Neutral and Ionic Co(II) Metal-Organic Frameworks with 2-Methylimidazole and Trimesate: Design and Evaluation for Molecule Encapsulation and Slow Release

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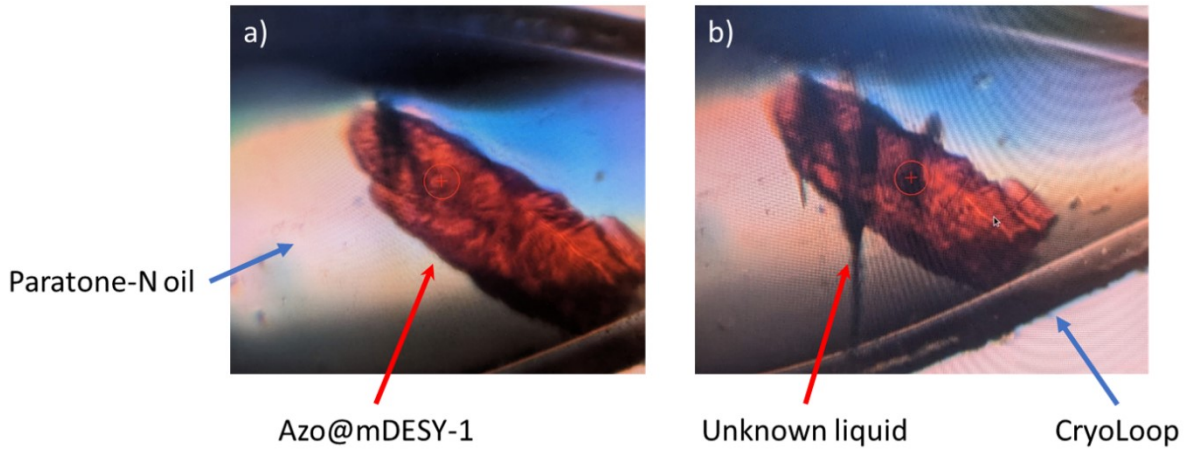

Figure S1. Azo@mDESY-1 mounted on a CryoLoop with paratone-N oil at the P11 beamline: a) before data collection and b) after data collection, showing the leaking of an unidentified liquid.

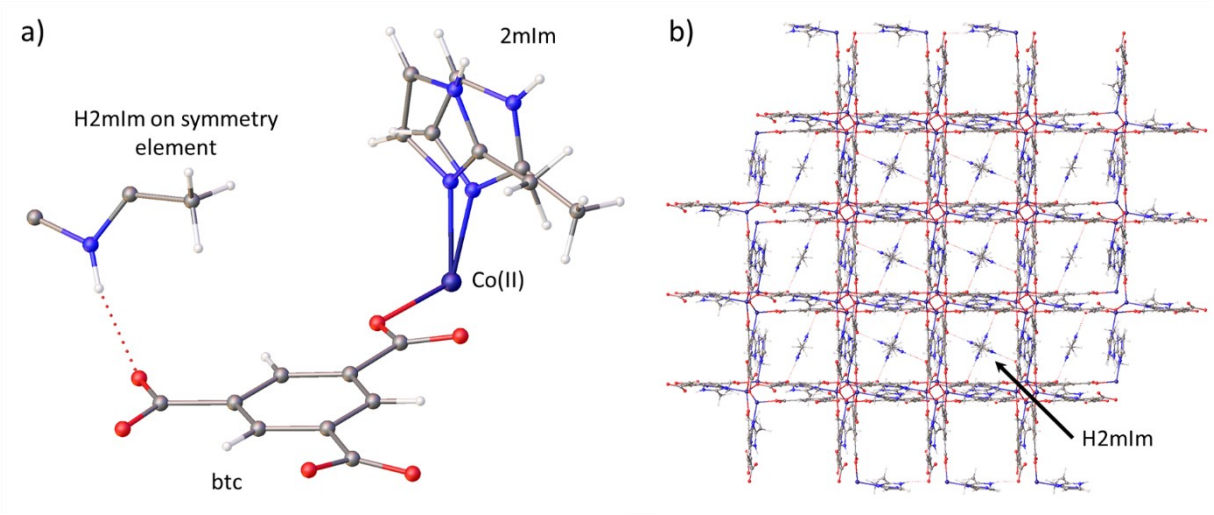

Figure S2. a) Asymmetric unit of mDESY-1 showing a HmIm laying on a symmetry element. b) Packing of mDESY-1 along the *c* axis, showing HmIm ions inside of the pores.

Table S1. Crystal data and Structure refinement parameters of mDESY-1 and mDESY-2 at 100 K.

Name	mDESY-1	mDESY-2
Temperature	100 K	100 K
Empirical Formula	$CoC_{13}H_9N_2O_6$	$Co_3C_{42}H_{42}N_{12}O_{12}$, $2(H_2O)$
Crystal colour/habit	Violet/Prismatic	Violet/Plate
Crystal size (mm)	0.12x0.05x0.02	0.05x0.05x0.01
Co-crystallizing solvent	None	Water
Crystal system/ Space group	Tetragonal/$I4_1/a$	Monoclinic/ $C2/c$
a (Å)	17.060 (2)	31.090 (6)
b (Å)	17.060 (2)	10.230 (2)
c (Å)	32.36 (7)	16.130 (3)
α (°)	90	90
β (°)	90	100.29 (3)

γ (°)	90	90
Volume (Å^3)	9418 (3)	5047.6 (18)
Z/Z'	16/1	4/0.5
Molecular Weight	348.15	1119.70
Calculated density (g/cm3)	0.982	1.473
F(000)	2816.0	2300
Radiation	Synchrotron (λ=0. 61990 Å)	Synchrotron (λ=0. 61990 Å)
θ range (°)	1.177/22.630	1.161/24.085
Scan type	ϕ	ϕ
Measured reflections	61623	36613
Unique reflections	4608	5878
Observed reflections [|F|> 4σ(F)]	3769	4998
Final R (%)	6.08	5.25
wR2 (%)	20.13	0.1516
Good-of-fit on F^2(S)	1.103	1.040
Δρ max (e. Å^{-3})	0.44	1.160
Δρ min (e. Å^{-3})	-0.40	-0.806
No of restrains/parameters	16/256	0/327
Data [|F|> 4σ(F)]-to-parameter ratio	14.7:1	18.0:1

Table S2. Crystal data and Structure refinement parameters of mDESY-1, azobenzene and Azo@mDESY-1 at room temperature.

Name	mDESY-1	Azobenzene	Azo@mDESY-1
Temperature	290 K	290 K	290 K
Empirical Formula	$C_{56}H_{43}Co_4N_{10}O_{24}$	$C_{12}H_{10}N_2$	
Crystal colour/habit	Purple/Prismatic	Reddish yellow/Rhombohedral	Reddish violet/irregular
Crystal size (mm)	0.351x0.092x0.08	1.00x0.6x0.15	0.05x0.05x0.05
Co-crystallizing solvent	None	None	None
Crystal system/ Space group	*P*-1	$P2_1/c$	*P*-1
a (Å)	17.290 (2)	15.2146 (14)	17.0443 (8)
b (Å)	17.269 (2)	5.7842 (6)	17.2874 (7)
c (Å)	20.254 (3)	12.1728 (11)	20.2570(9)
α (°)	115.202 (4)	90	64.843(2)
β (°)	115.230 (4)	112.487 (2)	65.454(2)
γ (°)	89.994 (5)	90	89.865(2)
Volume (Å^3)	4826.9 (12)	989.81 (16)	4803.1(4)

Z/Z’	2/1	4/1	2/1
Molecular Weight	1475.72	182.22	1824.17
Calculated density (g/cm3)	1.015	1.223	1.261
F(000)	1498	384	1870
Radiation	Mo K_α	Mo K_α	Mo K_α
θ range (°)	1.260/26.485	2.898/26.509	1.676/23.816
Scan type	ϕ and ω	ϕ and ω	ϕ and ω
Measured reflections	102405	26212	50291
Unique reflections	19845	2030	14704
Observed reflections [|F|> 4σ(F)]	15170	1745	11230
Final R (%)	5.17	4.6	7.3
wR2 (%)	16.95	13.04	22.07
Good-of-fit on F^2(S)	1.022	1.089	1.036
Δρ max (e. $Å^{-3}$)	0.654	0.220	1.021
Δρ min (e. $Å^{-3}$)	-0.343	-0.158	-1.045
No of restrains/parameters	0/907	1/142	281/1135
Data [|F|> 4σ(F)]-to-parameter ratio	16.7:1	14.3:1	9.9:1

Table S3. Selected bond lengths and bond angles for mDESY-1 and mDESY-2 at 100 K.

mDESY-1				mDESY-2			
Co1–O5	1.9546(19)	O5–Co1–O1	95.83(10)	Co1–O1	1.935 (2)	O1–Co1–O6	103.98(9)
Co1–O1	1.965(2)	O5–Co1–O4	120.52(9)	Co1–06	1.961 (2)	O1–Co1–N1	108.66(10)
Co1–O4	1.977(2)	O1–Co1–O4	122.70(11)	Co1–N1	1.980 (2)	O1–Co1–N3	115.47(10)
Co1–N1	2.015(5)	O5–Co1–N1	106.8(2)	Co1–N3	1.992 (2)	O6–Co1–N1	119.44(10)
Co1–N3	2.027(10)	O1–Co1–N1	108.9(3)	Co2–O4	1.938 (2)	O6–Co1–N3	96.35(9)
		O4–Co1–N1	101.3(2)	Co2–N5	1.991 (2)	N1–Co1–N3	112.60(10)
		O5–Co1–N3	93.0(3)			O4–Co2–O4	115.88(14)
		O1–Co1–N3	105.7(5)			O4–Co2–N5	106.61(11)
		O4–Co1–N3	113.9(4)			O4–Co2–N5	105.84(11)
						N5–Co2–N5	116.49(17)

Table S4. Selected bond lengths and bond angles for mDESY-1 in P-1 space group, azobenzene and Azo@mDESY-1 at room temperature.

mDESY-1 (P-1)		Azobenzene		Azo@mDESY-1	
Co1–O19	1.968(2)	C1–C2	1.387(2)	Co1–O24	1.994(4)
Co1–O18	1.986(2)	C1–C6	1.382(2)	Co1–O1	1.974(4)
Co1–O4	1.997(2)	C10–C11	1.365(3)	Co1–N13	2.030(5)
Co1–N12	2.014(3)	C12–C11	1.363(3)	Co1–O11	1.986(5)
Co2–O12	1.968(2)	C2–C3	1.381(2)	Co3–O3	2.001(4)
Co2–O23	1.984(2)	C3–C4	1.382(2)	Co3–O18	1.968(4)
Co2–O15	1.993(2)	C4–C5	1.377(3)	Co3–O21	2.004(4)
Co2–N10	2.021(3)	C6–C5	1.382(2)	Co3–N19	1.979(4)
Co3–O6	1.970(2)	C7–C8	1.384(3)	Co4–O7	1.994(4)
Co3–O7	1.984(2)	C7–C12	1.373(3)	Co4–O19	1.963(4)
Co3–O21	1.996(2)	C7–N3	1.466(14)	Co4–O16	1.990(4)
Co3–N6	2.019(3)	C8–C9	1.379(3)	Co4–N17	2.040(6)
Co4–O14	1.967(2)	C8–N3	1.965(17)	Co2–O13	1.981(4)
Co4–O2	1.982(2)	C8–H8	0.90(2)	Co2–O9	1.969(4)
Co4–O10	1.990(2)	C9–C10	1.378(3)	Co2–O6	1.977(4)
Co4–N8	2.021(3)	N1–N1	1.241(2)	Co2–N15	2.037(5)
O19–Co1–O18	117.78(10)	N1–C1	1.4323(17)	O24–Co1–N13	104.50(19)
O19–Co1–O4	95.98(10)	N2–N2	1.205(5)	O1–Co1–O24	115.44(18)
O19–Co1–N12	104.40(12)	N2–C7	1.456(4)	O1–Co1–N13	104.4(2)
O18–Co1–O4	123.68(11)	N3–N3	1.38(3)	O1–Co1–O11	93.03(19)
O18–Co1–N12	105.12(11)	N1–N1–C1	114.01(15)	O11–Co1–O24	128.5(2)
O4–Co1–N12	108.30(12)	C2–C1–N1	123.73(13)	O11–Co1–N13	108.7(2)
O12–Co2–O23	117.56(10)	C6–C1–N1	115.95(13)	O3–Co3–O21	125.69(19)
O12–Co2–O15	95.94(10)	C6–C1–C2	120.28(13)	O18–Co3–O3	121.15(18)
O12–Co2–N10	104.34(12)	C3–C2–C1	119.23(14)	O18–Co3–O21	94.77(19)
O23–Co2–O15	123.66(11)	N2–N2–C7	112.1(3)	O18–Co3–N19	99.9(2)
O23–Co2–N10	105.41(11)	C1–C6–C5	119.86(15)	N19–Co3–O3	105.3(2)
O15–Co2–N10	108.30(12)	C2–C3–C4	120.62(15)	N19–Co3–O21	106.8(2)
O6–Co3–O7	117.76(10)	C5–C4–C3	119.83(14)	O7–Co4–N17	103.8(3)
O6–Co3–O21	96.24(10)	C4–C5–C6	120.13(15)	O19–Co4–O7	122.05(18)
O6–Co3–N6	104.24(12)	C8–C7–N2	127.37(19)	O19–Co4–O16	96.81(19)
O7–Co3–O21	123.49(11)	C8–C7–N3	87.1(7)	O19–Co4–N17	101.0(3)
O7–Co3–N6	105.28(12)	C12–C7–N2	112.63(19)	O16–Co4–O7	122.64(19)
O21–Co3–N6	108.21(12)	C12–C7–C8	120.00(18)	O16–Co4–N17	108.2(2)
O14–Co4–O2	117.75(10)	C12–C7–N3	152.9(7)	O13–Co2–N15	105.98(19)
O14–Co4–O10	95.88(10)	C7–C8–N3	48.2(4)	O9–Co2–O13	119.02(18)
O14–Co4–N8	104.32(12)	C7–C8–H8	119.7(13)	O9–Co2–O6	95.53(19)
O2–Co4–O10	123.79(11)	C9–C8–C7	119.34(18)	O9–Co2–N15	104.9(2)
O2–Co4–N8	105.23(12)	C9–C8–N3	167.5(4)	O6–Co2–O13	122.52(19)
O10–Co4–N8	108.24(12)	C9–C8–H8	120.9(13)	O6–Co2–N15	107.3(2)
		N3–C8–H8	71.5(14)		
		C11–C12–C7	120.05(19)		
		C10–C9–C8	120.08(19)		
		C11–C10–C9	119.78(18)		
		C12–C11–C10	120.75(19)		
		C7–N3–C8	44.7(5)		
		N3–N3–C7	104.7(13)		
		N3–N3–C8	148.7(14)		

Table S5. Cell and fit parameters obtained from the Le Bail fitting for mDESY-1 measured at P02.1, PETRA III.

Unit cell parameters				Fit parameters	
a (Å)	17.34550(30)	α (°)	114.87971(254)	R_p	9.08
b (Å)	17.26511(61)	β (°)	115.51295(216)	R_{wp}	8.12
c (Å)	20.27012(66)	γ (°)	89.89168(282)	R_{exp}	4.22
				χ^2	3.70

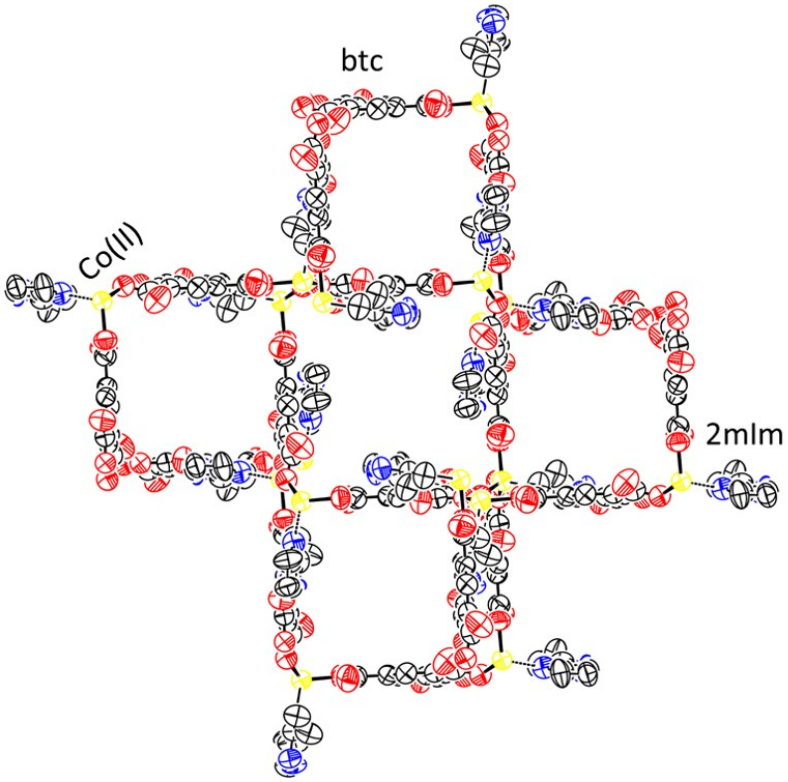

Figure. S3. Thermal ellipsoid plot (50 % of probability) for mDESY-1 at 100 K.

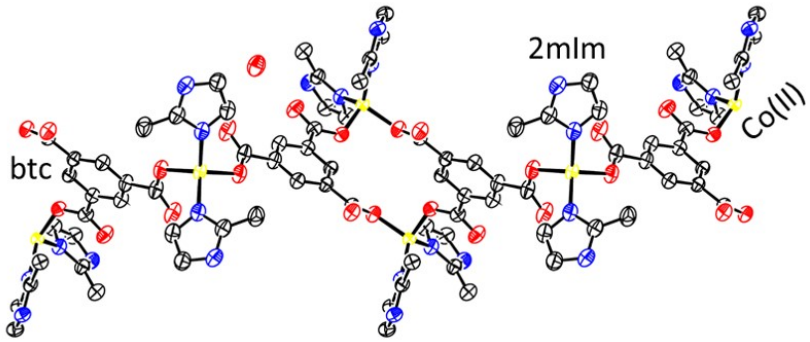

Figure. S4. Thermal ellipsoid plot (50 % of probability) for mDESY-2 at 100 K.

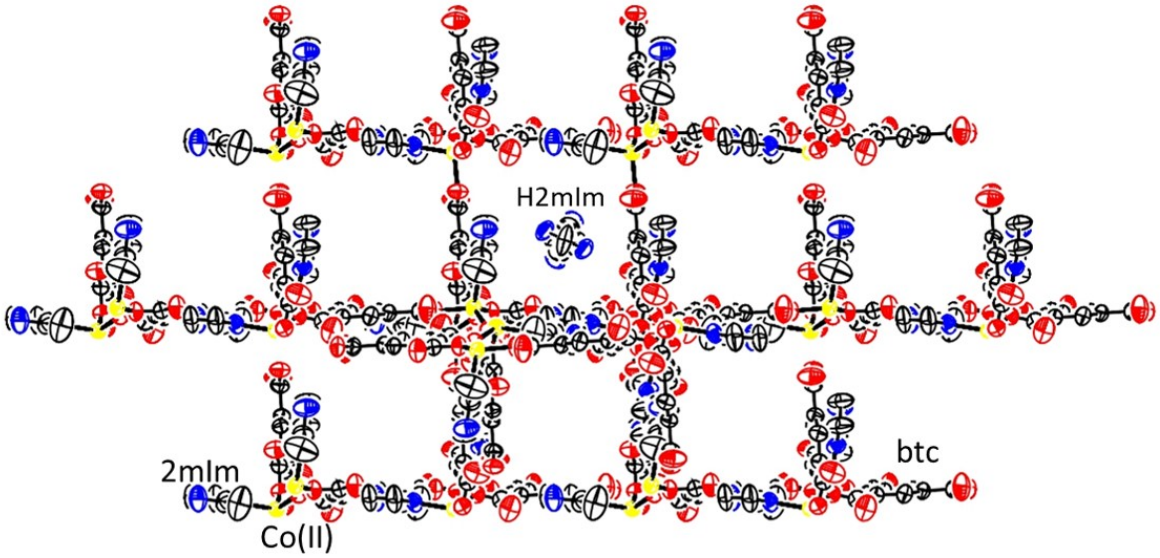

Figure. S5. Thermal ellipsoid plot (50 % of probability) for mDESY-1 in P-1 space group at room temperature.

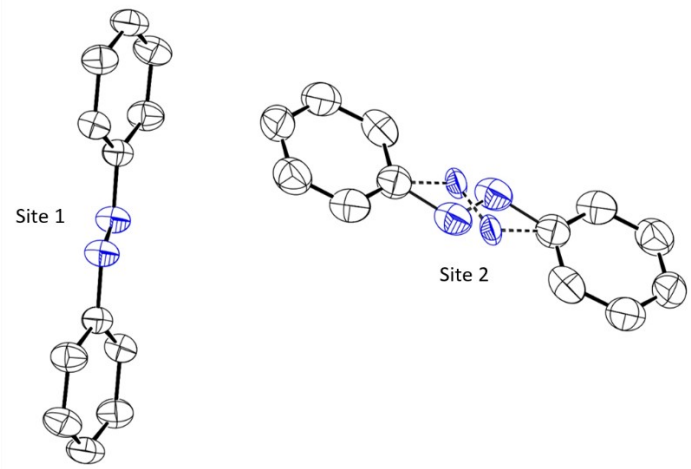

Figure. S6. Thermal ellipsoid plot (50 % of probability) for azobenzene at room temperature.

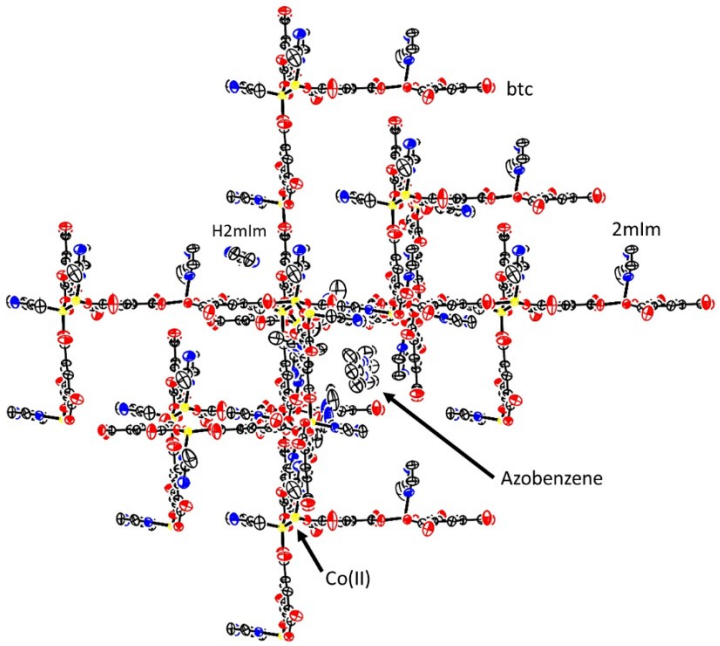

Figure. S7. Thermal ellipsoid plot (50 % of probability) for Azo@mDESY-1 at room temperature.

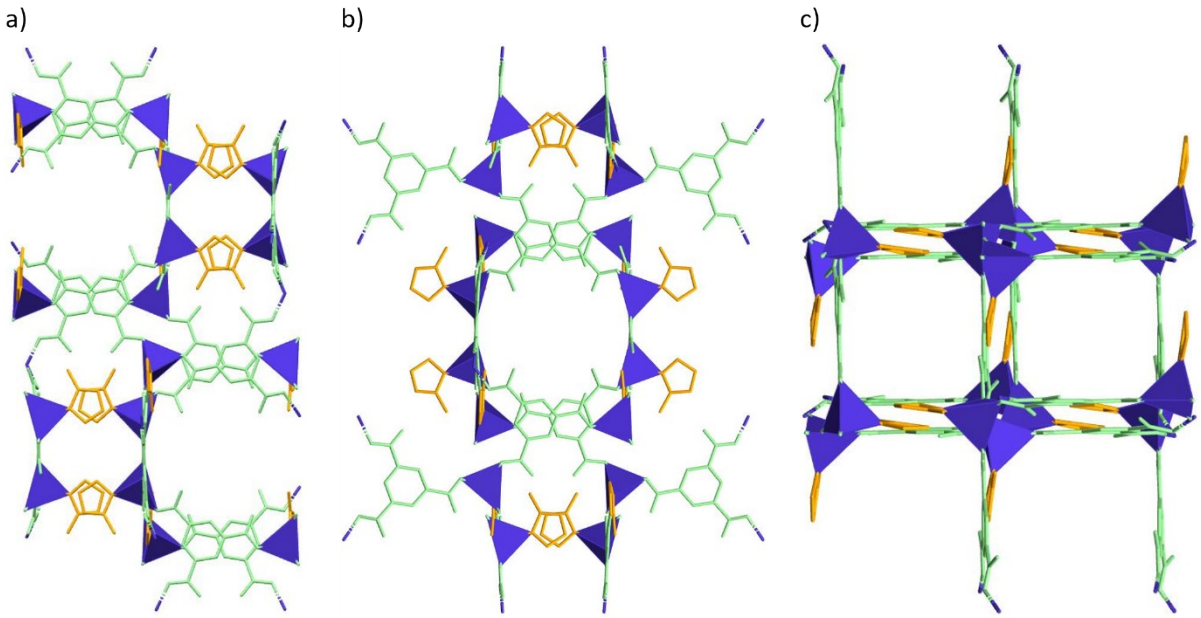

Figure S8. Images of the 3-D mDESY-1, view down the a-c) a, b and c axis. Neutral mIm ligands are drawn in yellow, btc ligands in light green and cobalt ions are drawn as purple polygons. Hydrogen atoms and counter ions were omitted for clarity.

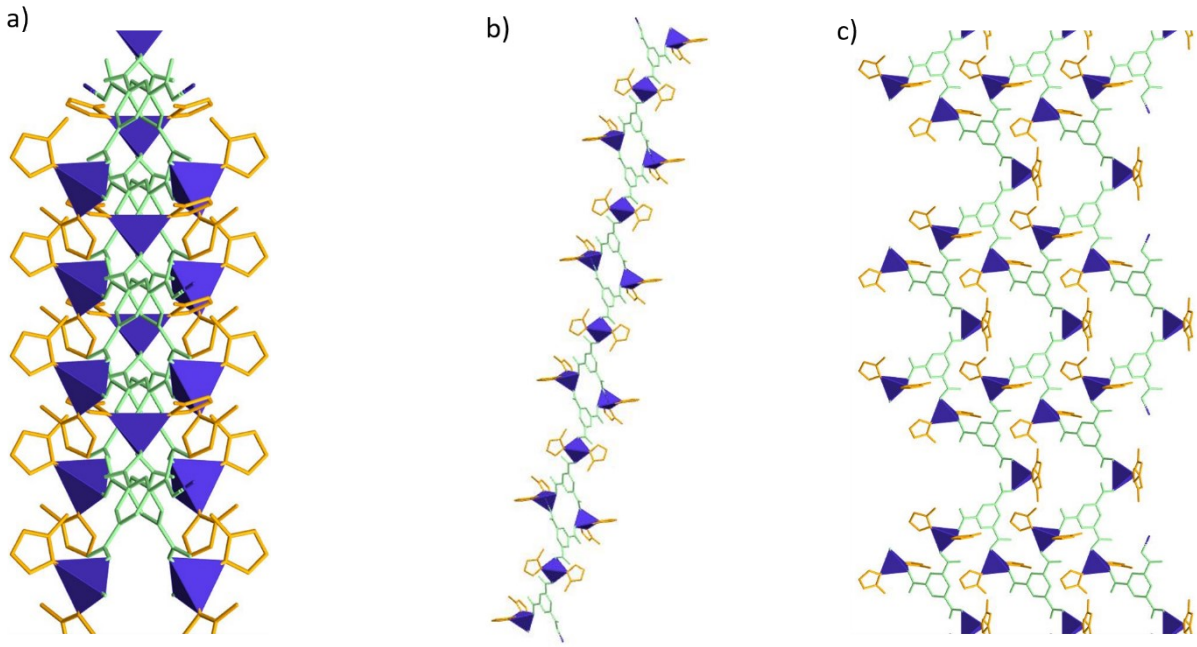

Figure S9. Images of the 2-D mDESY-2, view down the a-c) a, b and c axis. Neutral mIm ligands are drawn in yellow, btc ligands in light green and cobalt ions are drawn as purple polygons. Hydrogen atoms and co-crystallising water were omitted for clarity.

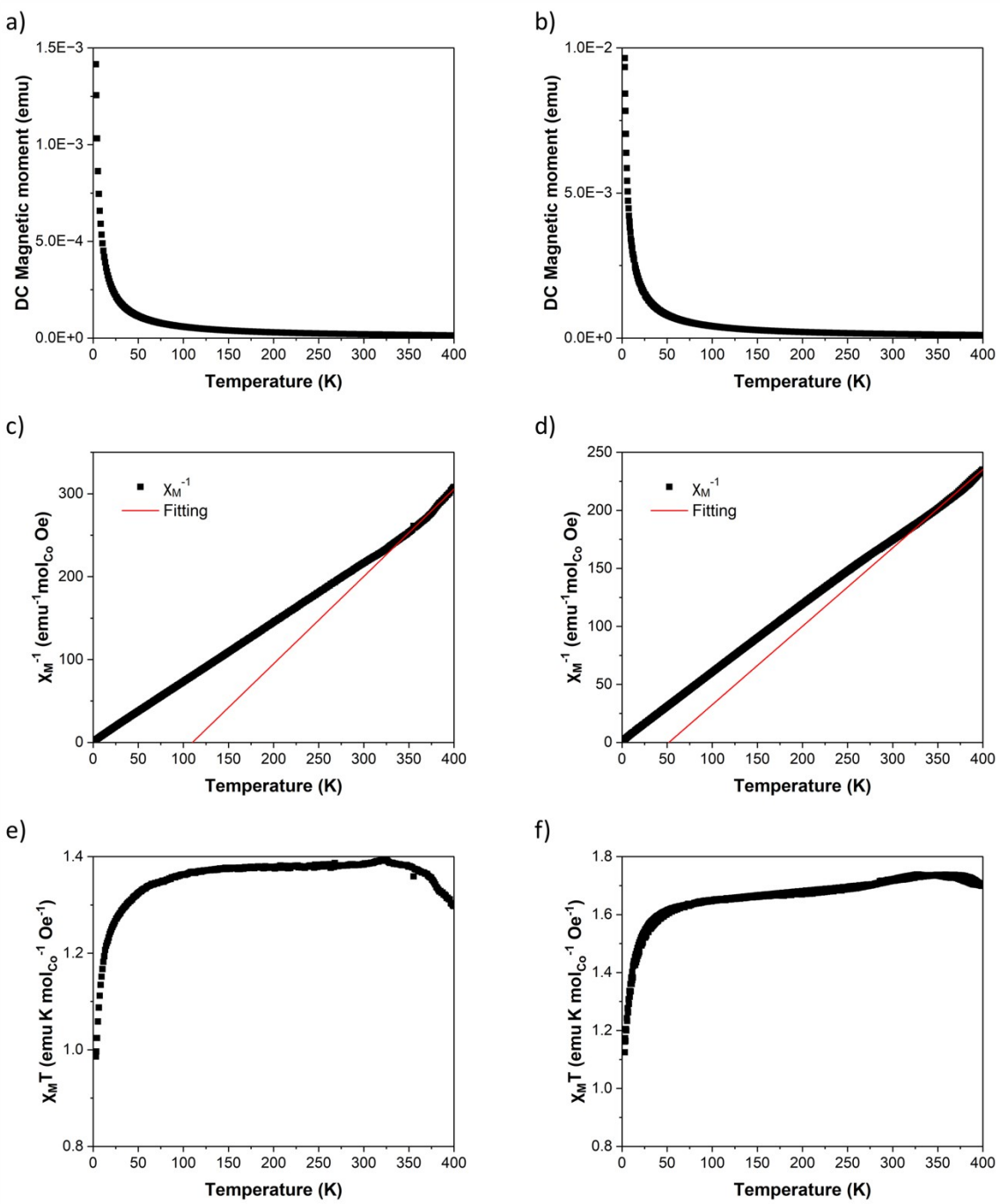

Figure S10. Magnetic characterisation of mDESY-1 and mDESY-2 measured at 1 T in the 3 – 400 K temperature range. Temperature dependence of DC magnetic moment for a) mDESY-1 and b) mDESY-2. Inverse molar magnetic susceptibility (χ_M^{-1}) vs temperature, including linear extrapolation to the zero level of a possible ferromagnetic ordering, for c) mDESY-1 and d) mDESY-2. The χ_MT vs temperature plot for e) mDESY-1 and f) mDESY-2.

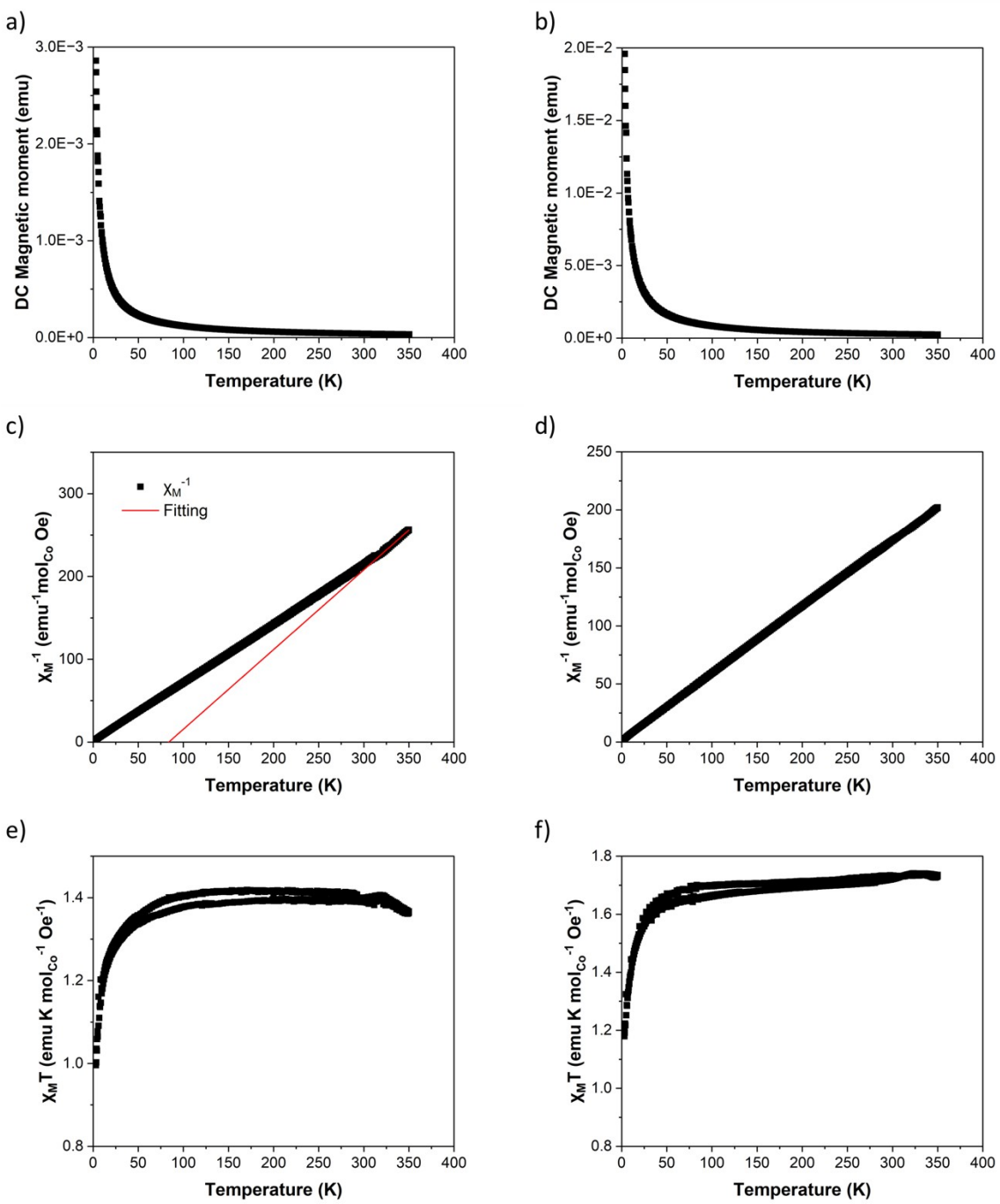

Figure S11. Magnetic characterisation of mDESY-1 and mDESY-2 measured at 2 T in the 3 – 350 K temperature range. Temperature dependence of DC magnetic moment for a) mDESY-1 and b) mDESY-2. Inverse molar magnetic susceptibility (χ_M^{-1}) vs temperature, including linear extrapolation to the zero level of a possible ferromagnetic ordering, for c) mDESY-1 and d) mDESY-2. The χ_MT vs temperature plot for e) mDESY-1 and f) mDESY-2.

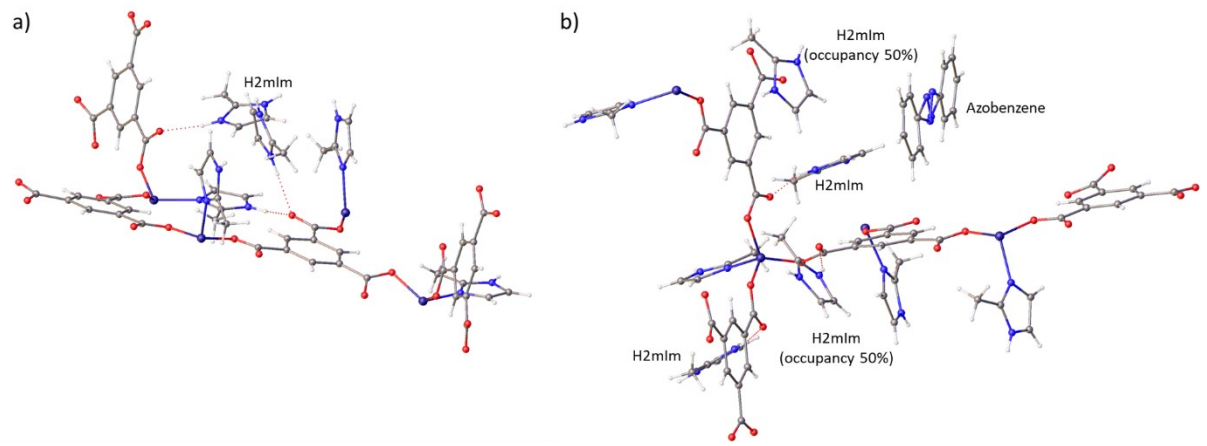

Figure S12. Asymmetric unit cell of a) mDESY-1 in P-1 space group and b) Azo@mDESY-1.

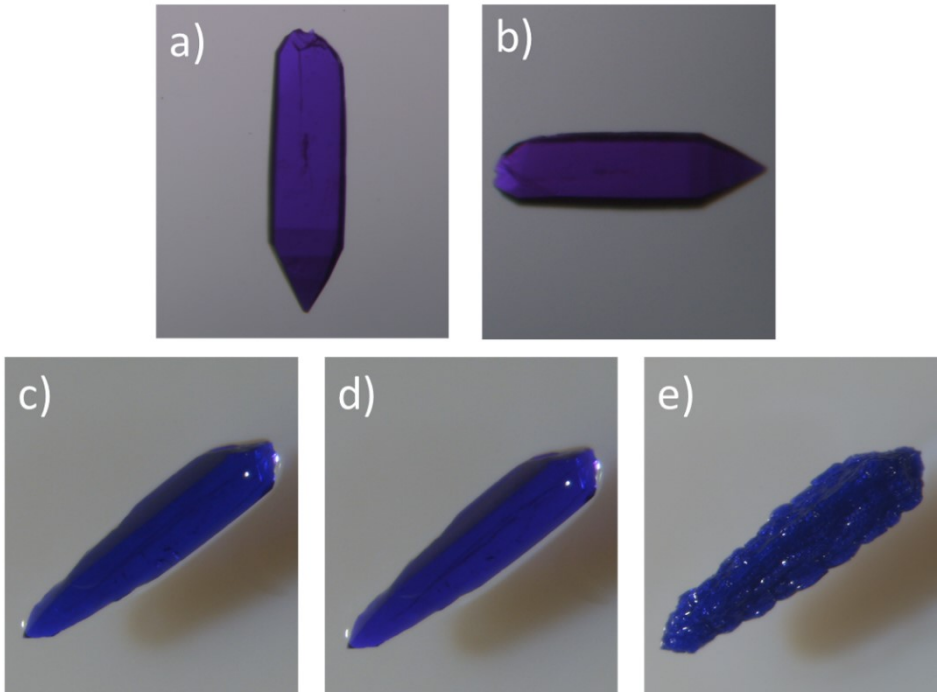

Figure S13. a) and b) Optical images of mDESY-1 at two different orientations, using transmission mode. Optical images of mDESY-1 at c) room temperature (17 °C) and 130 °C after d) 30 seconds and e) >1 min.

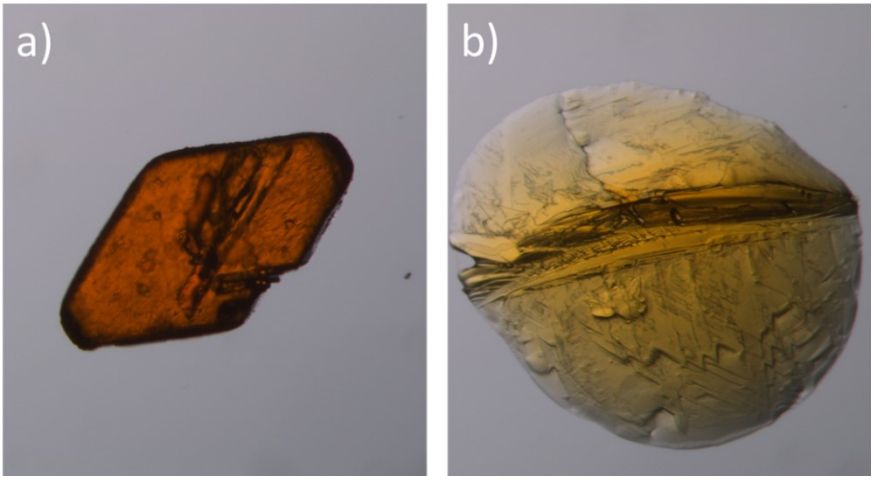

Figure S14. Optical images of azobenzene at a) room temperature (17 °C) and b) 68 °C.

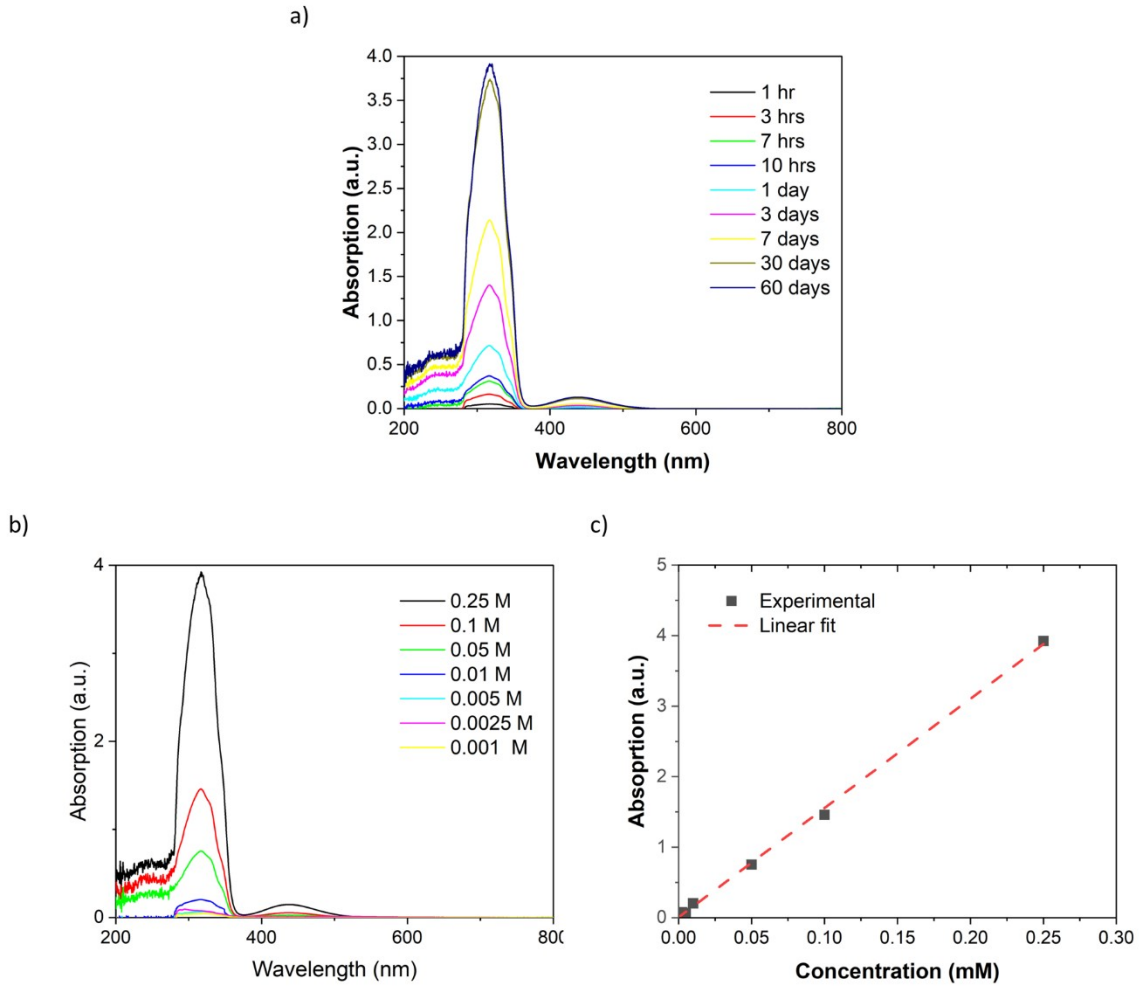

Figure S15. b) UV-vis spectra of the release of azobenzene in ethanol from mDESY-1 in a 2 month period, b) UV-vis spectra of azobenzene solution at different concentration used for the calibration curve and c) calibration curve used to calculate the concentration of released azobenzene.

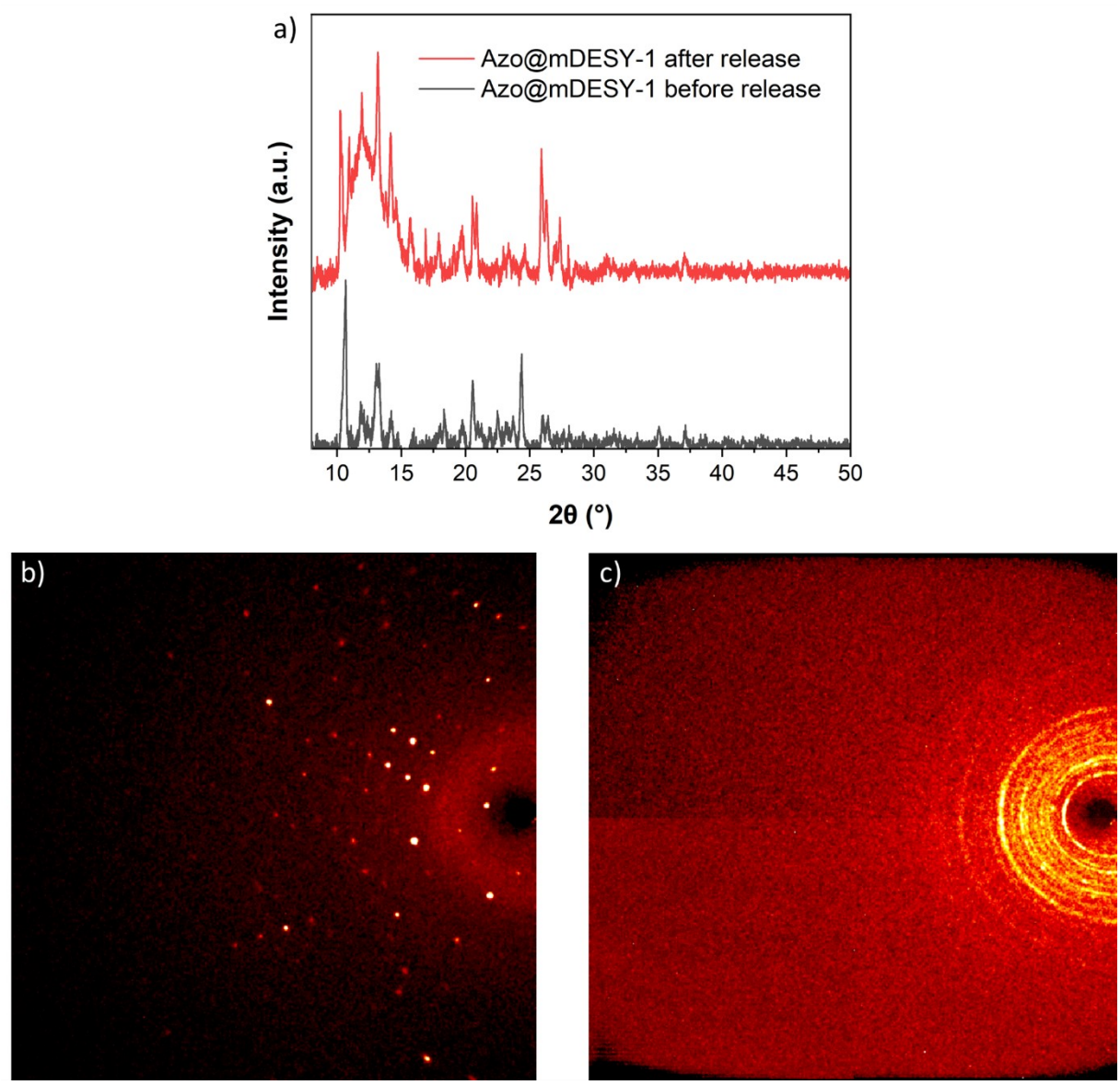

Figure S16. a) PXRD pattern of Azo@mDESY-1 before and after the release of azobenzene.

Diffraction images of a single crystal of Azo@mDESY-1 b) before and c) after release of azobenzene.

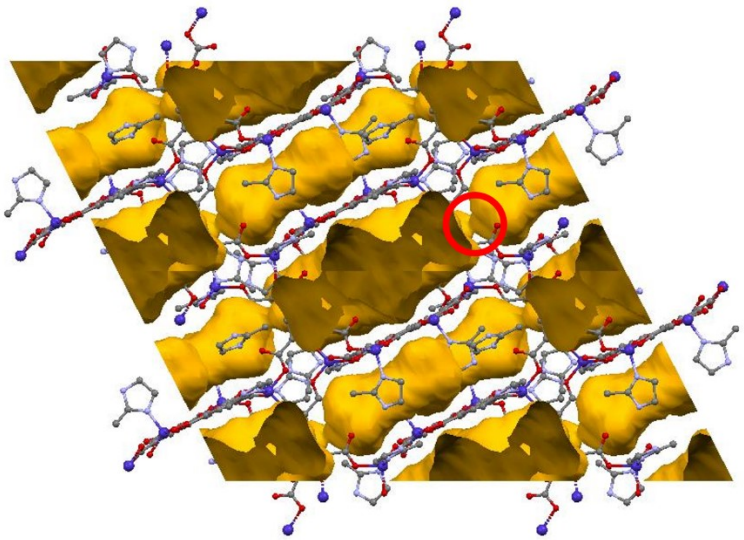

Figure S17. Calculated voids in Azo@mDESY-1, with Azobenzene molecules omitted during the calculation. The red circle highlights a constricted region within the channel.