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Пористые координационные полимеры: от синтеза и структуры к функциональным свойствам

ИНХ СО РАН

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ПЛАН ЛЕКЦИИ

1) Ведение
2) MOFs для сорбции и разделения
3) MOFs как сенсоры
4) MOFs для энантиоселективного разделения
5) Материалы с высокой протонной проводимостью
6) Заключение

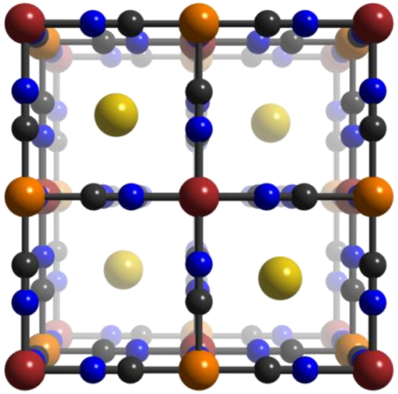
Координационные полимеры

Соединения с координационными связями металл-лиганд, в которых атомы металлов связаны мостиковыми лигандами с образованием регулярной структуры.

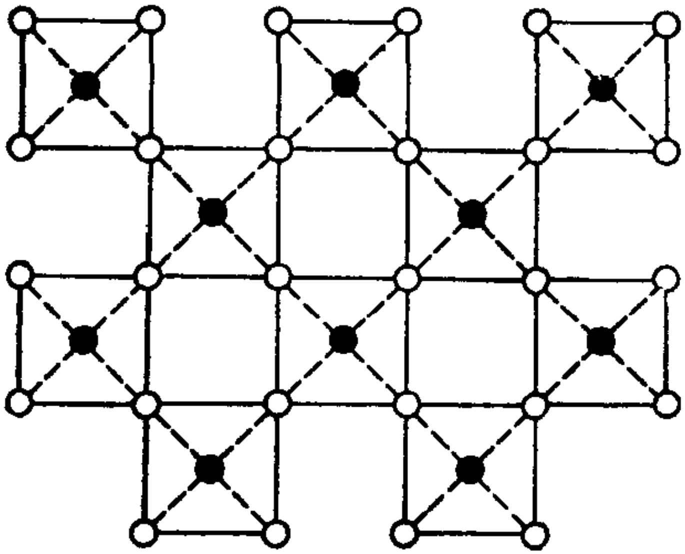
AgCN

… →Ag–C≡N→ Ag–C≡N →Ag–C≡N →

$KFe[Fe(CN)_6]$

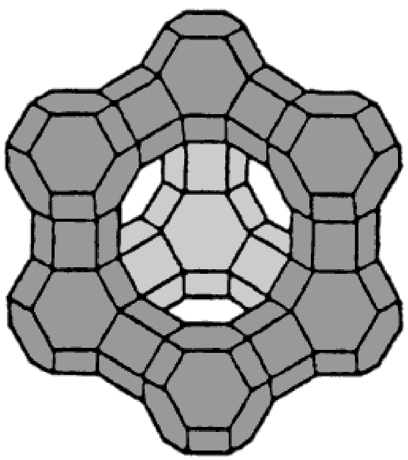


$Pd(CN)_2$

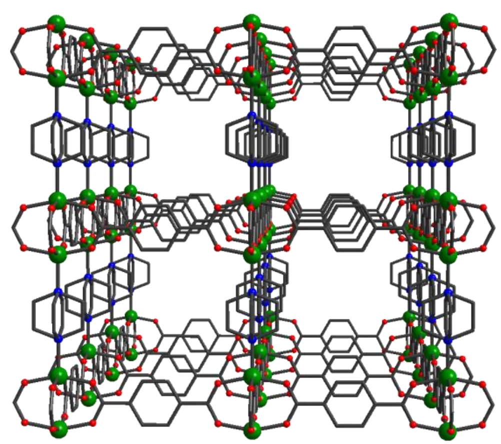


Питер ван дер Верфф, Погребение Христа (1709)

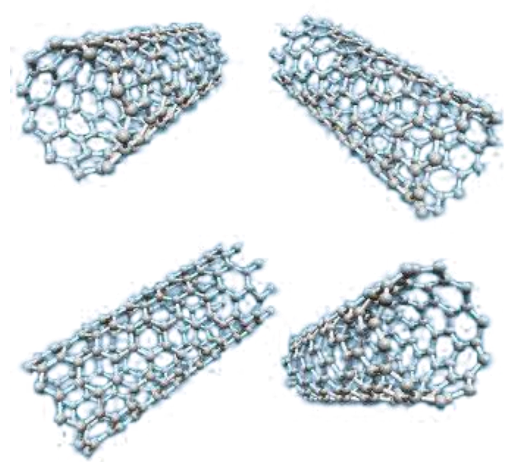
Примеры пористых материалов



Zeolites



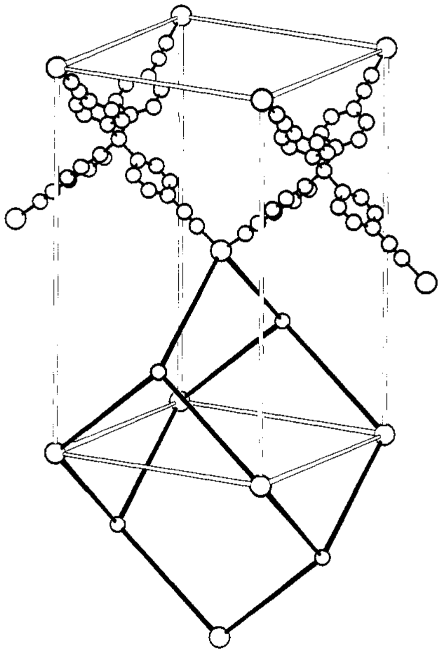
Metal-Organic Frameworks, MOFs



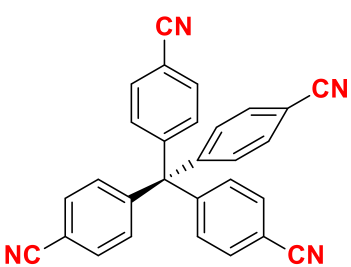
Nanocarbons

История MOF

Hoskins B.F., Robson R.,
J. Am. Chem. Soc. **1989**

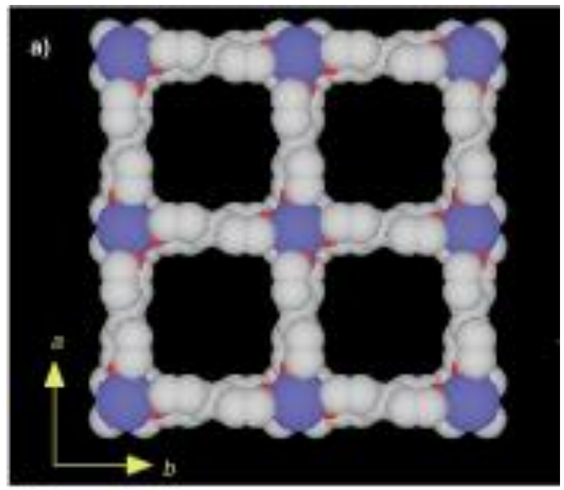


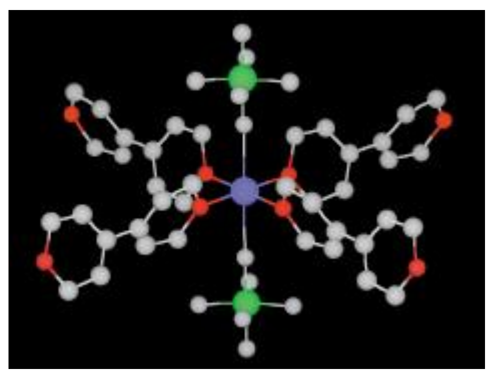
$[Cu^{I}(tpc)]BF_4$



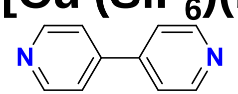
tpc

S. Noro, S. Kitagawa, et al.
Angew. Chem. Int. Ed. **2000**



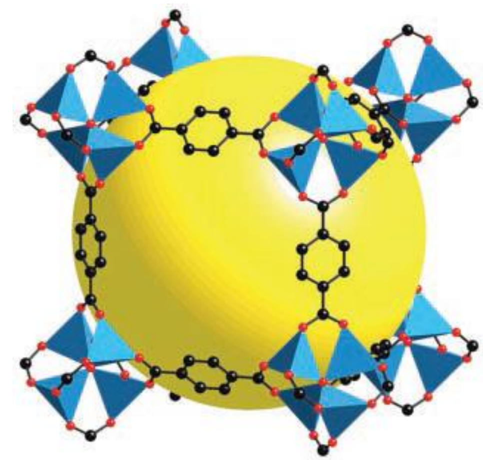


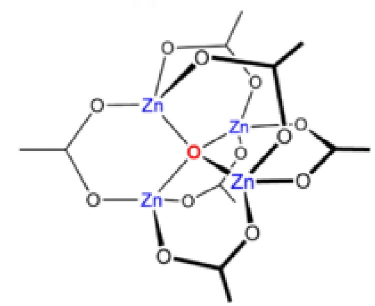
$[Cu^{I}(SiF_6)(bpy)]$



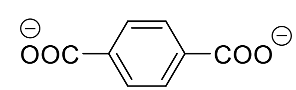
bpy

O.M. Yaghi et. al.
Science, **2003**





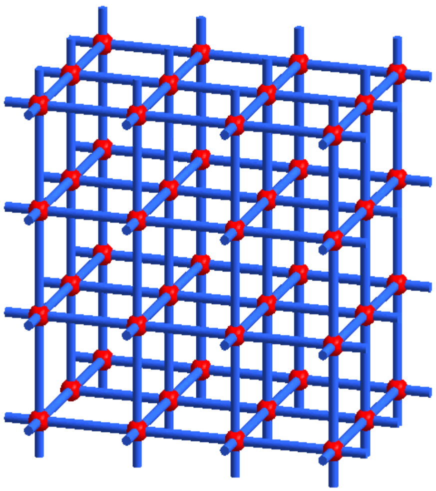
$[Zn_4O(bdc)_3]$ (MOF-5)

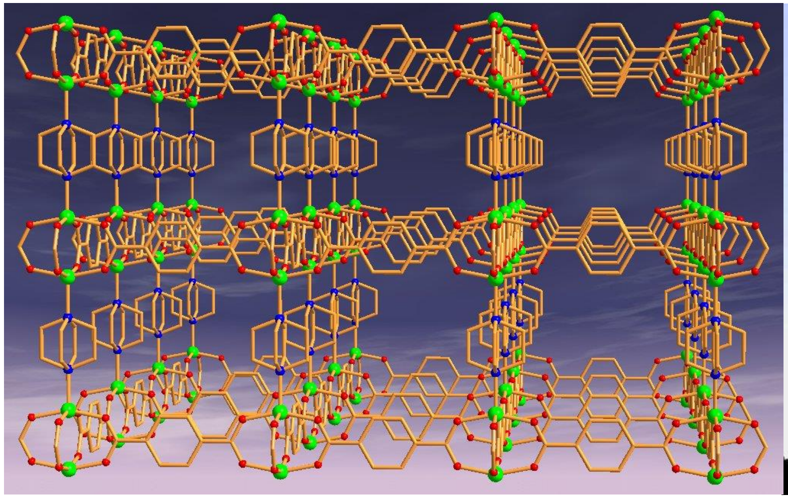


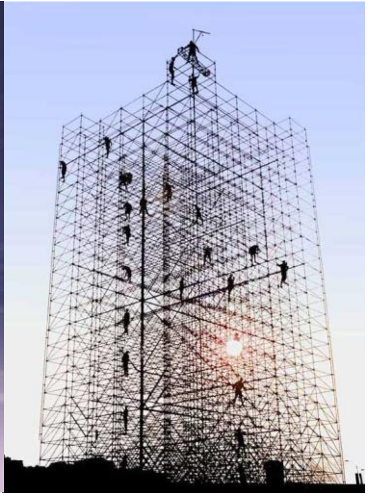
bdc^{2-}

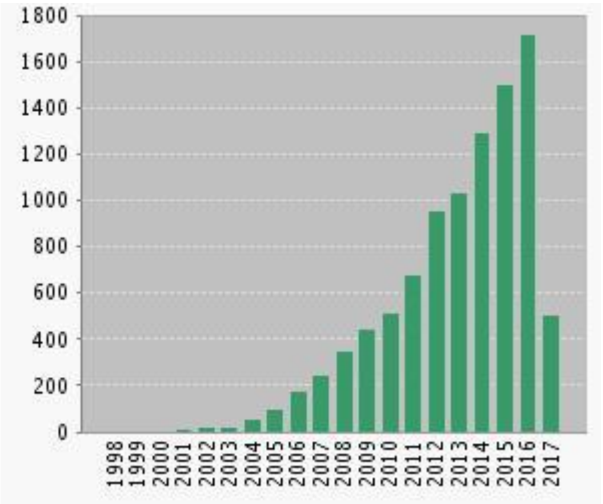
Porous coordination polymers (PCPs)

Metal-organic frameworks (MOFs)



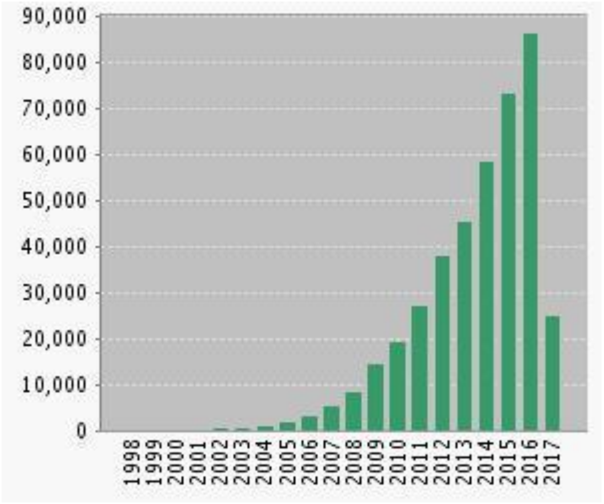




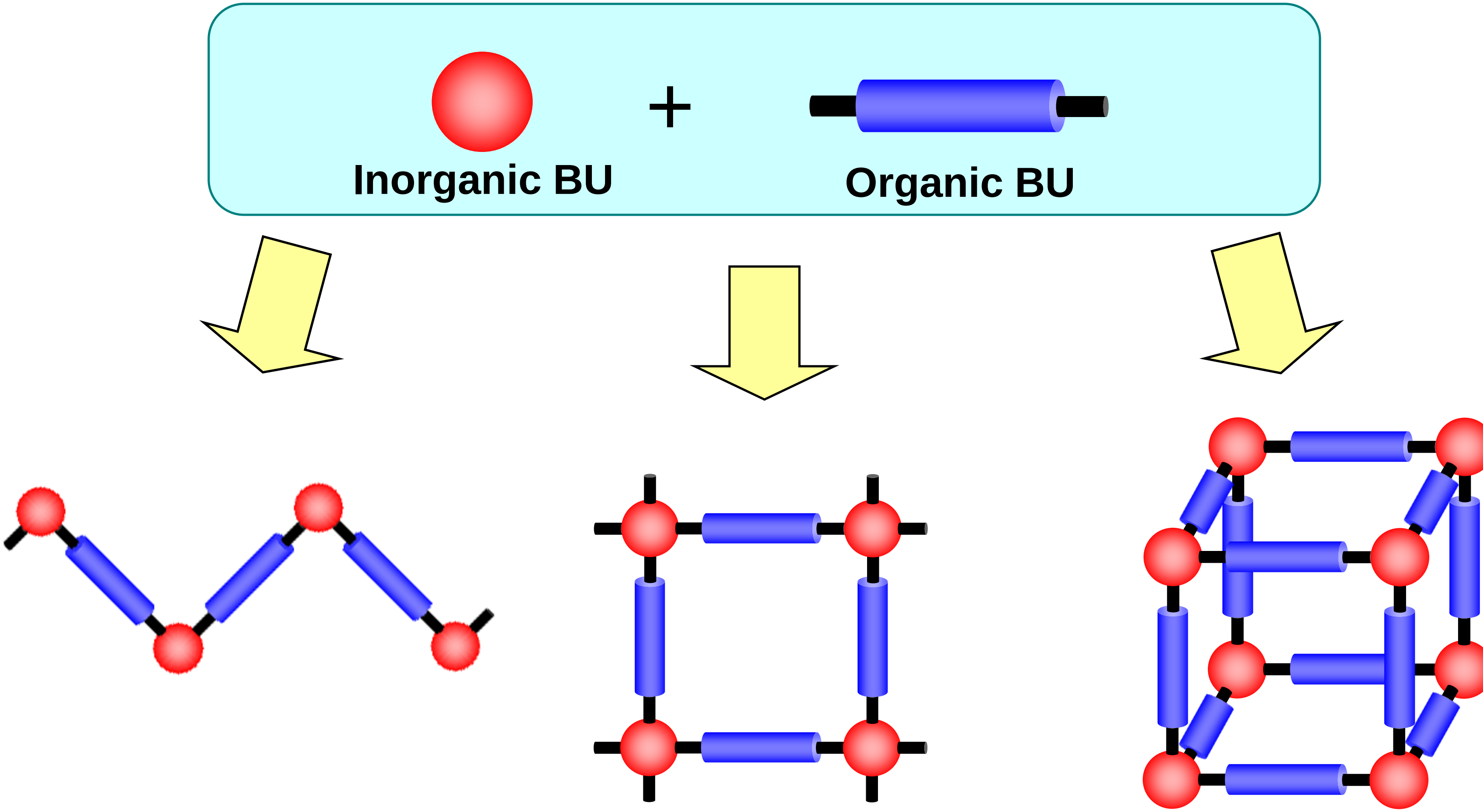


Web of Science
May 1, 2017
Search: **title**/metal-organic framework

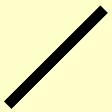
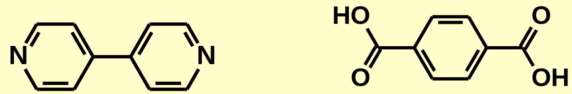
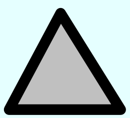
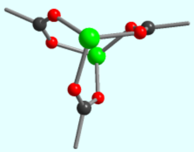
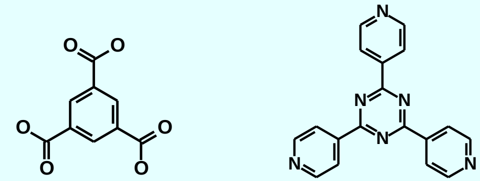
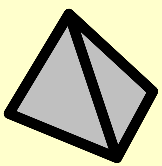
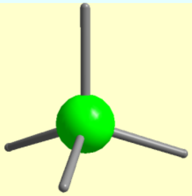
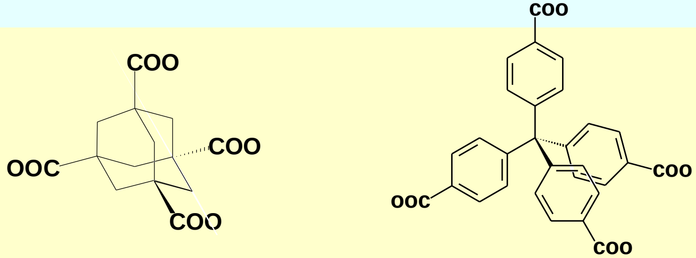
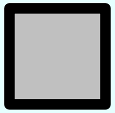
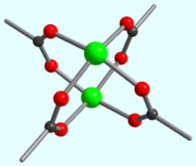
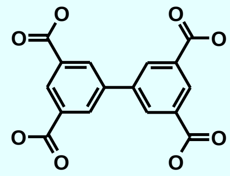
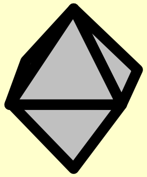
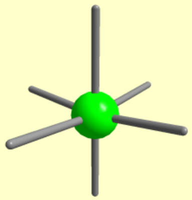
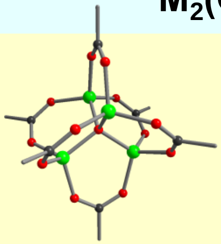
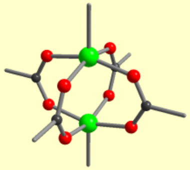
h-index = 253 (!!!)



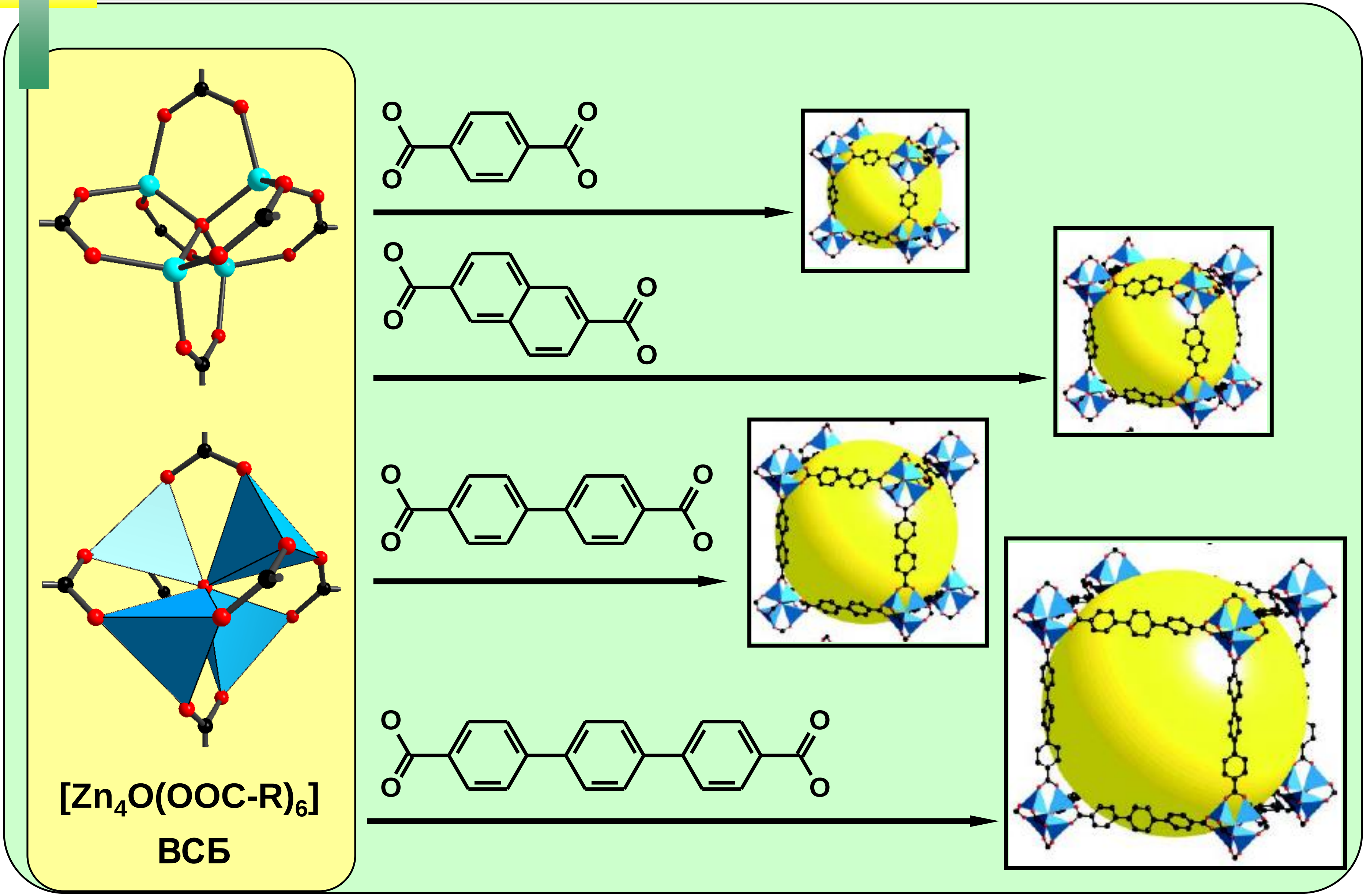
Metal-organic frameworks



Building units

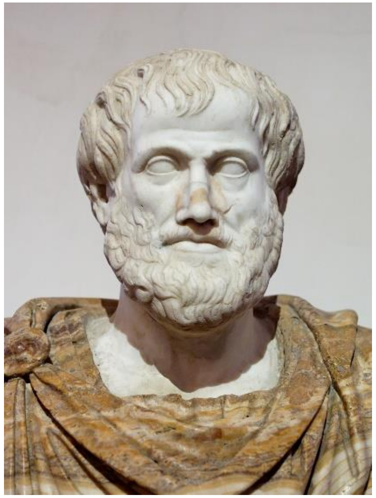
		Inorganic BU	Organic BU
	Linear		
	Triangular	 $M_2(COO)_3$	
	Tetrahedral		
	Square	 $M_2(COO)_4$	
	Octahedral	  $M_4O(COO)_6$  $M_2(COO)_4L_2$	

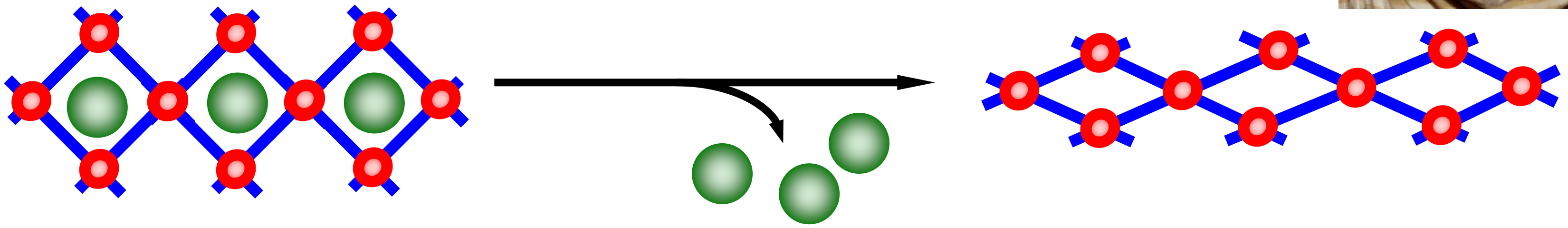
Примеры дизайна 3D пористых структур

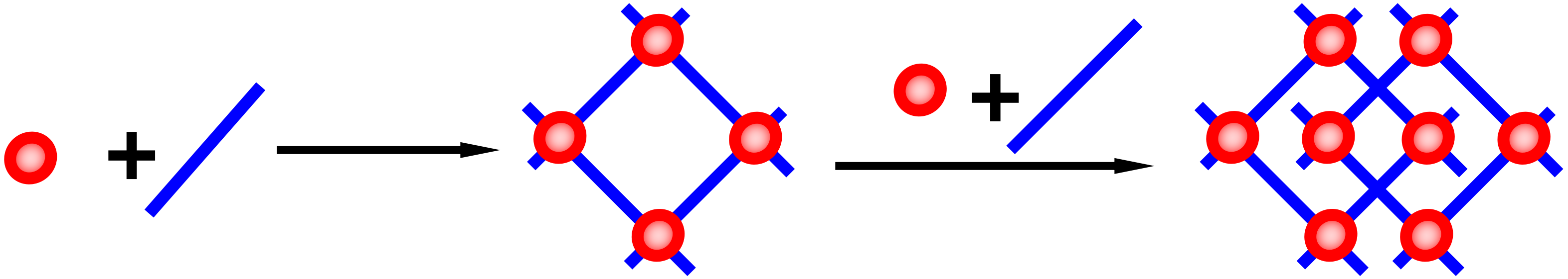


O.M. Yaghi et al., *Science*, **2002**, *295*, 469; *Nature*, **2003**, *423*, 705

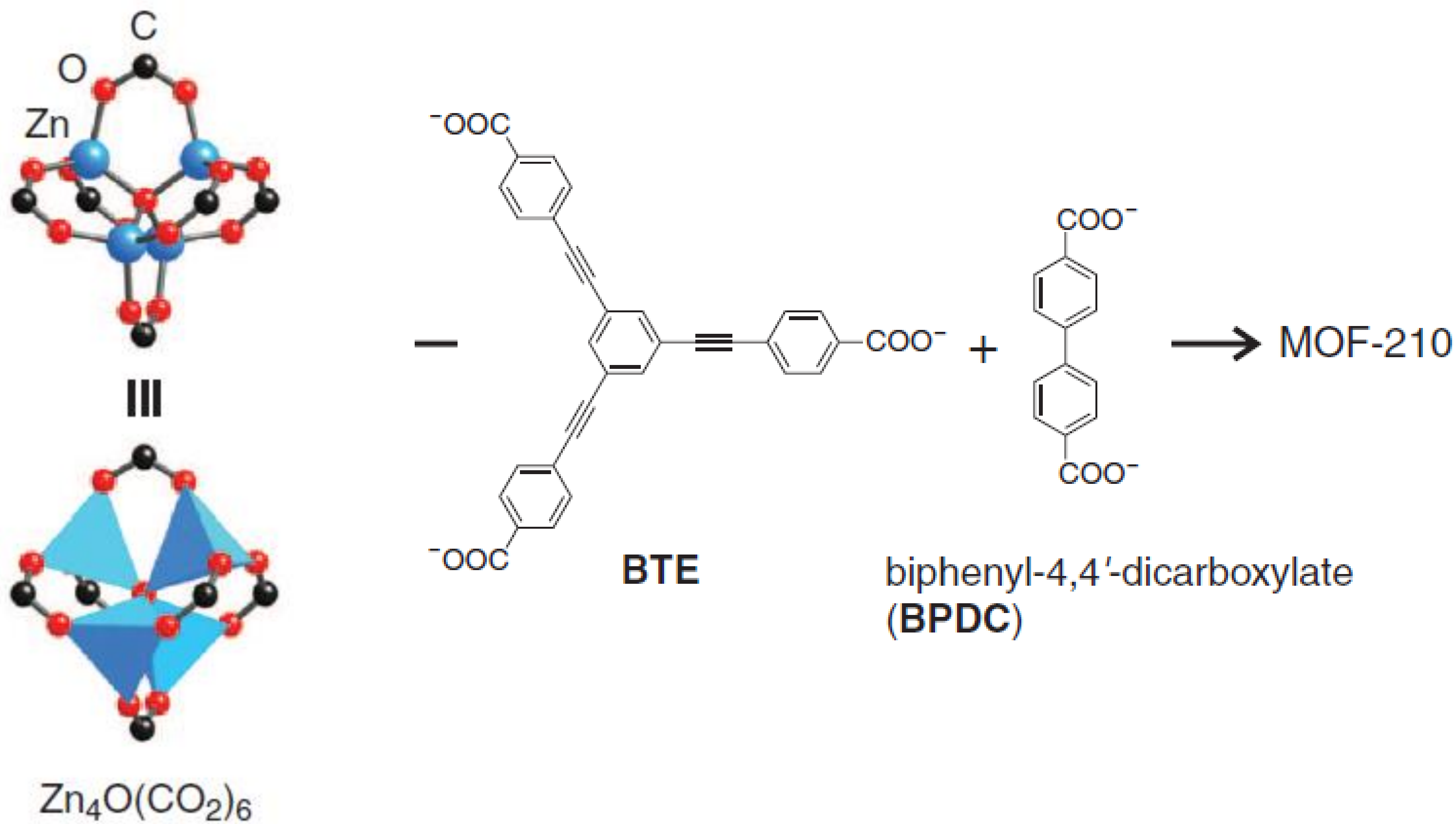
Natura abhorret vacuum







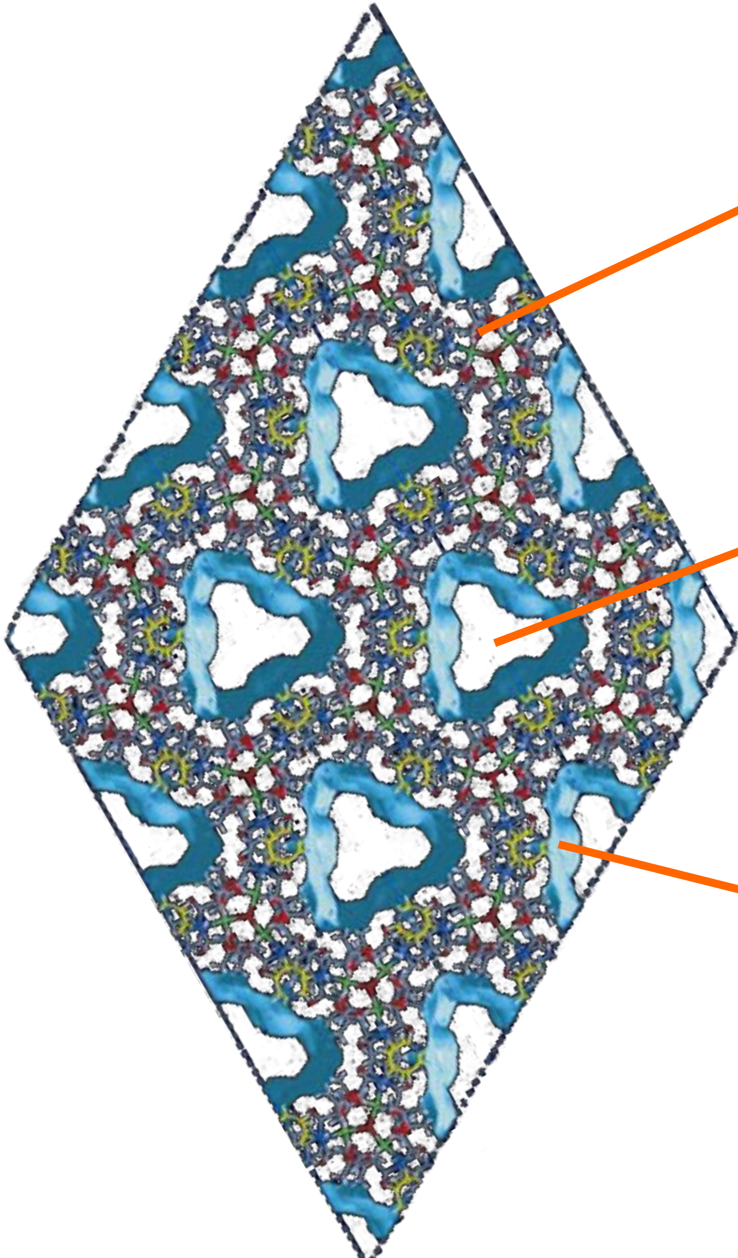
Рекорды в науке



Void volume = 89%; Crystal density = 0.25 g/cm^2;
S(BET) = 6240 m^2/g; S(Lang) = 10400 m^2/g

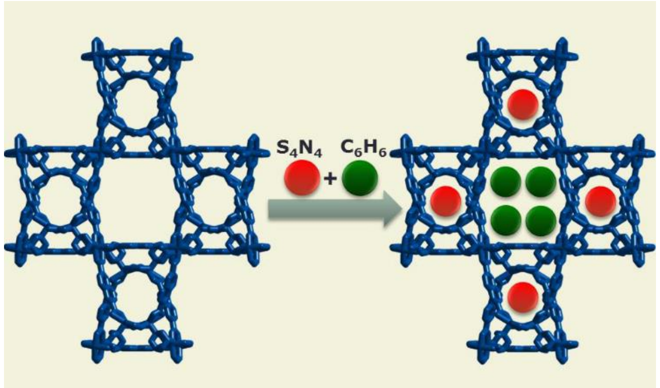
H. Furukawa et al., *Science* **2010**, *329*, 424

Основные особенности MOFs



- Framework
  - magnetic
  - electric
  - optical
  - dynamic (breathing) behavior
- Pores and channels
  - storage
  - separation
  - ion exchange
  - mediation of unique chemical reactions
- Surface
  - catalysis
  - adsorption
  - selective recognition
  - post-synthetic modifications

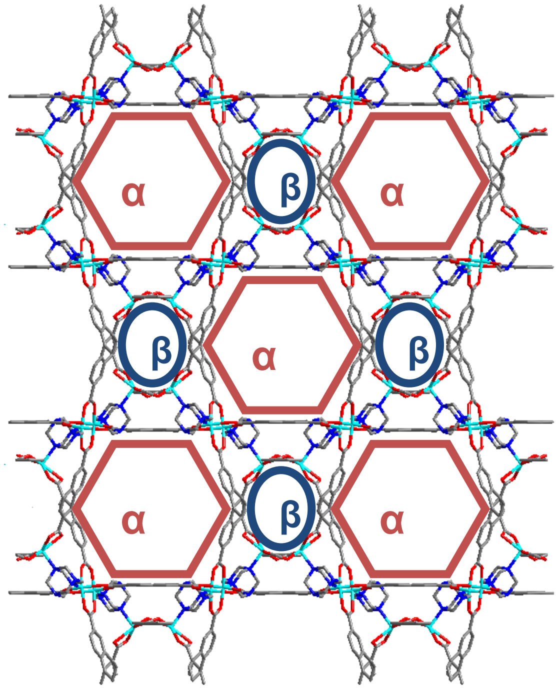
MOFs for sorption and separation

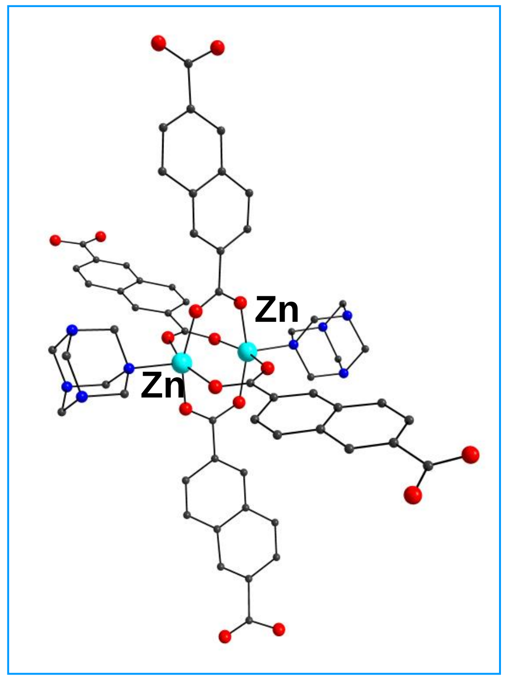


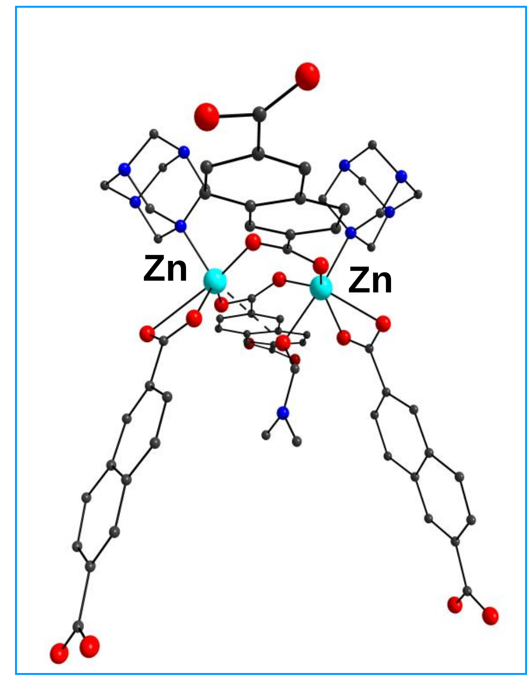
$[Zn_4(dmf)(ndc)_4(ur)_2]\cdot 5DMF\cdot H_2O$

$$Zn(NO_3)_2\cdot 6H_2O + H_2ndc + ur \xrightarrow[100^\circ C,\ 12\ h]{DMF} [Zn_4(dmf)(ndc)_4(ur)_2]\cdot 5DMF\cdot H_2O$$

Yield: 42%

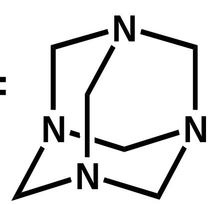




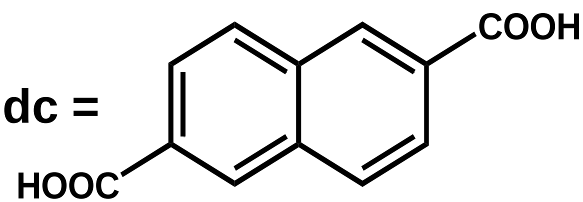


α channels: 9×11 Å
β channels: 6×9 Å

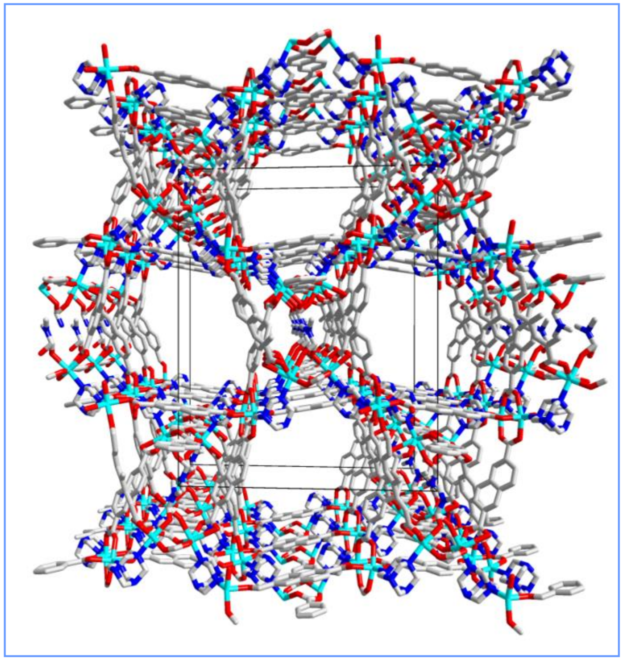
ur =



H_2ndc =



$[Zn_4(dmf)(ndc)_4(ur)_2]$: guest-free α channels



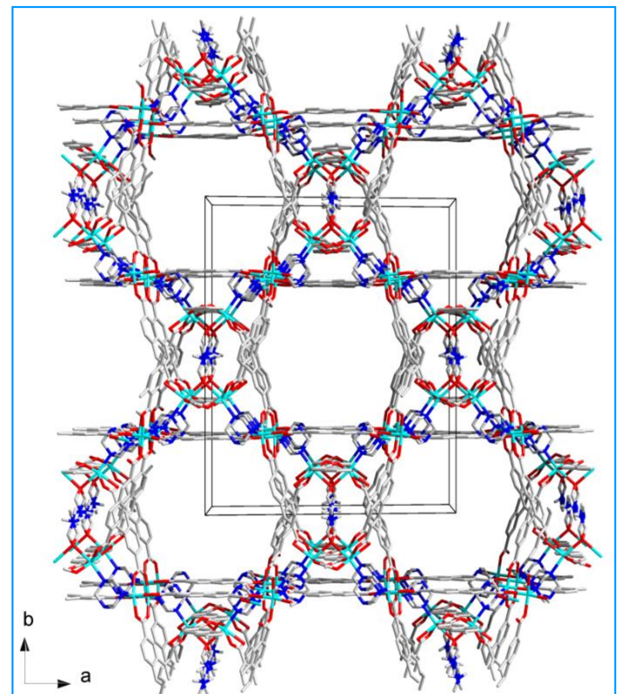
$[Zn_4(dmf)(ndc)_4(ur)_2]\cdot 5DMF\cdot H_2O$

1. CH_2Cl_2, 3 days
2. 50 °C, vacuum 1 day

$[Zn_4(dmf)(ndc)_4(ur)_2]$

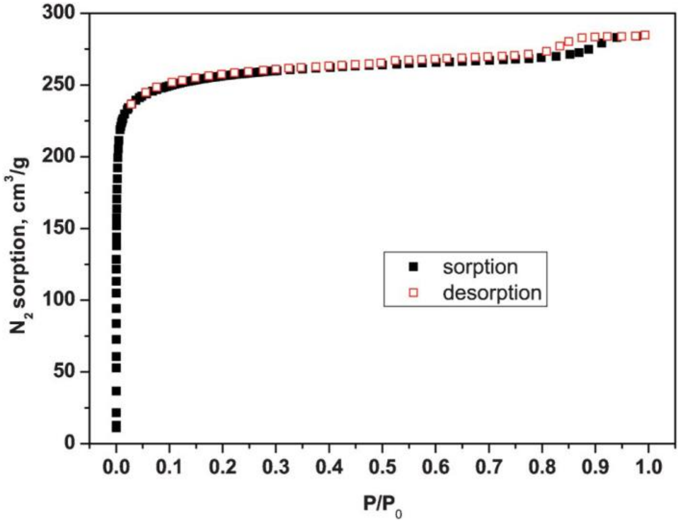
Monoclinic, Cc

Channels 9x11 Å

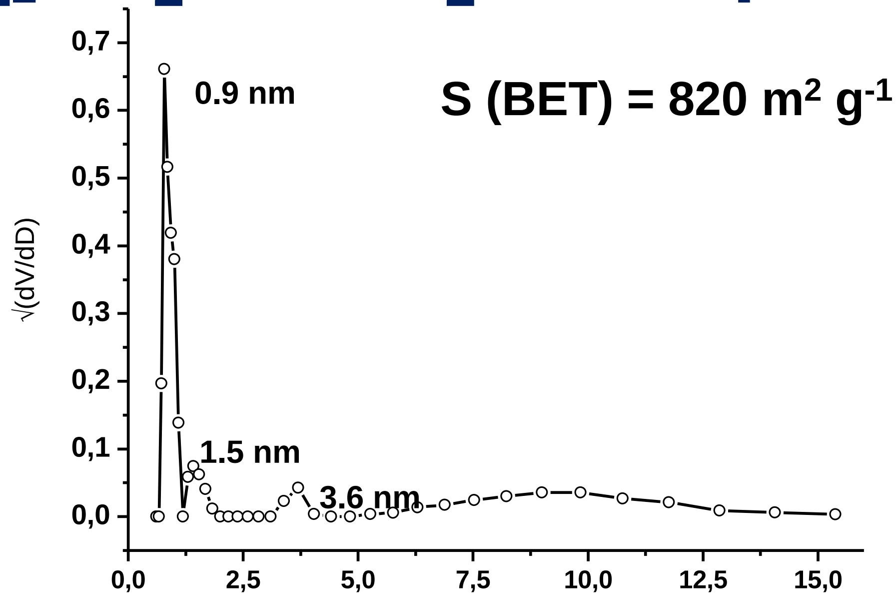


S.A. Sapchenko et al., *Dalton Trans*., **2011**, *40*, 2196

$[Zn_4(dmf)(ndc)_4(ur)_2]$: N_2 and H_2 adsorption

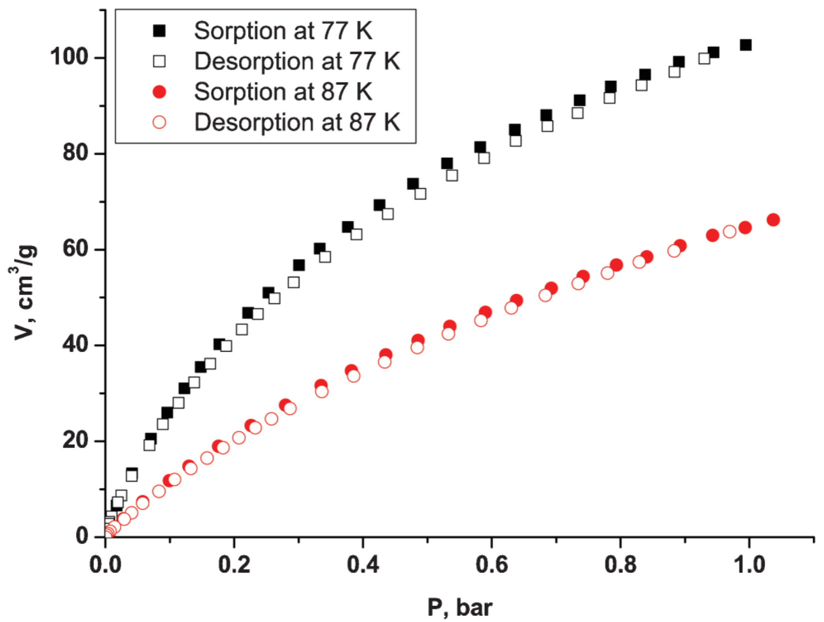


Nitrogen sorption isotherm at 77 K



77 K, 0.92 % H_2

ΔH_{ads} = 4.7 – 5.2 kJ/mol

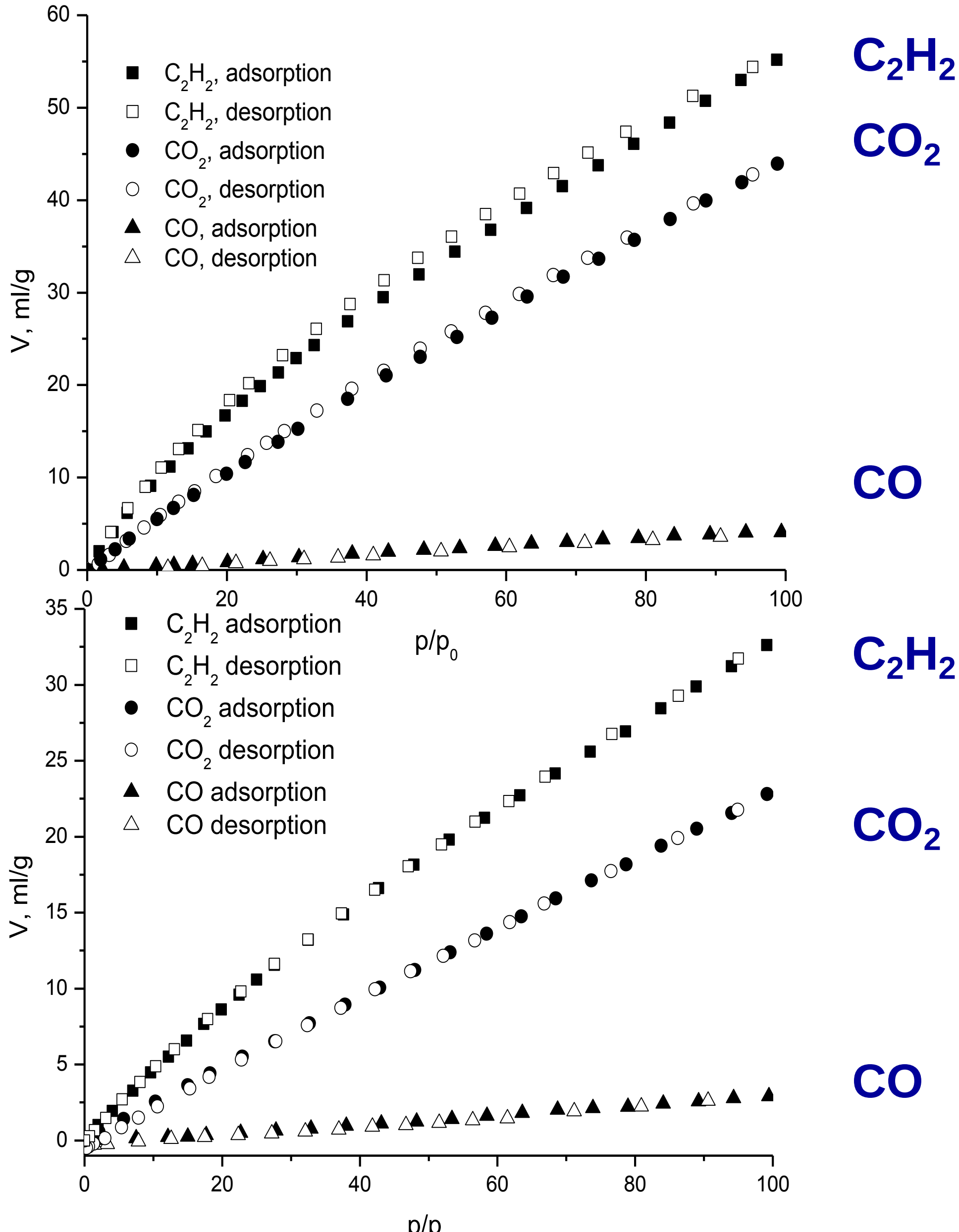


Hydrogen sorption isotherms at 77 and 87 K

[$Zn_4(dmf)(ndc)_4(ur)_2$]: C_2H_2, CO_2 and CO adsorption

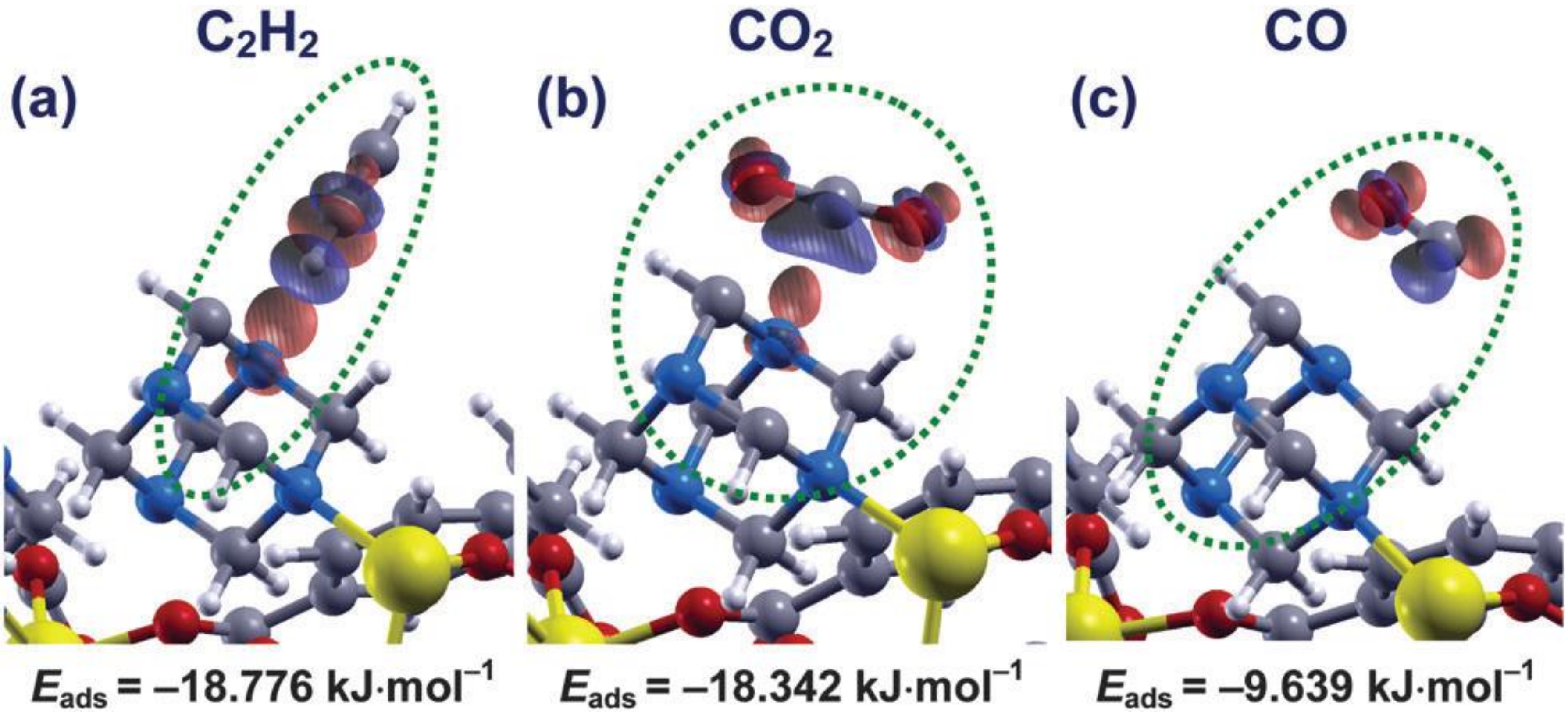
273 K

298 K



S.A. Sapchenko et al., *Chem. Commun.*, **2015**, *51*, 13918

DFT calculations

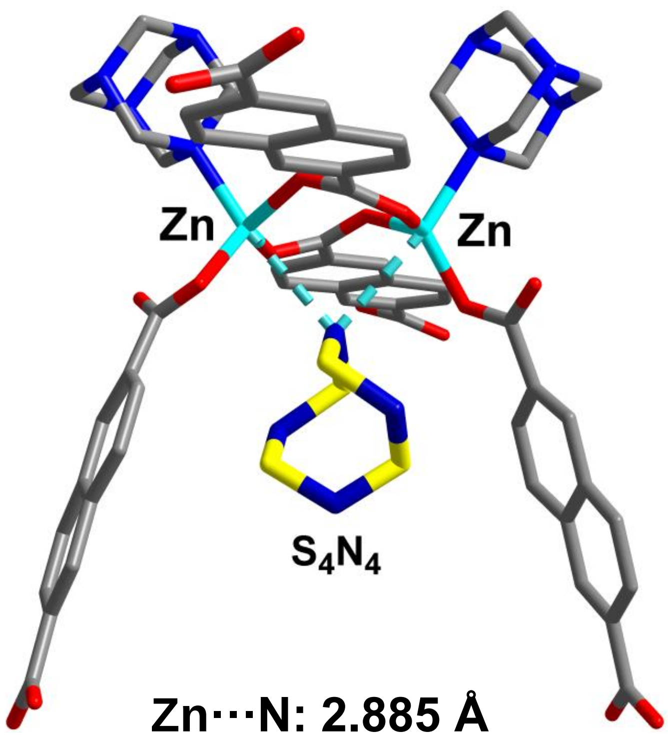


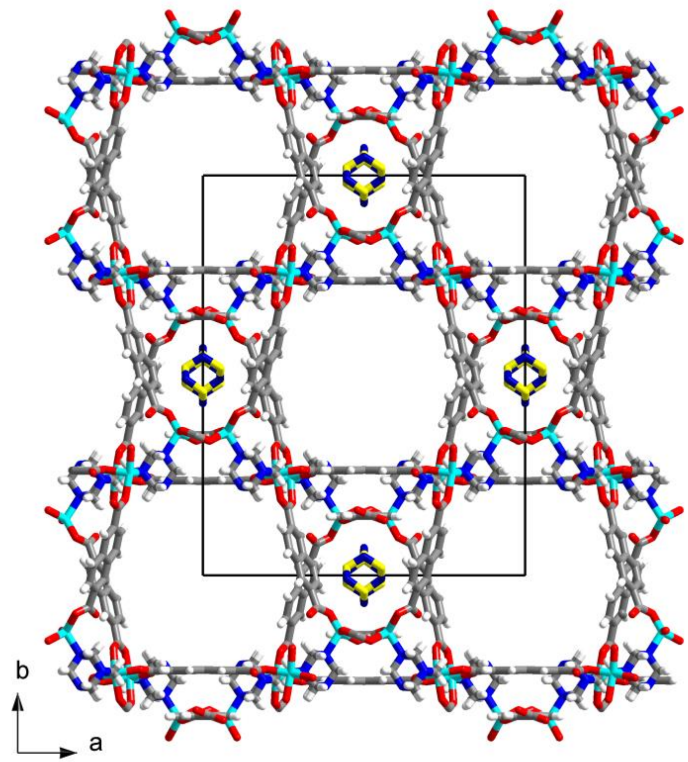
View of charge density isosurfaces for the interactions of (a) C_2H_2 , (b) CO_2 and (c) CO with the urotropine linker for the most favorable intermolecular interactions. Red represents the accumulation of electron density and blue the depletion of electron density.

S.A. Sapchenko et al., *Chem. Commun.*, **2015**, *51*, 13918

ZNU: inclusion of S_4N_4

$[Zn_2(\text{dmf})(ur)_2(ndc)_4] + S_4N_4 + x\text{Me}_2C{=}O \rightarrow [Zn_2(S_4N_4)(ur)_2(ndc)_4]\cdot x\text{Me}_2C{=}O + \text{DMF}$

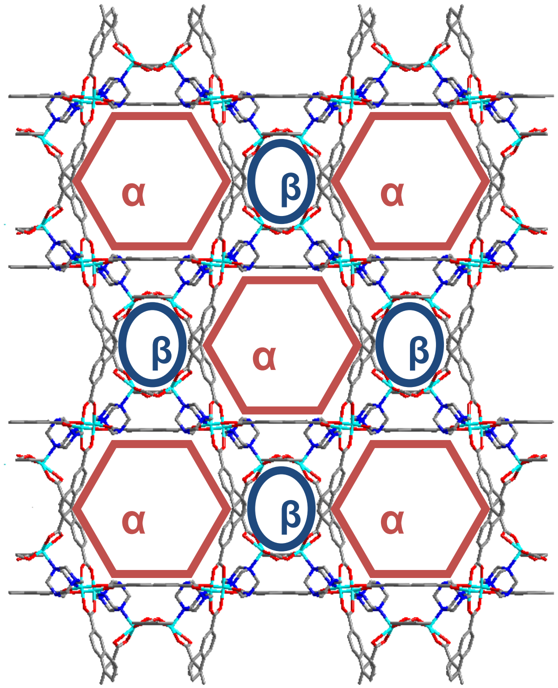




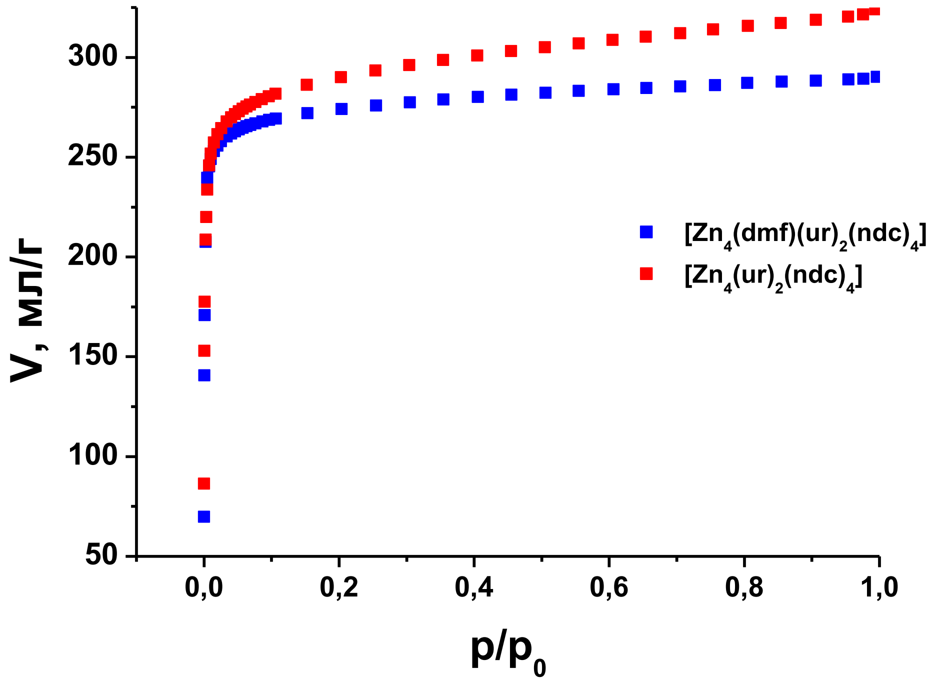
$[Zn_2(S_4N_4)(ur)_2(ndc)_4]\cdot x\text{Me}_2C{=}O + \text{Me}_2C{=}O \rightarrow [Zn_2(\text{Me}_2C{=}O)(ur)_2(ndc)_4]\cdot x\text{Me}_2C{=}O + S_4N_4$

$[Zn_2(\text{Me}_2C{=}O)(ur)_2(ndc)_4]\cdot x\text{Me}_2C{=}O \rightarrow [Zn_2(ur)_2(ndc)_4] + (x+1)\text{Me}_2C{=}O$ (*in vacuum*)

Step-by-step activation of biporous ZNU



α channels: 9×11 Å
β channels: 6×9 Å

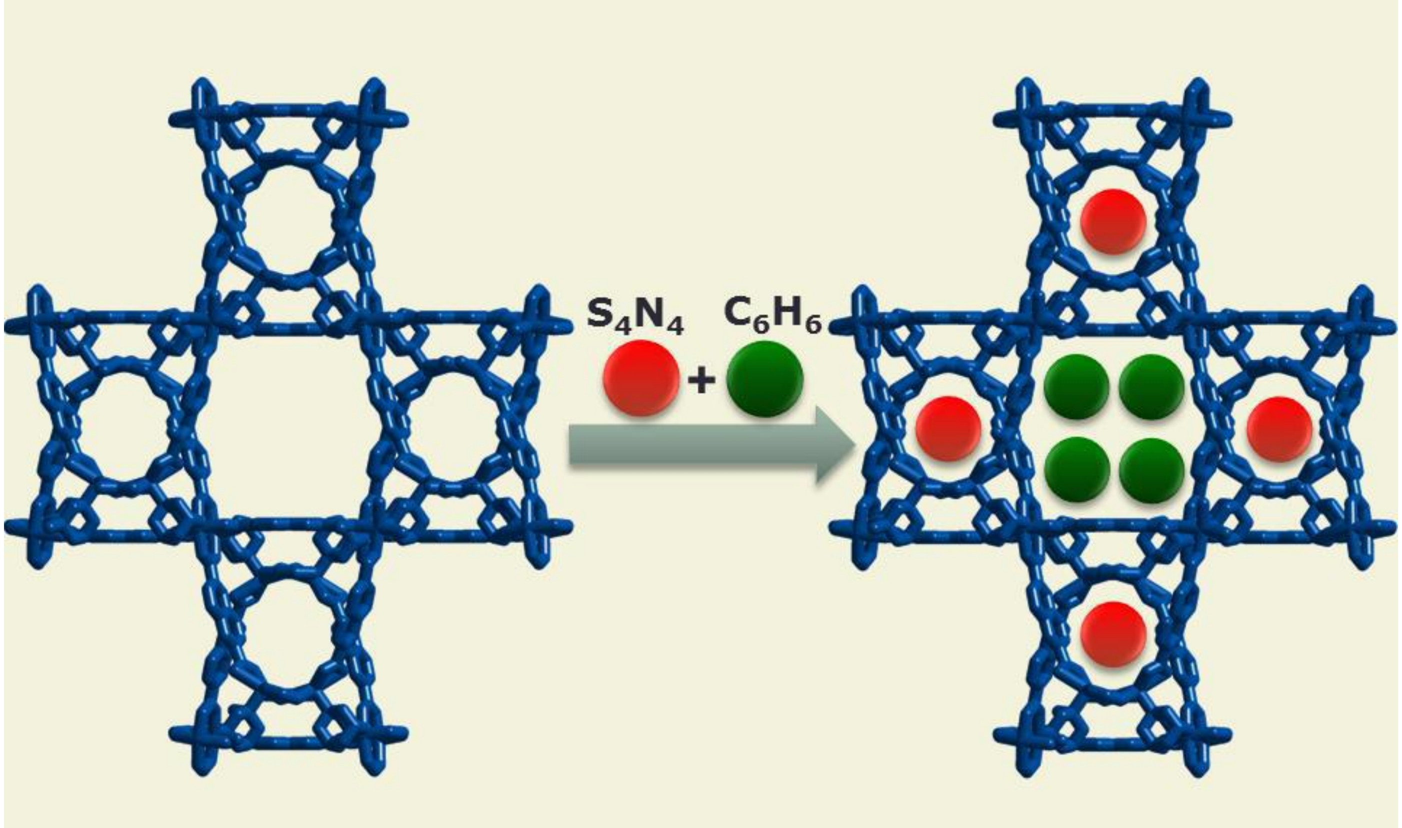


$[Zn_2($dmf$)(ur)_2(ndc)_4]$: S(BET) = 820 $m^2\ g^{-1}$

$[Zn_2(ur)_2(ndc)_4]$: S(BET) = 1113 $m^2\ g^{-1}$

S.A. Sapchenko et al., *Inorg. Chem.*, **2013**, *52*, 9702

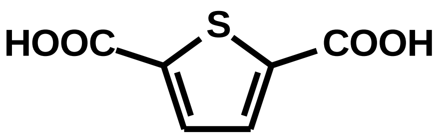
ZNU: selective separation



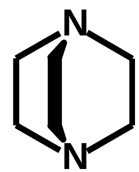
S.A. Sapchenko et al., *Inorg. Chem.*, **2013**, *52*, 9702

Porous zinc(II) thiophenedicarboxylate

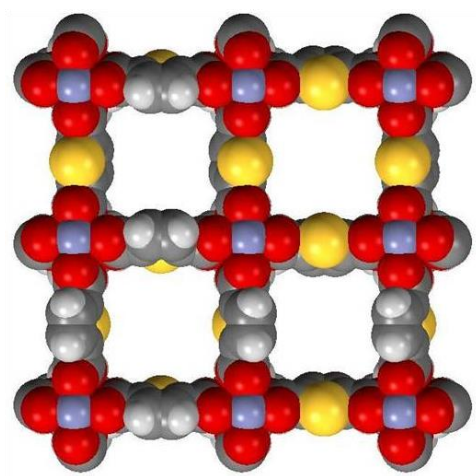
Zn^{2+} + H_2tdc + dabco $\xrightarrow{\Delta}$ **[Zn_2(tdc)$_2$dabco]·solv**



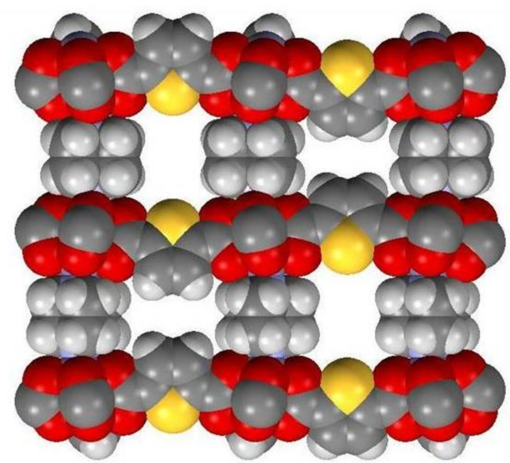
H_2tdc



dabco



Channels (7.5 x 7.5 Å)

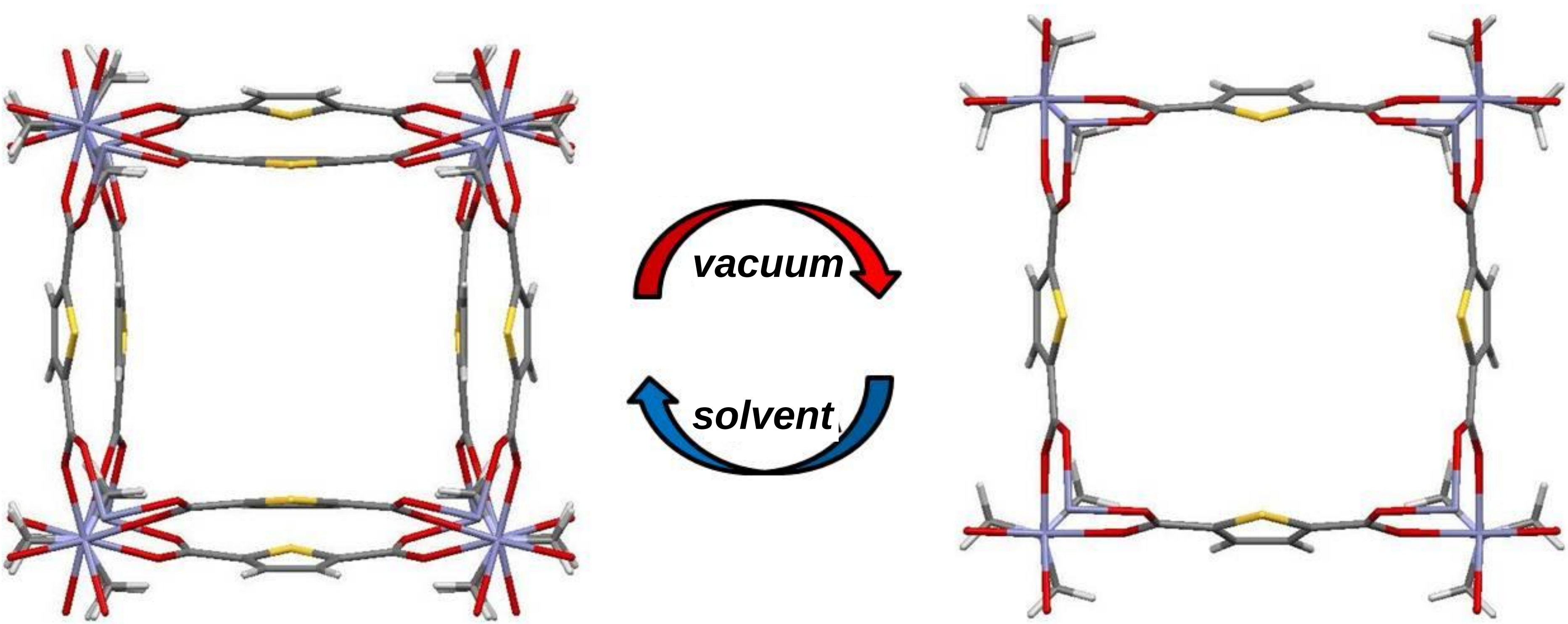


S-decorated windows (3×4 Å)

Very similar to the structure of [Zn_2(bdc)$_2$dabco] (D.N. Dybtsev et al., *ACIE*, **2004**, *43*, 5033)

V.A. Bolotov et al., **2017**, *MS in preparation*

[$Zn_2(tdc)_2dabco$]: Guest-dependent framework dynamics



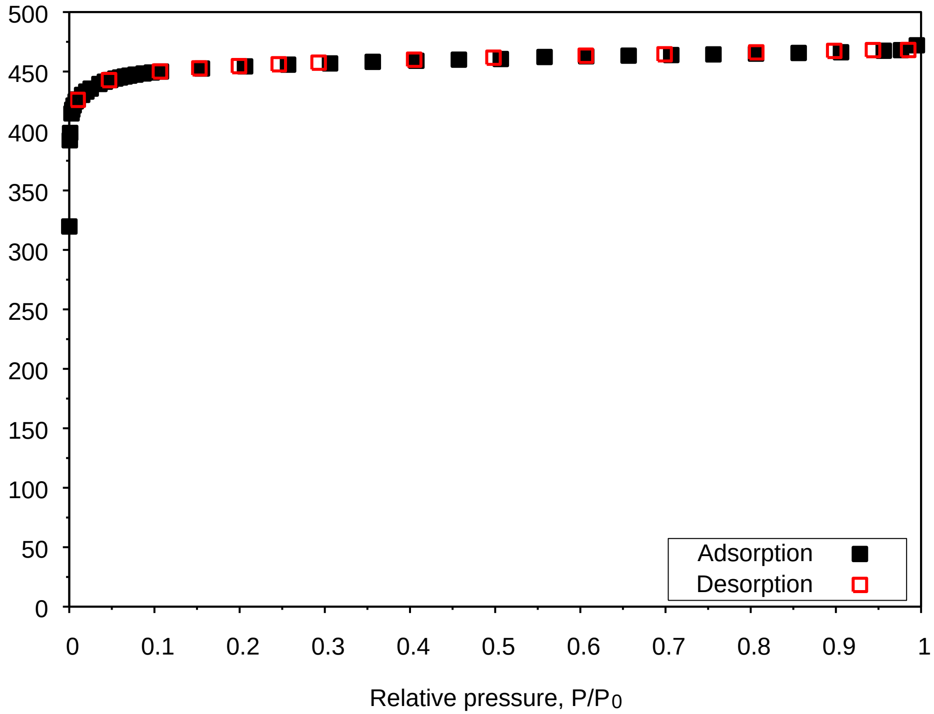
TDC ligands are bent

Fully reversible
V = -3%

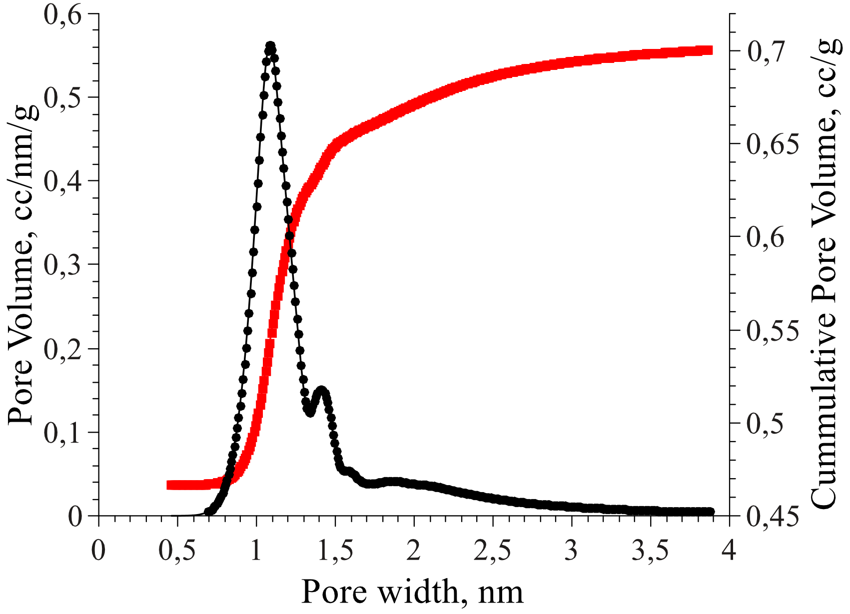
TDC ligands are linear

AGAIN: Very similar to [$Zn_2(bdc)_2dabco$] (D.N. Dybtsev et al., *ACIE*, **2004**, *43*, 5033)

$[Zn_2(tdc)_2dabco]$: nitrogen adsorption



N_2 adsorption isotherm at 77K



Pore-size distribution plot

Porous properties:

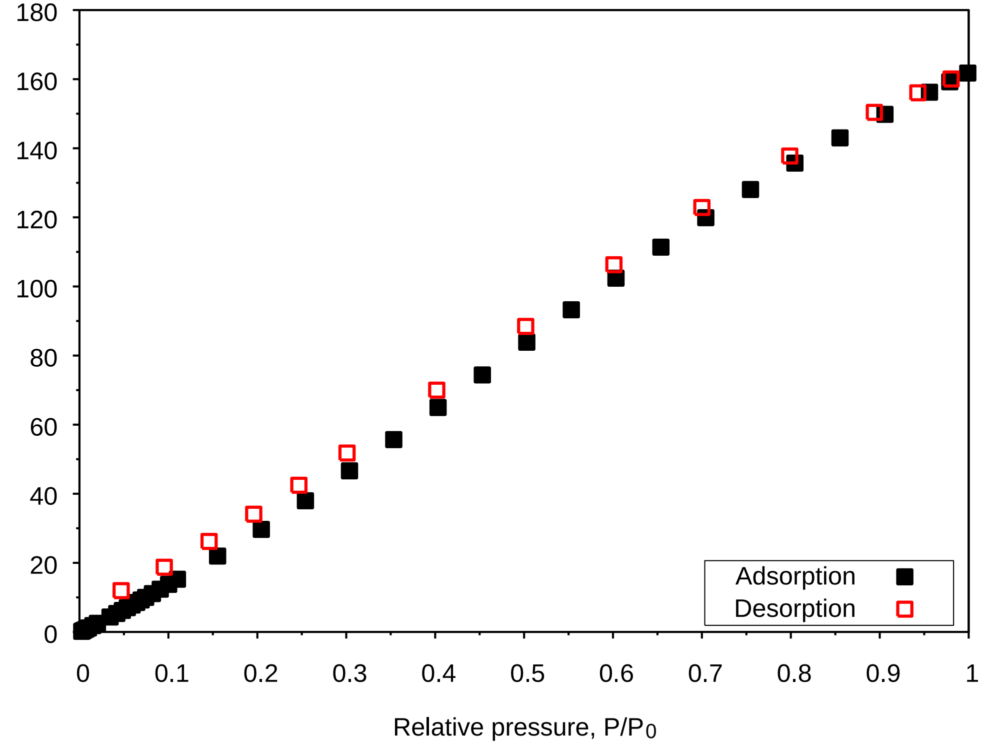
BET surface area = 1800 m^2/g

Langmuir = 2000 m^2/g

Pore volume = 0.7 ml/g

AGAIN: Very similar to the properties of $[Zn_2(bdc)_2dabco]$

[$Zn_2(tdc)_2$dabco]: CO_2 adsorption at 273 K



<u>CO_2 sorption summary:</u>

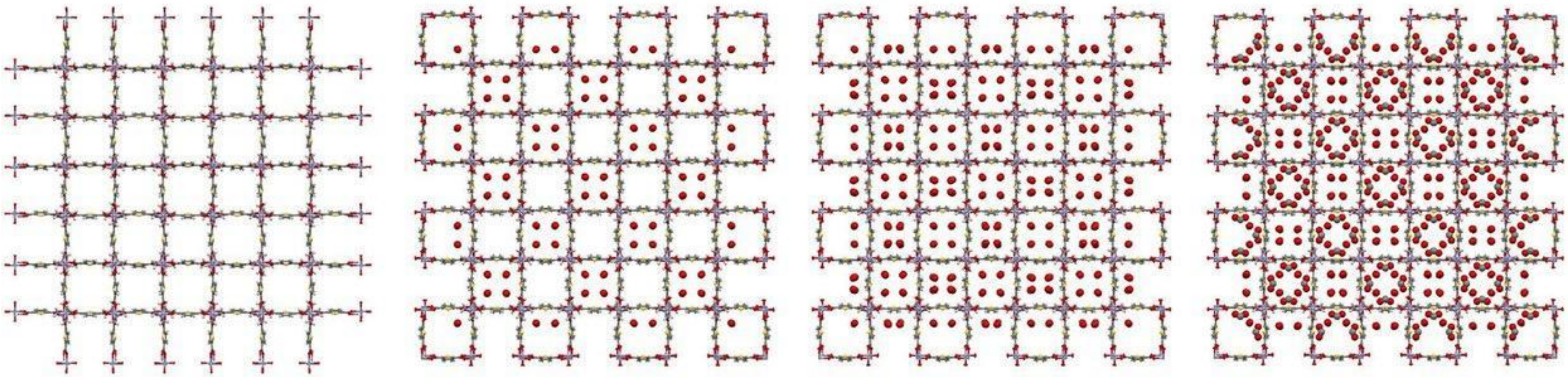
-- Highly unsaturated adsorption curve
-- At 1 bar (273 K) = **162 ml/g = 32 mass%**
-- formula: [Zn_2(tdc)dabco]•$4CO_2$

-- This number is higher than for any other porous MOF at this conditions, except for SNU-5 (38.5 mass%).

Suh, M. P. *et al.*, ACIE **2008**, *47*, 7741.
See also J. Long,. *et al*., Chem. Rev. **2012**, 112, 724.

Twice as higher than for [$Zn_2(bdc)_2$dabco] !!

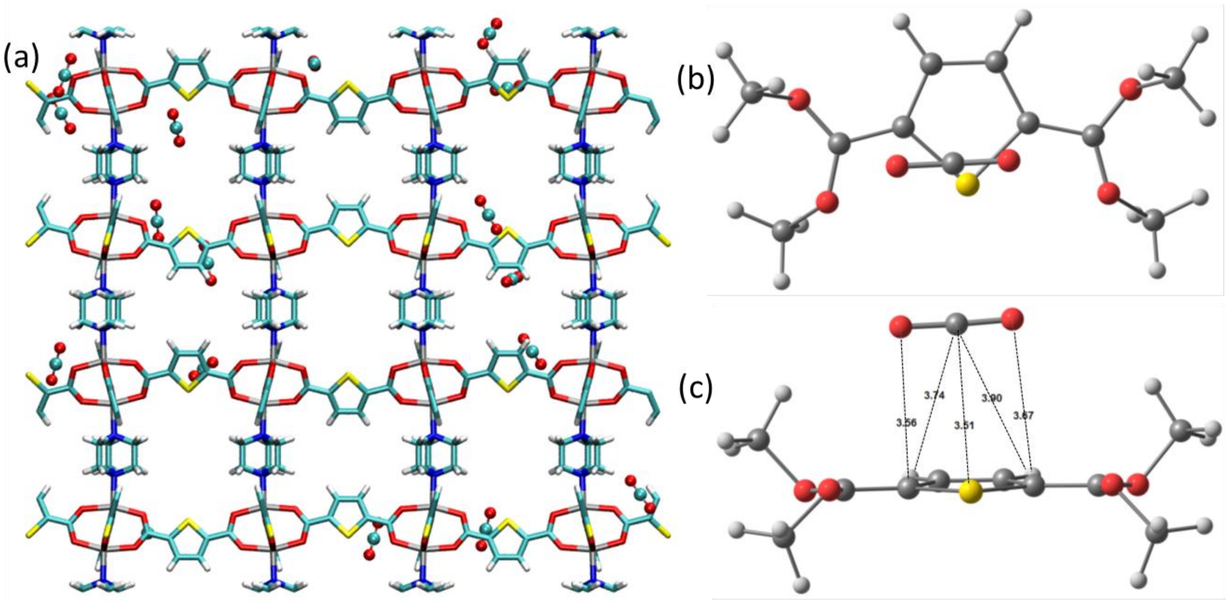
Evolution carbon dioxide storage in $[Zn_2(tdc)_2dabco]$ («Sevas Complex») detected by single-crystal X-ray diffraction data



$[Zn_2(tdc)_2dabco]$ $[Zn_2(tdc)_2dabco]@CO_2$ $[Zn_2(tdc)_2dabco]@2CO_2$ $[Zn_2(tdc)_2dabco]@3CO_2$

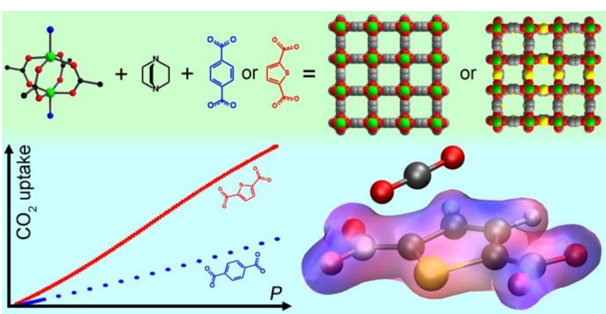
V.A. Bolotov et al., **2017**, *MS in preparation*

GCMC and DFT calculations



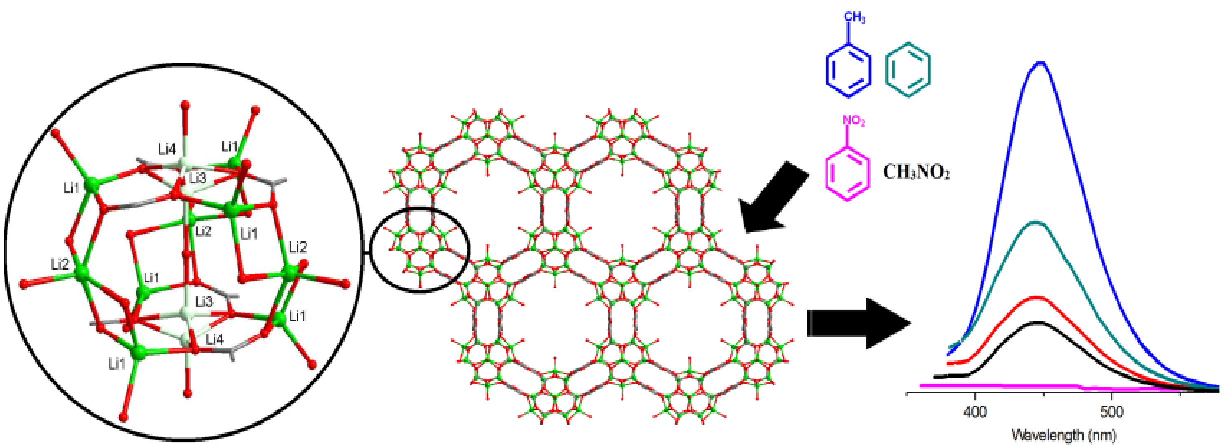
Snapshot from GCMC simulation at low pressure, in which the majority of CO_2 molecules were found to be located near to the thiophene ring (a). The DFT-optimised lowest-energy binding site for CO_2 viewed from above (b) and alongside the TDC fragment (c).

Calculated binding energies ranging from –15.7 to –18.3 kJ·mol^{-1}, *ca.* 3-10 kJ·mol^{-1} stronger than reported binding energies for CO_2 with benzene-based moieties



V.A. Bolotov et al., **2017**, *MS in preparation*

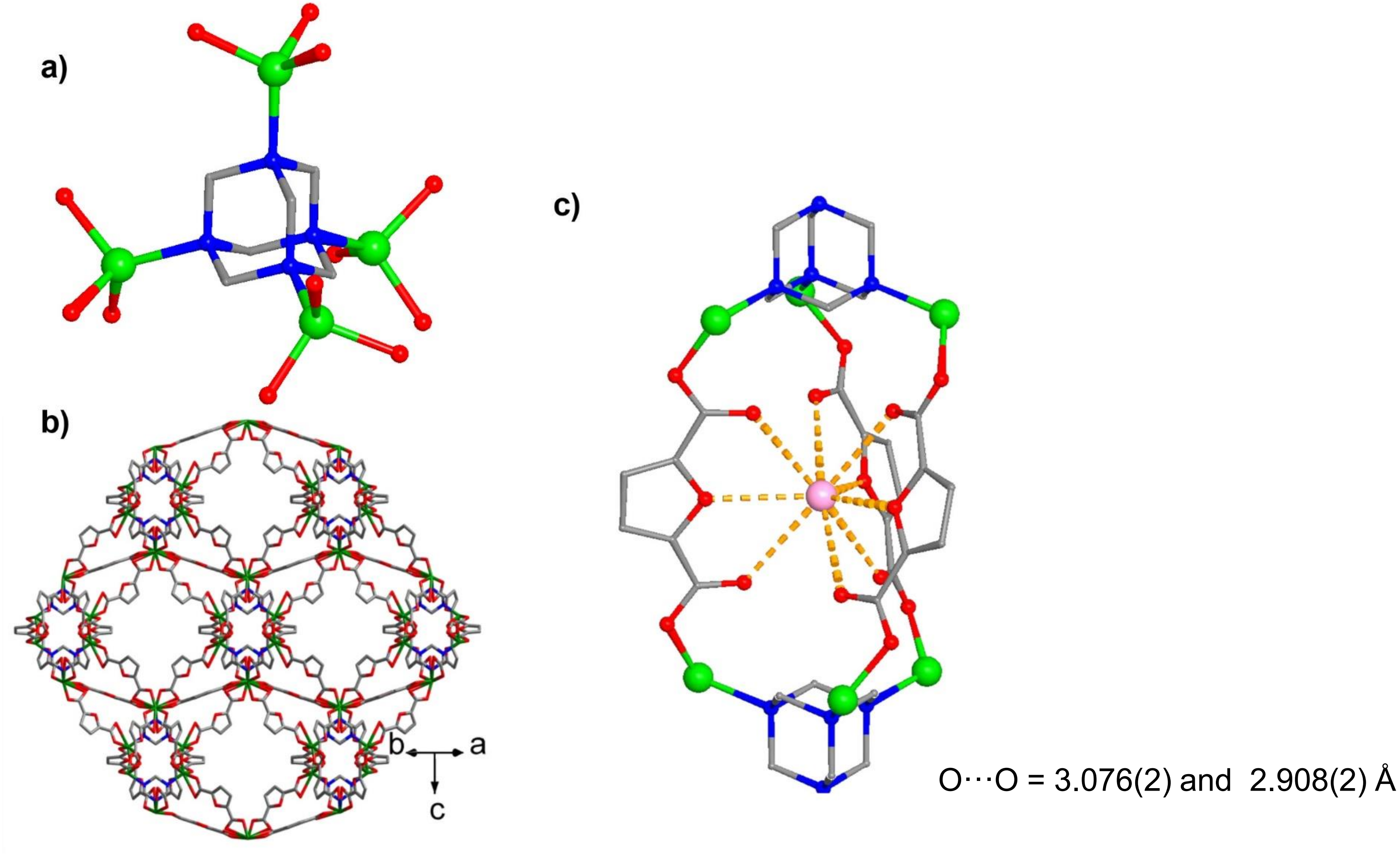
MOFs for sensor materials



$\{Li_{11}(H_2O)_5(RCOO)_{18}\}$ $(H_3O)[Li_{11}(H_2O)_5(Html)_6]$

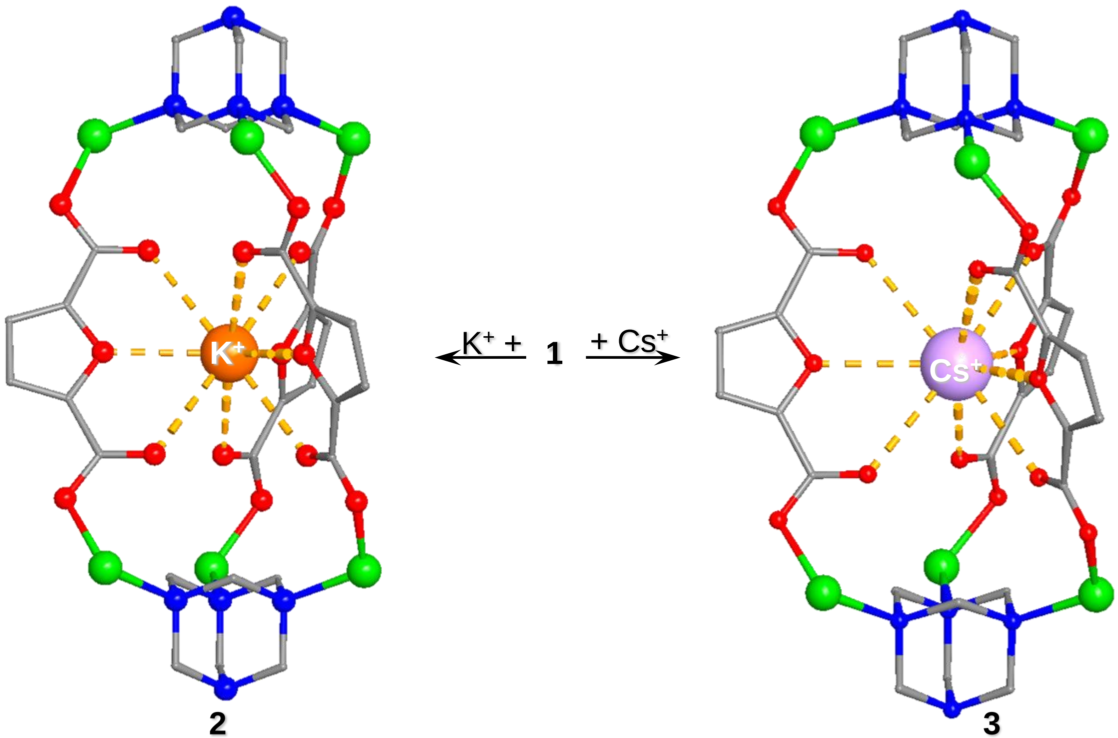
Cryptand-like MOF

$(H_3O)_2[Zn_4(ur)(Hfdc)_2(fdc)_4]\cdot G$



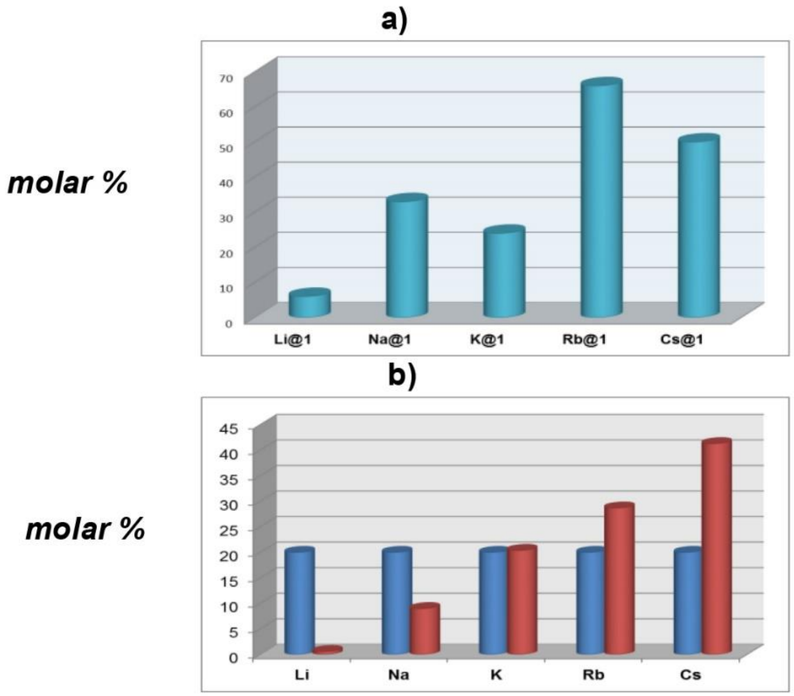
S.A. Sapchenko et al., *Chem. Eur. J.*, **2017**, *23*, 2286

Cations exchange



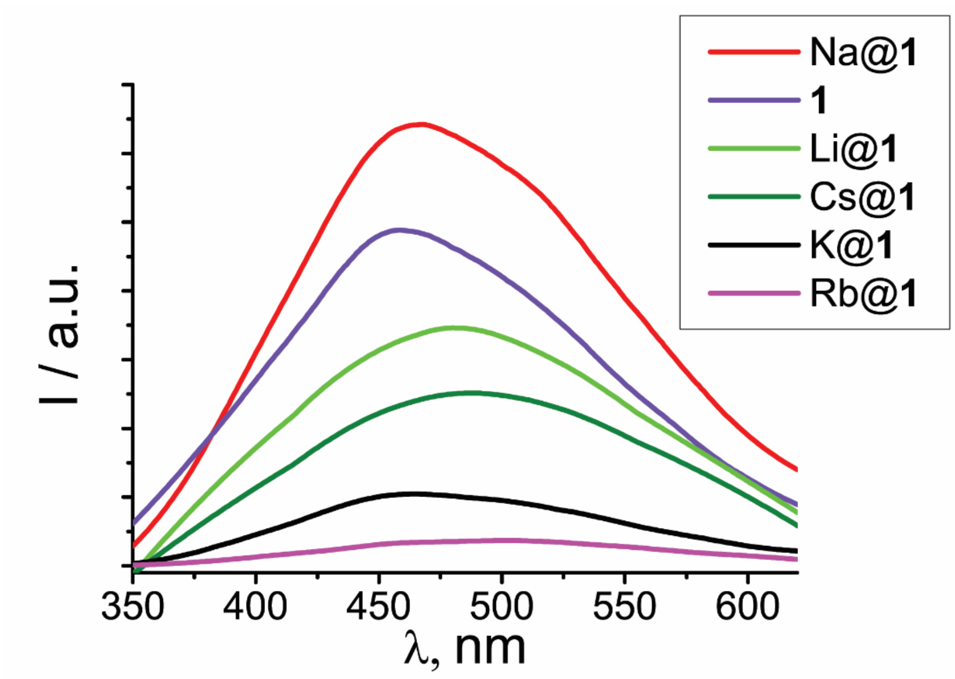
K···O(fdc) = 2.86 Å, K···O(COO) = 3.02 Å
Cs···O(fdc) = 3.10 Å, Cs···O(COO) = 3.14 Å

Extraction and detection of alkali metal cations



a) Molar fraction of alkali metal cation in the supramolecular adducts of compound **1** after immersion in 0.01 M MNO3 solution (M=Li, Na,K, Rb, Cs) in NMP.

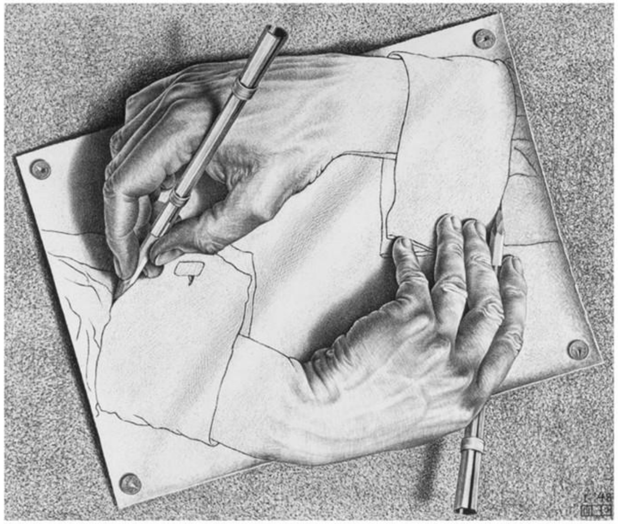
b) Molar fraction of alkali metal cation in a 0.001 M solution of alkali metals nitrates (blue) versus the molar fraction obtained within the supramolecular adduct of **1** (red).

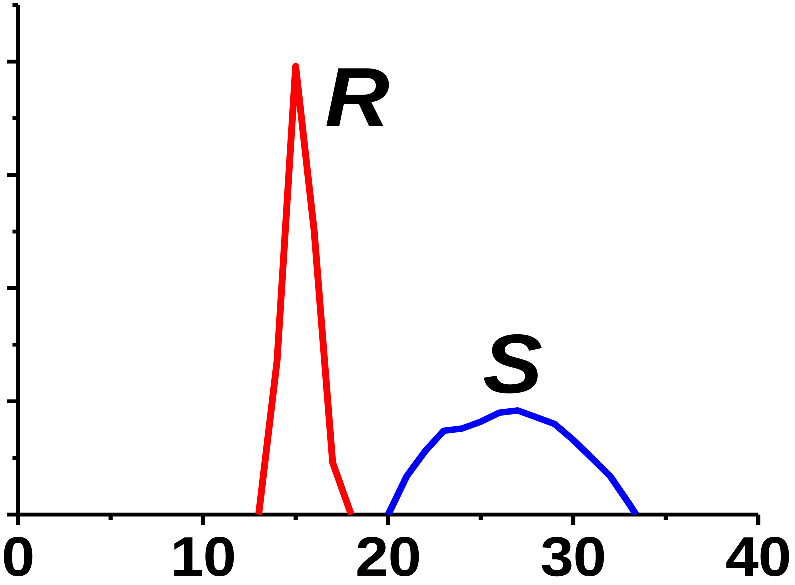


Solid-state photoluminescence spectra of compound **1** and its adducts with alkali metal cations.

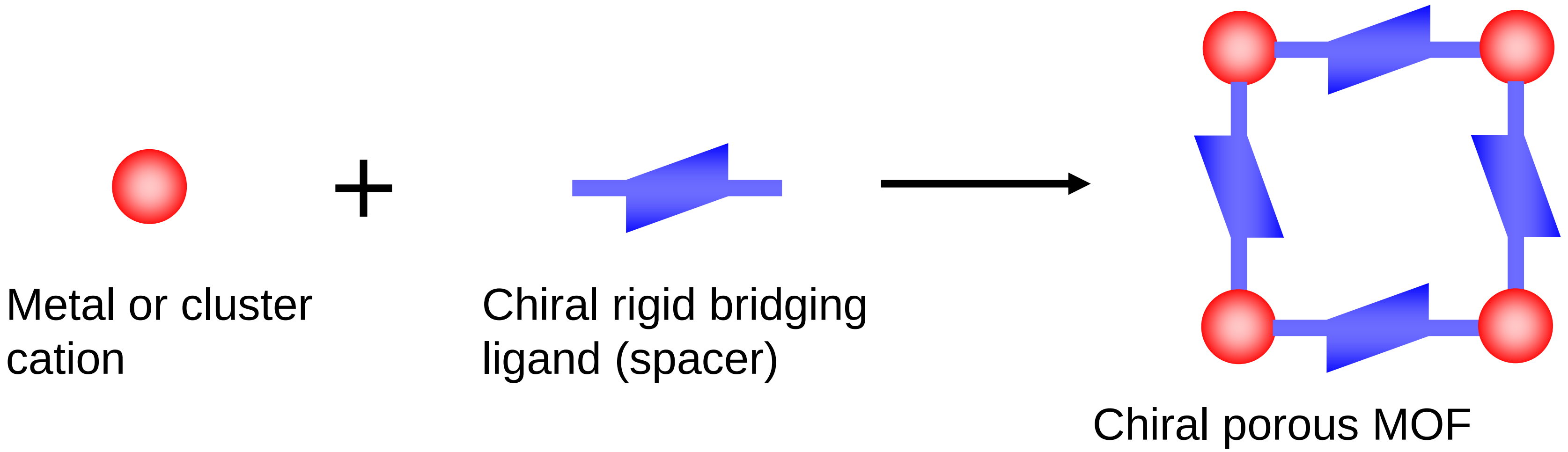
S.A. Sapchenko et al., *Chem. Eur. J.*, **2017**, *23*, 2286

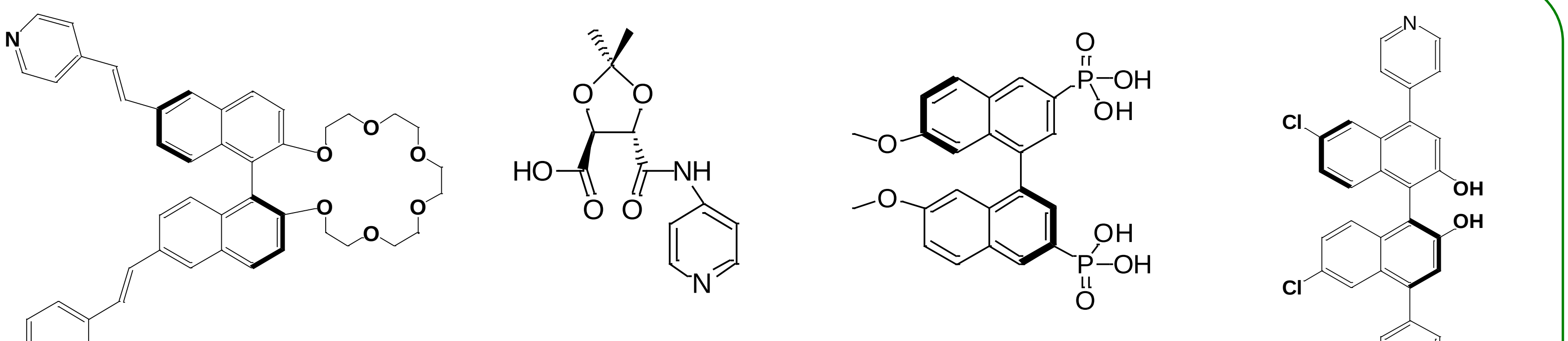
Chiral MOFs for enainioselective separation





Synthesis of chiral porous MOFs

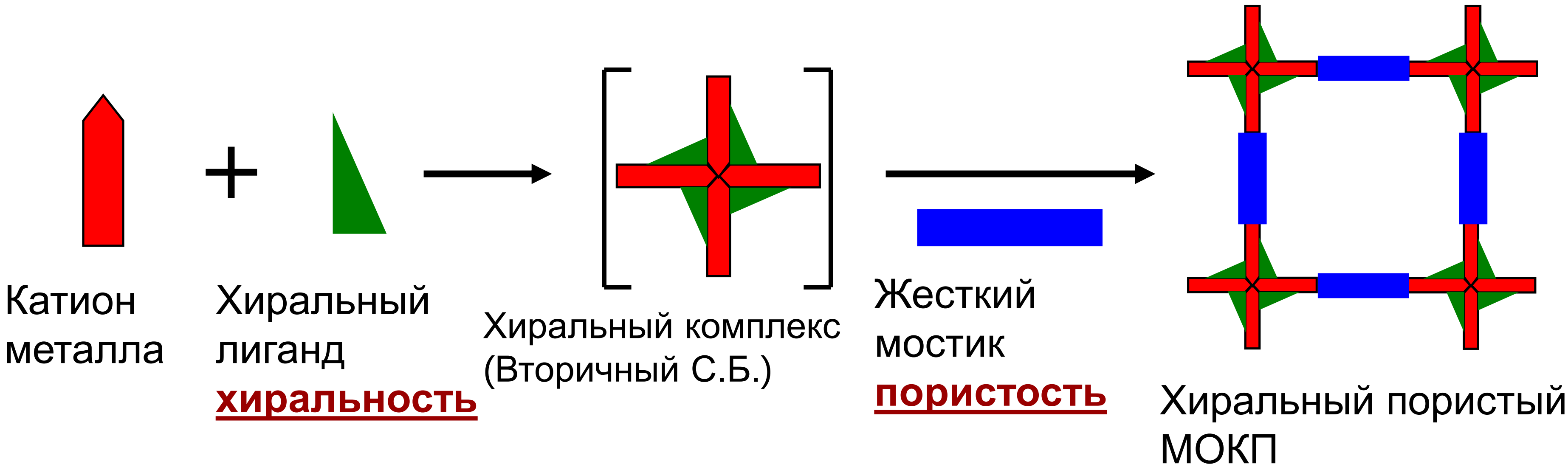




some examples of ligands, used for the synthesis

Новый подход к синтезу хиральных пористых МОКП

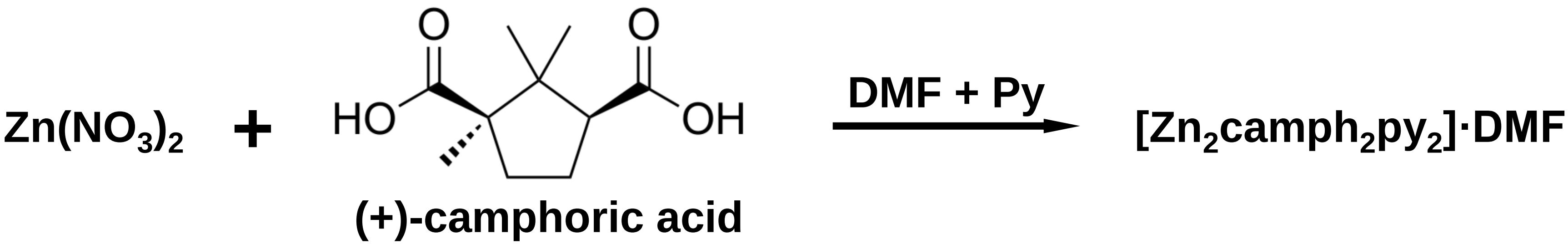
ДВА ЛИГАНДА ЛУЧШЕ ОДНОГО!

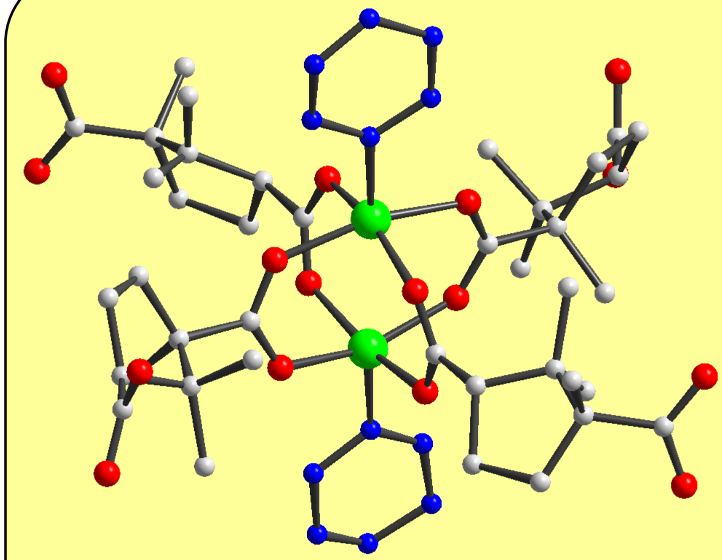


- **Позволяет использовать простые доступные хиральные лиганды природного происхождения**
- **Позволяет контролировать размер пор за счет изменения длины мостиковых лигандов.**

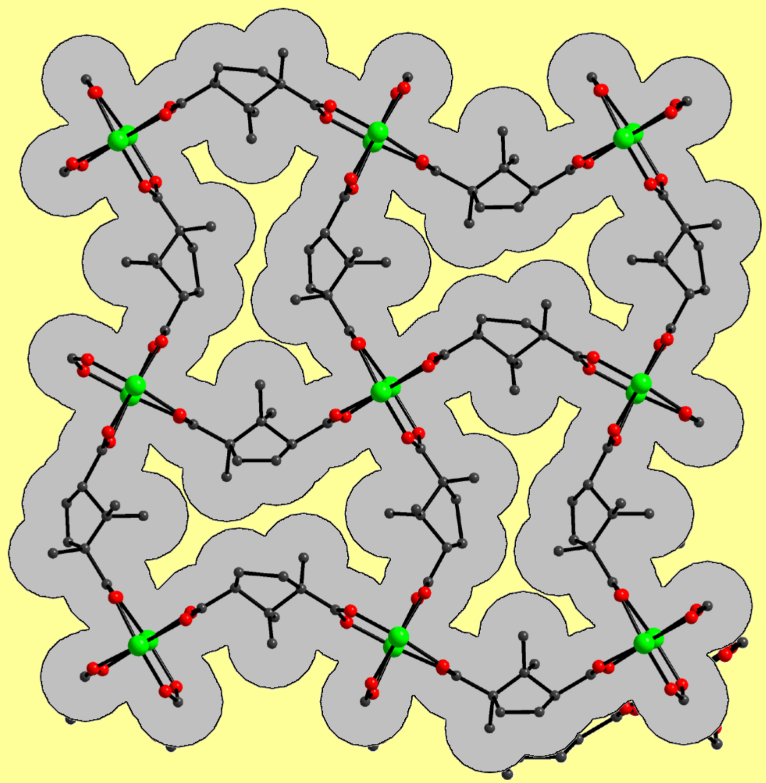
D.N. Dybtsev et al., Angew. Chem. Int. Ed., **2006**, *45*, 916

Zn(II) Camphorates





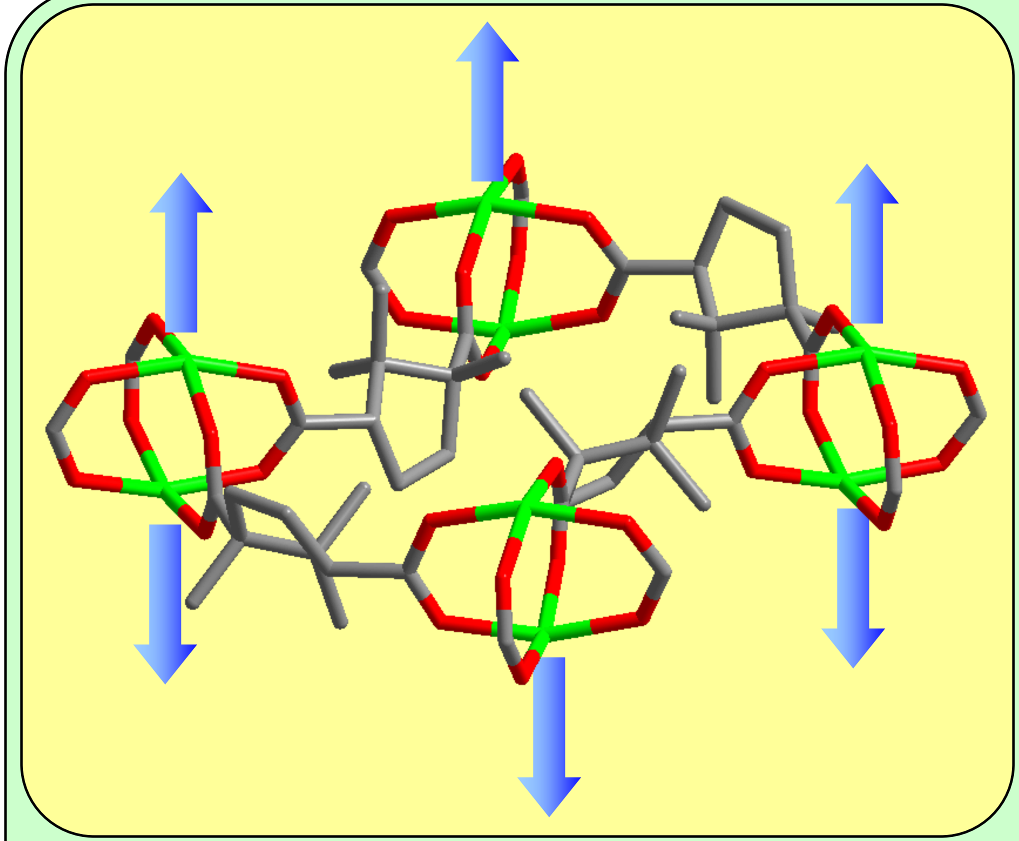
Structure of Zn_2 paddle-wheel

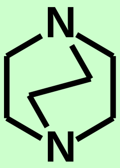


Layered zinc(II) camphorate

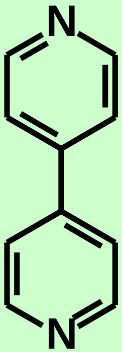
D.N. Dybtsev et al., *Inorg. Chem.*, **2007**, *46*, 6843

From chiral 2D layer to chiral 3D framework

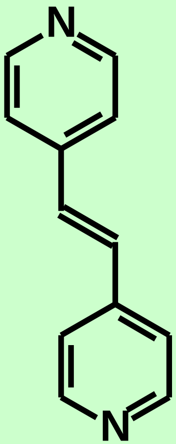




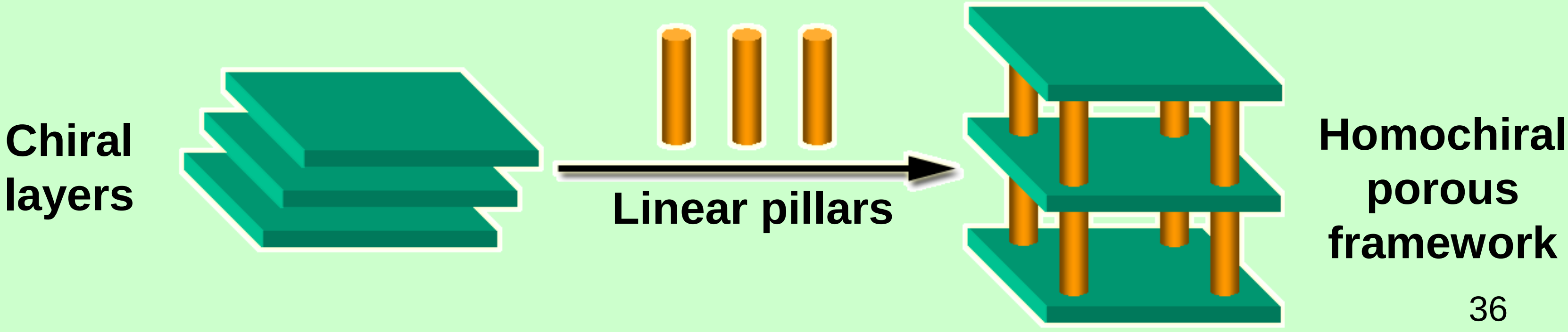
dabco



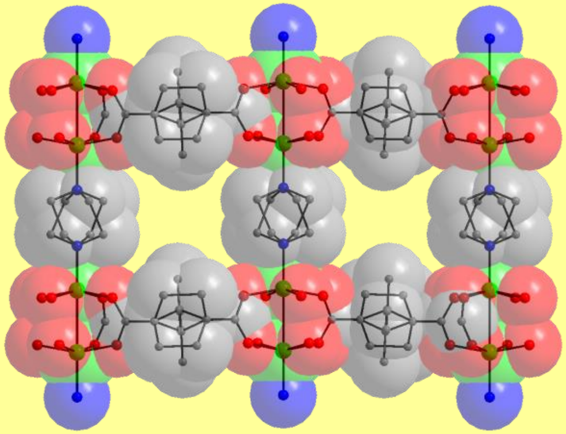
bipy



bpe



Isoreticular chiral porous MOFs

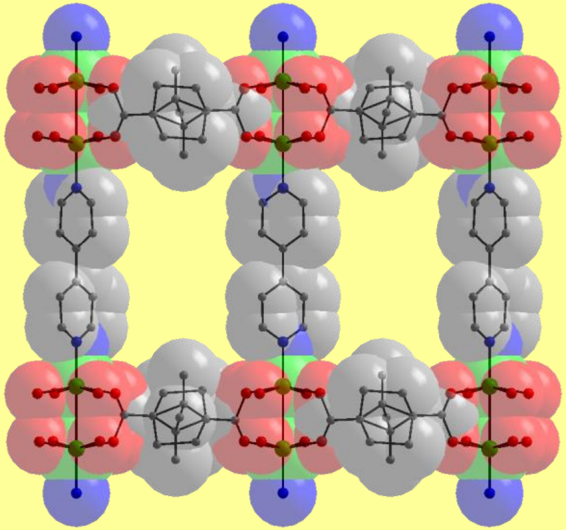


$[Zn_2camph_2dabco]$

V_{free} = 31%

∅ channel:
3 × 3.5 Å

S_{area} = 520 m²/g

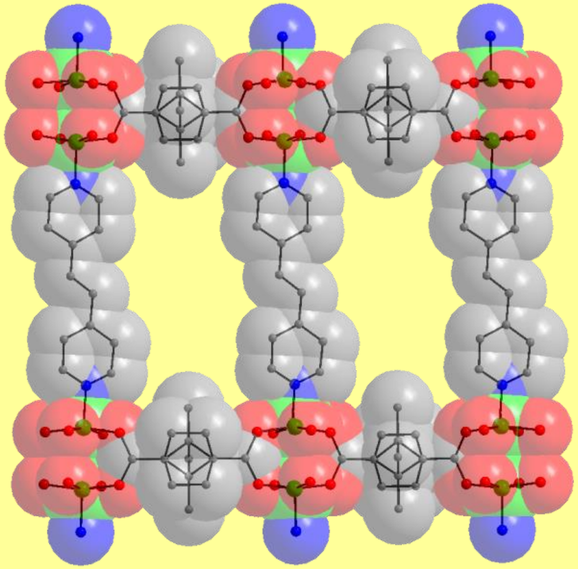


$[Zn_2camph_2bipy]$

V_{free} = 51%

∅ channel:
5 × 7 Å

S_{area} = 1040 m²/g



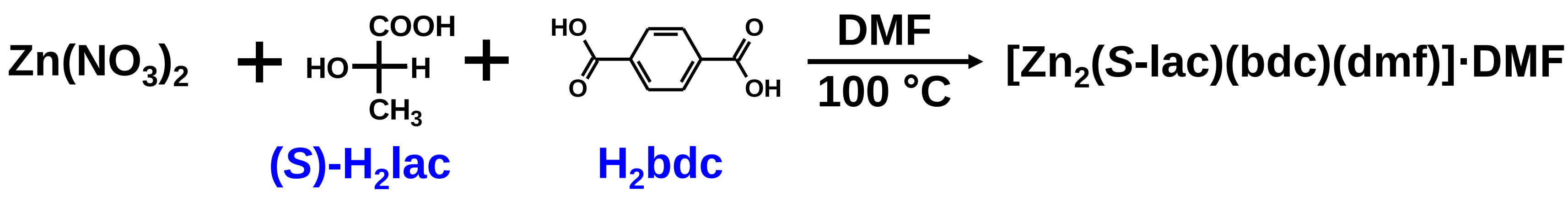
$[Zn_2camph_2bpe]$

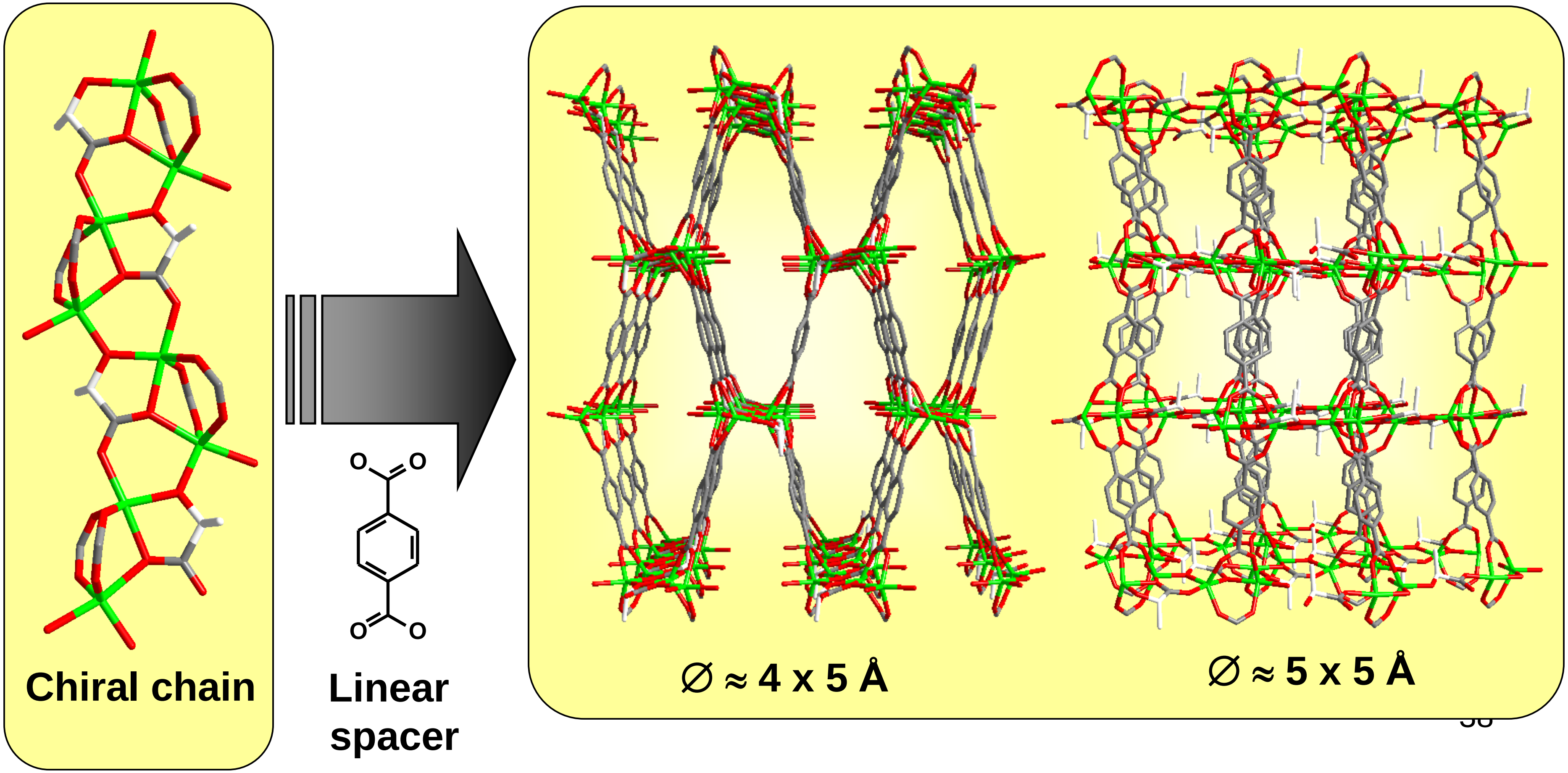
V_{free} = 56%

∅ channel:
5 × 10 Å

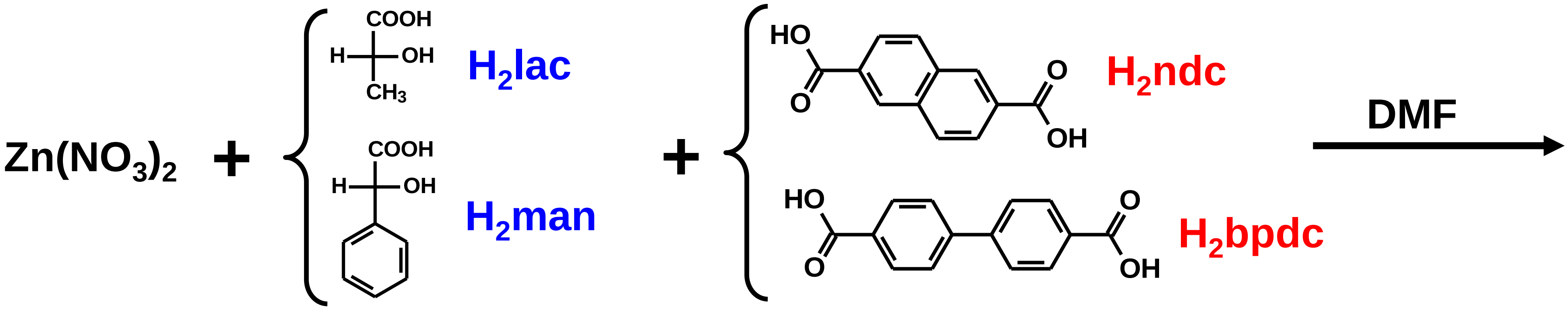
D.N. Dybtsev et al., *Inorg. Chem.*, **2007**, *46*, 6843

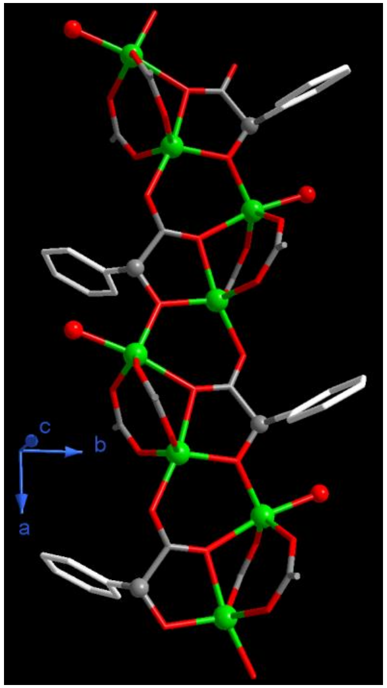
Porous Zn(II) lactate-terephtalate



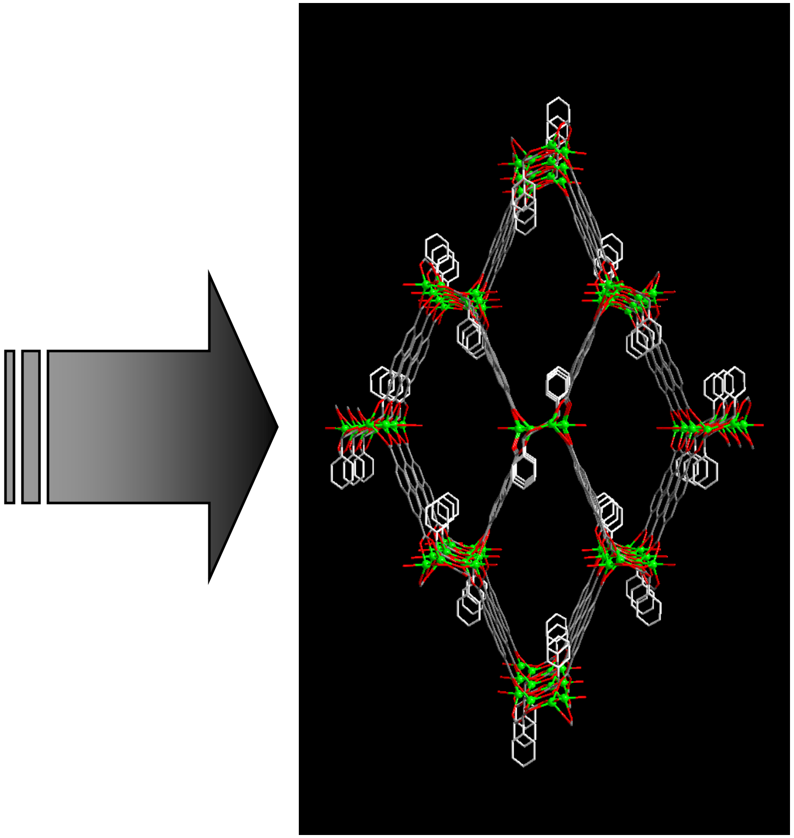


Chiral porous MOFs

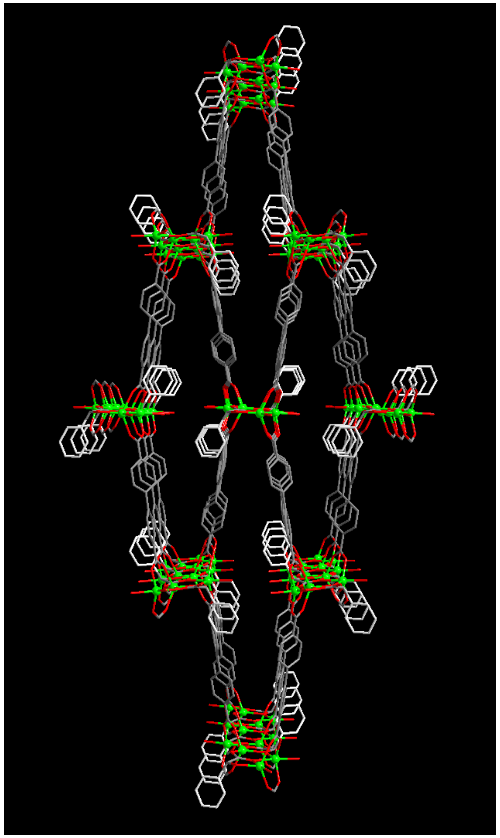




Chiral chain (SBU)

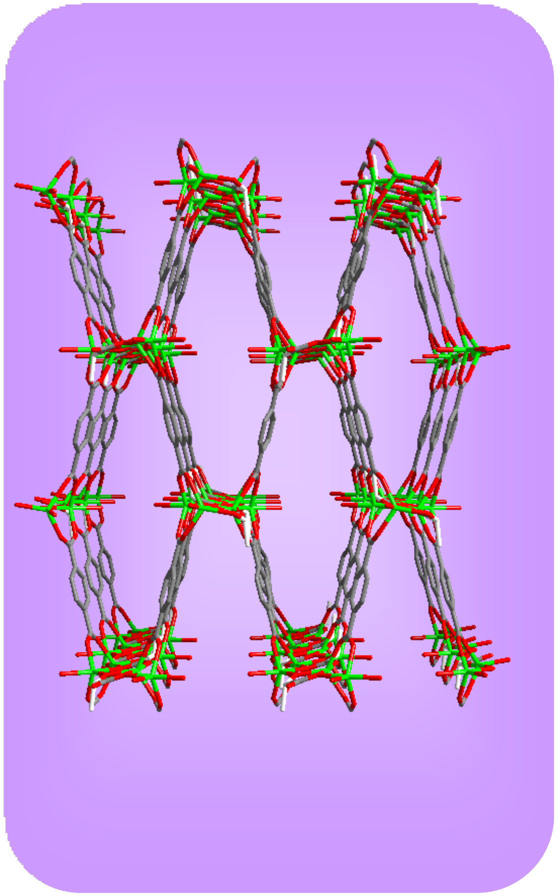


[Zn_2(ndc)(*R*-man)]



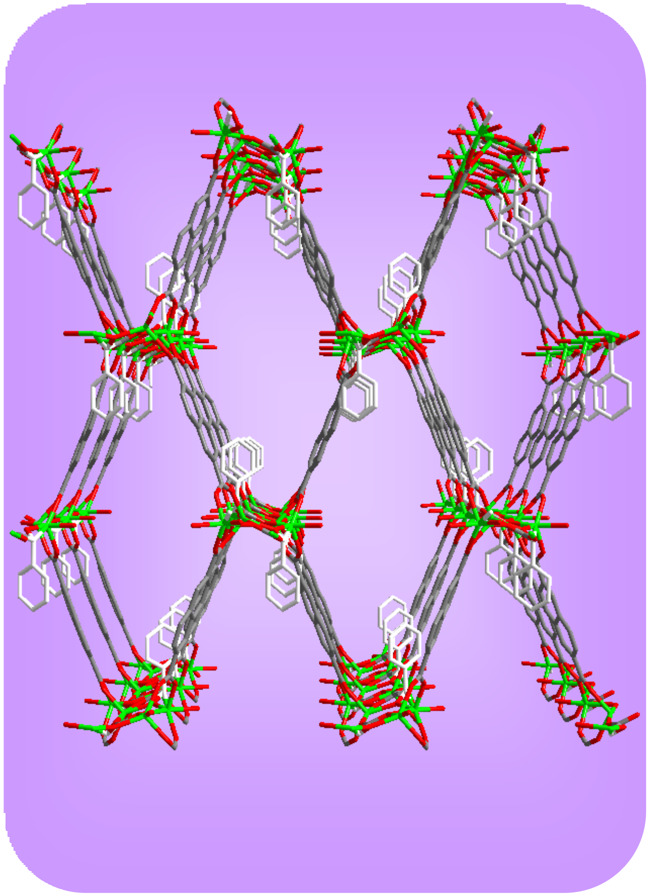
[Zn_2(bpdc)(*R*-man)]

Isoreticular chiral porous MOFs



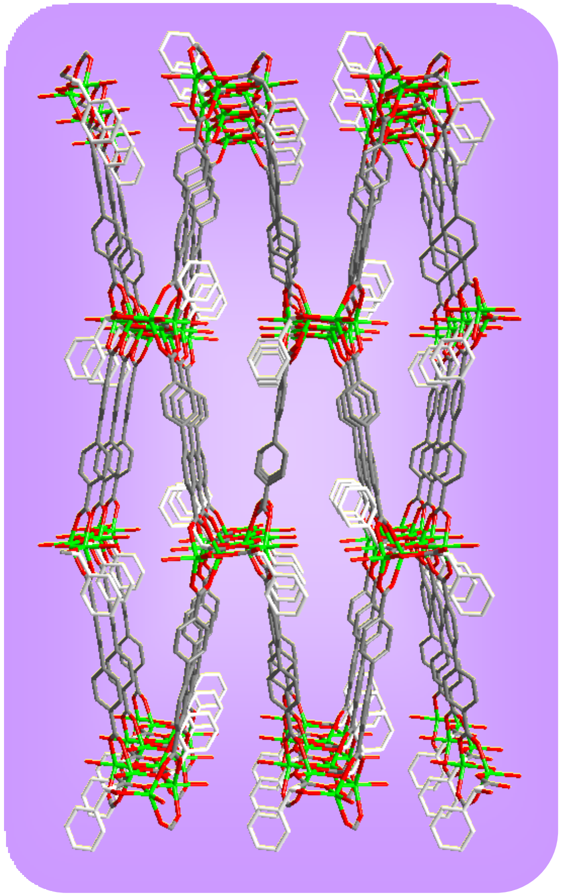
[Zn_2(bdc)(*S*-lac)]

∅ channel ≈ 4 x 5 Å
∅ window ≈ 5 x 5 Å



[Zn_2(ndc)(*R*-man)]

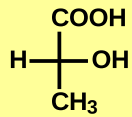
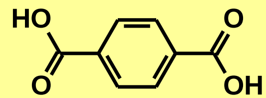
∅ channel ≈ 5 x 9 Å
∅ window ≈ 4 x 5 Å

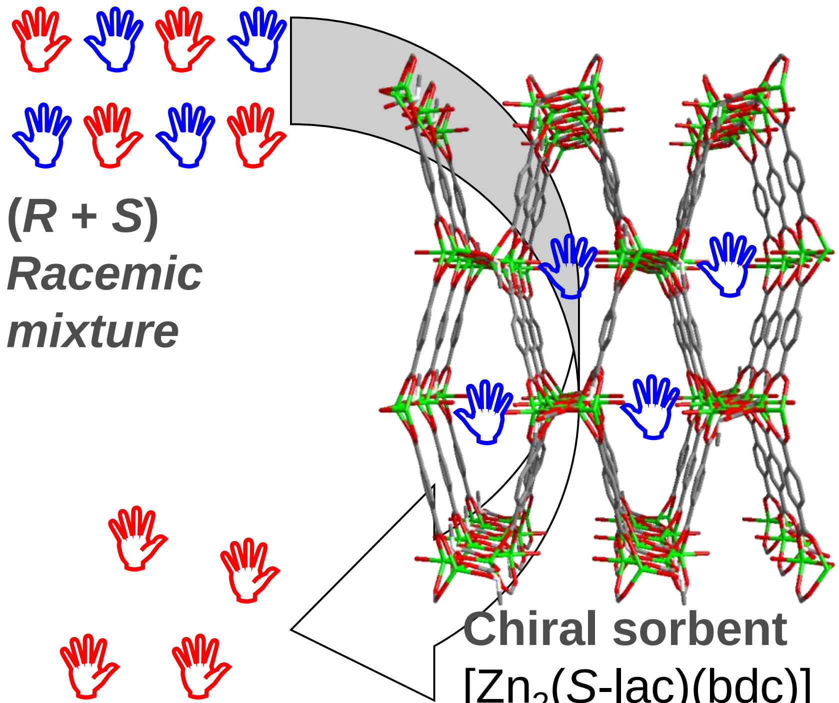


[Zn_2(bpdc)(*R*-man)]

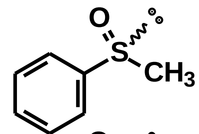
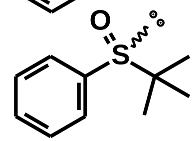
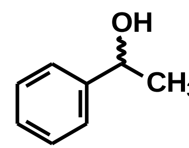
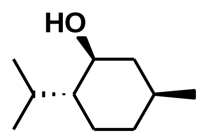
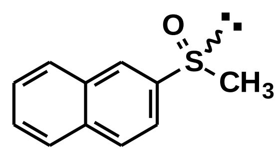
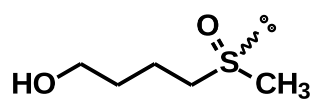
∅ channel ≈ 4 x 14 Å
∅ window ≈ 6 x 7 Å

Enantioselective sorption

$Zn(NO_3)_2$ +  +  ⟶ $[Zn_2(S\text{-lac})(bdc)]$



Stereoselective sorption

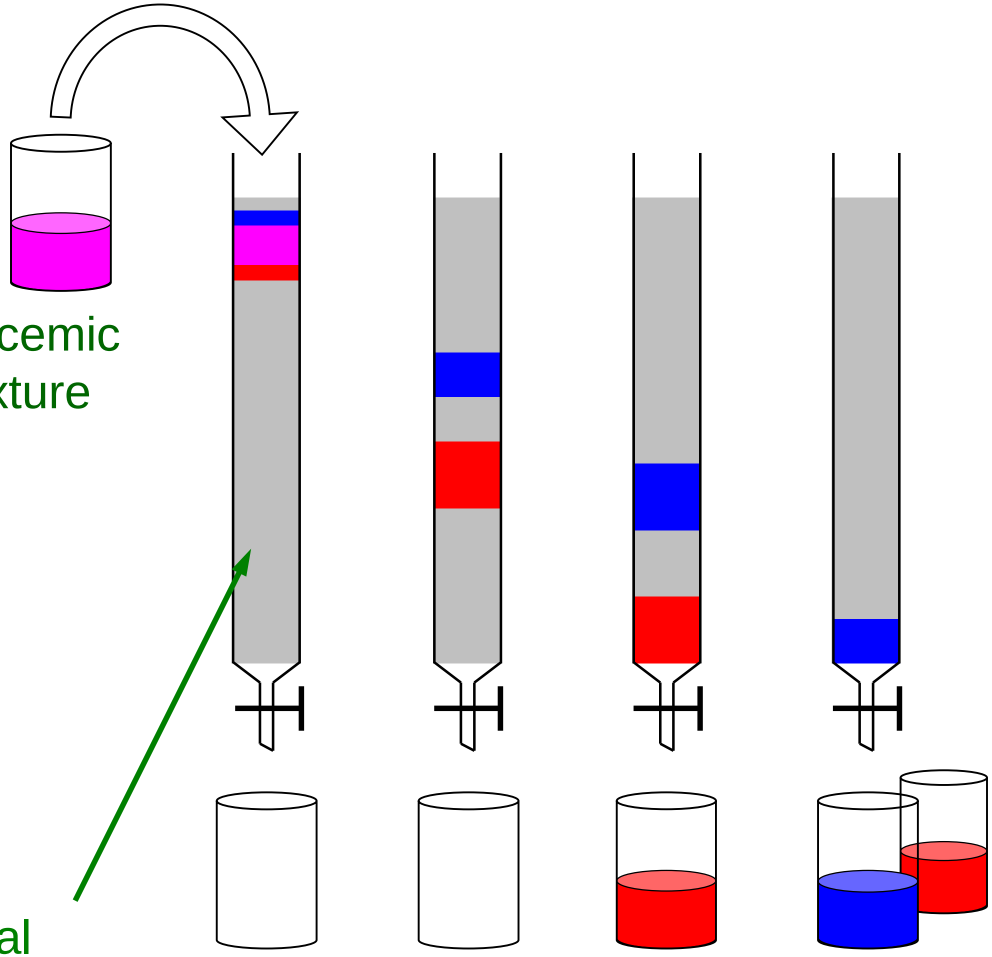
Substrate	*e.e.*(%)
	60 (*S*)
	55 (*S*)
	21 (*S*)
	25 (+)
	*no sorption*
 *Sulforaphane*	20 (*S*)

Enantiomeric excess (*e.e.*)

$$e.e. = ([R]-[S])/([R]+[S])$$

Angew. Chem. Int. Ed. **2006**, *45*, 916; *Chem. Eur. J.*, **2010**, *16*, 10348

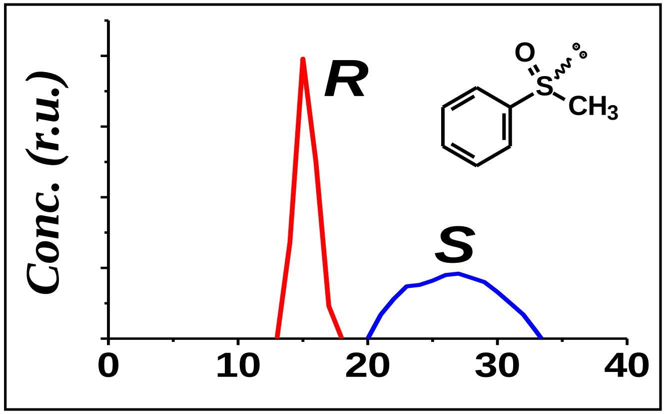
Enantioselective separation

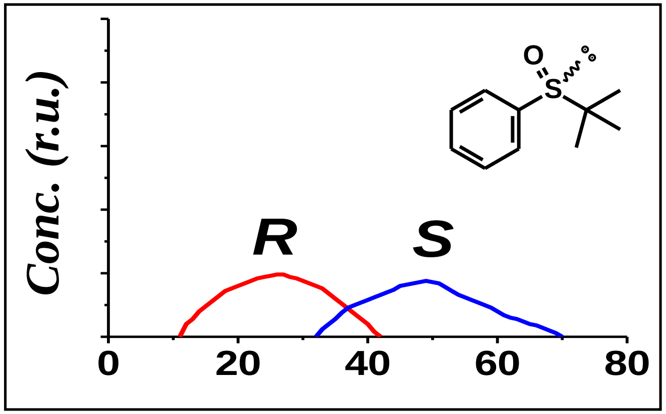


Racemic mixture

Chiral stationary phase $[Zn_2(bdc)(lac)]$

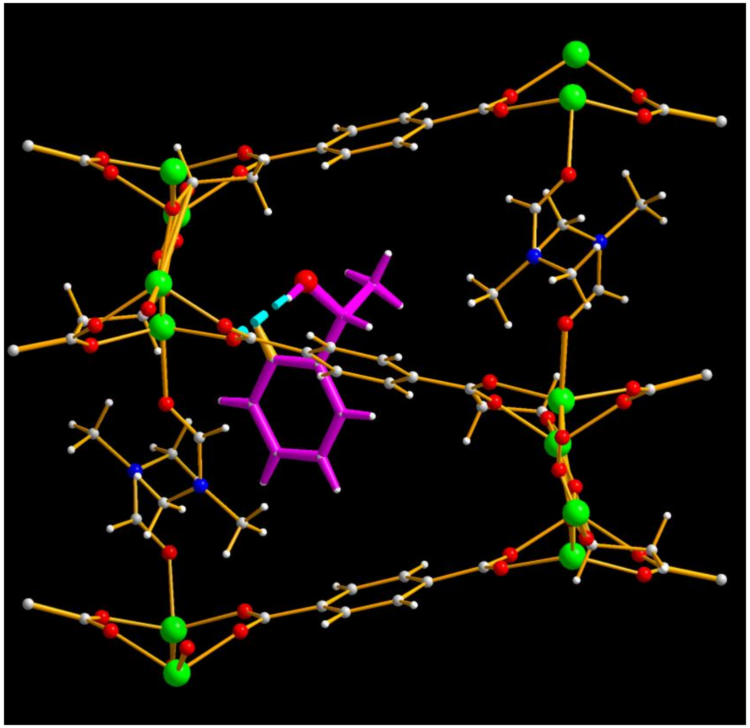
Separated optical isomers





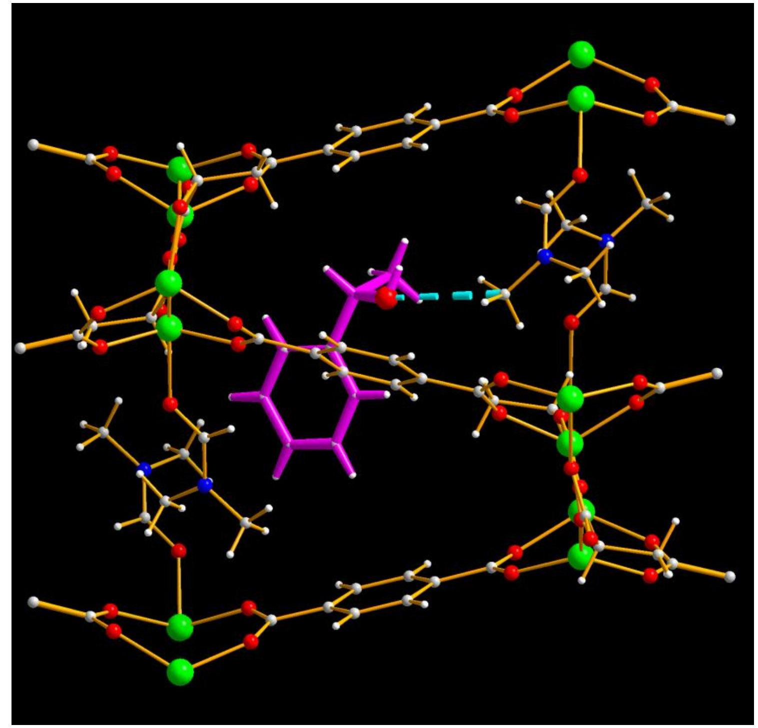
D.N. Dybtsev et al., *J. Am. Chem. Soc*., **2007**, *129*, 12958

Chiral guest in chiral host $[Zn_2(bdc)(S\text{-}lac)(dmf)]$



***R*-PhEtOH@MOF**

d(O…O) = 3.25 Å



***S*-PhEtOH@MOF**

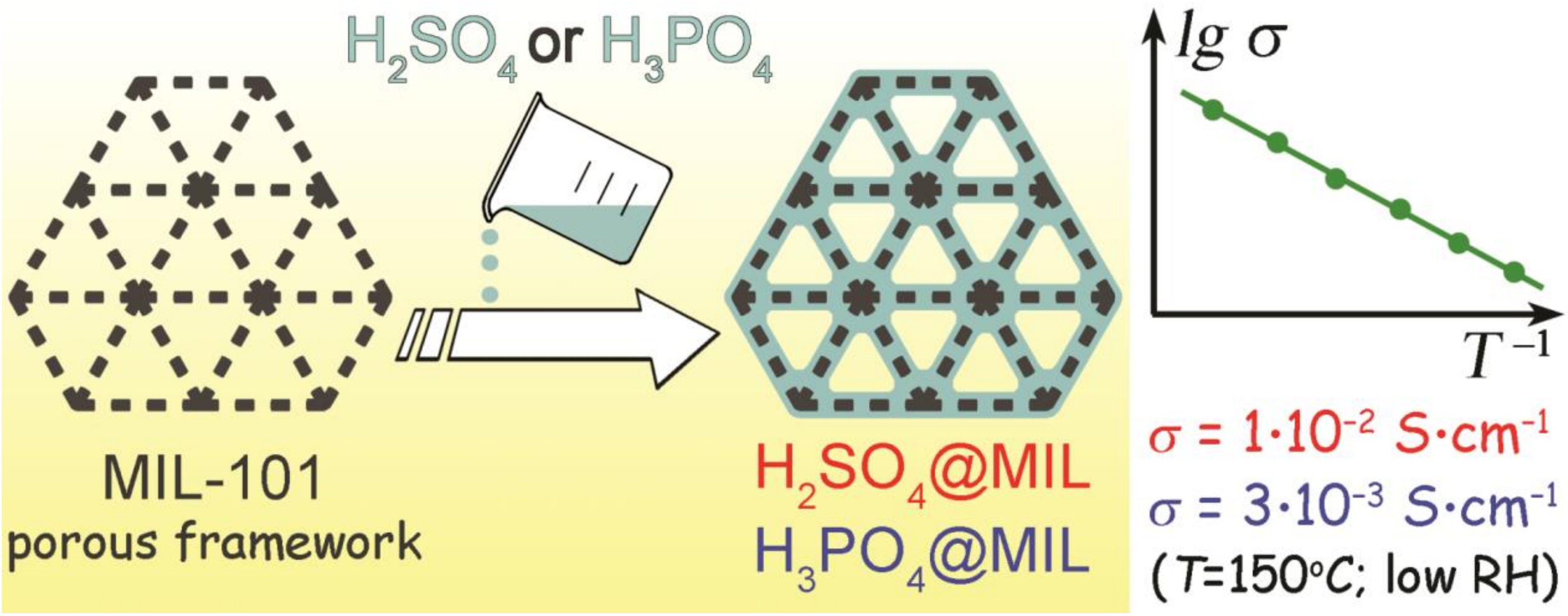
d(O…C) = 3.33 Å

1) *Эксперимент:* более высокое сродство каркаса к *S*-PhEtOH (e.e. = 21%)

2) *TG-DSC измерения*: разложение *S*-PhEtOH@**MOF** происходит труднее, чем *R*-PhEtOH@**MOF** (ΔH ≈ 20 kJ/mol)

K. Suh, M.P. Yutkin et al., *Chem. Commun*., **2012**, *48*, 513

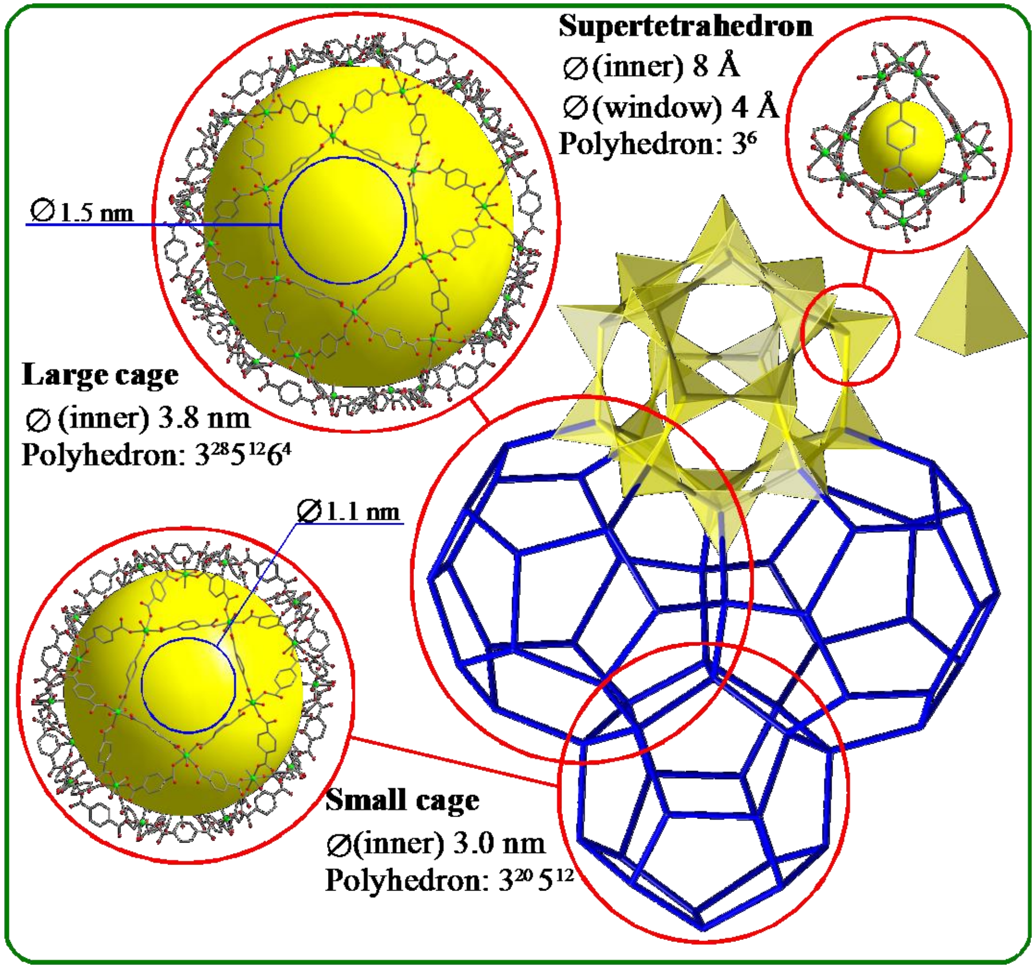
Materials with high proton-conductivity

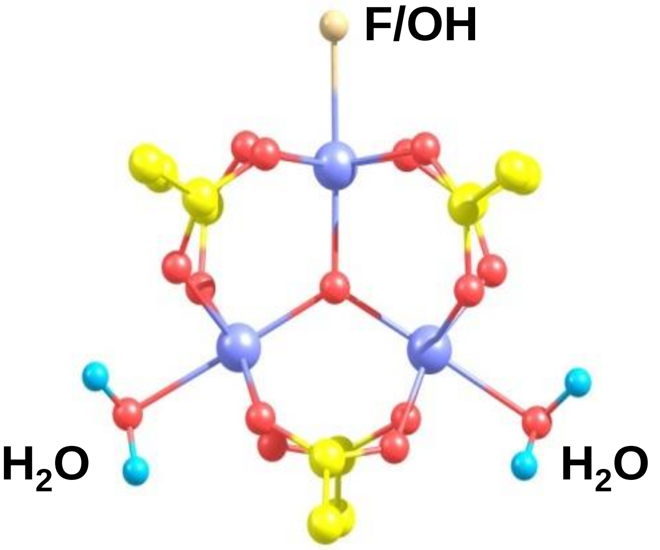


V.G. Ponomareva et al., *J. Am. Chem. Soc*., **2012**, *134*, 15640
D.N. Dybtsev et al., *ACS Appl. Mater. Interfaces*, **2014**, *6*, 5161
V.G. Ponomareva et al., *RCS Anvances*, **2017**, *7*, 403

MIL-101

$Cr_3OF(H_2O)_2\ [O_2CC_6H_4CO_2]_3 \cdot ca25H_2O$





Mesoporous MOF with MTN zeolytic topology

G. Ferey et al, Science 309 (2005) 2040

Imparting high proton conductivity to a MOF material by controlled acid impregnation

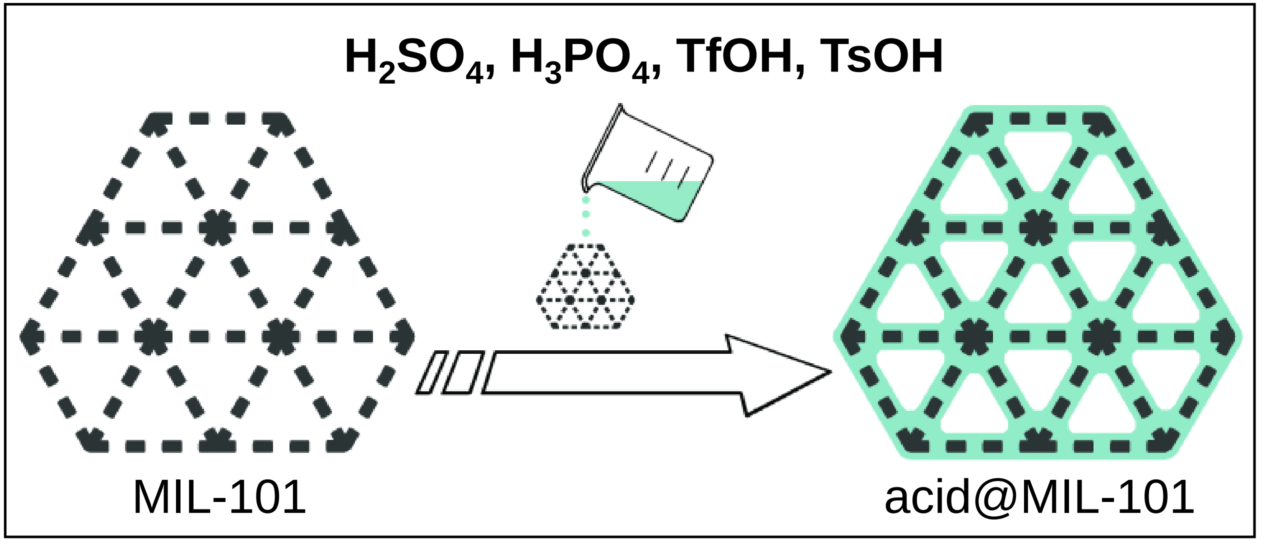
(Proton conductivity) ≈ (H^+ mobility) × (H^+ concentration)

Strong (mineral) acids = ideal proton conductors

1) Liquids can not be used for membranes **??**

2) Operating temperature of the fuel cell can must be 110 – 140 °C **??**

Inclusion of strong and/or non-volatile acids into mesoporous (and stable!) MIL-101 **!!!**



V.G. Ponomareva et al., *J. Am. Chem. Soc.*, **2012**, *134*, 15640; D.N. Dybtsev et al., *ACS Appl. Mater. Interfaces*, **2014**, *6*, 5161

How to make acid@MIL-101

1) Soaking crystalline MIL-101 in an aqueous acid solution (2 - 4 M) for 30 min at room temperature

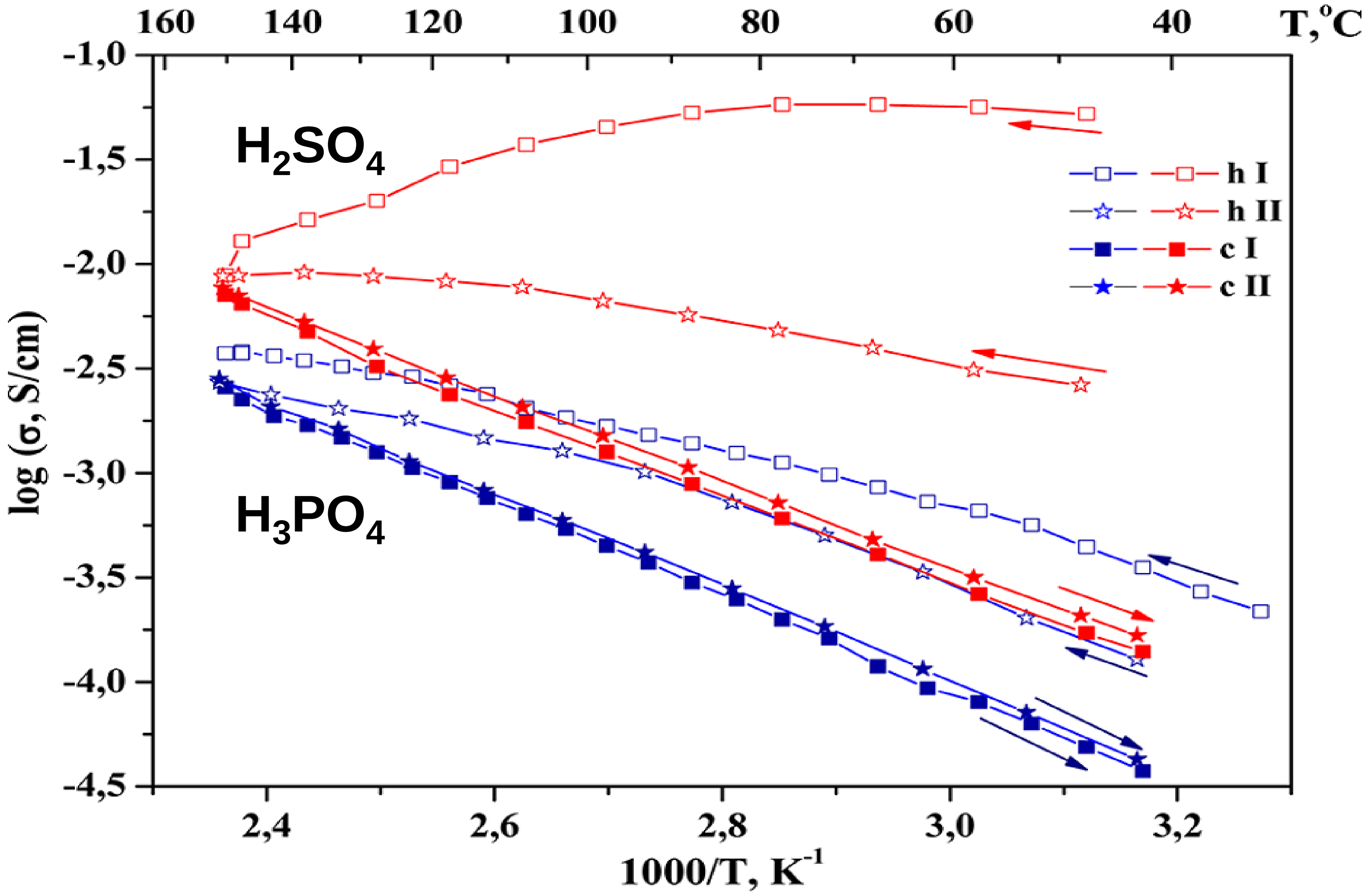
2) Filtration

3) drying at 60° C or in *vacuo*

H_2SO_4@MIL:	MIL·4.5H_2SO_4·10H_2O
H_3PO_4@MIL:	MIL·3.7H_3PO_4·5H_2O

The molar concentration of the acid in acid@MIL-101 corresponds to concentration of the initial aqueous solution (3 - 4 M).

H-conductivity of acid-impregnated MIL-101



1) Linear σ *vs T* plot as soon as the sample hydration is stabilized
2) Acid@MIL-101 materials are stable: no acid leeching, no framework deterioration after several measurements

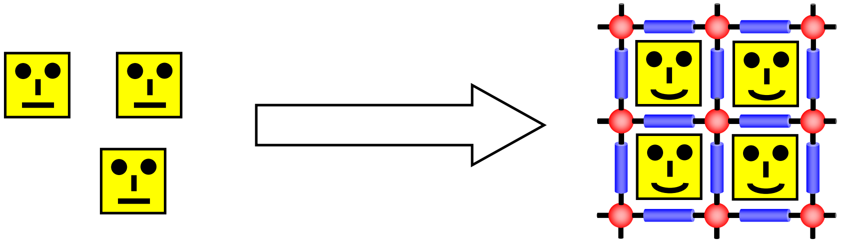
- Inclusion of strong acids does not destroy MIL-101 framework.

- Deviations in the values of proton conductivity in the heating and cooling regimes due to different moisture content in the sample. The amount of acid is not changed.
- Samples at a constant humidity give reproducible proton conductivity.
- Maximum proton conductivity: σ = 0.06 S/cm for H_2SO_4@MIL-101 at 80 °C and RH ≈ 10%.
- The proton conductivities of the H_2SO_4@MIL-101 and H_3PO_4@MIL-101 at T = 150 ºC and low humidity outperform any other MOF-based materials and could be compared with the best proton conductors, such as Nafion.

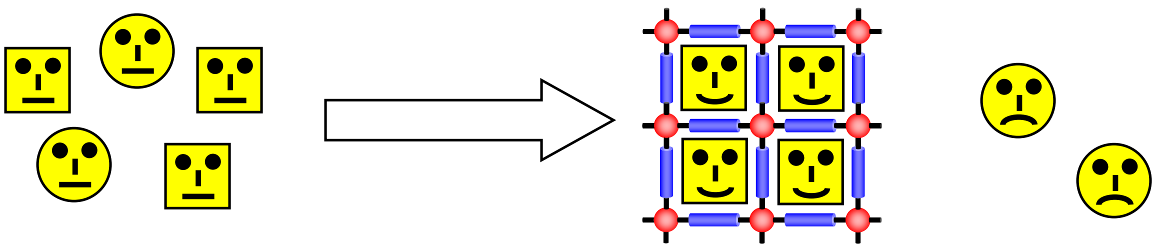
Nafion: $\sigma = 9 \cdot 10^{-3}$ S/cm at 80 °C and RH = 34%.

Applications for porous MOFs

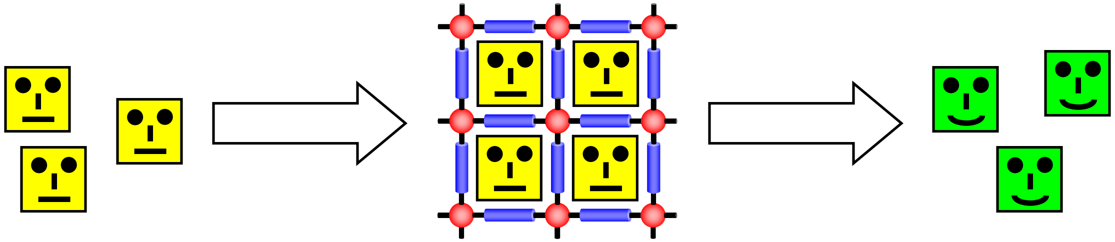
- Storage and delivery:
  - volatile gases (H_2, CH_4, C_2H_2, CO_2)
  - drugs



- Selective sorption:
  - gas molecules
  - enantioseparation



- Heterogeneous catalysis:
  - Chiral catalysis



«ВЫВОДЫ»

1) Химия пористых МОКП (MOFs) чрезвычайно интенсивно развивается в последние годы, но, по-прежнему, остается «новой» областью междисциплинарных исследований.

2) Многие исследовательские группы со всего мира сообщают о получении новых MOF с сенсорными свойствами, протонной, ионной, электронной проводимостью, нелинейными оптическим свойствами, магнитными свойствами и т.д.

3) Очевидно, много новых структур с интересными новыми свойствами и применениями будут открыты в ближайшее время.

4) ПОСМОТРИТЕ БОЛЕЕ ВНИМАТЕЛЬНО НА ЭТИ СОЕДИНЕНИЯ. ВОЗМОЖНО, ОНИ МОГУТ ОКАЗАТЬСЯ ПОЛЕЗНЫМИ ДЛЯ ВАШИХ ИССЛЕДОВАНИЙ. ☺

Лаборатория химии кластерных и супрамолекулярных соединений ИНХ СО РАН

Acknowledgments

Prof. K. Brilyakov and Prof. E. Talsi

Prof. O.A. Kholdeeva

Prof. V. Ponomareva

Prof. K. Kim

Prof. M. Schöder

Russian Science Foundation

Ministry of Science and Education

Russian Foundation for Basic Research

Новосибирский государственный университет
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АСПИРАНТУРА ИНХ СО РАН

ИНХ СО РАН является лидирующим научным центром России в области химии

Аспирантура ИНХ СО РАН аккредитована по направлению «Химические науки» по специальностям **неорганическая химия, физическая химия, аналитическая химия**

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- ✓ навыки работ на современном научном оборудовании
- ✓ международное сотрудничество и зарубежные стажировки
- ✓ стипендии им. А.В. Николаева, гранты и стипендии Президента РФ, другие престижные награды

Вступительные экзамены:
«общая химия»
«иностранный язык»

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Этот е-мэйл может изменить твою жизнь!