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Supporting Information

Investigation of the Preparation and Reactivity of Metal-Organic Frameworks of Cerium and Pyridine-2,4,6-Tricarboxylate

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Table S1: Crystal data for the Ce-PTC materials prepared in this work

Compound	**(1)**	**(2)**	**(3)**
CCDC reference	2110897	2110895	2110894
Empirical formula	$C_8H_6CeNO_{9.5}$	$C_{16}H_{16}Ce_2N_2O_{18}$	$C_{11}H_{13}CeN_2O_9$
Formula weight / gmol^{-1}	408.26	804.55	457.35
Temperature /K	150(2)	150(2)	150(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	Pc	Cc
a /Å	6.79808(15)	6.70661(9)	15.8285(3)
b /Å	12.0497(3)	9.44049(14)	10.1903(9)
c /Å	13.5329(3)	17.0698(2)	9.1832(3)
α /°	90	90	90
β /°	100.334(2)	92.4339(12)	90.062(4)
γ /°	90	90	90
Volume /Å^3	1090.56(5)	1079.77(3)	1481.22(15)
Z	4	2	4
ρ_{calc} g/cm^3	2.487	2.475	2.051
μ /mm^{-1}	4.227	4.264	3.123
F(000)	780.0	772.0	892.0
Crystal size /mm^3	0.124 × 0.116 × 0.074	0.2 × 0.16 × 0.06	0.16 × 0.08 × 0.04
Radiation (λ / Å)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.092 to 62.816	4.932 to 61.352	6.502 to 59.43
Index ranges	-9 ≤ h ≤ 9, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19	-9 ≤ h ≤ 9, -13 ≤ k ≤ 13, -24 ≤ l ≤ 24	-21 ≤ h ≤ 21, -13 ≤ k ≤ 13, -12 ≤ l ≤ 12
Reflections collected	17555	43697	10412
Independent reflections	3369 [R_{int} = 0.0457, R_{sigma} = 0.0354]	6306 [R_{int} = 0.0450, R_{sigma} = 0.0321]	3584 [R_{int} = 0.0265, R_{sigma} = 0.0289]
Data/restraints/parameters	3369/6/202	6306/26/379	3584/26/232
Goodness-of-fit on F^2	1.335	1.043	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0467, wR_2 = 0.0892	R_1 = 0.0211, wR_2 = 0.0427	R_1 = 0.0169, wR_2 = 0.0357
Final R indexes [all data]	R_1 = 0.0540, wR_2 = 0.0914	R_1 = 0.0228, wR_2 = 0.0437	R_1 = 0.0178, wR_2 = 0.0363
Largest diff. peak/hole / e Å^{-3}	2.04/–2.32	0.96/–0.70	0.38/–0.45
Flack parameter	-	–0.021(7)	–0.028(7)

Table S2: Comparison between the crystal structure of (1), (2) and (3) and previously reported structures. See Figure S1 for PTC binding modes.

Material	*a* / Å	*b*/ Å	*c* / Å	β (°)	*V* / Å^3	Space Group	Temp / K	PTC Binding Mode	Reference(s)
$[Pr(PTC)(H_2O)_2]\cdot 2H_2O$	6.754(5)	11.937(2)	13.456(5)	100.381(5)	1067.1	$P2_1/c$	100	Type VII	1
$[Nd(PTC)(H_2O)_2]\cdot 2H_2O$	6.751(5)	11.916(3)	13.457(5)	103.105(5)	1054.4	$P2_1/c$	100	Type VII	1
$[Pr(PTC)(H_2O)_2]\cdot 1.5H_2O$	6.7981(12)	11.978(2)	13.515(3)	100.174(2)	1083.1(3)	$P2_1/c$	293	Type VII	2
$[Ce(PTC)(H_2O)_2]\cdot H_2O$	6.8545(8)	12.077(1)	13.625(2)	100.035(1)	1110.6	$P2_1/c$	291	Type VII	3
$[Ce(PTC)(H_2O)_2]\cdot 1.5H_2O$	6.7970(3)	12.0415(6)	13.5364(7)	100.3156(47)	1090.0	$P2_1/c$	150	Type VII	**(1)** This work
$Ce(PTC)\cdot 3H_2O$	6.7066(1)	9.4405(1)	17.0698(2)	92.4339(12)	1079.78(3)	Pc	150	Type XII	**(2)** This work
$[Ce(PTC)(H_2O)_3]\cdot H_2O$	12.1373(5)	7.4129(3)	13.6653(5	96.508(2)	1221.6	$P2_1/c$	296	Type XI	4
$[Ce(PTC)(H_2O)_5]\cdot 4H_2O$	6.8437 (3)	13.3207(5)	17.9045 (7)	90	1632.23	$Pna2_1$	293	Type XIV	5
$[Ce(PTC)(H_2O)(DMF)]\cdot H_2O$	15.8285(3)	10.1903(9)	9.1832(3)	90.062	1481.22(15)	Cc	150	Type XIII	**(3)** This work

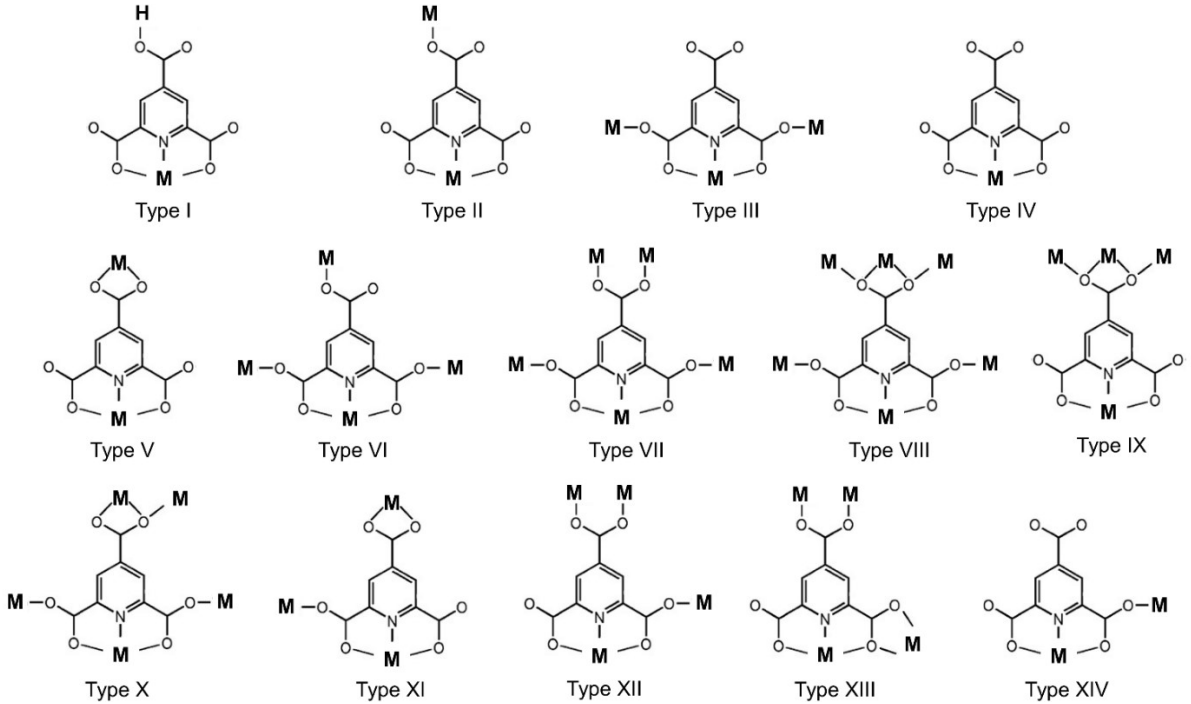

Figure S1: Binding modes for PTC seen in lanthanide and transition-metal coordination polymers using the classification of Das *et al.* (Types I-XI).[6] Type XII is an additional binding mode seen in (2), Type XIV is seen in the material, $[Ce(PTC)(H_2O)_5]\cdot 4H_2O$,[5] and Type XIII is seen in (3)

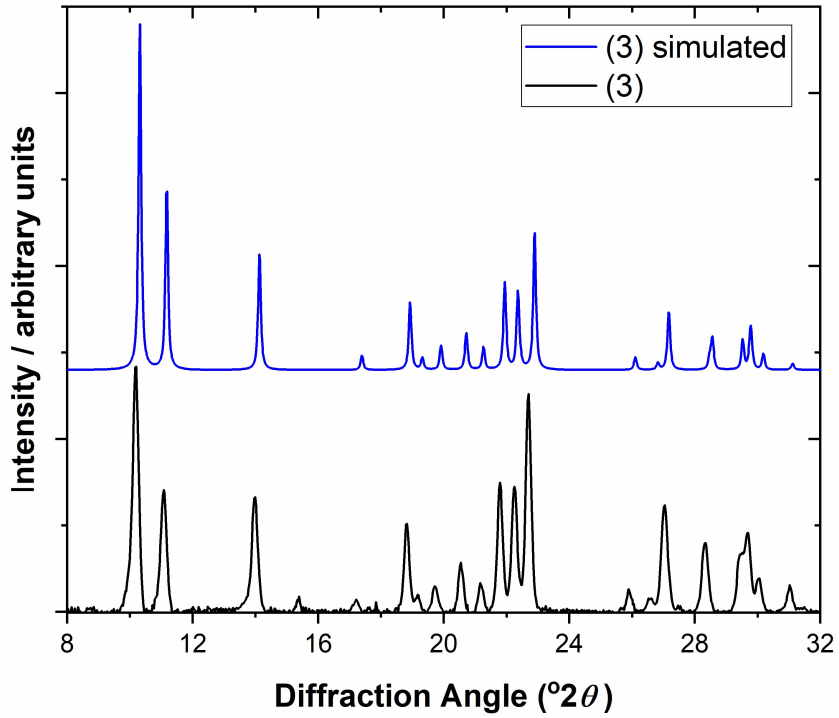

Figure S2: Simulated and measured powder XRD of (3)

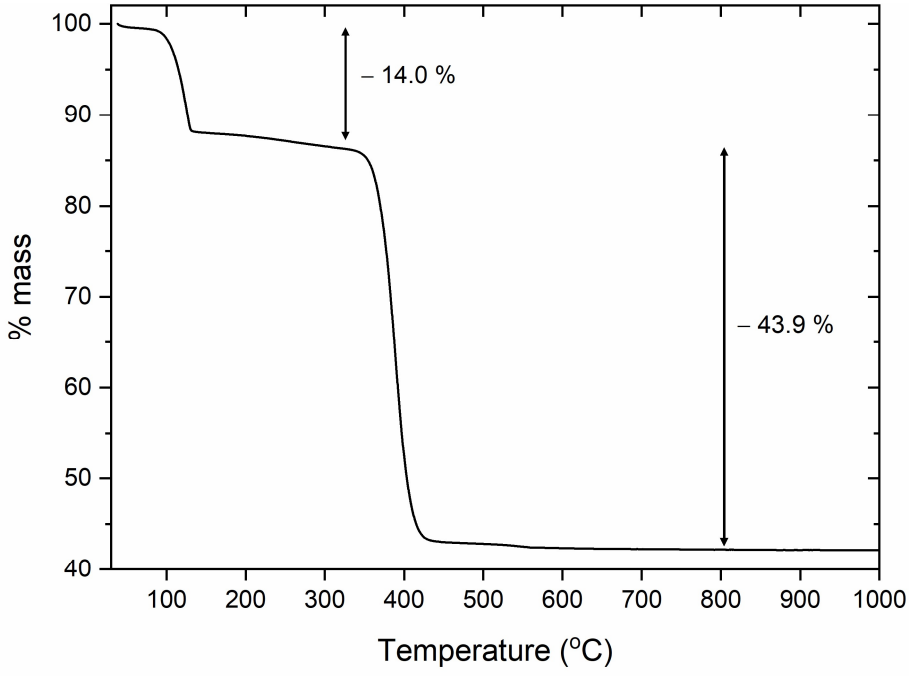

Figure S3: Thermogravimetric analysis of (1)

Table S3: Assignment of TGA of (1)

Decomposition step	**Calculated % Mass Loss**	**Observed % Mass Loss**
$[Ce(PTC)(H_2O)_2]\cdot 1.5H_2O$ → Ce(PTC)	15.3	14.0
Ce(PTC) → CeO_2	42.4	43.9

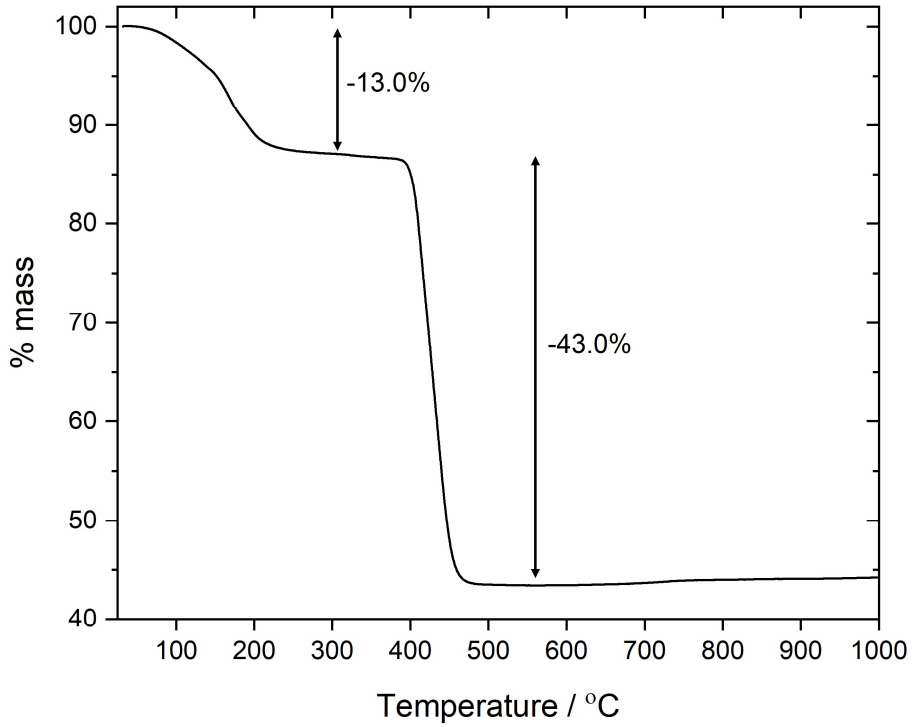

Figure S4: Thermogravimetric analysis of (2).

Table S4: Assignment of TGA of (2)

Decomposition step	**Calculated % Mass Loss**	**Observed % Mass Loss**
$Ce_2(PTC)_2 \cdot 6H_2O \rightarrow Ce_2(PTC)_2$	13.4	13.0
$Ce_2(PTC)_2 \rightarrow 2CeO_2$	43.9	43.0

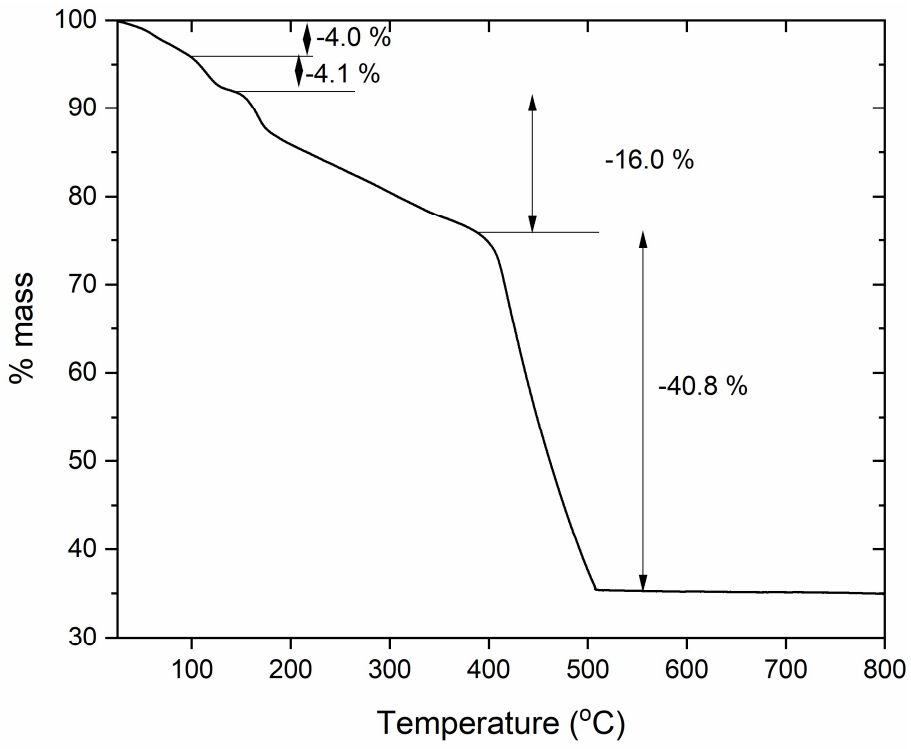

Figure S5: Thermogravimetric analysis of (3)

Table S5: Assignment of TGA of (3)

Decomposition step	**Calculated % Mass Loss**	**Observed % Mass Loss**
$[Ce(PTC)(H_2O)(DMF)]\cdot H_2O \rightarrow [Ce(PTC)(H_2O)(DMF)]$	3.94	4.0
$[Ce(PTC)(H_2O)(DMF)] \rightarrow [Ce(PTC)(DMF)]$	3.94	4.1
$[Ce(PTC)(DMF)] \rightarrow Ce(PTC)$	16.0	16.0
$Ce(PTC) \rightarrow CeO_2$	38.5	40.8

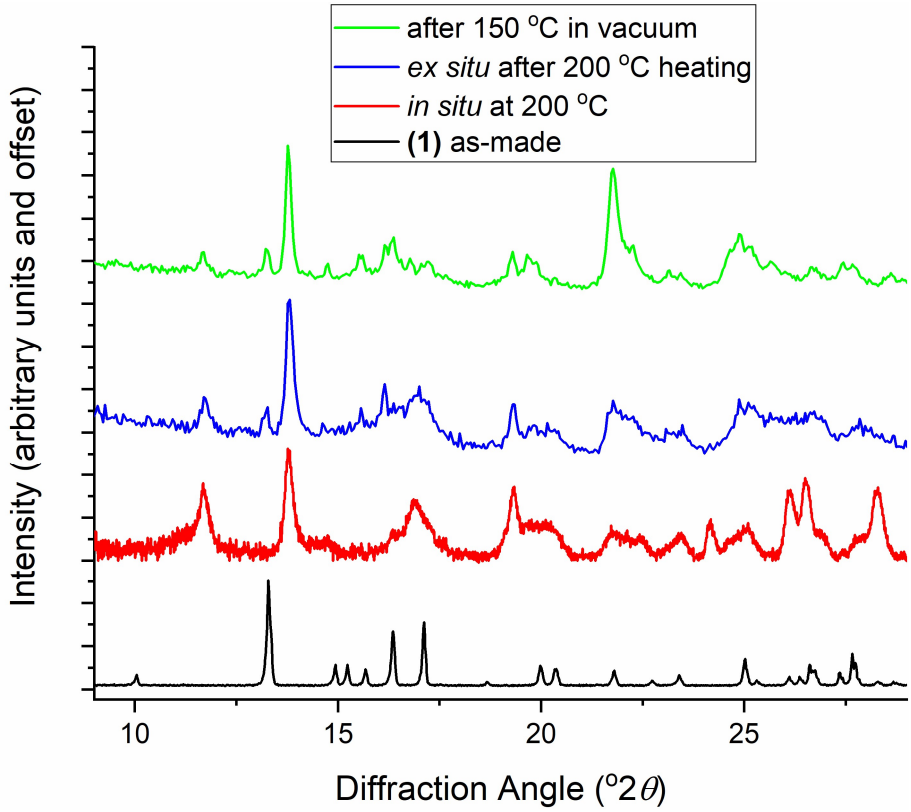

Figure S6: Powder XRD (1) after removal of water under different conditions.

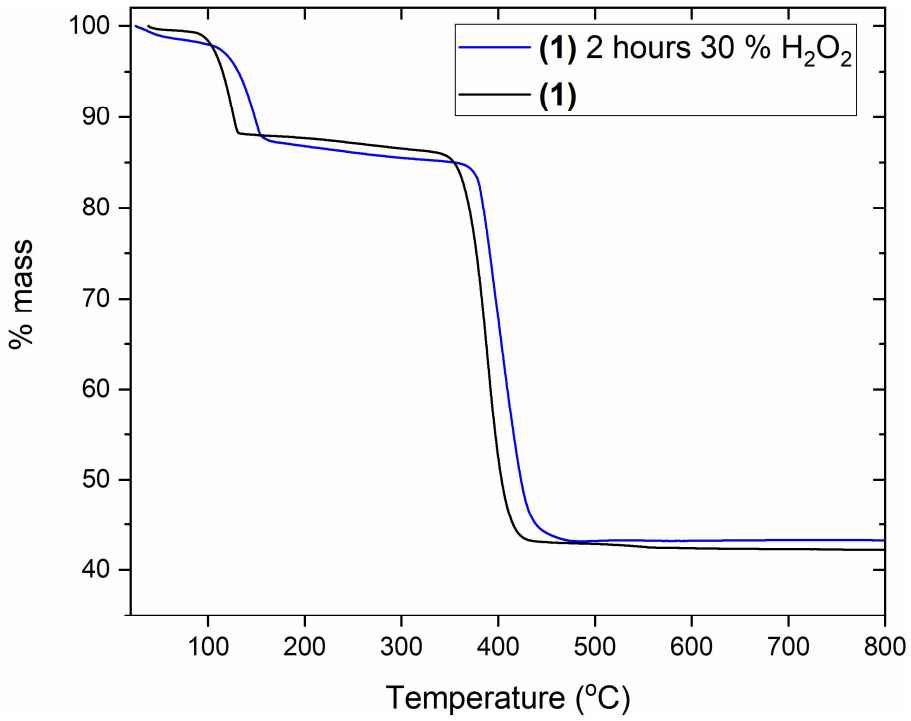

Figure S7: TGA of (1) before and after treatment with H_2O_2

Table S6: Crystal data for Na_3PTC

CCDC reference	2110896
Empirical formula	$C_8H_2NNa_3O_6$
Formula weight / gmol^{-1}	277.08
Temperature /K	150(2)
Crystal system	monoclinic
Space group	*Cc*
a /Å	3.42187(8)
b /Å	16.9689(4)
c /Å	15.1988(4)
α /°	90
β /°	91.590(2)
γ /°	90
Volume /Å^3	882.19(3)
Z	4
ρ_{calc} g/cm^3	2.086
μ /mm^{-1}	0.297
F(000)	552.0
Crystal size /mm^3	0.16 × 0.1 × 0.01
Radiation (λ / Å)	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.2 to 63.54°
Index ranges	-5 ≤ h ≤ 5, -24 ≤ k ≤ 24, -21 ≤ l ≤ 22
Reflections collected	12566
Independent reflections	2773[*R*(int) = 0.0229]
Data/restraints/parameters	2773/2/163
Goodness-of-fit on F^2	1.122
Final R indexes [I>=2σ (I)]	R_1 = 0.0229, wR_2 = 0.0631
Final R indexes [all data]	R_1 = 0.0234, wR_2 = 0.0635
Largest diff. peak/hole / e Å^{-3}	0.33/–0.21
Flack parameter	–0.08(7)

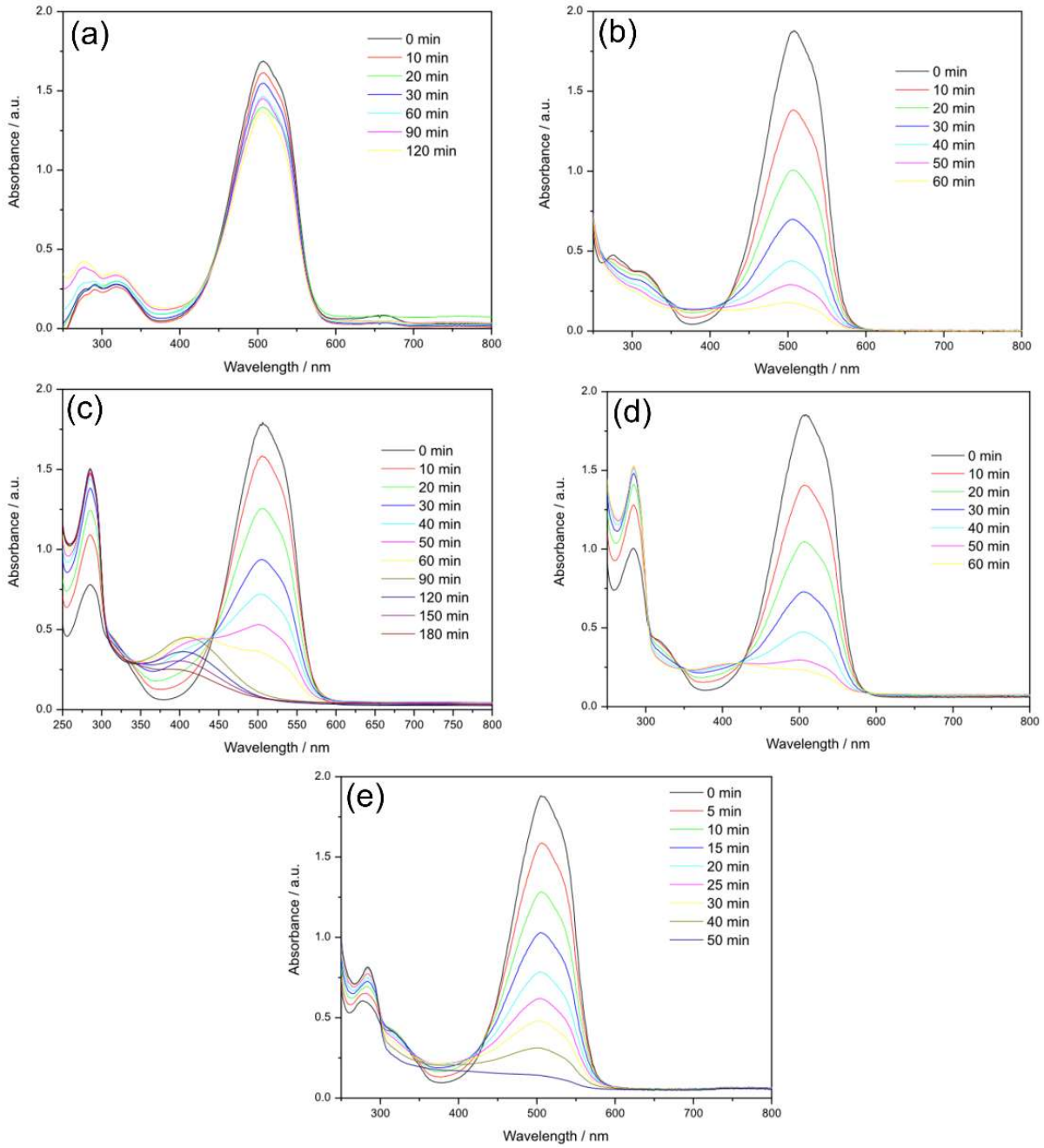

Figure S8: UV-Vis spectra recorded during photocatalysis experiments: a) in absence of catalyst, b) in absence of catalyst + H_2O_2, c) (1) alone, d) (1) previously oxidised and e) (1) alone + H_2O_2 (10 μL).

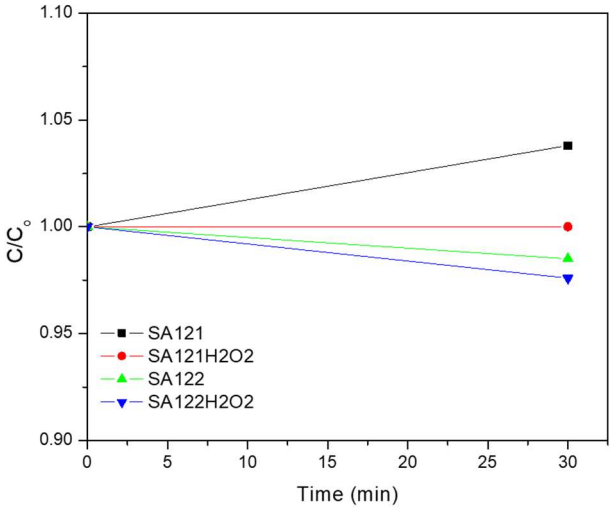

Figure S9: UV-Vis spectra recorded in darkness

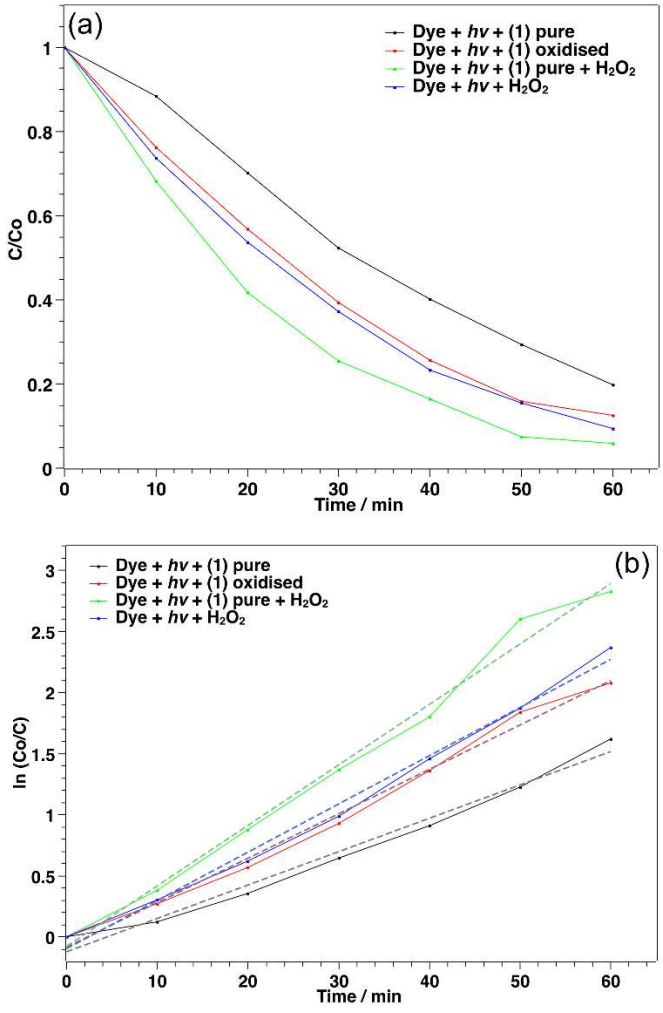

Figure S10: (a) Photodegradation of methyl orange at catalysts, 25 °C, UV light (250 W), and H_2O_2 (0.01 M) for blue and green curves. (a) Kinetic fit of the time trace and linear plots (pseudo first-order) of the UV–VIS band at λ_{max} = 505 nm. R^2 = 0.982 (black), 0.992 (red), 0.987 (green) and 0.992 (blue). k_{obs} = 0.0272 min^{-1} (black), 0.0363 min^{-1} (red), 0.0508 min^{-1} (green) and 0.0395 min^{-1} (blue).

Table S7: Likely hydrogen bonded interactions in the crystal structure of (1) **in the range 2.5 – 3 Å. Note that occluded water molecule sites O3, O4 and O5 are not fully occupied.**

Atom1	Atom2	Distance / Å
O1A	O9A	2.8699
	O2	2.9515
	O9B	2.9656
O8A	O1B	2.8381
	O2	2.9776
O9B	O1	2.9024
	O1A	2.9656
	O2	2.9988
O8B	O3	2.8248
O2	O5	2.6887
	O1A	2.9515
	O8A	2.9776
	O9B	2.9988
O9A	O1A	2.8699
	O5	2.8975
O1B	O8A	2.8381
O1	O3	2.7293
	O4	2.8915
	O9B	2.9024
O8A	O1B	2.8381
	O2	2.9776
O9B	O1	2.9024
	O1A	2.9656
	O2	2.9988
O8B	O3	2.8248
O9A	O1A	2.8699
	O5	2.8975
O1B	O8A	2.8381
O4	O3	2.6795
	O1	2.8915
O3	O5	2.5809
	O4	2.6795
	O5	2.7271
	O1	2.7293
	O8B	2.8248
O5	O3	2.5809
	O2	2.6887
	O3	2.7271
	O9A	2.8975

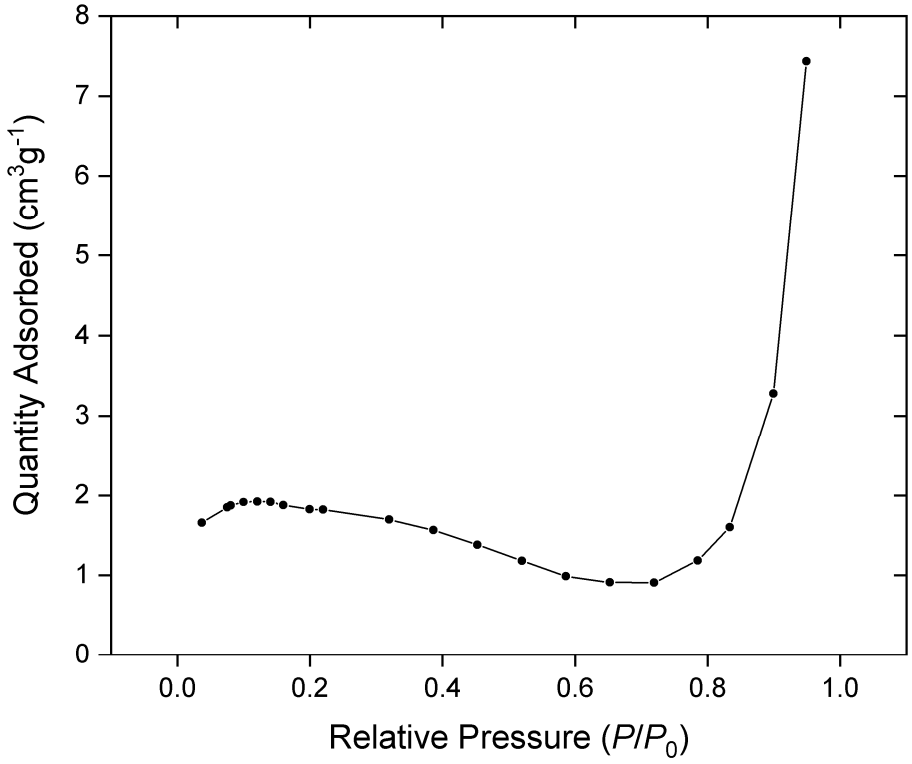

Figure S11: BET adsorption isotherm of (1) **(MicromeriticsASAP 2020) after activation of the sample at 150 °C in vacuum for 3 hours.**

References

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