

SUPPORTING INFORMATION

The Use of Rapid Precipitation to Synthesise Multivariate Metal-Organic Frameworks for Photocatalysis

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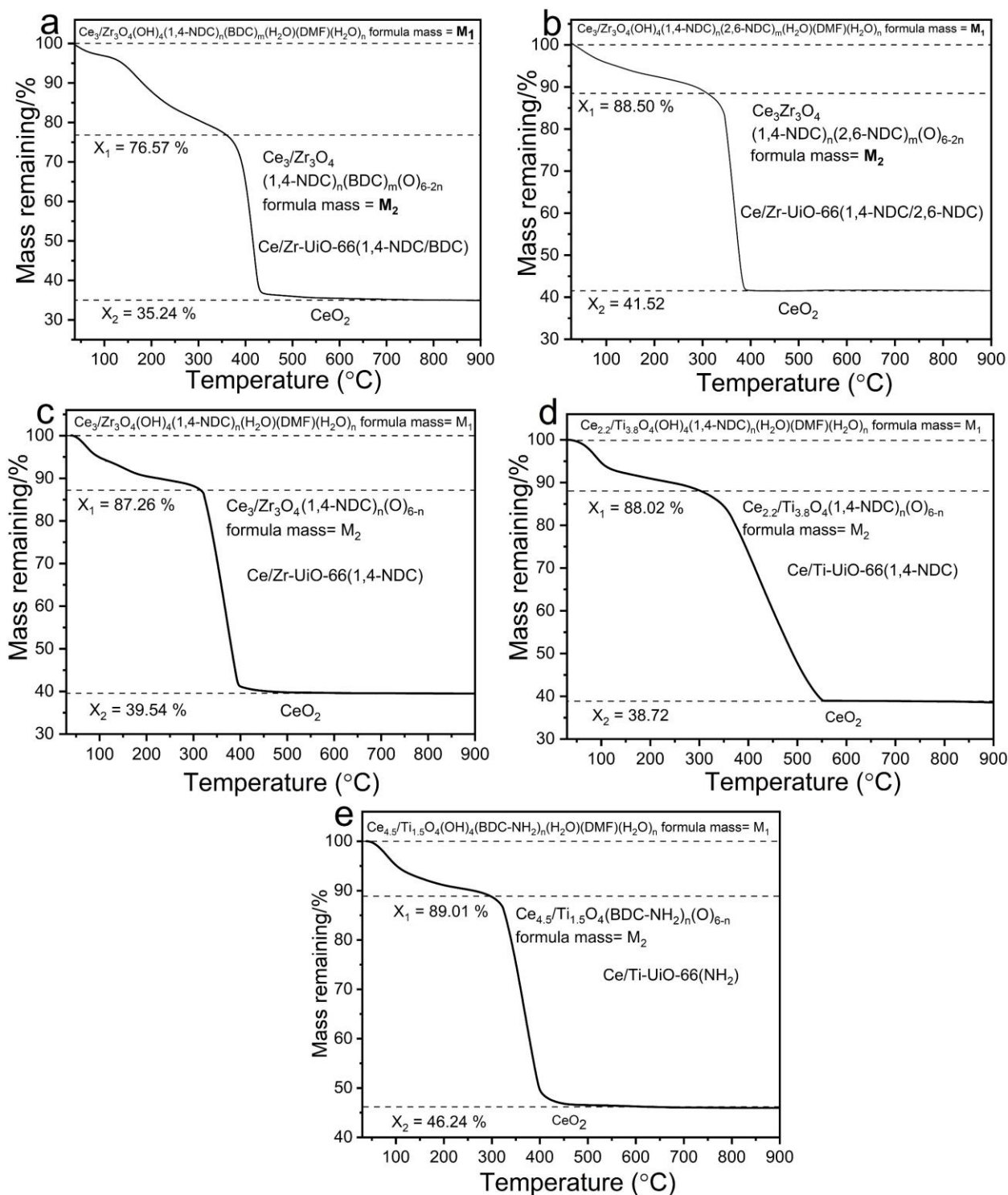


Figure S1: The thermogravimetric analysis (TGA) curves of MTV-MOFs series showing the continuous weight loss until ca. 500 °C, a) Ce/Zr-UiO-66(1,4-NDC/BDC), b) Ce/Zr-UiO-66(1,4-NDC/2,6-NDC), c) Ce/Zr-UiO-66(1,4-NDC), d) Ce/Ti-UiO-66(1,4-NDC), e) Ce/Zr-UiO-66(NH₂). thermal decomposition step is labelled X₁ and X₂ which is first mass loss(solvent, modulator, and water), and total ligand combustion, respectively. M₁ and M₂ are the theoretical and actual masses of MTV-MOFs, respectively.

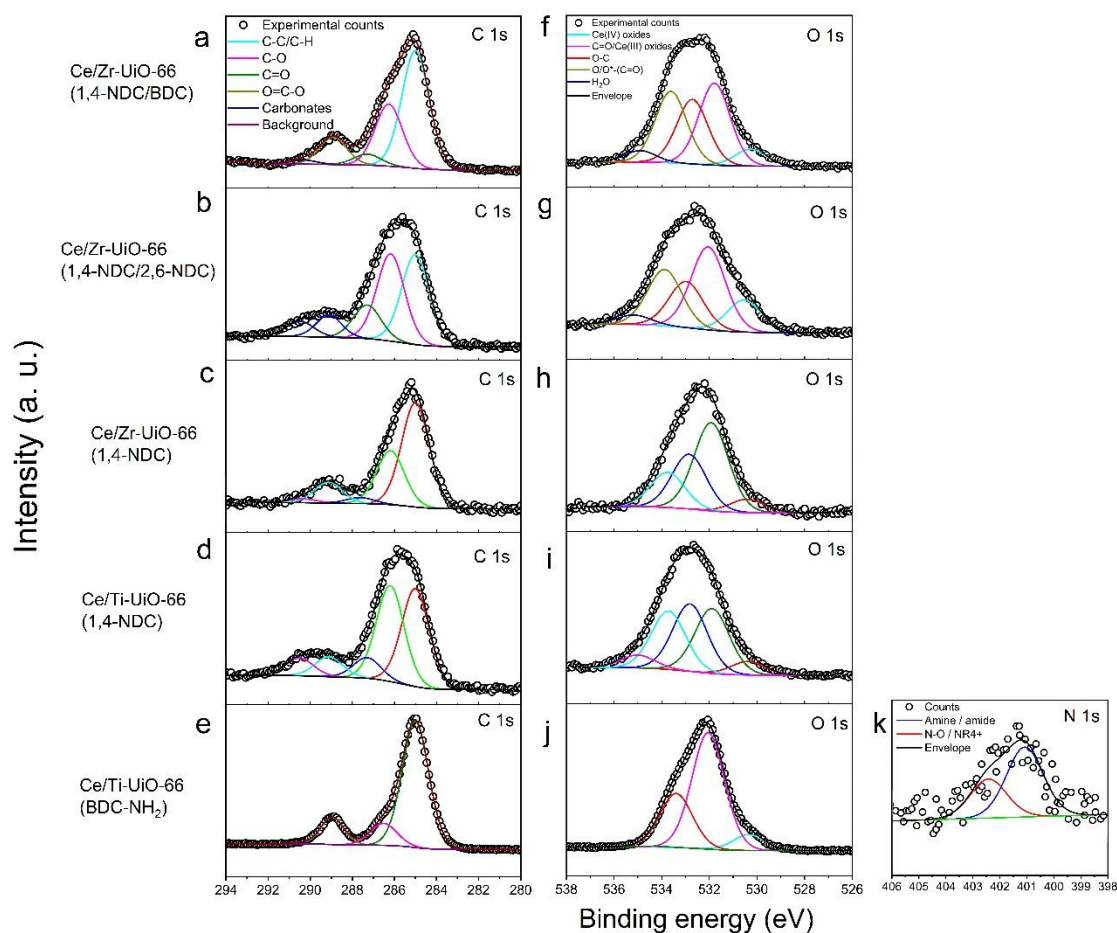


Figure S2: XPS spectra of C 1s: a) Ce/Zr-(1,4-NDC/BDC), b) Ce/Zr-(1,4-NDC/2,6-NDC), c) Ce/Zr-UiO-66(1,4-NDC), d) Ce/Ti-UiO(1,4-NDC), and e) Ce/Ti-UiO66(NH₂). O 1s: f) Ce/Zr-(1,4-NDC/BDC), g) Ce/Zr-(1,4-NDC/2,6-NDC), h) Ce/Zr-UiO-66(1,4-NDC), i) Ce/Ti-UiO(1,4-NDC), and j) Ce/Ti-UiO66(NH₂), N 1s: k) Ce/Ti-UiO66(NH₂).

Table S1a: Details of the deconvolution and ranges of energies of the features in the XPS spectrum of Ce/Zr-UiO-66(1,4-NDC/BDC) including binding energy, the nature of bonding in samples, and their percentages.

Ce 3d region			C 1s region			O 1s region		
Binding energy (eV)	% of region	Bonding environment	Binding energy (eV)	% of region	Bonding environment	Binding energy (eV)	% of region	Bonding environment
881.88	7.92	Ce 3d _{5/2} - Ce ³⁺	285	72.76	C-C/C-H	530.35	8.13	Ce ⁴⁺ oxides/ Metal oxides
885.82	25.7	Ce 3d _{5/2} - Ce ³⁺	286.51	12.68	C-O / C-N	532.05	62.44	O=C / Ce ³⁺ oxides
892.65	2.25	Ce 3d _{5/2} - Ce ³⁺	287.64	0.1	C=O	533.39	29	O-C
900.68	7.84	Ce 3d _{3/2} - Ce ³⁺	288.96	13.71	O=C-O	534.48	0.44	Atmos O / O*-(C=O)
904.62	27.91	Ce 3d _{3/2} - Ce ³⁺	290.67	0.74	Carbonates	-	-	-
909.99	2.25	Ce 3d _{3/2} - Ce ³⁺						
883.66	4.01	Ce 3d _{5/2} - Ce ⁴⁺	Zr 3d region					
889.38	3.88	Ce 3d _{5/2} - Ce ⁴⁺	<i>Binding energy (eV)</i>	<i>% of region</i>	<i>Bonding environment</i>			
898.69	5.27	Ce 3d _{5/2} - Ce ⁴⁺	183.13	50.78	Zr 3d _{5/2} - ZrO ₂			
902.01	3.99	Ce 3d _{3/2} - Ce ⁴⁺	185.51	49.22	Zr 3d _{3/2} - ZrO ₂			
908.19	3.73	Ce 3d _{3/2} - Ce ⁴⁺	-	-	-			
917.09	5.26	Ce 3d _{3/2} - Ce ⁴⁺	-	-	-			

Table S1b: Details of the deconvolution and ranges of energies of the features in the XPS spectrum of Ce/Zr-UiO-66(1,4-NDC/2,6-NDC) including binding energy, the nature of bonding in samples, and their percentages.

Ce 3d region			C 1s region			O 1s region		
Binding energy (eV)	% of region	Bonding environment	Binding energy (eV)	% of region	Bonding environment	Binding energy (eV)	% of region	Bonding environment
883.11	6.8	Ce 3d _{5/2} - Ce ³⁺	285	38.8	C-C/C-H	530.37	6.2	Ce ⁴⁺ oxides / Metal oxides
887.05	22.2	Ce 3d _{5/2} - Ce ³⁺	286.2	38.1	C-O / C-N	531.88	29.9	O=C / Ce ³⁺ oxides
893.88	1.9	Ce 3d _{5/2} - Ce ³⁺	287.29	8.2	C=O	532.81	31.1	O-C
901.9	6.8	Ce 3d _{3/2} - Ce ³⁺	289.12	7.9	O=C-O	533.71	26.9	Atmos O / O*-(C=O)
905.84	23.6	Ce 3d _{3/2} - Ce ³⁺	290.5	7	Carbonates	535	5.9	H ₂ O
911.22	1.9	Ce 3d _{3/2} - Ce ³⁺	Zr 3d region					
884.89	5.6	Ce 3d _{5/2} - Ce ⁴⁺						
890.6	5.4	Ce 3d _{5/2} - Ce ⁴⁺	Binding energy (eV)	% of region	Bonding environment			
899.91	7.4	Ce 3d _{5/2} - Ce ⁴⁺	183.23	27.2	Zr 3d _{5/2} - ZrO ₂			
903.23	5.6	Ce 3d _{3/2} - Ce ⁴⁺	185.66	26.4	Zr 3d _{3/2} - ZrO ₂			
909.42	5.2	Ce 3d _{3/2} - Ce ⁴⁺	184.51	23.5	Zr 3d _{5/2} - Unknown			
918.32	7.5	Ce 3d _{3/2} - Ce ⁴⁺	186.94	22.8	Zr 3d _{3/2} - Unknown			

Table S1c: Details of the deconvolution and ranges of energies of the features in the XPS spectrum of Ce/Zr-UiO-66(1,4-NDC) including binding energy, the nature of bonding in samples, and their percentages.

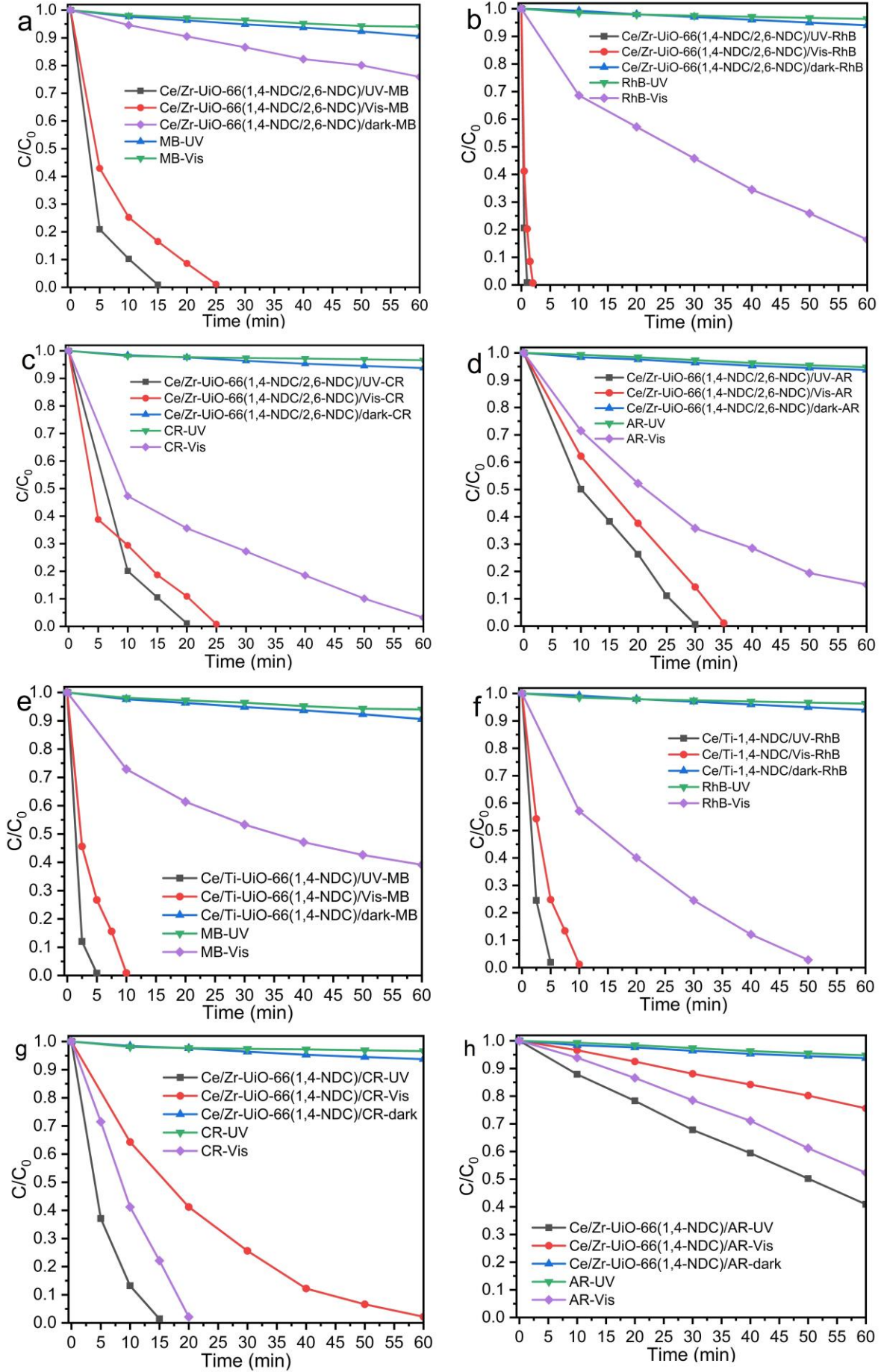
Ce 3d region			C 1s region			O 1s region		
Binding energy (eV)	% of region	Bonding environment	Binding energy (eV)	% of region	Bonding environment	Binding energy (eV)	% of region	Bonding environment
882.58	7.7	Ce 3d _{5/2} - Ce ³⁺	285	55.2	C-C/C-H	530.41	6.9	Ce ⁴⁺ oxides/Metal oxides
886.52	25	Ce 3d _{5/2} - Ce ³⁺	286.18	28.5	C-O / C-N	531.92	45.9	O=C / Ce ³⁺ oxides
893.35	2.2	Ce 3d _{5/2} - Ce ³⁺	287.63	3.2	C=O	532.85	28.5	O-C
901.38	7.6	Ce 3d _{3/2} - Ce ³⁺	289.13	11.1	O=C-O	533.75	18.3	Atmos O / O [*] -(C=O)
905.32	26.7	Ce 3d _{3/2} - Ce ³⁺	290.38	2.1	Carbonates	535.04	0.5	H ₂ O
910.69	2.2	Ce 3d _{3/2} - Ce ³⁺	Zr 3d region					
884.37	4.4	Ce 3d _{5/2} - Ce ⁴⁺						
890.08	4.2	Ce 3d _{5/2} - Ce ⁴⁺	Binding energy (eV)	% of region	Bonding environment			
899.39	5.7	Ce 3d _{5/2} - Ce ⁴⁺	182.93	29.6	Zr 3d _{5/2} - ZrO ₂			
902.71	4.3	Ce 3d _{3/2} - Ce ⁴⁺	185.36	28.7	Zr 3d _{3/2} - ZrO ₂			
908.9	4.1	Ce 3d _{3/2} - Ce ⁴⁺	184.09	21.2	Zr 3d _{5/2} - Unknown			
917.8	5.9	Ce 3d _{3/2} - Ce ⁴⁺	186.52	20.6	Zr 3d _{3/2} - Unknown			

Table S1d: Details of the deconvolution and ranges of energies of the features in the XPS spectrum of Ce/Ti-UiO-66(1,4-NDC) including binding energy, the nature of bonding in samples, and their percentages.

Ce 3d region			C 1s region			O 1s region		
Binding energy (eV)	% of region	Bonding environment	Binding energy (eV)	% of region	Bonding environment	Binding energy (eV)	% of region	Bonding environment
883.2	7.1	Ce 3d _{5/2} - Ce ³⁺	285	36.4	C-C/C-H	530.54	14.1	Ce ⁴⁺ oxides/Metal oxides
887.14	23.2	Ce 3d _{5/2} - Ce ³⁺	286.17	35.4	C-O / C-N	532.05	36.5	O=C / Ce ³⁺ oxides
893.97	2	Ce 3d _{5/2} - Ce ³⁺	287.29	13.6	C=O	532.98	20.4	O-C
902	7.1	Ce 3d _{3/2} - Ce ³⁺	289.11	8.3	O=C-O	533.88	24.9	Atmos O / O*-(C=O)
905.94	24.7	Ce 3d _{3/2} - Ce ³⁺	290.49	6.2	Carbonates	535.17	4.2	H ₂ O
911.31	2	Ce 3d _{3/2} - Ce ³⁺						
884.98	5.2	Ce 3d _{5/2} - Ce ⁴⁺	Ti 2p region					
890.7	5	Ce 3d _{5/2} - Ce ⁴⁺	Binding energy (eV)	% of region	Bonding environment			
900.01	6.8	Ce 3d _{5/2} - Ce ⁴⁺	460.78	24.4	Ti 2p _{3/2} - unknown			
903.33	5.1	Ce 3d _{3/2} - Ce ⁴⁺	466.55	24.7	Ti 2p _{1/2} - unknown			
909.51	4.8	Ce 3d _{3/2} - Ce ⁴⁺	459.26	25.3	Ti 2p _{3/2} - TiO ₂			
918.41	6.9	Ce 3d _{3/2} - Ce ⁴⁺	465.03	25.6	Ti 2p _{1/2} - TiO ₂			

Table S1e: Details of the deconvolution and ranges of energies of the features in the XPS spectrum of Ce/Ti-UiO-66(NH₂) including binding energy, the nature of bonding in samples, and their percentages.

Ce 3d region			C 1s region			O 1s region		
Binding energy (eV)	% of region	Bonding environment	Binding energy (eV)	% of region	Bonding environment	Binding energy (eV)	% of region	Bonding environment
882.78	6.6	Ce 3d _{5/2} - Ce ³⁺	285	52.9	C-C/C-H	530.27	6.8	Ce ⁴⁺ oxides/Metal oxides
886.72	21.4	Ce 3d _{5/2} - Ce ³⁺	286.27	27.9	C-O / C-N	531.78	33.3	O=C / Ce ³⁺ oxides
893.55	1.9	Ce 3d _{5/2} - Ce ³⁺	287.29	5	C=O	532.71	26.2	O-C
901.58	6.6	Ce 3d _{3/2} - Ce ³⁺	288.91	12.2	O=C-O	533.61	29.1	Atmos O / O*-(C=O)
905.52	22.9	Ce 3d _{3/2} - Ce ³⁺	290.38	1.9	Carbonates	534.9	4.7	H ₂ O
910.89	1.9	Ce 3d _{3/2} - Ce ³⁺	Ti 2p region			N 1s region		
884.56	5.9	Ce 3d _{5/2} - Ce ⁴⁺						
890.27	5.7	Ce 3d _{5/2} - Ce ⁴⁺	Binding energy (eV)	% of region	Bonding environment	Binding energy (eV)	% of region	Bonding environment
899.58	7.8	Ce 3d _{5/2} - Ce ⁴⁺	459.96	35.8	Ti 2p _{3/2} - unknown	399.51	48.3	Amine / amide
902.9	5.9	Ce 3d _{3/2} - Ce ⁴⁺	465.73	36.2	Ti 2p _{1/2} - unknown	400.85	51.7	N-O / NR ⁴⁺
909.09	5.5	Ce 3d _{3/2} - Ce ⁴⁺	458.44	13.9	Ti 2p _{3/2} - TiO ₂	N/A	0	Nitrates
917.99	8	Ce 3d _{3/2} - Ce ⁴⁺	464.21	14.1	Ti 2p _{1/2} - TiO ₂			



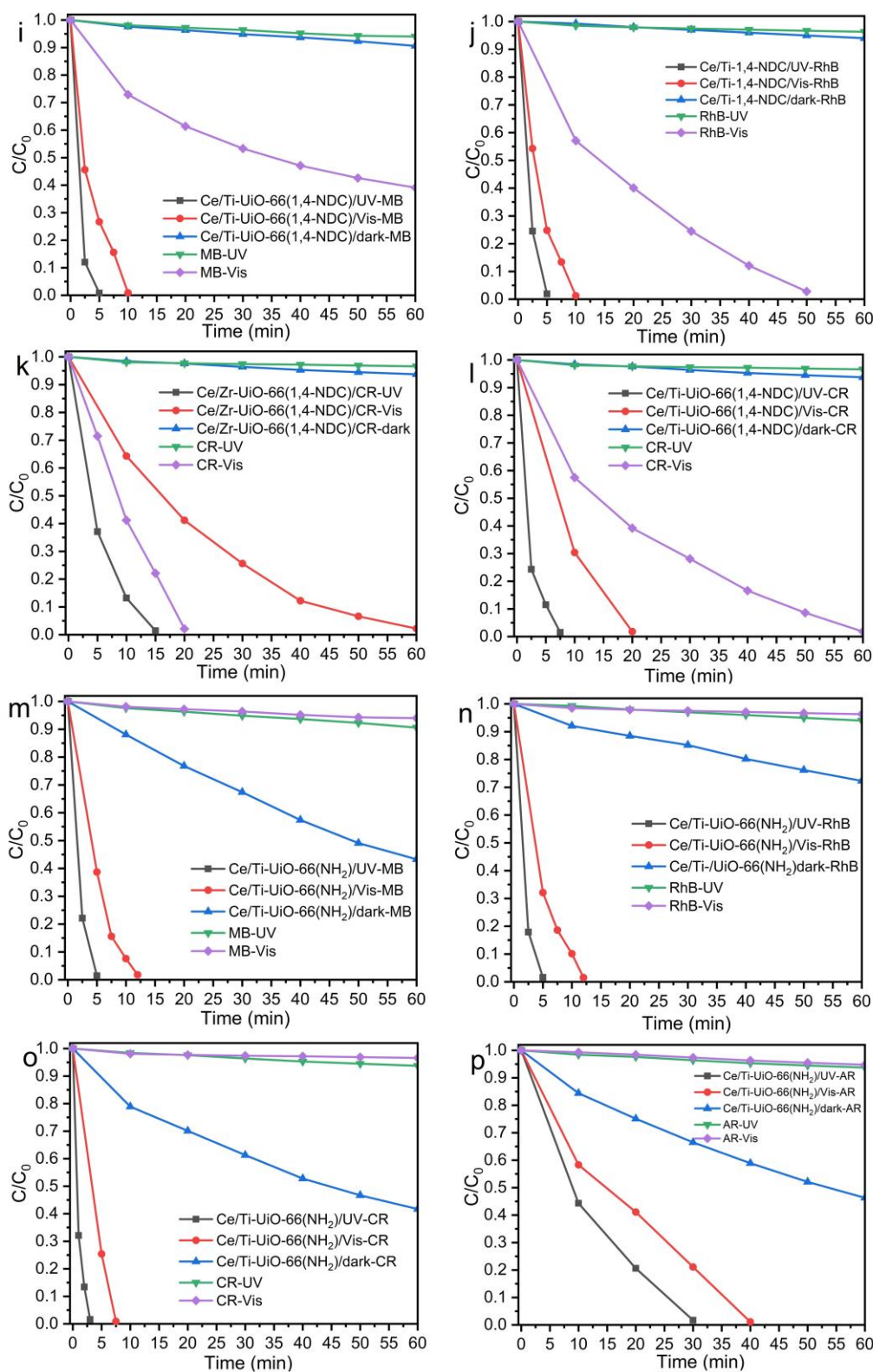


Figure S3: Photocatalytic activities, Ce/Zr-UiO-66(1,4-NDC/BDC), Ce/Zr-UiO-66(1,4-NDC/2,6-NDC), Ce/Zr-UiO-66(1,4-NDC), Ce/Ti-UiO-66(1,4-NDC), and Ce/Ti-UiO-66(NH₂) measured under UV, visible, and in MB, RhB, CR, and AR in 60 min.

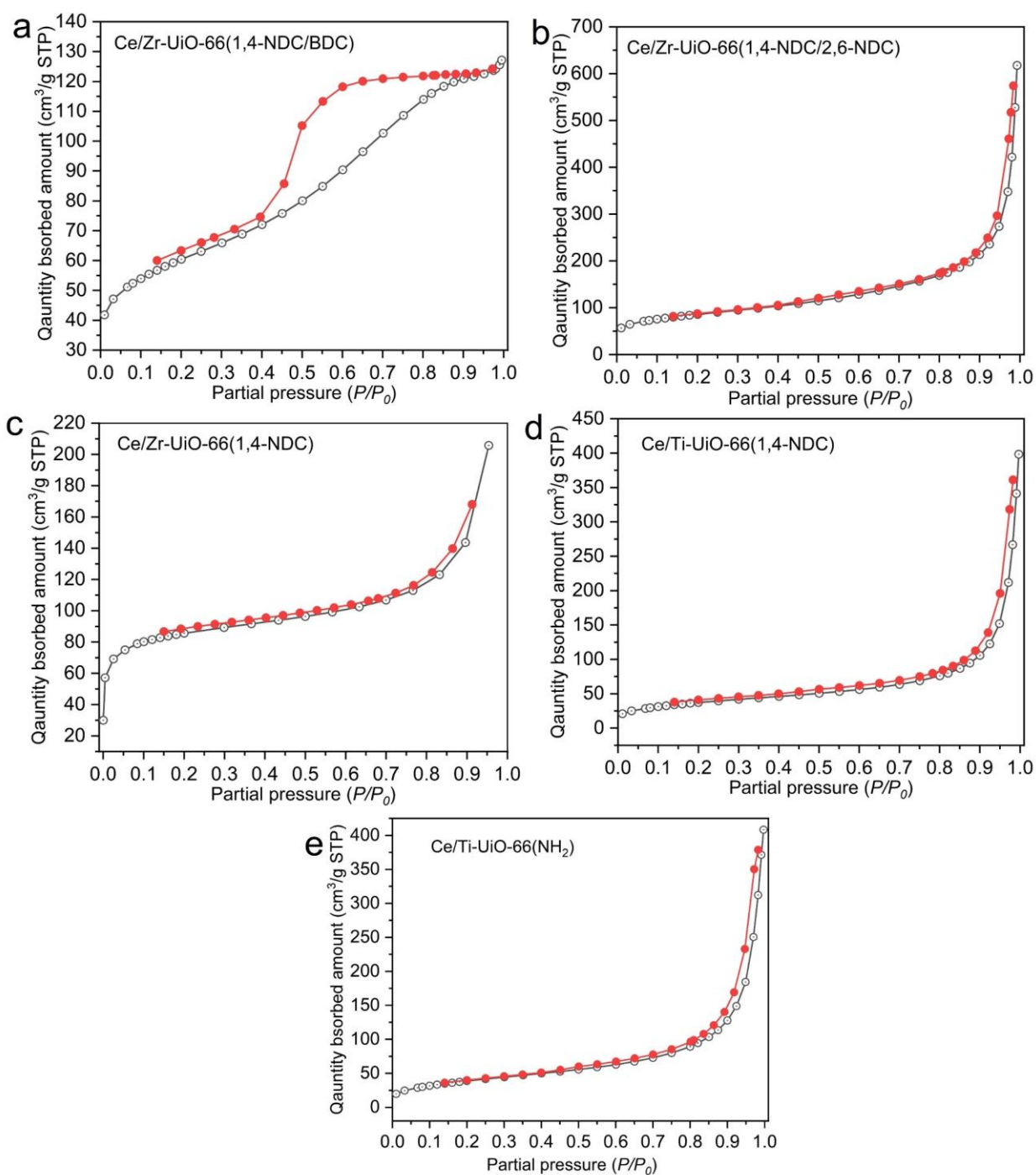


Figure S4: Nitrogen adsorption(black)–desorption(red) isotherms of MTV-MOFs, Ce/Zr-UiO-66(1,4-NDC/BDC), Ce/Zr-UiO-66(1,4-NDC/2,6-NDC), Ce/Zr-UiO-66(1,4-NDC), Ce/Ti-UiO-66(1,4-NDC), Ce/Ti-UiO-66(NH_2).

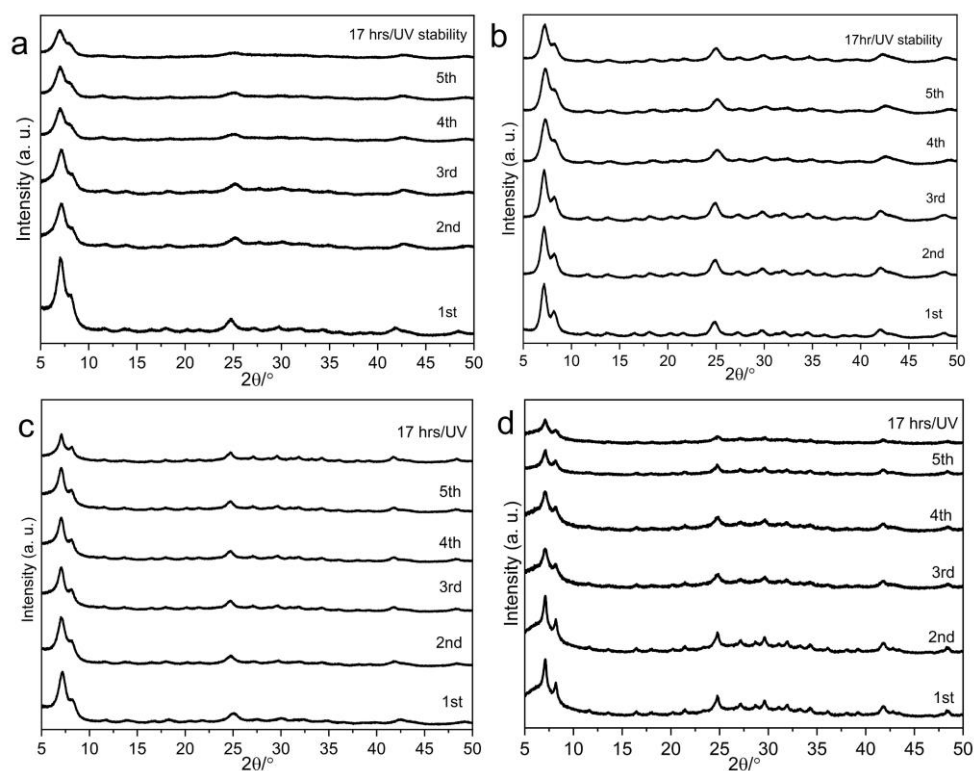
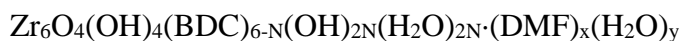


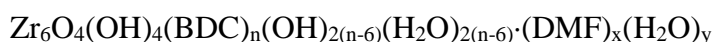
Figure S5: PXRD after 5 cycles and 17 hours of UV stability of MTV-MOFs, a) $\text{Ce/Zr-UiO-66-(1,4-NDC/2,6-NDC)}$, b) $\text{Ce/Zr-UiO-66(1,4-NDC)}$, c) $\text{Ce/Ti-UiO-66(1,4-NDC)}$, d) $\text{Ce/Ti-UiO-66(NH}_2\text{)}$.

Chemical Formula of MTV-MOFs(Multiple Metals and Linkers)

Multiple techniques are needed to define the chemical formula of MTV-MOFs (multiple metals and linkers). In this regard, XRF and NMR have been used to estimate the molar ratio of metals and organic linkers, respectively. The results of those analysis techniques and TGA assist in understanding the chemical formula of UiO-66. The results of the three techniques will be discussed in this section to define the chemical formula of structures containing two metals and two linkers. As shown in Figure 5.4, M_1 is an unknown chemical formula of a synthesised sample before starting the TGA analysis, and M_2 is an observed (or actual) mass of the samples after the loss of water and absorbed DMF. The empirical chemical formula in UiO-66 is written below:



If it sets $n = N-6$, then this formula can be written as:



The number of defects in the form of missing linkers is usually found in the UiO-66 structure. Each missing BDC di-anion introduces a net positive charge and creates two vacant oxygen sites within each cluster. To maintain charge balance, the simplest mechanism involves the inclusion of two compensating OH^- anions, followed by filling the remaining two vacant sites with water molecules.

When UiO-66 is heated in air to approximately 350°C , the solvent present in the structure evaporates, and the zirconium hydroxyoxide cluster undergoes dehydroxylation. The residual hydroxide and ligands are lost upon further heating, resulting in the formation of ZrO_2 . To account for the resulting ligand deficiency and maintain charge balance, the simplest representation of the product after the first mass loss is denoted as $\text{Zr}_6\text{O}_6(\text{BDC})_n\text{O}_{6-n}$. This illustration assumes that the charge imbalance is compensated by retained oxide species occupying the positions of the missing linkers while the remaining oxygen sites within the structure remain vacant, as reported by Oozeerally *et al.*⁹ This process also occurs for any other metals such as Ce and Ti clusters in MTV-MOFs and transforms them to CeO_2 and TiO_2 , respectively.

In the context of UiO-66, the unknown formula weights of the initial material (before any decomposition) and the intermediate product after solvent removal and dehydroxylation are

represented as M_1 and M_2 , respectively. The corresponding percentage masses measured at each thermal decomposition step are denoted as X_1 and X_2 . These measurements provide information about the weight loss and composition changes occurring during the thermal decomposition process of UiO-66.

Therefore, the calculation of empirical formula is:

$$M_1 = M_6O_4(OH)_4(L)_n(OH)_{2(n-6)}(H_2O)_{2(n-6)} \cdot (DMF)_x(H_2O)_y$$

After 350 °C the UiO-66 chemical formula is:

$$M_2 = \text{mass } (M_6O_6(L)_nO_{6-2n})$$

Regarding the MTV-MOFs, Ce/Zr-UiO-66(1,4-NDC/BDC) and Ce/Zr-UiO-66(1,4-NDC/2,6-NDC), these have been synthesised by two different metals and linkers with an equal feeding molar ratio, as shown in Figure 5.4. Regarding XRF results, the metals are distributed equally; therefore, the ratio of Ce toward Zr is found to be 1:1. In addition, the molar ratio between 1,4-NDC and BDC is 1:1, confirmed by $^1\text{H-NMR}$, as shown in Figure 5.5 and Table 5.2. the M_2 for Ce/Zr-UiO-66(1,4-NDC/BDC) formula can be rewritten as below:

$$= \text{Ce}_3/\text{Zr}_3\text{O}_6(1,4\text{-NDC})_n(\text{BDC})_n \text{O}_{(6-2n)}$$

The starting and finishing combustion mass percentages are X_1 and X_2 :

$$X_1 = 79.38 \%$$

$$X_2 = 35.4 \%$$

$$\text{so } X_1/X_2 = 2.163$$

Based on XRF results, the amount of Ce equals Zr, (Ce_3/Zr_3). The atomic weights of Ce and Zr are 140.11 and 91.22 g mol⁻¹, respectively. In addition, the atomic weight of 1,4-NDC and BDC is 216.16 and 164.13, respectively.

$$M_2 = \text{mass } (\text{Ce}_3/\text{Zr}_3\text{O}_6(\text{NDC})_n(\text{BDC})_n\text{O}_{6-2N})$$

$$M_2 = (3 \times 91.22) + (3 \times 140.11) + (6 \times 16) + (n \times 164.13) + (n \times 216.19) + [(6-2N) \times 16]$$

$$= 885.66 + 348.32 N$$

Therefore:

$$885.66 + 348.32 N = 798.22 X_1/X_2 (2.24)$$

$$N = \frac{[(885.66 \times 2.163) - 885.66]}{348.32}$$

The value of N is 2.95.

The molar ratio of linkers are equal based on NMR results as shown in Figure 5.5; therefore: $N = 2.95 + 2.95 = 5.9$

5.3.2.2. Determination of the Linkers' Ratio by NMR

As seen in Figure 5.5, the digested linkers of MTV-MOFs in ^1H -NMR can be detected as 1,4-NDC and BDC.^{10, 11} Regarding the labels of protons in the spectrum of 1,4-NDC, 'a' can be seen in singlet form at 7.338 ppm; however, both 'b' and 'c' appear as multiple signals at 7.376 and 7.967 ppm, respectively. In fact, 1,4-NDC has three protons, each of them has 3 types, and therefore the integral intensity of 1,4-NDC equals 6. Four protons of BDC are identified as the same type (label 'd') due to the structural symmetry appearing as a singlet signal at 7.642 ppm; therefore, the intensity of BDC spectra is equal to 4. To quantify the ratio of linkers, the number of protons must be divided by the integral peaks of linkers. For example, 1,4-NDC has 6 protons, the sum of the integral value of each signal is 3, and the ratio is 0.5; however, BDC has 4 protons, and the sum of integral values is 1.99, and the ratio is ~0.5; therefore, the ratio of each linker is equal in the MTV-MOF. As reported by Butova *et al.*, the molar ratio of 1,4-NDC and BDC in Zr-UiO-66(1,4-NDC/BDC) is equal, which is consistent with the results of Ce/Zr-UiO-66(1,4-NDC/BDC).¹¹ The results of digested linkers show that the initial and final ratio of 1,4-NDC toward BDC is consistent, as shown in Figure 5.5 (see section 5.2.2.1), and the chemical formula of MTV-MOF is:



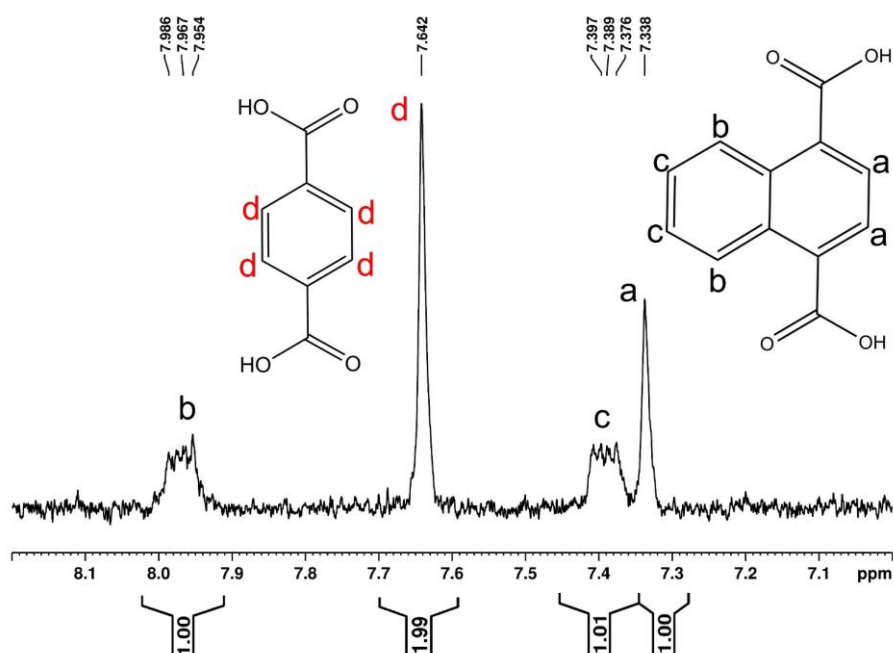


Figure S6: ^1H -NMR spectra obtained after digestion of Ce/Zr-UiO-66(1,4-NDC/BDC).

The estimation of Ce/Zr-UiO-66(1,4-NDC/2,6-NDC) chemical formula:

$$X_1 = 88.50$$

$$X_2 = 41.52$$

$$\text{so } X_1/X_2 = 2.131$$

Based on XRF results, Ce is equal to Zr.

$$M_2 = \text{mass } (\text{Ce}_3/\text{Zr}_3\text{O}_6(1,4\text{-NDC})_n(2,6\text{-NDC})_n\text{O}_{6-2N})$$

$$M_2 = (3 \times 91.22) + (3 \times 140.11) + (6 \times 16) + (n \times 216.19) + (n \times 216.19) + [(6-2N) \times 16]$$

$$= 885.66 + 400.38 N$$

$$\text{Therefore } 885.66 + 400.38 N = 885.66 X_1/X_2 (2.131)$$

Then:

$$N = \frac{[(885.66 \times 2.131) - 885.66]}{400.38}$$

N for MTV-UiO-66 is:

Therefore, the value of N is 2.50.

As shown in Figure 5.6, the ligand species and quantities have been labeled to identify 1,4-NDC and 2,6-NDC based on the previous reports in MTV-MOFs.^{9, 12} The results of NMR showed that the amount of 1,4-NDC is more than 2,6-NDC; therefore, the combination of two hetero linkers do not necessarily give an equal ratio in the final material, see Table 5.2. In addition, some unreacted ligands have been observed in Figure 5.1, which might be the reason for the unequal molar ratio of those linkers. Based on Tables 5.2 and 5.3, Figures 5.4d and 5.6, the molar ratio of 1,4-NDC toward 2,6-NDC is 1.46(~1.5); therefore, chemical formula is:

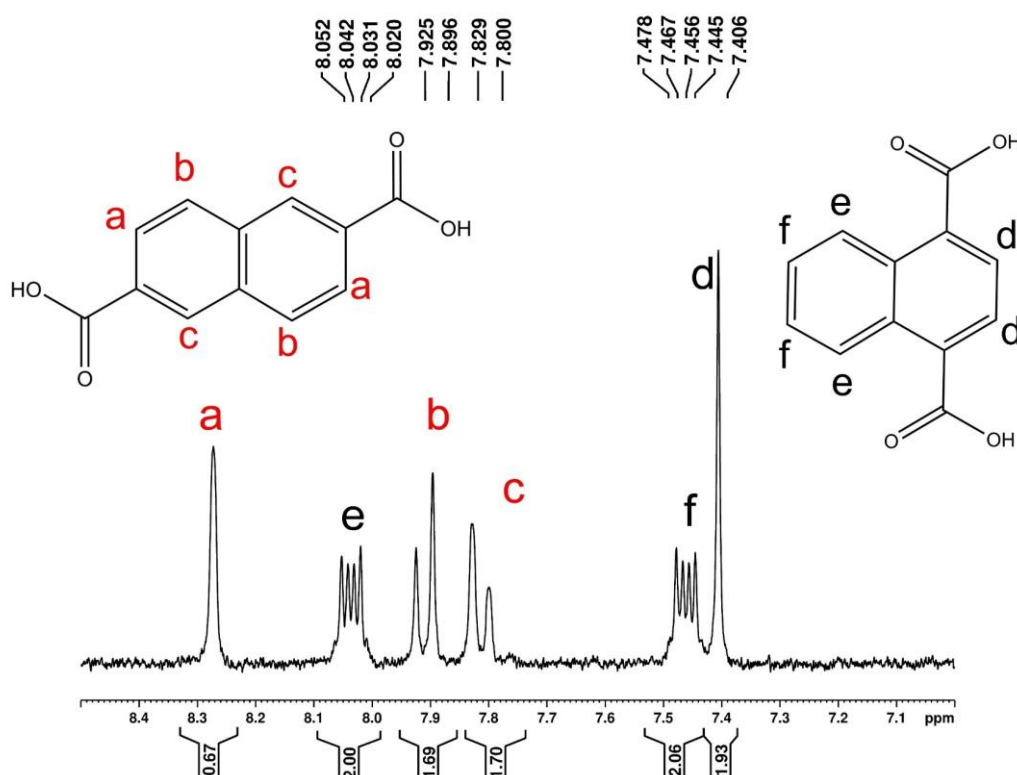


Figure S7: ¹H-NMR spectra obtained on the Ce/Zr-UiO-66(1,4-NDC/2,6-NDC).

Table S2: The number of protons, value of peak integrals, and calculation of the molar ratio of linkers in Ce/Zr-UiO-66(1,4-NDC/BDC) and Ce/Zr-UiO-66(1,4-NDC/2,6-NDC).

<i>Samples</i>	<i>Linkers</i>	<i>Peak integral</i>	<i>Protons</i>	<i>Normalised integral</i>	<i>Molar ratio</i>
Ce/Zr-UiO-66	1,4-BDC	1.99	4	$1.99/4 = 0.5$	1,4-NDC/BDC
(1,4-NDC/BDC)	1,4-NDC	3.01	6	$3/6 = 0.5$	= 1/1
Ce/Zr-UiO-66	1,4-NDC	5.99	6	$5.99/6 = 0.998$	(1,4/2,6-NDC)
(1,4NDC/2,6N-DC)	2,6-NDC	4.08	6	$3.395/6 = 0.680$	= 1/1.46