

Supporting Information

Ligand Effect on In-Ti-oxo Nanoclusters for Nanolithography

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I. General methods and materials.

All the reagents and solvents employed are purchased commercially and used as received without further treatment. $\text{InNO}_3 \cdot x\text{H}_2\text{O}$, salicylic acid, 5-fluorosalicic acid, $\text{Ti}(\text{O}^i\text{Pr})_4$ (96%) were purchased from Adamas. 5-nitrosalicic acid, Propylene glycol 1-monomethyl ether 2-acetate (PGMEA), 2-Heptanone, 4-Heptanone, 4-methyl-2-pentanone and ethyl lactate (EL) were purchased from Aladdin. 4-methylsalicylic acid were bought from Energy Chemical. While isopropanol (IPA), methanol, n-butanol, acetonitrile (CH_3CN), dimethyl formamide (DMF), and *tert*-butyl alcohol were bought from Sino pharm Chemical Reagent Beijing. Chemical. Powder X-ray diffraction (PXRD) analyses data were mounted on a Rigaku Mini Flex II diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) under ambient conditions. The Fourier transform infrared (FT-IR) spectra (ATR) were performed on Bruker VERTEX 70 over a range of $4000\text{--}400 \text{ cm}^{-1}$. Thermal stabilities were investigated by a Mettler Toledo TGA/SDTA 851e analyzer in N_2 atmosphere with a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ under N_2 atmosphere. Elemental analyses were measured on a Vario MICRO Elemental Analyzer instrument. The electrospray ionization mass spectrometry (ESI-MS) data were collected on Impact II UHR-TOF (Bruker). The DLS measurements were performed using a Zetasizer Nano instrument. Samples were dispersed in ethyl lactate at a concentration of 20 mg/mL , filtered, and analyzed at 23°C . Each measurement involved a continuous scan duration of 50 s at full laser power, with a count rate of 145.3 kcps; UV-Vis tests were performed on a Lambda 950 (PerkinElmer) at a scan rate of $266.75 \text{ nm}/\text{min}$ over a wavelength range of 200 to 800 nm; Surface chemical analyses were performed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher, ESCALAB 250Xi system); The X-ray reflectivity experiments were performed using a Rigaku Smartlab reflectometer with $\text{Cu K}\alpha$ X-ray source ($\lambda = 1.541 \text{ \AA}$) at China Spallation Neutron Source. The incident angle was increased continuously from 0.005° to 3° to finish the measurements of the three samples. The increase step was 0.005° and each step was counted by 60 s. The thickness of the sample was calculated from the equation of $d = \lambda / 2 \sin \theta$ by averaging the periodical Kiessig fringes The film thickness was measured by Ellipsometry-J. A. Woollam V-VASE. The film was exposed to an electron-beam using Raith quantum. The topography and the surface roughness of the sample are characterized by means of AFM-Bruker Dimension ICON and Asylum Research-Cypher. SEM images for patterns are performed by Zeiss Supra55.

II. Synthesis.

Synthesis of **InOC-20_v** $[\text{In}_4\text{Ti}_{12}(\text{SA})_{12}(\mu_3\text{-O})_4(\mu_2\text{-O})_{10}(\text{OCH}_3)_8(\text{H}_2\text{O})_6(\text{CH}_3\text{OH})_2] \cdot 4\text{CH}_3\text{OH}$

A mixture of $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (150mg, 0.50mmol), salicylic acid (138mg, 1mmol), CH_3OH (5mL) and $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.15mL, 0.49mmol) was sealed in a 20 mL vial and transferred to a oven at 80 °C for 3 days. When cooled to room temperature, block yellowish crystals formed. (yield: 32 mg, 22.81% based on Ti).

Synthesis of **InOC-21_v** $[\text{In}_4\text{Ti}_{12}(\text{SA-Me})_{12}(\mu_3\text{-O})_4(\mu_2\text{-O})_{10}(\text{OCH}_3)_8(\text{H}_2\text{O})_6(\text{CH}_3\text{OH})_2]$

A mixture of $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (100mg, 0.33mmol), 4-methylsalicylic acid (152mg, 1mmol), CH_3OH (2mL), *tert*-butanol (3mL) and $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.15mL, 0.49mmol) was sealed in a 20 mL vial and transferred to a oven at 80 °C for 4 days. When cooled to room temperature, block yellowish crystals formed. (yield: 33 mg, 23.24% based on Ti).

Synthesis of **InOC-22_v** $[\text{In}_4\text{Ti}_{12}(\text{SA-F})_{12}(\mu_3\text{-O})_4(\mu_2\text{-O})_{10}(\text{OCH}_3)_8(\text{H}_2\text{O})_6(\text{CH}_3\text{OH})_2] \cdot 2\text{CH}_3\text{OH}$

A mixture of $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (100mg, 0.33mmol), 5-fluorosalicic acid (156mg, 1mmol), CH_3OH (5mL) and $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.15mL, 0.49mmol) was sealed in a 20 mL vial and transferred to a oven at 80 °C for 5 days. When cooled to room temperature, plate yellowish crystals formed. (yield: 29 mg, 19.78% based on Ti).

Synthesis of **InOC-23_H** $(\text{H}_3\text{O})_2[\text{In}_4\text{Ti}_{12}(\text{SA-NO}_2)_{12}(\mu_3\text{-O})_4(\mu_2\text{-O})_{10}(\mu_2\text{-OH})_2(\text{OCH}_3)_8(\text{H}_2\text{O})_4]$

A mixture of $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (100mg, 0.33mmol), 5-nitrosalicic acid (183mg, 1mmol), CH_3OH (2mL), *n*-butanol (3mL) and $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.15mL, 0.49mmol) was sealed in a 20 mL vial and transferred to a oven at 80 °C for 5 days. When cooled to room temperature, block yellowish crystals formed. (yield: 32 mg, 20.45% based on Ti).

Synthesis of **InOC-20_{v(im)}** $[\text{In}_4\text{Ti}_{12}(\text{SA})_{12}(\mu_3\text{-O})_4(\mu_2\text{-O})_{10}(\text{OCH}_3)_8(\text{H}_2\text{O})_8] \cdot 12\text{H}_2\text{O}$

Immersion of **InOC-20_v** in water for 24h.

III. Single-Crystal X-ray diffraction.

The single-crystal diffraction data of **InOC-20_v**, **InOC-21_v**, **InOC-22_v**, **InOC-23_H** and **InOC-20_v(im)** were collected on Hybrid Pixel Array detector equipped with Ga-K α radiation ($\lambda = 1.3405$ Å) at 100 K. Using Olex2^[1], the crystal structures were determined by direct methods with ShelxT and refined by the full-matrix least-squares method based on F^2 with the SHELXL 2016^[2-4]. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms on C and O were bonded by theory. The obtained crystallographic data for **InOC-20_v** to **InOC-20_v(im)** are summarized in **Table S1** and **Table S2**.

Table S1 Crystal data and structure refinement for InOC-20_v to InOC-22_v.

Compound	InOC-20 _v	InOC-21 _v	InOC-22 _v
Crystal Formula	C ₉₈ H ₁₀₄ In ₄ O ₇₀ Ti ₁₂	C ₁₀₆ H ₁₁₄ In ₄ O ₆₆ Ti ₁₂	C ₉₆ H ₈₇ F ₁₂ In ₄ O ₆₈ Ti ₁₂
Formula weight	3435.89	3478.05	3590.73
Space group	P-42 ₁ C	P2 ₁ /n	P2 ₁ /n
Crystal system	tetragonal	monoclinic	monoclinic
a/Å	19.7706(2)	26.2798(2)	19.9080(4)
b/Å	19.7706(2)	20.9981(2)	22.5594(3)
c/Å	15.9534(2)	31.0613(3)	32.9320(8)
α/°	90	90	90
β/°	90	107.4470(10)	104.374(2)
γ/°	90	90	90
V/Å³	6235.81(15)	16351.9(3)	14327.2(5)
Z	2	4	4
ρ/g cm⁻³	1.830	1.413	1.665
μ/mm⁻¹	8.740	6.404	1.363
F(000)	3424.0	6952.0	7100.0
GOF on F₂	1.032	1.055	1.067
R₁^a/wR₂^b [I > 2(I)]	0.0415/ 0.1034	0.0581/0.1573	0.0720/0.1870
R₁^a/wR₂^b (all data)	0.0507/ 0.1090	0.0732/0.1675	0.01195/0.2117
^a R ₁ = $\Sigma F_0 - F_c /\Sigma F_0 $. ^b wR ₂ = $\{\Sigma[w(F_0^2 - F_c^2)]/\Sigma[w(F_0^2)]\}^{1/2}$.			

Table S2 Crystal data and structure refinement for InOC-23_H and InOC-20_{V(im)}.

Compound	InOC-23 _H	InOC-20 _{V(im)}
Crystal Formula	C ₉₂ H ₆₈ In ₄ N ₁₂ O ₈₈ Ti ₁₂	C ₉₂ H ₁₁₂ In ₄ O ₇₈ Ti ₁₂
Formula weight	3783.66	3499.89
Space group	P2 ₁ /n	P-42 ₁ c
Crystal system	monoclinic	tetragonal
a/Å	18.8550(4)	19.6806(4)
b/Å	16.9266(2)	19.6806(4)
c/Å	31.0947(5)	15.9007(4)
α/°	90	90
β/°	103.552(2)	90
γ/°	90	90
V/Å³	9647.6(3)	6158.8(3)
Z	2	2
ρ/g cm⁻³	1.302	1.887
μ/mm⁻¹	5.525	8.889
F(000)	3736.0	3496.0
GOF on F₂	1.041	1.066
R₁^a/wR₂^b [I > 2(I)]	0.0672/0.1920	0.0797/0.1991
R₁^a/wR₂^b (all data)	0.0819/0.2029	0.1069/0.2157
^a R ₁ = Σ F ₀ - F _c /Σ F ₀ . ^b wR ₂ = {Σ[w(F ₀ ² - F _c ²) ₂]/Σ[w(F ₀ ²) ₂]} ^{1/2} .		

IV. Bond valence sum calculations.

Bond valence sum calculations^[5] are performed on **InOC-20_v** (Table S3), **InOC-21_v** (Table S4), **InOC-22_v** (Table S5) and **InOC-23_H** (Table S6). The BVS values are consistent with the oxidation state +III for all In centers and +IV for all Ti ions. In addition, the BVS values suggest that some bridging oxygen positions are protonated with BVS value of ca. 1 (orange label) and some terminal oxygen positions are protonated with BVS value of ca. 0.4 (blue label).

Table S3 Bond valence sum values for oxygen atoms in **InOC-20_v**.

O1	−2.08	O2	−0.43	O5	−1.93
O11A	−0.53	O11B	−0.40	O12	−2.04
O18	−1.85				
Ti1	4.27	Ti2	4.19	Ti3	4.25
In1	3.22				

Table S4 Bond valence sum values for oxygen atoms in **InOC-21_v**.

O11	−2.07	O15	−2.08	O17	−2.07
O18	−1.96	O19	−2.08	O21	−2.05
O29	−2.08	O32A	−0.36	O32B	−0.36
O34	−1.68	O35	−1.80	O37	−2.03
O44	−0.42	O45	−1.85	O47	−0.45
O49	−0.39	O53	−0.43	O56A	−0.50
O56B	−0.50	O57	−1.59	O58	−1.91
O63	−1.96	O64A	−0.41	O64B	−0.50
O66A	−0.41	O66B	−0.44		
Ti1	4.31	Ti2	4.22	Ti3	3.94
Ti4	4.26	Ti5	4.25	Ti6	4.30

Ti7	4.25	Ti8	4.32	Ti9	4.15
Ti10	4.17	Ti11	4.23	Ti12	4.30
In1	3.25	In2	3.22	In3	3.221
In4	3.15				

Table S5 Bond valence sum values for oxygen atoms in **InOC-22_v**.

O2	−2.01	O4	−0.46	O7	−1.86
O8	−2.05	O9	−0.39	O12A	−0.43
O12B	−0.42	O14	−2.10	O17	−1.91
O27A	−0.42	O27B	−0.43	O34	−1.97
O35	−1.87	O38	−2.06	O40	−2.06
O41	−2.08	O43	−1.99	O45	−2.05
O46	−0.47	O53A	−0.44	O53B	−0.42
O57	−2.06	O58	−0.45	O67A	−0.35
O67B	−0.42	O68	−1.77		
Ti1	4.28	Ti2	4.24	Ti3	4.22
Ti4	4.24	Ti5	4.17	Ti6	4.29
Ti7	4.25	Ti8	4.21	Ti9	4.24
Ti10	4.17	Ti11	4.12	Ti12	4.29
In1	3.15	In2	3.15	In3	3.12
In4	3.10				

Table S6 Bond valence sum values for oxygen atoms in **InOC-23_H**.

O11	−1.22	O15	−0.47	O22	−0.46
O26	−2.05	O27	−1.98	O30	−2.01
O32	−2.17	O36	−2.16	O38	−2.00
O42	−2.01				

Ti1	4.32	Ti2	4.23	Ti3	4.23
Ti4	4.24	Ti5	4.28	Ti6	4.32
In1	3.09	In2	3.10		

V. Additional structural figures.

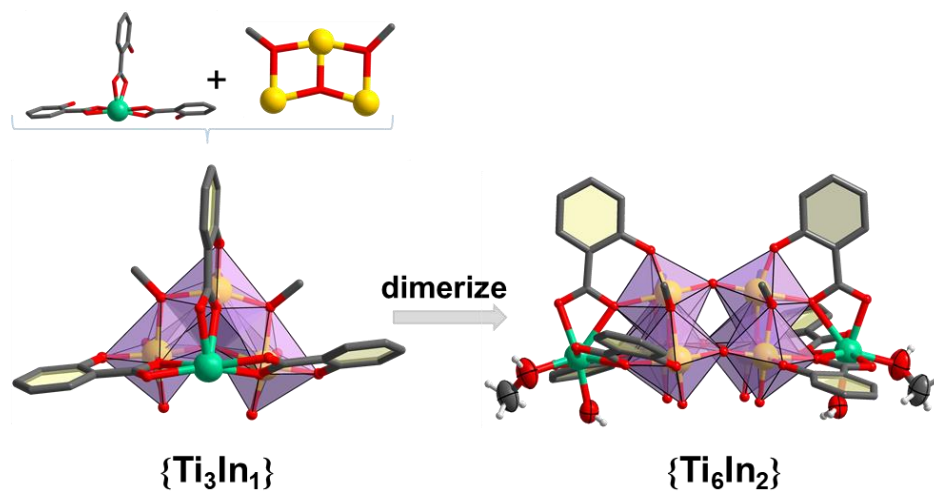


Figure S1 Processes for the formation of basic building units and second build units of **InOC-20_v**.

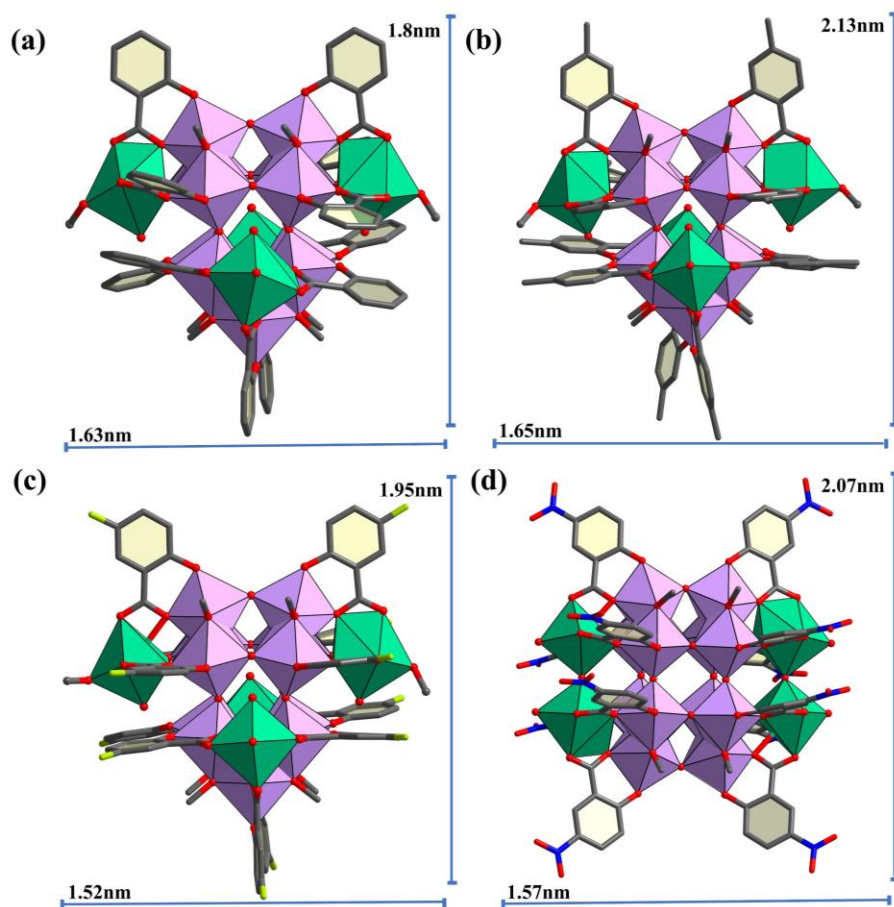


Figure S2 Molecular structure of **InOC-20_v** (a), **InOC-21_v** (b), **InOC-22_v** (c) and **InOC-23_H** (d). Some H atoms are omitted for clarity.

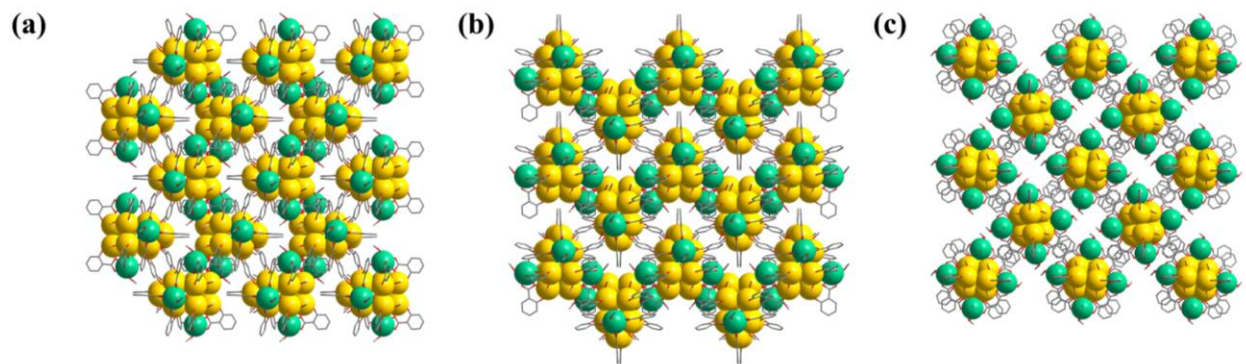


Figure S3 Packing mode of **InOC-20_v** along axis *a*, *b* and *c*.

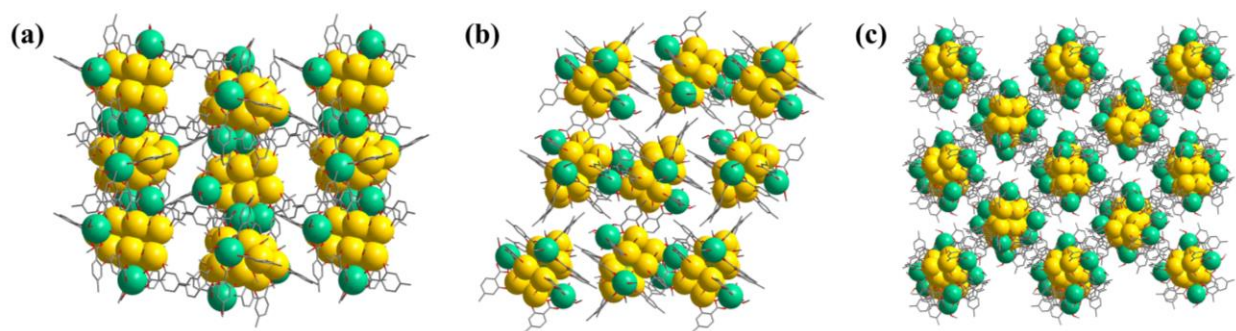


Figure S4 Packing mode of **InOC-21_v** along axis *a*, *b* and *c*.

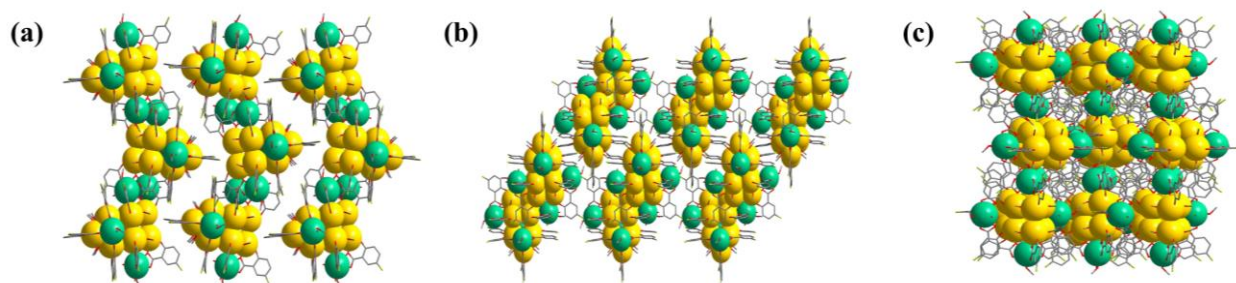


Figure S5 Packing mode of **InOC-22_v** along axis *a*, *b* and *c*.

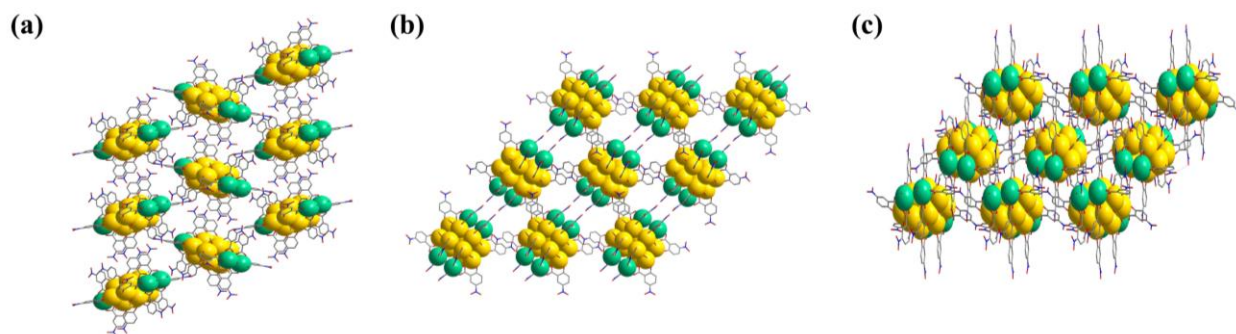


Figure S6 Packing mode of **InOC-23_H** along axis *a*, *b* and *c*.

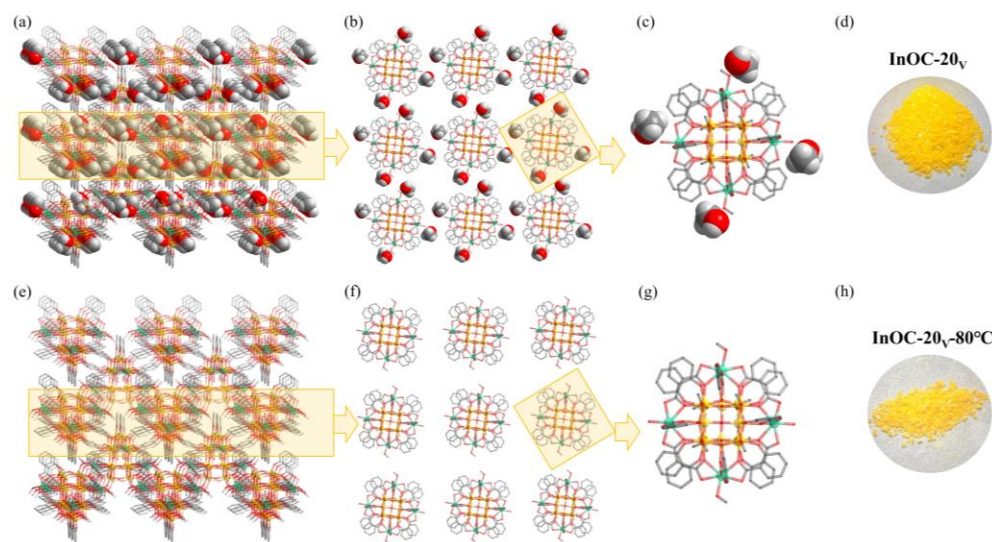


Figure S7 (a-d) individual structures, packing diagram and photographs of crystals of **InOC-20_V**; (e-h) individual structures, packing diagram and photographs of crystals of **InOC-20_V-80°C**.

VI. Powder-XRD.

There is a loss of solvent molecules and a change in crystal cell parameters, but the crystalline structure is unchanged.

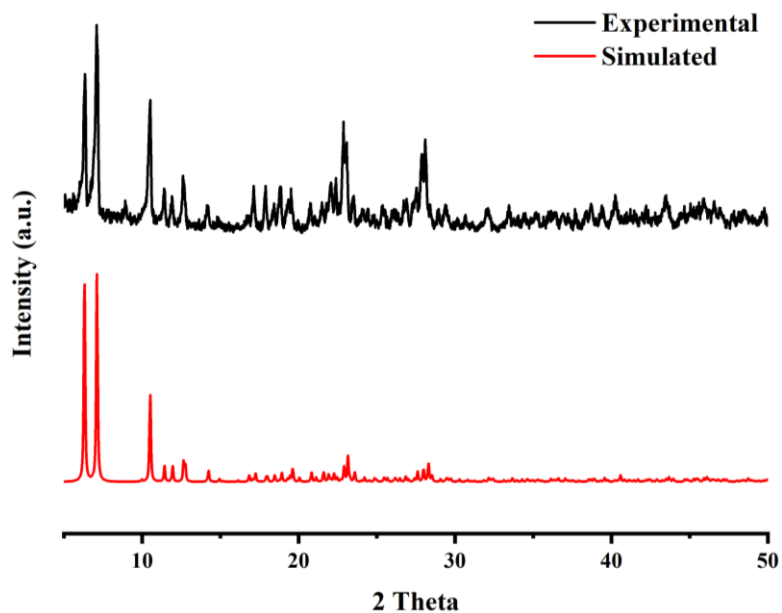


Figure S8 P-XRD analysis for InOC-20v.

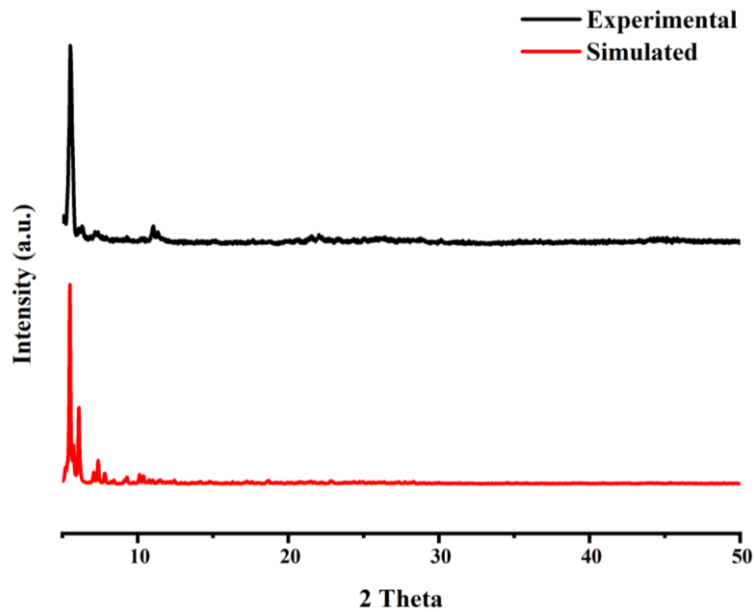


Figure S9 P-XRD analysis for InOC-21v.

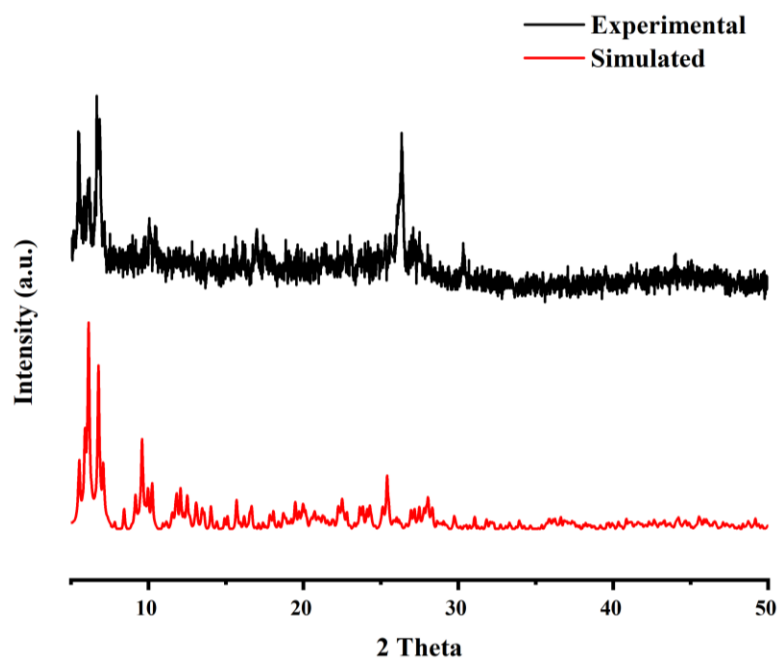


Figure S10 P-XRD analysis for **InOC-22_v**.

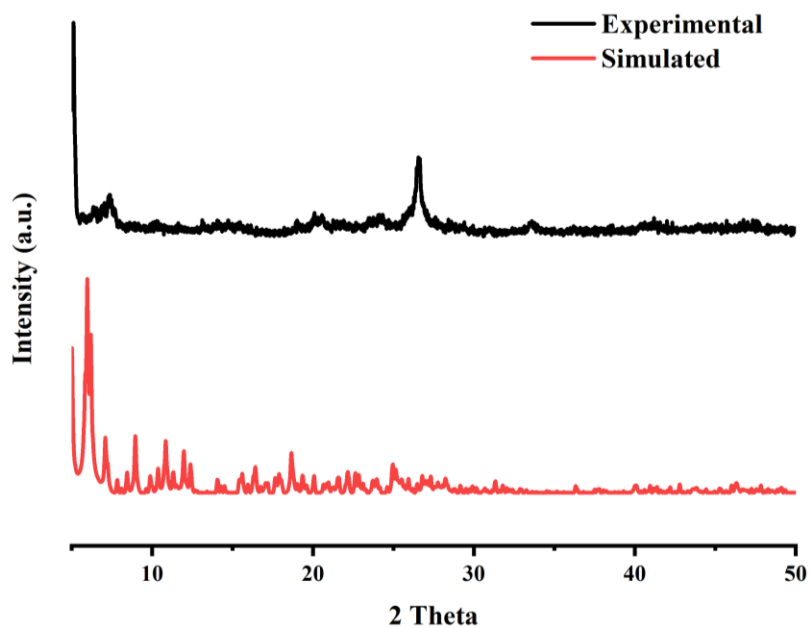


Figure S11 P-XRD analysis for **InOC-23_H**.

VII. Thermogravimetric analysis (TGA).

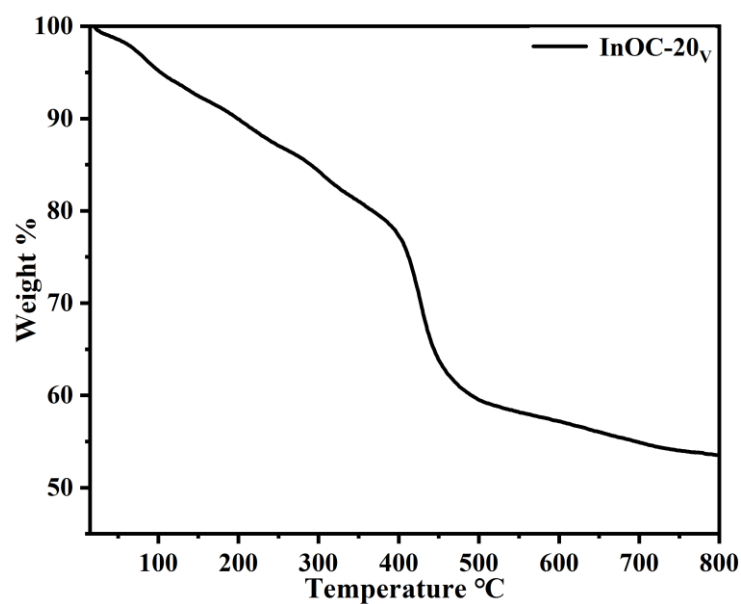


Figure S12 TG curve of compound **InOC-20_v** from room temperature to 800 °C under N₂ atmosphere.

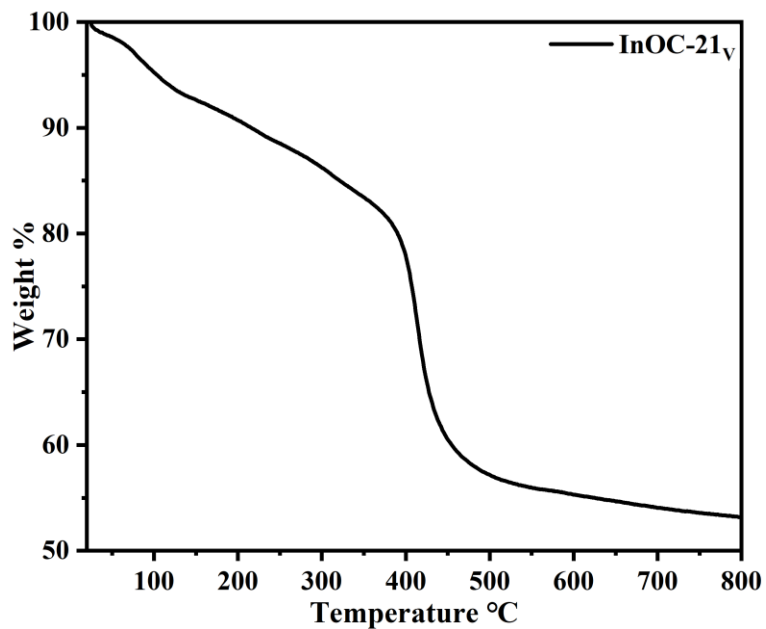


Figure S13 TG curve of compound **InOC-21_v** from room temperature to 800 °C under N₂ atmosphere.

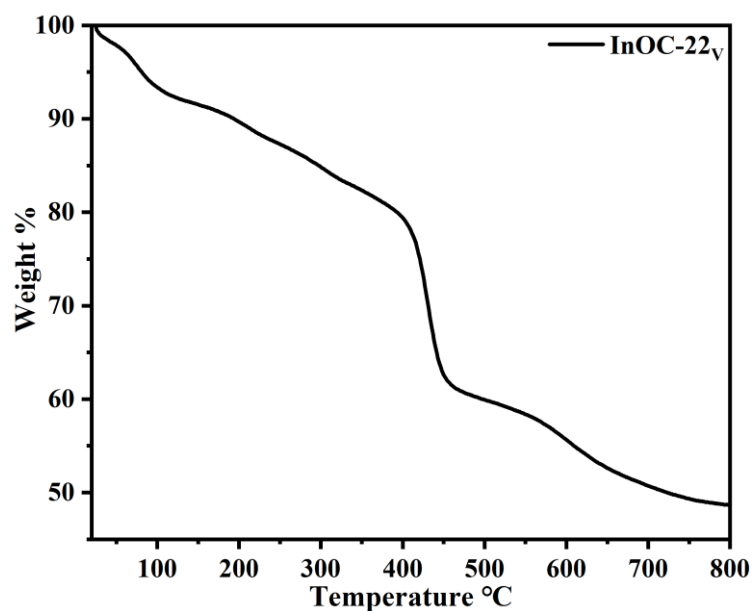


Figure S14 TG curve of compound **InOC-22_v** from room temperature to 800 °C under N₂ atmosphere.

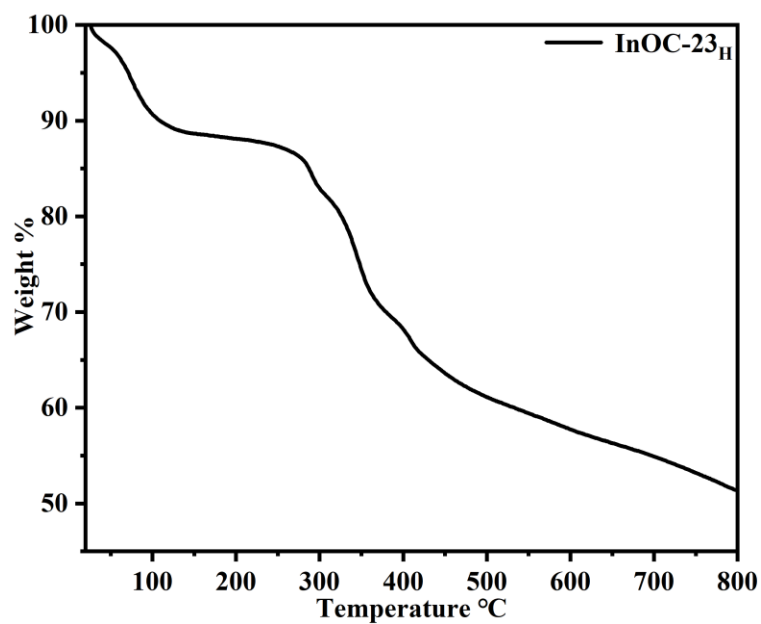


Figure S15 TG curve of compound **InOC-23_H** from room temperature to 800 °C under N₂ atmosphere.

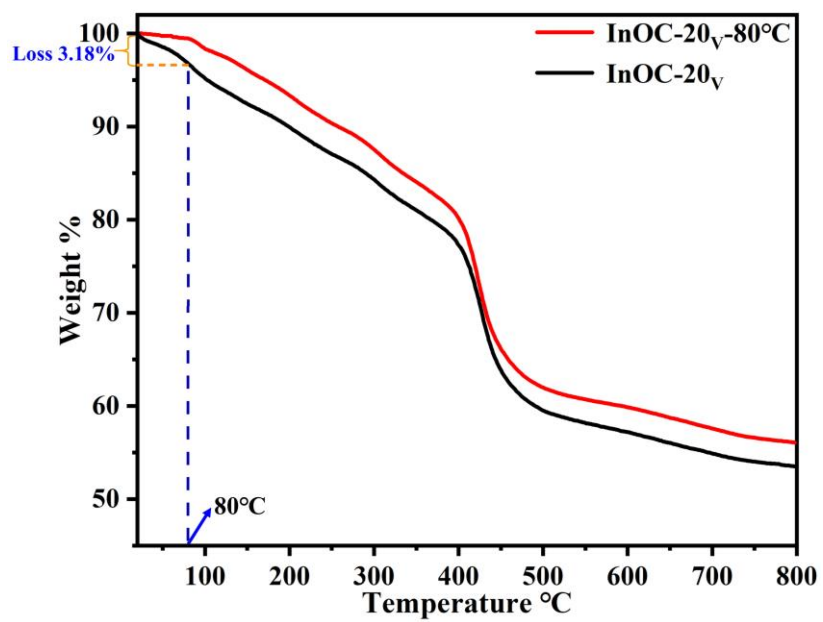


Figure S16 TG curve of compound **InOC-20_v** and **InOC-20_v-80°C** from room temperature to 800 °C under N₂ atmosphere.

VIII. IR spectra.

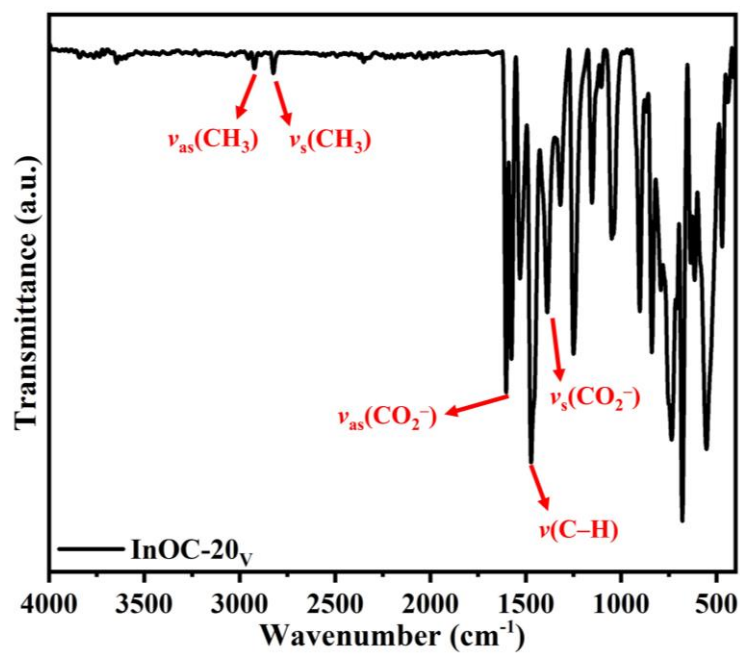


Figure S17 ATR FT-IR spectrum of InOC-20_v.

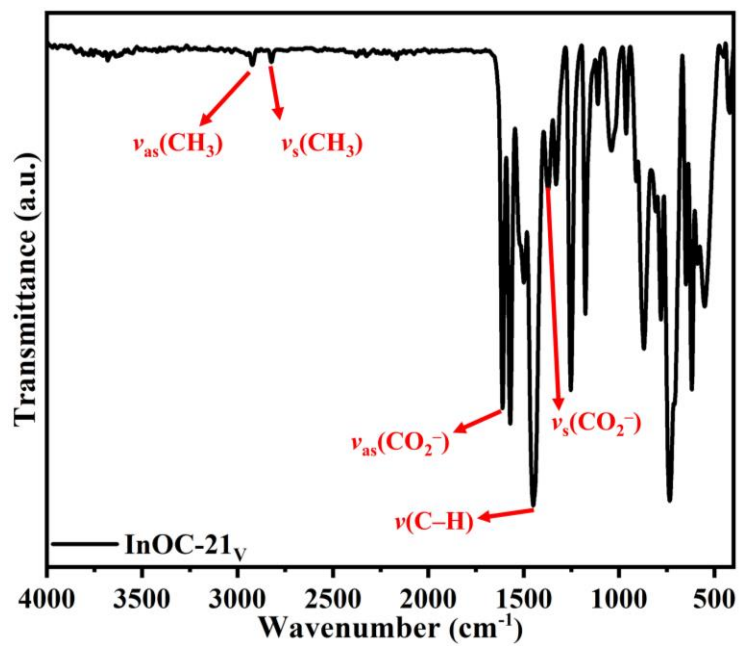


Figure S18 ATR FT-IR spectrum of InOC-21_v.

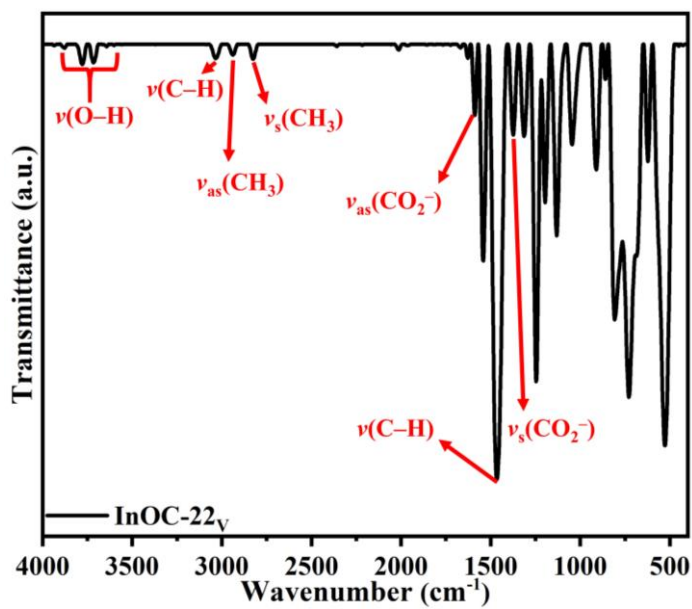


Figure S19 ATR FT-IR spectrum of InOC-22_v.

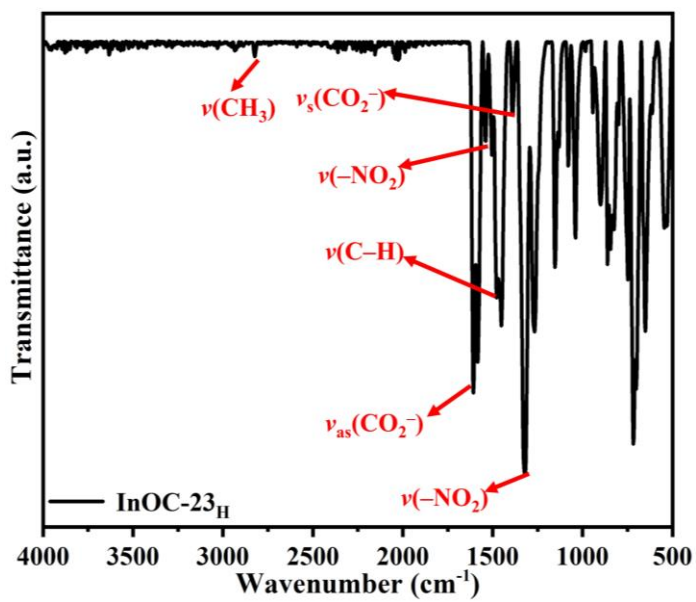


Figure S20 ATR FT-IR spectrum of InOC-23_H.

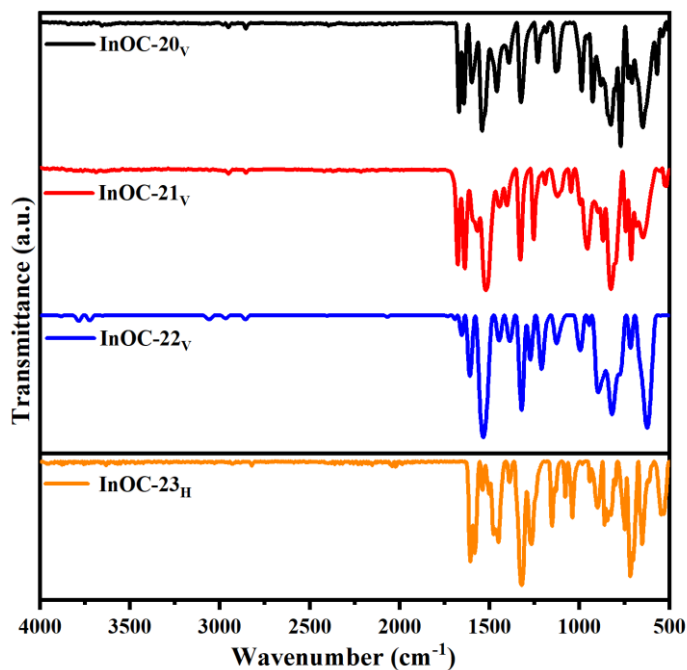


Figure S21 Comparison of ATR FT-IR spectrum **InOC-20_v** (black), **InOC-21_v** (red), **InOC-22_v** (blue), **InOC-23_H** (orange).

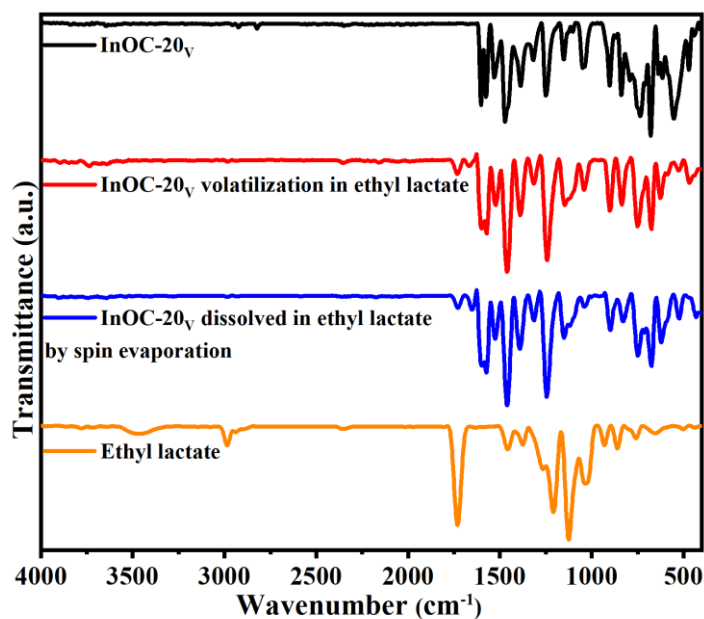


Figure S22 Comparison of ATR spectra of **InOC-20_v** (black), ethyl lactate (orange), **InOC-20_v** dissolved in ethyl lactate followed by volatilization (red) and **InOC-20_v** dissolved in ethyl lactate followed by spin evaporation (blue).

IX. UV-Vis parameters and bandgap.

Table S7 The concentration of the materials during the UV-Vis experiments.

Code	Concentration (mol/L)	Code	Concentration (mol/L)
InOC-20_v	3.02×10^{-5}	InOC-21_v	2.88×10^{-5}
InOC-22_v	2.86×10^{-5}		

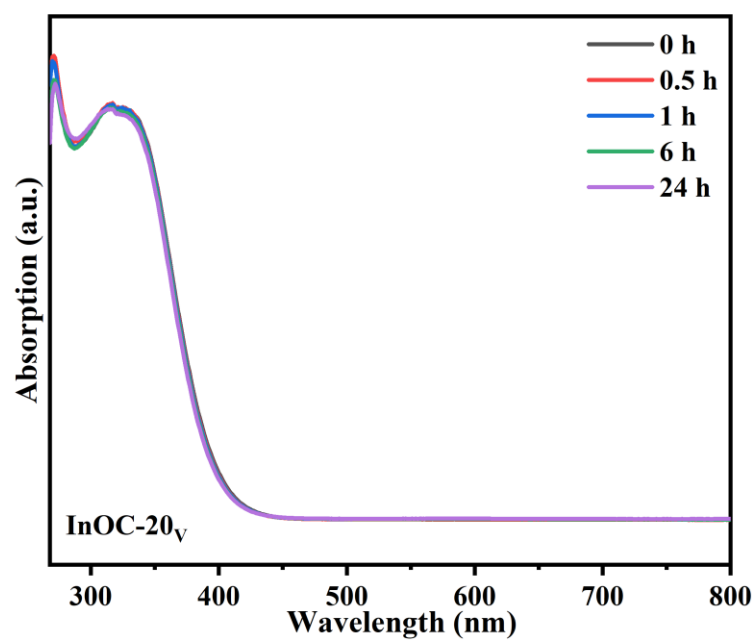


Figure S23 Comparative UV-Vis spectra of **InOC-20_v** in DMF at different time periods.

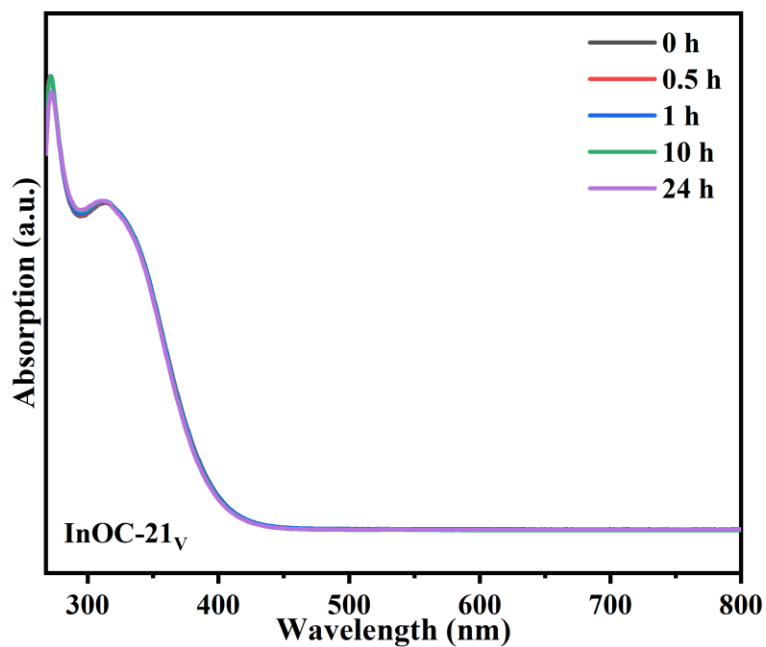


Figure S24 Comparative UV-Vis spectra of **InOC-21_v** in DMF at different time periods.

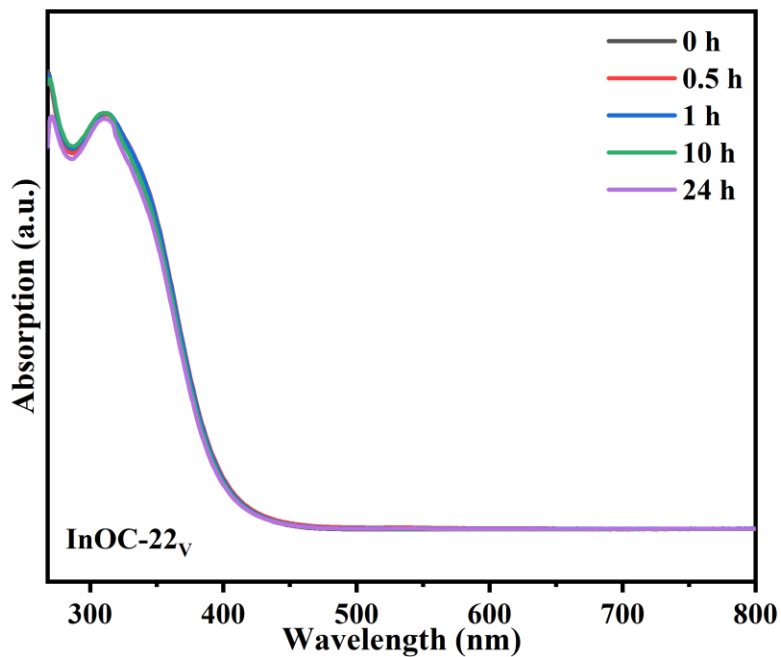


Figure S25 Comparative UV-Vis spectra of **InOC-22_v** in DMF at different time periods.

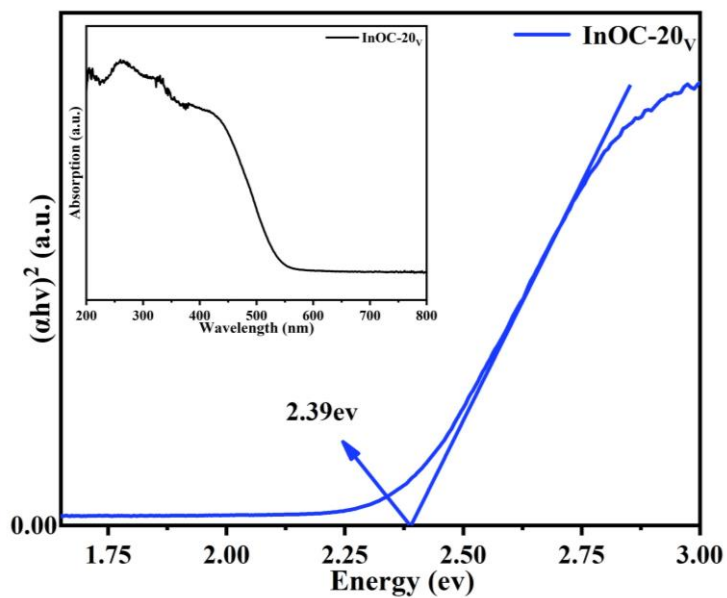


Figure S26 The absorption and bandgap spectra of InOC-20_v.

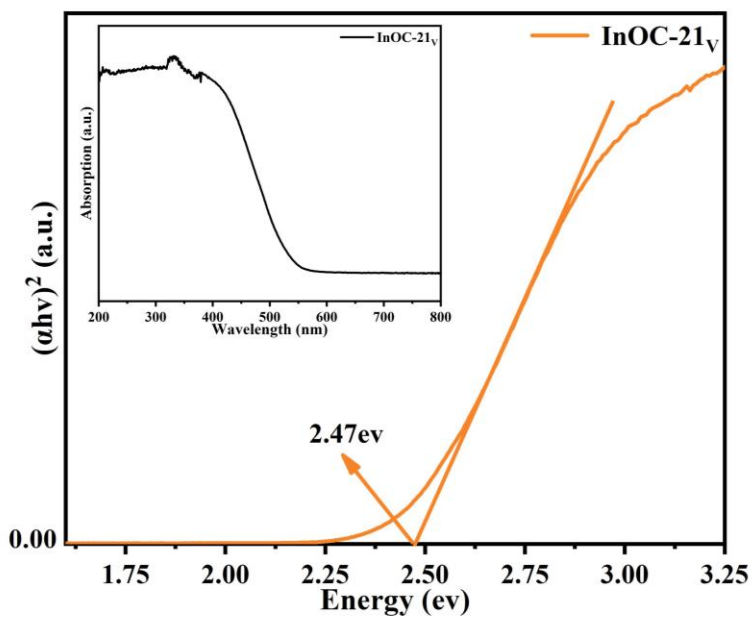


Figure S27 The absorption and bandgap spectra of InOC-21_v.

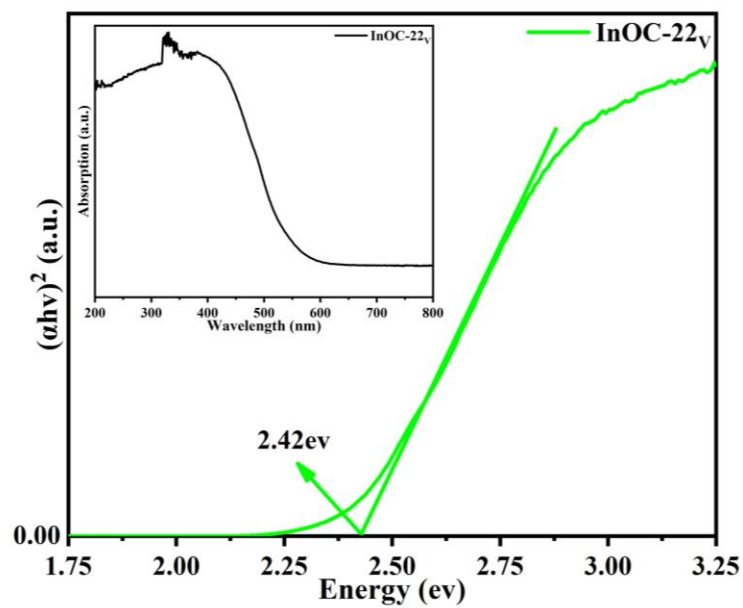


Figure S28 The absorption and bandgap spectra of InOC-22_v.

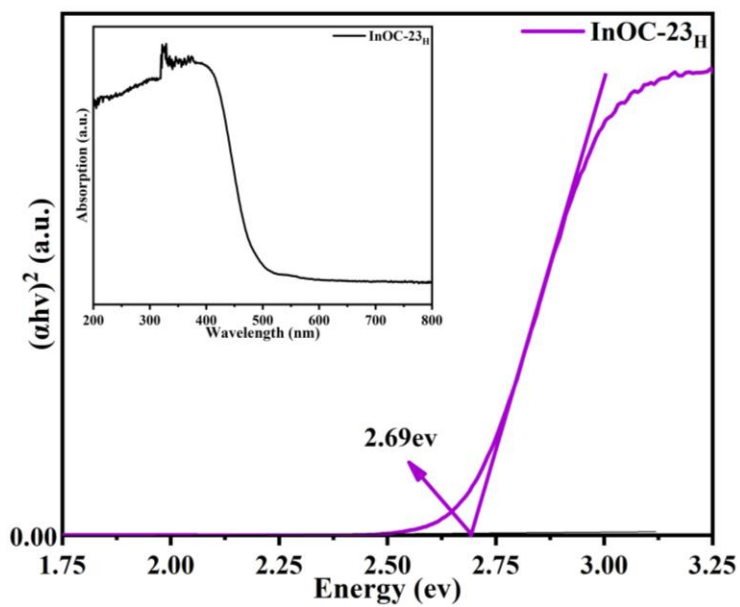


Figure S29 The absorption and bandgap spectra of InOC-23_H.

X. The energy dispersive X-ray spectroscopy (EDS) spectra.

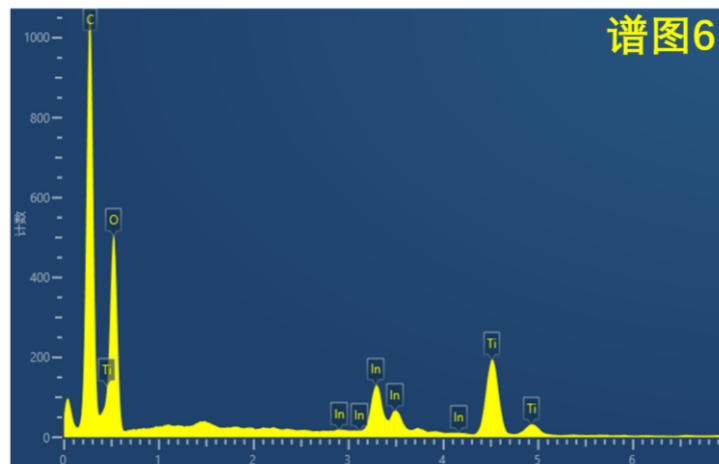


Figure S30 The EDS spectrum of InOC-20_v.

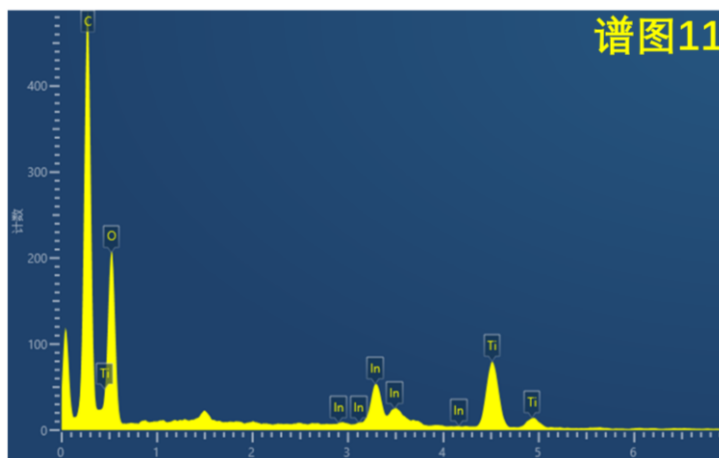


Figure S31 The EDS spectrum of InOC-21_v.

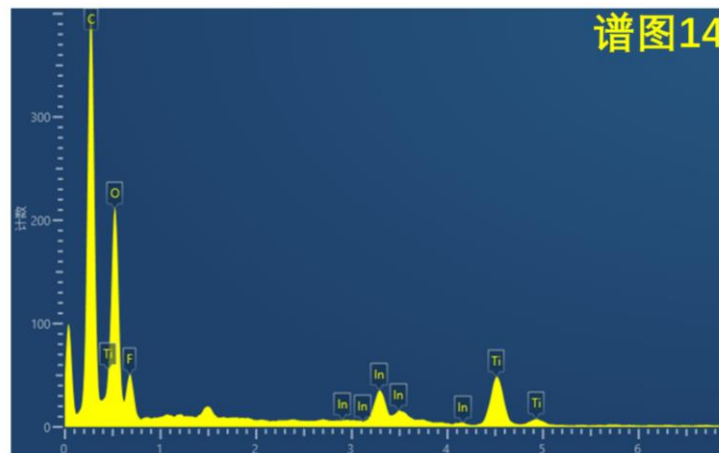


Figure S32 The EDS spectrum of InOC-22_v.

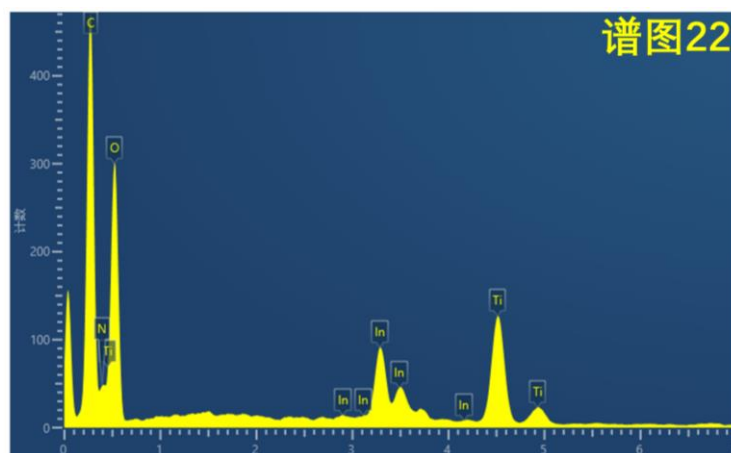


Figure S33 The EDS spectrum of **InOC-23_H**.

XI. Solubility, dynamic Light Scattering (DLS) data and contact angle measurements.

Table S8 InOC-20_v, InOC-21_v, InOC-22_v and InOC-23_H dissolution rate and saturation in different solvents.

code	InOC-20 _v		InOC-21 _v	
solvent	saturation capacity (mg/mL)	dissolution rate	saturation capacity (mg/mL)	dissolution rate
EL	>30	fast	<20	slow
DMF	>30	fast	<20	slow
H ₂ O	0	insoluble	0	insoluble
code	InOC-22 _v		InOC-23 _H	
solvent	saturation capacity (mg/mL)	dissolution rate	saturation capacity (mg/mL)	dissolution rate
EL	>30	slow	<5	slow
DMF	>30	fast	<5	slow
H ₂ O	0	insoluble	0	insoluble

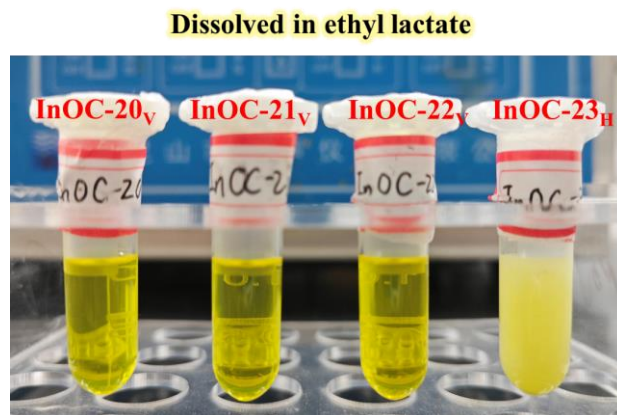


Figure S34 Dissolution rate of four compounds at 10mg in 1ml ethyl lactate for the same time.

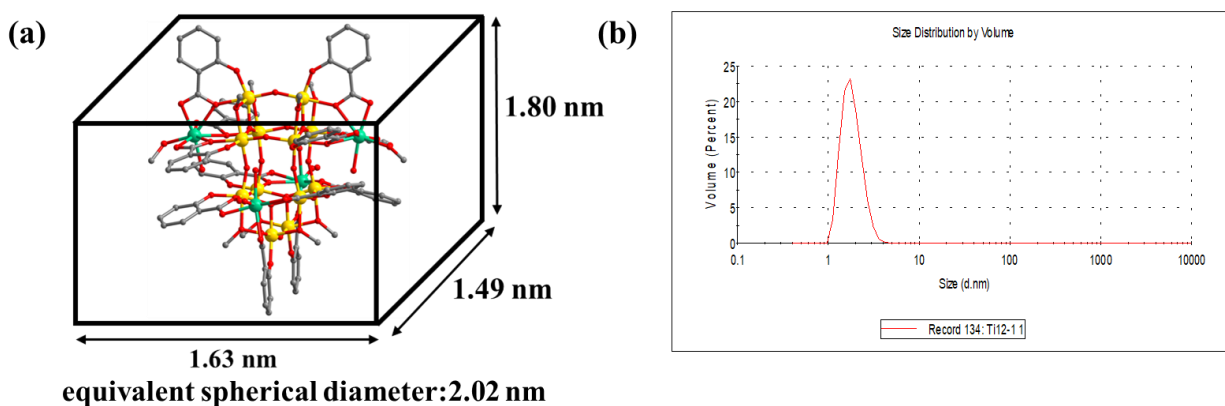


Figure S35 Molecular size of **InOC-20_v** (a) and cluster size distribution of the **InOC-20_v** (b).

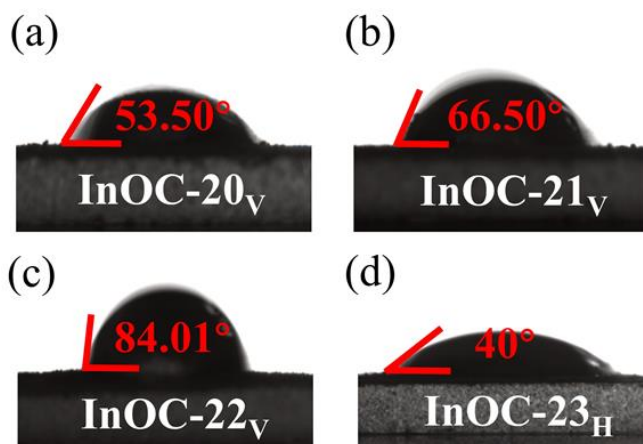


Figure S36 Contact angle patterns for water droplet on the crystal samples of **InOC-20_v** (a), **InOC-21_v** (b), **InOC-22_v** (c) and **InOC-23_H** (d).

XII. Electrospray ionization mass spectrometry measurements (ESI-MS).

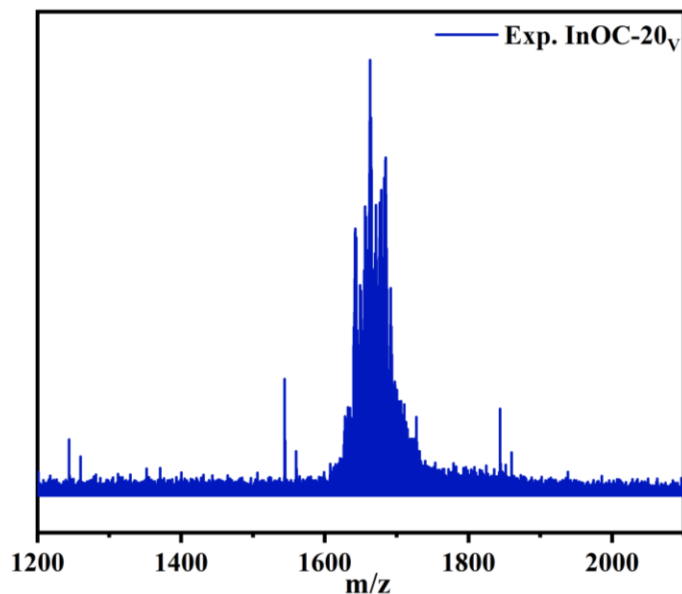


Figure S37 Positive-mode ESI-MS spectrum of **InOC-20_v** in IPA.

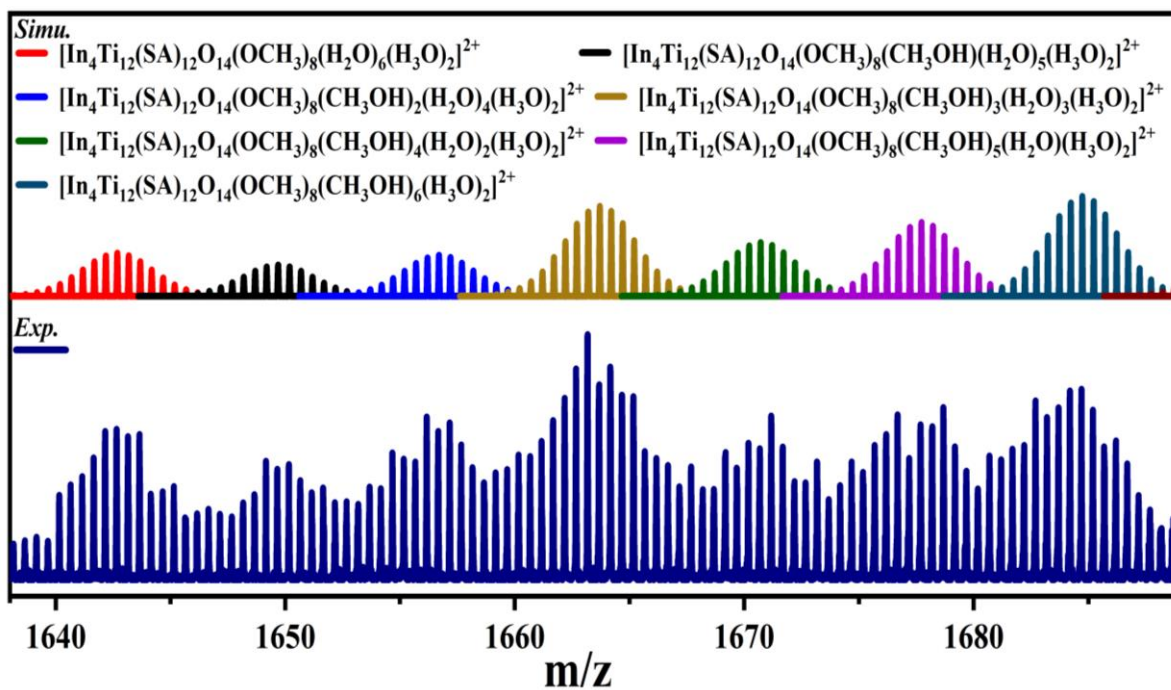


Figure S38 The comparison of experimental isotopic envelope with simulated patterns of the predominant species of +2 charged **InOC-20_v**.

Table S9 Peak assignments for positive mode ESI-MS of InOC-20_v in IPA.

Envelop assignment	charge	m/z (exp.)	m/z (cal.)
$[\text{In}_4\text{Ti}_{12}(\text{SA})_{12}(\mu_3\text{-O})_4(\mu_2\text{-O})_{10}(\text{OCH}_3)_8(\text{H}_2\text{O})_6(\text{H}_3\text{O})_2]^{2+}$	+2	1642.65	1642.68
$[\text{In}_4\text{Ti}_{12}(\text{SA})_{12}(\mu_3\text{-O})_4(\mu_2\text{-O})_{10}(\text{OCH}_3)_8(\text{CH}_3\text{OH})(\text{H}_2\text{O})_5(\text{H}_3\text{O})_2]^{2+}$	+2	1650.16	1649.69
$[\text{In}_4\text{Ti}_{12}(\text{SA})_{12}(\mu_3\text{-O})_4(\mu_2\text{-O})_{10}(\text{OCH}_3)_8(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_4(\text{H}_3\text{O})_2]^{2+}$	+2	1656.67	1656.70
$[\text{In}_4\text{Ti}_{12}(\text{SA})_{12}(\mu_3\text{-O})_4(\mu_2\text{-O})_{10}(\text{OCH}_3)_8(\text{CH}_3\text{OH})_3(\text{H}_2\text{O})_3(\text{H}_3\text{O})_2]^{2+}$	+2	1663.17	1663.71
$[\text{In}_4\text{Ti}_{12}(\text{SA})_{12}(\mu_3\text{-O})_4(\mu_2\text{-O})_{10}(\text{OCH}_3)_8(\text{CH}_3\text{OH})_4(\text{H}_2\text{O})_2(\text{H}_3\text{O})_2]^{2+}$	+2	1671.18	1670.72
$[\text{In}_4\text{Ti}_{12}(\text{SA})_{12}(\mu_3\text{-O})_4(\mu_2\text{-O})_{10}(\text{OCH}_3)_8(\text{CH}_3\text{OH})_5(\text{H}_2\text{O})(\text{H}_3\text{O})_2]^{2+}$	+2	1677.69	1677.72
$[\text{In}_4\text{Ti}_{12}(\text{SA})_{12}(\mu_3\text{-O})_4(\mu_2\text{-O})_{10}(\text{OCH}_3)_8(\text{CH}_3\text{OH})_6(\text{H}_3\text{O})_2]^{2+}$	+2	1684.19	1684.73

XIII. XPS spectra.

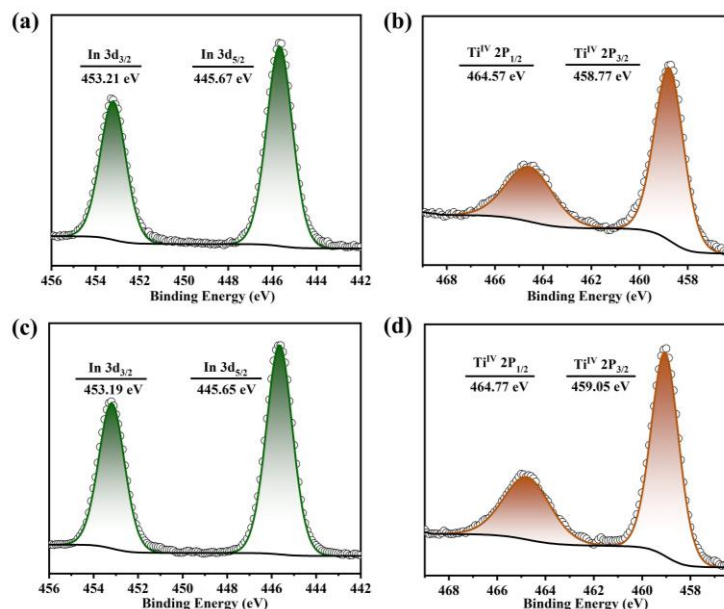


Figure S39 XPS signals for In^{III} 3d and Ti^{IV} 2p of **InOC-20_v** for initial materials (a,b) and the films subjected to EBL (c,d).^{[6][7]}

Table S10 Calculation of different C distribution obtained from C1s spectrum of **InOC-20_v**.

Element	C-C/Ti	C-O/Ti	C=O/Ti	In/Ti
Initial materials (normalization)	5.86	2.86	1	0.30
Films subjected to EBL (normalization)	5.27	1.27	0.73	0.33

Table S11 Calculation of different O distribution obtained from O1s spectrum of **InOC-20_v**.

Element	M-O-M/Ti	M-O-C/Ti	In/Ti
Initial materials (normalization)	1.71	4.57	0.30
Films subjected to EBL (normalization)	2.4	3.93	0.33

XIV. Neutron reflectivity (NR), and X-ray reflectivity (XRR) measurements.

As long as the neighboring layer has the enough SLD contrast (typically, it is true for the active layer and the substrate), the thickness can be correctly probed by either XRR or NR. Alternatively, XRR was used to present the high quality of the layers since XRR has large accessible Q range and high order reflectivity, which is especially important for checking the quality of thin films under 50 nm. However, neutron has much larger scattering cross section to compare to hydron element, NR is more suitable to measure the mass density of the layers.

NR measurements were carried out at the multipurpose reflectometer (MR) in China Spallation Neutron Source (CSNS, Dongguan, China).^[8] GenX reflectometry analysis package was used to fit both x-ray and neutron reflectivity data,^[9] both reflectivity data were fitted using the default layer model in Genx. Fitting result yields so called Scattering Length Density (SLD) profile, SLD is defined as the summation of the product of the scattering length and density of each atom which is written as:

$$\text{SLD} = \sum_j b_j \rho_j \quad (1)$$

where b_j is the scattering length and ρ_j is the particle number density, and j runs over all kind of atoms of the layer. And the mass density ρ was produced from the particle number density: $\rho = \rho_j / N_A * M_A$, where N_A is the Avogadro constant and M_A is the molar mass.

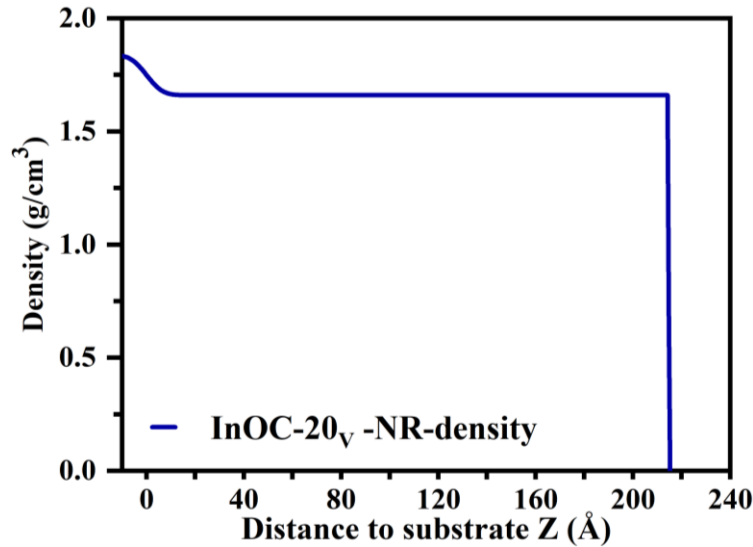


Figure S40 The density profiles as function of the thickness produced from the fitting of the NR reflectivity.

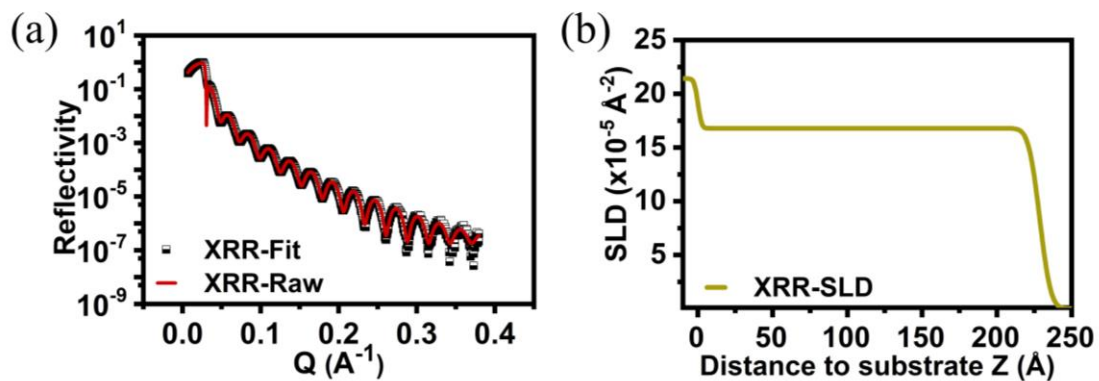


Figure S41 XRR profiles of InOC-20_v.

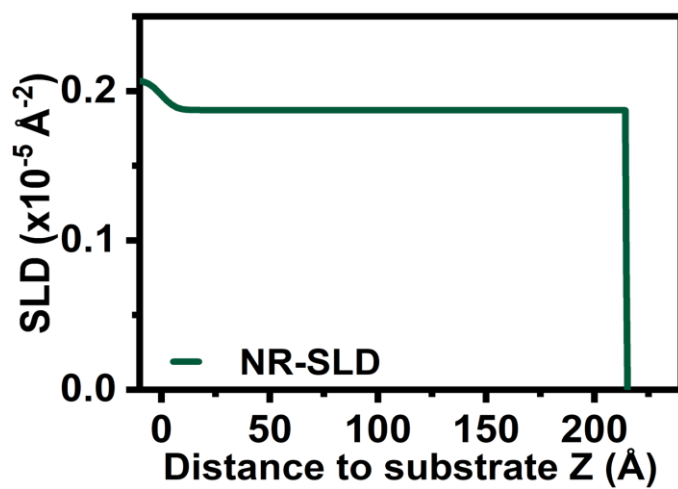


Figure S42 NR profiles of InOC-20_v.

XV. Patterning performance investigations.

The 20 mg/mL ethyl lactate solution of **InOC-20_v** was spin-coated onto a preclean silicon wafer at 3000 rpm for 30 seconds followed by baking on a hot plate at 80 °C for 60 seconds. In Figure S43, the developer used was a mixture of DMF/H₂O (3:2, v/v), with a development time of 60 seconds and no subsequent H₂O-based fixing step. The film was then exposed to electron beam radiation. As indicated in the scanning electron microscope (SEM) images, well-defined negative tone patterns were obtained after development.

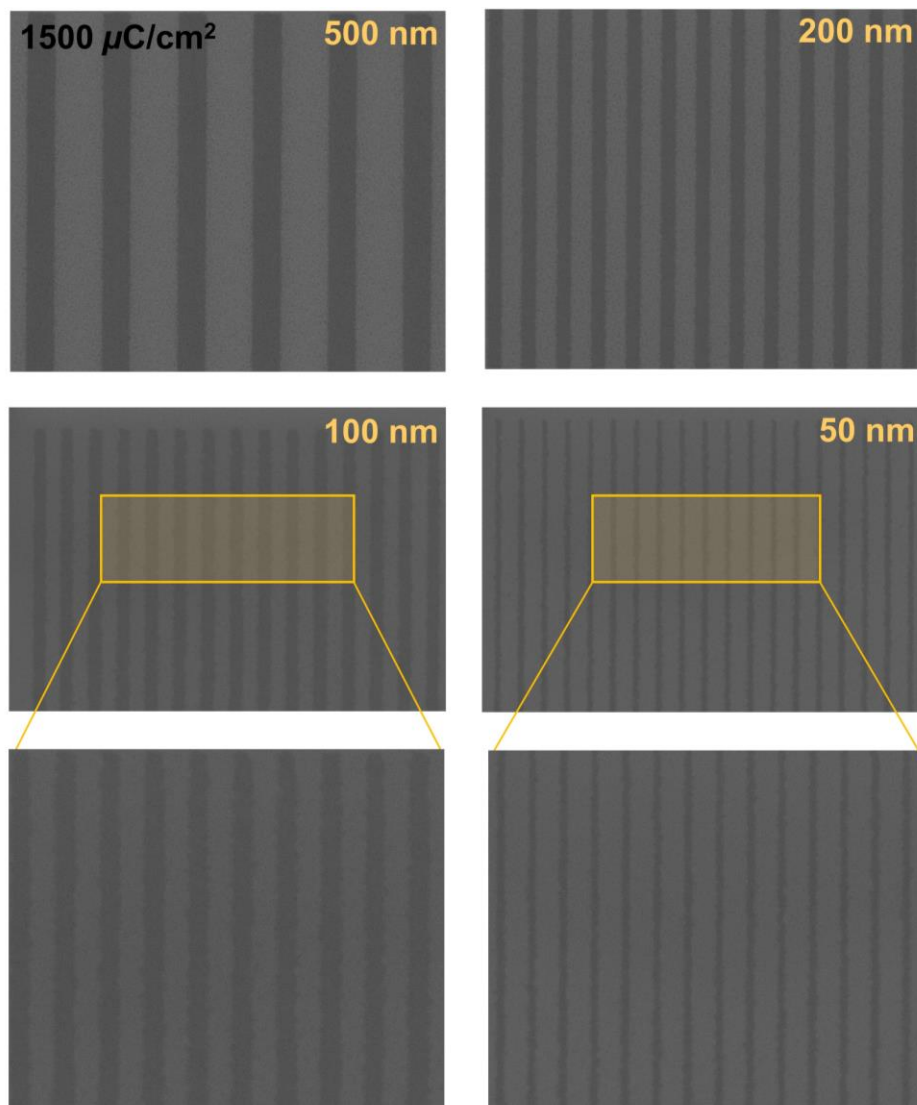


Figure S43 SEM images of patterns performed with dose of 1500 $\mu\text{C}/\text{cm}^2$ exhibiting different feature sizes of 500 nm, 200 nm, 100 nm and 50 nm for **InOC-20_v**.

XVI. Computational calculations.

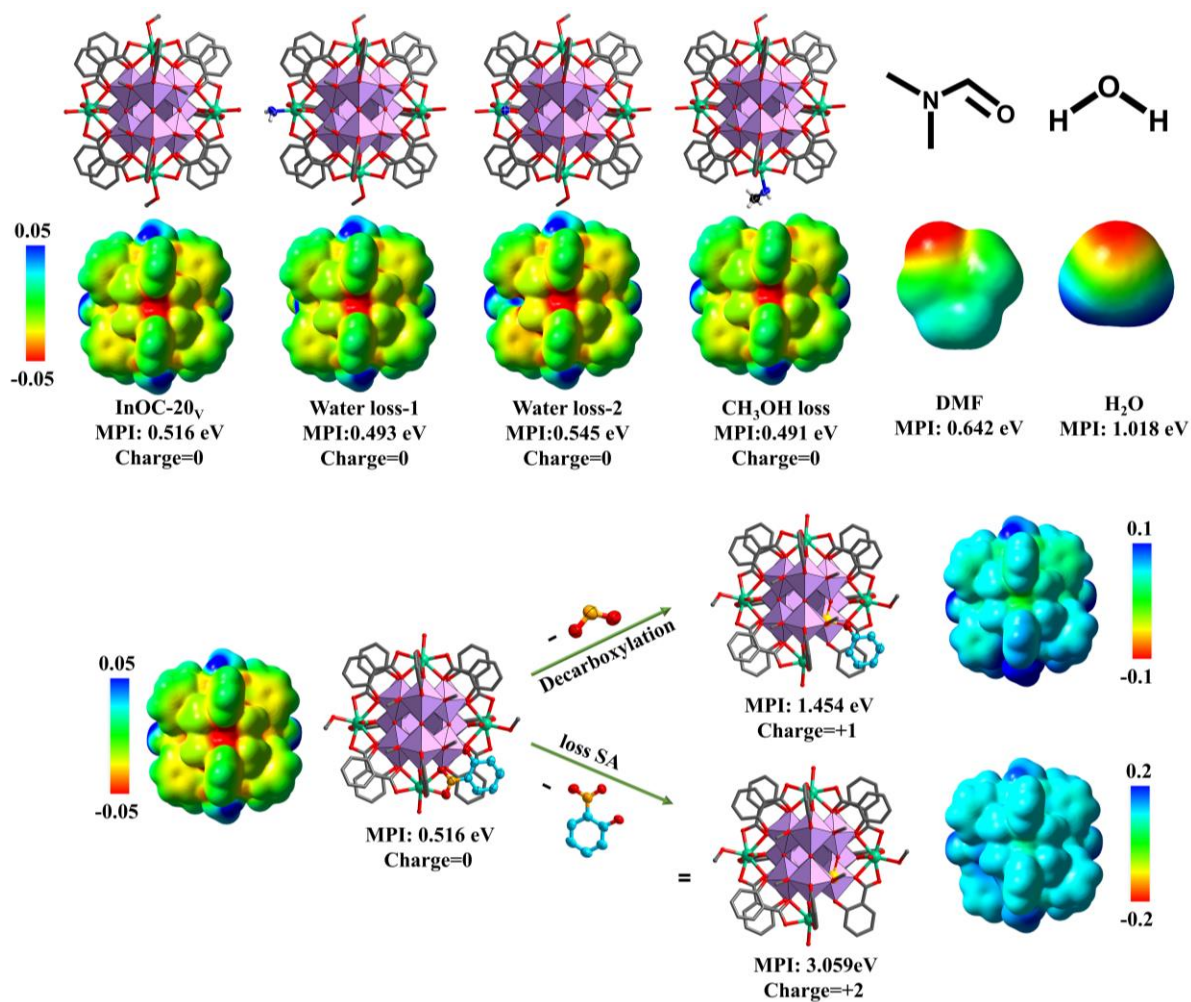


Figure S44 The ESP contours of DMF, H₂O and different segments lost from **InOC-20_v** calculated using DFT method. (The loss of segments are highlighted in ellipsoid-mode)

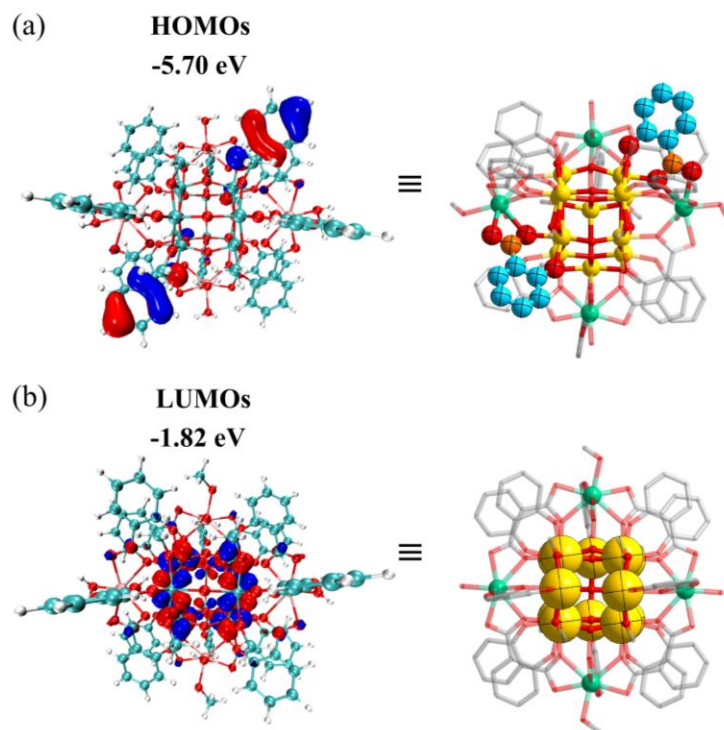


Figure S45 (a) HOMO and (b) LUMO orbitals of **InOC-20_v** (color code: blue ball, C; red ball, O; Pink ball, In; blue ball, Ti; white ball, H). the HOMO orbitals are predominantly localized around some salicylate ligands, while the LUMO orbitals are distributed around the metal-oxo-cores. Thus, upon irradiation, the electrons from HOMO orbitals would be excited, which weakens the Metal–O bonds, thereby facilitating the detachment of salicylate ligands.

All the calculations were implemented in Gaussian 16. The ground-state equilibrium geometries of these structures were fully optimized with density functional theory (DFT) using B3LYP functional and 6-31G(d,p) basis sets for C, H, O, and Lanl2DZ basis set for In, Ti with D3 dispersion correction of Grimme.^[10-19] In order to get a deeper understanding of the wave function, VMD software^[20] were used to analyze the electronic structures.

XVII. Long-term stability testing.

We have evaluated both the long-term solution stability and air stability of **InOC-20_v**. The FT-IR (Fig. S46) spectroscopy was used to confirm its long-term solution stability. Solution of **InOC-20_v** was tested at different time intervals, ranging from freshly dissolved to 2 days, and the resulting spin-coated film maintained unchanged FT-IR spectra for at least 2 days.

For air stability, FT-IR and single-crystal X-ray diffraction (SC-XRD) analyses were performed on the crystals after exposure to air for at least 10 months. The SC-XRD images demonstrate that **InOC-20_v** maintain good diffraction points after 10 months of air exposure (Fig. S48-S49). What's more, the FT-IR spectra strongly indicate that **InOC-20_v** is stable in air for at least 10 months (Fig. S47).

In summary, the experimental data demonstrate that **InOC-20_v** possess long-term stability both in solution and in air.

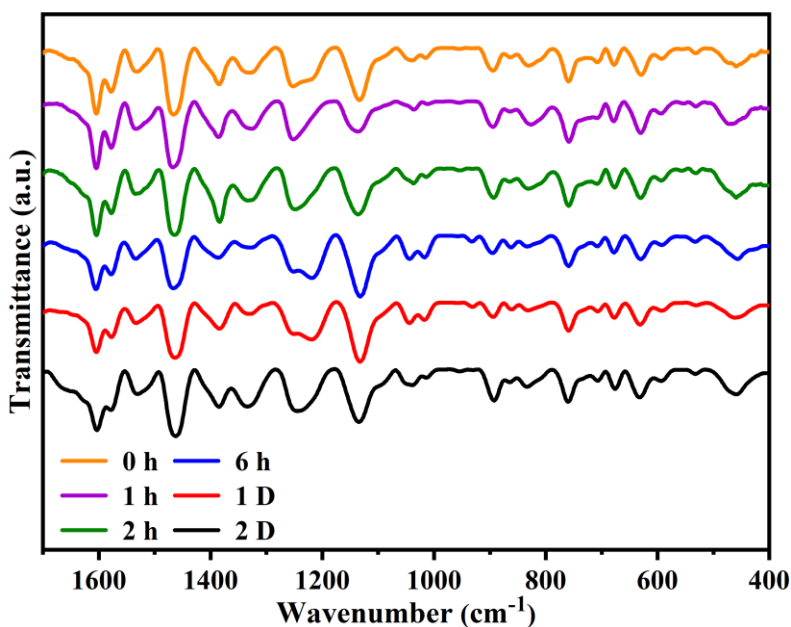


Figure S46 The FT-IR spectra of **InOC-20_v** in EA was measured at various intervals, from freshly dissolved up to 2 days, and sample was then spin-coated to fabricate films for ATR-IR measurements.

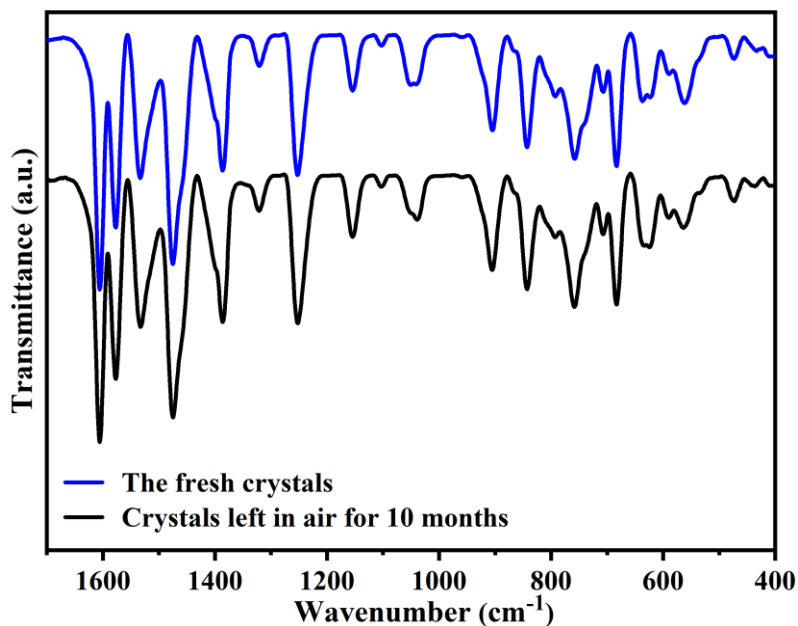


Figure S47 The FT-IR spectra of the fresh crystals and the crystals exposed to air for 10 months of **InOC-20_v**, which strongly illustrated its long-term stability in air.

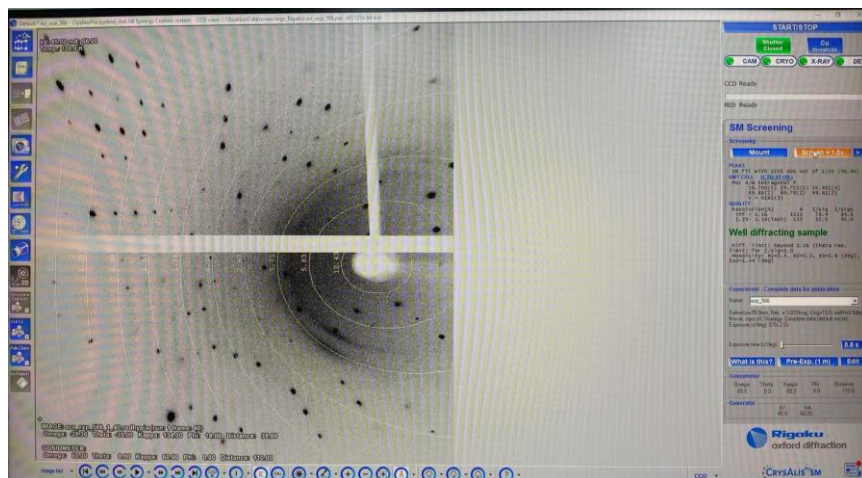


Figure S48 The single-crystal X-ray diffraction image of **InOC-20_v** crystal exposed to air for 10 months.

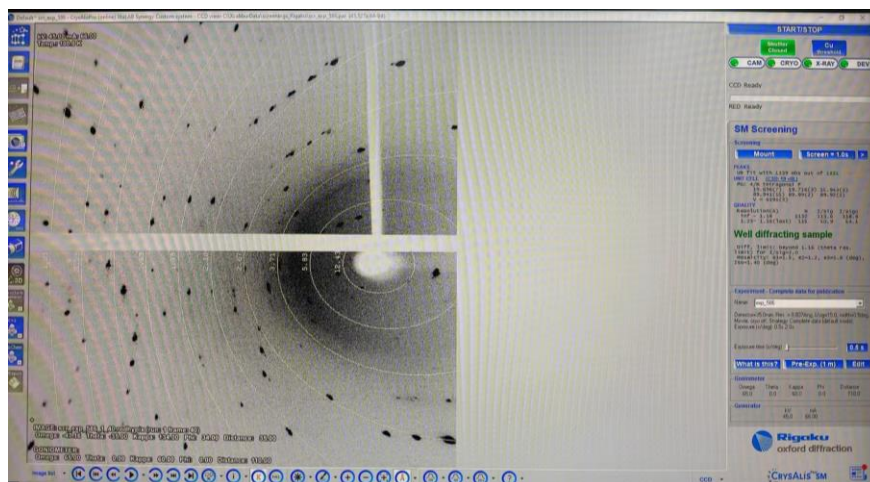


Figure S49 The single-crystal X-ray diffraction image of **InOC-20_v** crystal exposed to air for 1 day.

XVIII. Patterning performance investigations.

The ethyl lactate solution of **InOC-21_v**, **InOC-22_v**, and **InOC-23_H** was spin-coated onto a precleaned silicon wafer.

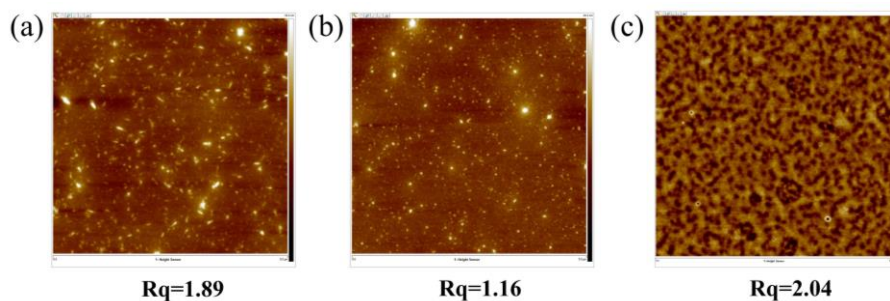


Figure S50 Topographic AFM images with Rq roughness of the spin-coated film of **InOC-21_v** (a), **InOC-22_v** (b) and **InOC-23_H** (c) over the areas of $5\ \mu\text{m} \times 5\ \mu\text{m}$. The films were prepared by spin-coating ethyl lactate solutions of **InOC-21_v**, **InOC-22_v**, and **InOC-23_H** onto hydrophilic silicon wafer.

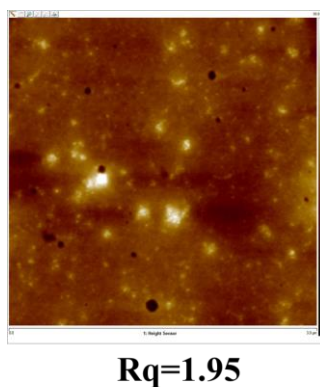


Figure S51 Topographic AFM images with Rq roughness of the spin-coated film of **InOC-20_v**. The films were prepared by spin-coating ethyl lactate solutions of **InOC-20_v** in 30 mg/mL onto hydrophilic silicon wafer.

XIX. Dose contrast curves.

InOC-20_v exhibits excellent solubility in DMF (N,N-Dimethylformamide) and EL (ethyl lactate) but is insoluble in H₂O. Notably, its solubility in EL is superior to that in DMF. Therefore, in our experiments, DMF or EL was used to dissolve the unexposed regions, enabling the formation of negative-tone patterns, while H₂O was introduced to moderate the developing strength. To systematically evaluate the developers, we tested solvent combinations of DMF/H₂O at different ratios (3:1, 3:2, and 1:1) and EL/H₂O at different ratios (3:2 and 1:1) and analyzed their dose contrast curves.

As shown in **Figures S49-S53**, the film thickness gradually increases with dose and eventually stabilizes, demonstrating clear negative-tone lithographic behavior. The D₁₀₀ of the resist developed in DMF/H₂O (3:2) (1500 $\mu\text{C}/\text{cm}^2$) is significantly better than that in DMF/H₂O (3:1) (3000 $\mu\text{C}/\text{cm}^2$) and EL/H₂O (3:2) (4500 $\mu\text{C}/\text{cm}^2$). However, when weaker developers such as DMF/H₂O (1:1) or EL/H₂O (1:1) are used, incomplete development occurs, resulting in poorly resolved patterns. Furthermore, 3D AFM imaging reveals that **InOC-20_v** developed in DMF/H₂O (3:2) exhibits superior patterning quality and uniform thickness compared to other developers. Based on these findings, we selected the DMF/H₂O (3:2) mixture as the optimal developer for lithography studies.

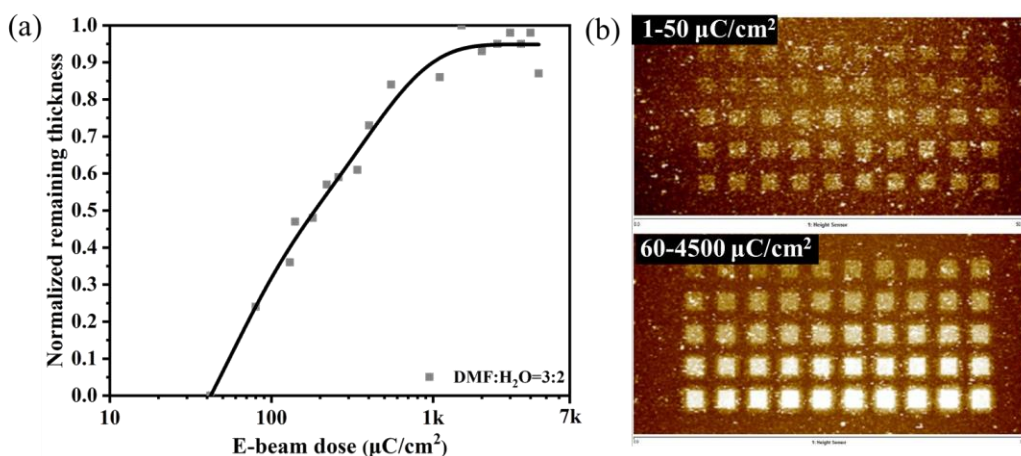


Figure S52 (a) Dose contrast curve of **InOC-20_v** after development in a DMF/H₂O (3:2) solvent, plotted as normalized remaining thickness vs. input dose; (b) AFM image of the **InOC-20_v** pattern after development. As the dose increases, the film thickness gradually rises and eventually stabilizes, demonstrating a clear negative-tone lithographic behavior. (Maximum patterned height reached 20.97 nm.)

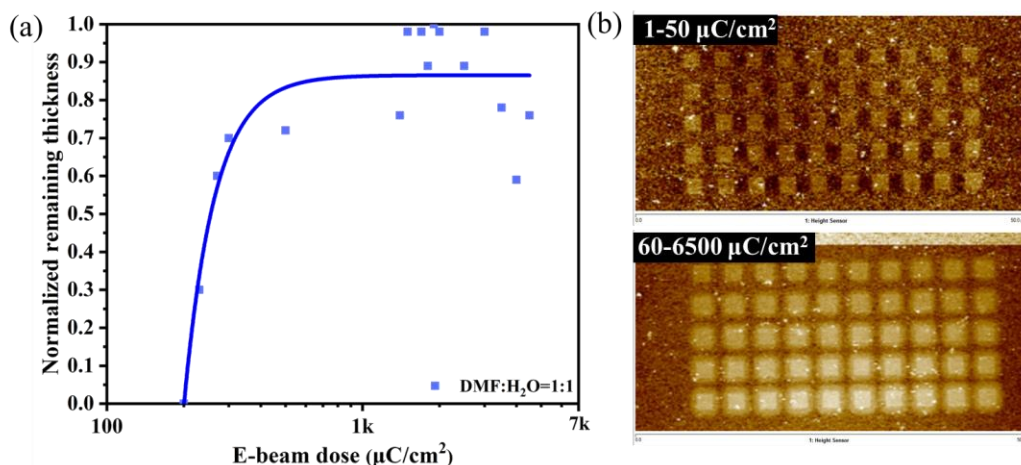


Figure S53 (a) Dose contrast curve of **InOC-20_v** after development in a DMF/H₂O (1:1) solvent, plotted as normalized remaining thickness vs. input dose; (b) AFM image of the **InOC-20_v** pattern after development. Under weak developing conditions, incomplete development results in the pattern not being displayed clearly. (Maximum patterned height reached 9.84 nm.)

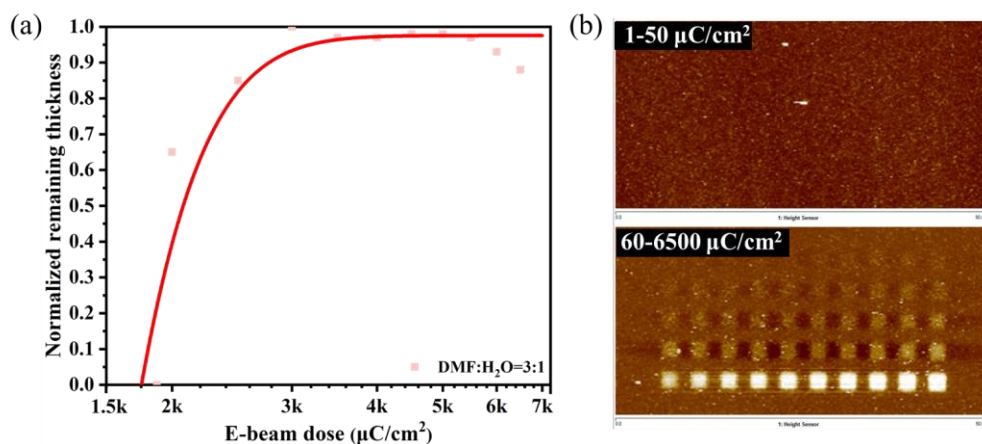


Figure S54 (a) Dose contrast curve of **InOC-20_v** after development in a DMF/H₂O (3:1) solvent, plotted as normalized remaining thickness vs. input dose; (b) AFM image of the **InOC-20_v** pattern after development. Under strong developing condition, most of the patterns were washed away, resulting in reduced lithographic sensitivity. (Maximum patterned height reached 12.84 nm.)

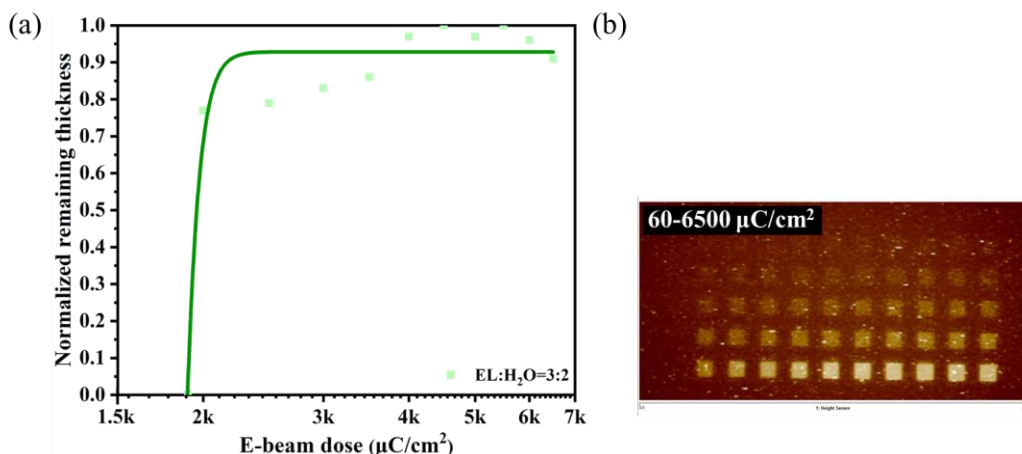


Figure S55 (a) Dose contrast curve of **InOC-20v** after development in a EL/H₂O (3:2) solvent, plotted as normalized remaining thickness vs. input dose; (b) AFM image of the **InOC-20v** pattern after development. Under strong developing condition, most of the patterns were washed away, resulting in reduced lithographic sensitivity. (Maximum patterned height reached 7.49 nm.)

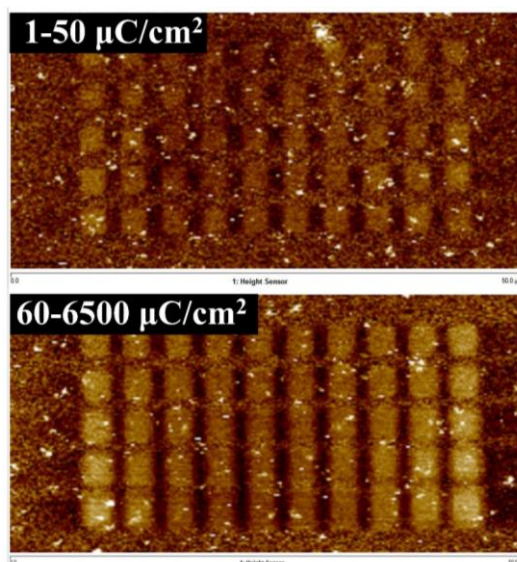


Figure S56 AFM image of the **InOC-20v** pattern after development in a EL/H₂O (1:1) solvent. Under weak developing conditions, incomplete development results in the pattern not being displayed clearly.

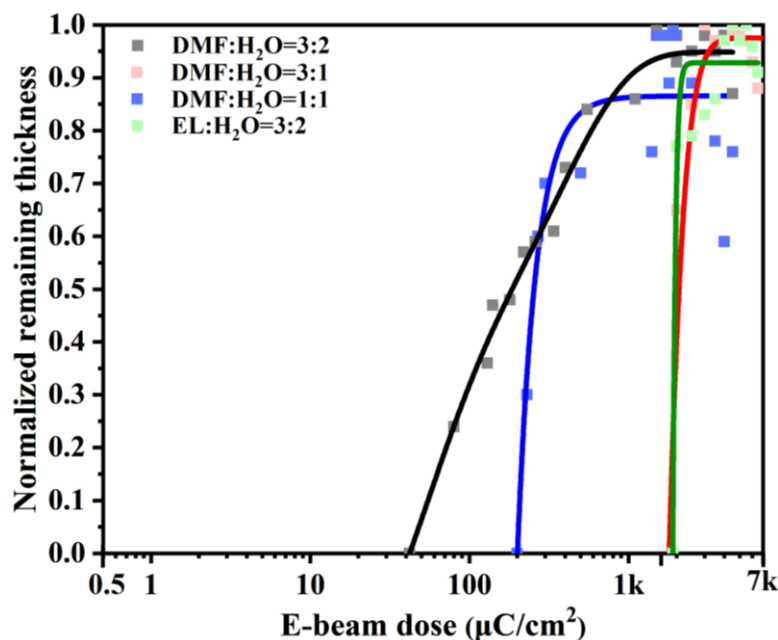


Figure S57 Contrast curves of the **InOC-20_v** resist derived for different developers.

Table S12 Sensitivity, contrast values and maximum patterned height for different developers obtained from EBL of the **InOC-20_v** resist.

Developer	Sensitivity (D_{50}), $\mu\text{C}/\text{cm}^2$	D_{100} , $\mu\text{C}/\text{cm}^2$	Contrast, γ	maximum patterned height, nm
DMF : H ₂ O = 3:2	189.42	1500	0.64	20.97
DMF : H ₂ O = 3:1	2068	3000	5.04	12.84
DMF : H ₂ O = 1:1	258.90	1900	1.02	9.84
EL : H ₂ O = 3:2	1948.96	4500	2.67	7.49

The sensitivity of a resist is the exposure dose that provides a thickness of the remaining film equal to 50% of the original value. The contrast is defined as $\gamma = |\log(D_{100}/D_0)|^{-1}$, where D_0 and D_{100} correspond to EBL doses at 0 and 100% of the remaining film thickness, respectively.

Table S12 reveals that when using DMF : H₂O = 3:1 as the developer, the **InOC-20_v** resist exhibits higher contrast but requires a higher dose for patterning. In contrast, with a DMF : H₂O = 3:2 developer, the resist achieves optimal sensitivity and the highest pattern height of 20.97 *nm*, closely matching the initial film thickness of ~21.4 *nm* before exposure.

XX. Reference.

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