Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Shape Assisted Fabrication of Fluorescent Cages of Squarate based Metal-Organic Coordination Frameworks

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Experimental Section

Materials

All the reagents and solvents employed were commercially available and used as supplied without further purification. $Co(OH)_2$, Squaric acid and polyvinylpyrrolidine were obtained from Aldrich chemical company.

Synthetic procedure for $[M(C_4O_4)(H_2O)_2]_n$ cages: In a typical synthesis $M(OH)_2$ (0.75 mmol) (where M = Co, Zn and Cd) is dissolved in water (8 ml) and mixed with polyvinylpyrrolidine (0.122 g, M_w = 25,000). To this solution, squaric acid (0.5 mmol) dissolved in deionized water (5 ml) is added in a quick succession. The mixture is then transferred to a teflon container (23 ml capacity) and stirred for 30 min. The container is then put inside a steel autoclave and heated at 180°C for 96 h in a temperature-controlled oven (Additionally, the reaction time is varied to 1 h, 5h, 24 h, 48 h, and 72 h for arresting the intermediate structures during formation). After 96 h of reaction time, the solid obtained is washed thoroughly with water and ethanol and dried at room temperature for further analysis.

Sample characterization: The morphologies of the samples obtained in all the experiments were examined with field emission scanning electron microscope (FESEM, FEI Nova-Nano SEM-600, The Netherlands) and TEM (JEOL JEM-3010 with an accelerating voltage at 300 KV). Powder X-ray diffraction (XRD) patterns were measured by using BRUKER Discover D8 diffractometer employing Cu-K_α radiation. Thermogravimetric analysis (TGA) was performed using Mettler Toledo TGA 850 instrument. N_2 adsorption-desorption isotherms were measured using QUANTACHROME QUDRASORB™ surface area analyzer at liquid N_2 temperature (77 K) and BELSORB aqua III adsorption instrument (JAPAN) for solvent adsorption measurements. The IR spectra were recorded using Fourier-transform infrared instrument (FT-IR, Bruker, IFS 66 V/s) in the range of 400 - 4000 cm^{-1}. Confocal Microscopy imaging was taken at room temperature using a Zeiss LSM 510META laser scanning confocal microscope. The microscope objective of 40X (NA 0.75) and 100X (NA 1.3) were employed. To excite CSP, a 514 nm line (Argon laser) with a band pass filter of 525-670 nm was used and emission spectra were recorded using a META PMT detector array.

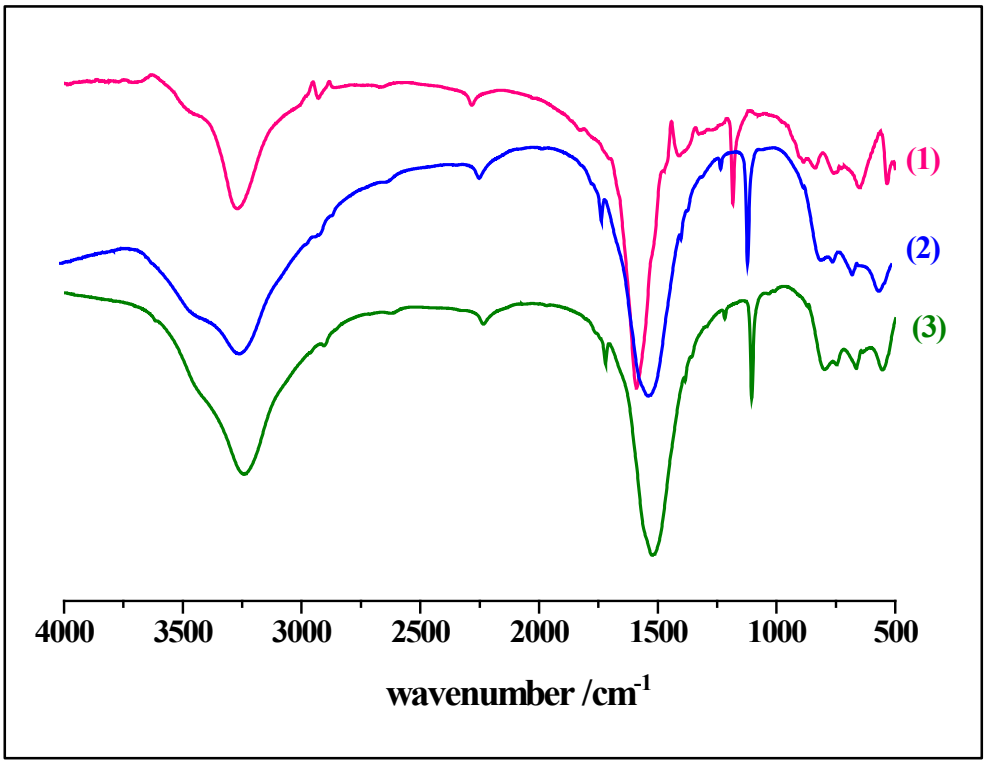

Fig. S1. FT-IR spectra of $[Co(C_4O_4)(H_2O)_2]$ (**1**), $[Zn(C_4O_4)(H_2O)_2]$ (**2**) and $[Cd(C_4O_4)(H_2O)_2]$ (**3**) cage.

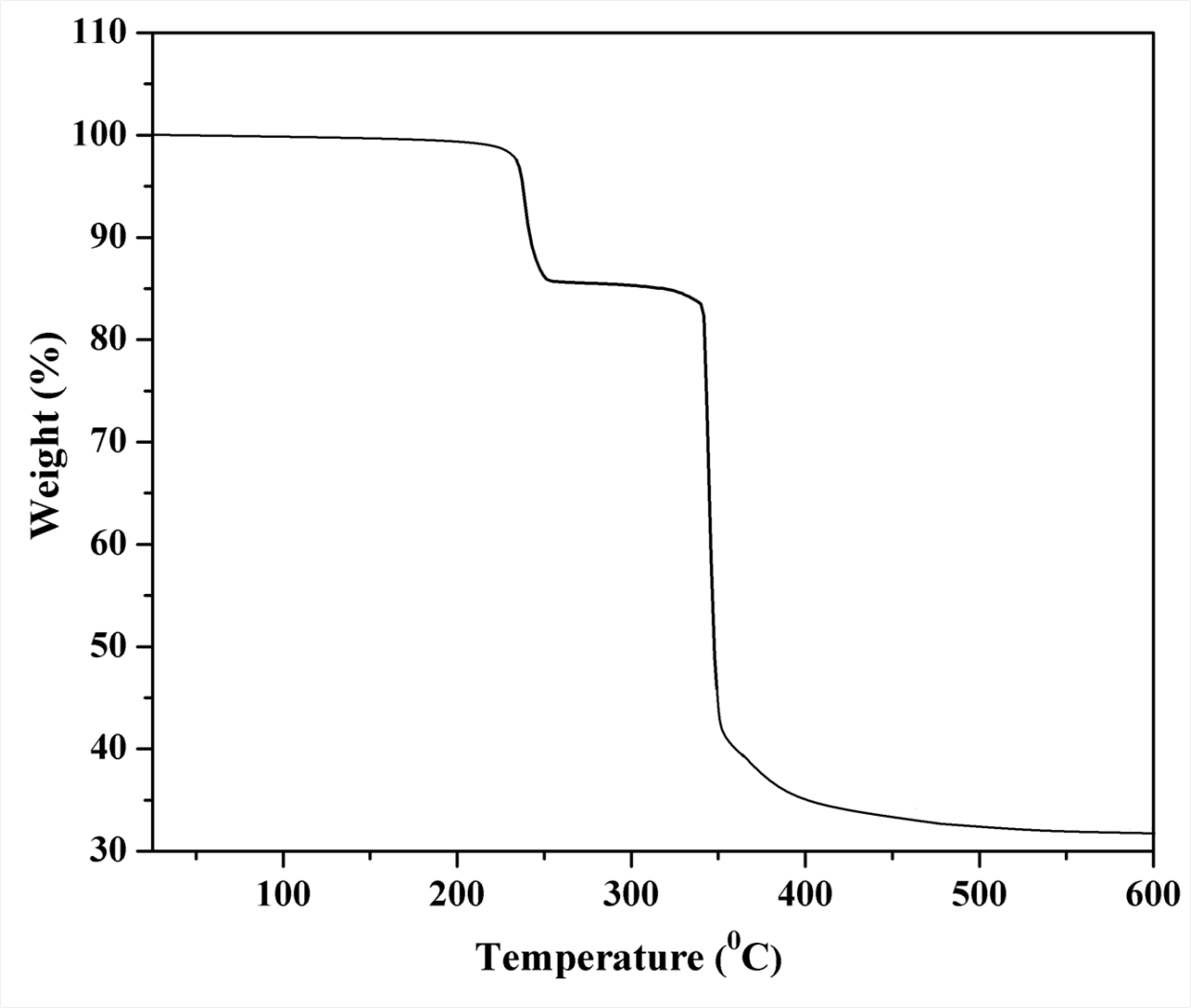

Fig. S2a. Thermogravimetric analysis (TGA) of cage of $[Co(C_4O_4)(H_2O)_2]$ (**1**).

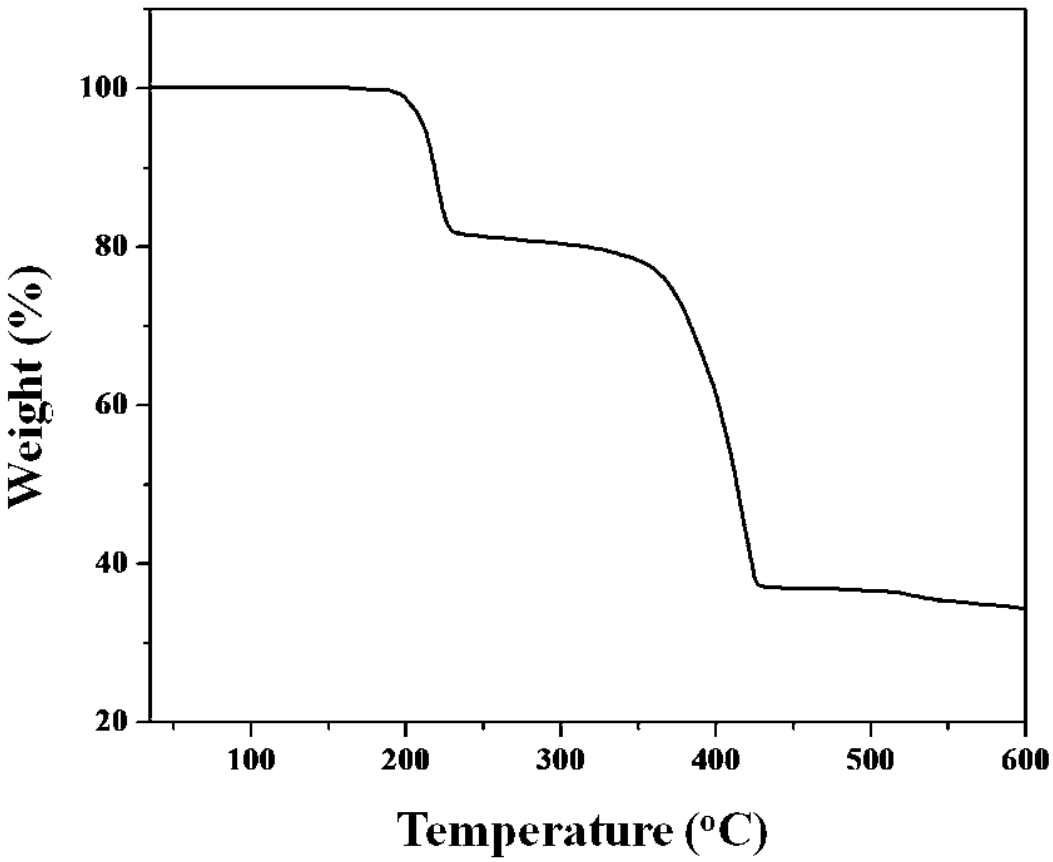

Fig. S2b. Thermogravimetric analysis (TGA) ofcage of $[Zn(C_4O_4)(H_2O)_2]$ (**2**).

Table S1. Elemental analyses data for the cages.

	$Co(C_4O_4).2H_2O$ (1)		$Zn(C_4O_4).2H_2O$ (2)		$Cd(C_4O_4).2H_2O$ (3)	
	Carbon (%)	Hydrogen (%)	Carbon (%)	Hydrogen (%)	Carbon (%)	Hydrogen (%)
Experimental	23.17	1.89	22.36	1.91	18.54	1.62
Calculated	23.12	1.93	22.49	1.87	18.43	1.53

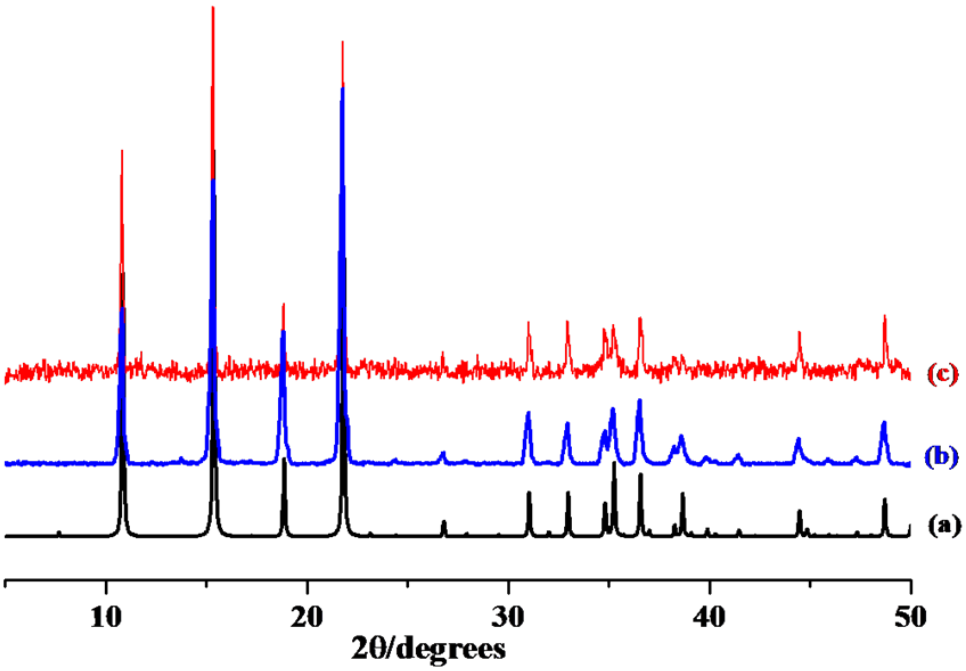

Fig. S3. Powder X-ray diffraction (PXRD) pattern of the nanocages. (a) simulated pattern of $[Co(C_4O_4)(H_2O)_2]_n$; (b) assynthesized nanocage of $[Zn(C_4O_4)(H_2O)_2]_n$; (c) assynthesized cage of $[Cd(C_4O_4)(H_2O)_2]_n$.

Table S2. Indexing result from the powder data of cage $[Co(C_4O_4)(H_2O)_2]_n$ (1).

From TREOR programme

a = 16.248(1) b = 16.248(1) c = 16.248(1)Å, $\alpha = \beta = \gamma$ = 90.00°

UNIT CELL VOLUME = 4290.12 Å^3

H	K	L	SST-OBS	SST-CALC	DELTA	2TH-OBS	2TH-CALC	D-OBS
2	0	0	.008997	.008989	.000007	10.886	10.881	8.1211
2	2	0	.017987	.017979	.000008	15.415	15.411	5.7435
2	2	2	.026998	.026968	.000030	18.914	18.904	4.6881
6	2	0	.089959	.089895	.000064	34.907	34.894	2.5683
5	4	0	.092151	.092142	.000009	35.343	35.342	2.5375
6	2	2	.098908	.098884	.000024	36.661	36.656	2.4493
7	0	0	.110030	.110121	-.000091	38.745	38.762	2.3222

NUMBER OF OBS. LINES = 7

NUMBER OF CALC. LINES = 7

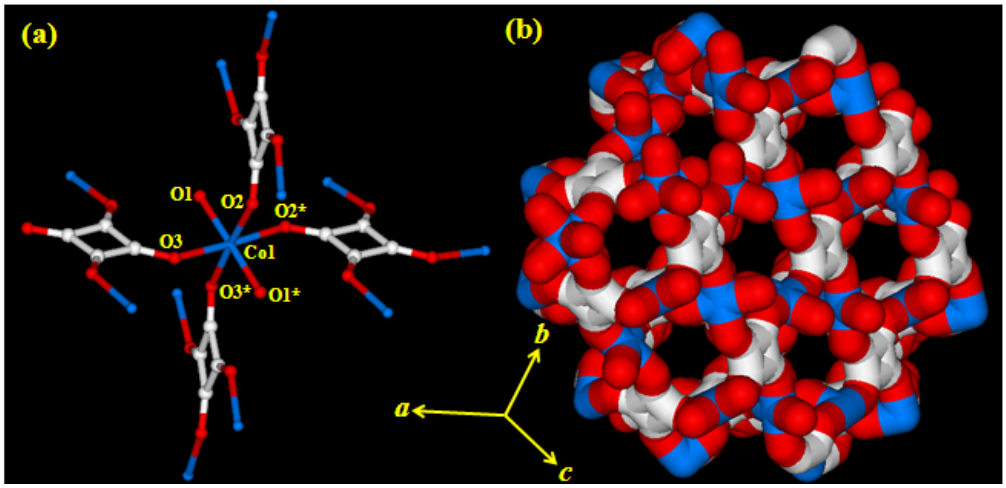

Fig. S4. (a) View of the coordination environment of Co(II) and binding of the squarate dianion in $[Co(C_4O_4)(H_2O)_2]_n$ (**1**); (b) View of the hexagonal channels along [110] direction.

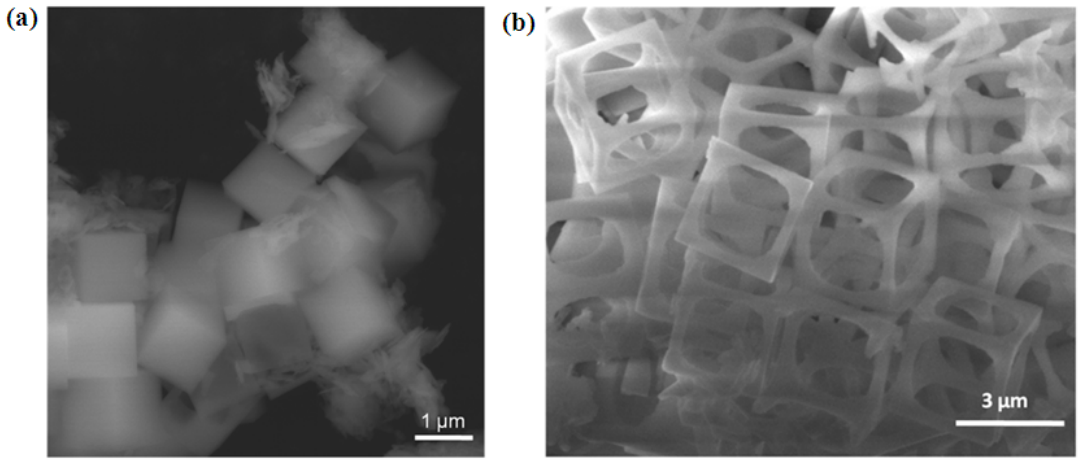

Fig. S5a. (a) Cubes of $[Co(C_4O_4)(H_2O)_2]$ (**1**) obtained in good yield after 24 h of reaction time. (b) Cages of $[Co(C_4O_4)(H_2O)_2]$ (**1**) obtained in good yield after 96 h of reaction time.

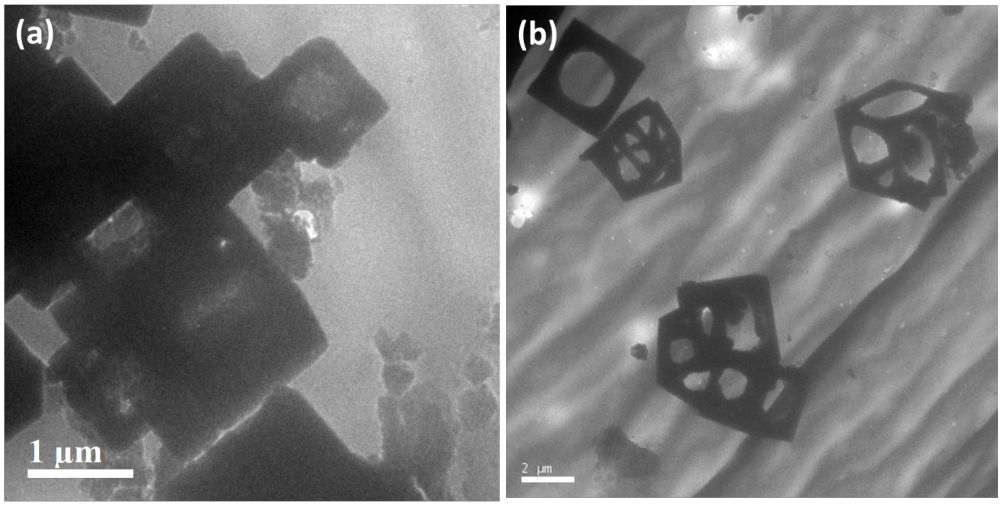

Fig. S5b. TEM images of (a) $[Zn(C_4O_4)(H_2O)_2]$ (**2**) ; (b) $[Cd(C_4O_4)(H_2O)_2]$ (**3**) showing micronic cages throughout the sample.

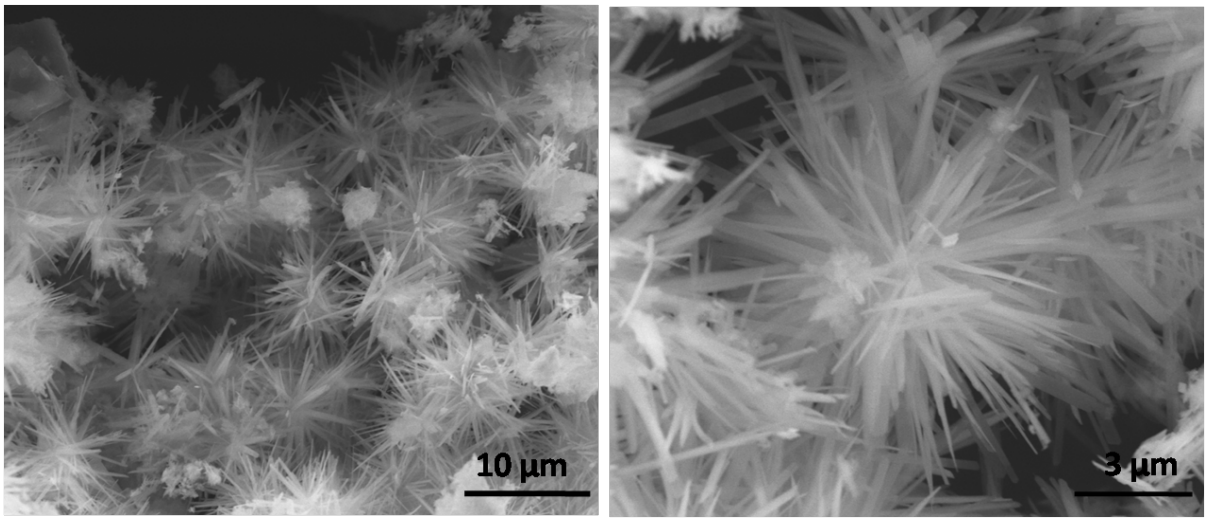

Fig. S6. Dandelion-like nanostructures obtained after 24 h reaction time while using lower amount of PVP.

Table S3. Details of the different experiments performed.

Change of Morphology with PVP

Template	**PVP (M. Wt. 25,000)**	**PVP (M. Wt. 1,00,000)**	**PVP (M. Wt. 5,000)**
Morphology	Cubes/cages	Flaky particles	Flaky particles

Conditions: [Temperature =180 °C, Time = 72 h, PVP =(polyvinylpyrrolidine, PVA= poly vinyl alcohol), $Co(OH)_2$ = (0.069g, 0.75mmol,) and squaric acid = (0.5 mmol, 0.057g)]

Temperature

Temperature	**Room Temp**	**100 °C**	**120 °C**	**180 °C**	**200 °C**
Morphology	Flakes	Flakes	Rods	Cube/cage	flakes

Conditions: Time = 72 h, PVP = (1.09 mmol, 0.122 g, M. Wt. 25000), $Co(OH)_2$ = (0.75 mmol 0.069 g) and squaric acid = (0.5 mmol, 0.057 g)

Metal Anions

Anion (X)	**Hydroxyl**	**Chloride**	**Acetate**	**Nitrate**	**perchlorate**
Morphology	Cubes/cages	No cube/cages	No cube/cages	No cube/cages	No cube/cages

Conditions: Time = 72 h, PVP = (1.09 mmol, 0.122 g), Temperature = 180 °C and squaric acid (0.5 mmol, 0.057g)

Metal precursor to PVP ratio:

$M(OH)_2$ (X) **PVP (Y)**	**5 h**	**24 h**	**48 h**	**72 h**	**96 h**	**120 h**
X: Y/5	Cubes/ partly cages	Dandelion-like / cubes	Flaky particles	Flaky particles	Flaky particles	Broken cages
X: Y	flakes	cubes	Partially etched cubes	Cubes/ cages	**Cages**	Broken cages
X: 2Y	Cubes/faceted cages	Cubes/faceted cages	Broken cages	Broken cages	Broken cages	Broken cages

Conditions:
X= $M(OH)_2$ [$Co(OH)_2$ (0.75 mmol 0.069 g]Y = PVP [1.09 mmol, 0.122 g], (monomeric unit's molecular weight has been considered as 1 mol) All experiment at temperature = 180 °C; and squaric acid (0.5 mmol, 0.057g)

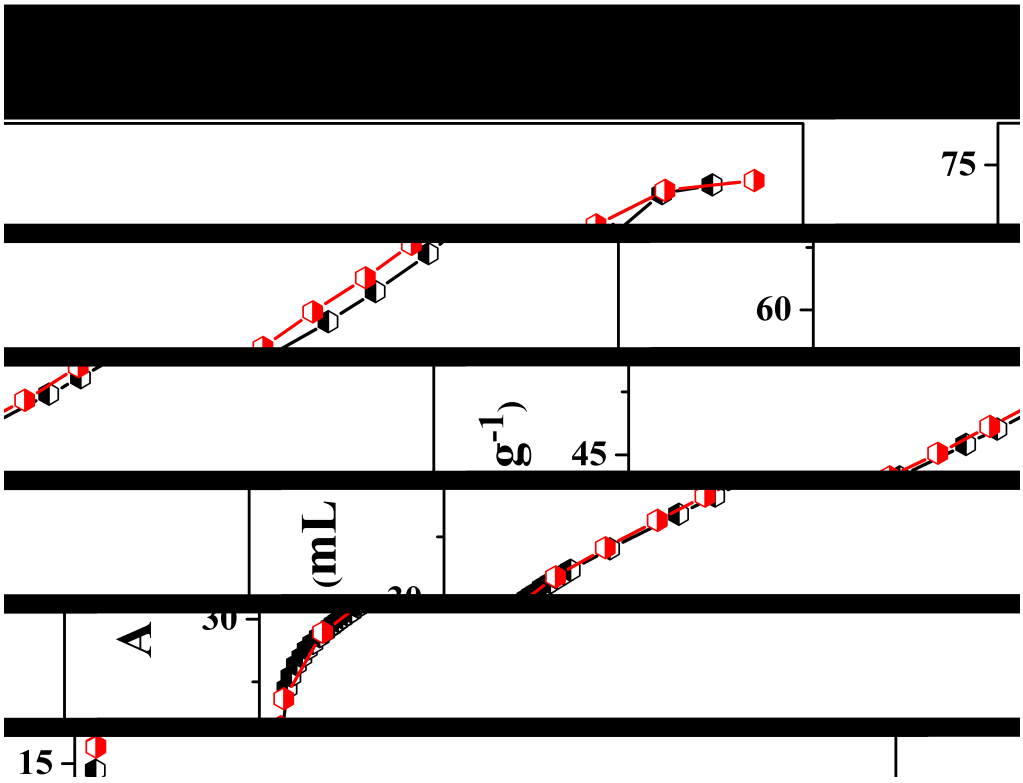

Fig. S7. Nitrogen adsorption isotherm for the dehydrated cage structure of $[Co(C_4O_4)(H_2O)_2]_n$ at 77 K

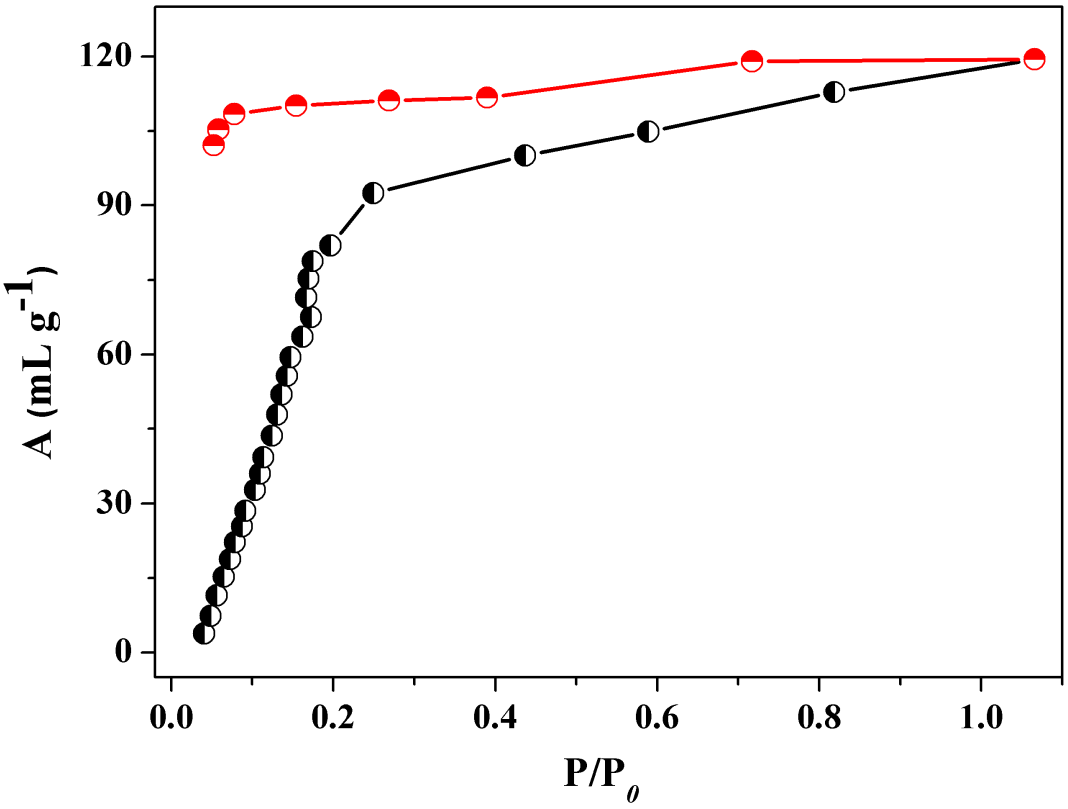

Fig. S8. Water sorption isotherms of dehydrated cage $[Co(C_4O_4)(H_2O)_2]$ (**1**) H_2O at 298 K (P_o is the saturated vapor pressure of the adsorbates at the corresponding temperature, blue curve for adsorption and red curve for desorption).

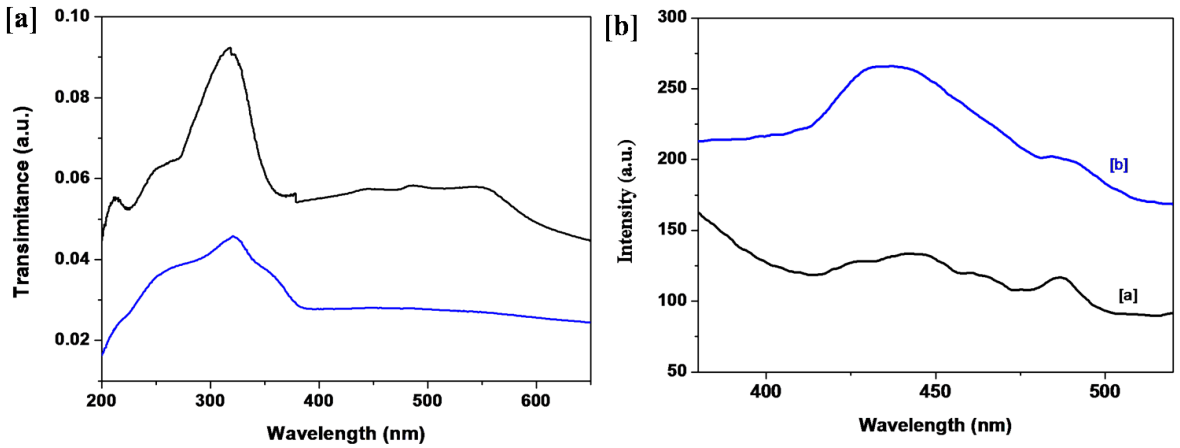

Fig. S9. [a] UV-vis spectra and [b] emission spectra of squaric acid and $[Zn(C_4O_4)(H_2O)_2]_n$ (**2**) cages. [black line for squaric acid and blue line for $[Zn(C_4O_4)(H_2O)_2]_n$ nanocages)

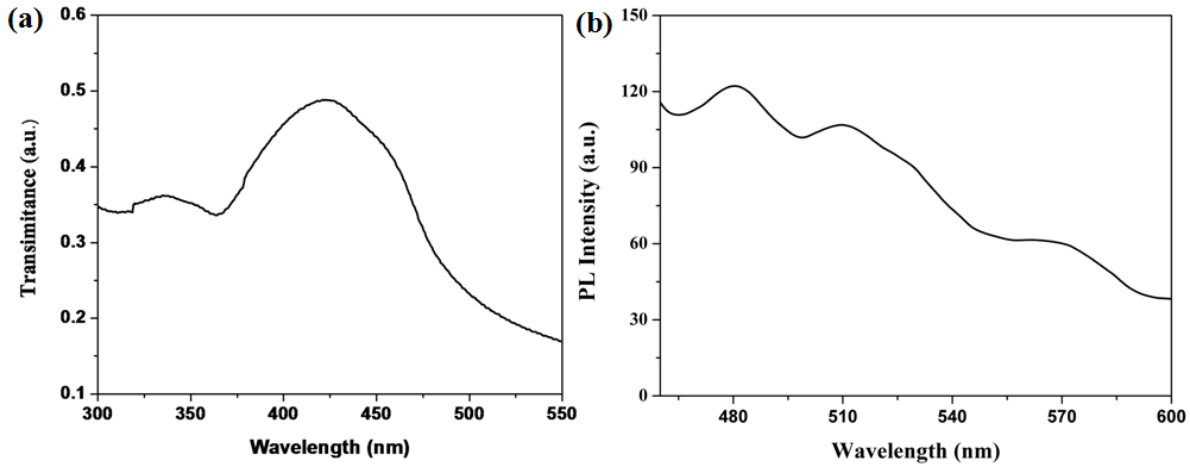

Fig. S10. (a) UV-vis and (b) emission spectra of OPV-NH_2 in solid state.

Post-synthetic modifications of metal-organic nanostructures (cage/cubes):

2 mg of $[M(C_4O_4)(H_2O)_2]_n$ nanocubes or nanocages were immersed in 2 ml of ethanol solution containing OPV-NH_2 (0.00914g, 0.01mmol) for 48 h. After this, the resulting nanocubes or nanocages were separated by decantation and then washed with ethanol several times and then dried at room temperature for 6 h. Confocal laser scanning microscopy (CLSM) measurements were performed on a glass slide by drop casting one drop of above solution containing cubes and cages.

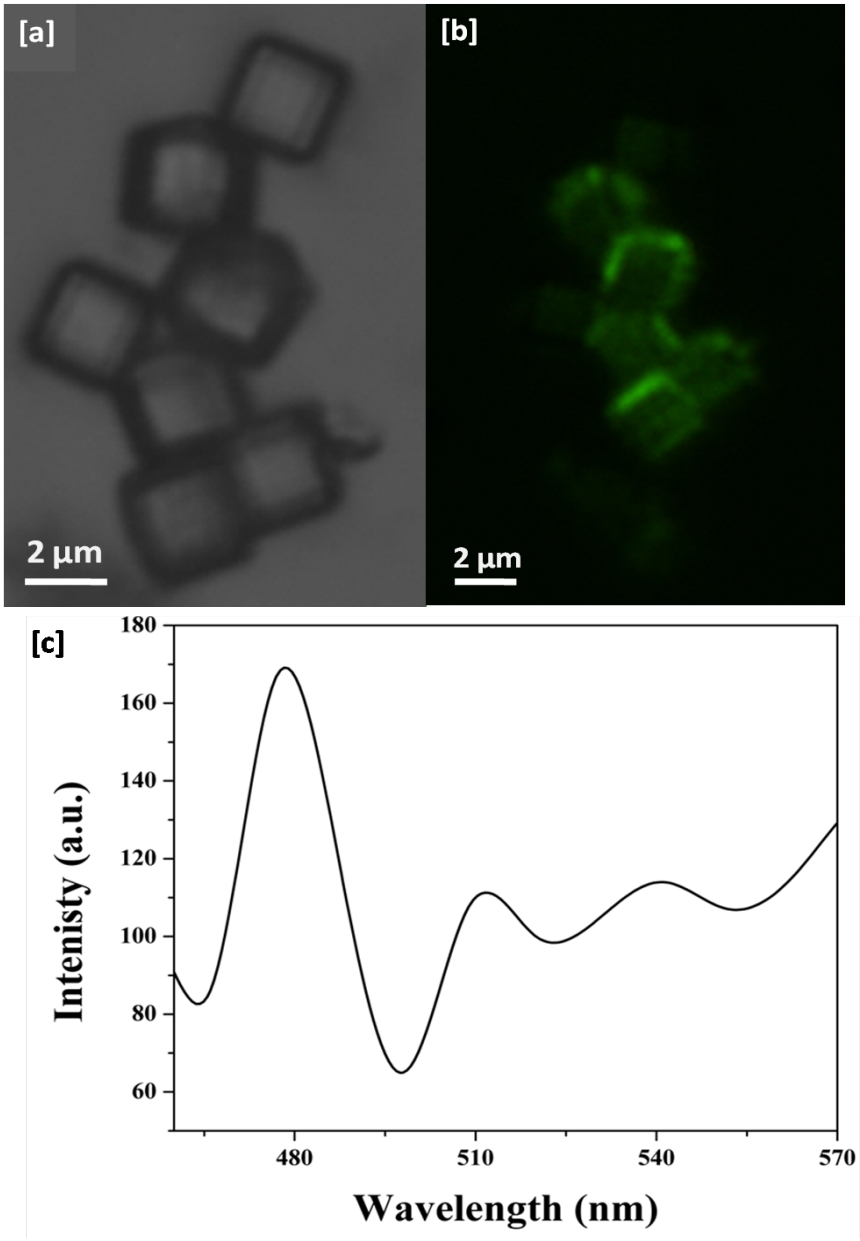

Fig. S11. Confocal laser scanning microscopic images (CLSM) of $[Zn(C_4O_4)(H_2O)_2]$ cubes after functionalization with OPV-NH_2. cubes (a) without excitation (b) with excitation at 421 nm showing green fluorescent cubes and (c) corresponding emission spectra of the cubes obtained under the confocal microscope.