Electronic Supplementary Information (ESI) For

Dynamically Controlled One-pot Synthesis of Heterogeneous Core-shell MOF Single Crystals using Guest Molecules

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1. Experimental Section

1.1. General procedures and instrumentations

All chemicals used during this investigation were reagent grade and used as received. The synthesis of $Ru(bpy)_3(PF_6)_2$ was using a modified method.¹ Elemental analyses of C, H and N was carried out with a VarioEL analyzer. X-ray powder diffraction (XRD) data were collected on a D8 Focus (Bruker) diffractometer at 40 kV and 30 mA with monochromated Cu Ka radiation ($\lambda =$ 1.5405 Å). Thermogravimetric analysis (TGA) was carried out on a Thermal Analysis Instrument (SDT 2960, TA Instruments, New Castle, DE) from room temperature to 900 °C in N₂ atmosphere with a heating rate of 10 °C/min. The infrared (IR) spectrum was measured within the 650-4000 cm⁻¹ region on a Nicolet iS10 spectrometer with ITR mode. EDS spectrums were collected by the Bruker AXS XFlash detector 4010 associated in the FE-SEM (Hitachi S4800) at an accelerating voltage and current of 20 kV and 15 μ A. Solid UV-vis spectrums were recorded on a Hitachi Model U-4100 spectrophotometer from 800 to 200 nm region. Microscope images of compound 1, 2 and 1@2 were photographed using a light transmission microscope (Olympus BX51, Olympus, Melville, NY). The photoluminescence (PL) excitation and emission spectra were recorded with F7000 luminescence spectrometer equipped with a Xenon lamp of 450 W as an excitation light source. The photoluminescence lifetimes of the solid samples were measured with a Lecroy Wave Runner 6100 Digital Oscilloscope (1GHz) using a tunable laser (pulse width = 4 ns) as the excitation source (Continuum Sunlite OPO). Oxygen sensitivity experiment was carried out by monitoring the fluorescence intensity of the compounds upon switching between vacuum and certain oxygen concentration in the quartz cuvette.

1.2. Synthesis and preparation of compound 1, 2 and 1@2

General process for synthesis compound 1, 2 and 1@2.

Method A.

 $0.5 \text{ ml In}(NO_3)_3 \cdot 5H_2O$ (200 mg in 10 ml DMF), 0.5 ml pydc (88 mg in 10 ml DMF), 0.5 ml H₂O and 0.5 ml designed Ru(bpy)₃²⁺ (0-16 mg Ru(bpy)₃(PF₆)₂ in 1 ml DMF) were mixed with added 1-4 drops 6 M HAc in a 20 ml glass vial. The mixture was allowed to stand in a capped vial at 358 K and observed at different reaction time.

Compound 1 can be widely obtained in the range of 1.8 mg/ml to 16 mg/ml [Rubpy]. The typical synthesis for **1** is loading 0.5 ml Ru(bpy)₃²⁺ (2 mg Ru(bpy)₃(PF₆)₂ in 1 ml DMF). After 26 hours, red hexagonal block crystals were obtained, washed with DMF and dried under air (yield 85% Based on Ru). CHN analysis calcd (%) for **1**: C 41.70, H 3.47, N 9.12; found: C 40.47, H 3.42, N 9.06.

Compound 2 was synthesized through 48 hours reaction without adding $Ru(bpy)_3(PF_6)_2$. Colorless hexagonal block crystals **2** were washed with DMF and dried under air for the further examination (yield 75% Based on pydc). CHN analysis calcd (%) for **2**: C 38.02, H 4.2, N 9.33; found: C 37.96, H 3.83, N 9.24.

For core-shell MOF crystal 1@2, it can be prepared in the range of 0.2 mg/ml to 1.8 mg/ml Ru(bpy)₃²⁺ in a 20 ml glass vial, but the pure core-shell phases merely yield in a narrow concentration (0.8-1.2 mg/ml Rubpy).



Fig. S1 Reaction time vs concentration plot of the compound 1, 2 and core-shell phases 1@2



Fig. S2 The color of mixture liquids with increasing initial $Ru(bpy)_3^{2+}$ concentration from 0.2 mg/ml to 18 mg/ml before reaction (a) and after reaction (b)

Reaction time *vs* concentration plot of the compound **1**, **2** and core-shell phases **1@2** are recorded in Fig. S1. For reaction time, more than 36 h and 48 h are needed to obtain the well-shaped coreshell crystals **1@2** and pure colorless crystals **2** respectively while only 18 h is required for core MOF **1**. For initial concentration of $\text{Ru}(\text{bpy})_3^{2+}$, the **1@2** can be prepared in a wide range of 0.2 mg/ml to 1.8 mg/ml Ru(bpy)_3²⁺, but the pure phase merely yields in a narrow concentration (0.8-1.2 mg/ml Ru(bpy)_3²⁺).

Method B. (Crystal seeds method)

A piece of core 1 were added to the mixture of 0.5 ml $In(NO_3)_3 \cdot 5H_2O$ (200 mg in 10 ml DMF), 0.5 ml pydc (88 mg in 10 ml DMF) and 1 ml H₂O-DMF (1:1) in a 20 ml glass vial. After 48 h, core-shell crystals 1@2 were obtained. In a reverse process, adding shell 2 to the mixture of $In(NO_3)_3 \cdot 5H_2O$, pydc, $Ru(bpy)_3(PF_6)_2$ could not afford core-shell crystals 2@1 but only 1 was obtained.

2. Structure determinations

A suitable single crystal of **compound 1** and **2** was selected for single-crystal X-ray diffraction analysis. The data were collected on a Bruker AXS SMART APEX II diffractometer in the range of 0.73 to 26.08 ° for 1 and 1.68 to 26.04 ° for 2 at the temperature of 296(2) K using graphitemonochromated Mo-Ka radiation ($\lambda = 0.71073$ Å). Data processing was accomplished with the SAINT processing program.² For 1, a total of 36766 reflections were collected, of which 7988 reflections were unique. For 2, a total of 22233 reflections were collected, of which 2486 reflections were unique. Both the structures of 1 and 2 were solved by direct method and refined by full matrix least-squares technique with the SHELXTL 97 crystallographic software package.³ All non-H atoms of framework were located from a difference Fourier map and refined anisotropically. The remained solvent molecules and $H_2NMe_2^+$ cations within compound 1 and 2 were disordered and could not be modeled properly, the program $SOUEEZE^4$ was used to calculate the solvent and cations disorder area and remove its contribution to the overall intensity data. The ISOR instructions were used to restrain the Rubpy molecule so that there were 18 restraints in the data of compound 1. All the H atoms of pydc ligands and Rubpy guests were added geometrically. All of the crystal data and structure refinement details for compound 1 and 2 are given in Table S1. Selected bond and angle for compound 1 and 2 are given in Table S2. (CCDC: 997132-997133)

Identification code	1	2
Empirical formula*	$C_{186}H_{102}N_{30}O_{72}In_9Ru_2$	$C_{14}H_6N_2O_8In$
Formula weight*	5144.5	445.03
Temperature	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Trigonal, P321	Trigonal, R-3c
Unit cell dimensions	a = 15.7780(13) Å	<i>a</i> = 15.7069(13) Å
	b = 15.7780(13) Å	<i>b</i> = 15.7069(13) Å
	c = 28.032(5) Å	c = 52.887(9) Å
Volume	6043.5(12) Å ³	11299(2) Å ³
Z, Calculated density	1, 1.414 Mg/m ³	18, 1.177 Mg/m ³
Absorption coefficient	1.044 mm ⁻¹	0.971 mm ⁻¹
<i>F</i> (000)	2533	3906
Crystal size	0.40 x 0.40 x 0.20 mm	0.35 x 0.35 x 0.20 mm
Theta range for data collection	0.73 to 26.08 deg.	1.68 to 26.04 deg.
Limiting indices	-19≤ <i>h</i> ≤19, -19≤ <i>k</i> ≤15, -34≤ <i>l</i> ≤33	-18≤h≤19, -19≤k≤19, -62≤l≤64
Reflections collected / unique	36766 / 7988 [<i>R</i> (int) = 0.0639]	22233 / 2486 [<i>R</i> (int) = 0.1186]
Completeness to theta = 26.08	99.40%	99.80%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.8184 and 0.6802	0.8295 and 0.7275
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7988 / 18 / 451	2486 / 0 / 114
Goodness-of-fit on F^2	1.066	0.868
Final R indices [I>2sigma(I)]	$R_1 = 0.0701, wR_2 = 0.1681$	$R_1 = 0.0362, wR_2 = 0.0680$

Table S1 The crystal data and structure refinement details for compound 1 and 2

R indices (all data)	$R_1 = 0.0810, wR_2 = 0.1742$	$R_1 = 0.0674, wR_2 = 0.0744$
Largest diff. peak and hole	2.734 and -2.413 e.Å-3	0.333 and -0.468 e.Å ⁻³

* Not included the solvent molecules.

 $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \ wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$

Table S2 Selected bond and angle for $compound \ 1$ and 2

1	In(1)-O(5)	2.140(8)	Ru(1)-N(5)#1	2.007(11)
	In(1)-O(1)#3	2.143(7)	Ru(1)-N(5)#2	2.007(11)
	In(1)-O(7)	2.183(7)	Ru(1)-N(5)	2.007(11)
	In(1)-O(3)#4	2.227(7)	Ru(1)-N(4)	2.077(8)
	In(1)-N(1)#3	2.276(8)	Ru(1)-N(4)#1	2.077(8)
	In(1)-N(2)#4	2.303(8)	Ru(1)-N(4)#2	2.077(8)
	In(2)-O(11)	2.132(9)	Ru(1)-N(5)#1	2.007(11)
	In(2)-O(11)#5	2.132(9)	In(2)-O(9)#7	2.184(8)
	In(2)-O(9)#6	2.184(8)	In(2)-N(3)#7	2.287(9)
	O(5)-In(1)-O(1)#3	84.0(3)	O(11)-In(2)-O(11)#5	93.4(5)
	O(5)-In(1)-O(7)	92.9(3)	O(11)-In(2)-O(9)#6	85.5(3)
	O(1)#3-In(1)-O(7)	124.7(3)	O(11)#5-In(2)-O(9)#6	121.7(3)
	O(5)-In(1)-O(3)#4	122.6(3)	O(11)-In(2)-O(9)#7	121.7(3)
	O(1)#3-In(1)-O(3)#4	142.9(3)	O(11)#5-In(2)-O(9)#7	85.5(3)
	O(7)-In(1)-O(3)#4	82.8(3)	O(9)#6-In(2)-O(9)#7	142.1(4)
	O(5)-In(1)-N(1)#3	154.0(4)	O(11)-In(2)-N(3)#7	86.4(4)
	O(1)#3-In(1)-N(1)#3	73.7(3)	O(11)#5-In(2)-N(3)#7	155.6(3)
	O(7)-In(1)-N(1)#3	89.1(3)	O(9)#6-In(2)-N(3)#7	82.7(3)
	O(3)#4-In(1)-N(1)#3	83.4(3)	O(9)#7-In(2)-N(3)#7	74.0(3)
	O(5)-In(1)-N(2)#4	86.7(3)	O(11)-In(2)-N(3)#6	155.6(3)
	O(1)#3-In(1)-N(2)#4	85.0(3)	O(11)#5-In(2)-N(3)#6	86.4(4)
	O(7)-In(1)-N(2)#4	150.2(3)	O(9)#6-In(2)-N(3)#6	74.0(3)
	O(3)#4-In(1)-N(2)#4	72.6(3)	O(9)#7-In(2)-N(3)#6	82.7(3)
	N(1)#3-In(1)-N(2)#4	104.1(3)	N(3)#7-In(2)-N(3)#6	103.6(5)
	N(5)#1-Ru(1)-N(5)#2	95.6(4)	N(5)-Ru(1)-N(4)#1	92.9(4)
	N(5)#1-Ru(1)-N(5)	95.6(4)	N(4)-Ru(1)-N(4)#1	95.1(4)
	N(5)#2-Ru(1)-N(5)	95.6(4)	N(5)#1-Ru(1)-N(4)#2	92.9(4)
	N(5)#1-Ru(1)-N(4)	169.4(4)	N(5)#2-Ru(1)-N(4)#2	77.3(4)
	N(5)#2-Ru(1)-N(4)	92.9(4)	N(5)-Ru(1)-N(4)#2	169.4(4)
	N(5)-Ru(1)-N(4)	77.3(4)	N(4)-Ru(1)-N(4)#2	95.1(4)
	N(5)#1-Ru(1)-N(4)#1	77.3(4)	N(4)#1-Ru(1)-N(4)#2	95.1(4)
	N(5)#2-Ru(1)-N(4)#1	169.4(4)		

Symmetry transformations: #1 -x+y+1,-x+1,z; #2 -y+1,x-y,z; #3 -x+y+2,-x+2,z; #4 -y+2,x-y+1,z; #5 y, x,-z;

#6 -x+1,-x+y,-z; #7 -x+y,-x+1,z

In(1)-O(4)#1	2.158(2)	In(1)-O(1)	2.197(2)

In(1)-O(4)#2	2.158(2)	In(1)-N(1)#3	2.276(3)	
In(1)-O(1)#3	2.197(2)	In(1)-N(1)	2.276(3)	
O(4)#1-In(1)-O(4)#2	95.28(14)	O(1)#3-In(1)-N(1)#3	73.25(9)	
O(4)#1-In(1)-O(1)#3	125.93(10)	O(1)-In(1)-N(1)#3	82.32(10)	
O(4)#2-In(1)-O(1)#3	83.00(10)	O(4)#1-In(1)-N(1)	151.74(10)	
O(4)#1-In(1)-O(1)	83.00(10)	O(4)#2-In(1)-N(1)	86.73(10)	
O(4)#2-In(1)-O(1)	125.93(10)	O(1)#3-In(1)-N(1)	82.32(10)	
O(1)#3-In(1)-O(1)	139.63(13)	O(1)-In(1)-N(1)	73.25(9)	
O(4)#1-In(1)-N(1)#3	86.73(10)	N(1)#3-In(1)-N(1)	104.63(14)	
O(4)#2-In(1)-N(1)#3	151.74(10)			
Symmetry transformations: #1 x-y+4/3,-y+5/3,-z+1/6; #2 -y+2,x-y+1,z; #3 y+1/3,x-1/3,-z+1/6				



Fig. S3 Structure of {In(bpdc)₂} anionic skeleton with six-member windows (left) and Rubpy guest shown in space-filling mode (right)



Fig. S4 Structure of 2-D {In(bpdc)₂}•Rubpy layer of **compound 1** along *c* direction and Rubpy guest with space-filling mode

3. Characterization Section

3.1. Microscope images



Fig. S5 Microscope images of core-shell MOF crystals 1@2



Fig. S6 Microscope images of shell crystals 2







Fig. S8 The experimental and simulated PXRD patterns of core crystals 1 (green), shell crystals 2 (black) and core-shell crystals 1@2 (blue). The simulated PXRD of 1 and 2 draw in red color (all the sample without grinding)

The pure phase was determined by the PXRD patterns. The encapsulation of larger Rubpy guest into the anionic $\{In(pydc)_2\}$ frameworks may slightly increase the lattice parameters (see the structure determination in section 2). The PXRD patterns of core and shell MOFs in the area of the light blue shadow exhibit obvious difference. The consistence in the PXRD patterns of core-shell crystals 1@2 and shell crystal 2 clearly indicates the successful formation of shell crystals 2 encapsulated core-shell MOF crystal.

3.3. Energy Dispersive Spectrometer (EDS) analysis



Fig. S9 The EDS of core crystals 1 synthesized under different initial Rubpy concentration (2 mg/ml (a), 4 mg/ml (b), 6 mg/ml (c) and 8 mg/ml (d))

 Table S3 The amount of Ru, In and Ru: In rate within compound 1 synthesized under different initial Rubpy concentration

Name	Ru (at. %)	In (at. %)	In: Ru
Compound 1 (2mg/ml)	0.89	4.28	4.81
Compound 1 (4mg/ml)	2.69	14.43	4.72
Compound 1 (6mg/ml)	3.63	16.85	4.64
Compound 1 (8mg/ml)	0.84	3.70	4.41

In order to determine the content of Rubpy within a series of as-synthesized **compound 1** (the initial Rubpy concentration of 2 mg/ml, 4 mg/ml, 6 mg/ml and 8 mg/ml), the rate of Ru: In was obtained by the EDS shown in Fig. S9 and Table S3. All the Ru: In rate within those as-synthesized **compound 1** is agree with the value 4.5 calculated from the single crystal data. Combining with the experimental section and single crystal data, both Rubpy guests and H₂NMe₂⁺ cations exist within **compound 1** in order to compensate the charge balance of anionic {In(pydc)₂} frameworks. Moreover, although the initial Rubpy concentrations change in the large scope form 1.8 mg/ml to 18 mg/ml (the required initial Rubpy concentrations for fully charge balance of skeleton is 6.85 mg/ml), the final amount of Rubpy within as-synthesized **compound 1** remain the same Ru: In ratio of 2:9.

3.4. Thermogravimetric analysis



Fig. S10 The thermogravimetric curves of core crystals 1 (red) and shell crystals 2 (black) under N_2 atmosphere

For **compound 1**, thermogravimetric curve decrease gently from RT to 900 °C. The first stage form RT to 100 °C attributes to the loss of 18 crystallized water molecules (cat. 5.4 %, exp. 5.16 %). The second stage with the loss weight (3.95 %) form 100 °C to 200 °C belongs to the decomposition of H₂NMe₂⁺ cations (cat. 3.83 %). The third stage in the range of 200 °C to 337 °C belongs to the weight loss of four DMF solvent (cat. 4.87 %, exp. 5.18 %). The whole weight loss (%) in the range from RT to 615 °C is 56.74 % (cat. 59.26 %). Combining with the CHN and EDS data, the formula of **compound 1** is {(H₂NMe₂)₅(Rubpy)₂} {In₉(pydc)₁₈}•18H₂O•4DMF.

For **compound 2**, thermogravimetric curve decrease rapidly from RT to 900 °C. The weight loss (%) from RT to 100 °C is 5.76%, which belong to the loss of two crystallized water molecules (cat. 5.98%). The next weight loss in the range from 100 °C to 200 °C is 7.64 %, which belong to the loss of H₂NMe₂⁺ cations (cat. 7.83%). The next weight loss from 200 °C to 400 °C attributes to decompose of pydc ligands and DMF solvent. The whole weight loss (%) in the range from RT to 400 °C is 50.79 % (cat. 51.32%). Combining with the CHN data, the formula of **compound 2** is $\{H_2NMe_2\}\{In(pydc)_2\}\bullet 2H_2O\bullet DMF.$

3.5. The FT-IR spectra



Fig. S11 The FT-IR spectra of **compound 1** (black), **compound 2** (blue) and **1@2** (red) The IR spectra of synthesized **1**, **2** and **1@2** are similar with adsorption peaks location at 539(w, γ_{C-H}), 655(m, γ_{C-H}), 685(m, γ_{C-H}), 763(s, γ_{C-H}), 831(s, γ_{C-H}), 890(w, γ_{C-H}), 958(w, δ_{C-H}), 1035(m, δ_{C-H}), 1094(w, δ_{C-H}), 1172(w, δ_{C-H}), 1280(s, v_{C-O}), 1338(s, v_{C-O}), 1473(w, $v_{C=C}$), 1616(s, $v_{C=C}$), 1666(m, v_{C-H}), 2800(w, v_{C-H}), 2929(w, v_{C-H}), 2970(w, v_{C-H}), 3073(m, v_{C-H}) and 3460(w, v_{N-H}) cm⁻¹.

3.6. The UV-vis spectrum



Fig. S12 The solid UV-vis spectrum of core crystals 1 (green), shell crystals 2 (black) and coreshell crystals 1@2 (red) in the range of 800 to 200 nm

The successful encapsulation of $\text{Ru}(\text{bpy})_3^{2+}$ molecules in { $\text{In}(\text{pydc})_2$ } frameworks was further confirmed by the UV-vis spectroscopy. The absorption pink at around 450 nm of compound 1 and core-shell 1@2 belong to the triplet metal to ligand charge transfer state (³MLCT) of Rubpy. Furthermore, the 1@2 exhibit two obvious synergetic absorption spectra came from the 2 shell and 1 core respectively.



3.7. The lifetime of Ru(bpy)₃(PF₆)₂, compound 1 and core-shell 1@2

Fig. S13 The lifetime of Ru(bpy)₃(PF₆)₂ (a), core crystals 1 (b) and core-shell crystals 1@2 in the solid state at room temperature, excited by 450 nm

The fluorescence decays of core crystals 1, core-shell crystals 1@2 and Rubpy were analyzed using Origin 7.0 software. The following formula was used to analyze the experimental fluorescence decays:

$$P(t) = b + \sum_{i}^{n} \alpha_{i} \exp(-t/\tau_{i})$$

b is a baseline correction, *n* is the number of discrete emissive species, and α_i and τ_i are the preexponential factors and excited-state fluorescence lifetimes associated with the *i*_{th} component, respectively. For bi-exponential decays (*n* = 2), the lifetimes are given in τ_1 and τ_2 .

The average lifetimes ($<\tau$ >) are calculated by the following formula:

$$\langle \tau_i \rangle = \sum_{i=1}^2 \alpha_i \tau_i^2 / \sum_{i=1}^2 \alpha_i \tau_i$$

Table S4 Decay parameters for $Ru(bpy)_3(PF_6)_2$, core crystals 1 and core-shell crystals 1@2 in the solid state at room temperature

Compound	$\lambda_{\max}(\mathbf{nm})$	Bi-exponential fitting		< 7 >°	R ²
	_	$ au_1(\alpha_1)^{\mathbf{b}} (\mathbf{ns})^{\mathbf{a}}$	$\tau_2(\alpha_2)^{\mathbf{b}} (\mathrm{ns})^{\mathbf{a}}$		
$Ru(bpy)_3(PF_6)_2$ in solid	578	43.5 (0.25%)	315 (99.75%)	316	0.99269
core-shell crystals 1@2	576	381 (8.49%)	2790 (91.51%)	2760	0.99753
core crystals 1	583	196 (4.71%)	1760 (85.29%)	1750	0.99685

^{*a*} Lifetimes excitation at 450 nm. ^{*b*} Relative amplitude. ^{*c*} Average lifetime.

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