Supporting Information

Flexible Chiral Pyrazolate-Based Metal-Organic Framework containing saddle-type Cu^{I}_{4}(pyrazolate)$_4$ units

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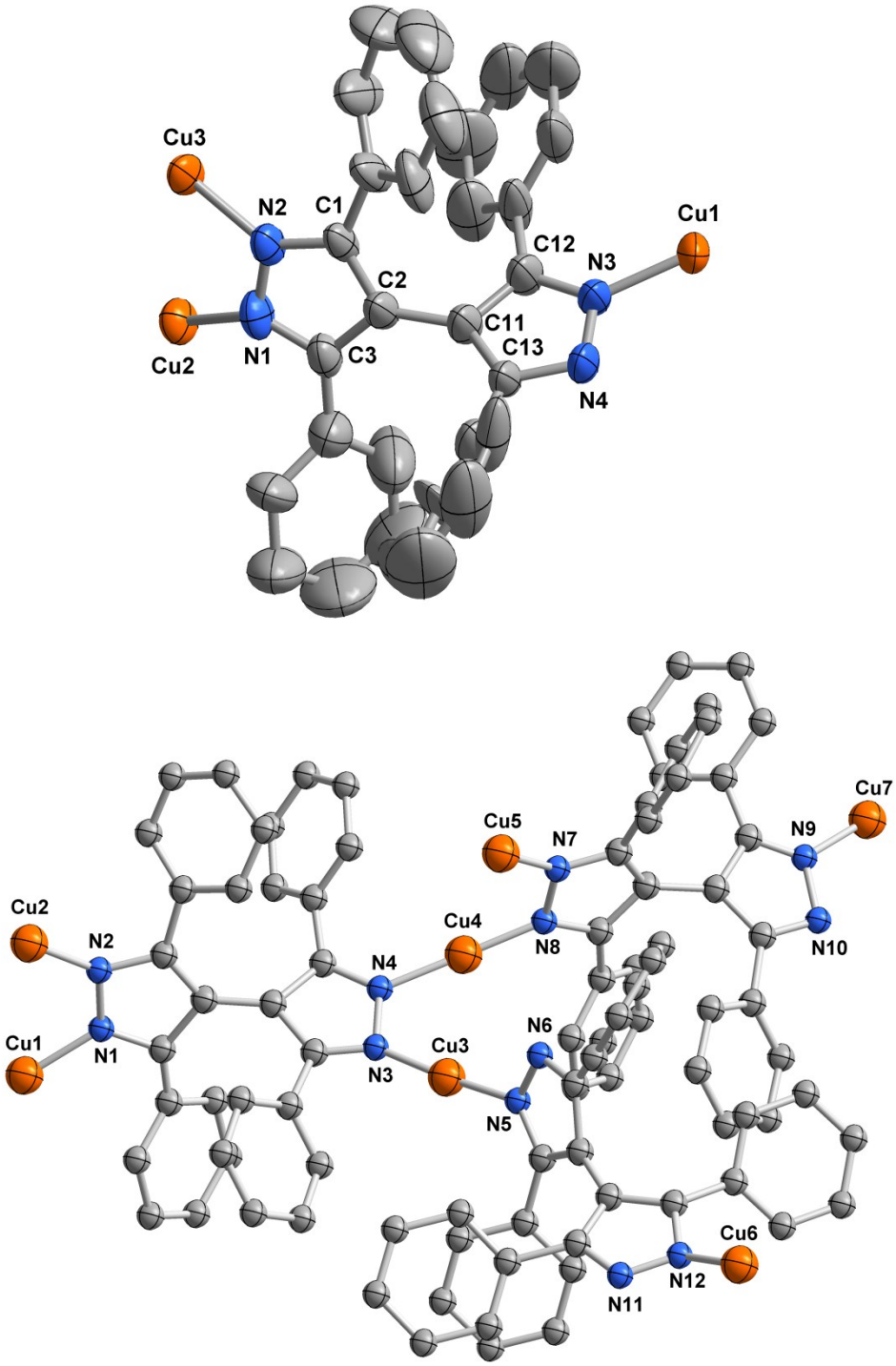

Fig. S1 Ortep-style plot of the asymmetric units of **lp-CFA-9** (top) and **np-CFA-9** (bottom). Thermal ellipsoids probability: 50 %. Hydrogen atoms and disordered carbon atoms from phenyl groups are omitted for clarity.

Table S1. Selected bond distances in **lp-** and **np-CFA-9**.

Bond	**lp-CFA-9**	Bond	**np-CFA-9**
Cu1-N3	1.840(3)	Cu1-N1	1.859(12)
Cu1-N3[a]	1.840(3)	Cu1-N11[d]	1.916(13)
Cu2-N1	1.861(3)	Cu2-N2	1.775(16)
Cu2-N1[b]	1.861(3)	Cu2-N2[d]	1.775(16)
Cu3-N4[c]	1.838(4)	Cu3-N3	1.774(15)
Cu3-N2	1.847(3)	Cu3-N5	1.799(14)
		Cu4-N8	1.800(14)
		Cu4-N4	1.872(14)
		Cu5-N10[e]	1.819(13)
		Cu5-N7	1.828(12)
		Cu6-N12[f]	1.825(14)
		Cu6-N12	1.825(14)
		Cu7-N6[g]	1.861(13)
		Cu7-N9	1.896(12)
		N6-Cu7[e]	1.861(13)
		N10-Cu5[g]	1.819(13)
		N11-Cu1[h]	1.916(13)

Symmetry transformations used to generate equivalent atoms:

[a]x-y+1,-y+2,-z+4/3; [b]y,x,-z+2; [c]-x+1,-x+y,-z+5/3; [d] -x+1/2,y+1/2,-z; [e] -x,-y+1,z [f] x-1/2,-y+1/2,-z+1; [g] x+1/2,-y+1/2,-z+1; [h]-x+1/2,y-1/2,-z

Topology analysis with TOPOS program.[2]

lp_CFA-9

3:C31 H24 Cu2 N4 O/intercluster bonds and atoms at rings>5
##
Topology for Sc1

Atom Sc1 links by bridge ligands and has
Common vertex with R(A-A)
Sc 1 1.0000 0.5260 0.3333 (1 1 0) 10.661A 1
Sc 1 0.0000 0.5260 0.3333 (0 1 0) 10.661A 1
Sc 1 0.5260 0.0000 -0.3333 (1 0-1) 10.661A 1
Sc 1 0.5260 1.0000 -0.3333 (1 1-1) 10.661A 1

Structural group analysis

Structural group No 1

Structure consists of 3D framework with Sc
Coordination sequences

Sc1: 1 2 3 4 5 6 7 8 9 10
Num 4 12 30 52 80 116 156 204 258 318

[2] V. A. Blatov, IUCr CompComm Newsletter, 2006, **7**, 4–38.

Cum 5 17 47 99 179 295 451 655 913 1231

TD10=1231
Vertex symbols for selected sublattice

Sc1 Point symbol:{6^4.8^2}
Extended point symbol:[6.6.6(2).6(2).8(9).8(9)]

Point symbol for net: {6^4.8^2}
4-c net; uninodal net
Topological type: qtz Quartz; 4/6/h1 (topos&RCSR.ttd) {6^4.8^2} - VS [6.6.6(2).6(2).8(7).8(7)] (61079 types in 9 databases)
Elapsed time: 9.36 sec.

np-CFA9

##########
4:C30 H20 Cu2 N4/intercluster bonds and atoms at rings>5
##########
Topology for Sc1

Atom Sc1 links by bridge ligands and has

Common vertex with				R(A-A)	
Sc 2	-0.3834	0.7072	0.3475	(0 1 0)	10.009A 1
Sc 2	0.3834	0.2928	0.3475	(0 0 0)	10.009A 1
Sc 2	-0.1166	0.2072	-0.3475	(-1 0 0)	11.270A 1
Sc 2	0.1166	0.7928	-0.3475	(0 0 0)	11.270A 1

Topology for Sc2

Atom Sc2 links by bridge ligands and has

Common vertex with				R(A-A)	
Sc 1	0.0000	0.5000	0.0940	(0 0 0)	10.009A 1
Sc 2	-0.1166	0.2072	0.6525	(-1 0 1)	10.660A 1
Sc 2	0.8834	0.2072	0.6525	(0 0 1)	10.660A 1
Sc 1	0.5000	0.0000	-0.0940	(0 0 0)	11.270A 1

Structural group analysis

Structural group No 1

Structure consists of 3D framework with Sc

Coordination sequences

Sc1: 1 2 3 4 5 6 7 8 9 10
Num 4 12 30 52 80 116 156 204 258 318
Cum 5 17 47 99 179 295 451 655 913 1231

Sc2: 1 2 3 4 5 6 7 8 9 10
Num 4 12 30 52 80 116 156 204 258 318
Cum 5 17 47 99 179 295 451 655 913 1231

TD10=1231

Vertex symbols for selected sublattice

Sc1 Point symbol:{6^4.8^2}
Extended point symbol:[6.6.6(2).6(2).8(9).8(9)]

Sc2 Point symbol:{6^4.8^2}
Extended point symbol:[6.6.6(2).6(2).8(9).8(9)]

Point symbol for net: {6^4.8^2}
4-c net; uninodal net

Topological type: qtz Quartz; 4/6/h1 (topos&RCSR.ttd) {6^4.8^2} - VS [6.6.6(2).6(2).8(7).8(7)] (61079 types in 9 databases)
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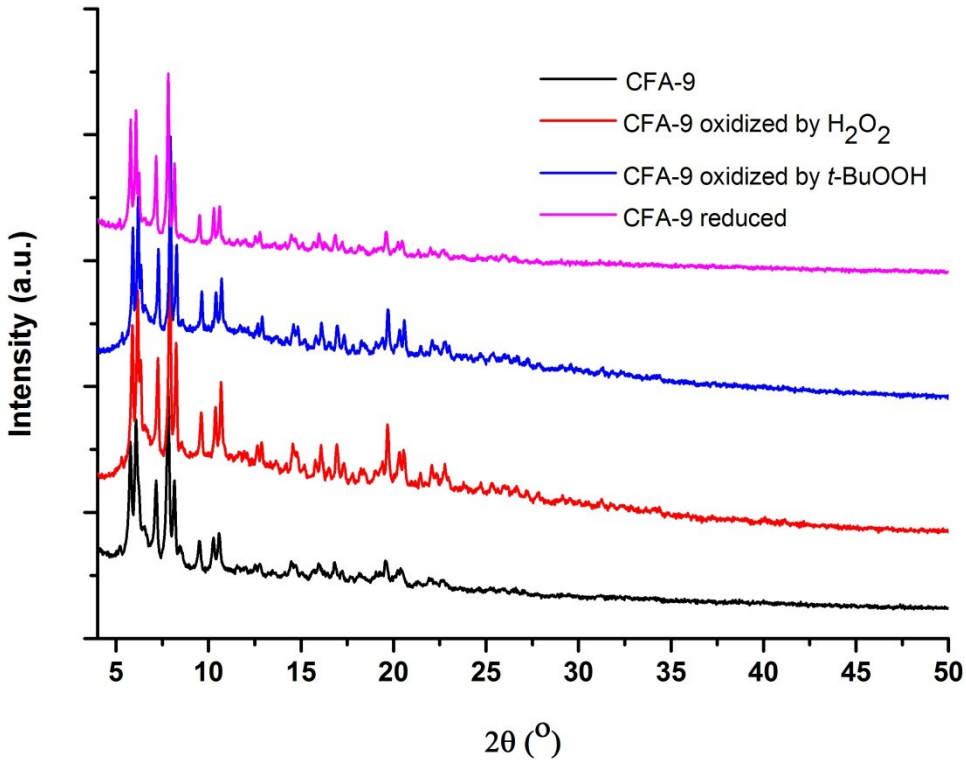

Fig. S2 XRPD patterns of **CFA-9**: black line – **CFA-9**, red – **CFA-9** oxidized by H_2O_2, blue – oxidized by *t*-BuOOH, magenta- **CFA-9** reduced by heating in DMF at 120 °C during 4 hours.

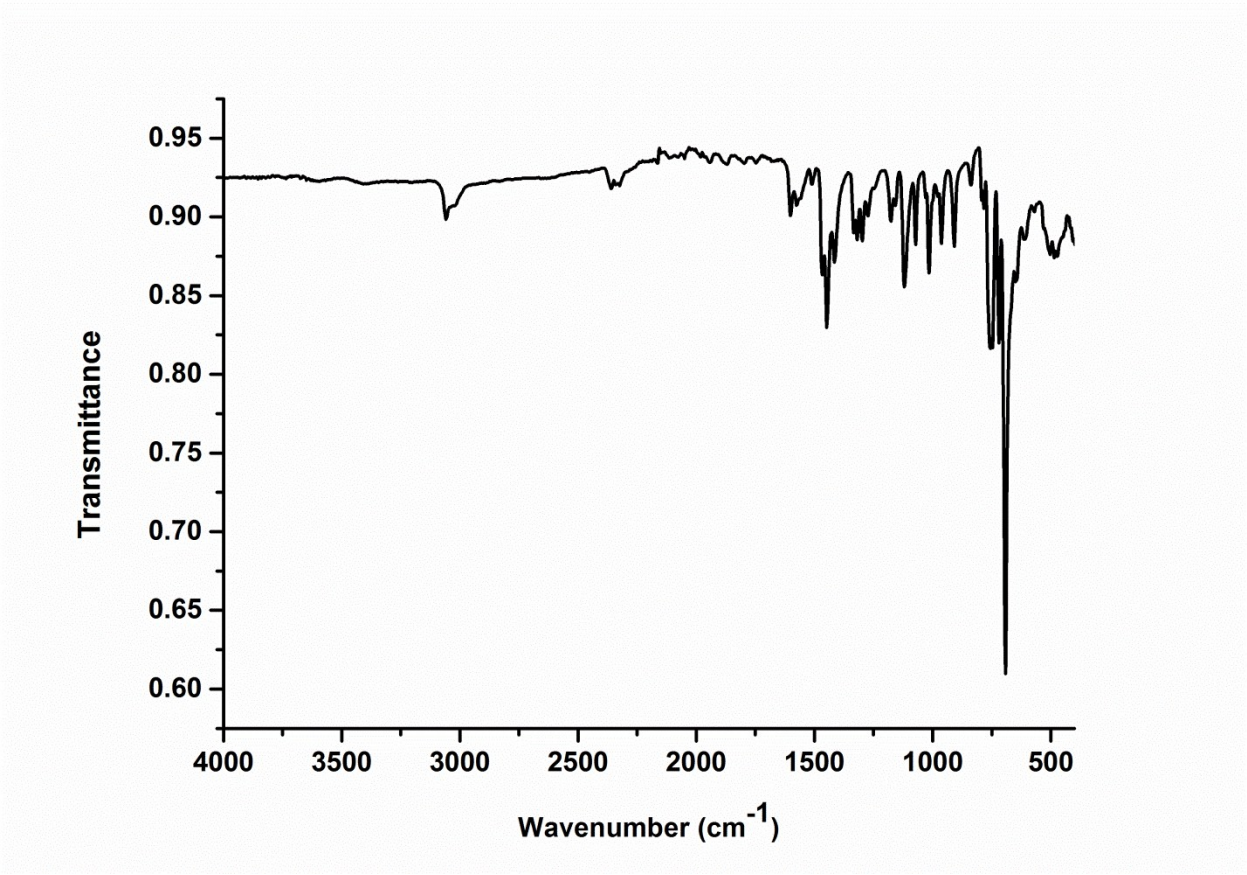

Fig. S3 IR spectrum of **CFA-9**.

Gas sorption measurements

The isosteric heats of adsorption were calculated from the measured isotherms (Fig. S 5-6) using the Clausius-Clapeyron equation (**I**). The slopes of linear plots ln P versus 1/RT for different loadings (Fig. S 7-8) give the adsorption enthalpies, according to the equation (**II**).

$$Q_{st} = -R\left(\frac{\partial(\ln P)}{\partial(1/T)}\right)_{\theta}$$ (**I**), Θ – surface coverage

$$\ln P = -\frac{Q_{st}}{R}\left(\frac{1}{T}\right) + C$$ (**II**), C – integration constant

The isosteric heat of O_2 adsorption at zero limit surface coverage (initial heat of adsorption) has been determined using Henry's constants K_H, obtained as a slope from the linear ranges of isotherms at low pressure (Table S2 and Fig. S9). In this range the dependence of amount adsorbed (n) on the pressure can be expressed with Henry's law (**III**). The initial isosteric heat of adsorption can be obtained in a similar way by using the Clausius-Clapeyron equation (**IV**) (Fig. S10).

$n = K_H \bullet P$ (**III**)

$$\lim_{n\to 0}(Q_{st}) = Q_{st}^0 = R\left(\frac{\partial(\ln K_H)}{\partial(1/T)}\right) \quad \textbf{(IV)}$$

Table S2. Henry's constants for O_2 adsorption on **CFA-9**, $cm^3\ g^{-1}\ kPa^{-1}$

T / K	163	173	183	193
K_H	1.2192	0.6277	0.3548	0.2076

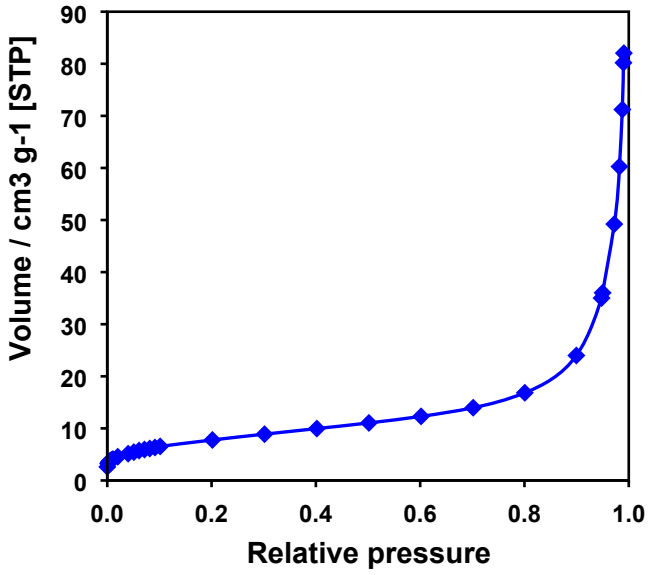

Fig. S4 Argon adsorption isotherm at 87.3 K for **CFA-9**.

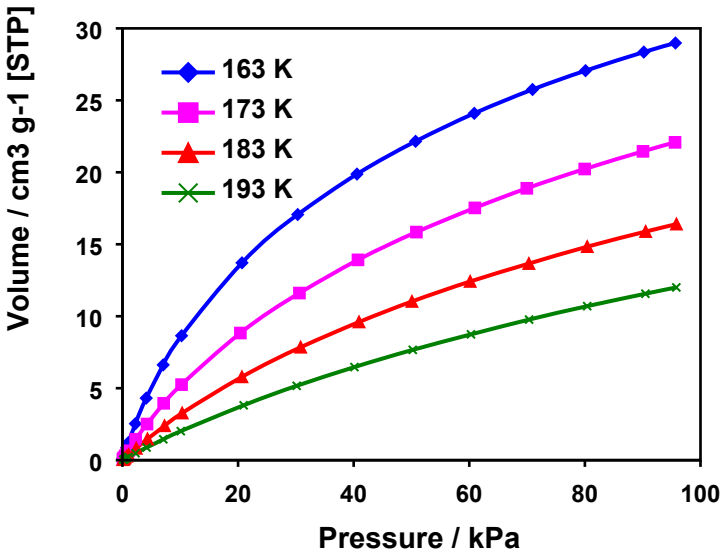

Fig. S5 O_2 adsorption isotherms for **CFA-9** at different temperatures for the determination of the isosteric heat of adsorption.

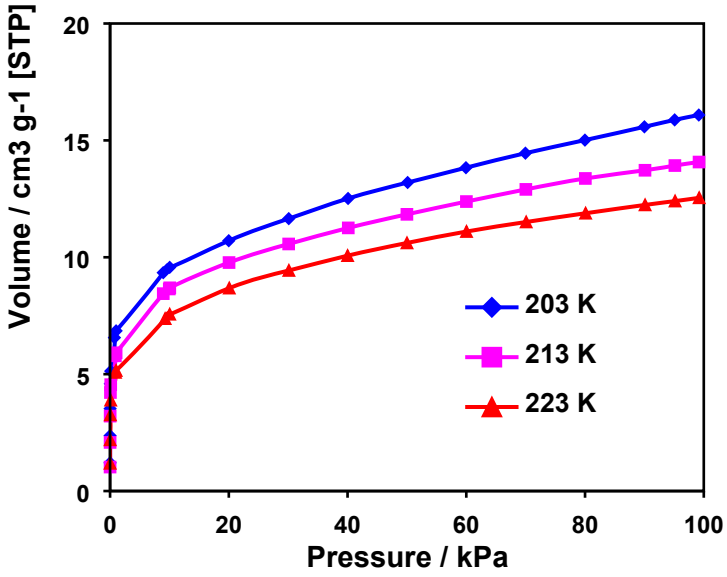

Fig. S6 CO adsorption isotherms for **CFA-9** at different temperatures for the determination of the isosteric heat of adsorption.

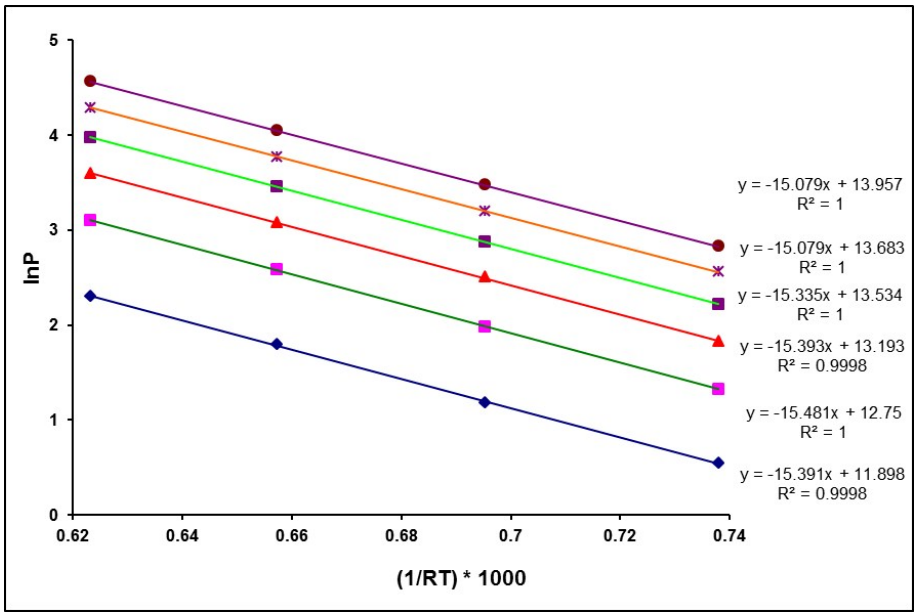

Fig. S7 ln P versus 1/RT plots for different loadings for O_2 adsorption on **CFA-9**.

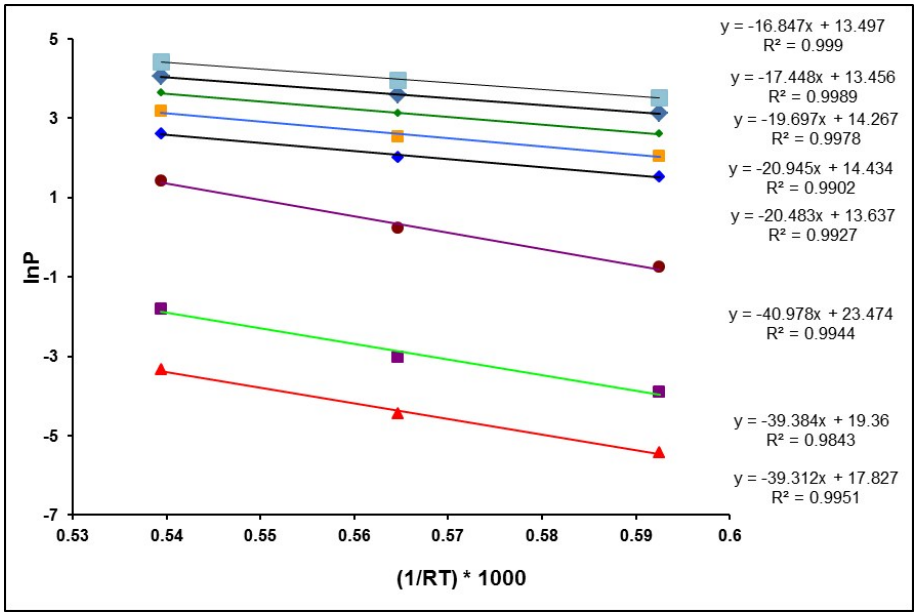

Fig. S8 ln P versus 1/RT plots for different loadings for CO adsorption on **CFA-9**.

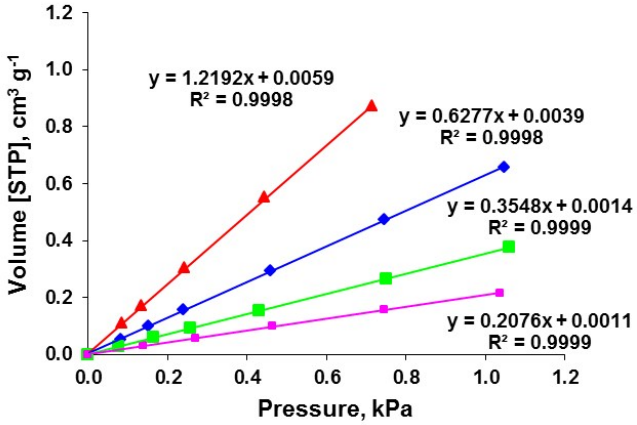

Fig. S9 Determination of Henry's constants for O_2 adsorption on **CFA-9**.

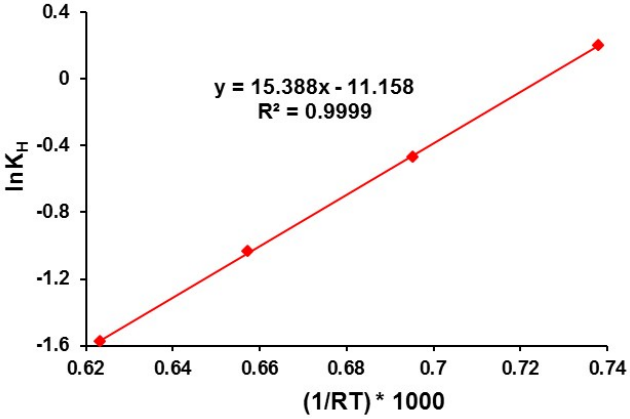

Fig. S10 $\ln K_H$ versus 1/RT plots for O_2 adsorption on **CFA-9**.