Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

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A robust Viologen and Mn-based porous coordination polymer with two types of Lewis acid sites providing high affinity for H_2O, CO_2 and NH_3.

I- Synthesis of (H_4*pc3*)$(Cl)_2$

The synthesis of the (H_4*pc3*)$(Cl)_2$ has been obtained in two steps according to the Zincke reaction (Figure S1). The first step is the synthesis of the Zincke salt of 4,4'-bipyridinium, 1,1'bis-(2,4-dinitrophenyl) dichloride. In a 50 mL flask, 1.562g (10 mmol, 1 eq) of 4,4'-bipyridine is added to 4.051g (20 mmol, 2 eq) of 1-chloro-2,4-dinitrobenzene, and 25 mL of ethanol (96%). The mixture was heated under reflux and stirred for 48 hours, then the precipitate was filtered off and washed with ethanol (96%), acetone and dried with diethyl ether. The second step is the synthesis of the expected salt. In a 50 mL flask, 5.613g (10 mmol, 1eq) of 4,4'-bipyridinium-1,1'bis-(2,4-dinitrophenyl) dichloride are added to 3.623g (20 mmol, 2 eq) of 5-aminoisophtalic acid, and 25 mL of ethanol (96%). The mixture was heated under reflux and stirred for 48 hours. The solid was filtered off and washed with ethanol (96%), acetone and dried with diethyl ether. The compound was characterized by ^1H NMR (300 MHz – olid solubilized in DMSO-d_6) (Figure S2). The general yield of the synthesis is 32%

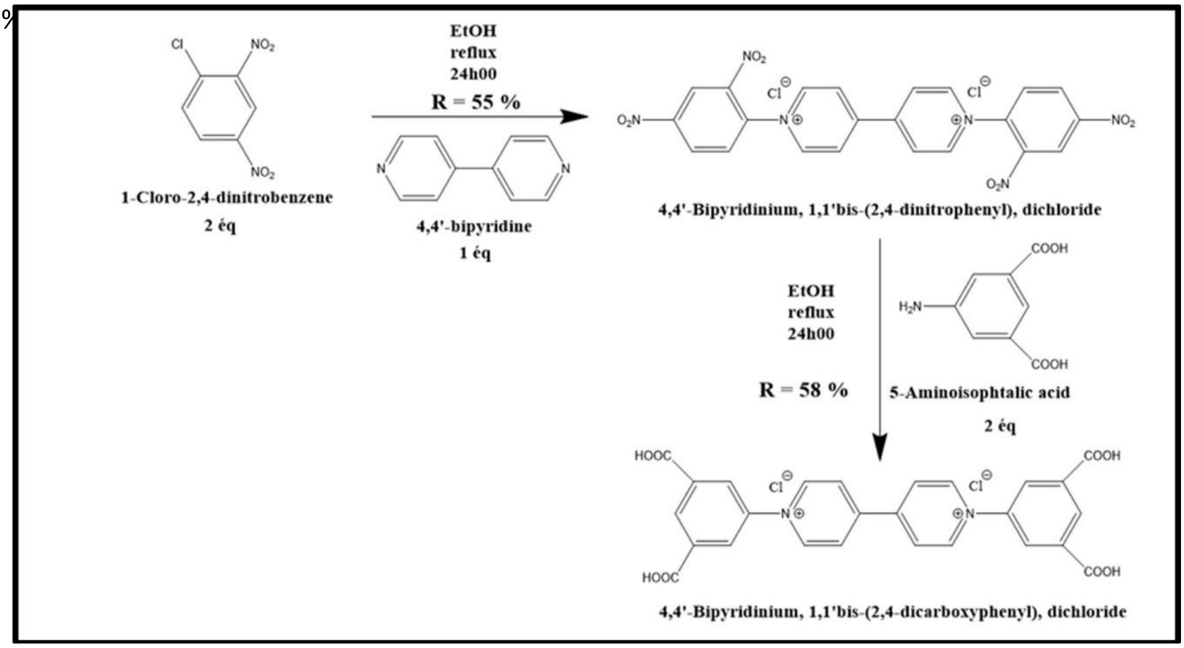

Figure S1 : Synthesis (H_4*pc3*)$(Cl)_2$ leading to a general yield of 32%.

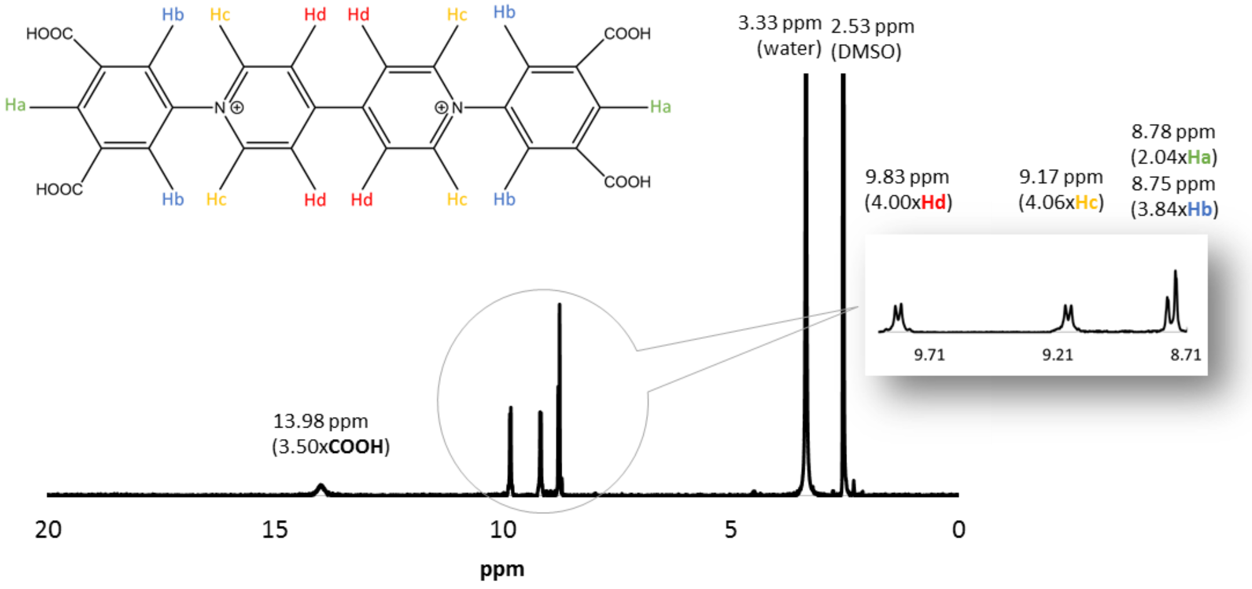

Figure S2 : 1H NMR of $(H_4\textit{pc}3)(Cl)_2$ solubilzed in deuterated DMSO.

II- Synthesis of $[Mn(\textit{pc}3)(H_2O)_2].xH_2O$

The PCP $[Mn(\textit{pc}3)(H_2O)_2]x.H_2O$ ($x \approx 3.5$) was obtained as pure phase by hydrothermal method : 3mg of $(H_4\textit{pc}3)(Cl)_2$ are added to 8mL of a saturated water solution of $(H_4\textit{pc}3)(Cl)_2$ whose pH was fixed to pH=7 thanks to the addition of a suitable quantity of triethylamine ; then 100mg of $MnCl_2.4H_2O$ were added to this solution ; the heating program was set to : 50 hours from RT to 160°C, 160 °C for 20 hours, and a final cooling step from 160 °C to RT for 12 hours. The sample was filtered off and dried in air. In Fig. S3, the XRPD pattern of the sample is compared to the theoretical one calculated from the crystal structure of **1**. All positions of experimental lines well fit with the expected ones showing that the phases has been obtained as a pure phase. Moreover, the C, N, H elemental analyses which have been carried out, the values well corresponding to the expected ones for a formulation of $[Mn(\textit{pc}3)(H_2O)_2]3.5\ H_2O$ (exp: C: 48.65, N: 4.29, H: 3.80; calc: C: 49.02, N: 4.40, H: 3.92).

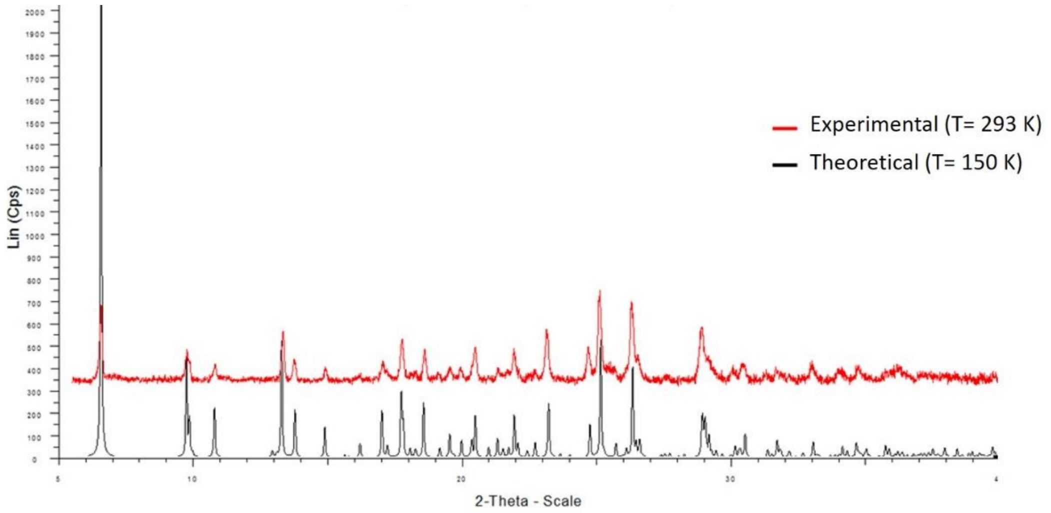

Figure S3 : Experimental and theoretical XRPD of $[Mn(\textit{pc}3)(H_2O)_2]x.H_2O$.

III- Crystal structure of [Mn(*pc3*)(H_2O)$_2$].3H_2O

While the TGA analysis and elemental analysis give a formulation of [Mn(*pc3*)(H_2O)$_2$]x.H_2O with x ≈ 3.5, the single crystal structure analysis leads to a formulation of [Mn(*pc3*)(H_2O)$_2$]3.H_2O, the three water molecules in pores being well located..

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      Empirical formula                   C26 H24 Mn N2 O13
                            Ou     C26 H14 N2 O8, Mn, 5 H2 O

    Formula weight                       627.41
    Temperature                          150.0(1) K
    Wavelength                           1.54184 A
    Crystal system, space group          Monoclinic,  P 21/c
    Unit cell dimensions        a = 14.4605(8) A   alpha = 90 deg.
                                b = 10.4594(5) A beta = 111.925(7) deg.
                                c = 18.7370(10) A   gamma = 90 deg.
    Volume                               2629.0(3) A^3
    Z, Calculated density                4,  1.585 Mg/m^3
    Absorption coefficient               4.755 mm^-1
    F(000)                               1292
    Crystal size                         0.156 x 0.087 x 0.042 mm
    Theta range for data collection      3.295 to 76.515 deg.
    Limiting indices                  -18<=h<=17, -12<=k<=8, -23<=l<=19
    Reflections collected / unique       10699 / 5314 [R(int) = 0.0452]
    Completeness to theta = 74.000       98.4 %
    Absorption correction                Semi-empirical from equivalents
    Max. and min. transmission           1.00000 and 0.55219
    Refinement method                 Full-matrix least-squares on F^2
    Data / restraints / parameters       5314 / 0 / 376
    Goodness-of-fit on F^2               1.041
    Final R indices [I>2sigma(I)] R1 = 0.0656, wR2 = 0.1816  [4003 Fo]
    R indices (all data)                 R1 = 0.0860, wR2 = 0.1956
    Largest diff. peak and hole          1.910 and -0.725 e.A^-3
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Table S1 : Summary of crystallographic data for [Mn(*pc3*)(H_2O)$_2$]3.H_2O.

IV- Unit cell determination of the dehydrated phase

The unit cell of the dehydrated phase has been tentatively determined using the TREOR program from the XRPD collected at 150°C under nitrogen flux (main text). Despite the poor quality of the pattern, a unit cell which is correlated to the one of the initial compound is found, showing the decreasing of two parameters, a and b, while the c parameter doesn’t change.

```
Position of lines (° 2θ)
       7.208650
        9.707850
       10.502800
       11.479400
       13.767410
       14.453670
       14.758610
       16.750259
       17.202049
       17.955030
       18.435989
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       19.131201
       19.481440
       20.477520
       21.606991
       22.698811
       23.691589
       24.415751
       25.371889
       26.388411
       26.927259
       29.701530
       31.056890
  Proposed unit cell :
   A = 19.088408  0.022803 A   ALFA = 90.000000  0.000000 DEG
   B =  9.614204  0.012613 A   BETA =114.822639  0.137194 DEG
   C = 13.483883  0.026756 A  GAMMA = 90.000000  0.000000 DEG
   UNIT CELL VOLUME =   2245.94 A**3

TOTAL NUMBER OF LINES =    23  NUMBER OF CALC. LINES =    37
    H   K   L SST-OBS  SST-CALC   DELTA   2TH-OBS 2TH-CALC D-OBS
    0   0   1 0.003956 0.003962 -0.000005    7.212   7.217 12.2466
   -2   0   1 0.007156 0.007170 -0.000014    9.705   9.715  9.1057
    1   0   1          0.008288                     10.447
    1   1   0 0.008377 0.008396 -0.000019   10.503  10.515  8.4162
   -1   1   1 0.010002 0.010008 -0.000006   11.479  11.483  7.7023
    2   1   0          0.014327                     13.749
   -2   0   2 0.014365 0.014356  0.000009   13.767  13.763  6.4270
    2   0   1 0.016423 0.016569 -0.000146   14.726  14.791  6.0109
   -3   1   1 0.021215 0.021124  0.000091   16.750  16.714  5.2886
    0   1   2 0.022366 0.022266  0.000100   17.202  17.163  5.1507
    1   0   2          0.022523                     17.263
    3   1   0 0.024351 0.024211  0.000139   17.955  17.903  4.9363
    0   2   0 0.025661 0.025678 -0.000016   18.436  18.442  4.8086
    1   2   0 0.027615 0.027654 -0.000040   19.131  19.145  4.6354
   -4   0   2 0.028625 0.028679 -0.000054   19.481  19.500  4.5529
    3   0   1          0.028803                     19.542
    4   0   0 0.031595 0.031630 -0.000035   20.478  20.489  4.3336
   -4   1   2 0.035134 0.035099  0.000036   21.607  21.596  4.1096
    3   1   1          0.035222                     21.634
   -3   1   3 0.038727 0.038720  0.000007   22.699  22.697  3.9143
   -1   2   2          0.038802                     22.721
    0   1   3 0.042139 0.042075  0.000064   23.692  23.673  3.7525
    2   2   1          0.042246                     23.722
    1   0   3 0.044715 0.044682  0.000033   24.416  24.407  3.6428
   -5   1   1          0.048054                     25.326
   -5   1   2          0.048191                     25.362
    1   2   2 0.048227 0.048201  0.000026   25.372  25.365  3.5076
   -4   2   1 0.052099 0.051870  0.000229   26.388  26.329  3.3748
   -2   0   4          0.052498                     26.491
    3   1   2 0.054209 0.054157  0.000052   26.927  26.914  3.3084
   -4   2   2          0.054357                     26.965
    3   2   1          0.054480                     26.996
    2   3   0 0.065691 0.065682  0.000009   29.702  29.699  3.0054
   -5   0   4          0.065816                     29.730
    1   3   1          0.066063                     29.787
    5   1   1 0.071672 0.071552  0.000121   31.057  31.030  2.8773
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IV- Adsorption measurements

Adsorption−desorption isotherms of H_2O, CO_2 and NH_3 on **1** were measured at 25 °C using a home-built McBain-type thermobalance. Before measurements, the samples (ca. 15 mg) were outgassed at 180 °C under vacuum (10^{-5} hPa) overnight. Then, measurement of the adsorption branch of the isotherms was started by introducing the gas into the balance, with the pressure increasing incrementally from 0.1 to 30 hPa for H_2O and up to 1000 hPa. After the introduction of each dose of adsorptive, the sample weight was measured continuously until its stabilization. The values of the pressure and weight gain at each equilibrium state were used to construct the adsorption isotherm. Once the highest pressure value had been attained, the desorption branch of the isotherm was measured by progressively decreasing the pressure. The estimated experimental error on the adsorbed amount was about 1 mg g^{-1}. The accuracy of the pressure measurement was 1%, and the temperature was maintained within 1 °C.

CO2 adsorption

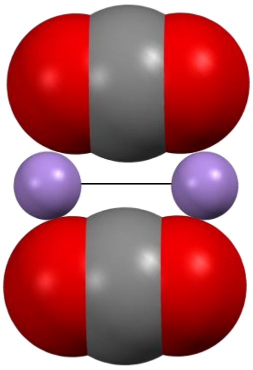

Figure S4 : Hypothetical scheme of interaction between CO_2 molecules (gray: C, red: O) and Mn^{2+} (violet) of dimeric units. The sketch is drawn to scale using the following parameters: d(Mn-Mn) = 3.5 Å, $r(Mn^{2+})$ = 0.72 Å, d(C-O) = 1.2 Å, r_{VdW}(O) = 1.52 Å.

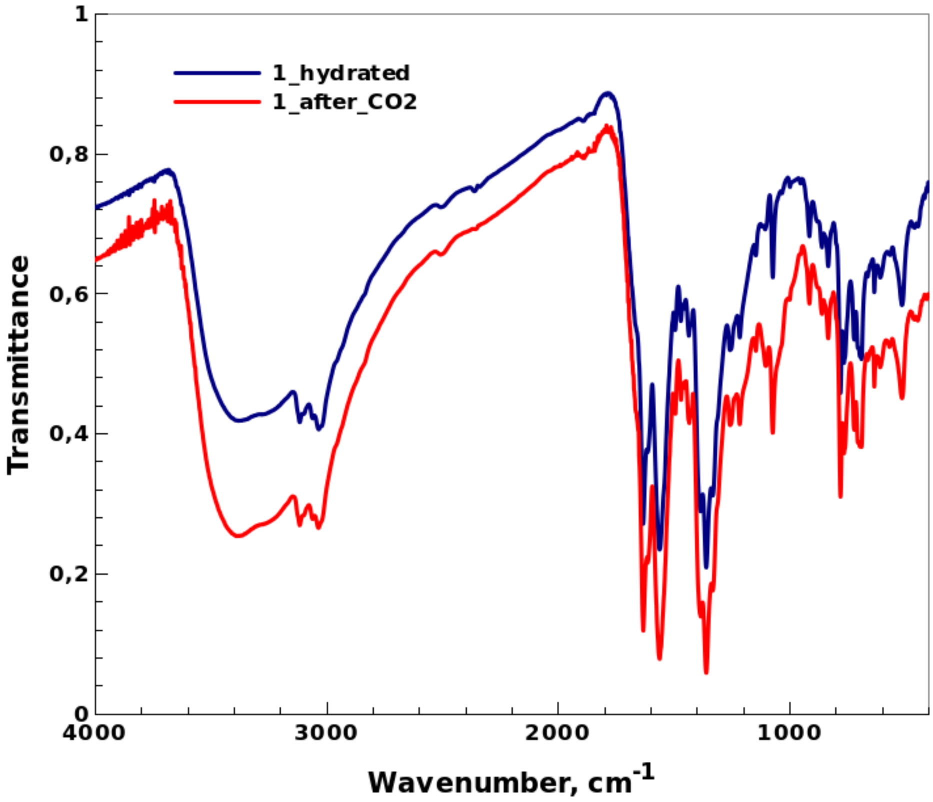

Figure S5: FTIR spectra of hydrated **1** before (blue) and after adsorption-desorption cycle of CO_2 at 298K (red). The spectra are offset by 0.1 to facilitate comparison.

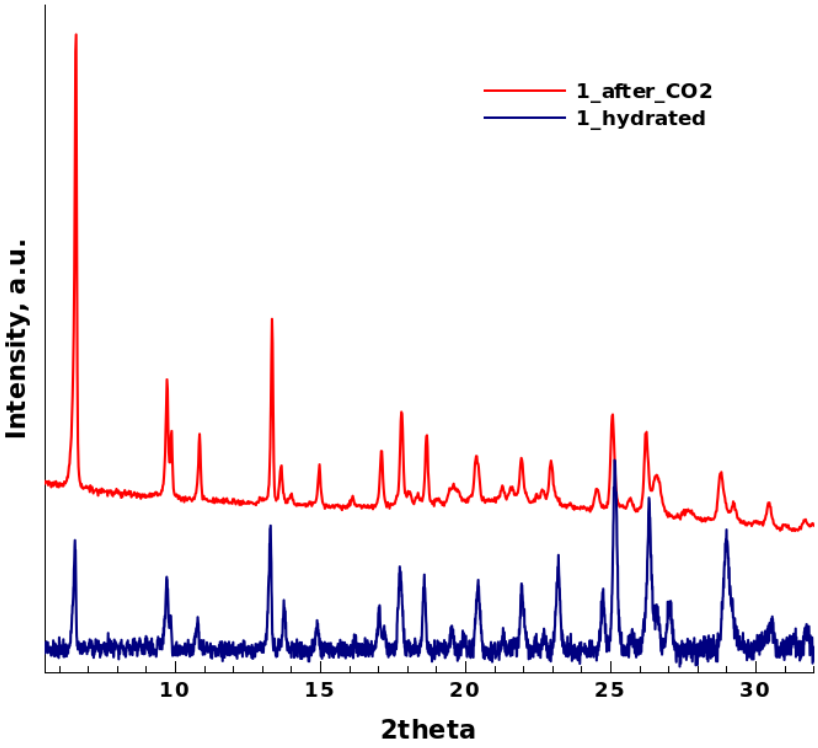

Figure S6: XRD patterns of hydrated **1** before (blue) and after adsorption-desorption cycle of CO_2 at 298K (red).

In situ PXRD of 1 in the presence of ammonia

The XRD pattern of **1** in the presence of NH_3 was recorded using the *in situ* capillary technique. To realize the measurements **1** was placed in a Pyrex capillary of 0.5 mm external diameter. The capillary was connected to a McBain thermobalance which contained the same sample in the measurement crucible. Given that both samples (inside the capillary and in the measurement crucible) were exposed to the same atmosphere at the same temperature, measuring the weight of one of them gives us the information about the amount of NH_3 adsorbed on the sample placed in the capillary. After outgassing at 180°C under a residual pressure of 10^{-5} hPa for 15 h the sample was cooled and exposed to the same atmosphere as the solid in the balance. After attaining 960 hPa the capillary was sealed off and the XRD pattern of the sample was recorded at room temperature using Cu $K\alpha_1\alpha_2$ radiation on a Bruker D8-A25 Discover diffractometer equipped with a LynxEyeXE detector.

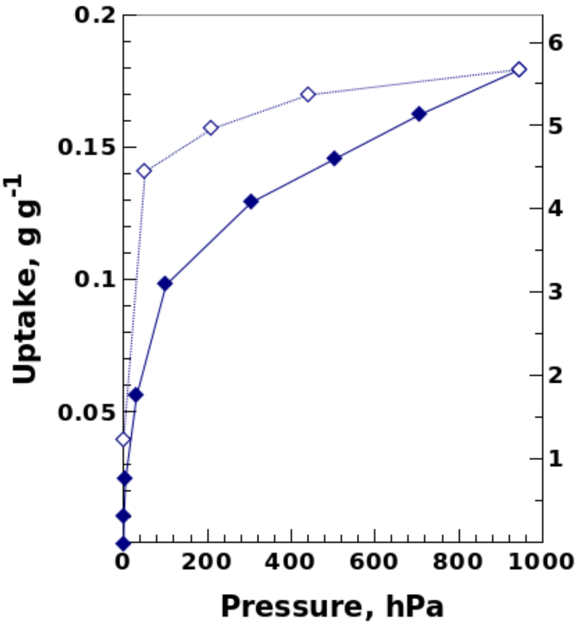

Figure S7 : Adsorption isotherm of NH_3 on **1** at 298K: full symbols – adsorption, open symbols - desorption.