Solvatomorphism, CO_2 adsorption and luminescence properties of non-aromatic bis-hydroxamate-based metal-organic frameworks

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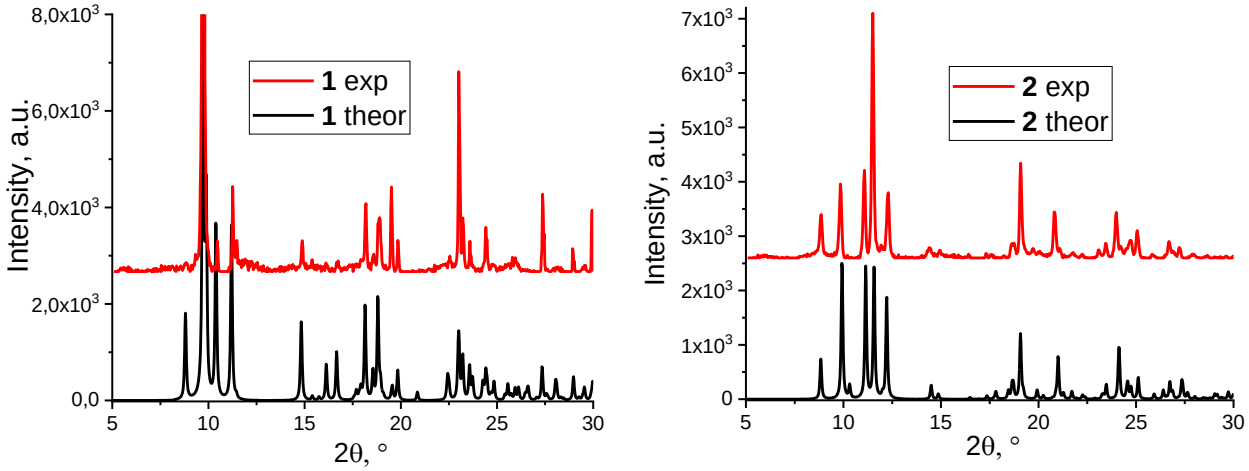
Electronic supplementary information

Table S1. Single-crystal X-ray diffraction experiment and structure refinement details

	1	**2**
Chemical formula	$C_{28}H_{52}N_6O_{16}Tb_2$	$C_{24}H_{46}N_4O_{16}Tb_2$
M_r, g·mol^{-1}	1046.59	964.49
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Temperature, K	150	150
a, Å	10.5916(3)	9.7692(4)
b, Å	10.6052(5)	10.1377(4)
c, Å	11.5225(4)	10.6609 (6)
α, °	113.549(4)	72.938(4)
b, °	95.905(3)	72.646(4)
γ, °	115.253(4)	63.374(4)
V, Å^3	1013.11 (8)	884.97(8)
Z	1	1
F(000)	520	476
$D_{(calc.)}$, g·cm^{-3}	1.715	1.810
μ, mm^{-1}	3.53	4.03
Crystal size, mm	0.37 × 0.30 × 0.19	0.18 × 0.14 × 0.10
θ range for data collection, °	2.04 < θ < 25.35	2.04 < θ < 28.95
No. of reflections: measured / independent / obs. [I > 2σ(I)]	14616 / 3718 / 3472	7595 / 3886 / 3537
R_{int}	0.0560	0.0246
Index ranges	$-12 \le h \le 12$ $-12 \le k \le 12$ $-13 \le l \le 13$	$-13 \le h \le 12$ $-13 \le k \le 10$ $-12 \le l \le 14$
Final R indices [I > 2σ(I)]	R_1 = 0.0314 wR_2 = 0.0736	R_1 = 0.0243 wR_2 = 0.0495
Final R indices (all data)	R_1 = 0.0343 wR_2 = 0.0757	R_1 = 0.0295 wR_2 = 0.0521
Goodness-of-fit on F^2	1.030	1.034
Largest diff. peak, hole, e/Å^3	1.32, –1.04	0.75, –0.89



a b

Figure S1. PXRD patterns for **1** (a) and **2** (b) compared to the theoretical ones.

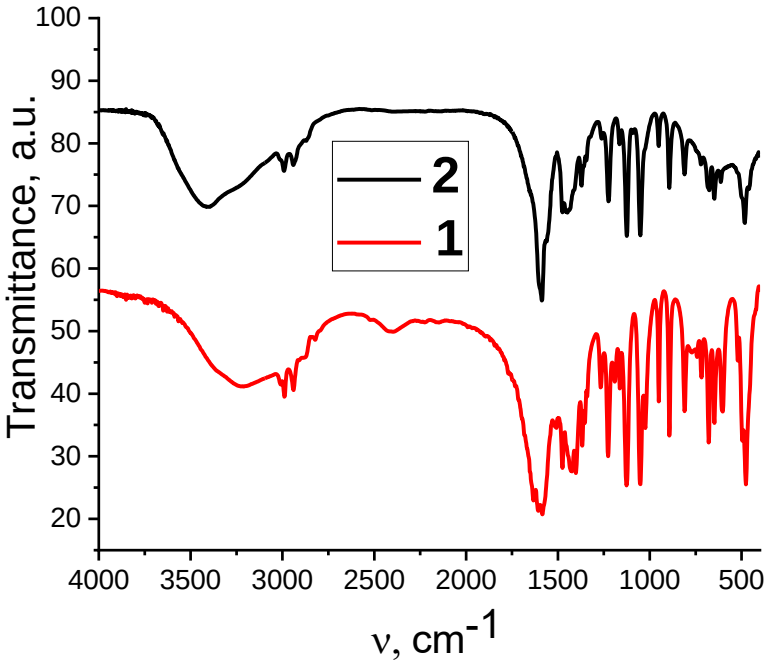
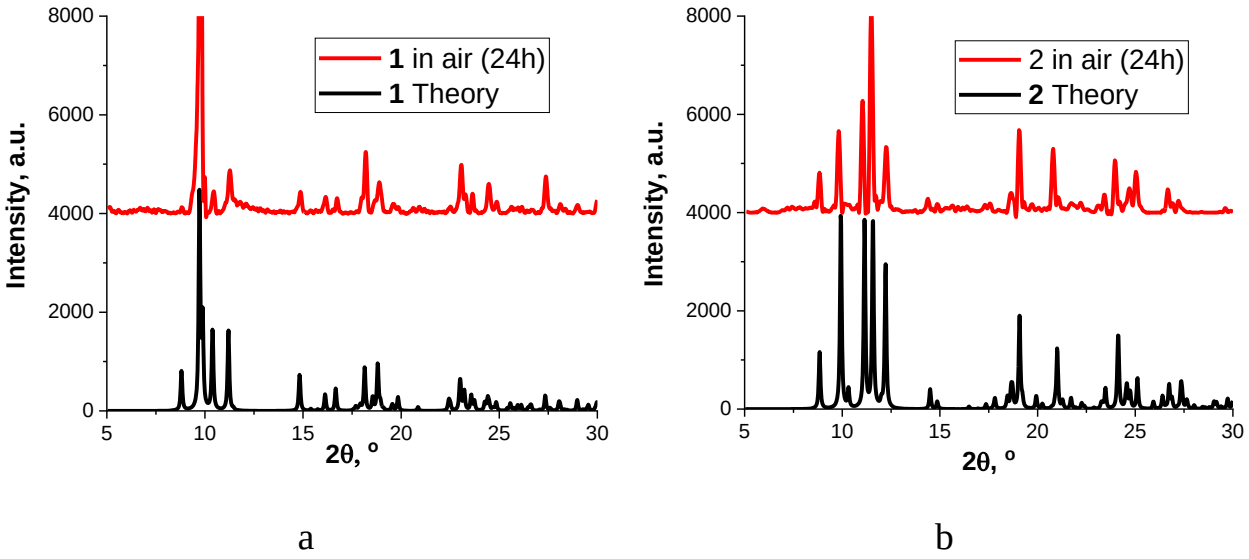


Figure S2. IR spectra for **1** and **2**



a b

Figure S3. PXRD patterns for the polycrystalline powders of **1** and **2** after 24h storage in air.

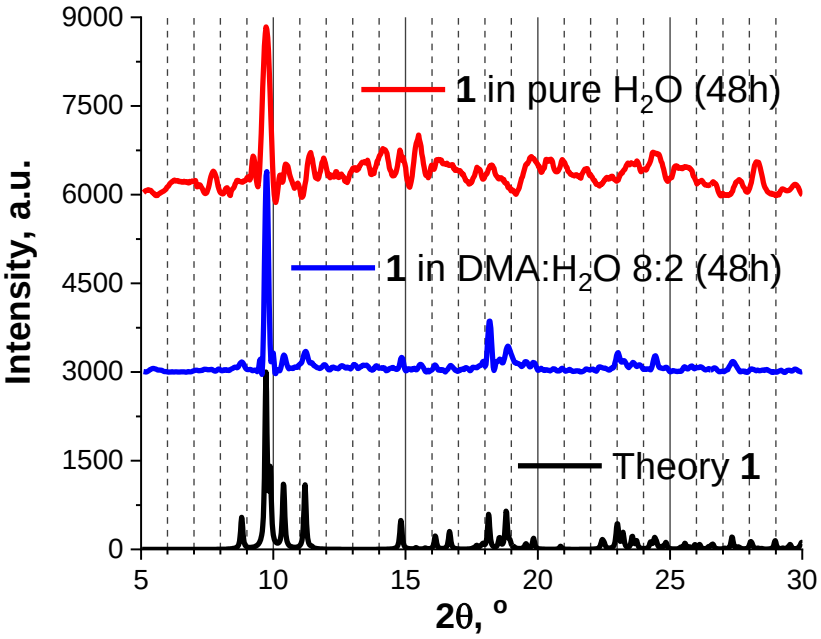


Figure S4. PXRD patterns for the polycrystalline powders of **1** after 48h storage in H_2O or DMA-H_2O mixture.

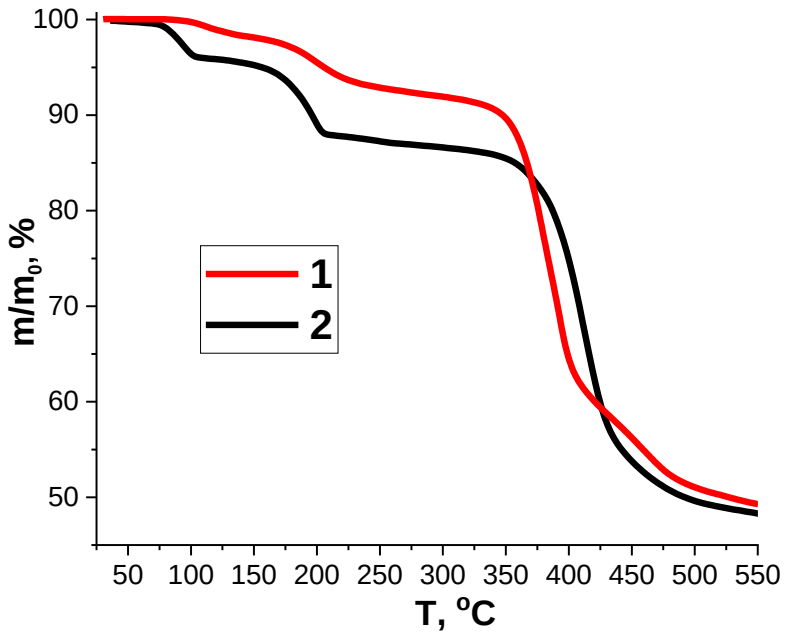


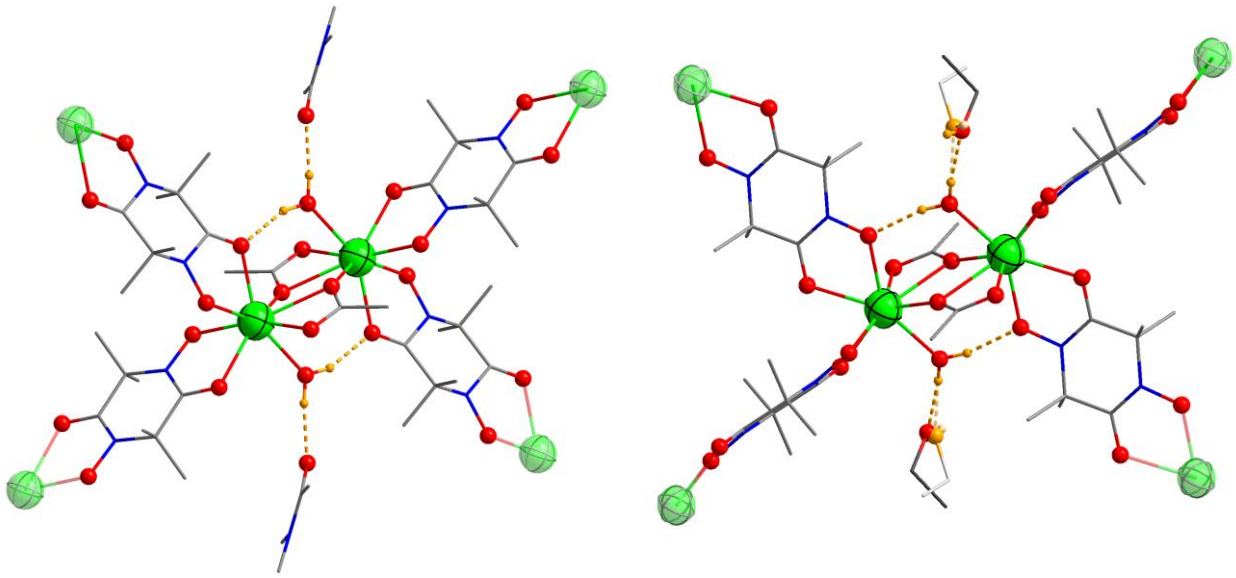
Figure S5. TGA plots for **1** and **2**.

Table S2. Bond lengths in Tb^{3+} coordination environments.

		Structure (bond lengths are given in Å)	
Part of the trigonal do-decahedron	Atom type	**1**	**2**
Trigonal "base"	O(–C_L) / O(–N_L)	2.21(2); 2.369(7); 2.375(5) / 2.28(3); 2.286(5); 2.41(3)	2.291(10); 2.358(5); 2.38(4) / 2.240(17); 2.40(7); 2.40(2)
Upper "square"	O(–C_L) / O(–N_L)	2.30(3) / 2.348(5)	2.26(6) / 2.334(4)
	O(H_2O)	2.352(3)	2.360(2)
	O(μ-κ^1:κ^2-COO)	2.385(3); 2.481(3)	2.340(2); 2.449(3)
Cap		2.494(3)	2.539(2)

Table S3. Deviation criteria for different geometries of metal coordination polyhedra, according to Shape 2.1 [MS74] nomenclature.

Structure [ML8]	**1**	**2**
OP-8	31.270	32.814
HPY-8	21.106	21.193
HBPY-8	15.168	15.140
CU-8	10.364	13.723
SAPR-8	**2.068**	4.400
TDD-8	2.909	**1.931**
JGBF-8	12.902	10.652
JETBPY-8	24.973	26.140
JBTPR-8	3.226	3.578
BTPR-8	2.947	3.206
JSD-8	4.783	3.279
TT-8	10.775	14.154
ETBPY-8	19.586	22.738



a b

Figure S6. Hydrogen bond arrangements in **1** (a) and **2** (b). Tb atoms are shown green, O atoms – red, N atoms – blue, C atoms – grey, O-bonded H atoms orange, C-bonded H atoms are not shown. Hydrogen bonds are shown by orange dashed lines. Two disordered positions of EtOH molecules in (b) are shown in different shades.

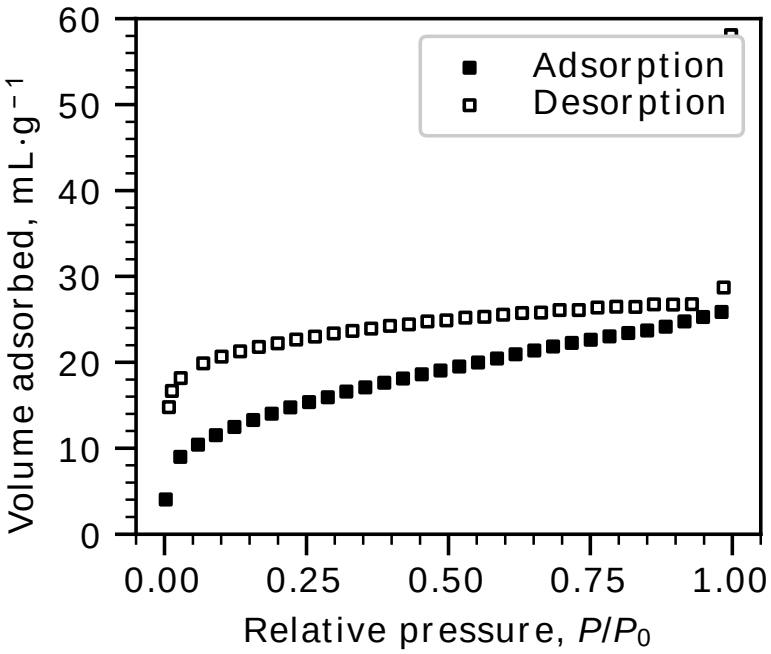


Figure S7. CO_2 adsorption-desorption isotherm for the sample **1a** at 195 K.

Details of surface area and pore volume calculations

1. BET

BET equation in linear form:

$$\frac{1}{n\left(\frac{P_0}{P}-1\right)} = \frac{1}{wC} + \frac{C-1}{wC}\frac{P}{P_0} \quad (1)$$

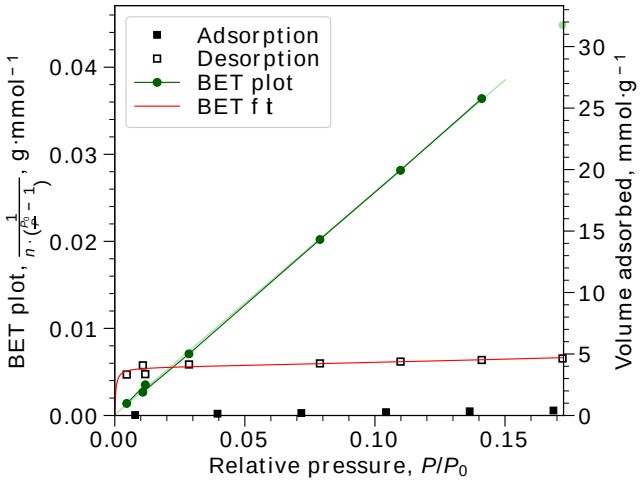
n — uptake in mmol·g^{-1}, P/P_0 — relative pressure, w — monolayer capacity in mmol·g^{-1}, C — BET constant.

BET surface area was calculated using equation:

$$S_{BET} = w \cdot a_m \cdot N_A \quad (2)$$

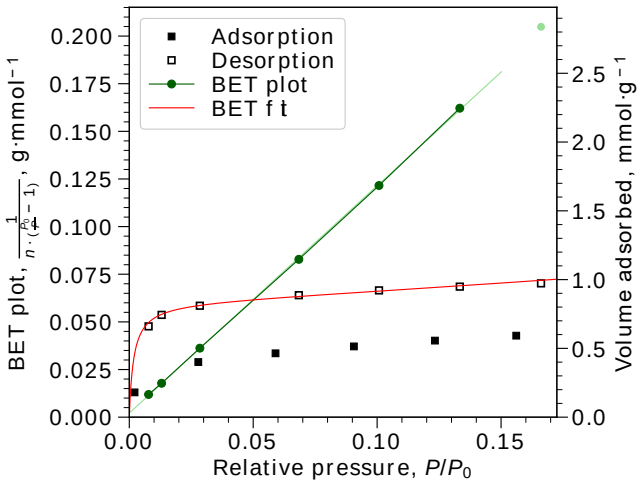
a_m = 21.0 Å^2, carbon dioxide cross-section area, N_A — Avogadro number.

The right and left pressure limits were chosen according to consistency criteria [Ref. 62 in the MS]. The corresponding BET plot and calculated parameters are shown below.



Parameter	Value
Pressure range, P/P_0	0.001, 0.15
Slope	0.256
Intercept	$9.89 \cdot 10^{-5}$
R^2	1.000
C_{BET}	2591.5
Monolayer capacity, mmol·g^{-1}	3.903
BET area, m^2·g^{-1}	493±4

Figure S8. BET surface area calculations for **2a** based on carbon dioxide adsorption isotherm at 195 K.



Parameter	Value
Pressure range, P/P_0	0.001, 0.15
Slope	1.193
Intercept	0.002124
R^2	1.000
C_{BET}	562.5
Monolayer capacity, mmol·g^{-1}	0.838
BET area, m^2·g^{-1}	105.8±0.7

Figure S9. BET surface area calculations for **1a** based on carbon dioxide adsorption isotherm at 195 K.

Langmuir

Langmuir equation in linear form:

$$\frac{P/P_0}{n} = \frac{1}{wK} + \frac{P/P_0}{w} \quad (3)$$

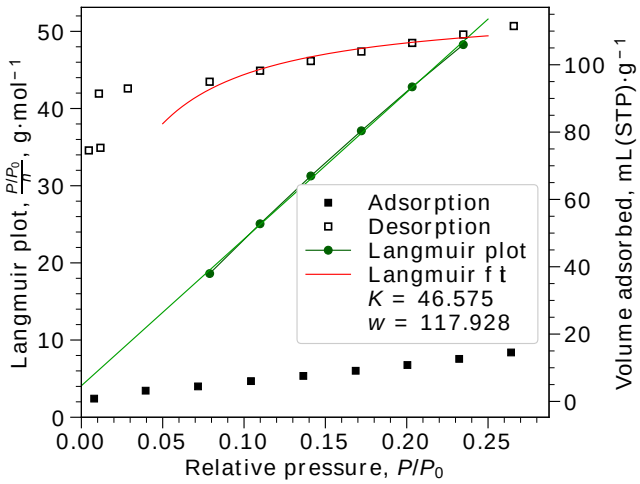
n — uptake in mL·g^{-1}, P/P_0 — relative pressure, w — monolayer capacity in mL·g^{-1}, K — Langmuir equilibrium constant.

Langmuir surface area was calculated using equation:

$$S_{Langmuir} = \frac{w \cdot a_m \cdot N_A}{V_M} \quad (4)$$

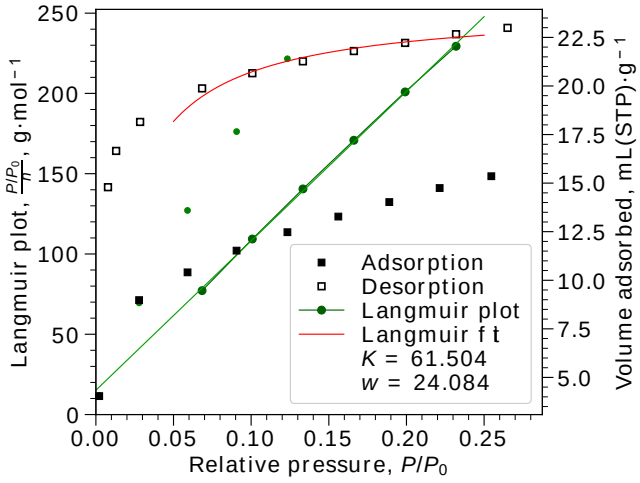
a_m = 21.0 Å^2, carbon dioxide cross-section area, N_A — Avogadro number, V_M — molar volume at STP.

The right and left pressure limits were chosen to provide good linearity of Langmuir plot. The corresponding Langmuir plot and calculated parameters are shown below.



Parameter	Value
Pressure range, P/P_0	0.05, 0.25
Slope	0.0085
Intercept	0.000182
R^2	0.999
K	46.57
Monolayer capacity, mL·g^{-1}	117.9
Langmuir area, m^2·g^{-1}	665±11

Figure S10. Langmuir surface area calculations for **2a** based on carbon dioxide adsorption isotherm at 195 K.



Parameter	Value
Pressure range, P/P_0	0.05, 0.25
Slope	0.0415
Intercept	0.000675
R^2	0.999
K	61.50
Monolayer capacity, mL·g^{-1}	24.08
Langmuir area, m^2·g^{-1}	135.9±1.6

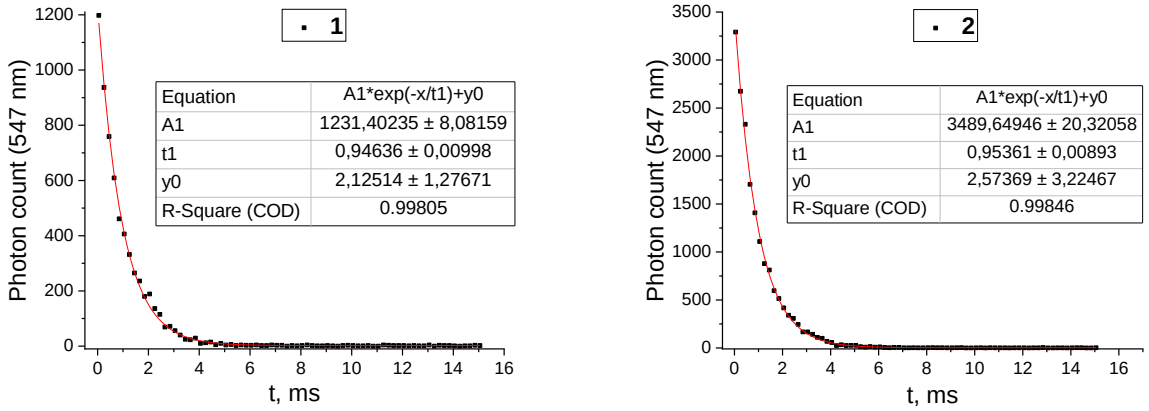
Figure S11. Langmuir surface area calculations for **1a** based on carbon dioxide adsorption isotherm at 195 K.

3. Pore volume

Pore volume were calculated using equation:

$$V_{\text{total}} = \frac{V_{ads} M}{V_M \rho} \tag{5}$$

ρ = 1.564 g·cm^{-3}, density of condensed carbon dioxide, M =43.99 g·mol^{-1}, CO_2 molar mass.



a b

Figure S12. Phosphorescence decay fitting curves for **1** (a) and **2** (b)