

Supporting Information

**Molecular Bixbyite-Like In₁₂-Oxo Clusters with Tunable Functionalization Sites for
Lithography Patterning Applications**

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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. Propylene glycol 1-monomethyl ether 2-acetate (PGMEA), *p*-fluorophenol and InBr₃ were purchased from energy chemical. *p*-nitrophenol and InCl₃·4H₂O were purchased from Aladdin. While isopropanol (IPA), methanol, phenol, tetrahydrofuran and diethanolamine were bought from Sino pharm Chemical Reagent Beijing. Powder X-ray diffraction (PXRD) analyses data were mounted on a Rigaku Mini Flex II diffractometer using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) under ambient conditions. The Fourier transform infrared (FT-IR) spectra (KBr pellets) were performed on Bruker VERTEX 70 over a range of 400-4000 cm⁻¹. Thermal stabilities were investigated by a Mettler Toledo TGA/SDTA 851e analyzer in N₂ atmosphere with a heating rate of 10 °C/min under N₂ atmosphere. The electrospray ionization mass spectrometry (ESI-MS) data were collected on Impact II UHR-TOF (Bruker). Elemental analyses were measured on a Vario MICRO Elemental Analyzer instrument. The UV-vis absorption spectra are recorded at room temperature on a Lamda35 UV spectrophotometer and scanned at 268-800 nm. The energy dispersive spectroscopy (EDS) analyses of single crystals were performed on a JEOL JSM6700F field-emission scanning electron microscope equipped with an Oxford INCA system. 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-1**: A mixture of $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ (293 mg, 1 mmol), diethanolamine (1 mL), CH_3OH (3 mL) was sealed in a 20 mL vial and transferred to an oven at 100 °C for 2 days. When cooled to room temperature, block colorless crystals formed. (yield: 210 mg, 95.56% based on In). Elemental analysis (%) for $\text{C}_{36}\text{H}_{86}\text{Cl}_6\text{In}_{12}\text{N}_8\text{O}_{26}$, *calc.*: C, 16.39; H, 3.29; N, 4.25; found: C, 16.36; H, 3.46; N, 4.23.

Synthesis of **InOC-2**: A mixture of $\text{InBr}_3 \cdot 4\text{H}_2\text{O}$ (354 mg, 1 mmol), diethanolamine (1.5 mL), CH_3OH (3 mL) was sealed in a 20 mL vial and transferred to an oven at 100 °C for 2 days. When cooled to room temperature, block colorless crystals formed. (yield: 155mg, 61.99% based on In). Elemental analysis (%) for $\text{C}_{39}\text{H}_{98}\text{Br}_6\text{In}_{12}\text{N}_8\text{O}_{29}$, *calc.*: C, 15.61; H, 3.29; N, 3.73; found: C, 15.87; H, 3.27; N, 3.87.

Synthesis of **InOC-3**: A mixture of $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ (293 mg, 1 mmol), *p*-nitrophenol (700 mg, 5 mmol), diethanolamine (1 mL), tetrahydrofuran (4 mL) was sealed in a 20 mL vial and transferred to an oven at 100 °C for 2 days. When cooled to room temperature, block yellowish crystals formed. The crystals are washing with tetrahydrofuran before collected. (yield: 120mg, 46.97% based on In). Elemental analysis (%) for $\text{C}_{56}\text{H}_{90}\text{Cl}_6\text{In}_{12}\text{N}_{12}\text{O}_{34}$, *calc.*: C, 21.94; H, 2.96; N, 5.48; found: C, 22.16; H, 2.84; N, 5.40.

Synthesis of **InOC-4**: A mixture of $\text{InBr}_3 \cdot 4\text{H}_2\text{O}$ (354 mg, 1 mmol), *p*-nitrophenol (700 mg, 5 mmol), diethanolamine (0.5 mL), tetrahydrofuran (4 mL) was sealed in a 20 mL vial and transferred to a oven at 100 °C for 2 days. When cooled to room temperature, block yellowish crystals formed. (yield: 171mg, 61.58% based on In). Elemental analysis (%) for $\text{C}_{56}\text{H}_{90}\text{Br}_6\text{In}_{12}\text{N}_{12}\text{O}_{34}$, *calc.*: C, 20.18; H, 2.72; N, 5.04; found: C, 18.59; H, 3.02; N, 4.82.

Synthesis of **InOC-5**: A mixture of $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ (293 mg, 1 mmol), *p*-fluorophenol (550 mg, 5 mmol), diethanolamine (1 mL), tetrahydrofuran (4 mL) was sealed in a 20 mL vial and transferred to a oven at 100 °C for 2 days. When cooled to room temperature, block light crystals formed. (yield: 115mg, 46.67% based on In). Elemental analysis (%) for $\text{C}_{56}\text{H}_{90}\text{Cl}_6\text{F}_4\text{In}_{12}\text{N}_8\text{O}_{26} \cdot 2\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$, *calc.*: C, 24.26; H, 3.56; N, 4.42; found: C, 25.31; H, 3.44; N, 4.21.

III. Single-crystal X-ray diffraction

Single-crystal diffraction data for **InOC-1** and **InOC-2** were collected on Hybrid Pixel Array detector equipped with Ga-K α radiation ($\lambda = 1.3405 \text{ \AA}$) at about 293~298 K, while **InOC-3**, **InOC-4** and **KLD-5** were collected on Supernova single crystal diffractometer equipped with graphite-monochromatic Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$) at about 100 K. Using Olex2,^[1] the structures were solved with the dual-direct methods using ShelxT and refined with the full-matrix least-squares technique based on F^2 using the *SHELXL*.^[2] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically. The obtained crystallographic data for **InOC-1** to **InOC-5** summarized in Table S1 to Table S5. The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC 2078614-2078618 (**InOC-1** to **InOC-5**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Crystal data and structure refinement for **InOC-1**.

Crystal formula	C ₃₆ H ₈₄ Cl ₆ In ₁₂ N ₈ O ₂₆
Formula weight	2635.65
Temperature/K	293(2)
Crystal system	monoclinic
Space group	I2
a/ \AA	16.05120(10)
b/ \AA	11.42060(10)
c/ \AA	20.21170(10)
$\alpha/^\circ$	90
$\beta/^\circ$	90.1940(10)
$\gamma/^\circ$	90
Volume/ \AA^3	3705.07(4)
Z	2
$\rho_{\text{calc}}/\text{g/cm}^3$	2.362
μ/mm^{-1}	21.288
F(000)	2508.0
Crystal size/ mm^3	0.8 \times 0.7 \times 0.6
Radiation	GaK α ($\lambda = 1.3405$)
Index ranges	-21 \leq h \leq 20, -15 \leq k \leq 14, -27 \leq l \leq 27
Reflections collected	43834

Independent reflections	9088 [$R_{\text{int}} = 0.0720$, $R_{\text{sigma}} = 0.0361$]
Data/restraints/parameters	9088/1/400
Goodness-of-fit on F^2	1.036
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0335$, $wR_2 = 0.0911$
Final R indexes [all data]	$R_1 = 0.0340$, $wR_2 = 0.0915$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.13/-1.33

Table S2 Crystal data and structure refinement for **InOC-2**.

Crystal formula	$\text{C}_{36}\text{H}_{84}\text{Br}_6\text{In}_{12}\text{N}_8\text{O}_{26}$
Formula weight	2902.41
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
$a/\text{\AA}$	11.5427(3)
$b/\text{\AA}$	26.8196(3)
$c/\text{\AA}$	26.8568(5)
$\alpha/^\circ$	101.1820(10)
$\beta/^\circ$	102.181(2)
$\gamma/^\circ$	96.092(2)
Volume/ \AA^3	7878.3(3)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	2.447
μ/mm^{-1}	21.535
F(000)	5448.0
Crystal size/ mm^3	$0.1 \times 0.08 \times 0.06$
Radiation	$\text{GaK}\alpha$ ($\lambda = 1.3405$)
Index ranges	$-14 \leq h \leq 14$, $-34 \leq k \leq 34$, $-28 \leq l \leq 34$
Reflections collected	104803
Independent reflections	34943 [$R_{\text{int}} = 0.0750$, $R_{\text{sigma}} = 0.0721$]
Data/restraints/parameters	34943/14/1602
Goodness-of-fit on F^2	1.045
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0754$, $wR_2 = 0.1826$

Final R indexes [all data]	$R_1 = 0.1138$, $wR_2 = 0.2024$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	2.39/-1.93

Table S3 Crystal data and structure refinement for **InOC-3**.

Crystal formula	$C_{56}H_{88}Cl_6In_{12}N_{12}O_{34}$
Formula weight	3063.92
Temperature/K	100.0(2)
Crystal system	tetragonal
Space group	I-4
$a/\text{\AA}$	15.9892(2)
$b/\text{\AA}$	15.9892(2)
$c/\text{\AA}$	20.3659(5)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ \AA^3	5206.63(18)
Z	2
$\rho_{\text{calc}}/\text{g/cm}^3$	1.954
μ/mm^{-1}	22.853
F(000)	2940.0
Crystal size/ mm^3	$0.11 \times 0.1 \times 0.05$
Radiation	$\text{CuK}\alpha$ ($\lambda = 1.54184$)
Index ranges	$-15 \leq h \leq 19$, $-16 \leq k \leq 19$, $-25 \leq l \leq 24$
Reflections collected	19375
Independent reflections	5146 [$R_{\text{int}} = 0.0559$, $R_{\text{sigma}} = 0.0410$]
Data/restraints/parameters	5146/61/276
Goodness-of-fit on F^2	1.048
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0565$, $wR_2 = 0.1445$
Final R indexes [all data]	$R_1 = 0.0601$, $wR_2 = 0.1484$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.23/-1.40

Table S4 Crystal data and structure refinement for **InOC-4**.

Crystal formula	C ₅₆ H ₆₈ Br ₆ In ₁₂ N ₁₂ O ₃₄
Formula weight	3310.52
Temperature/K	100.01(12)
Crystal system	tetragonal
Space group	I-4
a/Å	16.1018(4)
b/Å	16.1018(4)
c/Å	20.4257(8)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	5295.7(3)
Z	2
ρ _{calc} /cm ³	2.076
μ/mm ⁻¹	23.728
F(000)	3116.0
Crystal size/mm ³	0.12 × 0.1 × 0.06
Radiation	CuKα (λ = 1.54184)
Index ranges	-11 ≤ h ≤ 19, -19 ≤ k ≤ 16, -24 ≤ l ≤ 17
Reflections collected	7312
Independent reflections	4325 [R _{int} = 0.0407, R _{sigma} = 0.0464]
Data/restraints/parameters	4325/156/276
Goodness-of-fit on F ²	1.067
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0759, wR ₂ = 0.1999
Final R indexes [all data]	R ₁ = 0.0793, wR ₂ = 0.2069
Largest diff. peak/hole / e Å ⁻³	1.71/-2.14

Table S5 Crystal data and structure refinement for **InOC-5**.

Crystal formula	C ₅₆ H ₈₈ Cl ₆ F ₄ In ₁₂ N ₈ O ₂₆
Formula weight	2955.88
Temperature/K	100.03(19)
Crystal system	tetragonal
Space group	I-4
a/Å	15.9744(2)
b/Å	15.9744(2)
c/Å	19.4804(5)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	4971.04(18)
Z	2
ρ _{calc} /cm ³	1.975
μ/mm ⁻¹	23.891
F(000)	2828.0
Crystal size/mm ³	0.08 × 0.06 × 0.05
Radiation	CuKα (λ = 1.54178)
Index ranges	-17 ≤ h ≤ 17, -17 ≤ k ≤ 16, -21 ≤ l ≤ 21
Reflections collected	10192
Independent reflections	3465 [R _{int} = 0.0303, R _{sigma} = 0.0257]
Data/restraints/parameters	3465/36/254
Goodness-of-fit on F ²	1.086
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0275, wR ₂ = 0.0709
Final R indexes [all data]	R ₁ = 0.0280, wR ₂ = 0.0712
Largest diff. peak/hole / e Å ⁻³	1.48/-0.58

IV. Bond valence sum calculations

Bond valence sum calculations^[3] are performed on **InOC-1 (Table S6)**, **InOC-2 (Table S7)**, **InOC-3 (Table S8)**, **InOC-4 (Table S9)** and **InOC-5 (Table S10)**. The BVS values for the oxygen atoms suggest that there exists protonation of some oxygen positions in the skeleton of these In₁₂-oxo-clusters with BVS value of *ca.* 1.

Table S6 Bond valence sum values for oxygen atoms in **InOC-1**.

O00J	-1.98	O1	-1.98	O2	-1.95	O3	-1.91	O4	-2.04
O5	-1.05	O6	-1.97	O7	-2.07	O8	-1.96	O9	-1.93
O10	-2.01	O11	-1.01	O12	-2.05	O13	-1.96		

Table S7 Bond valence sum values for oxygen atoms in **InOC-2**.

O1	-1.95	O2	-1.96	O3	-1.94	O4	-1.00	O5	-1.83
O6	-1.95	O7	-2.01	O8	-2.06	O9	-1.95	O10	-1.90
O11	-1.99	O12	-2.10	O13	-1.80	O14	-1.98	O15	-2.03
O16	-2.05	O17	-1.94	O18	-2.03	O19	-2.03	O20	-1.92
O21	-2.01	O22	-1.02	O23	-2.00	O24	-2.02	O25	-2.04
O26	-1.94	O27	-1.93	O28	-2.03	O29	-1.03	O30	-2.06
O31	-1.97	O32	-2.08	O33	-1.94	O34	-1.98	O35	-1.99
O36	-2.06	O37	-2.10	O38	-1.87	O39	-2.00	O40	-1.98
O41	-2.05	O42	-1.89	O43	-2.03	O44	-1.73	O45	-1.95
O46	-1.83	O47	-2.05	O48	-2.02	O49	-2.03	O50	-1.96
O51	-1.06	O52	-2.01						

Table S8 Bond valence sum values for oxygen atoms in **InOC-3**.

O3	-2.43	O4	-2.03	O5	-2.05	O6	-1.08	O7	-2.17
O8	-1.89	O9	-2.04						

Table S9 Bond valence sum values for oxygen atoms in **InOC-4**.

O3	-2.11	O4	-2.26	O5	-1.08	O6	-2.04	O7	-1.91
O8	-2.08	O9	-1.88						

Table S10 Bond valence sum values for oxygen atoms in **InOC-5**.

O1	-2.00	O2	-1.07	O3	-2.19	O4	-2.03	O5	-2.02
O6	-1.87	O7	-2.03						

V. Additional structural pictures

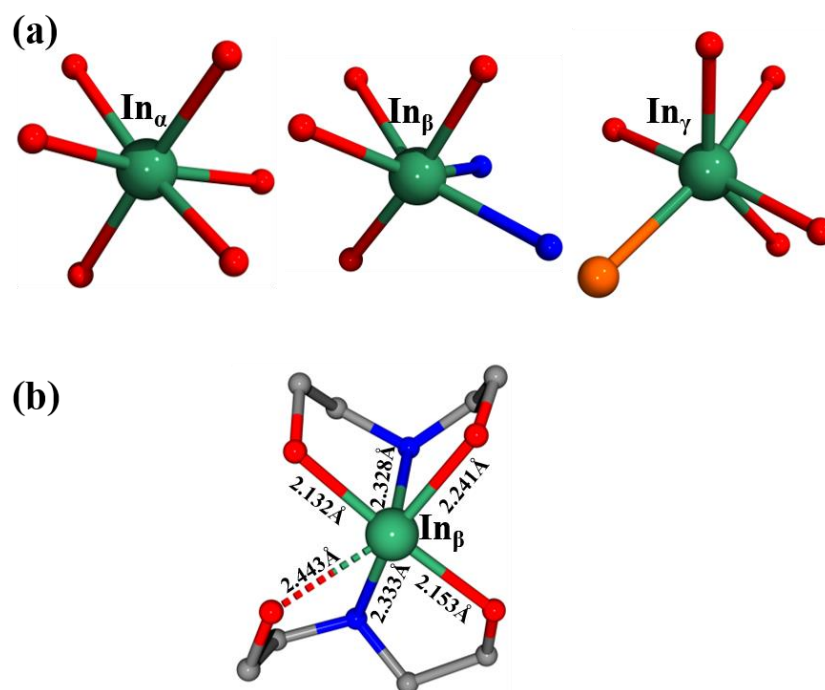


Figure S1 (a) The coordination environment of In_α $\{\text{InO}_6\}$, In_β $\{\text{InO}_5\text{Cl}\}$ and In_γ $\{\text{InO}_4\text{N}_2\}$ in **InOC-1** to **InOC-5**. **(b)** Structural details and coordination modes of diethanol amine in **InOC-1** to **InOC-5**.

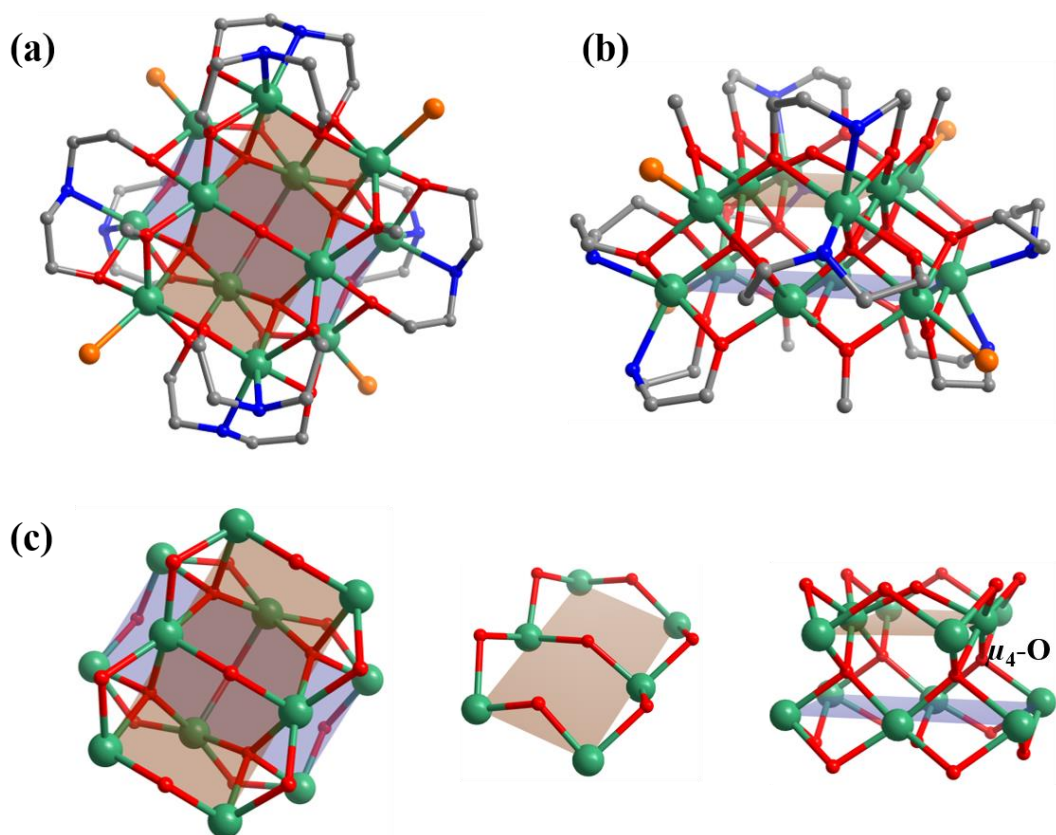


Figure S2 Top view (a) and side view (b) towards molecular structure of **InOC-1** with highlighted In₆ building units. (c) Illustration of the rectangular In₆ building units and the arrangements of two pairs of In₆-rectangle in **InOC-1** to **InOC-5**.

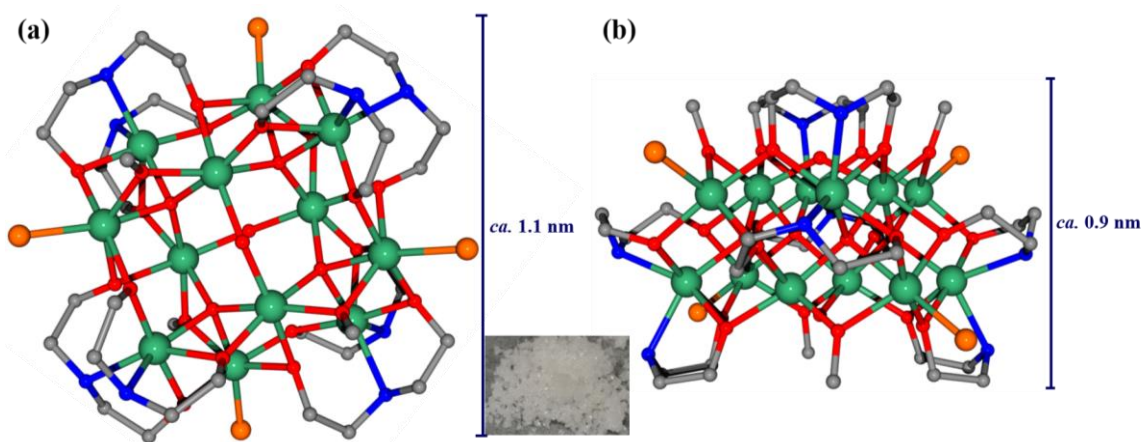


Figure S3 Molecular structure of **InOC-1** in top view (a) and side view (b). The side length and thickness are also presented.

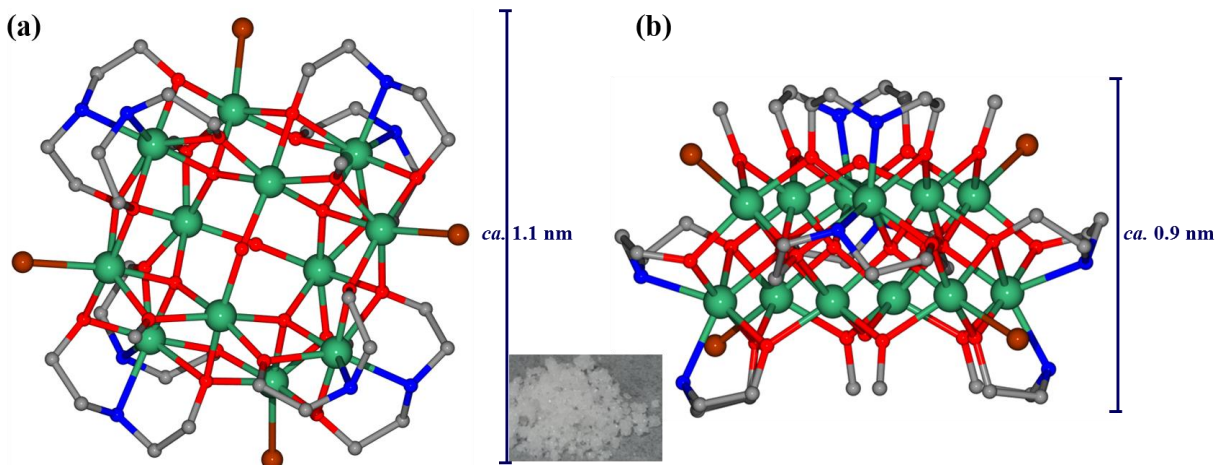


Figure S4 Molecular structure of **InOC-2** in top view **(a)** and side view **(b)**. The side length and thickness are also presented.

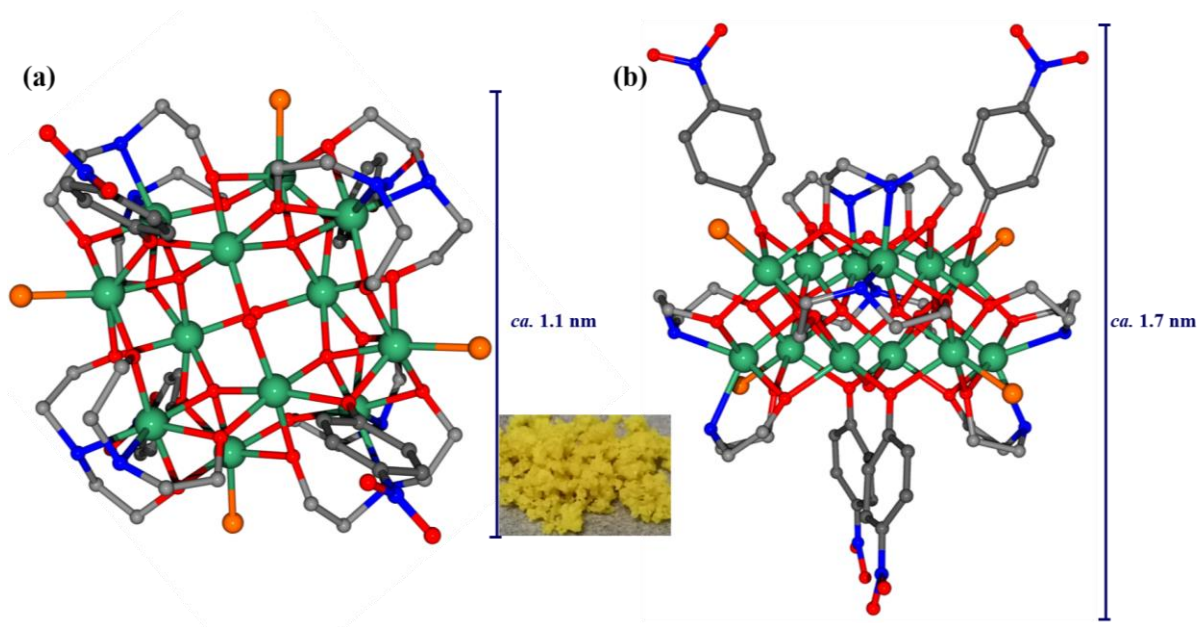


Figure S5 Molecular structure of **InOC-3** in top view **(a)** and side view **(b)**. The side length and thickness are also presented.

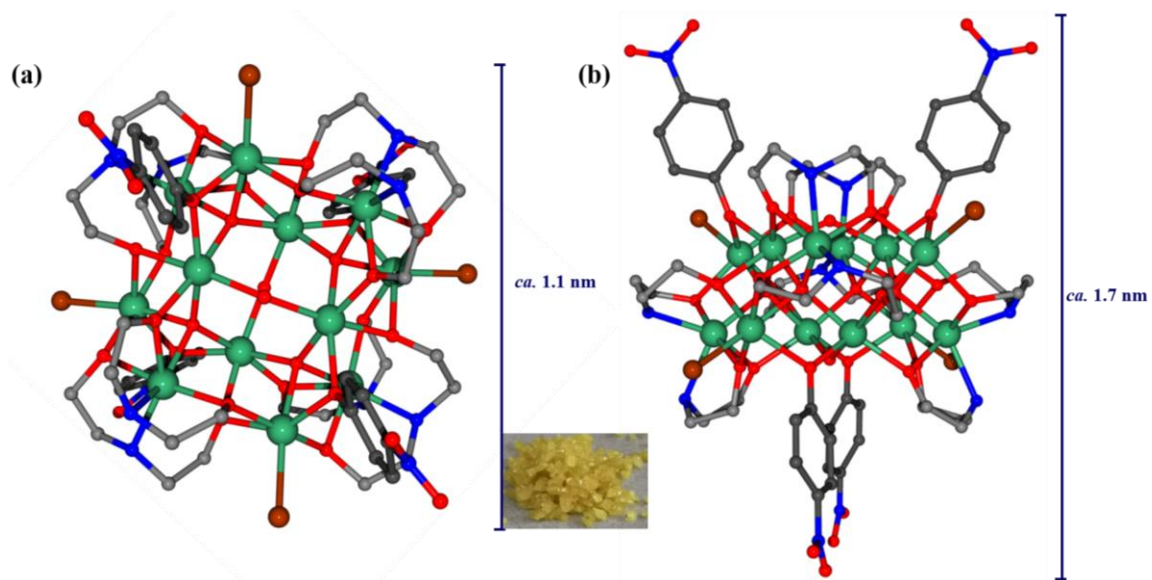


Figure S6 Molecular structure of **InOC-4** in top view (a) and side view (b). The side length and thickness are also presented.

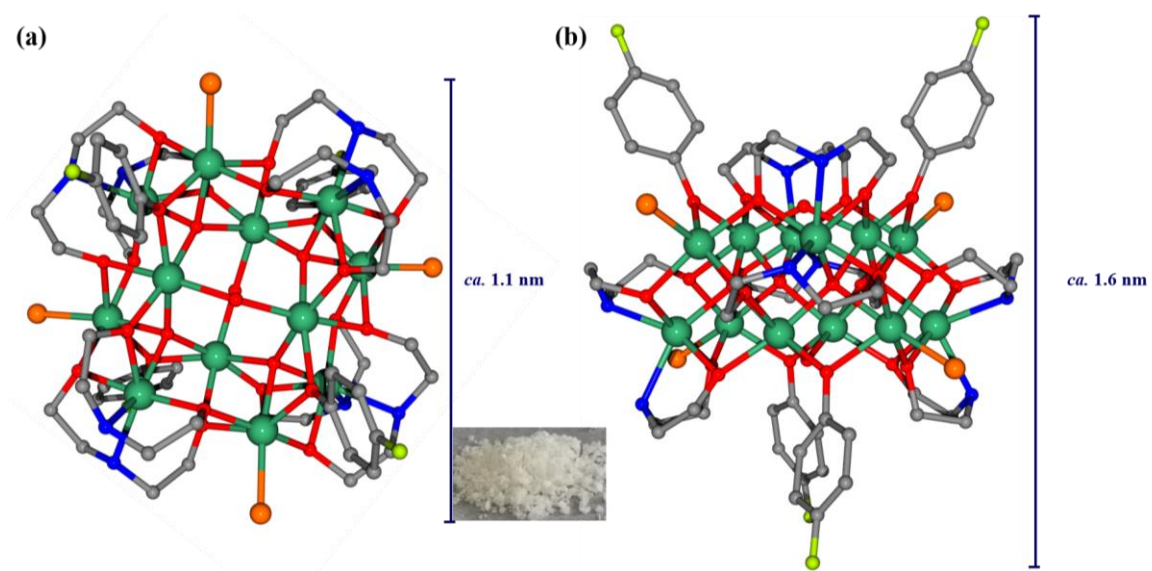


Figure S7 Molecular structure of **InOC-5** in top view (a) and side view (b). The side length and thickness are also presented.

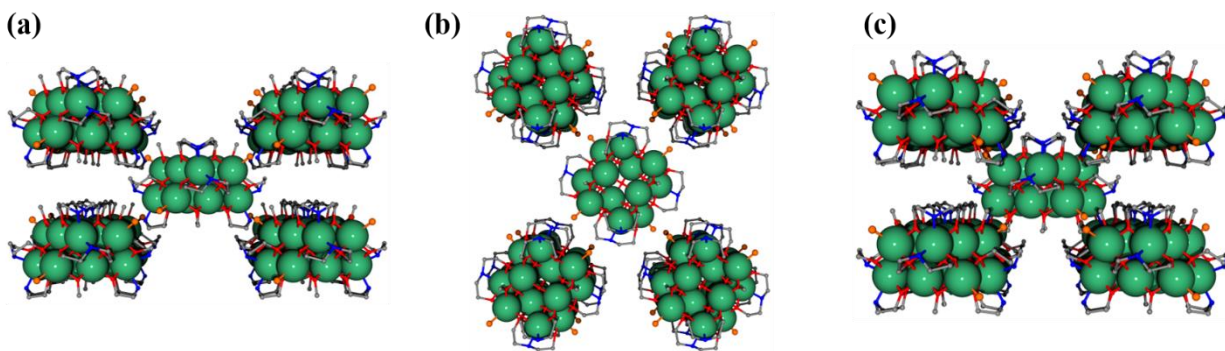


Figure S8 Packing mode of **InOC-1** along axis *a*, *b* and *c*.

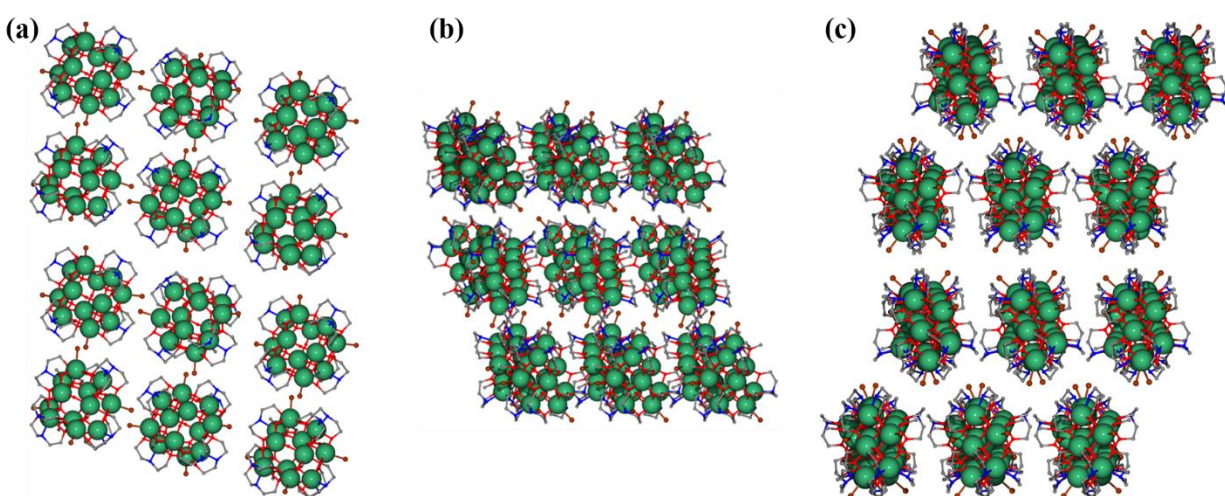


Figure S9 Packing mode of **InOC-2** along axis *a*, *b* and *c*.

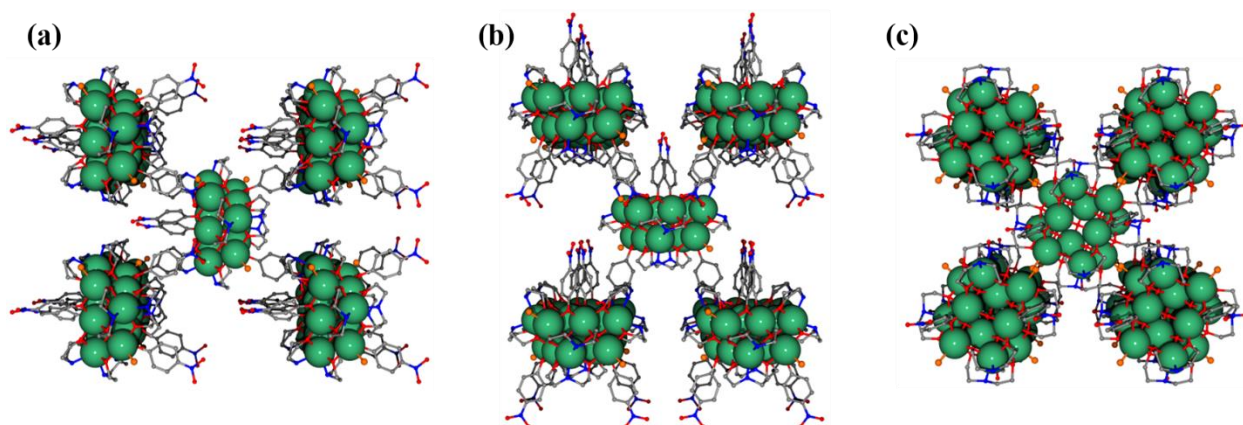


Figure S10 Packing mode of **InOC-3** along axis *a*, *b* and *c*.

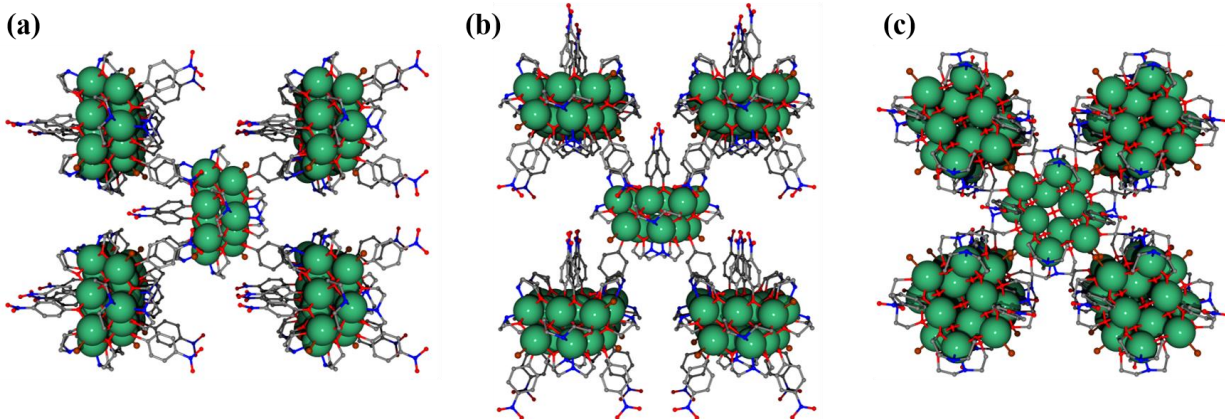


Figure S11 Packing mode of **InOC-4** along axis *a*, *b* and *c*.

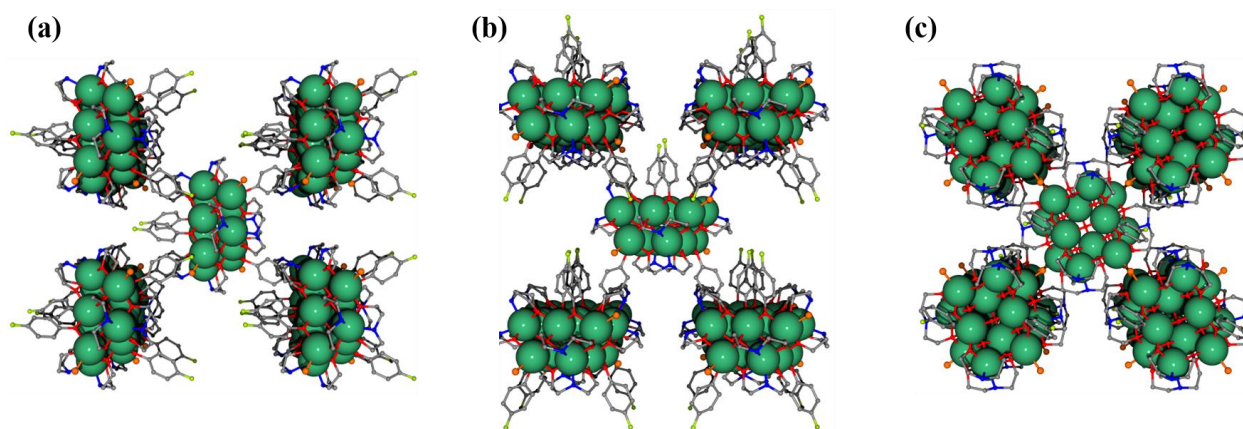


Figure S12 Packing mode of **InOC-5** along axis *a*, *b* and *c*.

VI. Powder-XRD patterns

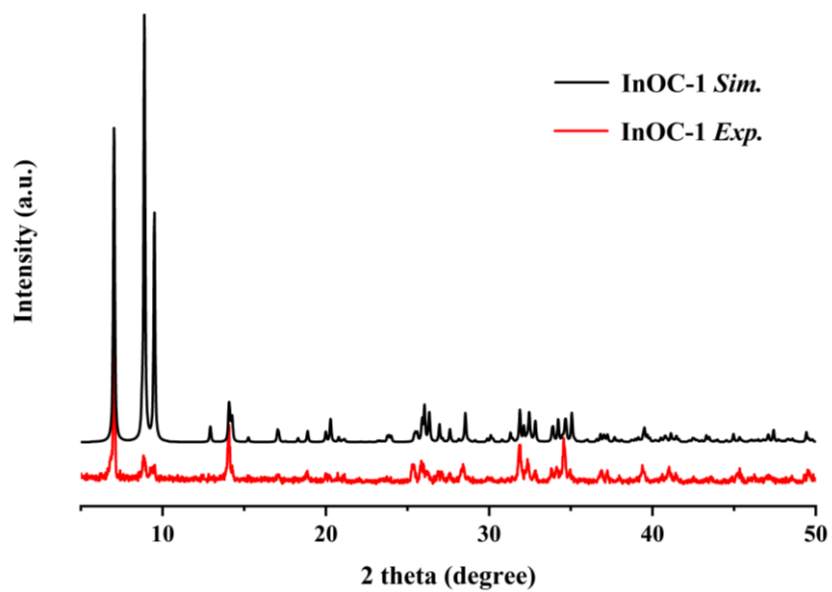


Figure S13 P-XRD analysis for InOC-1.

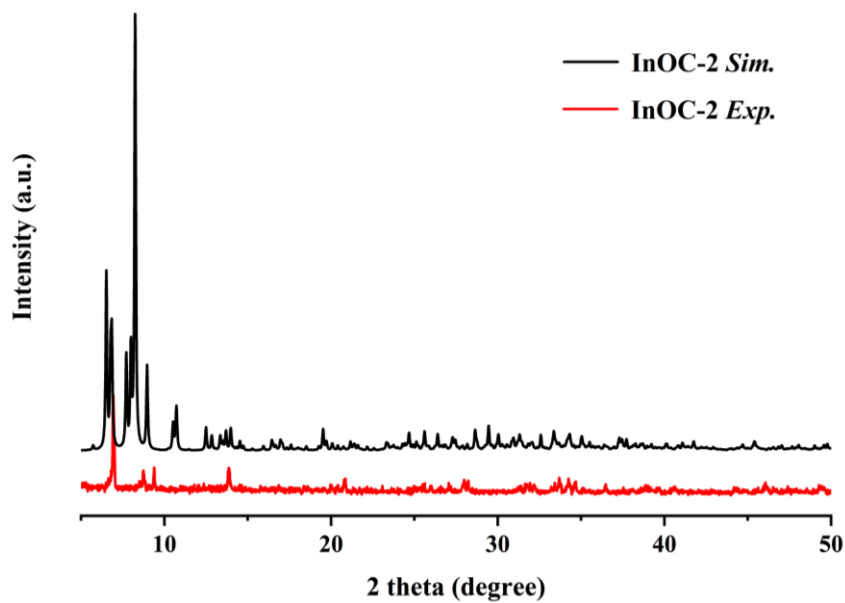


Figure S14 P-XRD analysis for InOC-2.

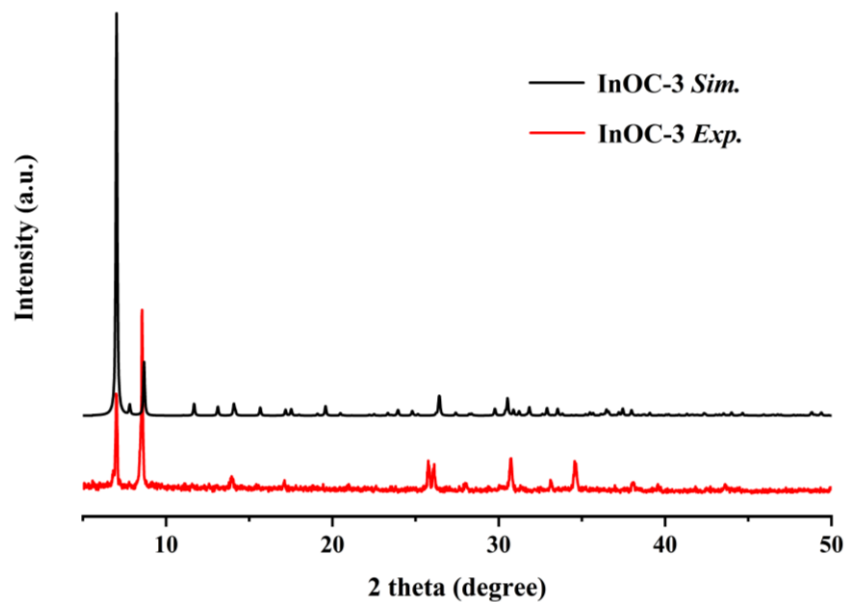


Figure S15 P-XRD analysis for **InOC-3**.

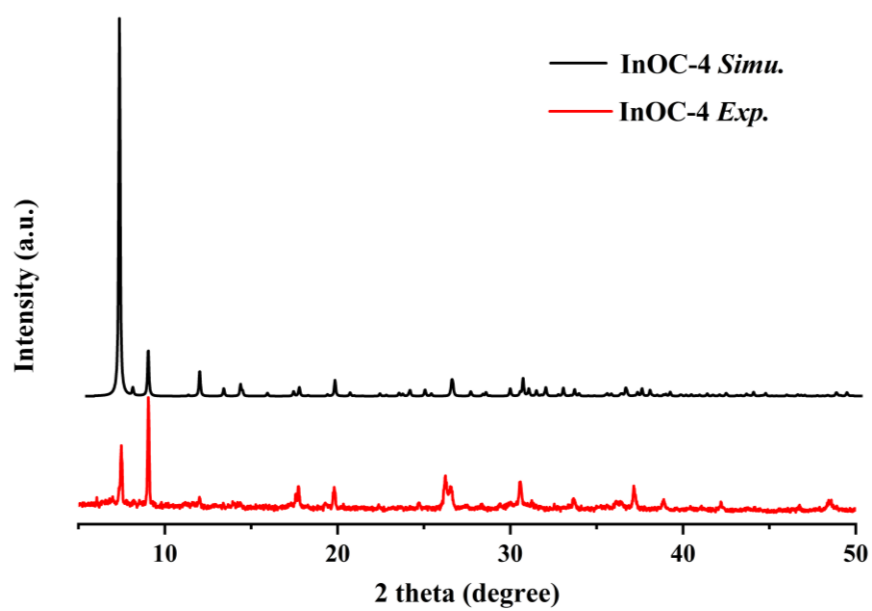


Figure S16 P-XRD analysis for **InOC-4**.

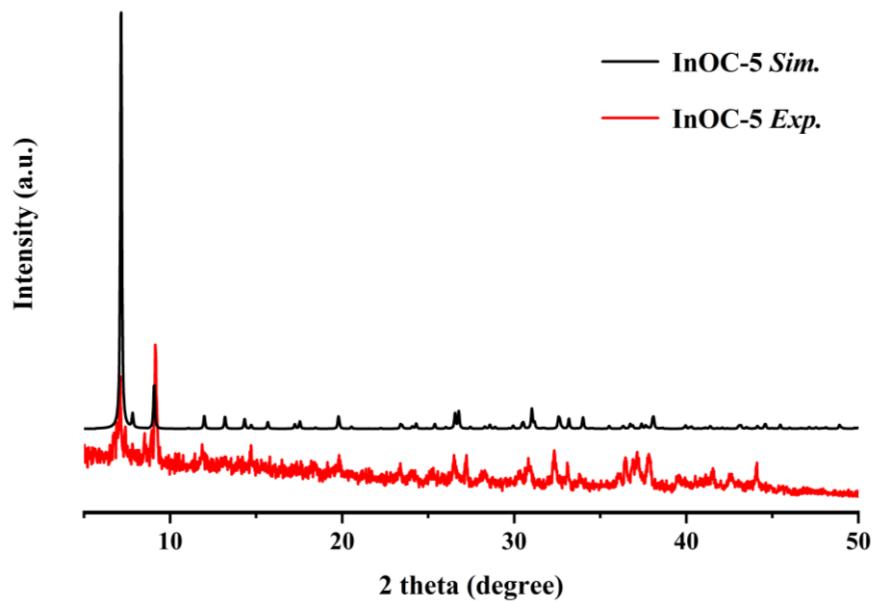


Figure S17 P-XRD analysis for **InOC-5**.

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

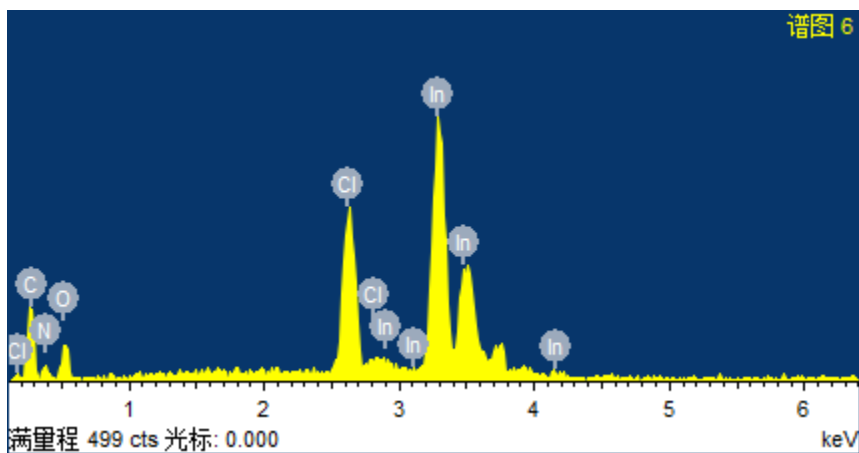


Figure S18 The EDS spectrum of InOC-1

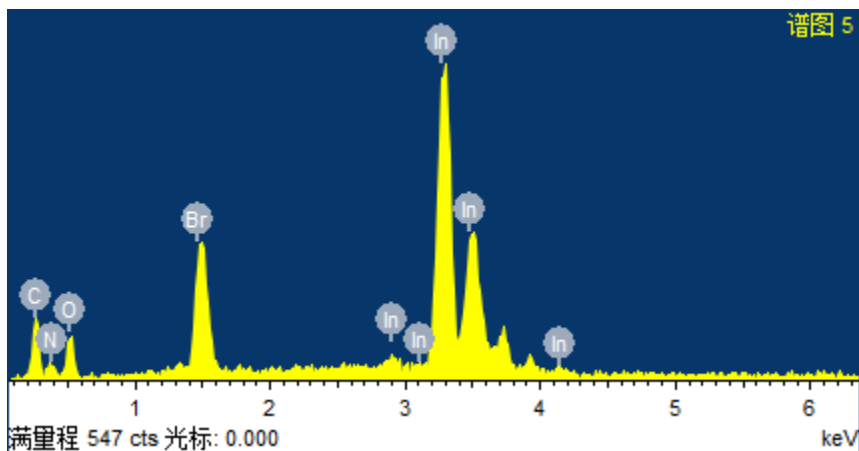


Figure S19 The EDS spectrum of InOC-2

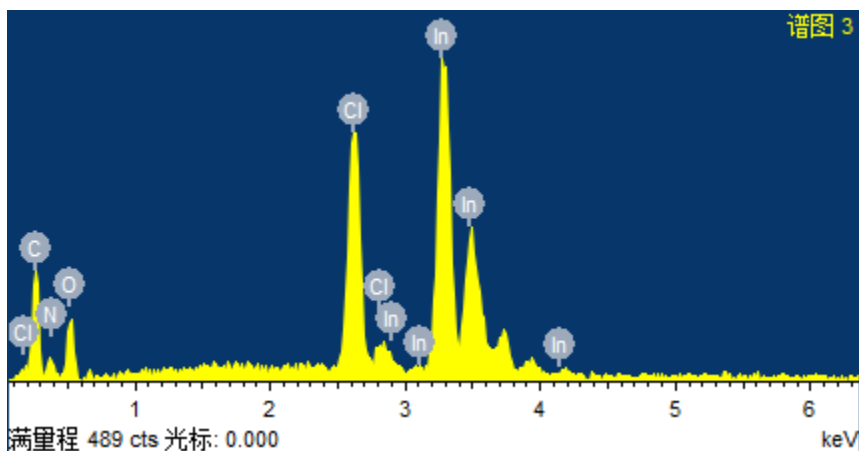


Figure S20 The EDS spectrum of InOC-3

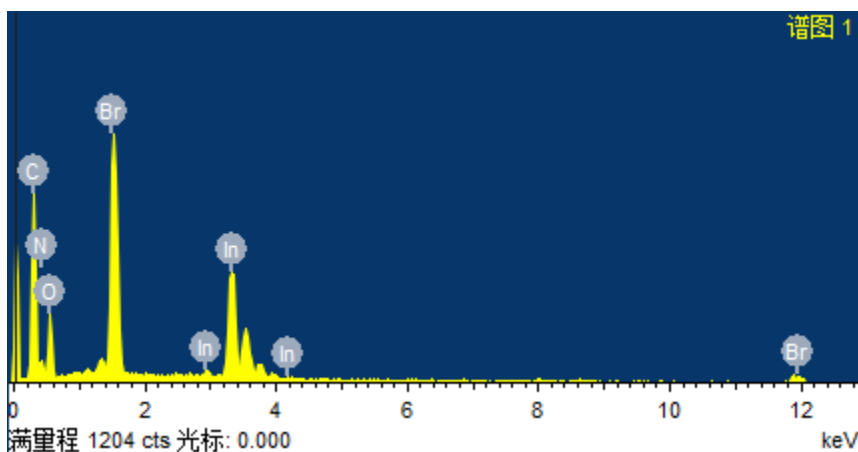


Figure S21 The EDS spectrum of **InOC-4**

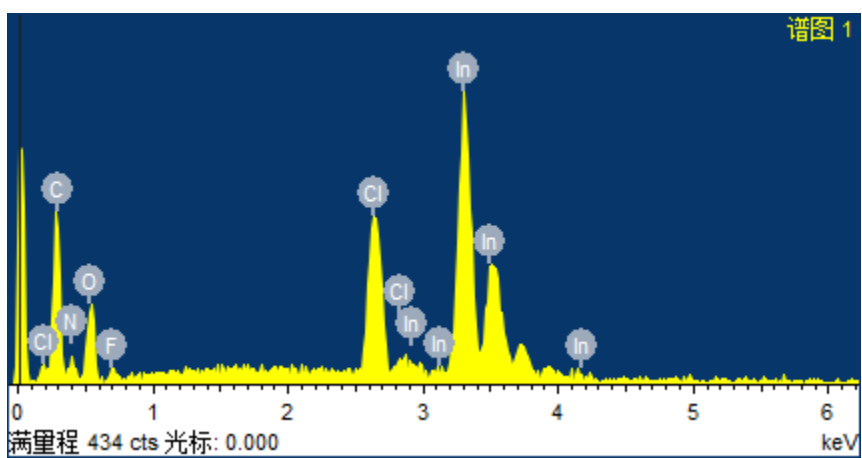


Figure S22 The EDS spectrum of **InOC-5**

VIII. Thermogravimetical analysis (TGA)

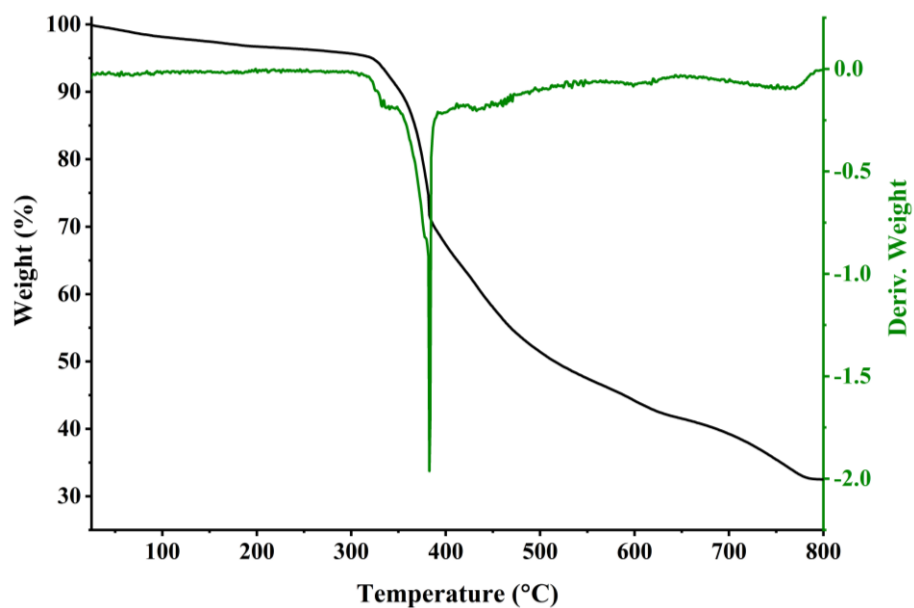


Figure S23 TGA (black), derivative TGA (green) and curves for **InOC-1** from room temperature to 800 °C under N₂ atmosphere.

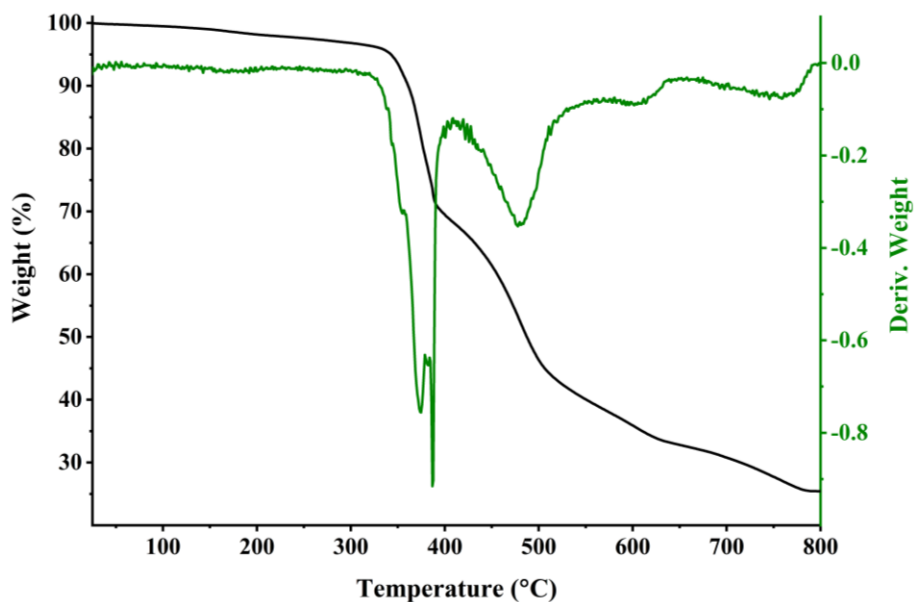


Figure S24 TGA (black), derivative TGA (green) and curves for **InOC-2** from room temperature to 800 °C under N₂ atmosphere.

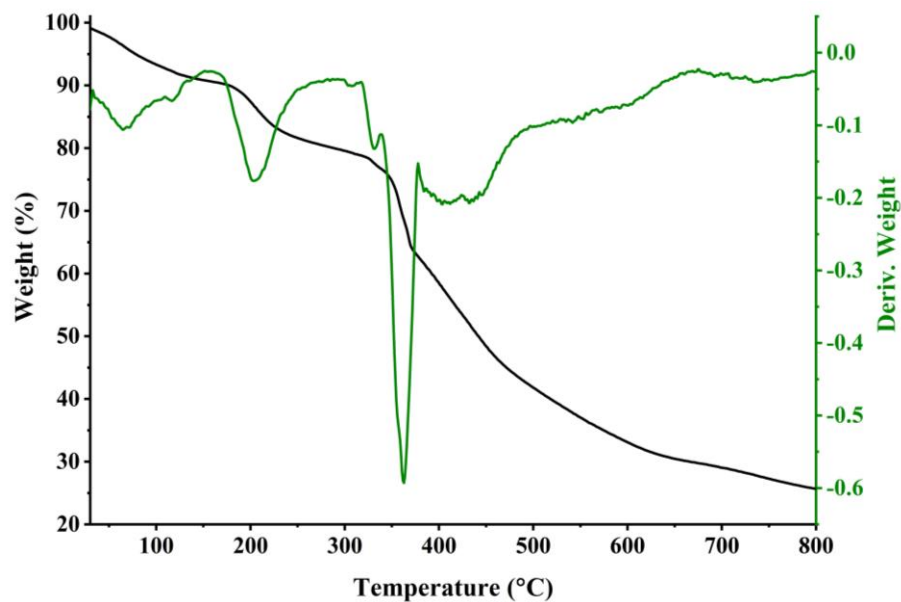


Figure S25 TGA (black), derivative TGA (green) and curves for **InOC-3** from room temperature to 800 °C under N₂ atmosphere.

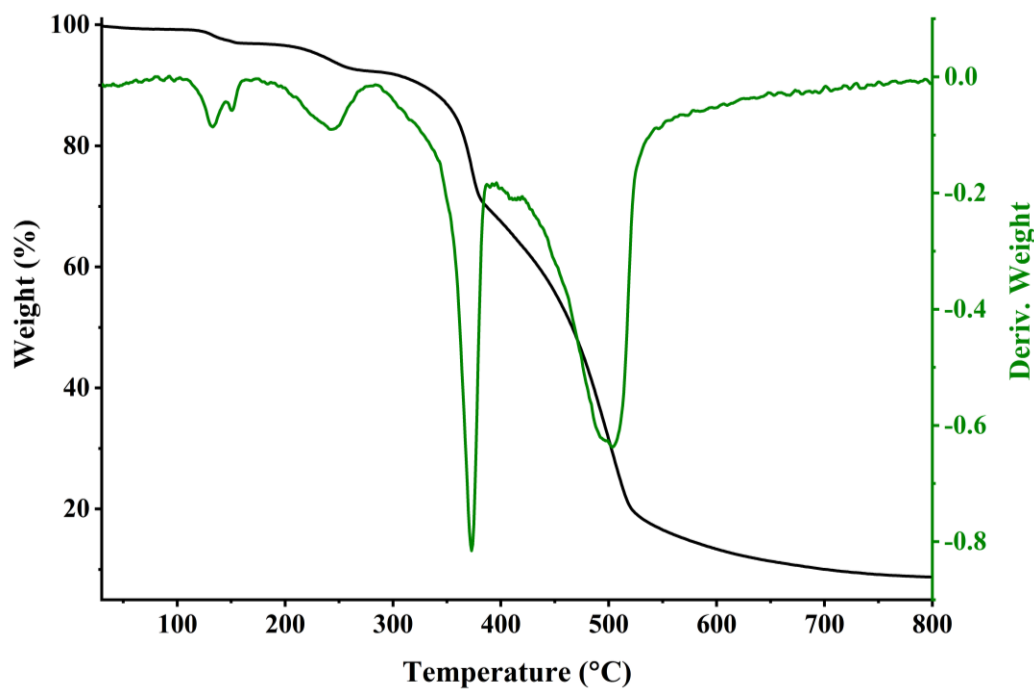


Figure S26 TGA (black), derivative TGA (green) and curves for **InOC-4** from room temperature to 800 °C under N₂ atmosphere.

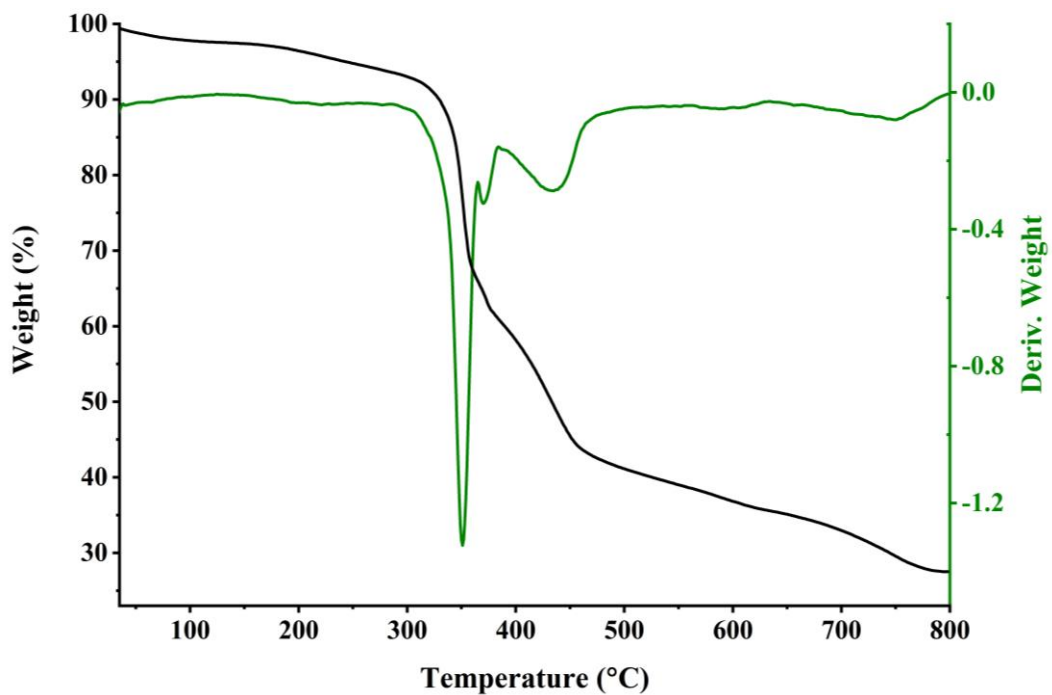


Figure S27 TGA (black), derivative TGA (green) and curves for **InOC-5** from room temperature to 800 °C under N₂ atmosphere.

IX. IR spectra

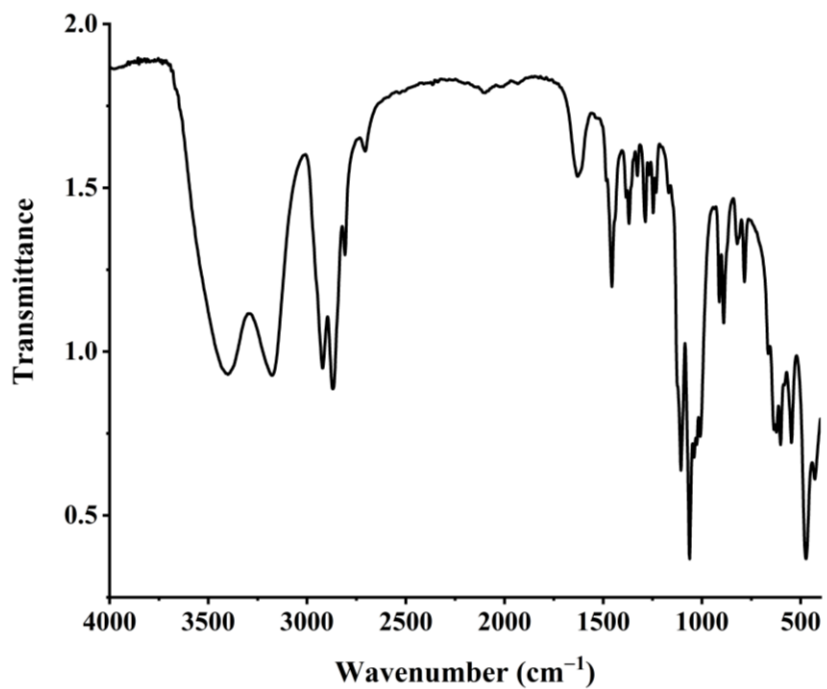


Figure S28 FT-IR spectrum of InOC-1.

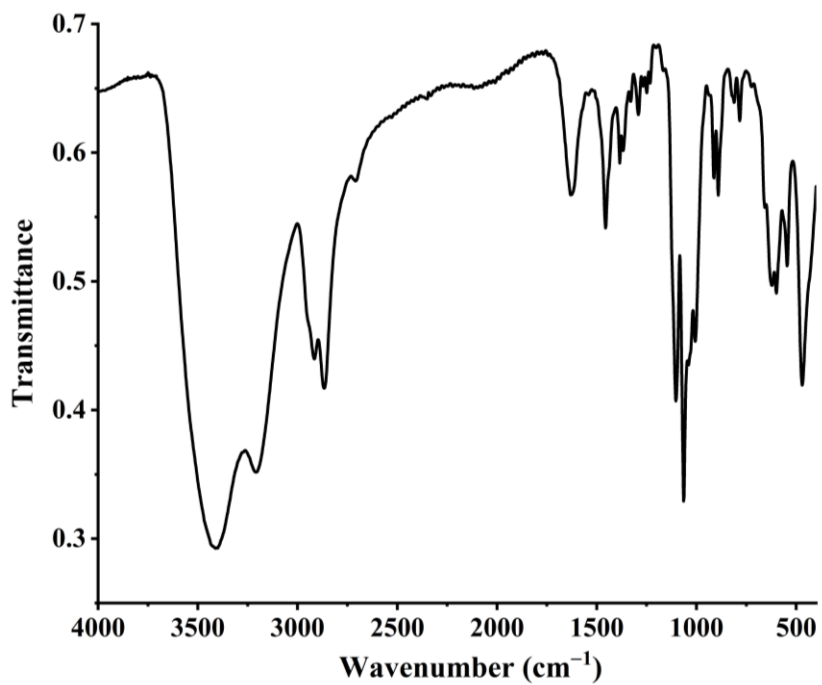


Figure S29 FT-IR spectrum of InOC-2.

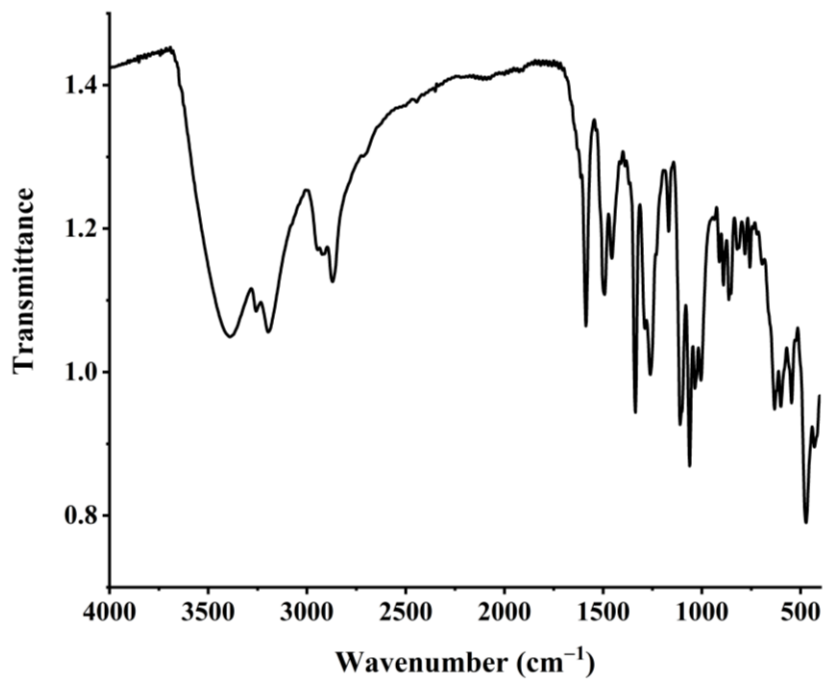


Figure S30 FT-IR spectrum of **InOC-3**.

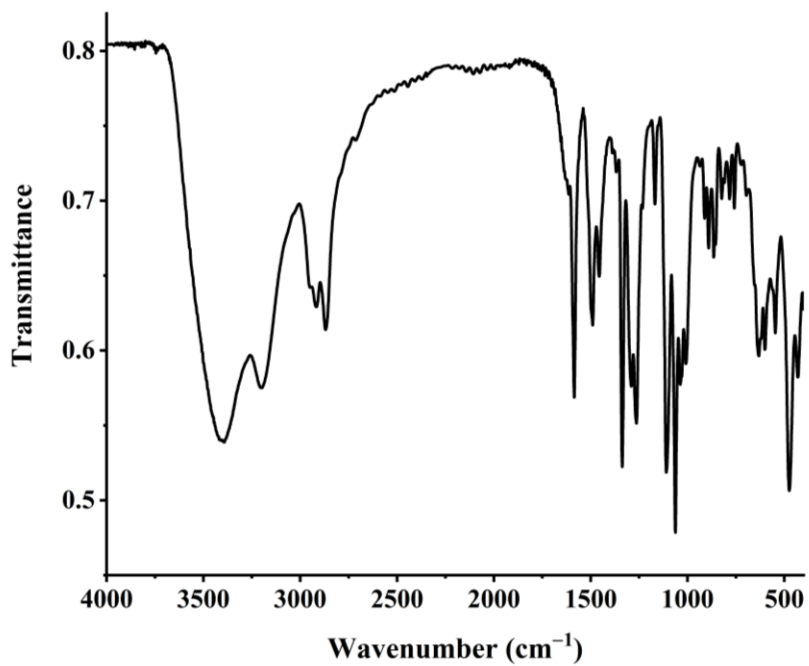


Figure S31 FT-IR spectrum of **InOC-4**.

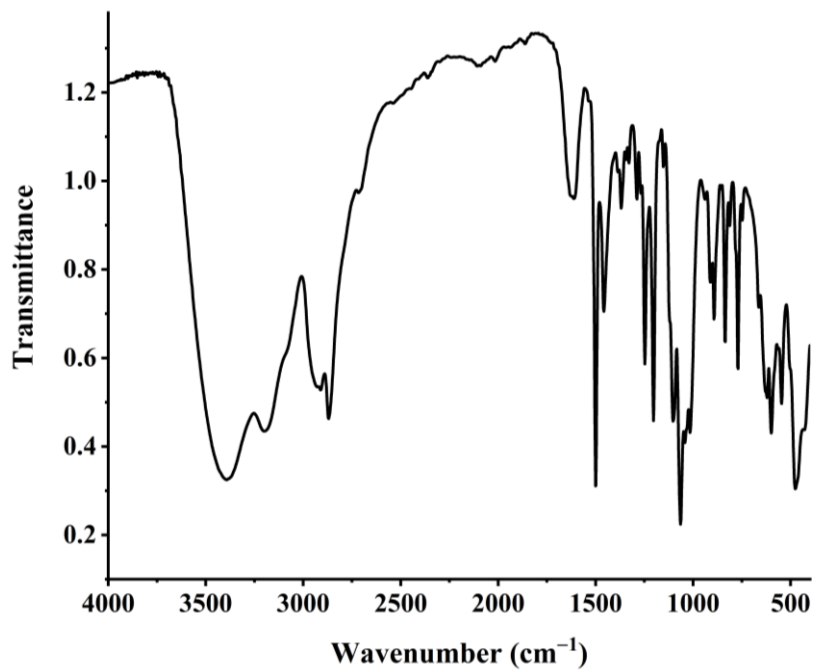


Figure S32 FT-IR spectrum of **InOC-5**.

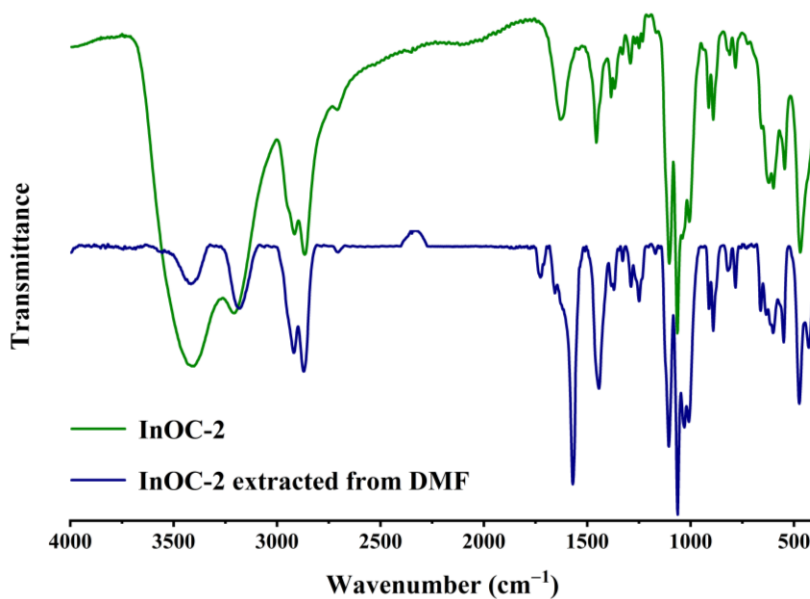


Figure S33 Comparison of FT-IR spectra of **InOC-2** (olive) and **InOC-2** dissolved in DMF followed by extraction with assistance of PGMEA (navy).

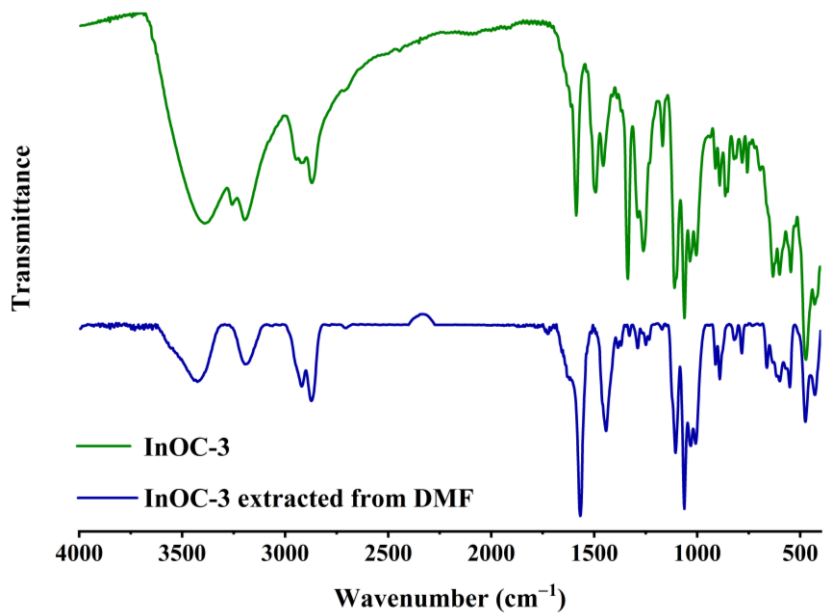


Figure S34 Comparison of FT-IR spectra of **InOC-3** (olive) and **InOC-3** dissolved in DMF followed by extraction with assistance of PGMEA (navy).

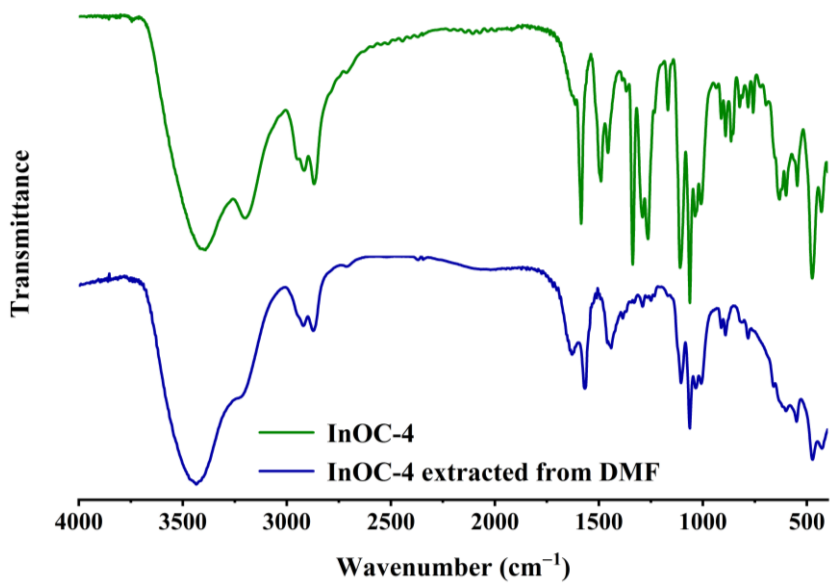


Figure S35 Comparison of FT-IR spectra of **InOC-4** (olive) and **InOC-4** dissolved in DMF followed by extraction with assistance of PGMEA (navy).

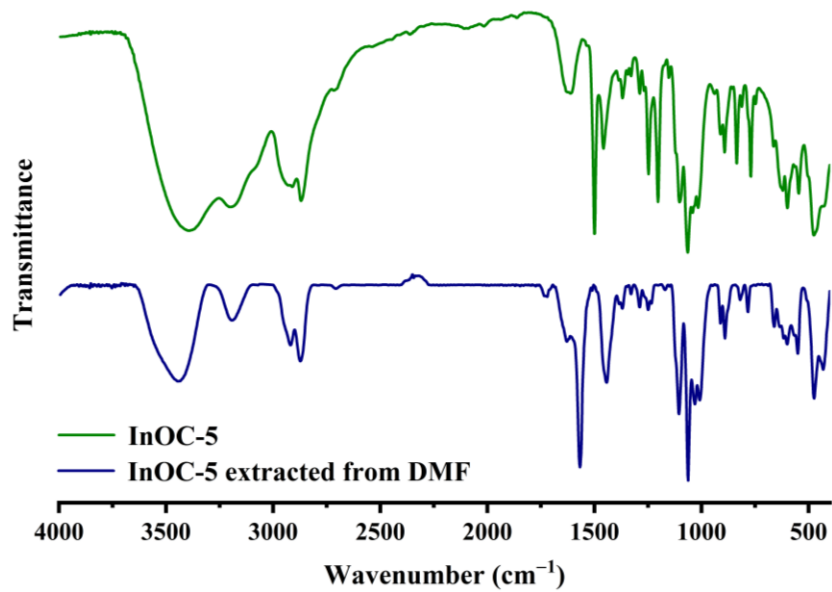


Figure S36 Comparison of FT-IR spectra of **InOC-5** (olive) and **InOC-5** dissolved in DMF followed by extraction with assistance of PGMEA (navy).

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

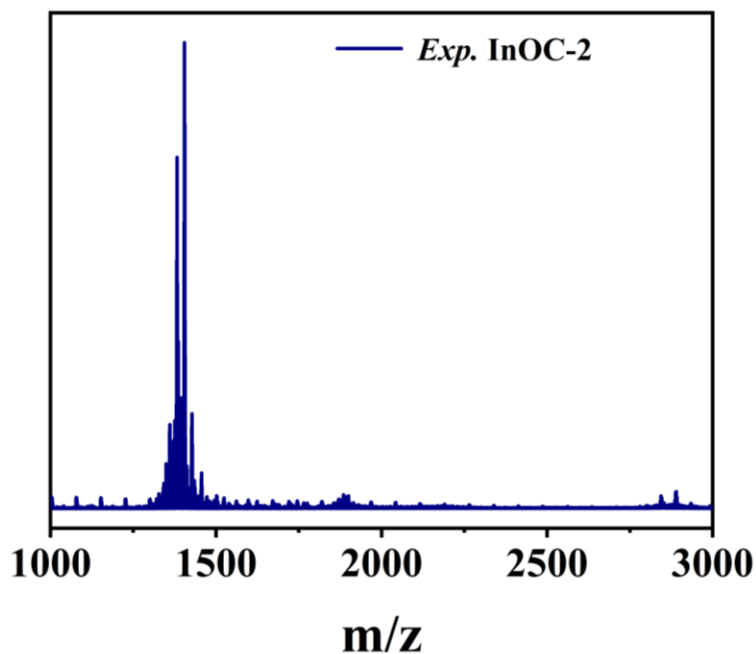


Figure S37 Positive-mode ESI-MS spectrum of the mother liquor of **InOC-2**.

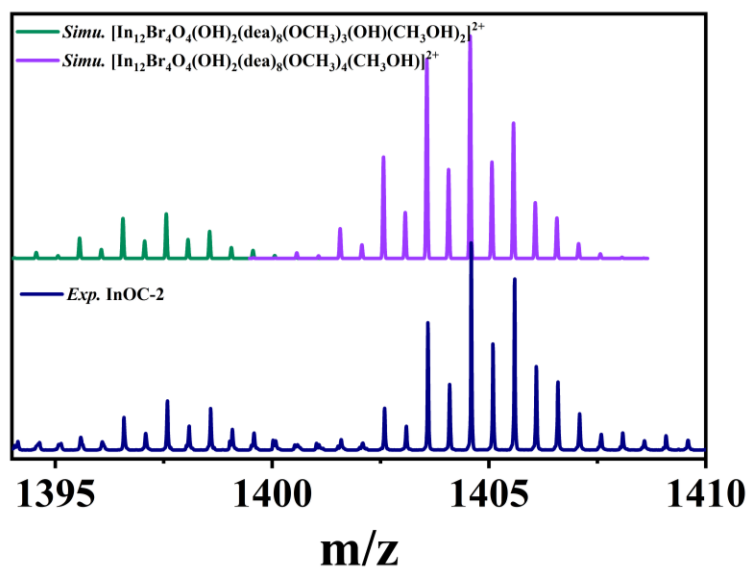


Figure S38 The comparison of experimental isotopic envelope with simulated patterns of the predominant species of +2 charged $\{\text{In}_{12}\text{-cluster}\}^{2+}$ **InOC-2**.

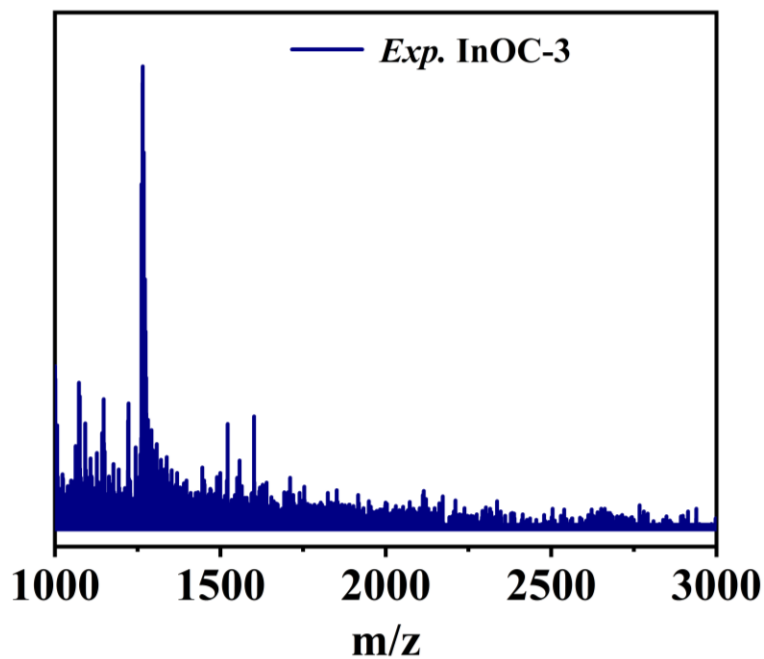


Figure S39 Positive-mode ESI-MS spectrum of **InOC-3** in DMF.

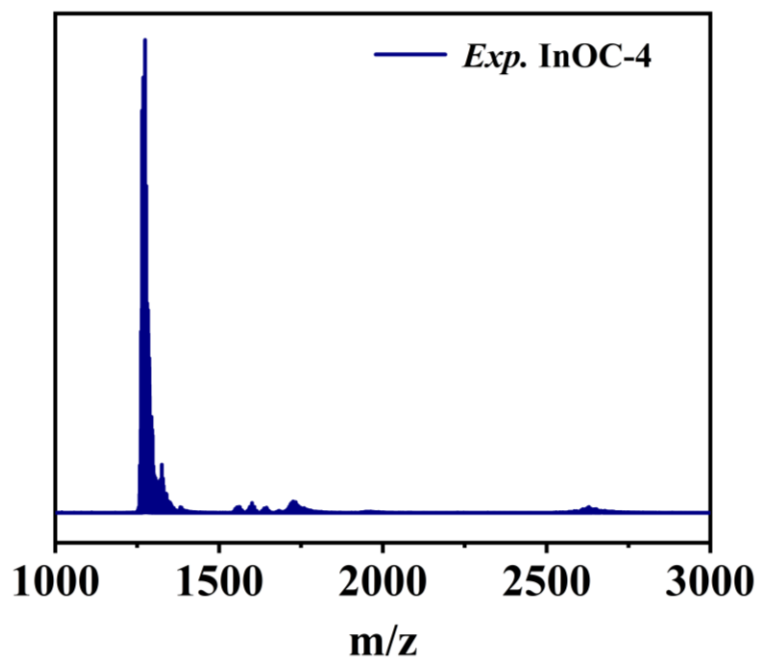


Figure S40 Positive-mode ESI-MS spectrum of **InOC-4** in DMF.

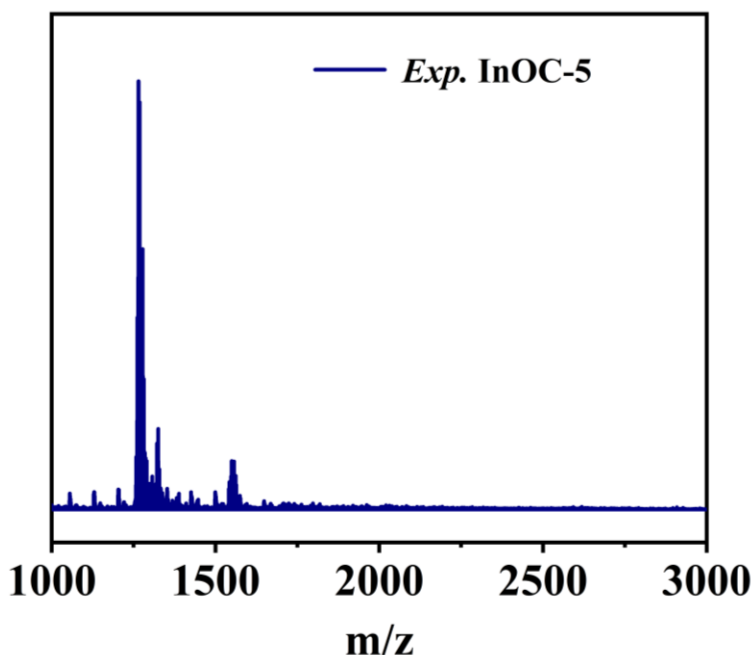


Figure S41 Positive-mode ESI-MS spectrum of **InOC-5** in DMF.

Table S11 Peak assignments for positive mode ESI-MS of **InOC-1** in DMF.

Envelop assignment	charge	m/z (<i>exp.</i>)	m/z (<i>cal.</i>)
$[\text{In}_{12}\text{Cl}_4\text{O}_4(\text{OH})_2(\text{OCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{O})_8(\text{OH})_4]^{2+}$	+2	1254.57	1254.61
$[\text{In}_{12}\text{Cl}_3\text{O}_4(\text{OH})_2(\text{OCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{O})_8(\text{OCH}_3)_3(\text{OH})]^{2+}$	+2	1258.09	1258.15
$[\text{In}_{12}\text{Cl}_4\text{O}_4(\text{OH})_2(\text{OCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{O})_8(\text{OCH}_3)(\text{OH})_3]^{2+}$	+2	1261.59	1261.61
$[\text{In}_{12}\text{Cl}_3\text{O}_4(\text{OH})_2(\text{OCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{O})_8(\text{OCH}_3)_4]^{2+}$	+2	1265.09	1265.18
$[\text{In}_{12}\text{Cl}_4\text{O}_4(\text{OH})_2(\text{OCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{O})_8(\text{OCH}_3)_2(\text{OH})_2]^{2+}$	+2	1268.51	1268.62

Table S12 Peak assignments for positive mode ESI-MS of **InOC-2** mother liquor.

Envelop assignment	charge	m/z (<i>exp.</i>)	m/z (<i>cal.</i>)
$[\text{In}_{12}\text{Br}_4\text{O}_4(\text{OH})_2(\text{OCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{O})_8(\text{OCH}_3)_4(\text{CH}_3\text{OH})_2]^{2+}$	+2	1402.60	1402.57
$[\text{In}_{12}\text{Br}_4\text{O}_4(\text{OH})_2(\text{OCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{O})_8(\text{OCH}_3)_3(\text{OH})(\text{CH}_3\text{OH})_2]^{2+}$	+2	1395.56	1395.56

XI. UV-Vis parameters

Table S13 The concentration of the materials during the UV-Vis experiments.

Code	Concentration (mol/L)	Code	Concentration (mol/L)
InOC-3	$5.92 \cdot 10^{-5}$	InOC-4	$6.112 \cdot 10^{-5}$
InOC-5	$1.16 \cdot 10^{-4}$	<i>p</i>-Nitrophenol	$1.02 \cdot 10^{-3}$
<i>p</i>-Flurophenol	$2.86 \cdot 10^{-3}$		

XII. Patterning performance investigations

The 12~14 mg/mL DMF solution of **InOC-1**, **InOC-2** and **InOC-3** was spin-coated onto a pre-clean silicon wafer at 2000 or 3000 rpm for 30 seconds followed by baking on a hot plate at 70 °C for 30 seconds. The film with a thickness of ca. 14 to 20 nm was then exposed to electron beam radiation with doses of 10 to 1200 $\mu\text{C}/\text{cm}^2$. As indicated in the scanning electron microscope (SEM) and atomic force microscope (AFM) images, well-defined negative tone patterns were obtained after development. Unfortunately, no matter on the hydrophilic or hydrophobic Si-substrate, **InOC-4** or **InOC-5** only formulated poor quality films unsuitable for EBL evaluations. We think the subtle fluctuations in the structures or compositions of the In_{12} -oxo clusters dominate their Hansen solubility parameters (HSP) and surface tension of the resulting solution, which determine whether smooth films can be formed on the Si-substrate.

Table S14 Film thickness of **InOC-1** to **InOC-3** on the Si-wafer.

Code	Thickness (nm)	Code	Thickness (nm)	Code	Thickness (nm)
InOC-1	15	InOC-2	18	InOC-3	14

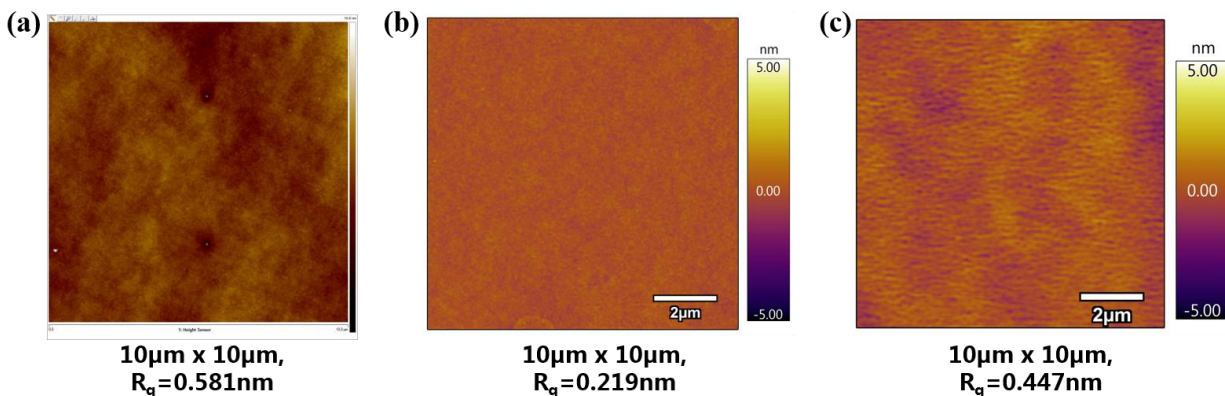


Figure S42 Topographic AFM images with R_q roughness in the areas of 10 μm x 10 μm for **InOC-1** (a), **InOC-2** (b), **InOC-3** (c). R_q roughness is defined here as the square root of the arithmetic mean of the squares of each z value measured on an AFM image.

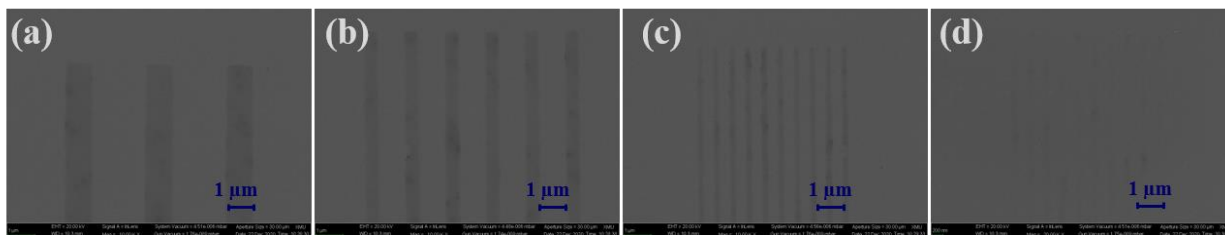


Figure S43 SEM images of patterns performed with dose of $1000 \mu\text{C}/\text{cm}^2$ exhibiting different feature sizes of $1 \mu\text{m}$ (a), 500 nm (b), 200 nm (c) and 100 nm (d) for **InOC-1**.

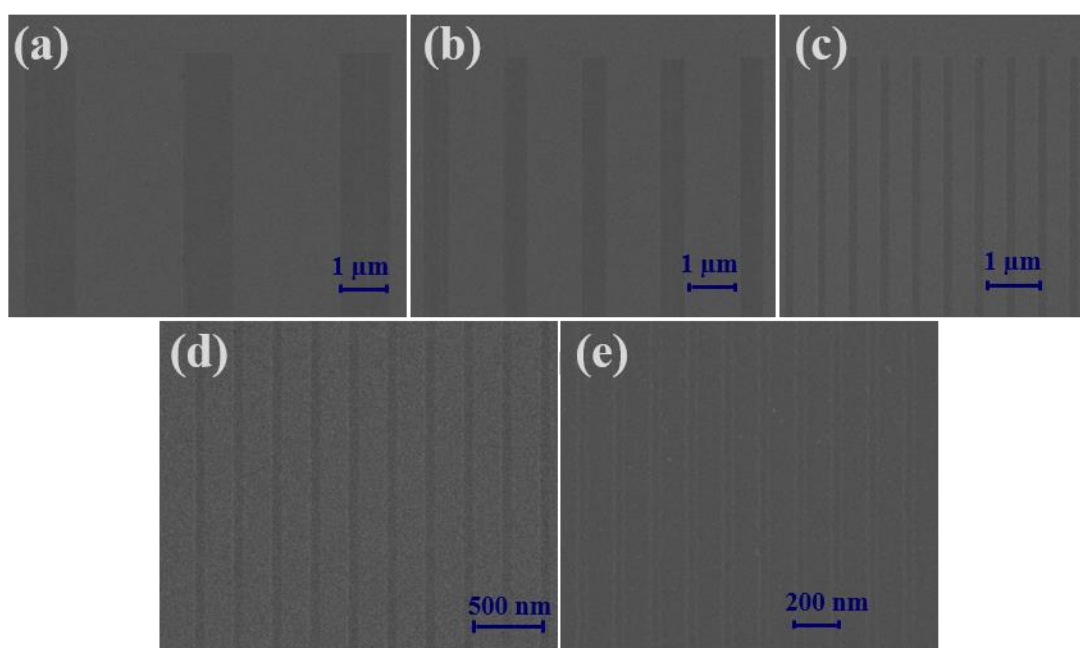


Figure S44 SEM images of patterns performed with dose of $1000 \mu\text{C}/\text{cm}^2$ exhibiting different feature sizes of $1 \mu\text{m}$ (a), 500 nm (b), 200 nm (c), 100 nm (d) and 50 nm (e) for **InOC-2**.

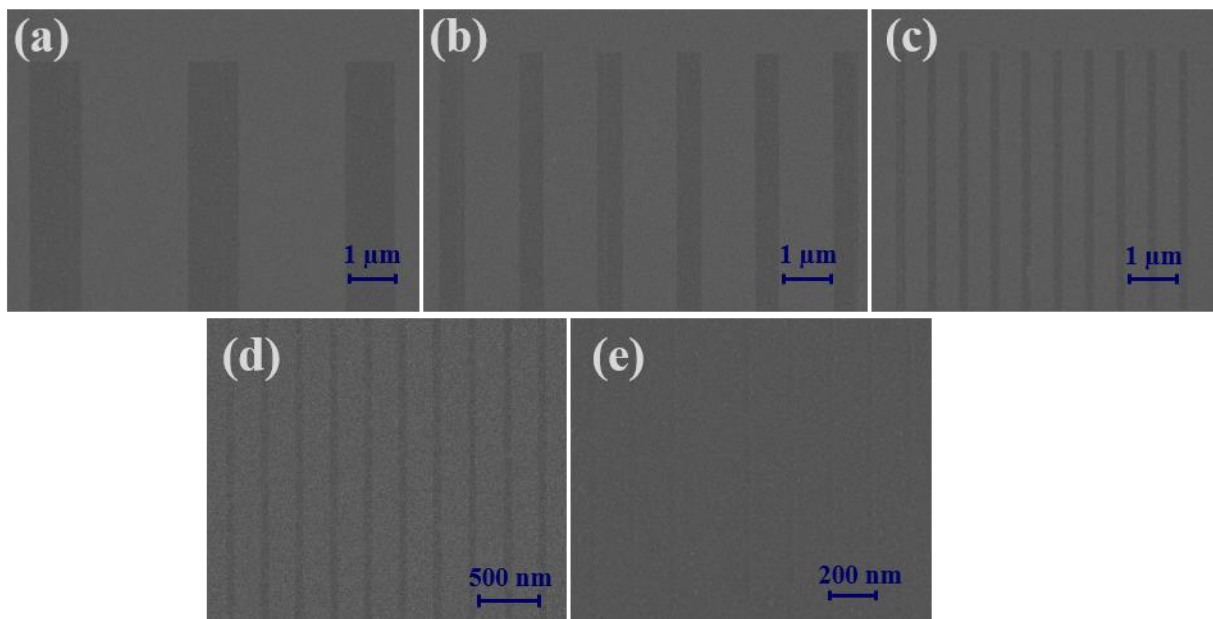


Figure S45 SEM images of patterns performed with dose of $1000 \mu\text{C}/\text{cm}^2$ exhibiting different feature sizes of $1 \mu\text{m}$ (a), 500 nm (b), 200 nm (c), 100 nm (d) and 50 nm (e) for **InOC-3**.

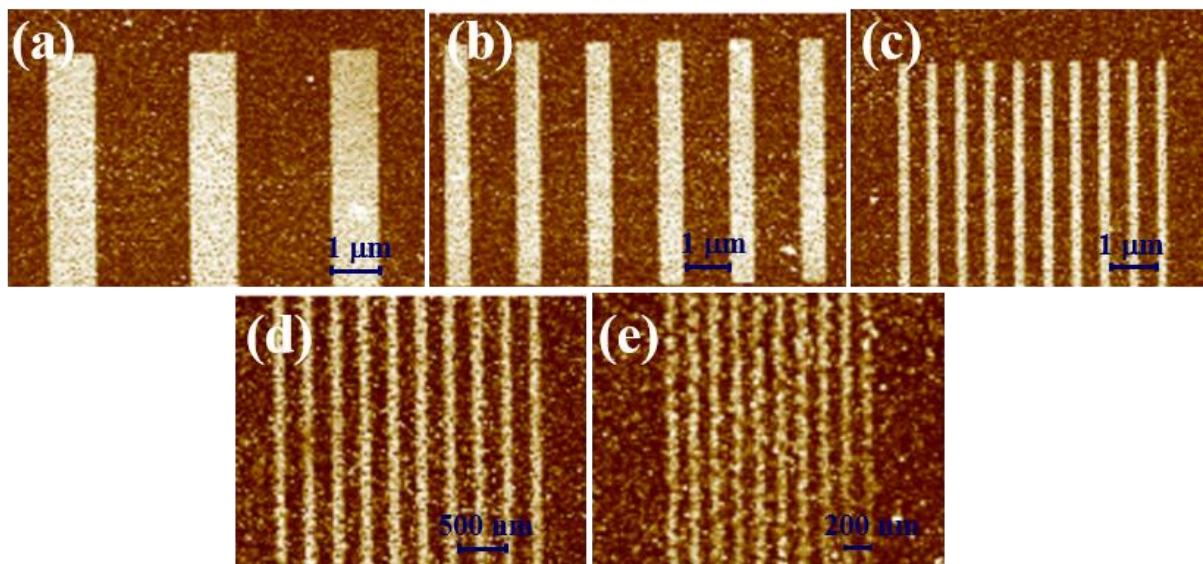


Figure S46 AFM images of patterns performed with dose of $500 \mu\text{C}/\text{cm}^2$ exhibiting different feature sizes of $1 \mu\text{m}$ (a), 500 nm (b), 200 nm (c), 100 nm (d) and 50 nm (e) for **InOC-3**.

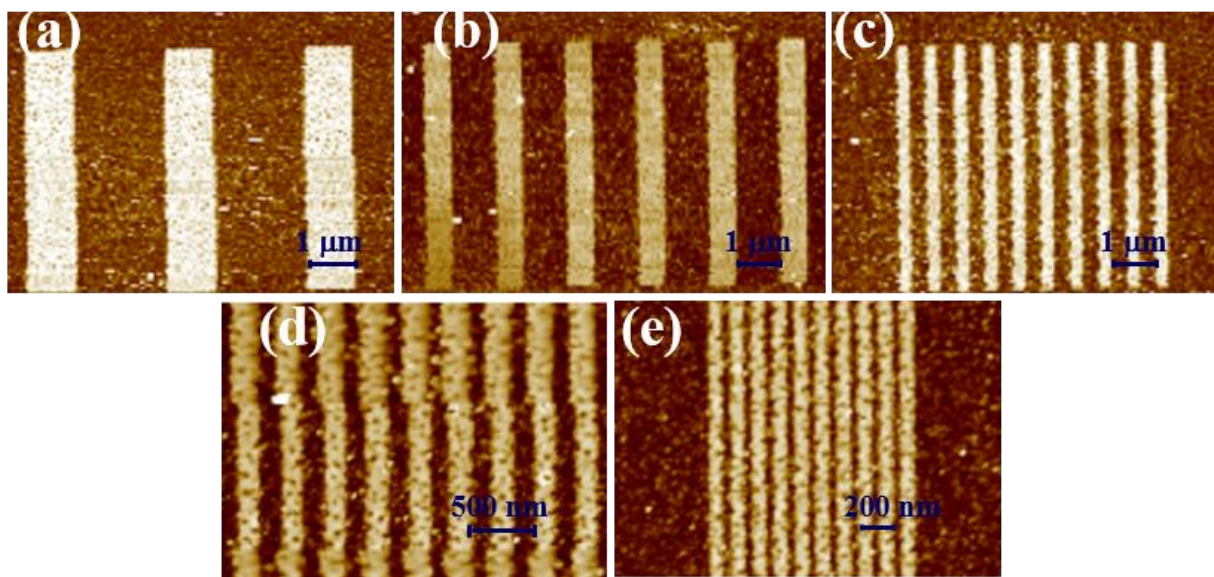


Figure S47 AFM images of patterns performed with dose of $1000 \mu\text{C}/\text{cm}^2$ exhibiting different feature sizes of $1 \mu\text{m}$ (a), 500 nm (b), 200 nm (c), 100 nm (d) and 50 nm (e) for **InOC-3**.

- [1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339-341.
- [2] a) G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3-8; b) G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112-122.
- [3] a) I. D. Brown, D. Altermatt, *Acta Crystallogr.* **1985**, *B41*, 244-247; b) K. Knížek, *Kalvados – Software for crystal structure and powder diffraction*; see <http://www.fzu.cz/~knizek/kalvados/index.html>.