Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

Polyaniline-intercalated MIL-101: selective CO_2 sorption and supercapacitor properties

Sokhrab B. Aliev, Denis G. Samsonenko, Evgeny A. Maksimovskiy, Ekaterina O. Fedorovskaya, Sergey A. Sapchenko and Vladimir P. Fedin

Table S1. Adsorption characteristics of selected Cr-MOFs and MOFs with -N and -O sites

Compounds	BET surface area, m^2/g	CO_2 uptake, mmol/g	T, K	Selectivity CO_2/N_2	Ref.
MIL-101(Cr)	3500	2.90	288	12	1
DETA@MIL-101(Cr)	1560	0.97	273	–	2
Ag@MIL-101(Cr)	1417	1.4	298	–	3
PEI@MIL-101(Cr)-NH_2	947	3.5	298	–	4
MIL-101(Cr)-pNO_2	2195	2.76	273	15	5
MIL-101(Cr)-pNO_2	2195	1.66	298	24	
MIL-101(Cr)-NH_2	2687	5	273	73	
MIL-101(Cr)-NH_2	2687	3.6	293	100	
mmen-Cu-BTTri	870	3.49	298	165	6
Mg_2(dobdc)	1470	8.00	303	44	7
bio-MOF-11	1040	3.44	298	45	8

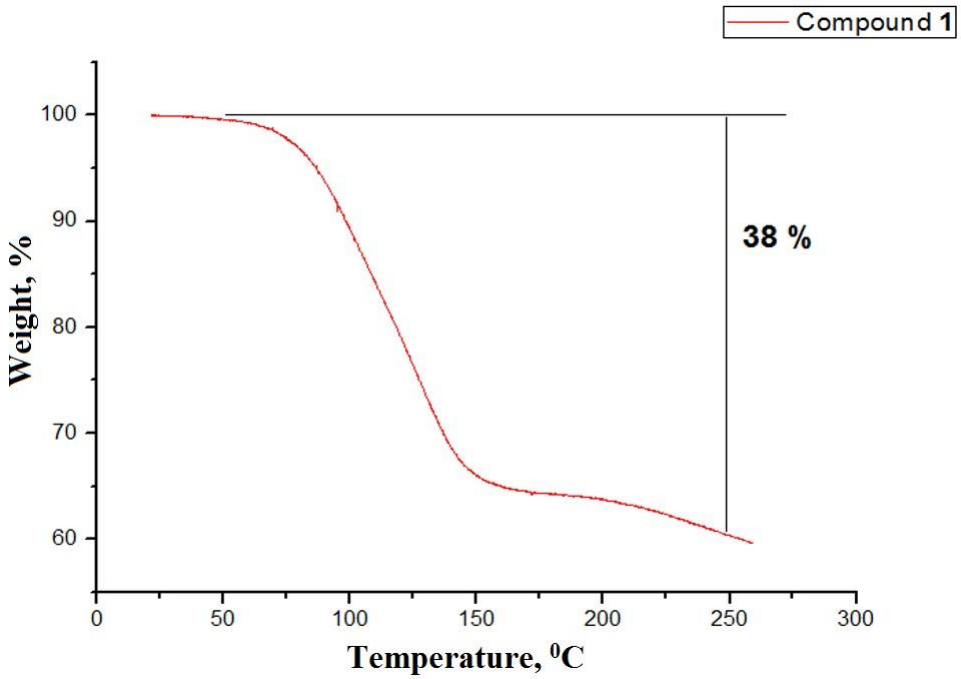


Fig. S1 TG plot of the compound **1**

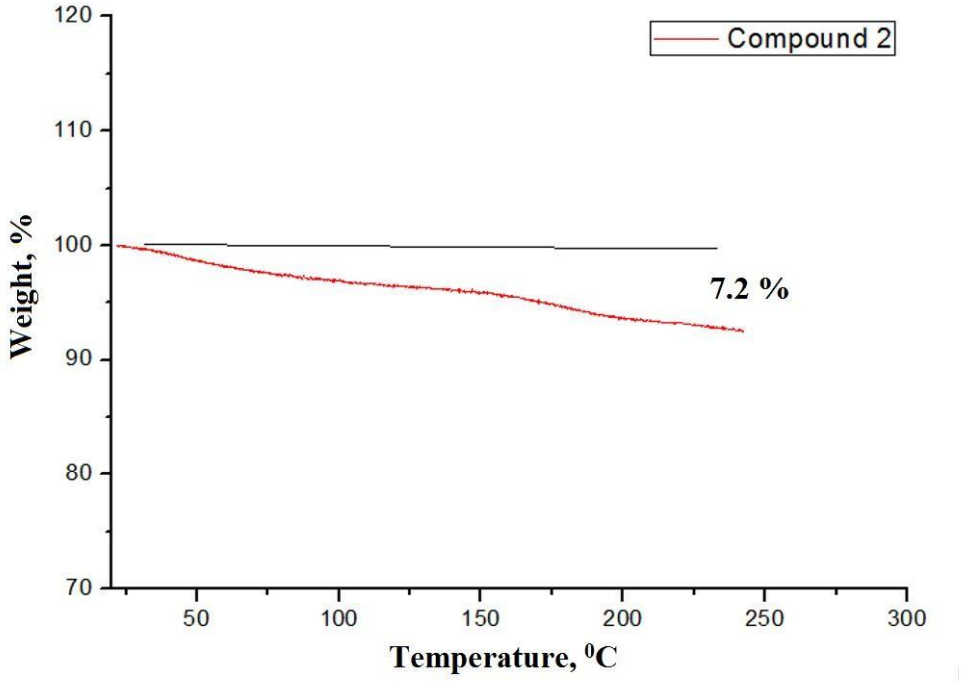


Fig. S2 TG plot of the compound **2**

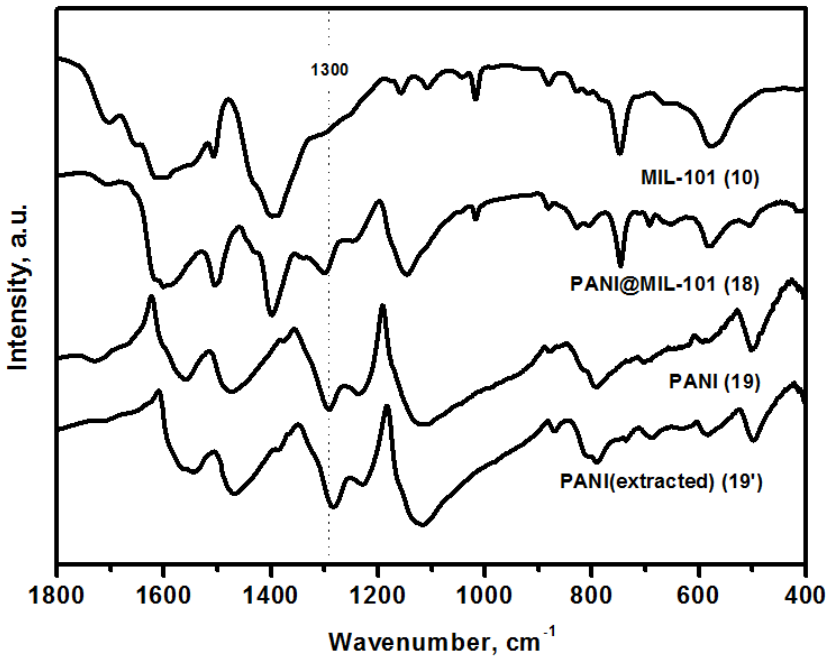


Fig. S3 IR spectra of MIL-101, PANI@MIL-101 , PANI(pristine) and PANI extracted from PANI@MIL-101 channels.

PANI molecular weight measurements:

Four solutions with different concentrations of PANI were prepared by the dissolving the extracted PANI in concentrated sulfuric acid and the viscosimetric technique was used. The reduced viscosities (η) of these samples were determined at 25°C using an Ubbelohde viscometer according to the equation:

$$\eta = \frac{t - t^0}{ct^0},$$

where t^0 is the dripple time of a pure sulfuric acid, t is the dripple time for a polyaniline solution of a known concentration c (g/dL). η was then plotted versus the polyaniline concentration. The linear extrapolation of the plot to zero concentration revealed the value of $[\eta]$ = 0.479 dL/g (Fig. S4, S5**)**.

Average molecular weights for incapsulated and free PANI were calculated using the Mark–Houwink equation:

$$[\eta] = K M^{\alpha}$$

with constants $K = 1.95 \cdot 10^{-6}$ and $\alpha = 1.36$ for PANI [9].

The average molecular weight of the extracted PANI was found to be 9176 Da (Fig. S6**)**. This value corresponds to the average chain length of 101 aniline monomers. Same operations were performed for pristine PANI, the molecular weight was 9990 Da and corresponded to the chain length of ca. 110 aniline monomers.

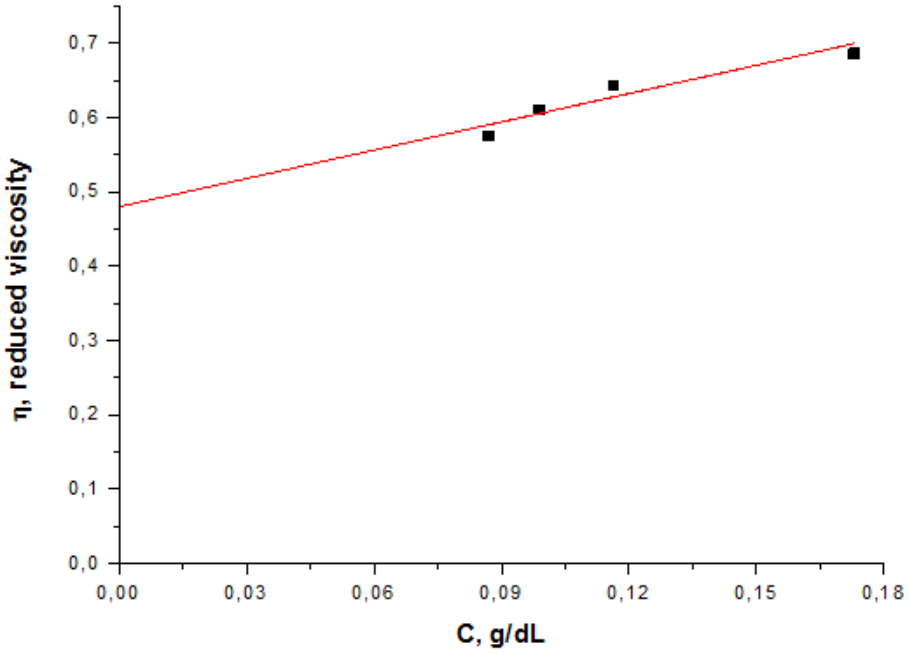


Fig. S4 Dependence of reduced viscosity on concentration of PANI extracted from **2** in sulfuric acid solution

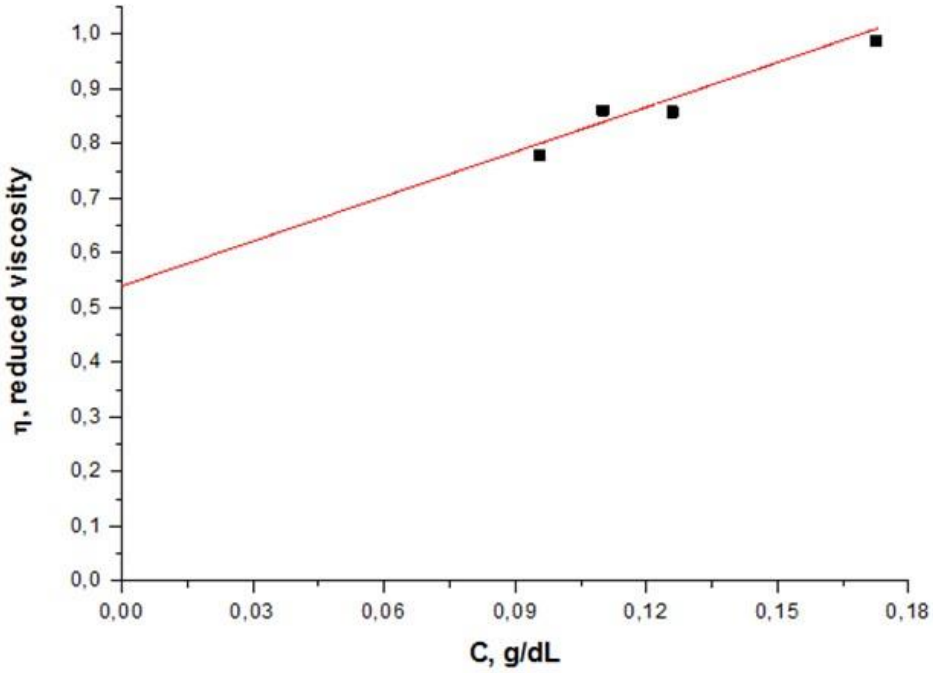
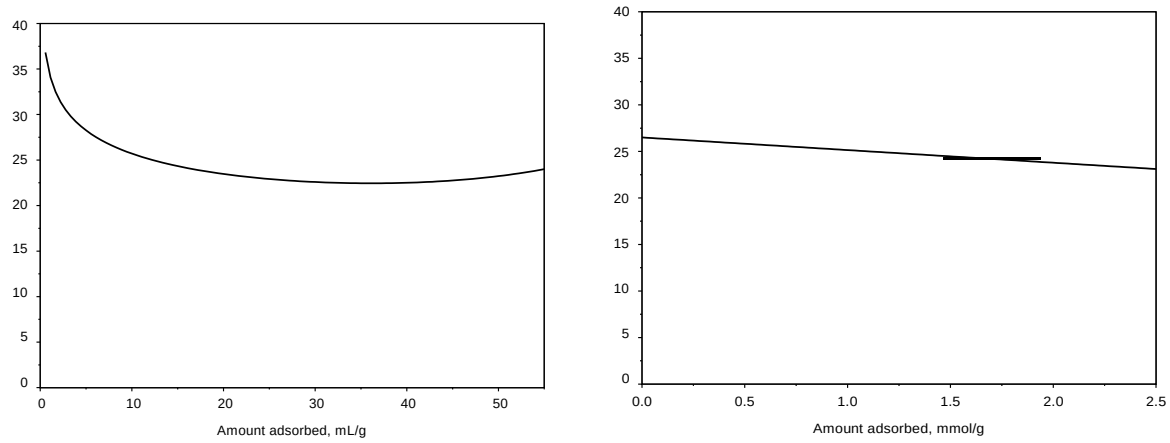


Fig. S5 Dependence of reduced viscosity on concentration of PANI obtained in a free form in sulfuric acid solution



a) b)

Fig. S6 Adsorption enthalpies of CO_2 for compound **2** as functions of gravimetric uptake. calculated from (a) Clausius–Clapeyron relation. (b) virial equation of state

Enthalpy Calculations

a) Adsorption enthalpies calculated by fitting the sorption plots at 273 and 293 K with Clausius–Clapeyron relation

$$\frac{\omega}{\omega_m} = \frac{BP^{1/t}}{1+BP^{1/t}},$$

where ω –adsorbed amount of CO_2, ω_m –adsorbed amount of CO_2 at saturation, P – pressure, B and t are constants.

The found parameters for both isotherms:

ω_{m1} = 109.921 ± 2.267 (2.062%)

B_1 = 0.00373906 ± $4.812\cdot10^{-5}$ (1.287%)

t_1 = 1.24985 ± 0.0102 (0.8158%)

ω_{m2} = 92.0159 ± 3.25 (3.532%)

B_2 = 0.00162636 ± $2.803\cdot10^{-5}$ (1.723%)

T_2 = 1.13076 ± 0.01212 (1.072%)

The enthalpy of sorption can be calculated according to the formula:

$$\Delta H_{ads} = R\frac{T_1T_2}{T_2 - T_1} ln\frac{P_1}{P_2}$$

where T_1=273 K, T_2=293 K, and pressure P was calculated by the formula:

$$P = \left(\frac{\frac{\omega}{\omega_m}}{B - B\frac{\omega}{\omega_m}} \right)^t$$

b) Adsorption enthalpies calculated by fitting the sorption plots with the virial equation of state

$\ln p(n,T) = \ln n + (a_0 + a_1 \cdot n)/T + b_0$,

where p is pressure (normalized to p_0=1 atm), n is coverage (mol g^{-1}), T is temperature, and a_i and b_i are temperature independent empirical parameters. Their values are given below:

a_0 = −3187.47 ± 55.16 (1.731%)

a_1 = 163.268 ± 3.158 (1.934%)

b_0 = 9.71839 ± 0.1929 (1.985%).

The isosteric heat of adsorption was determined as a function of coverage:

Qst = $-R(a_0 + a_1 n)$.

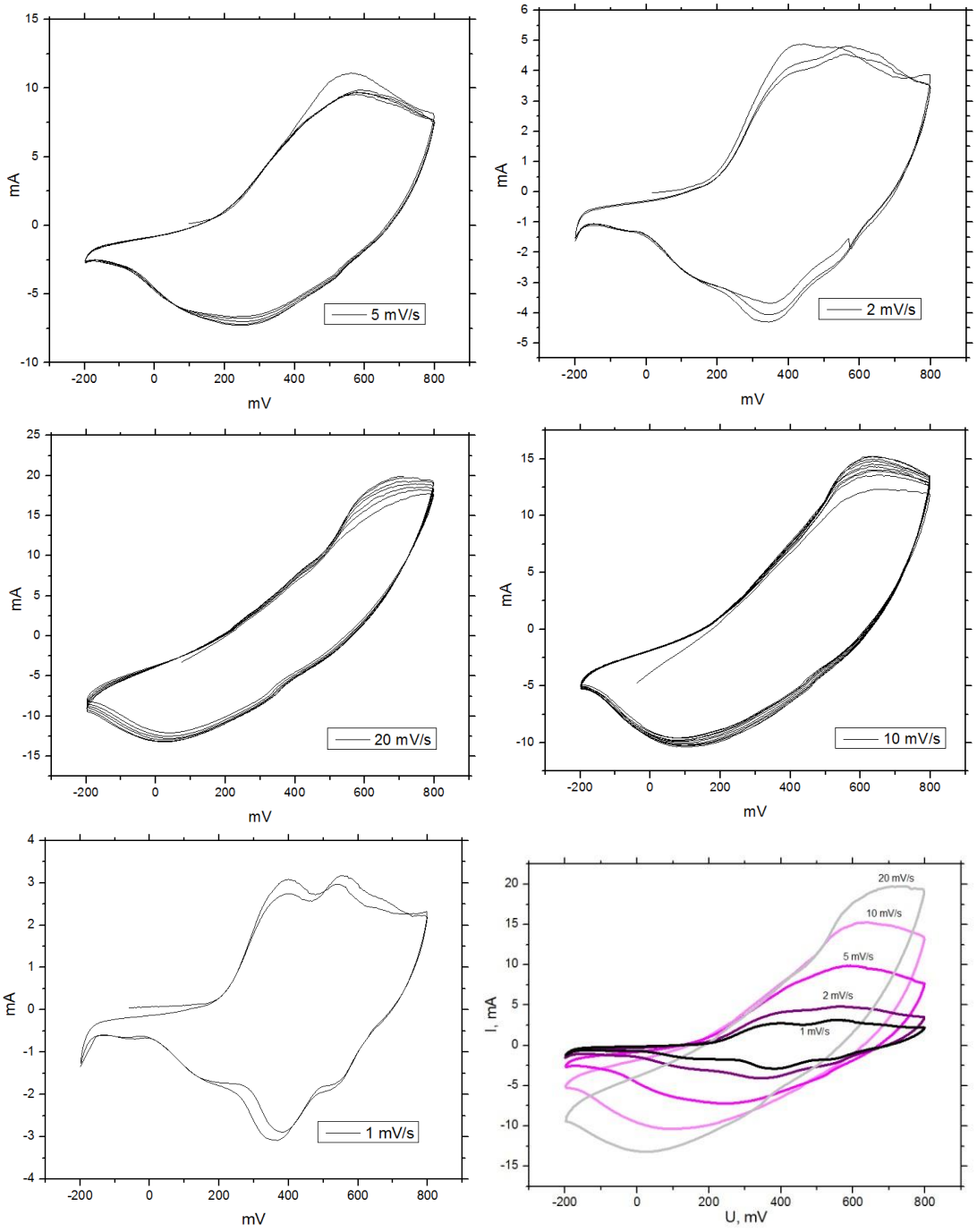


Fig. S7 Cyclic voltammograms of **2** measured at 20, 10, 5, 2 and 1 mV/s rates of the potential scan

References

1. K. Munusamy, G. Sethia, D. V. Patil, P. B. S. Rallapalli, R. S. Somani and H. C. Bajaj, *Chem. Eng. J.*, 2012, **195-196**, 359.
2. S. Kim, S. Yang, J. Kim, J. Park and W. Ahn, *Cryst. Eng. Comm*, 2012, **14**, 4142.
3. X. Liu, J. Ma, Z. Niu, G. Yang and P. Cheng, *Angew. Chem. Int. Ed.*, 2014, **54**, 988.
4. Q. Xin, J. Ouyang, T. Liu, Z. Li, Z. Li, Y. Liu, S. Wang, H. Wu, Z. Jiang and X. Cao, *ACS Appl. Mater. Interfaces*, 2015, **7**, 1065.
5. A. Khutia and C. Janiak, *Dalton Trans.*, 2014, **43**, 1338.
6. T. M. McDonald, D. M. D'Alessandro, R. Krishna and J. R. Long, *Chem. Sci.*, 2011, **2**, 2022.
7. S. R. Caskey, A. G. Wong-Foy and Adam J. Matzger, *J. Am. Chem. Soc.*, 2008, **130**, 10870.
8. J. An, S. J. Geib and N. L. Rosi, *J. Am. Chem. Soc.*, 2010, **132**, 38.
9. S. C. Hobaica, *J. Polym. Sci.: Polym. Phys.*, 2003, **41**, 807.