Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information (SI):

1. Structure of MIL-101(Cr) framework:

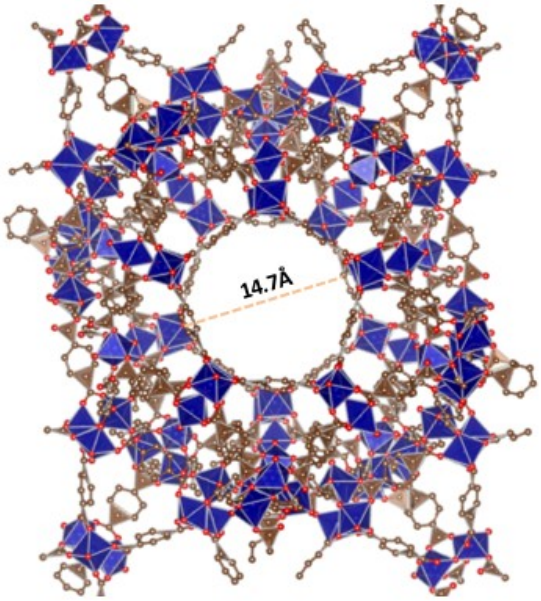

Fig. 1s. Schematic of MIL-101(Cr) framework

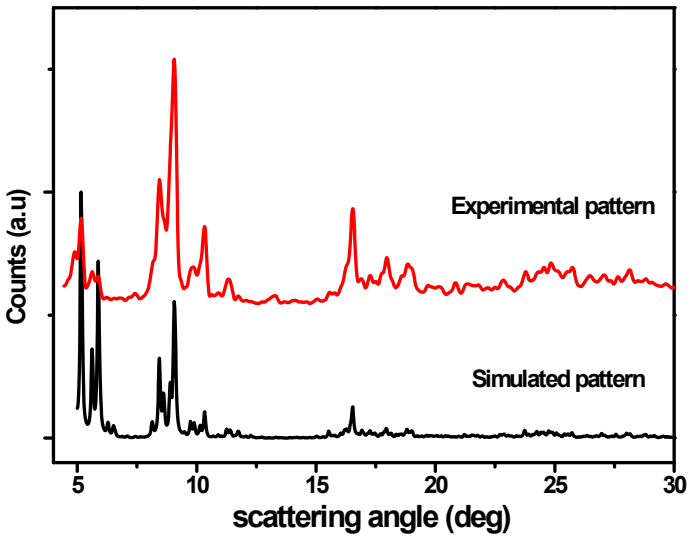

Fig. 2s: Powder X-ray diffraction pattern of the bare MIL-101(Cr) framework and comparison with the simulated pattern (Cu-Kα radiation) at room temperature.

2. Pore size of MIL-101(Cr) framework:

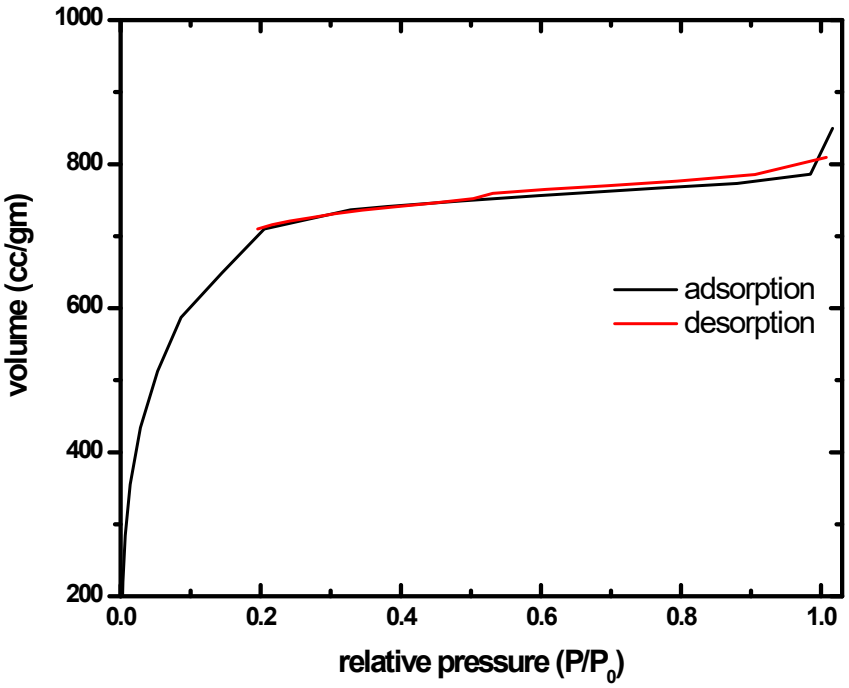

Fig.3s. BET nitrogen gas adsorption-desorption isotherm in MIL-101(Cr) framework.

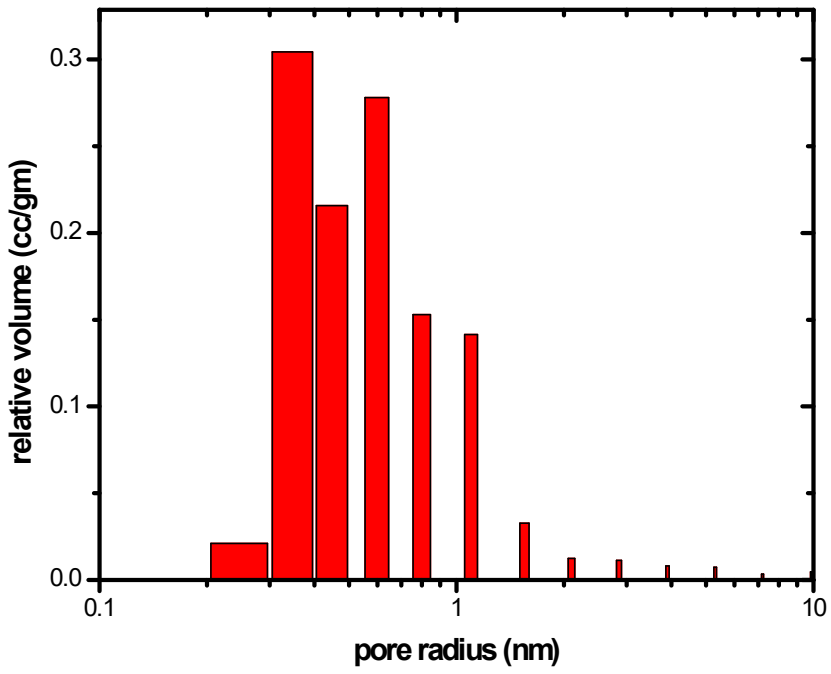

Fig 4s: Pore radius distribution in MIL-101(Cr) framework as obtained from BJH method in the desorption branch of BET nitrogen adsorption-desorption isotherm.

3. Variable energy positron annihilation spectroscopic result:

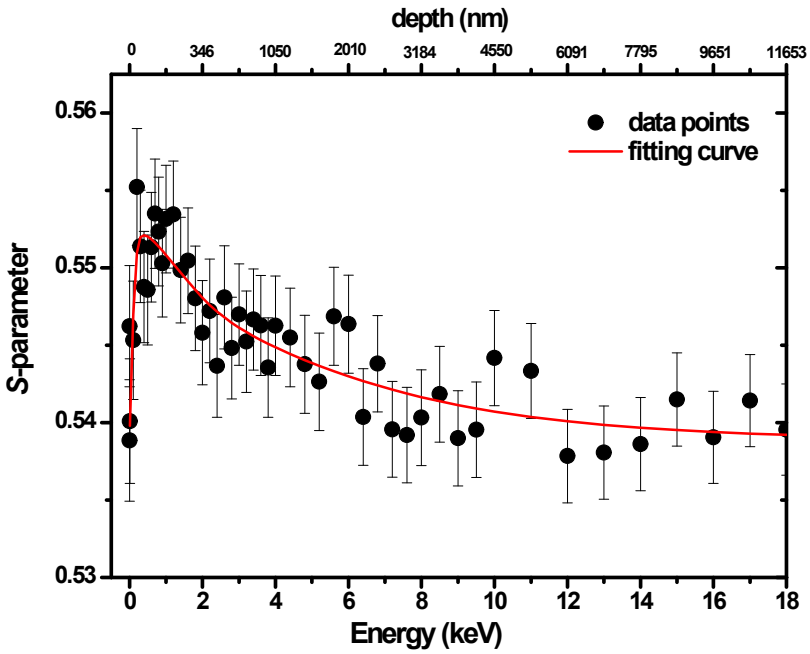

Fig 5s. Depth profile of *S*-parameter (*S*-*E* profile) of MIL-101(Cr) film deposited on Si-substrate. The solid line shows the fitting of *S*-*E* profile using VEPFIT analysis program. The estimated diffusion length of positronium (pore-interconnection length) by fitting the experimental data is found 130±30 nm.

4. MIL-101(Cr) structure before and after water adsorption:

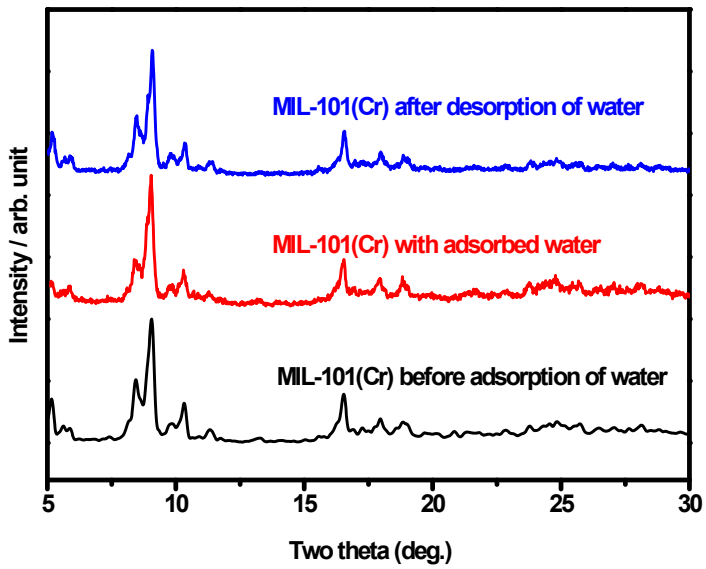

Fig. 6s: Comparison of XRD pattern of MIL-101(Cr) before and after water adsorption and desorption. The comparison shows that the structure of MIL-101(Cr) framework remains unchanged after adsorption and desorption of water.

4. Estimation of volume fraction of water monolayer inside the pore

Van der Waals radius of water molecule: 1.7Å [1].

Cross sectional area of water molecule =9.08 $Å^2$

The specific pore surface area (from BET) of MIL-101=2564 m^2/gm

Total number of water molecules to cover the pore surface=2564 X 10^{20}/ 9.08 =280.4 X 10^{20}

Weight of monolayer water= 280.4 X 10^{20} X 18/(6.023 X10^{23})

=840 X 10^{-3} gm

=0.84gm

Volume of this amount of water=0.84cc

Specific pore volume (from BET) of MIL-101=1.21cc/gm

Volume fraction of monolayer water w.r.t. the pore volume=(0.84/1.21)X 100

=70%

Ref:

[1]. A. J. Li and R. Nussinov R. **Proteins,** 1998, **32(1)**:111-27. PMID: 9672047