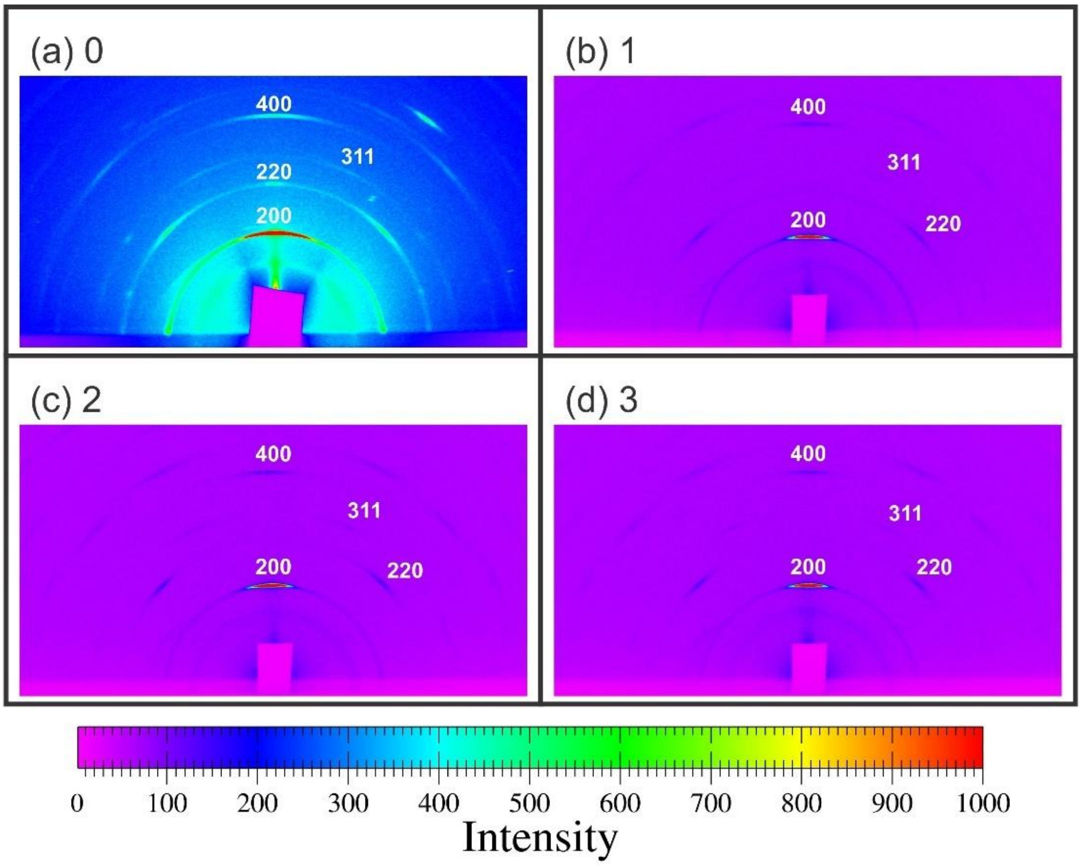


Figure S17 2D-GIXRD patterns of **Zn-ME** films fabricated at 40 °C via integration of coordination modulation with LPE fabrication process without self-seeding layer; using $Zn_4O(OAc)_6$ 0.5 mM, H_2ME 0.5 mM and acetic acid as coordination modulator by mixing it with the $Zn_4O(OAc)_6$ solutions with $r_M = 0 - 3$. The synchrotron parameters are X-ray wavelength 1.0013 Å, incidence angle 0.6° and refined sample-to-detector distance 440.0 mm.

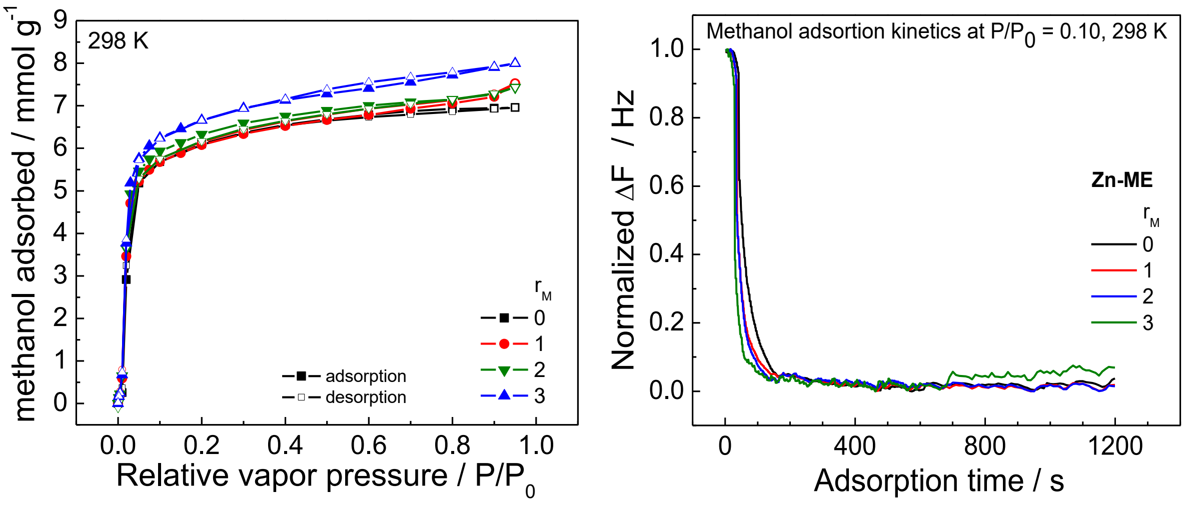


Figure S18 Methanol sorption isotherms at 25 °C and adsorption kinetics at $P/P_0 = 0.10$ measured using the environmentally controlled quartz crystal microbalance (QCM) of **Zn-ME** films fabricated at 40 °C via integration of coordination modulation with LPE fabrication process; using $Zn_4O(OAc)_6$ 0.5 mM, H_2DM 0.5 mM as precursor solutions and acetic acid as coordination modulator by mixing it with the $Zn_4O(OAc)_6$ solutions with $r_M = 0 – 3$.

C. Zn-DE films

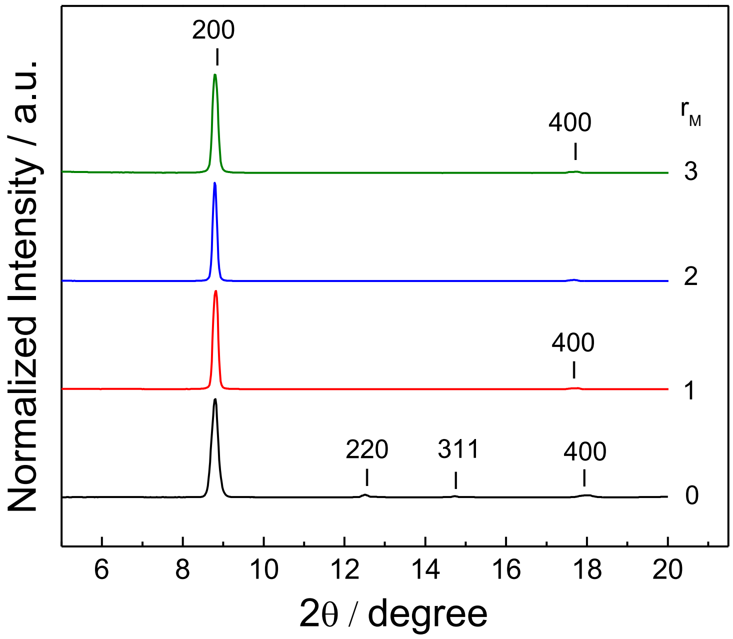


Figure S19 Powder X-ray diffraction patterns (XRD) of **Zn-DE** films fabricated at 40 °C via integration of coordination modulation with LPE fabrication process; using $Zn_4O(OAc)_6$ of (a) 0.5 mM and (b) 1.0 mM, H_2DE 0.5 mM as precursor solutions and acetic acid as coordination modulator by mixing it with the $Zn_4O(OAc)_6$ solutions with $r_M = 0 – 3$.

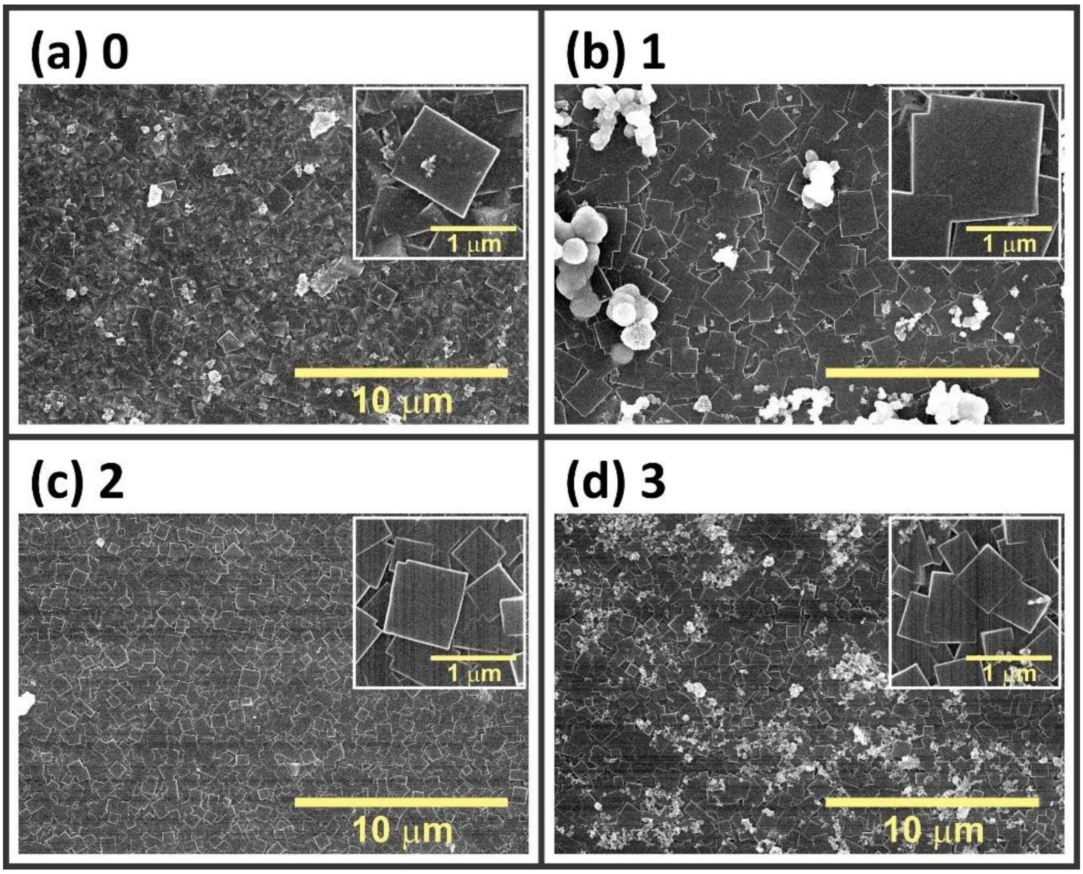


Figure S20 SEM images of the surfaces of **Zn-DE** films fabricated at 40 °C via integration of coordination modulation with LPE fabrication process; using $Zn_4O(OAc)_6$ 0.5 mM, H_2DE 0.5 mM and acetic acid as coordination modulator by mixing it with the $Zn_4O(OAc)_6$ solutions with $r_M = 0 – 3$.

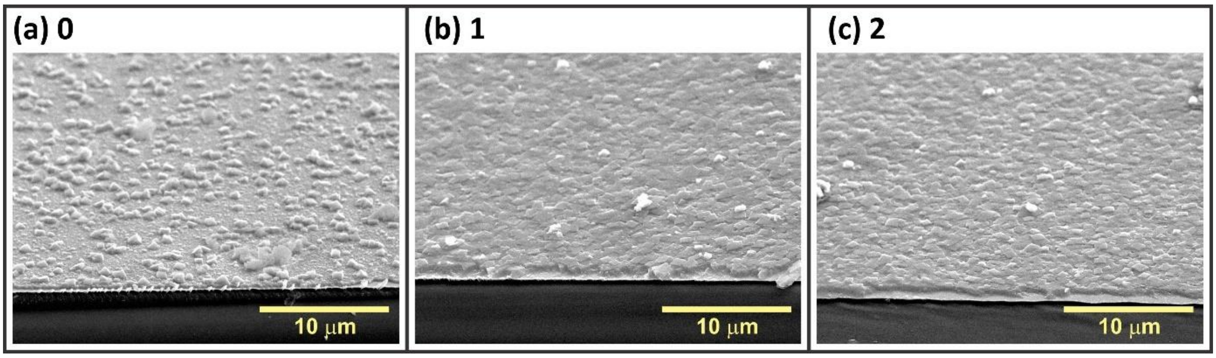


Figure S21 Cross-sectional view SEM images of **Zn-DE** films fabricated at 40 °C via integration of coordination modulation with LPE fabrication process using $r_M = 0 – 3$.

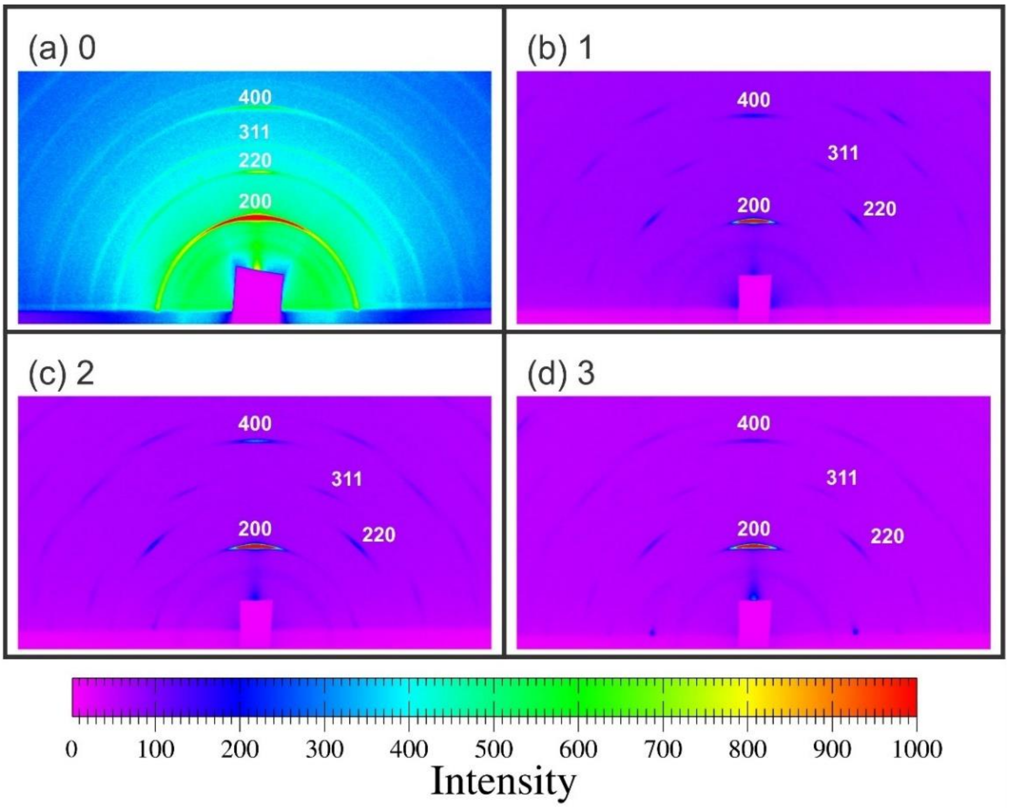


Figure S22 2D-GIXRD patterns of **Zn-DE** films fabricated at 40 °C via integration of coordination modulation with LPE fabrication process without self-seeding layer; using $Zn_4O(OAc)_6$ 0.5 mM, H_2DE 0.5 mM and acetic acid as coordination modulator by mixing it with the $Zn_4O(OAc)_6$ solutions with $r_M = 0 - 3$. The synchrotron parameters are X-ray wavelength 1.0013 Å, incidence angle 0.6° and refined sample-to-detector distance 440.0 mm.

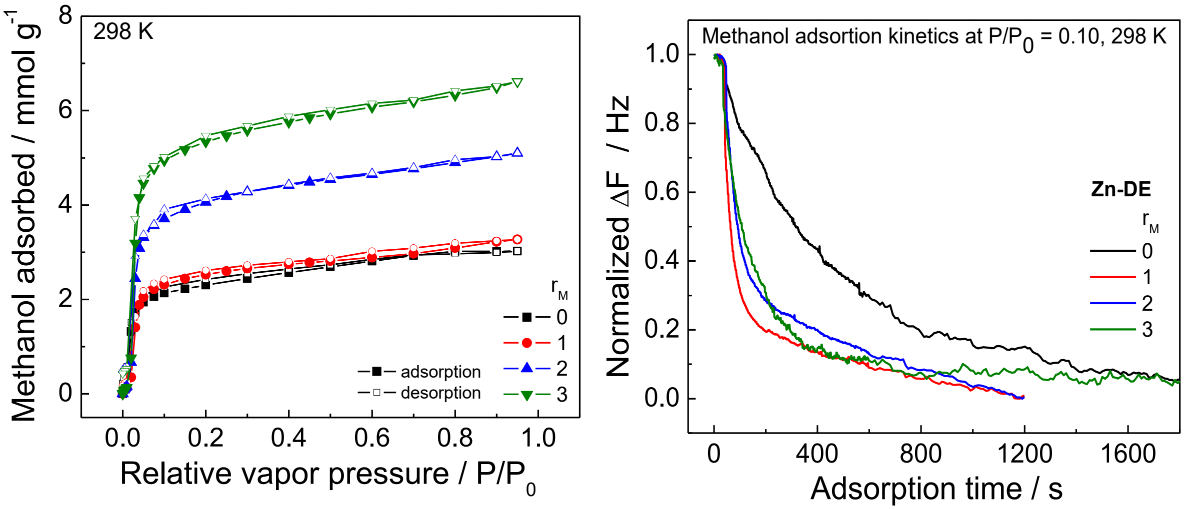


Figure S23 Methanol sorption isotherms at 25 °C and adsorption kinetics at $P/P_0 = 0.10$ measured using the environmentally controlled quartz crystal microbalance (QCM) of **Zn-DE** films fabricated at 40 °C via integration of coordination modulation with LPE fabrication process; using $Zn_4O(OAc)_6$ 0.5 mM, H_2DM 0.5 mM as precursor solutions and acetic acid as coordination modulator by mixing it with the $Zn_4O(OAc)_6$ solutions with $r_M = 0 - 3$.

3. Probing the role of coordination modulation in optimizing LPE fabrication

A. Zn-DM films fabricated on self-seeding Zn-DM layer prepared by conventional LPE process

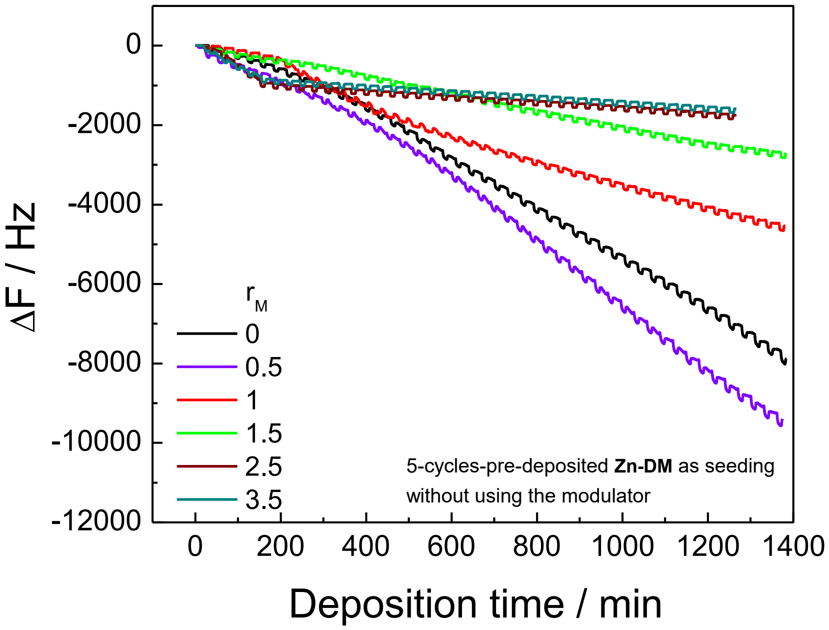


Figure S24 In-situ monitoring of QCM frequency during the fabrication of **Zn-DM** films at 40 °C via integration of coordination modulation with LPE fabrication process on the 5-cycles-pre-deposited **Zn-DM** films fabricated without using modulator as a self-seeding layer; using $Zn_4O(OAc)_6$ 0.5 mM, H_2DM 0.5 mM as precursor solutions and acetic acid as coordination modulator by mixing it with the $Zn_4O(OAc)_6$ solutions with $r_M = 0 – 3.5$.

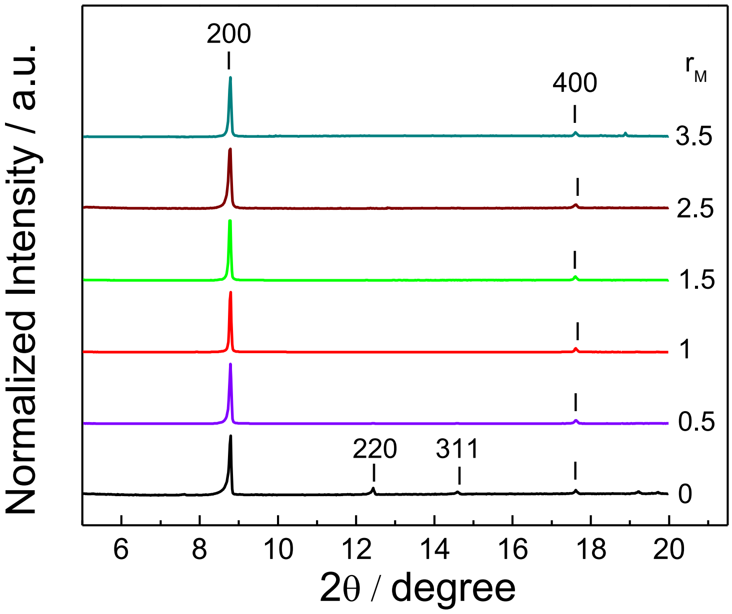


Figure S25 XRD patterns of **Zn-DM** films fabricated at 40 °C with various r_M ratio via integration of coordination modulation with LPE fabrication process on the pre-deposited, self-seeding **Zn-DM** layer fabricated without using the modulator for 5 cycles (corresponding with the growth data in Figure S24)

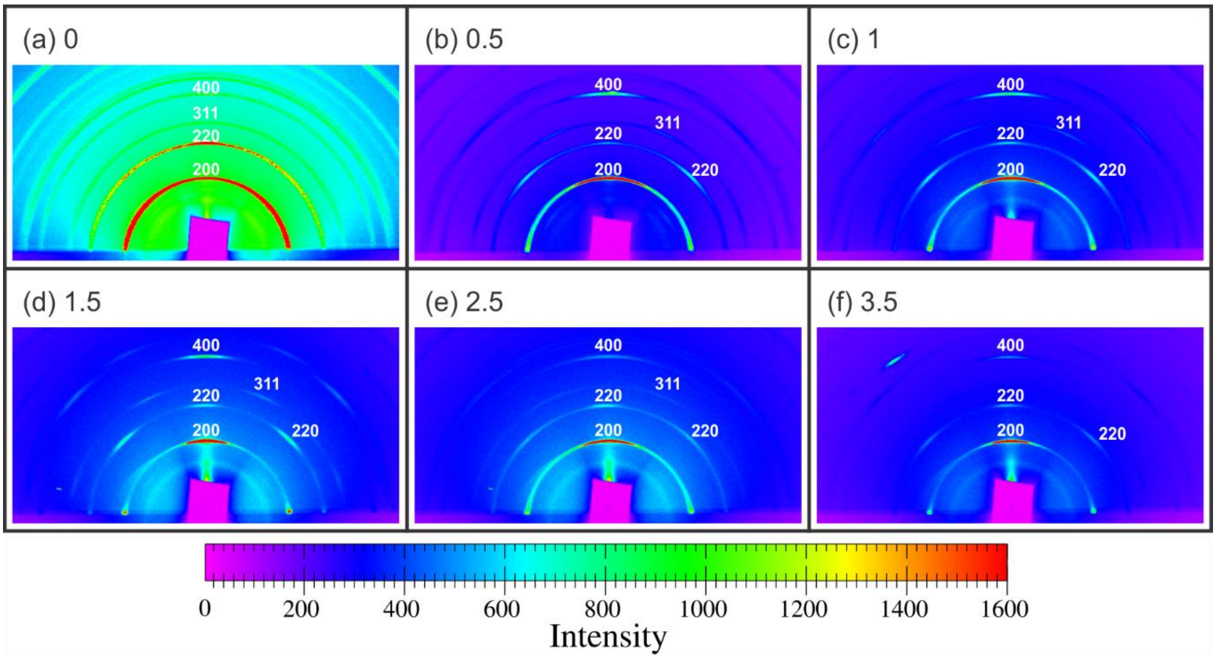


Figure S26 GIXRD patterns of **Zn-DM** films fabricated at 40 °C with various r_M ratio by employing coordination modulation method in conjunction with LPE process on the pre-deposited, self-seeding **Zn-DM** layer fabricated without using the modulator for 5 cycles. Synchrotron parameters are X-ray wavelength 1.0013 Å, incidence angle 0.6° and refined sample-to-detector distance 487.3 mm.

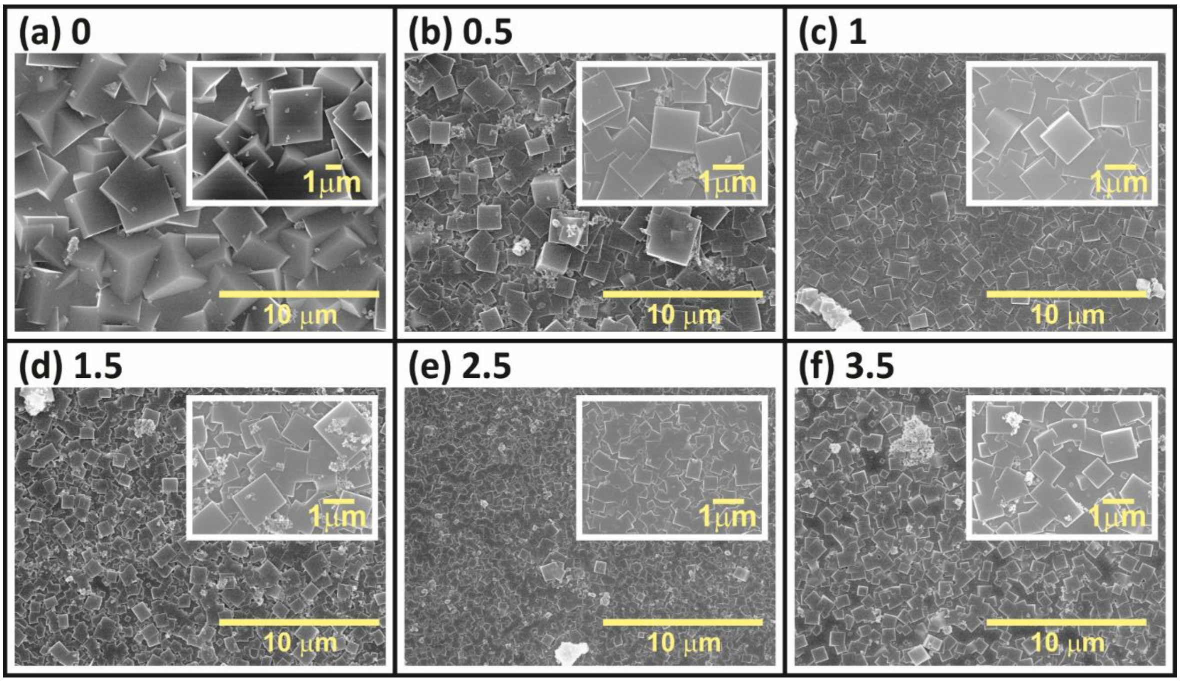


Figure S27 SEM images of the surfaces of **Zn-DM** films fabricated at 40 °C with various r_M ratio via integration of coordination modulation with LPE fabrication process on the pre-deposited, self-seeding **Zn-DM** layer fabricated without using the modulator for 5 cycles.

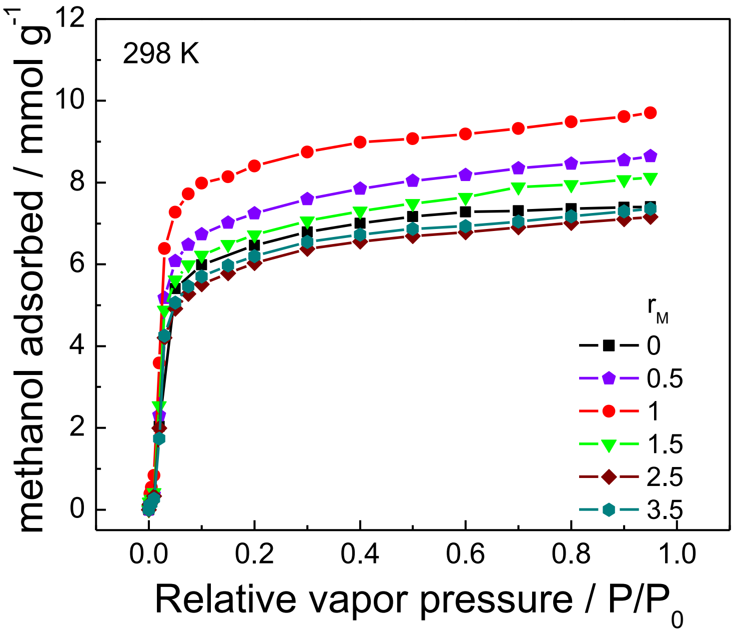


Figure S28 Methanol adsorption isotherms at 25 °C using the environmentally controlled quartz crystal microbalance (QCM) of **Zn-DM** films fabricated at 40 °C with various r_M ratio via integration of coordination modulation with LPE fabrication process on the self-seeding **Zn-DM** layer fabricated without using the modulator for 5 cycles

B. Zn-DM films fabricated by the coordination modulation-controlled LPE process by mixing acetic acid

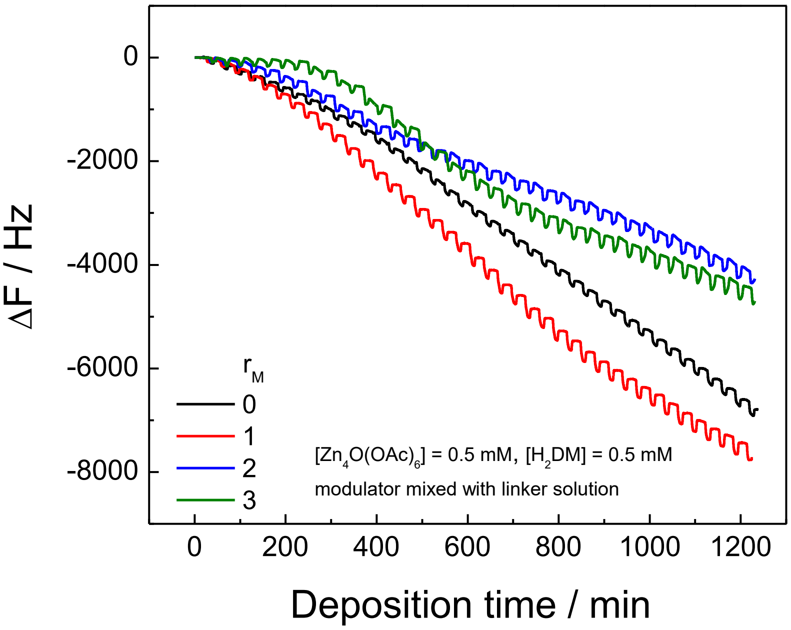


Figure S29 In-situ monitoring of QCM frequency during the fabrication of **Zn-DM** films at 40 °C via integration of coordination modulation with LPE fabrication process without seeding layer; using $Zn_4O(OAc)_6$ 0.5 mM and H_2DM 0.5 mM as precursor solutions, and acetic acid as coordination modulator by mixing it with the H_2DM solutions with various r_M ratio

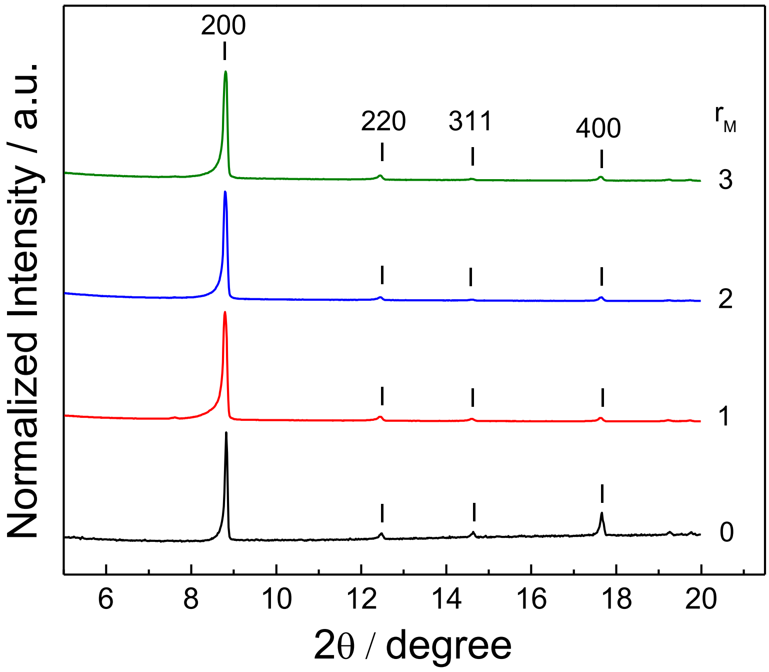


Figure S30 XRD patterns of **Zn-DM** films fabricated at 40 °C via integration of coordination modulation with LPE fabrication process; using $Zn_4O(OAc)_6$ 0.5 mM and H_2DM 0.5 mM as precursor solutions, and acetic acid as coordination modulator by mixing it with the H_2DM solutions with various r_M ratio (corresponding with the growth data in Figure S29)

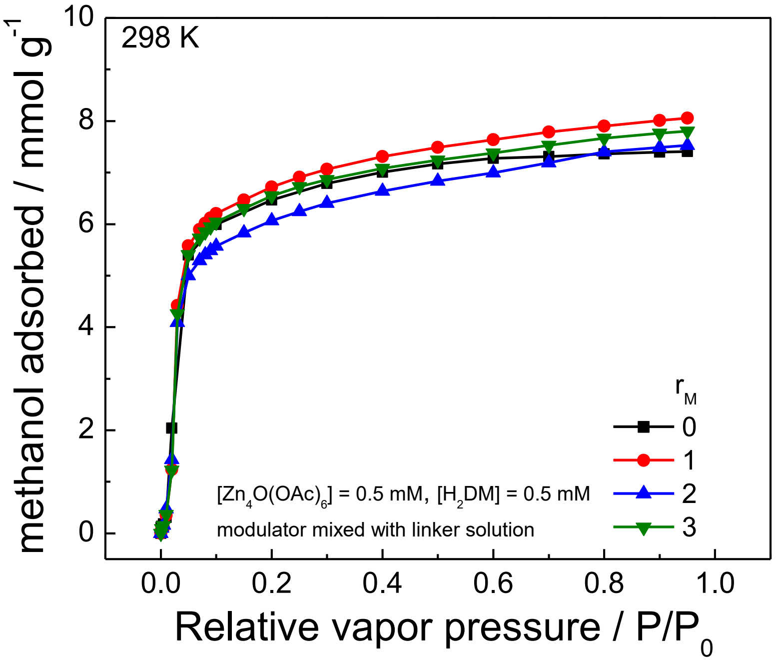


Figure S31 Methanol adsorption isotherms at 25 °C using the environmentally controlled quartz crystal microbalance (QCM) of **Zn-DM** films fabricated at 40 °C via integration of coordination modulation with LPE fabrication process without self-seeding layer; using $Zn_4O(OAc)_6$ 0.5 mM and H_2DM 0.5 mM as precursor solutions and acetic acid as coordination modulator by mixing it with the H_2DM solution with various r_M ratio