Electronic Supplementary Information for:

Three-dimensional Cd(II) Porphyrin Metal-Organic Frameworks for the Colorimetric Sensing of Electron Donors

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Table S1. Crystal data and structure refinement details for **1, 2** and **3** in this study.

	$[Cd_2(CdTCPP)(bpe)(H_2O)]$ (**1**)	$[Cd_2(ZnTCPP)(bpe)(H_2O)]$ (**2**)	$[Cd_2(bpaz)(CdTCPP)H_2O]$ (**3**)
Formula	$C_{60}H_{34}Cd_3N_6O_9$	$C_{60}H_{34}Cd_2N_6O_9Zn$	$C_{58}H_{32}Cd_3N_8O_9$
M/g mol^{-1}	1320.13	1273.10	1322.11
Temperature (K)	100(2)	100(2)	100(2)
Crystal system	Tetragonal	Tetragonal	Tetragonal
Space Group	*P*4/*m*	*P*4/*m*	*P*4/*m*
Crystal size (mm^3)	0.20 × 0.15 × 0.12	0.16 × 0.08 × 0.06	0.08 × 0.04 × 0.03
Crystal Colour	Purple	Purple	Purple
Crystal Habit	Block	Block	Block
a (Å)	18.53870(10)	18.53870(10)	18.20082(11)
b (Å)	18.53870(10)	18.53870(10)	18.20082(11)
c (Å)	16.41120(10)	16.41120(10)	16.58899(13)
V (Å^3)	5640.26(7)	5640.26(7)	5495.43(8)
Z	2	2	2
ρ_{calc} (mg/mm^3)	0.777	0.750	0.799
λ(CuKα)	1.54178 Å	1.54178 Å	1.54178 Å
μ(CuKα)	4.741 mm^{-1}	3.492 mm^{-1}	4.872 mm^{-1}
Reflections collected	93674/6268 [R_{merge} = 0.0712, R_{sigma} = 0.0247]	73075/6277 [R_{merge} = 0.0728, R_{sigma} = 0.0305]	71352/6053 [R_{merge} = 0.0738, R_{sigma} = 0.0265]
Data/parameters	6268/199	6277/199	6053/195
Final R indexes [all data]	R_1 = 0.0863, wR_2 = 0.2315	R_1 = 0.0612, wR_2 = 0.1799	R_1 = 0.0842, wR_2 = 0.2185
Goodness-of-fit on F^2	1.111	1.175	1.133
Largest diff. peak/hole (e$^-$Å^{-3})	–1.09, 2.13	–1.22, 1.95	–0.81, 1.51

Table S2. Analysis of the possible coordination geometries using the SHAPE program for the 7-coordinate M(II) centres in compounds **1-3**

Geometry	Symmetry	1	2	3
HP-7	D_{7h}	31.737	31.522	31.466
HPY-7	C_{6v}	21.003	21.088	20.836
PBPY-7	D_{5h}	8.616	8.606	8.532
COC-7	C_{3v}	3.906	3.912	3.807
CTPR-7	C_{2v}	**2.810**	**2.775**	**2.725**
JPBPY-7	D_{5h}	12.684	12.678	12.698
JETPY-7	C_{3v}	18.242	18.171	18.591

HP-7 = Heptagon; HPY-7 = Hexagonal pyramid; PBPY-7 = Pentagonal bipyramid; COC-7 = Capped octahedron; CTPR-7 = Capped trigonal prism; JPBPY = Johnson pentagonal bipyramid J13; JETPY-7 = Johnson elongated triangular pyramid J7. The minima values are indicated in bold.

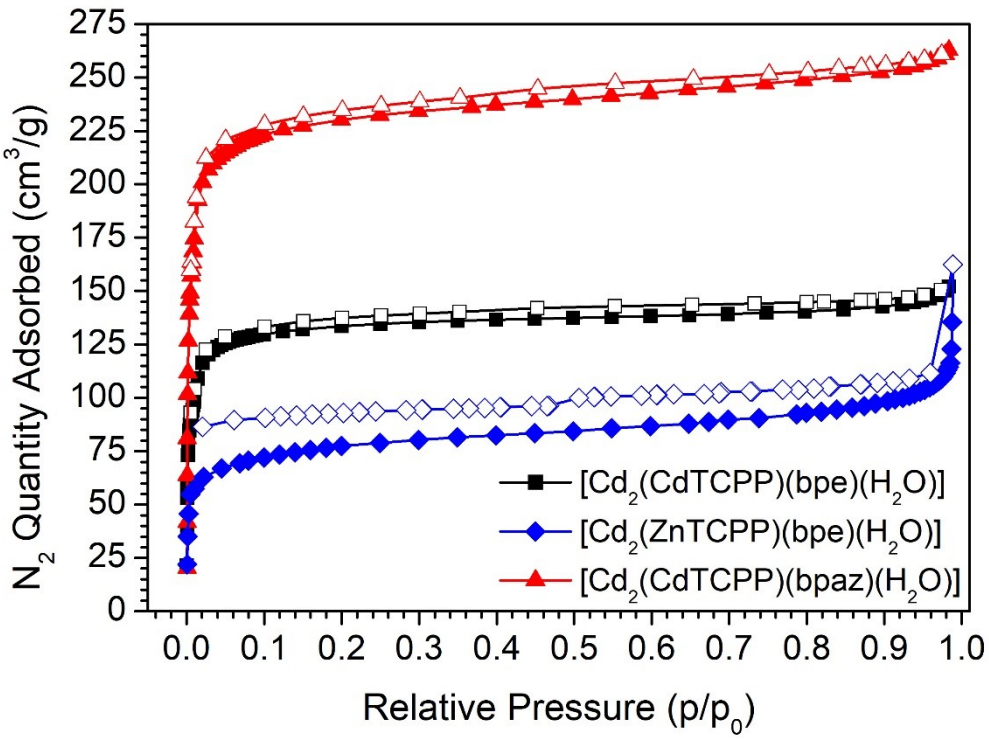

Figure S1. Nitrogen gas sorption isotherms collected at 77 K for $[Cd_2(bpe)(CdTCPP)(H_2O)]$ (**1**), $[Cd_2(bpe)(ZnTCPP)(H_2O)]$ (**2**) and $[Cd_2(bpaz)(CdTCPP)(H_2O)]$ (**3**) where the filled symbols show the adsorption isotherm and hollow symbols show the desorption isotherm.

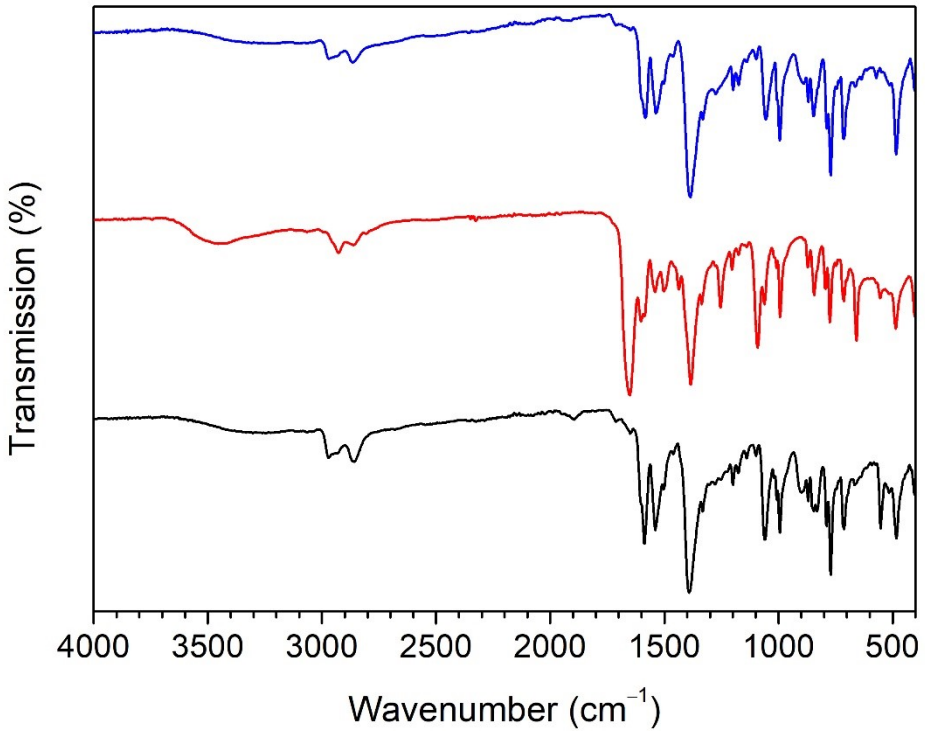

Figure S2. ATR Fourier transform infrared spectra (FT-IR) of [Cd_2(CdTCPP)(bpe)(H_2O)] (**1**) (black), [Cd_2(ZnTCPP)(bpe)(H_2O)] (**2**) (red), [Cd_2(CdTCPP)(bpaz)(H_2O)] (**3**) (blue) between 4000 and 400 cm^{-1}.

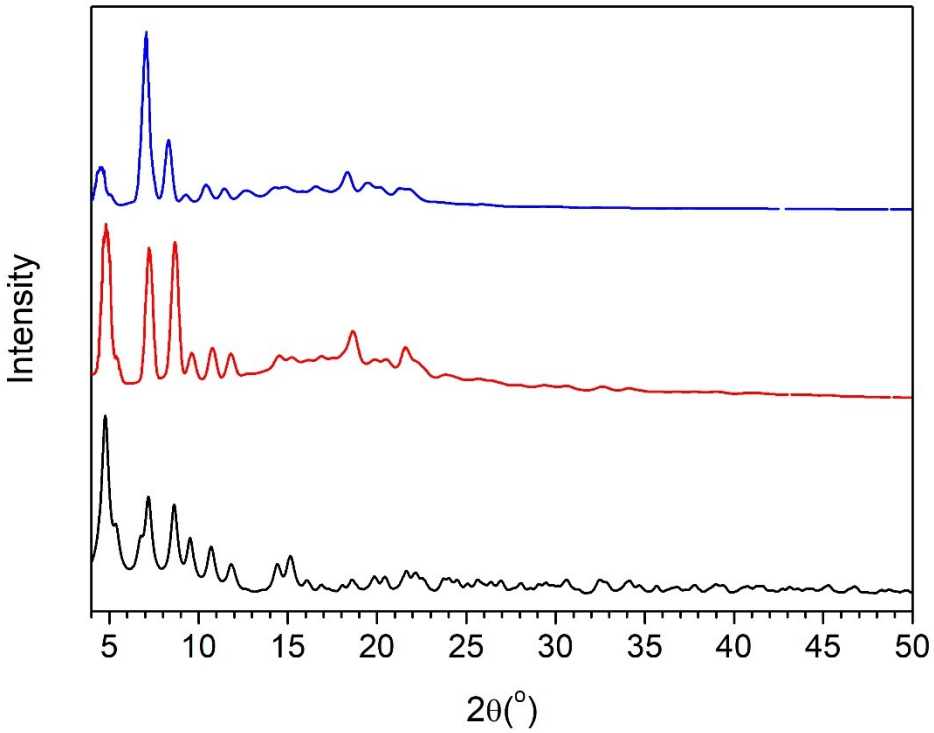

Figure S3. PXRD patterns of [Cd_2(CdTCPP)(bpe)(H_2O)] (**1**), calculated (black), as synthesised (red) and desolvated (blue) between 5 and 50° 2θ.

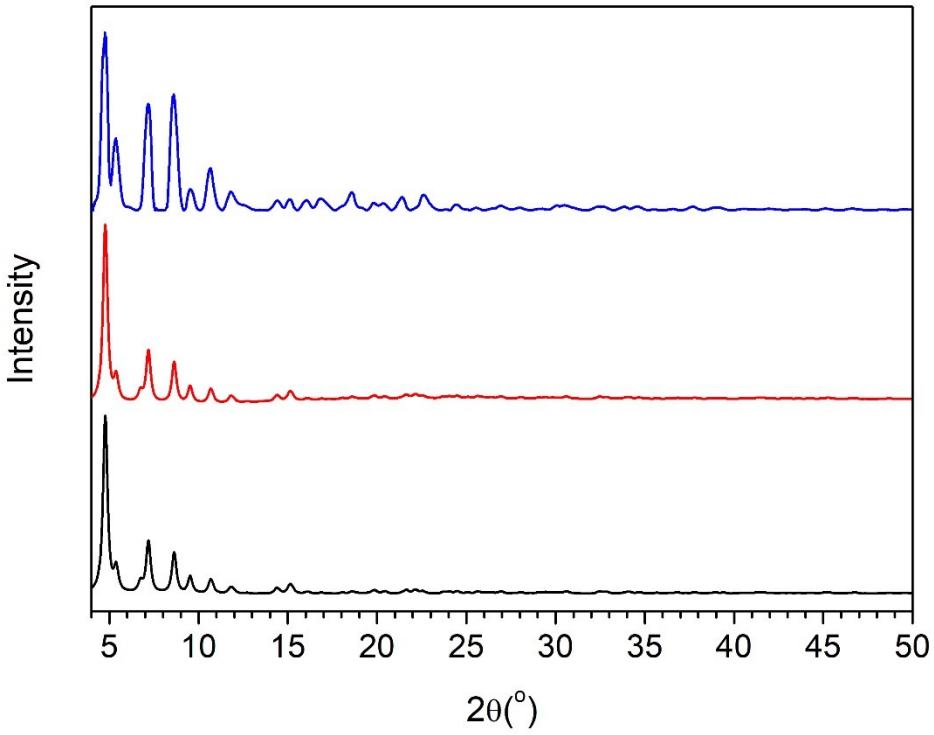

Figure S4. PXRD patterns of [Cd_2(ZnTCPP)(bpe)(H_2O)] (**2**), calculated (black), as synthesised (red) and desolvated (blue) between 5 and 50° 2θ.

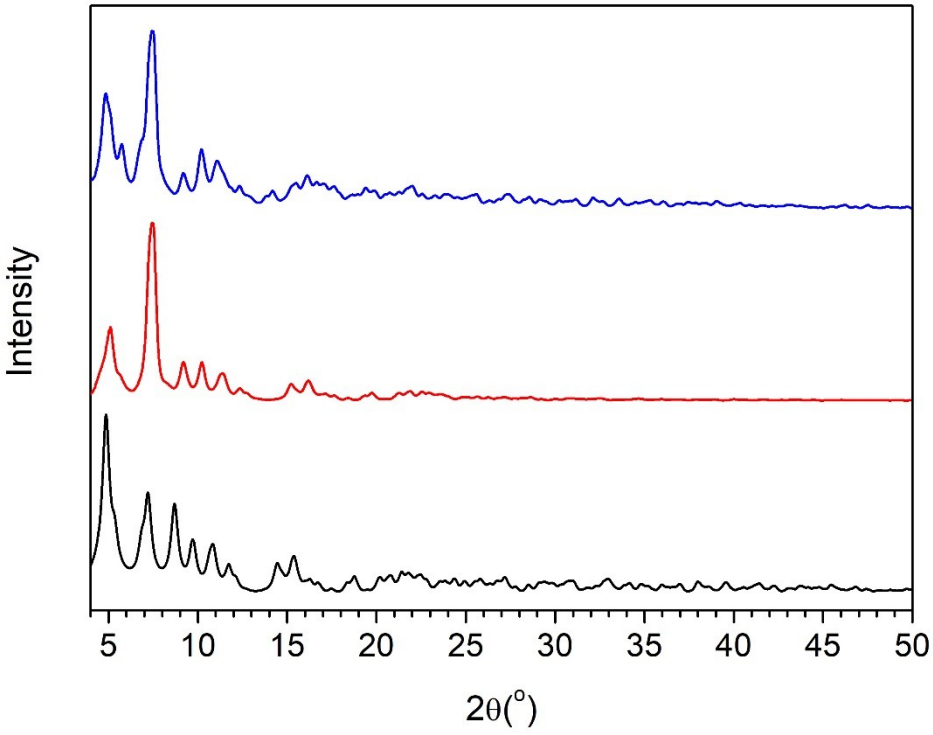

Figure S5. PXRD patterns of [Cd_2(bpaz)(CdTCPP)H_2O], calculated, as synthesised, solvent exchanged with THF and desolvated between 5 and 50° 2θ.

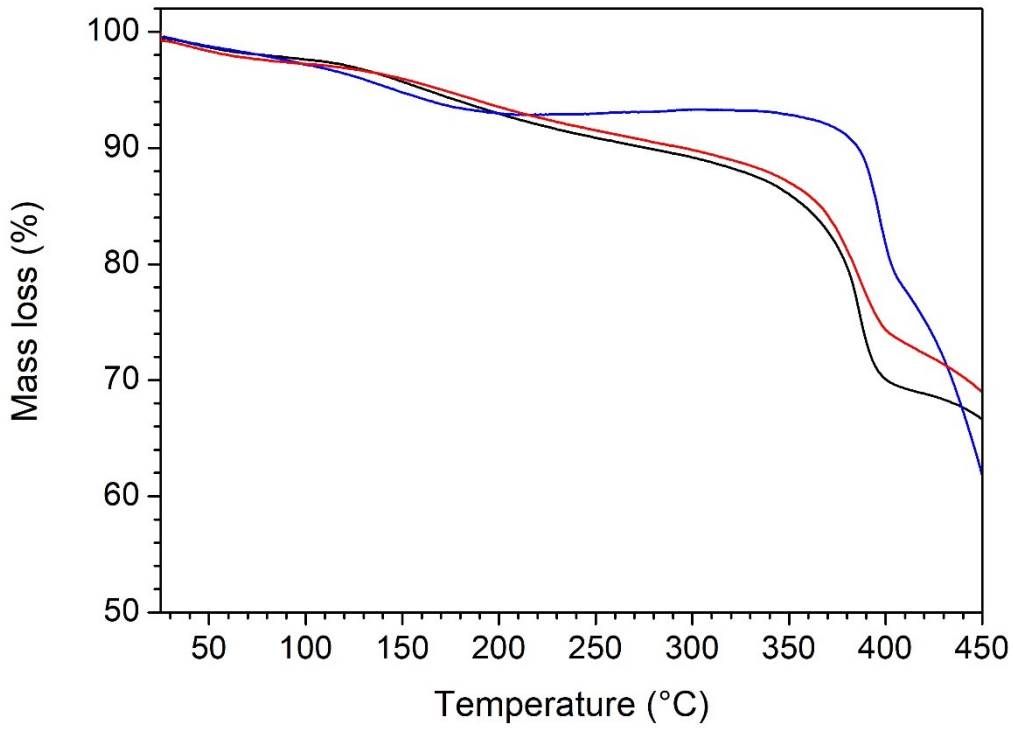

Figure S6. Thermal Gravimetric Analysis (TGA) of [Cd_2(CdTCPP)(bpe)(H_2O)] (**1**) (black), [Cd_2(CdTCPP)(bpaz)(H_2O)] (**3**) (red), [Cd_2(ZnTCPP)(bpe)(H_2O)] (**2**) (blue) under N_2 between 25 and 450 °C, heated at a rate of 5 °C/min.

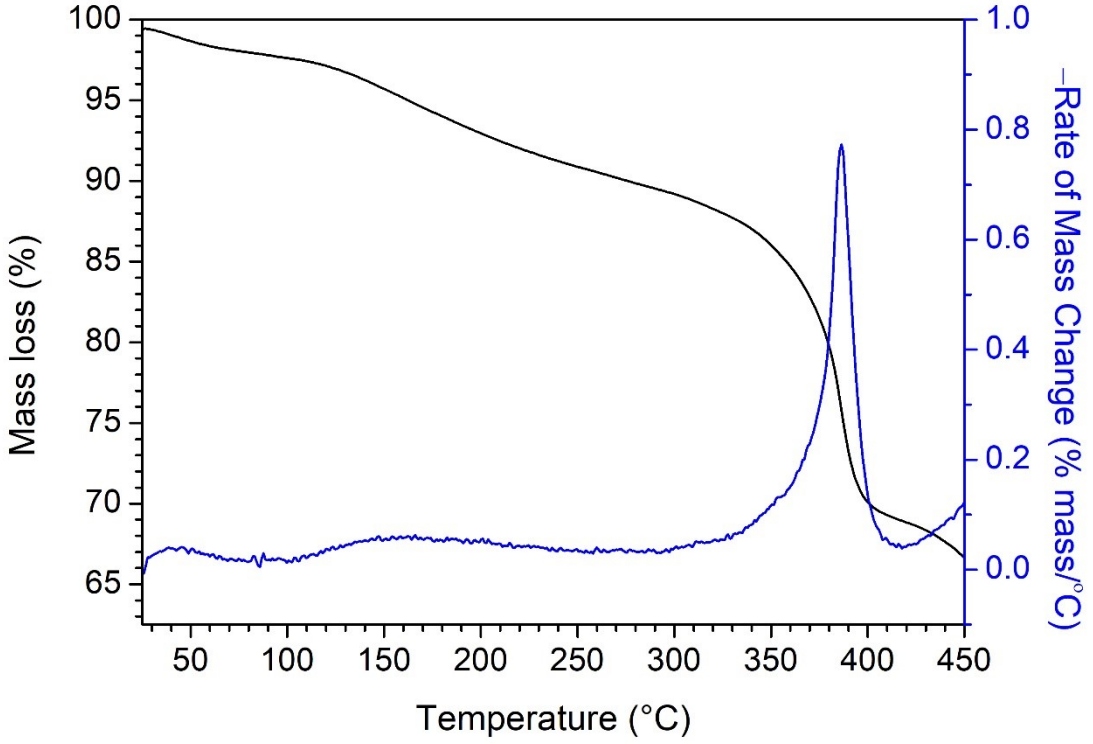

Figure S7. Thermal Gravimetric Analysis (TGA) of [Cd_2(CdTCPP)(bpe)(H_2O)] (**1**) under N_2 between 25 and 450 °C, heated at a rate of 5 °C/min.

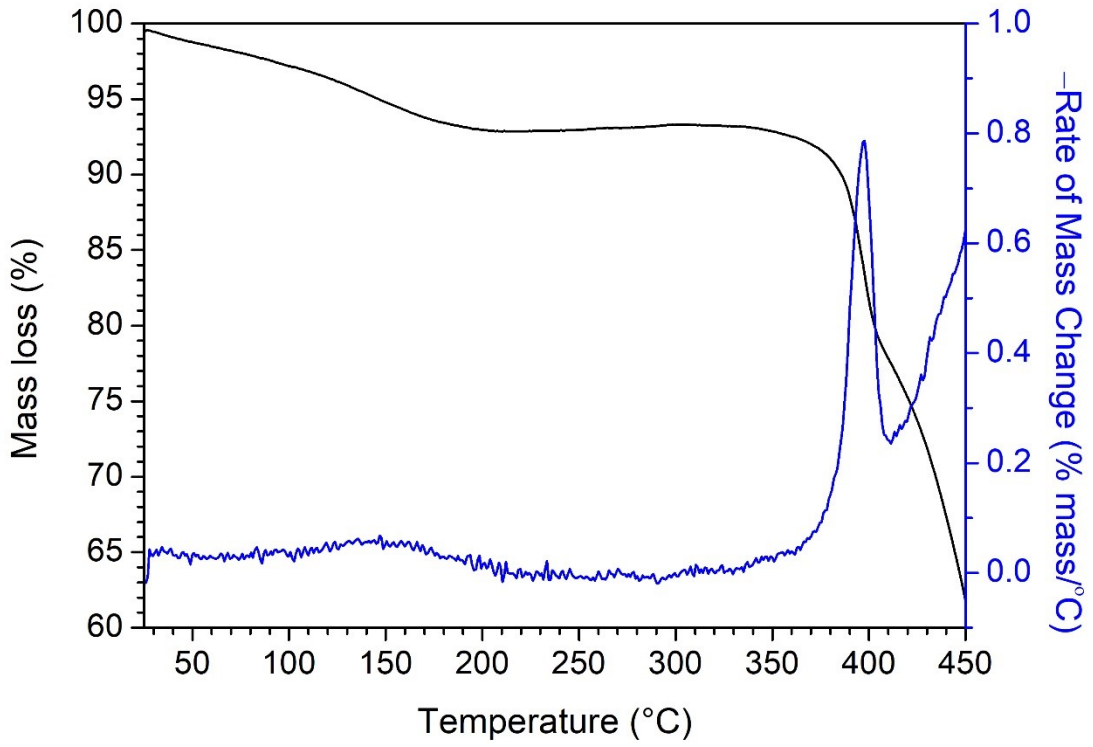

Figure S8. Thermal Gravimetric Analysis (TGA) of [Cd_2(ZnTCPP)(bpe)(H_2O)] (**2**) under N_2 between 25 and 450 °C, heated at a rate of 5 °C/min.

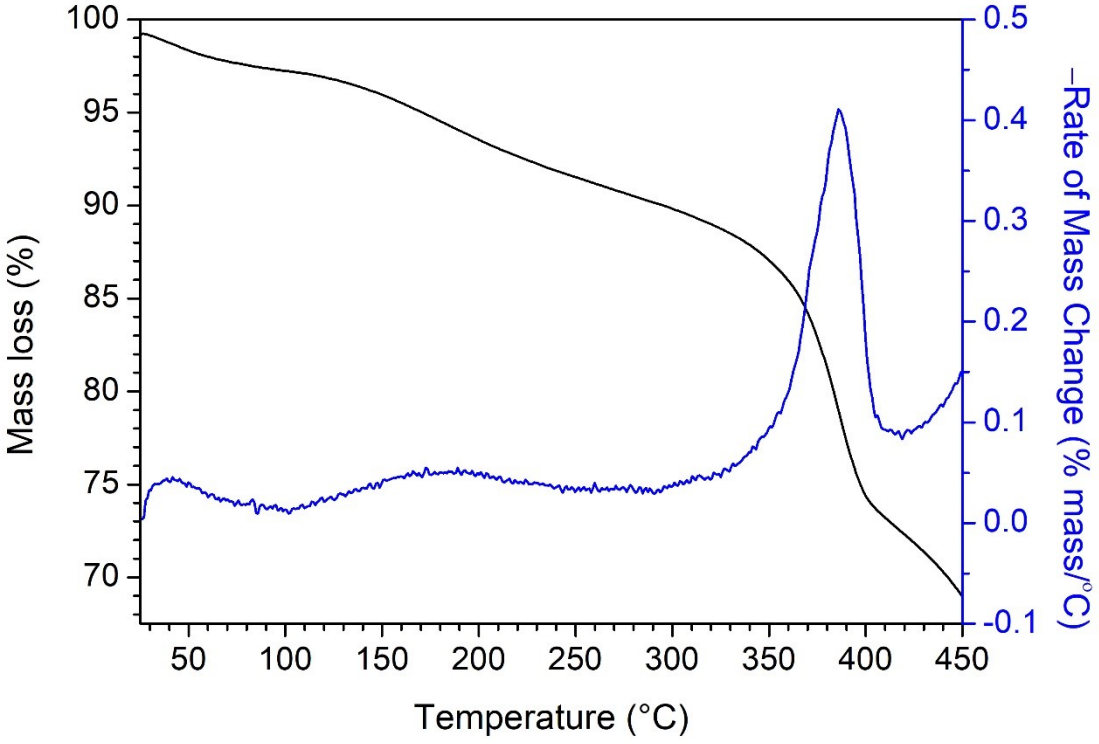

Figure S9. Thermal Gravimetric Analysis (TGA) of [Cd_2(CdTCPP)(bpaz)(H_2O)] (**3**) under N_2 between 25 and 450 °C, heated at a rate of 5 °C/min.

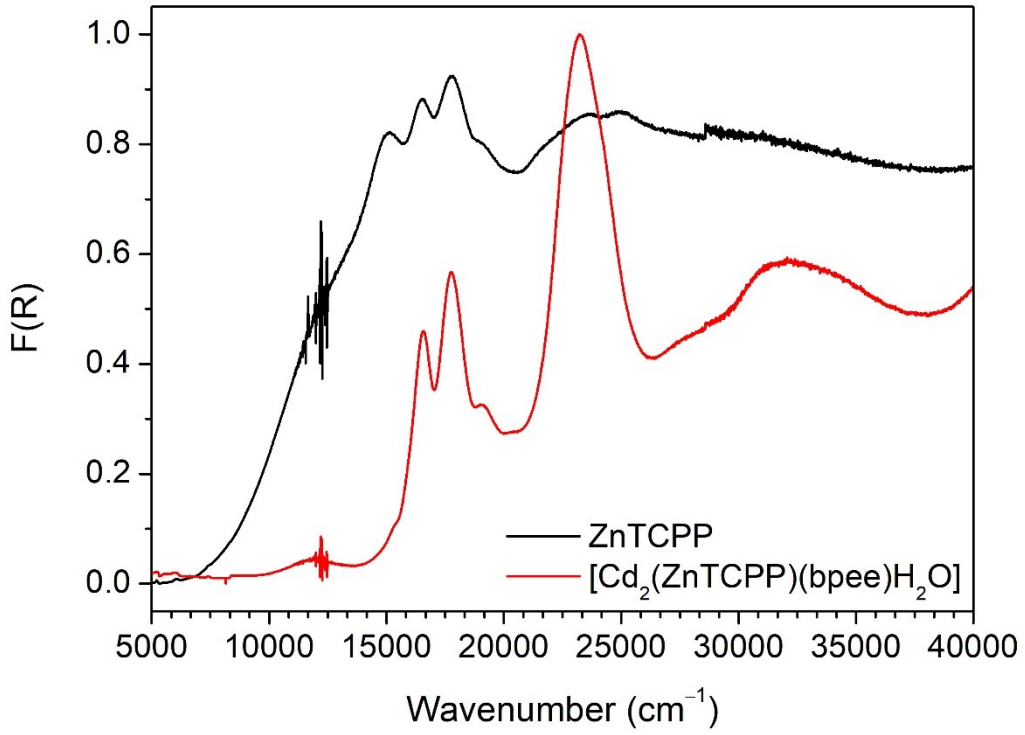

Figure S10. Solid state UV-Vis-NIR spectra of ZnTCPP (black) and [Cd_2(ZnTCPP)(bpe)(H_2O)] (**2**) (red) between 5000 – 40000 cm^{-1}.

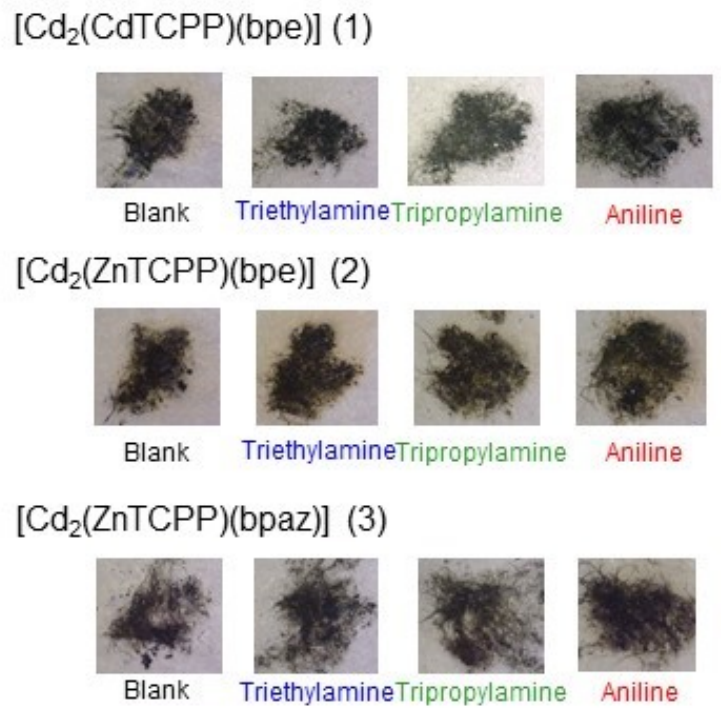

Figure S11. Photos of the colour change of (a) [Cd_2(CdTCPP)(bpe)] (**1**), (b) [Cd_2(ZnTCPP)(bpe)] (**2**) and (c) [Cd_2(CdTCPP)(bpaz)] (**3**) upon exposure to triethylamine, tripropylamine and aniline.

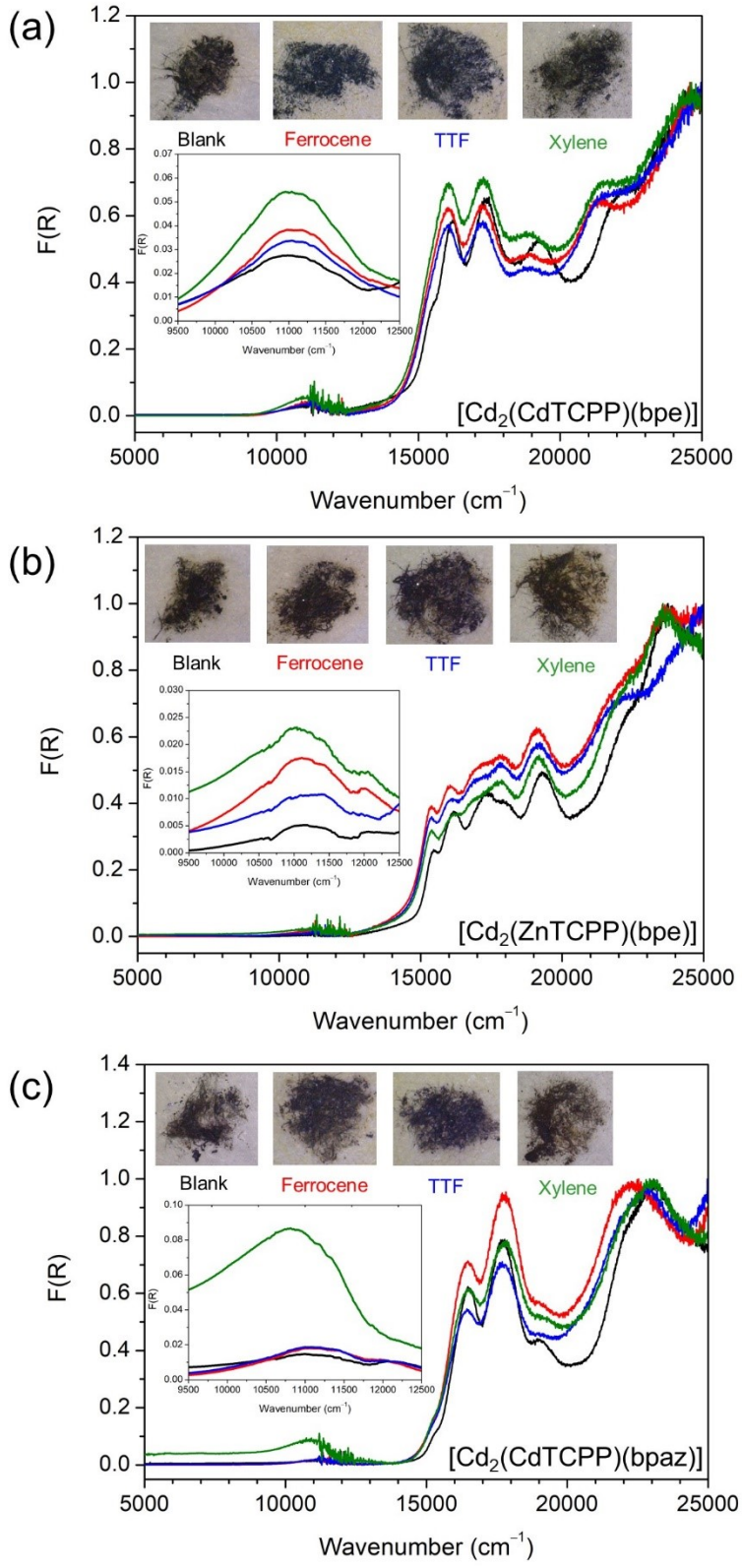

Figure S12. Normalised Vis-NIR spectra (black) of (a) [Cd_2(CdTCPP)(bpe)] (**1**), (b) [Cd_2(ZnTCPP)(bpe)] (**2**) and (c) [Cd_2(CdTCPP)(bpaz)] (**3**) upon exposure to ferrocene (red), TTF (blue) and xylene (green) vapour. The inset graph shows an expanded view of the NIR region and the inset photos show the colour change observed upon exposure of the framework to amine vapour.