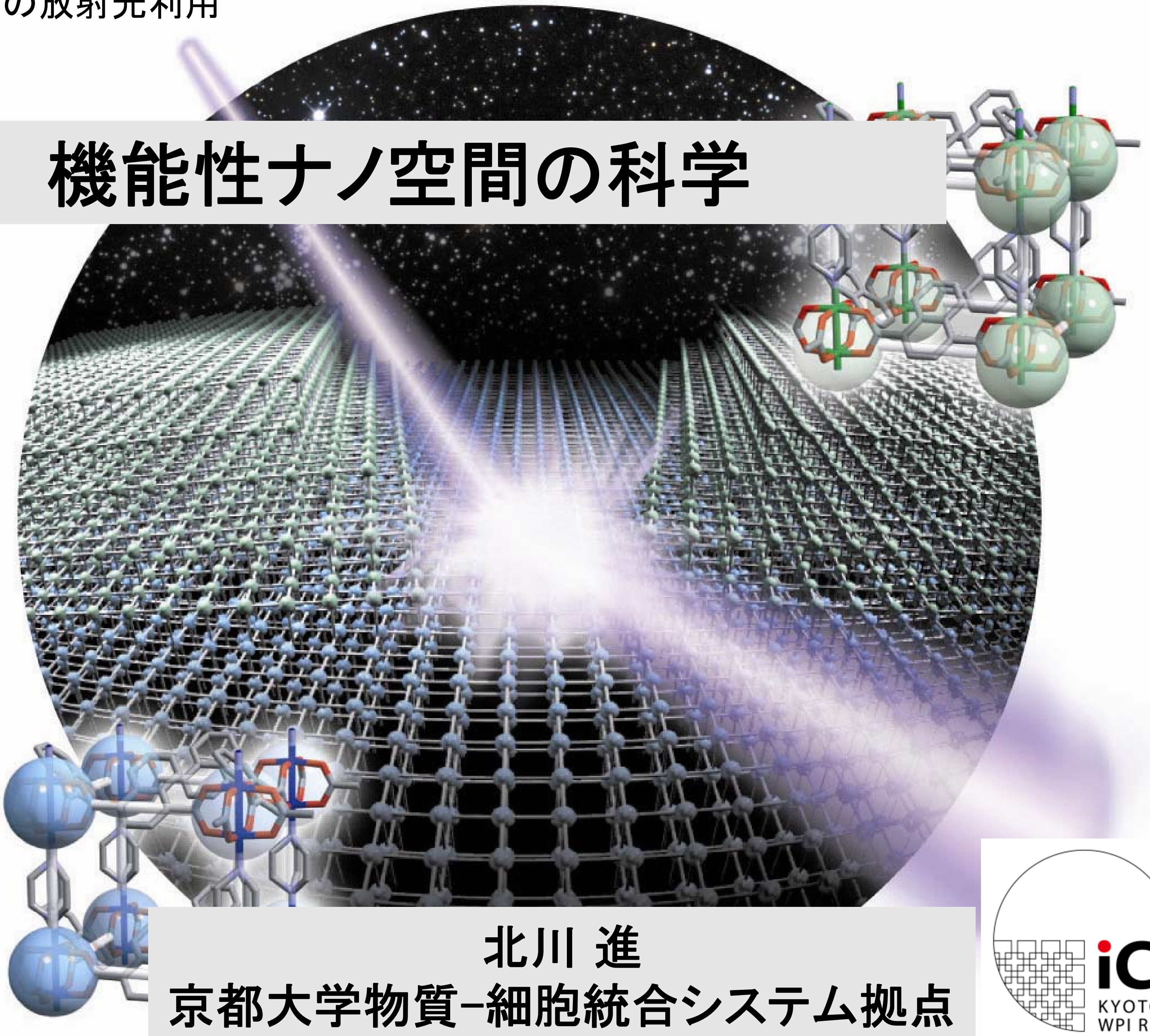
機能性ナノ空間の科学



北川 進
京都大学物質−細胞統合システム拠点

iCeMS
KYOTO UNIVERSITY
WPI Research Center


無用之用
「人皆知有用之用、而莫知无用之用也
内篇(人間世篇、第四)」
莊子, the 4th century B.C.

空间

space

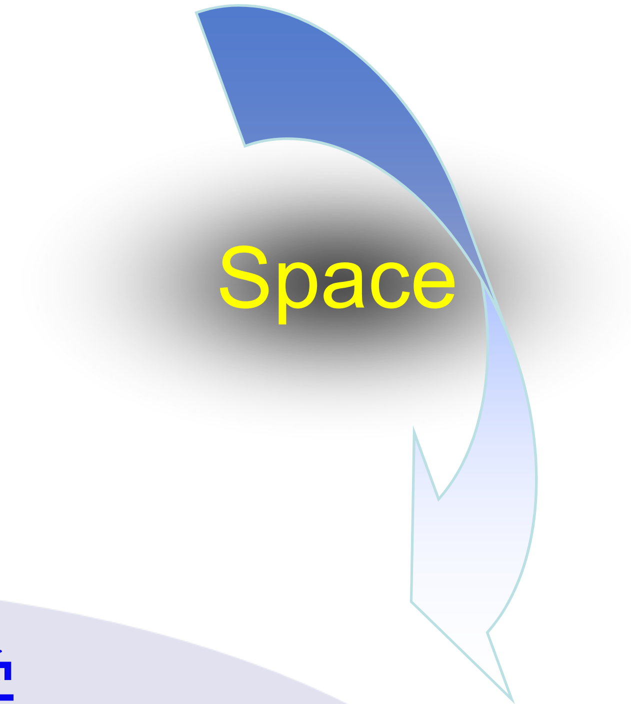
“空間”は単に何もない空隙ではなく、
機能の宝庫である

“Space” is not a simple void
but an entity with functionality

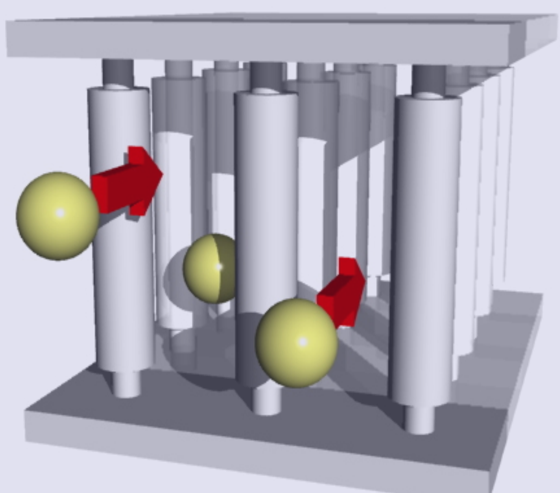
空間を科学する

Creative Science for Space

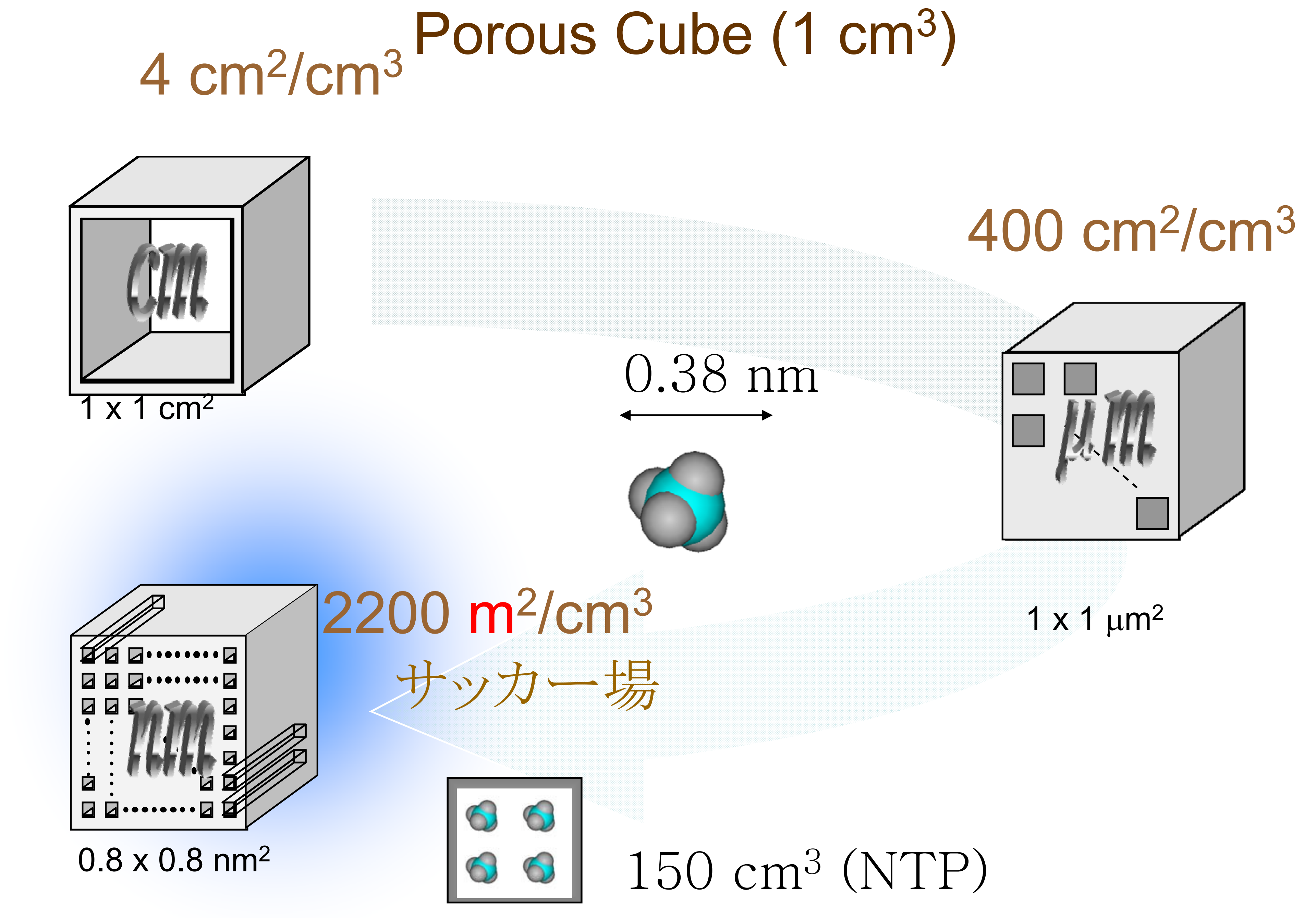
“メートル(*m*)” scale



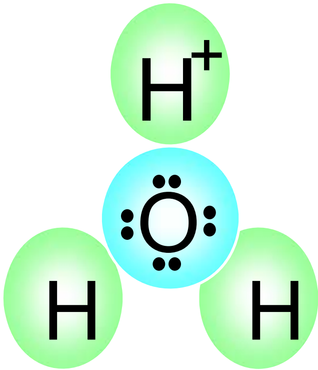
配位空間の化学

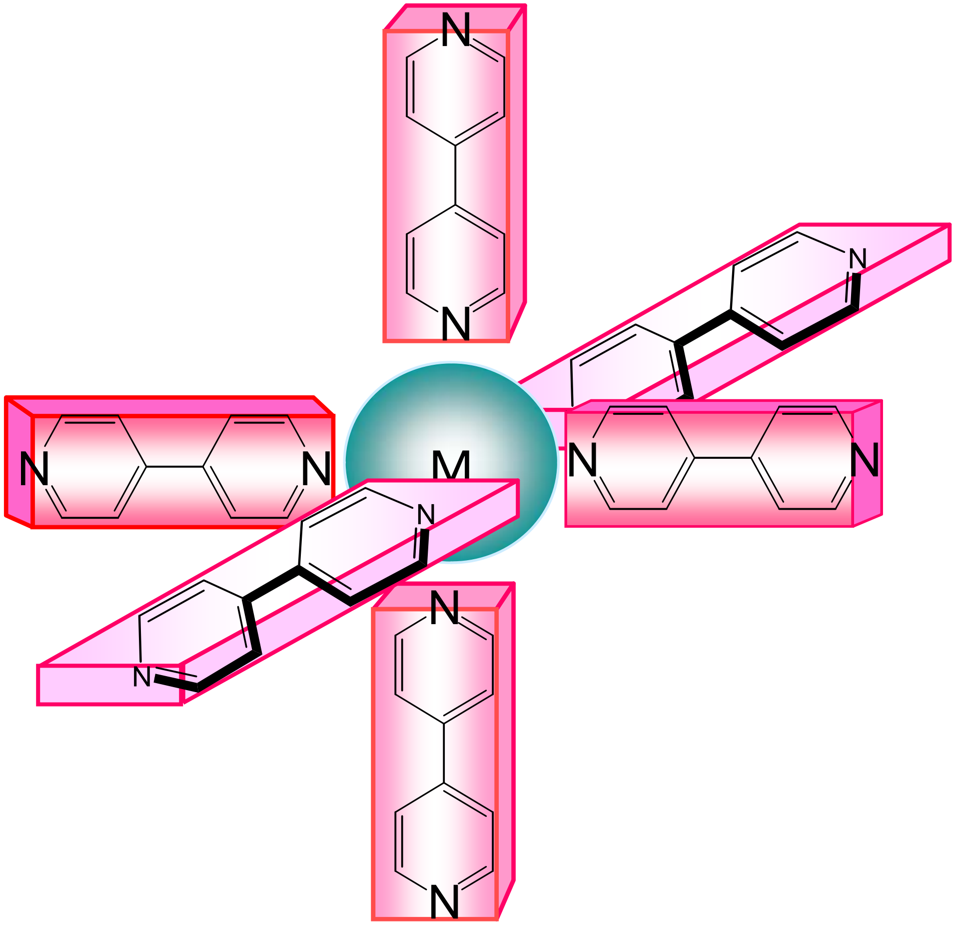


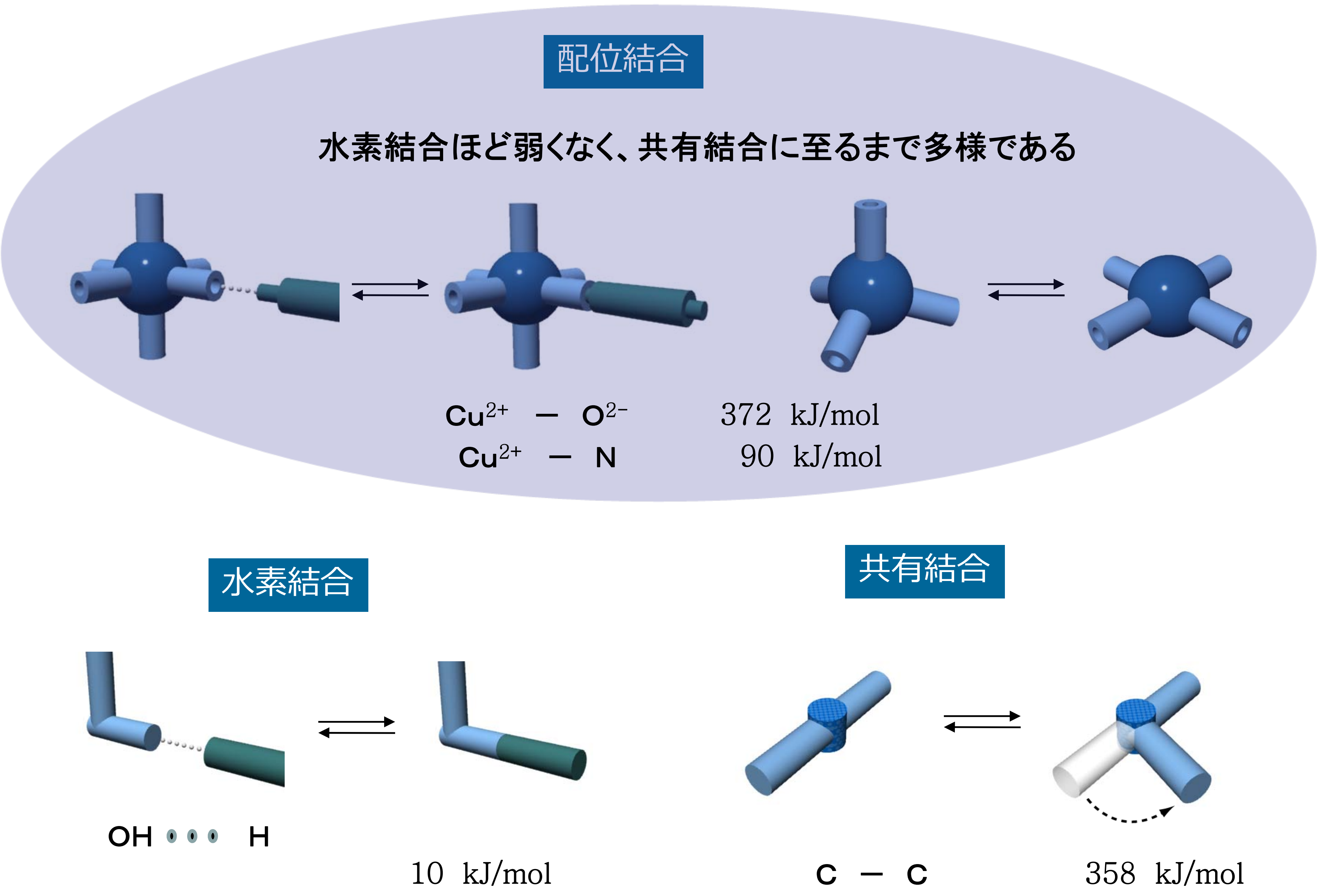
“< 2 ナノメートル(*nm*)” scale


Porous Cube (1 cm3)
4 cm2/cm3
cm
1 x 1 cm2
400 cm2/cm3
0.38 nm
μm
1 x 1 μm2
2200 m2/cm3
サッカー場
nm
0.8 x 0.8 nm2
150 cm3 (NTP)

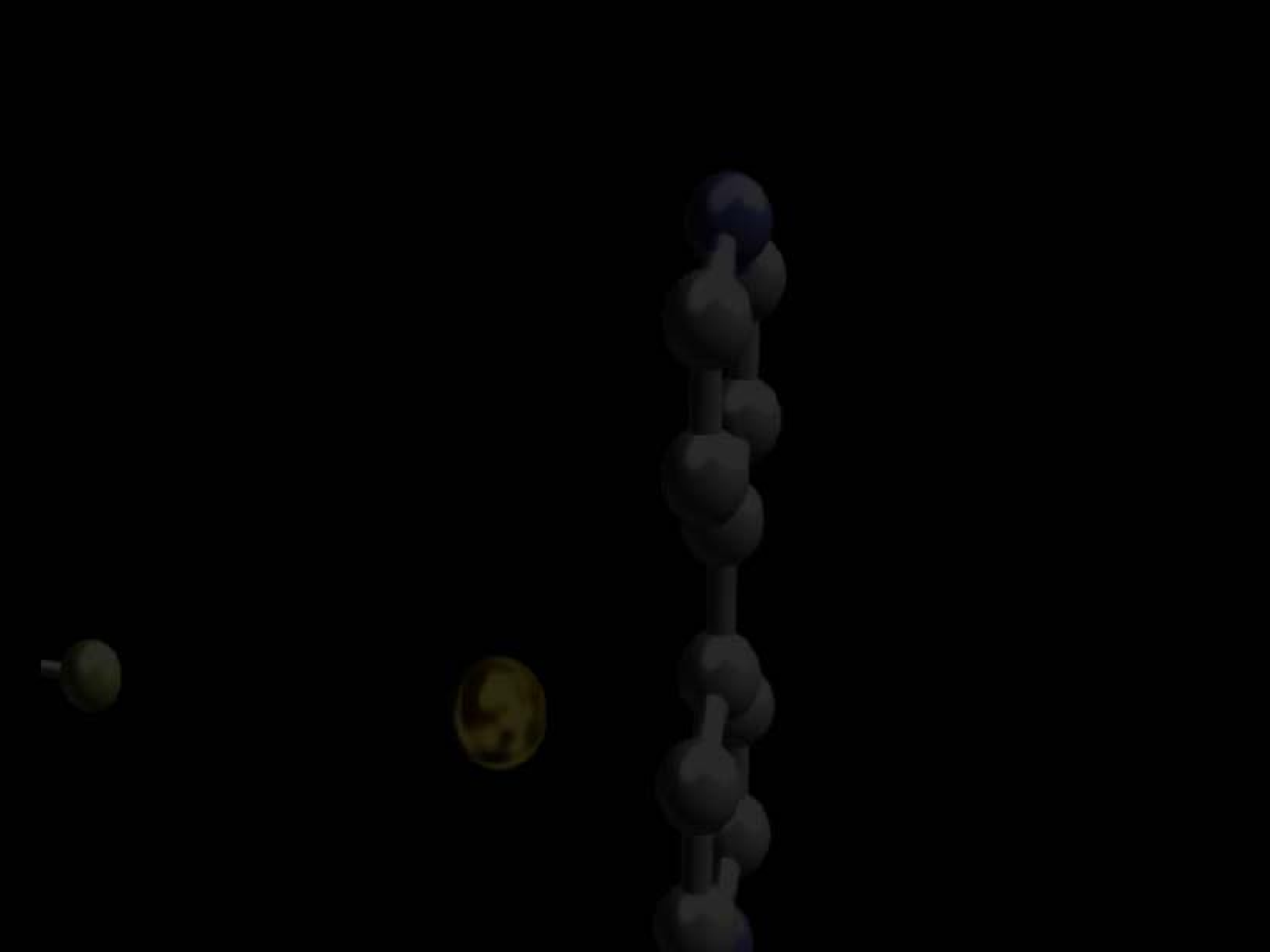
Key － 配位結合

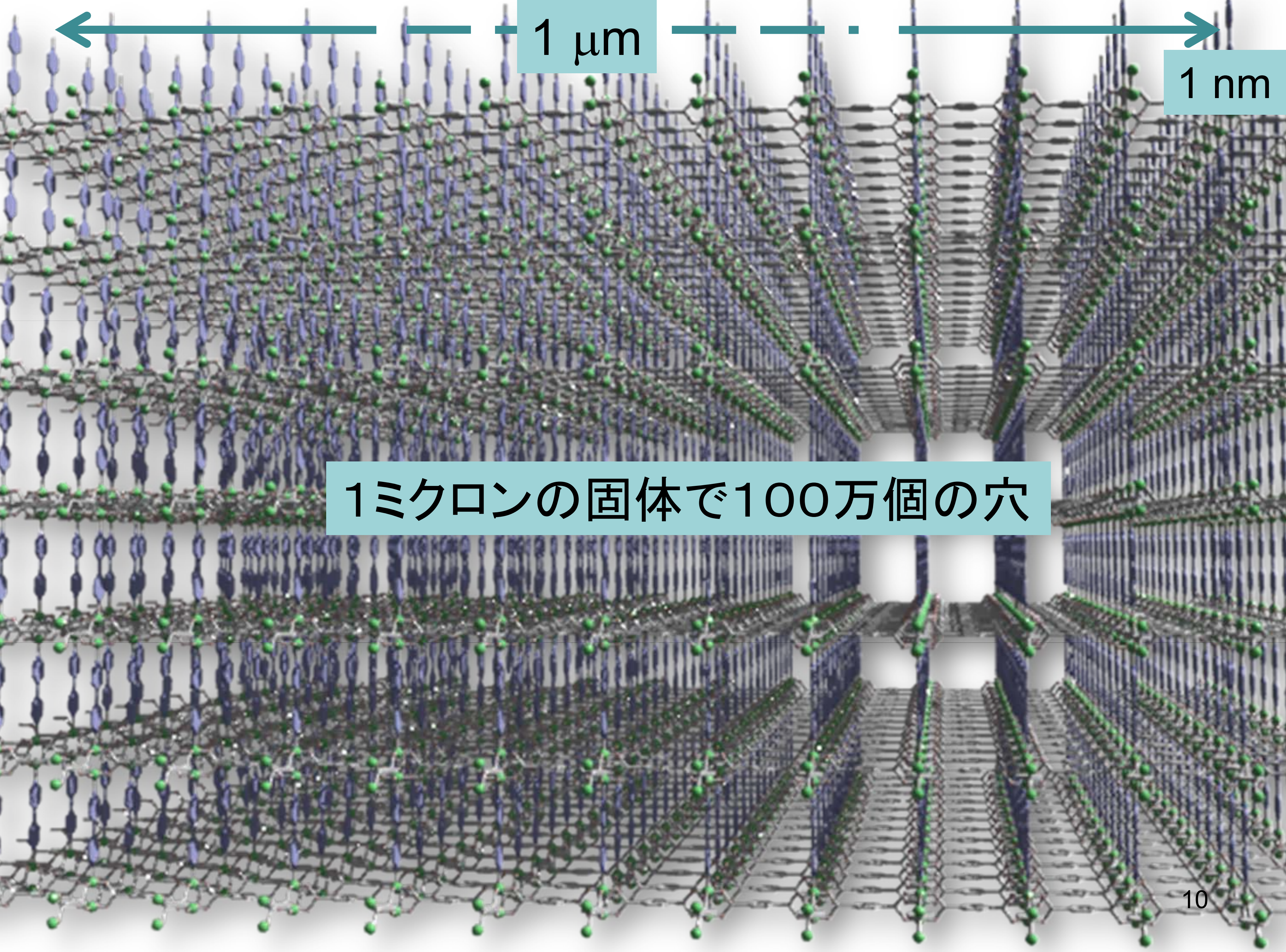


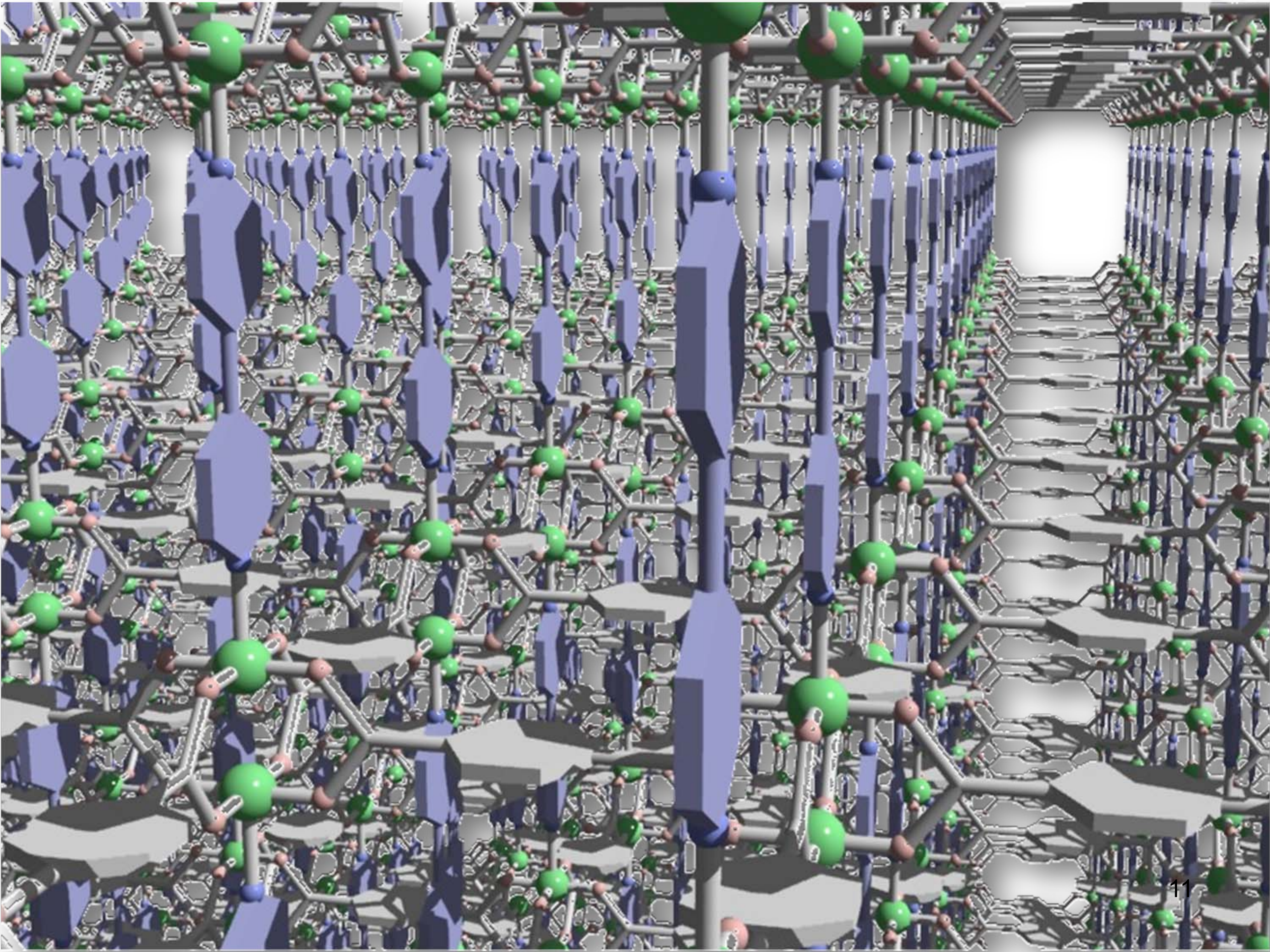




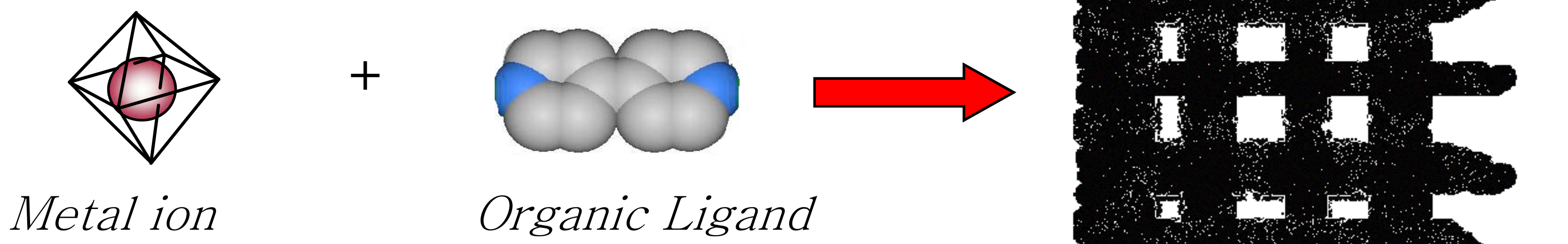
配位結合
水素結合ほど弱くなく、共有結合に至るまで多様である
Cu^{2+} — O^{2-} 372 kJ/mol
Cu^{2+} — N 90 kJ/mol
水素結合
OH ••• H
10 kJ/mol
共有結合
C — C
358 kJ/mol



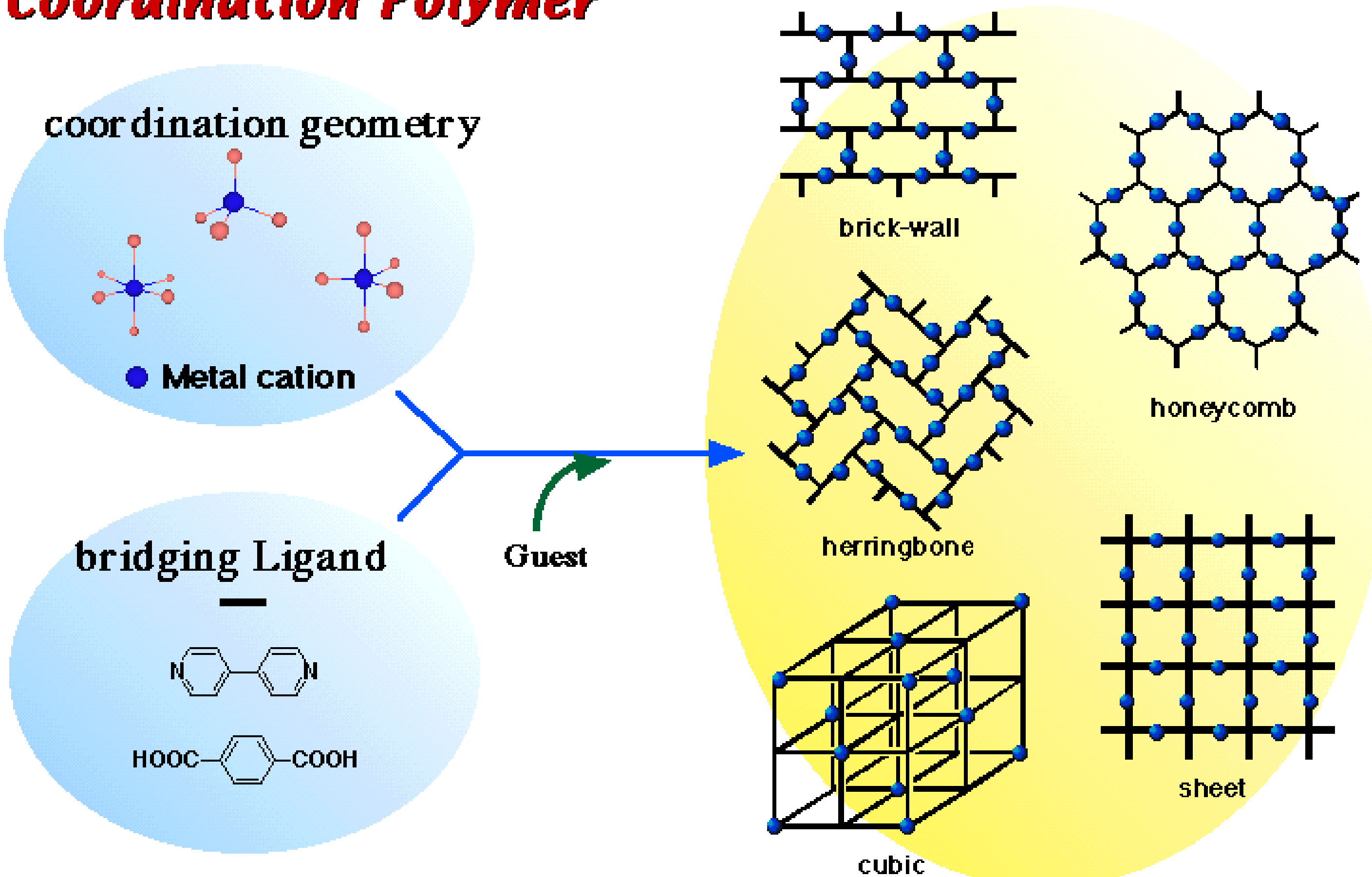

1 μm
1 nm
1ミクロンの固体で100万個の穴



Self-assembling at ambient condition

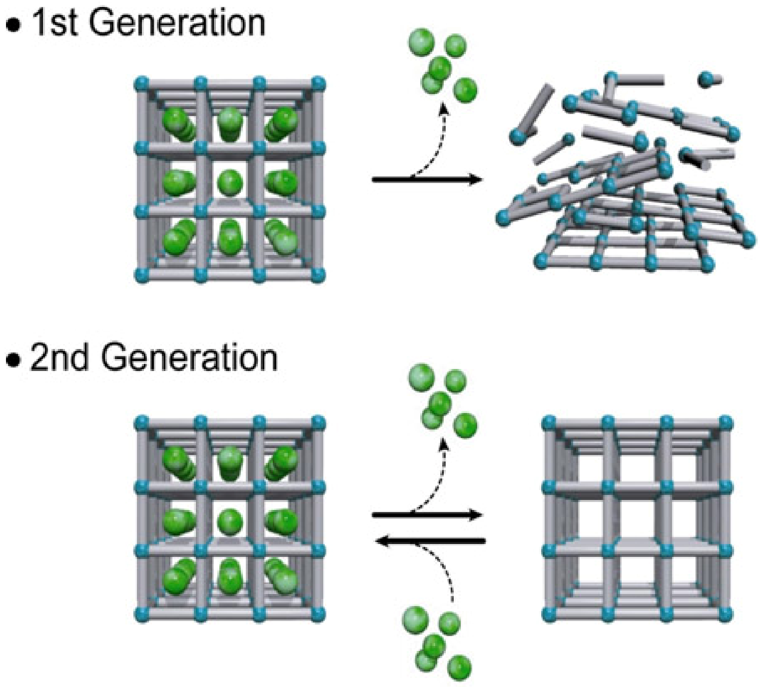


Coordination Polymer



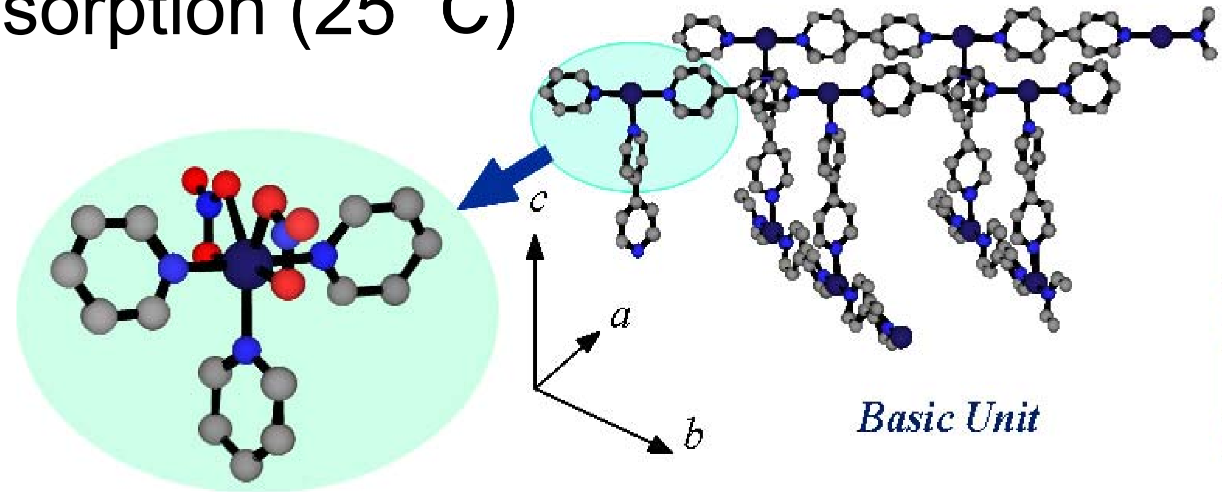
Natura abhorret a vacuo.

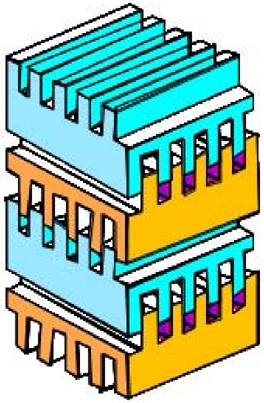
(Nature abhors a vacuum, Aristotle the 4th century B.C.)



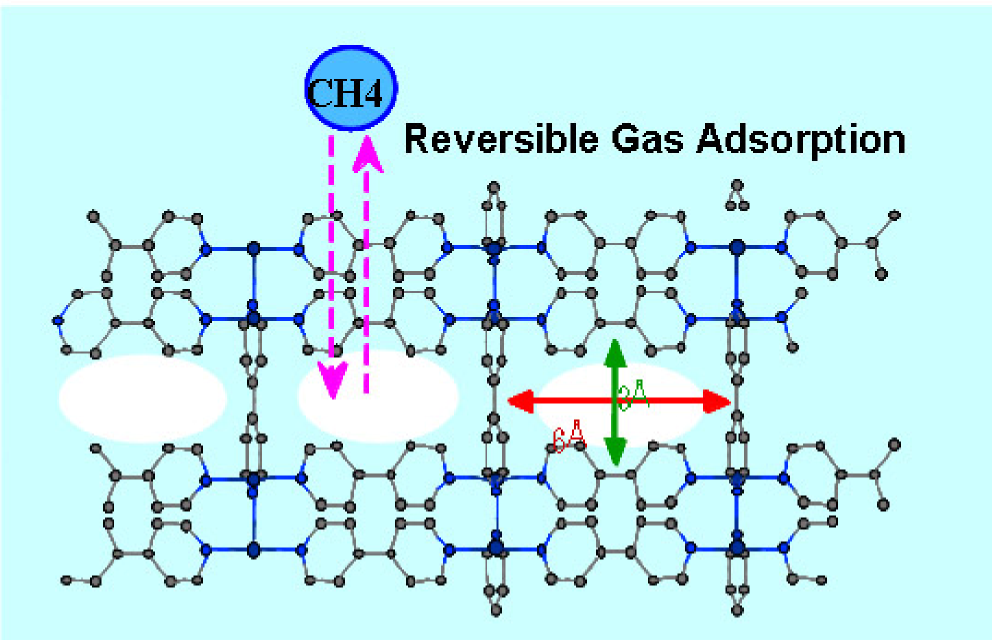
Bull.Chem.Soc.Jpn. Accounts 1998, 71,1739.

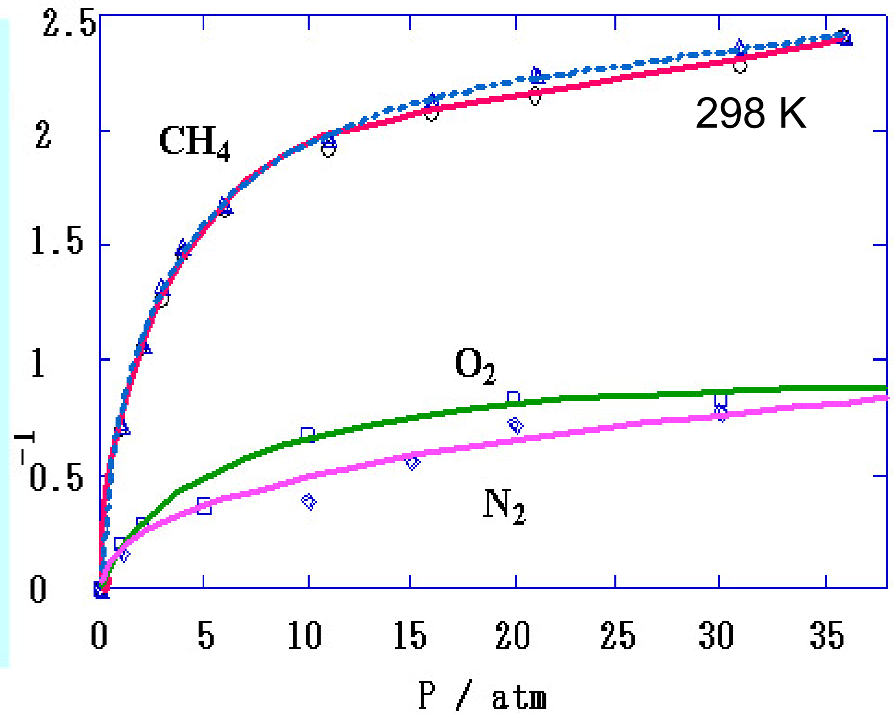
First Gas Adsorption (25 ℃)





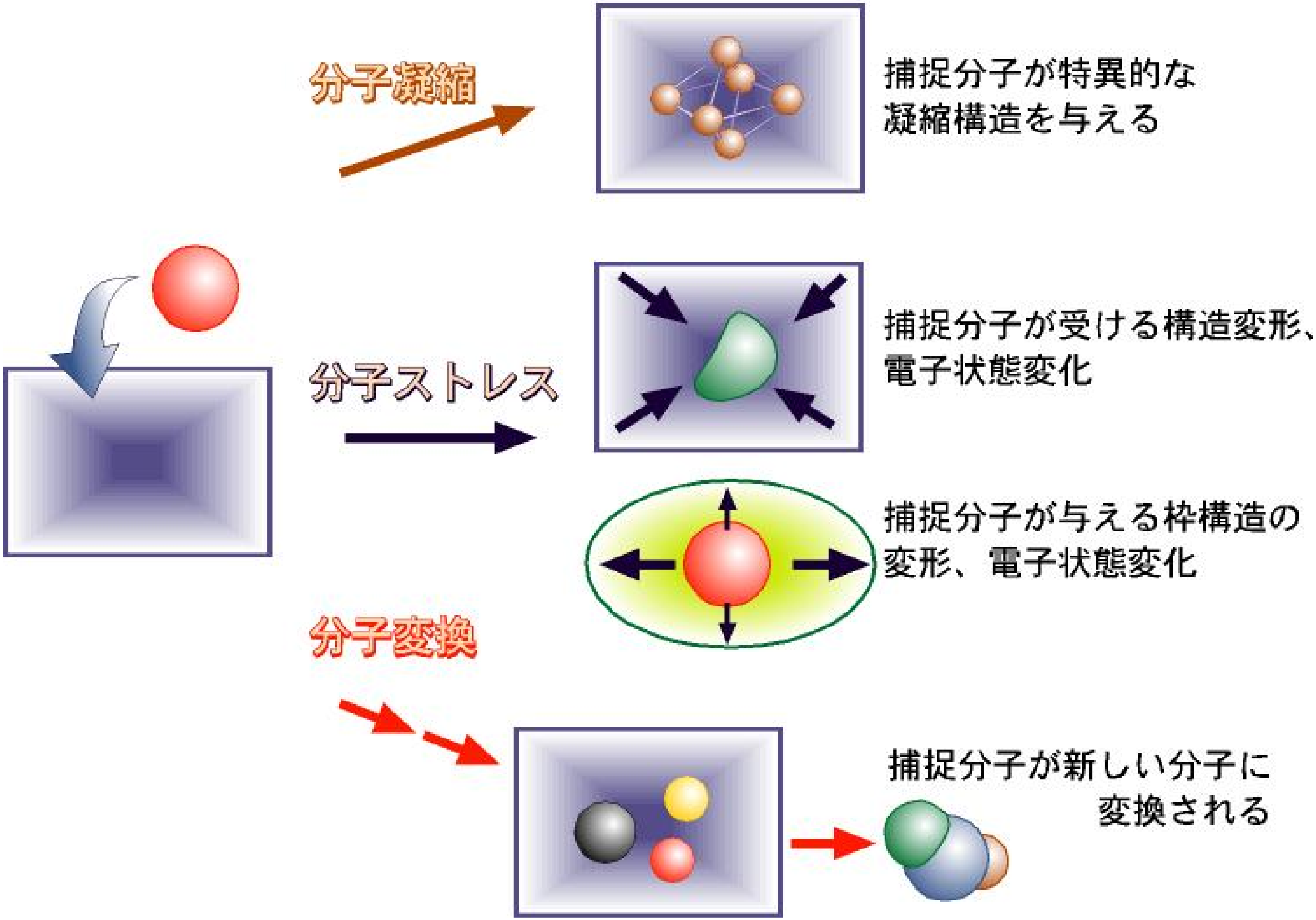
$[Co_2(4,4'\text{-bpy})_3(NO_3)_4]$

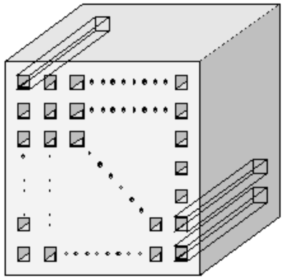




Angew.Chem.Int.Ed. 1997, 36,1725.

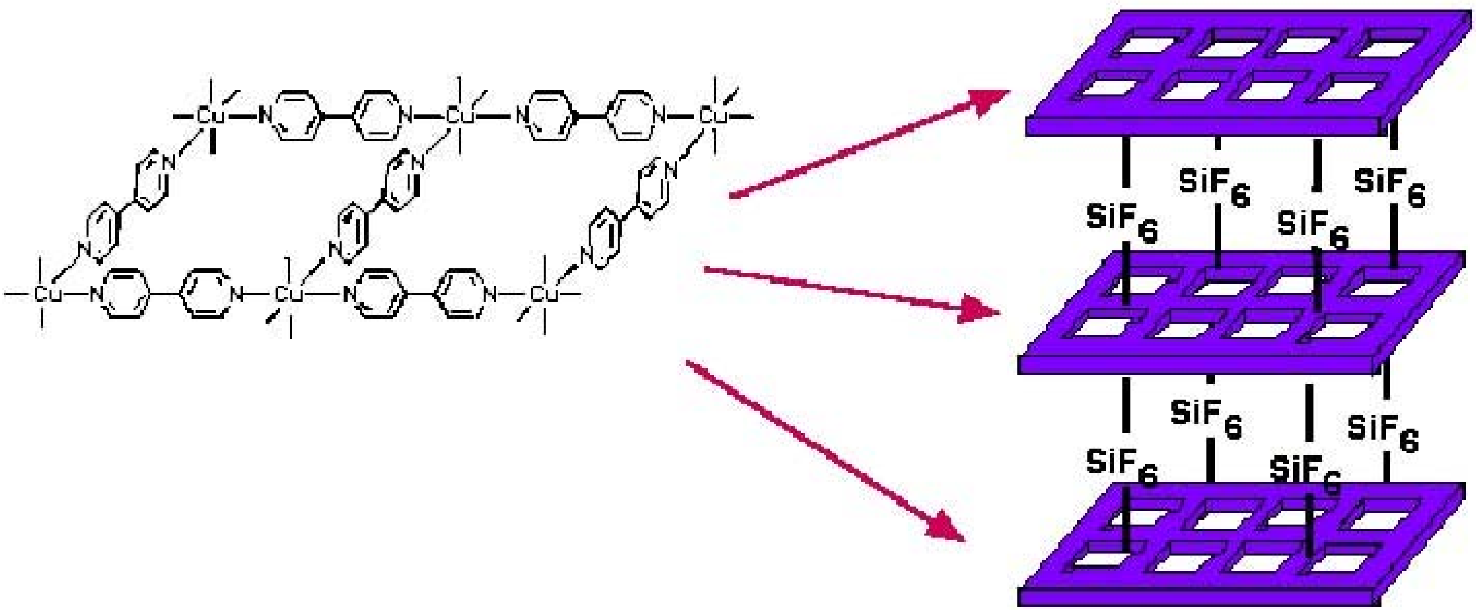
配位空間の機能


分子凝縮
捕捉分子が特異的な
凝縮構造を与える
分子ストレス
捕捉分子が受ける構造変形、
電子状態変化
捕捉分子が与える枠構造の
変形、電子状態変化
分子変換
捕捉分子が新しい分子に
変換される



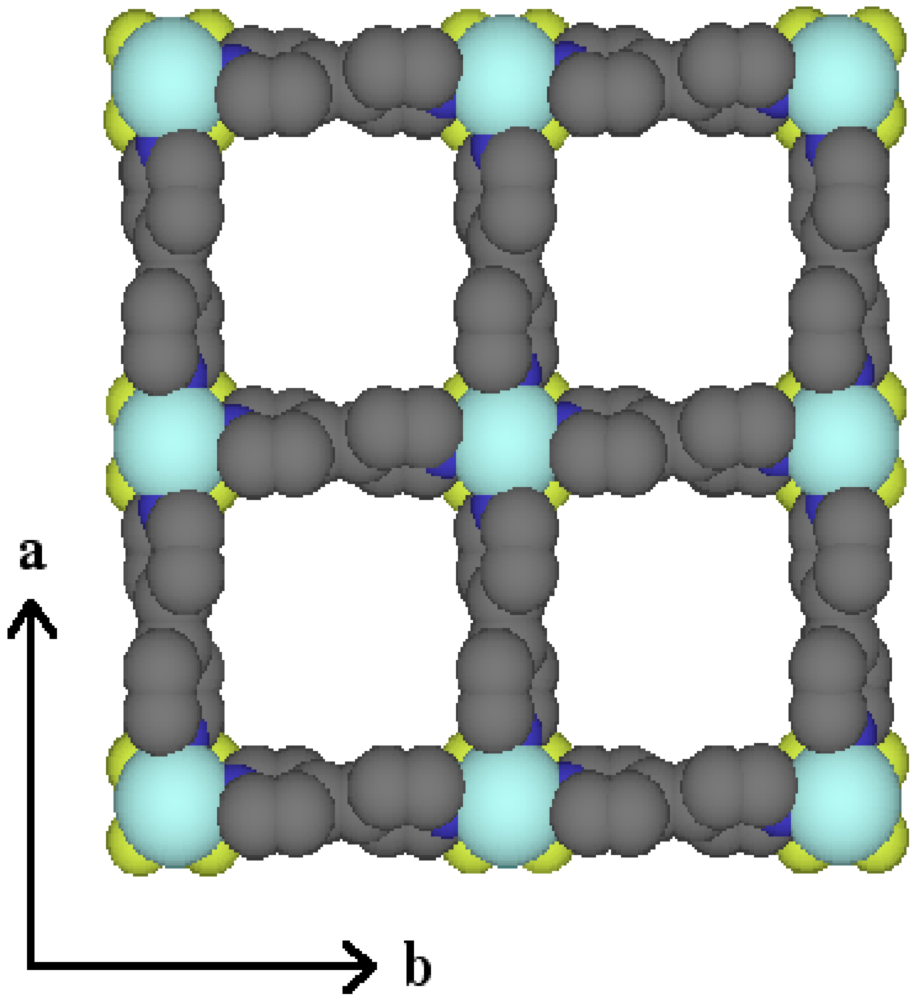
$Cu(BF_4)_2 6H_2O$ + $(NH_4)_2SiF_6$ + 4,4'-bpy

$\xrightarrow{H_2O/\text{ethyleneglycol}}$ $[Cu(4,4'\text{-bpy})_2(SiF_6)]8H_2O$

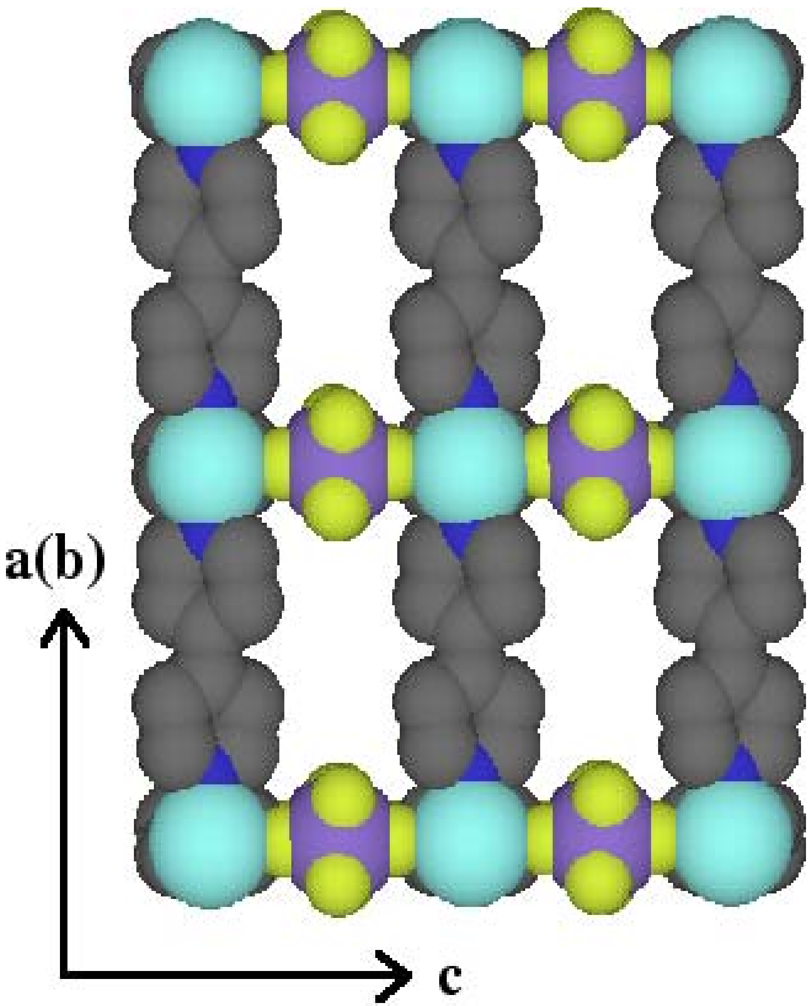


Angew.Chem.Int.Ed.2000,39,2081.
J.Am.Chem.Soc.2002,124,2568.

Space-Filling Type Framework of [Cu(4,4'-bpy)$_2$(SiF$_6$)]

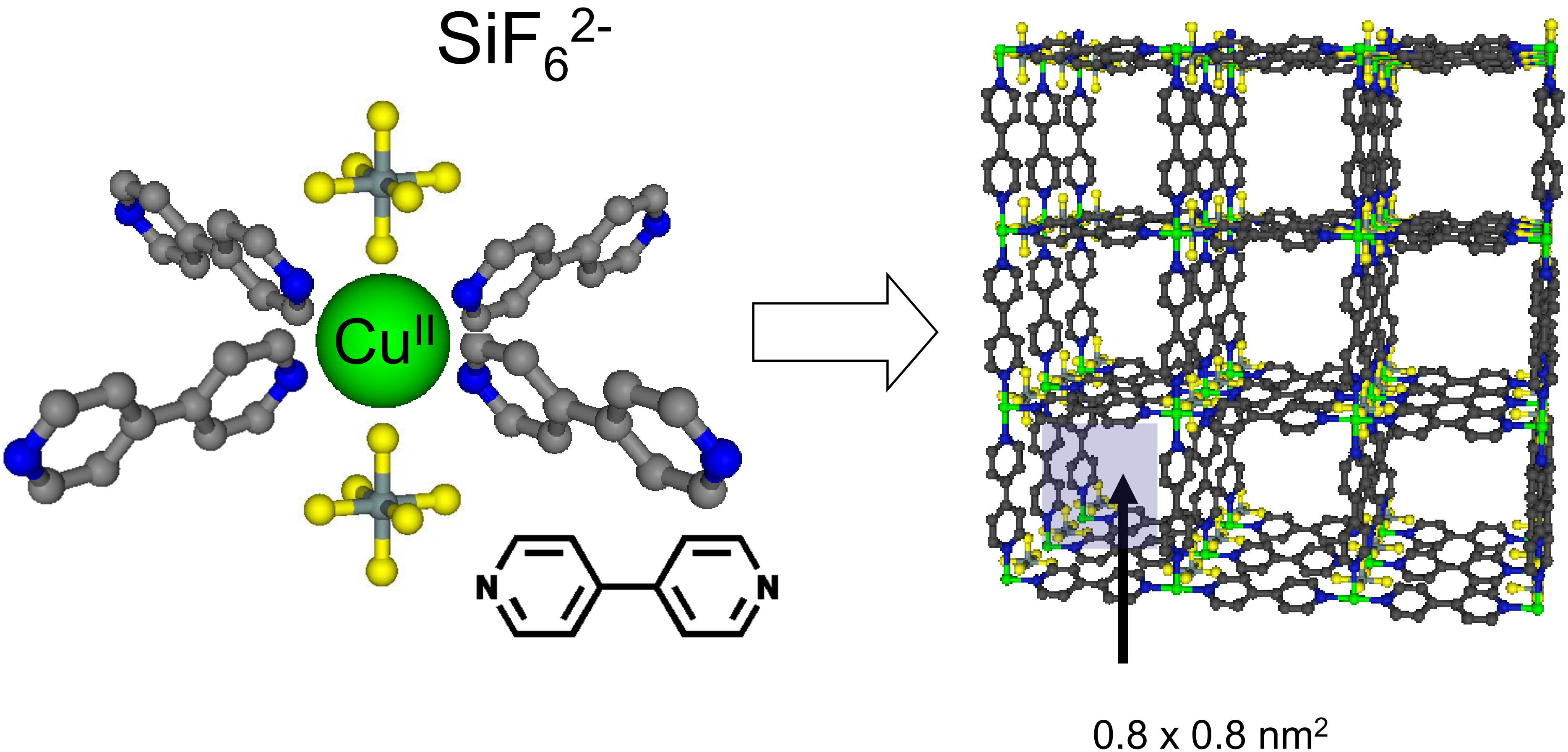


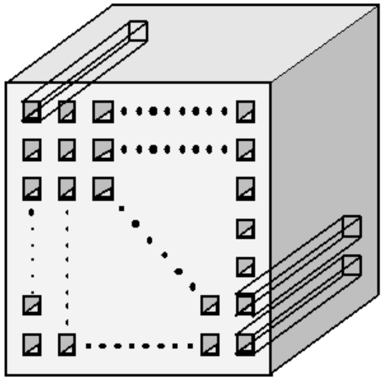
Channel Size 8.0 x 8.0 Å^2



Channel Size 8.0 x 4.0 Å^2

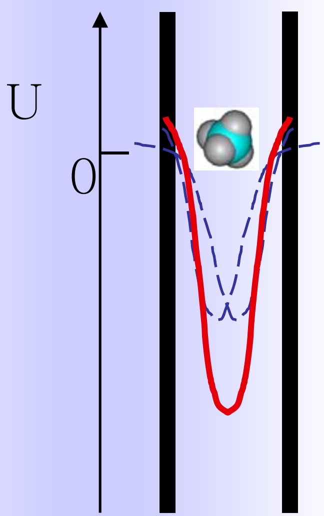
Self-assembly Process of Cation, Anion and Neutral Ligand

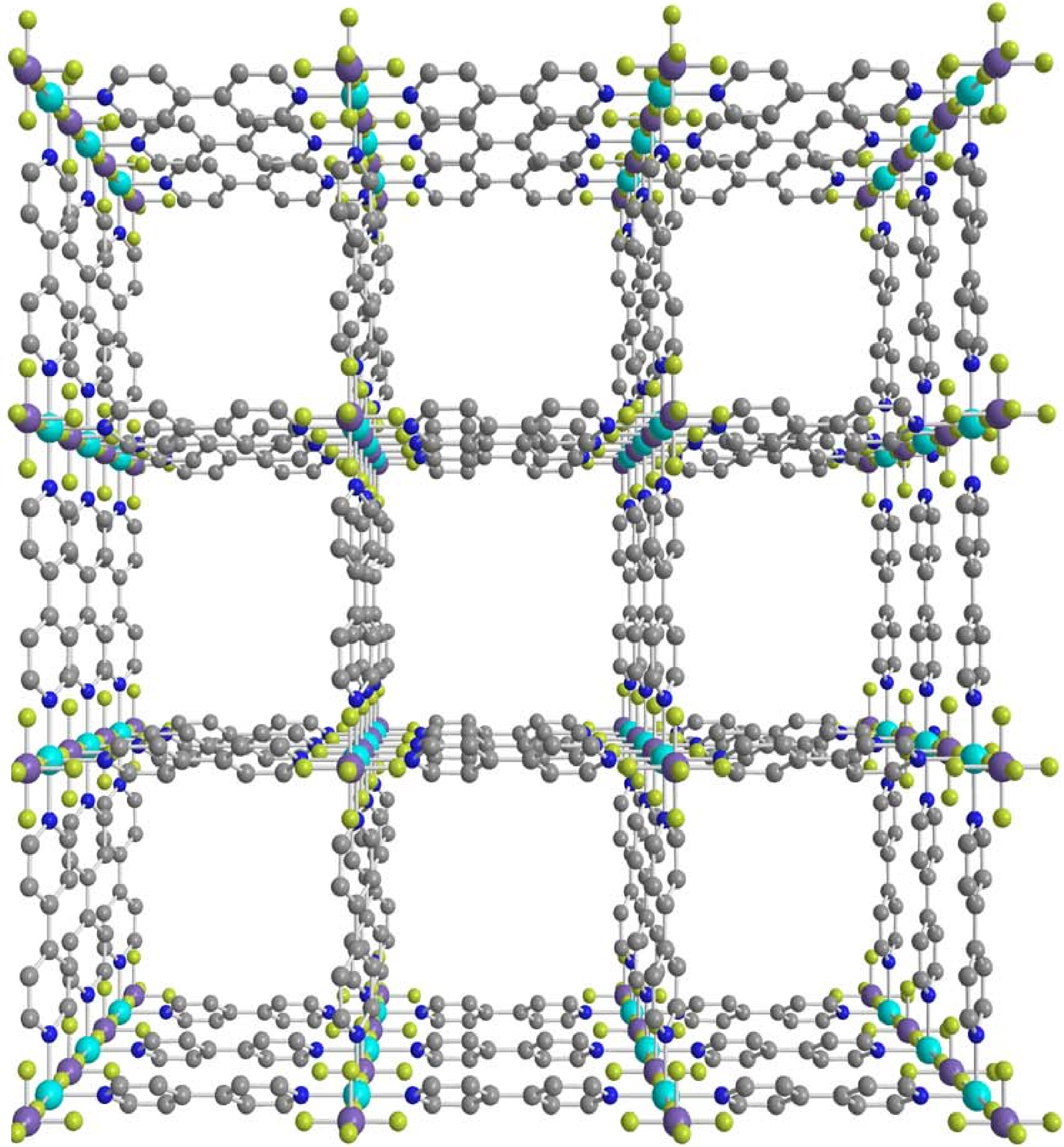




Pore < 2nm

Micropore Filling

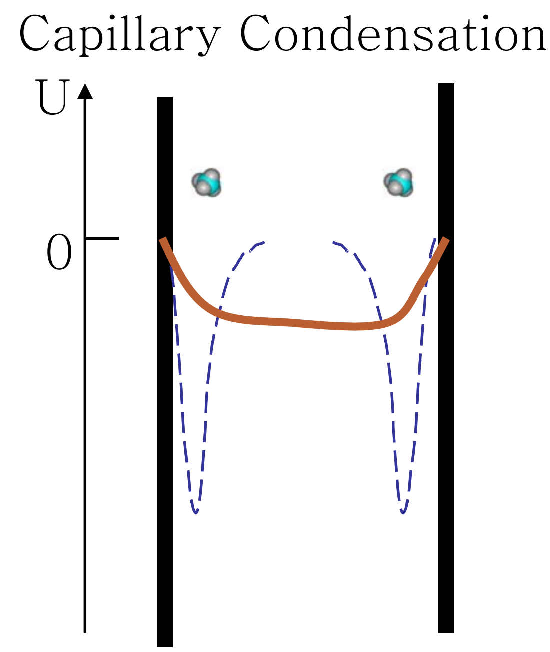


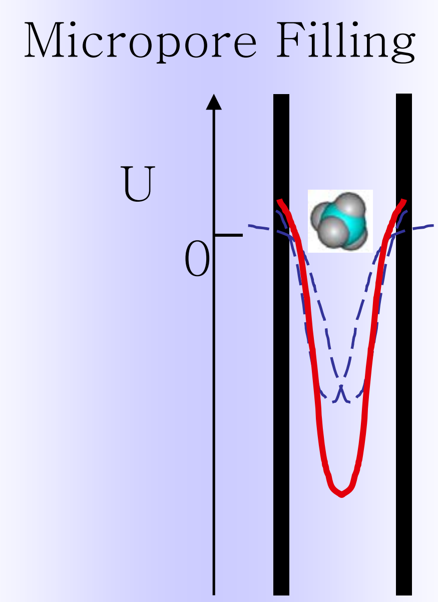


細孔の分類

	細孔径
マクロ孔	> 50 nm
メソ孔	2 nm～50 nm
マイクロ孔	< 2 nm
スーパーマイクロ孔	0.7 ～ 2 nm
ウルトラマイクロ孔	< 0.7 nm

"IUPAC Mannual of Symbols and Terminology", *Pure and Appl. Chem.* 31,578(1972).

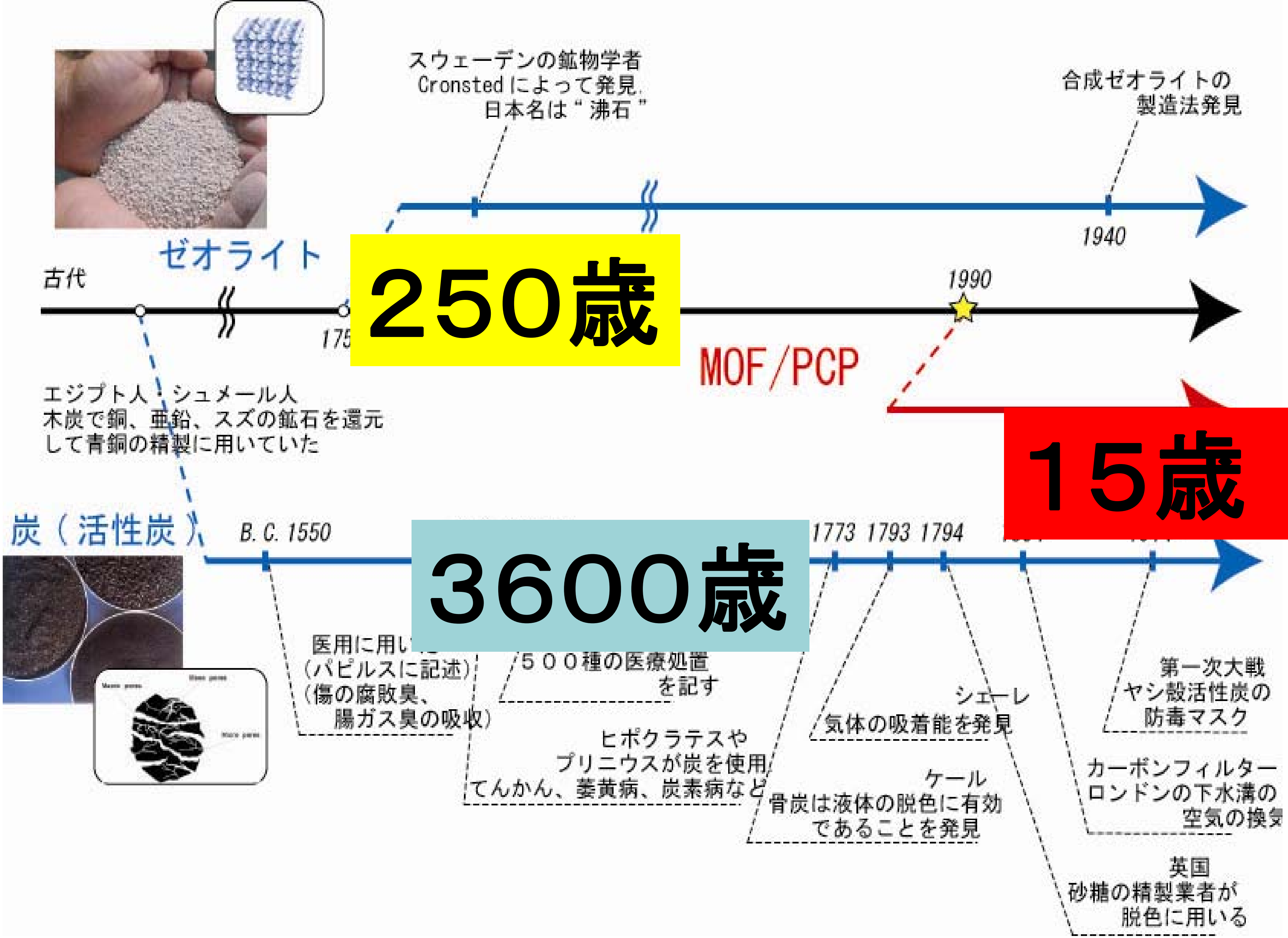




従来の多孔性材料

無機材料（ゼオライト、…）

炭素材料（活性炭、…）



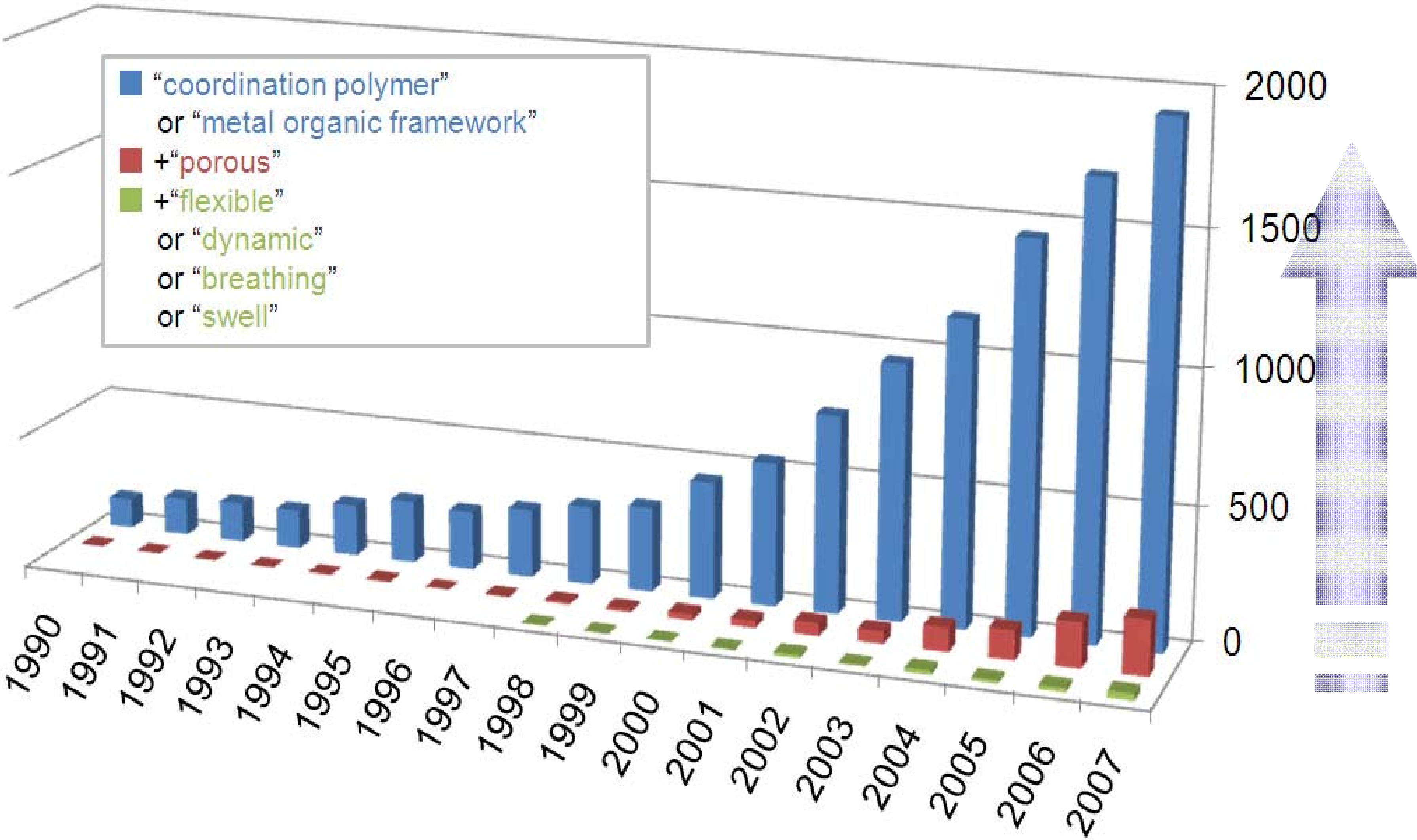
スウェーデンの鉱物学者
Cronsted によって発見
日本名は“沸石”
合成ゼオライトの
製造法発見
1940
ゼオライト
古代
250歳
1990
MOF/PCP
エジプト人・シュメール人
木炭で銅、亜鉛、スズの鉱石を還元
して青銅の精製に用いていた
15歳
炭（活性炭）
B. C. 1550
3600歳
1773
1793
1794
医用に用い
（パピルスに記述）
（傷の腐敗臭、
腸ガス臭の吸収）
５００種の医療処置
を記す
ヒポクラテスや
プリニウスが炭を使用
てんかん、萎黄病、炭素病など
シェーレ
気体の吸着能を発見
ケール
骨炭は液体の脱色に有効
であることを発見
英国
砂糖の精製業者が
脱色に用いる
第一次大戦
ヤシ殻活性炭の
防毒マスク
カーボンフィルター
ロンドンの下水溝の
空気の換

新しい物質群

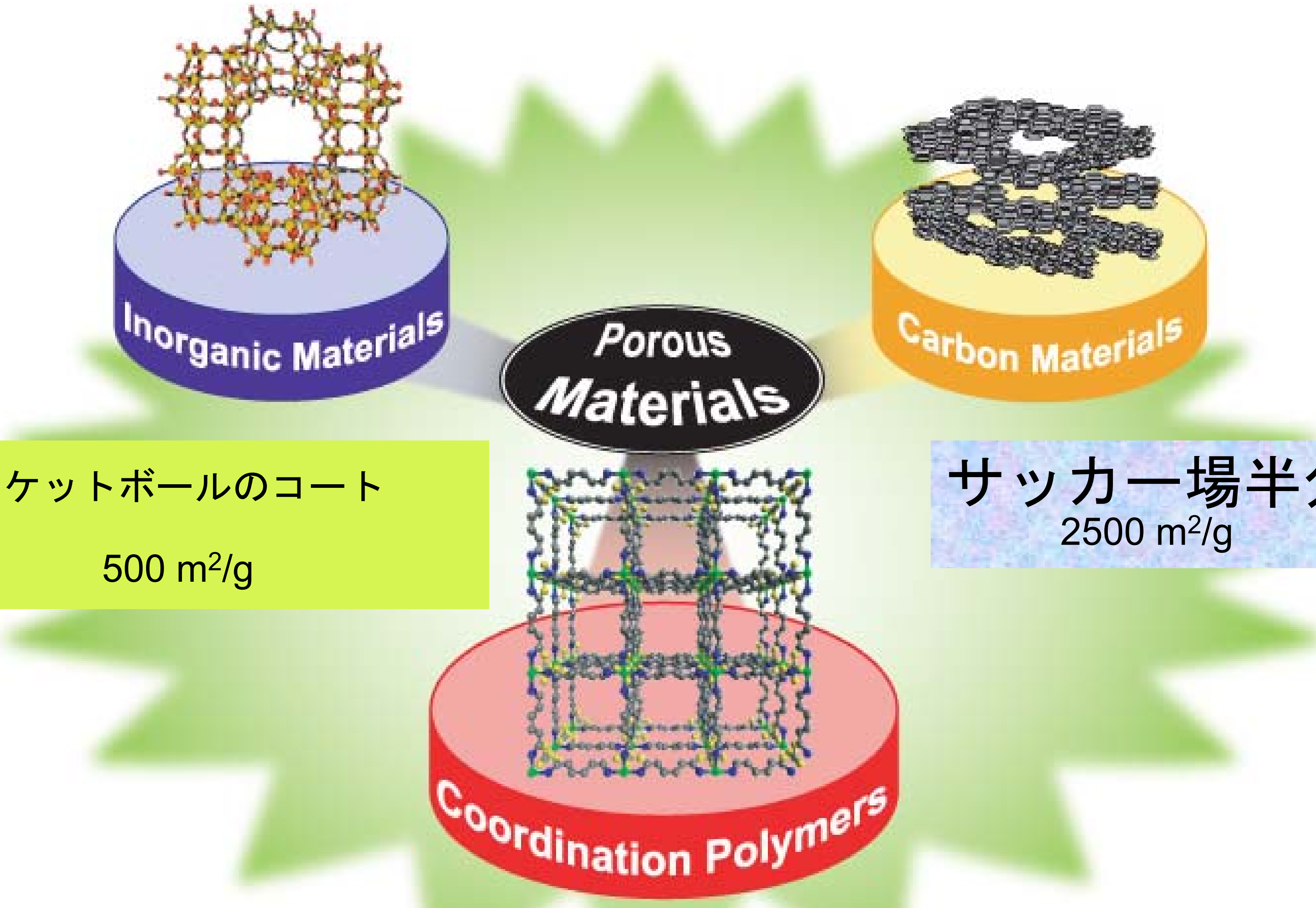
配位高分子(coordination polymers)

または

金属ー有機骨格体(Metal-Organic Frameworks)



Reviews ***Angew.Chem.Int.Ed. 2004,43,2334.***
cited 2067 (Web of Science, Sept.7, 2009)



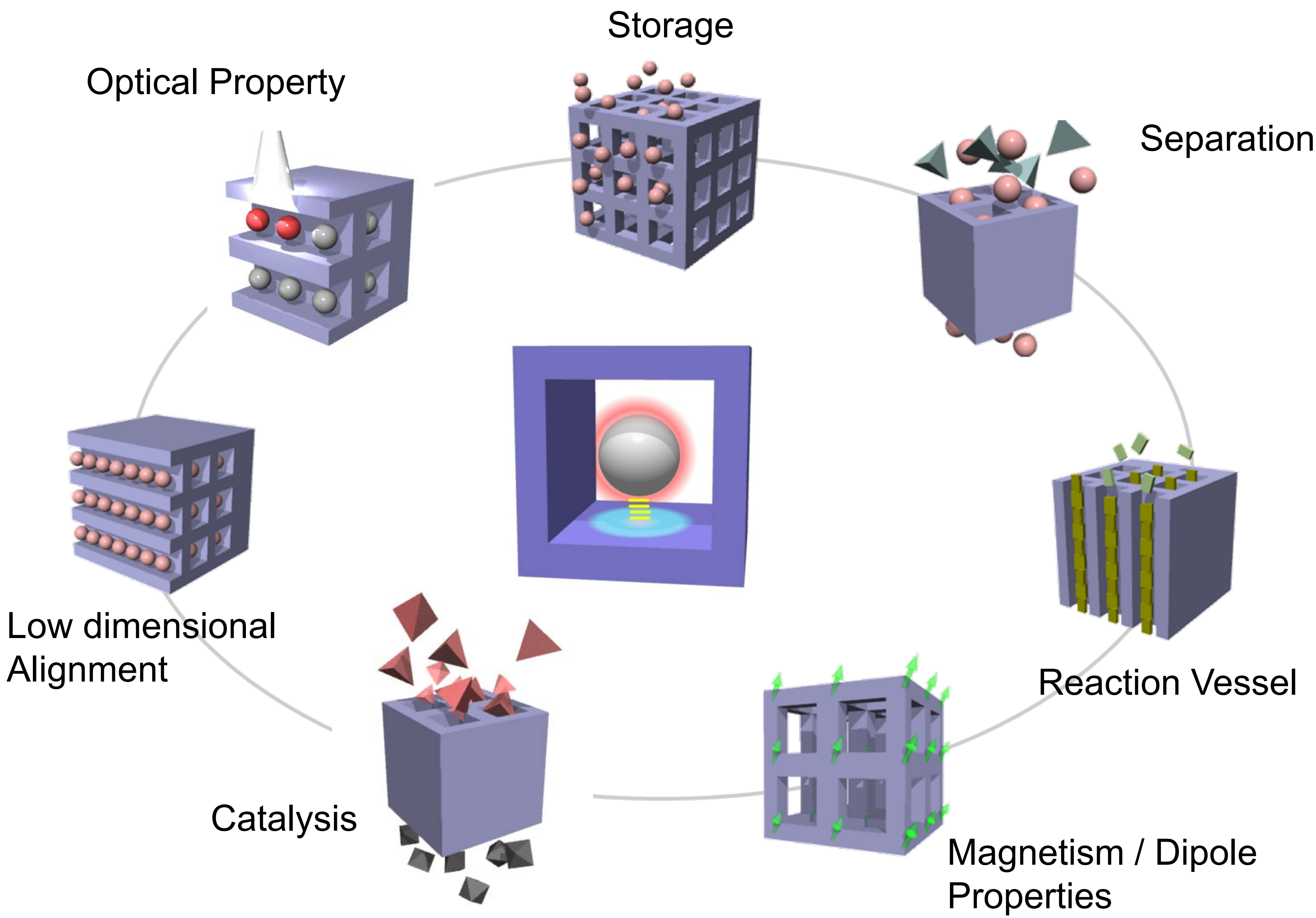
バスケットボールのコート

500 m^2/g

サッカー場半分

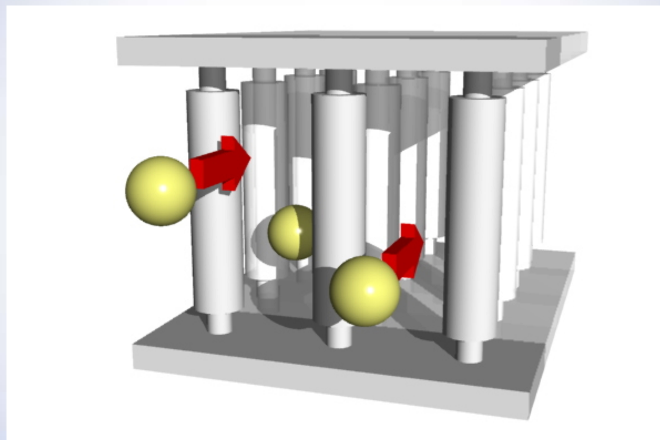
2500 m^2/g

サッカー場 4500 m^2/g

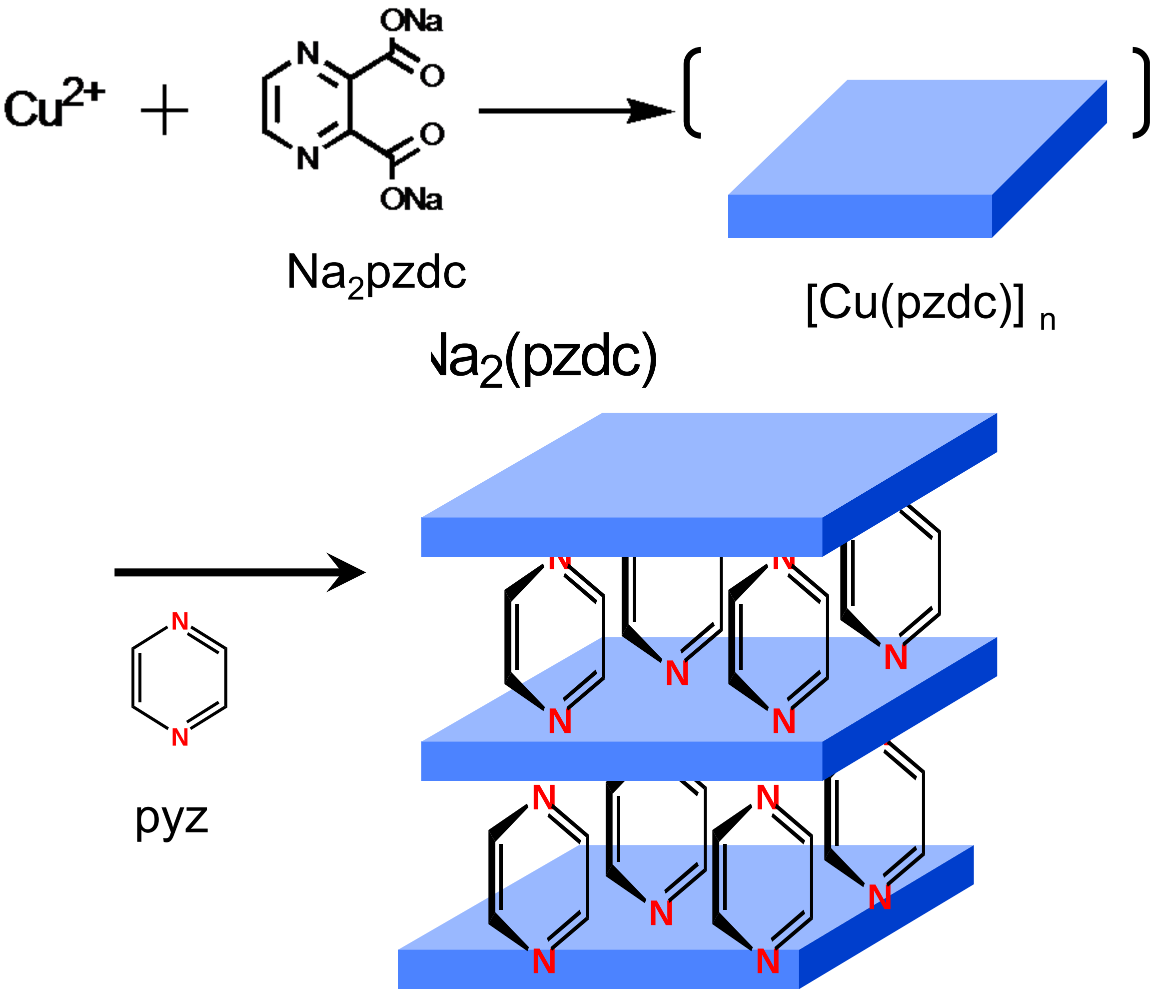

Storage
Optical Property
Separation
Reaction Vessel
Magnetism / Dipole Properties
Catalysis
Low dimensional Alignment

Pillared Layer Structures

Molecular World of Pillared Layer Architecture

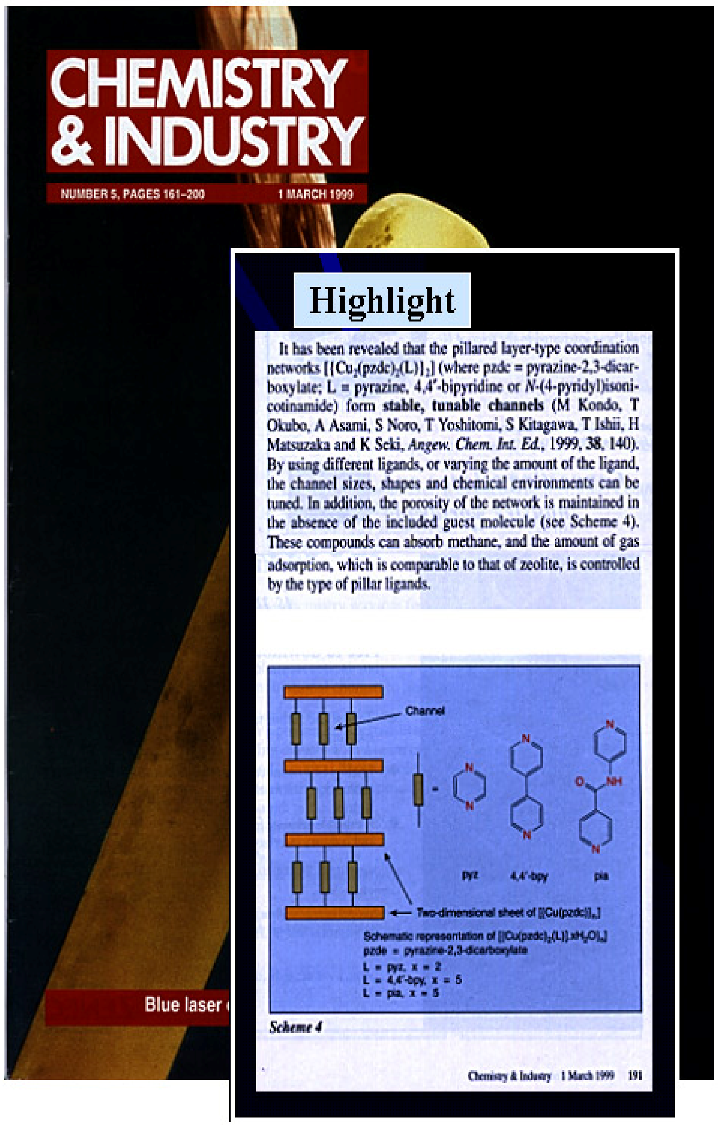


Coordination Pillared Layer Structure (CPL Series)



$[Cu_2(pzdc)_2(pyz)]_n$ (CPL1)

Chemistry & Industry, 191,1999



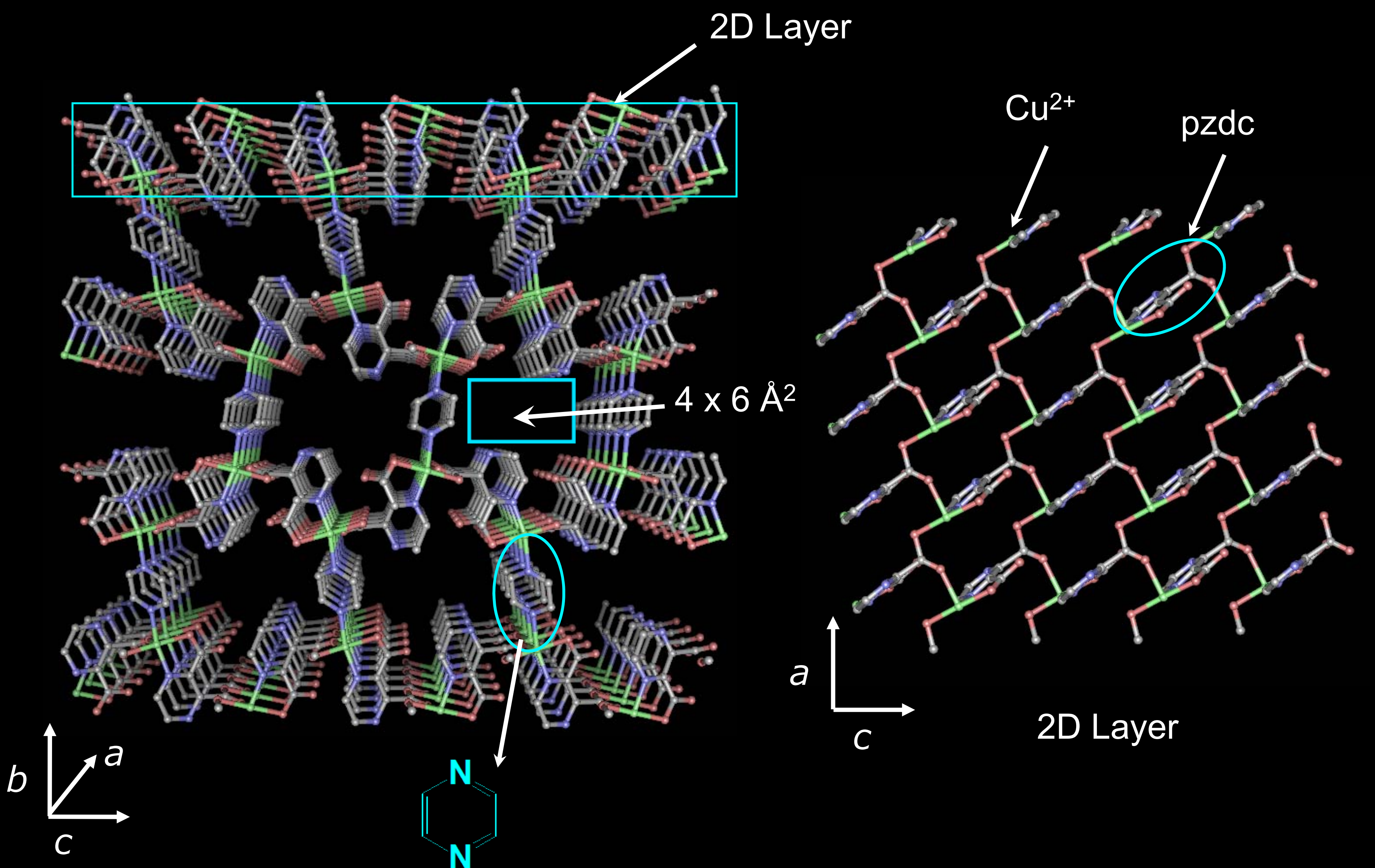
Highlight

It has been revealed that the pillared layer-type coordination networks $[\{Cu_2(pzdc)_2(L)\}_n]$ (where pzdc = pyrazine-2,3-dicarboxylate; L = pyrazine, 4,4′-bipyridine or *N*-(4-pyridyl)isonicotinamide) form **stable, tunable channels** (M Kondo, T Okubo, A Asami, S Noro, T Yoshitomi, S Kitagawa, T Ishii, H Matsuzaka and K Seki, *Angew. Chem. Int. Ed.*, 1999, 38, 140). By using different ligands, or varying the amount of the ligand, the channel sizes, shapes and chemical environments can be tuned. In addition, the porosity of the network is maintained in the absence of the included guest molecule (see Scheme 4). These compounds can absorb methane, and the amount of gas adsorption, which is comparable to that of zeolite, is controlled by the type of pillar ligands.

Scheme 4

Angew.Chem.Int.Ed.1999,38,

3-D Structure of [Cu_2(pzdc)$_2$(pyz)] (CPL1)

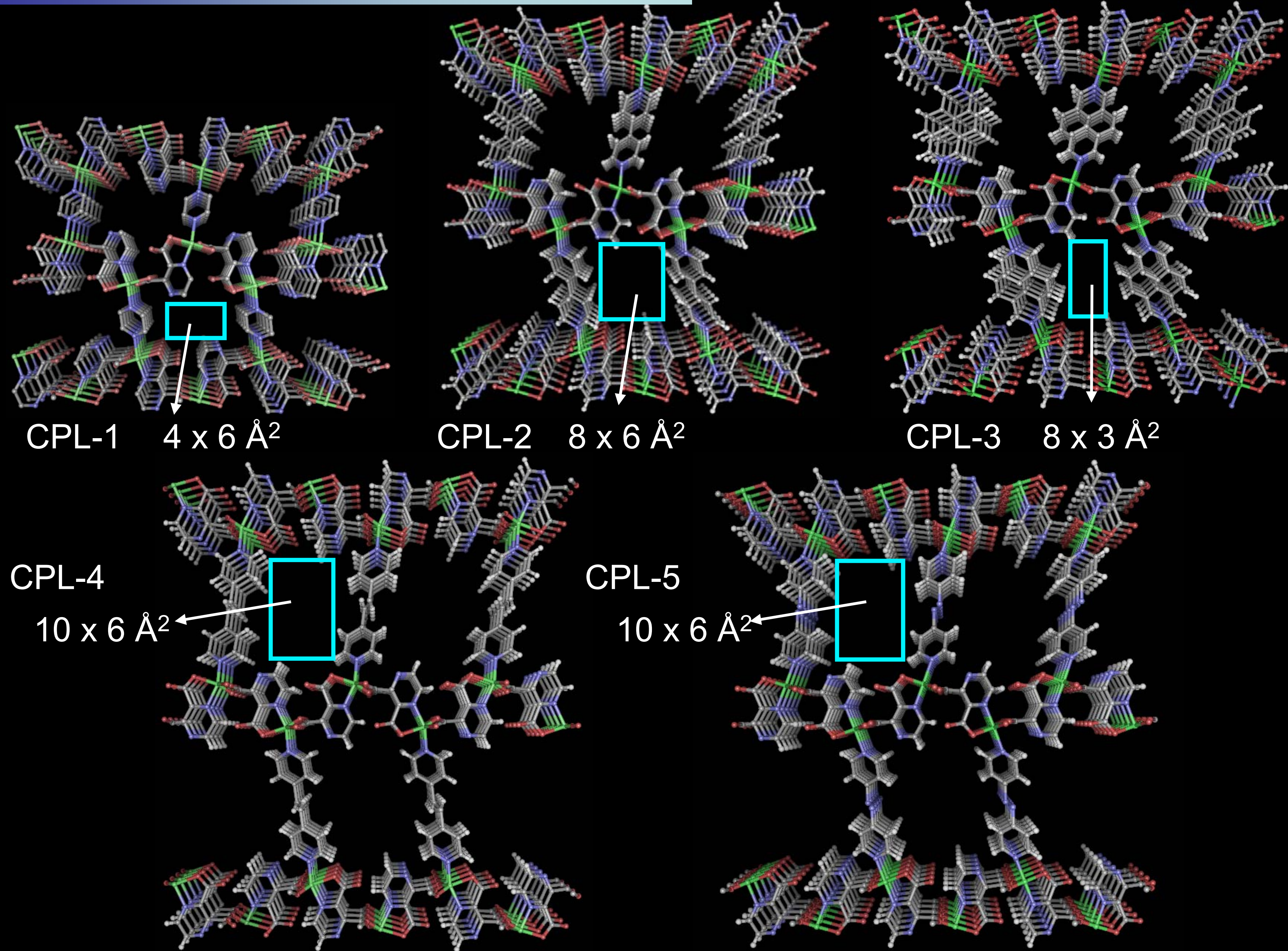


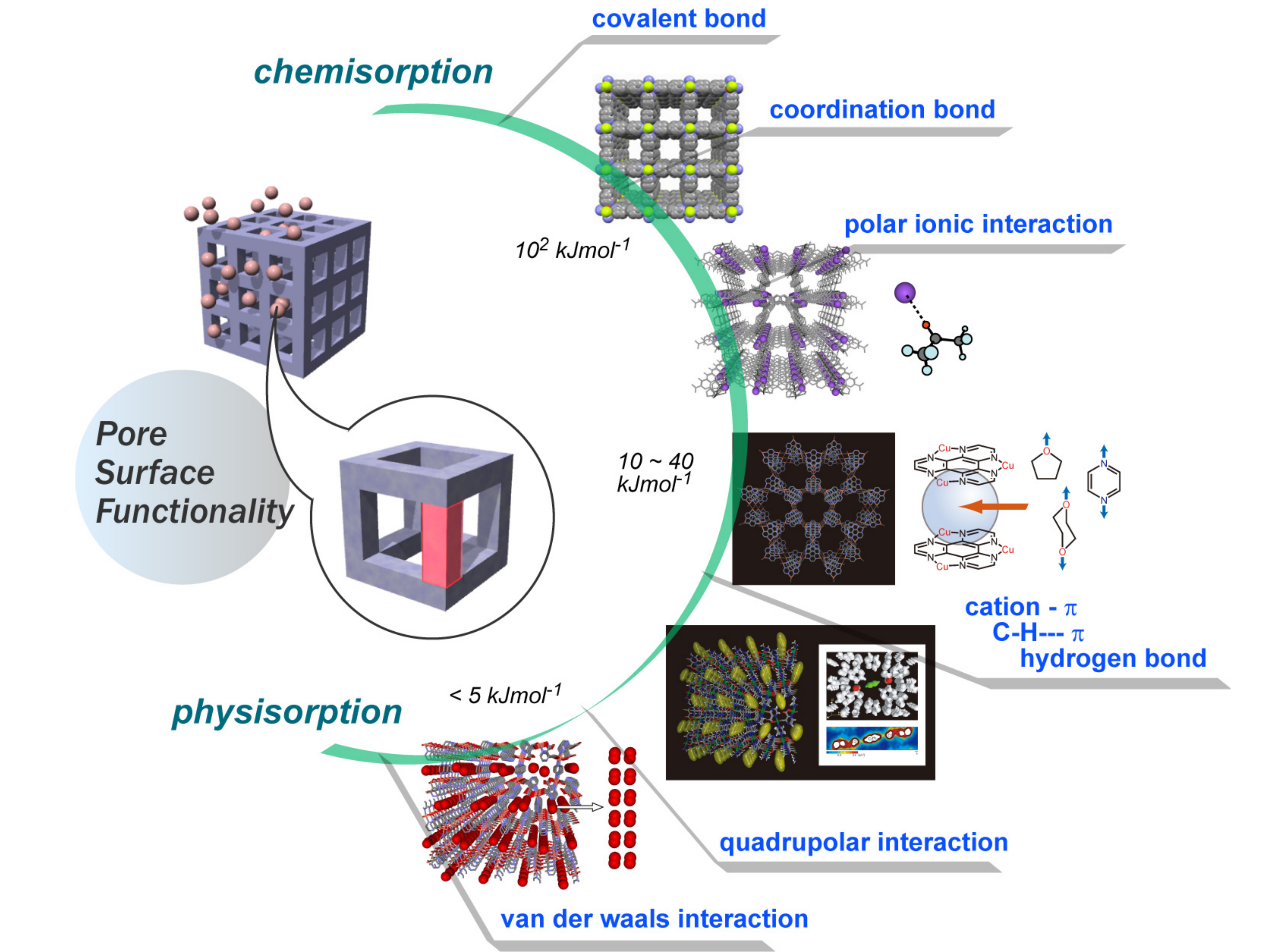
多孔性金属錯体　CPL系

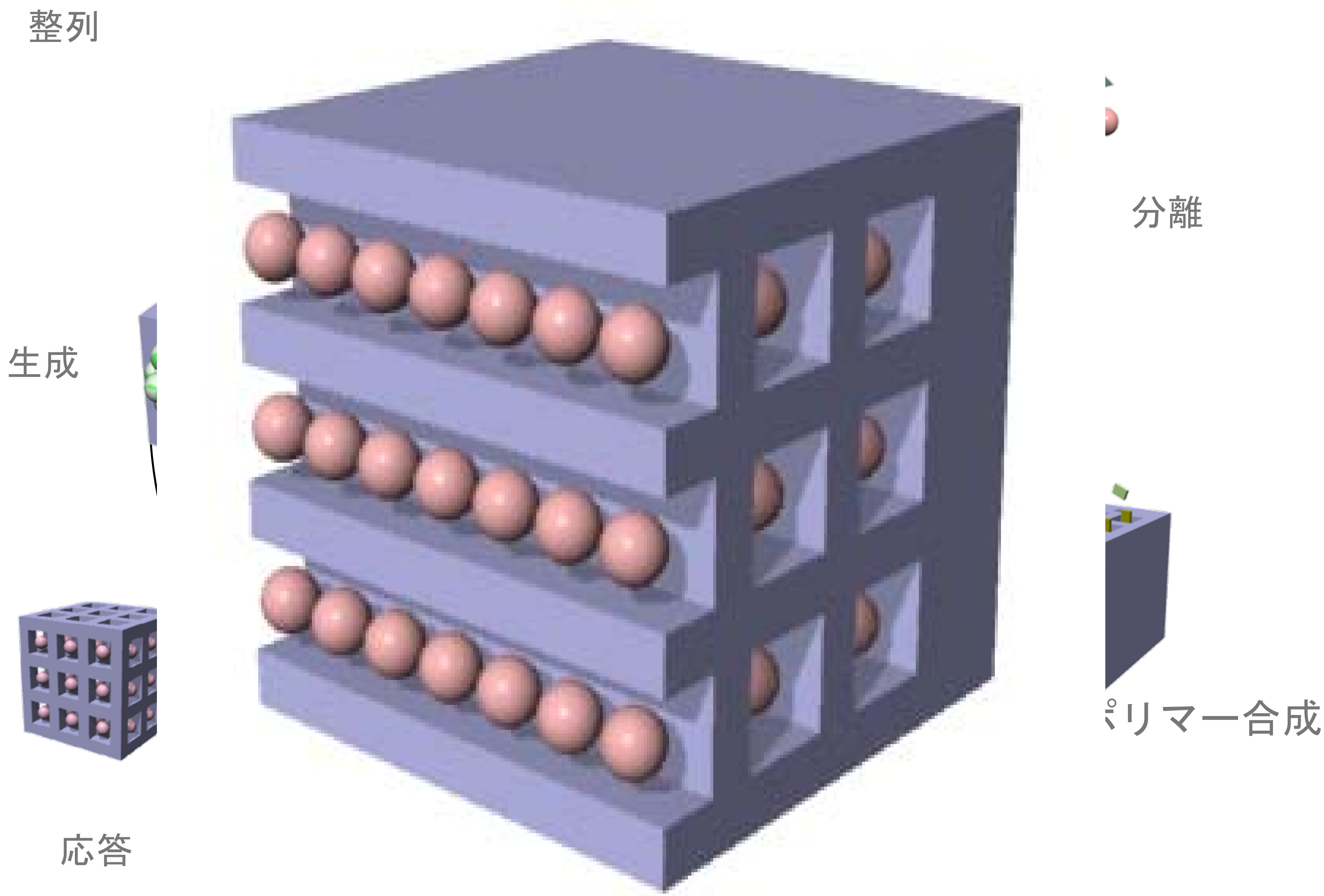
CPL1

- 青色粉末結晶
- 250℃まで安定な細孔骨格
- 大量合成できる
- 空気中で取り扱い可
- 多数回の吸脱着

Coordination Pillared Layer Structures (CPLs)

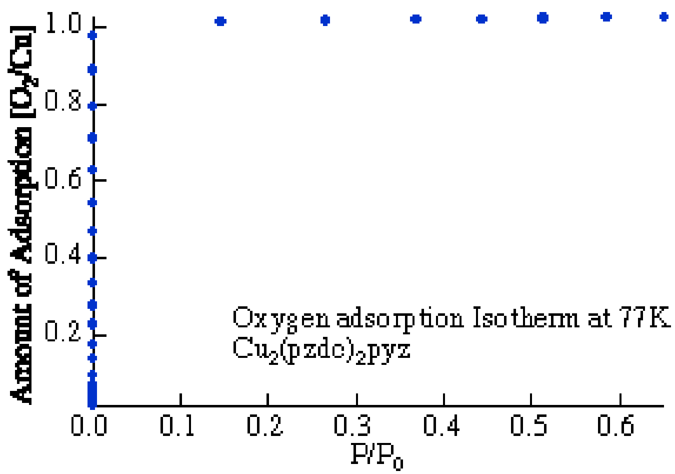


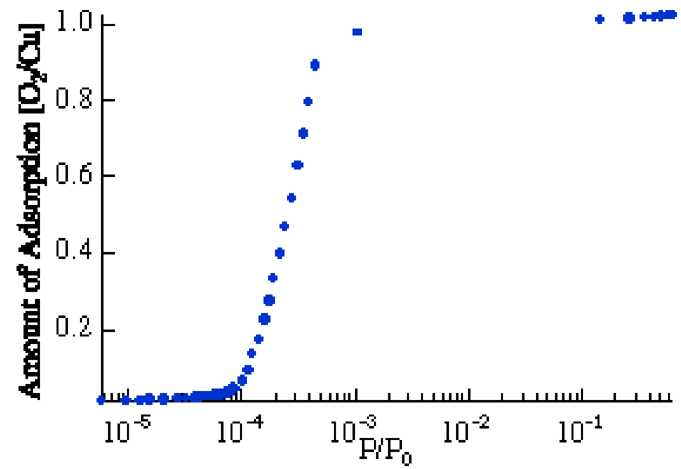

covalent bond
chemisorption
coordination bond
polar ionic interaction
10^2 kJmol^-1
Pore
Surface
Functionality
10 ~ 40
kJmol^-1
cation - π
C-H--- π
hydrogen bond
< 5 kJmol^-1
physisorption
quadrupolar interaction
van der waals interaction


整列
分離
生成
リマー合成
応答

Adsorption Properties of CPL-1

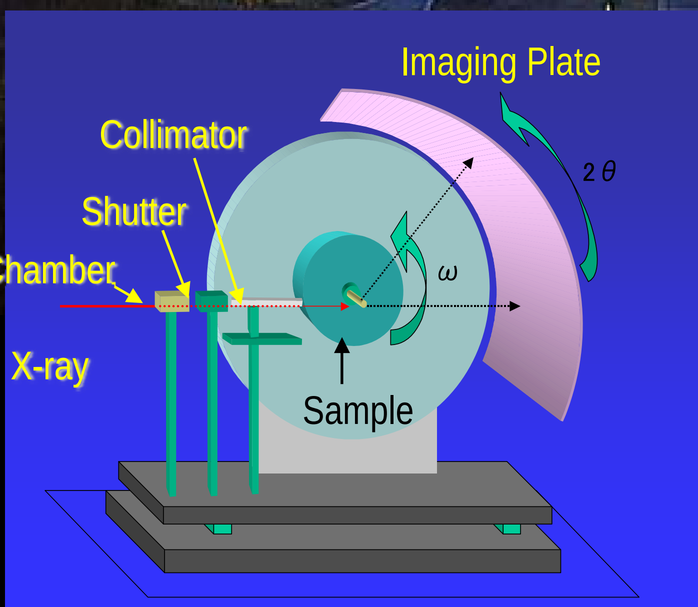
$[O_2]/[Cu] = 1$

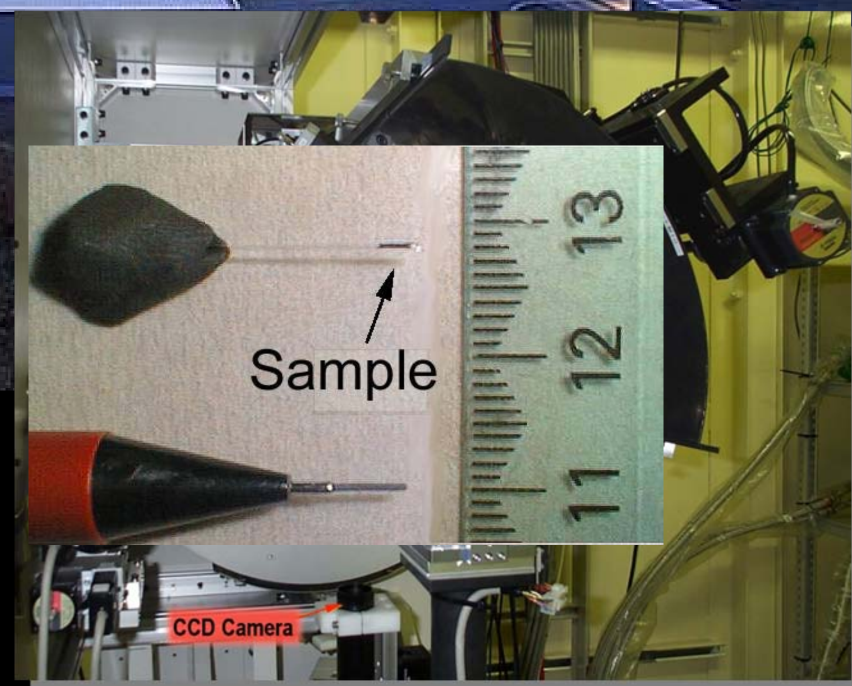




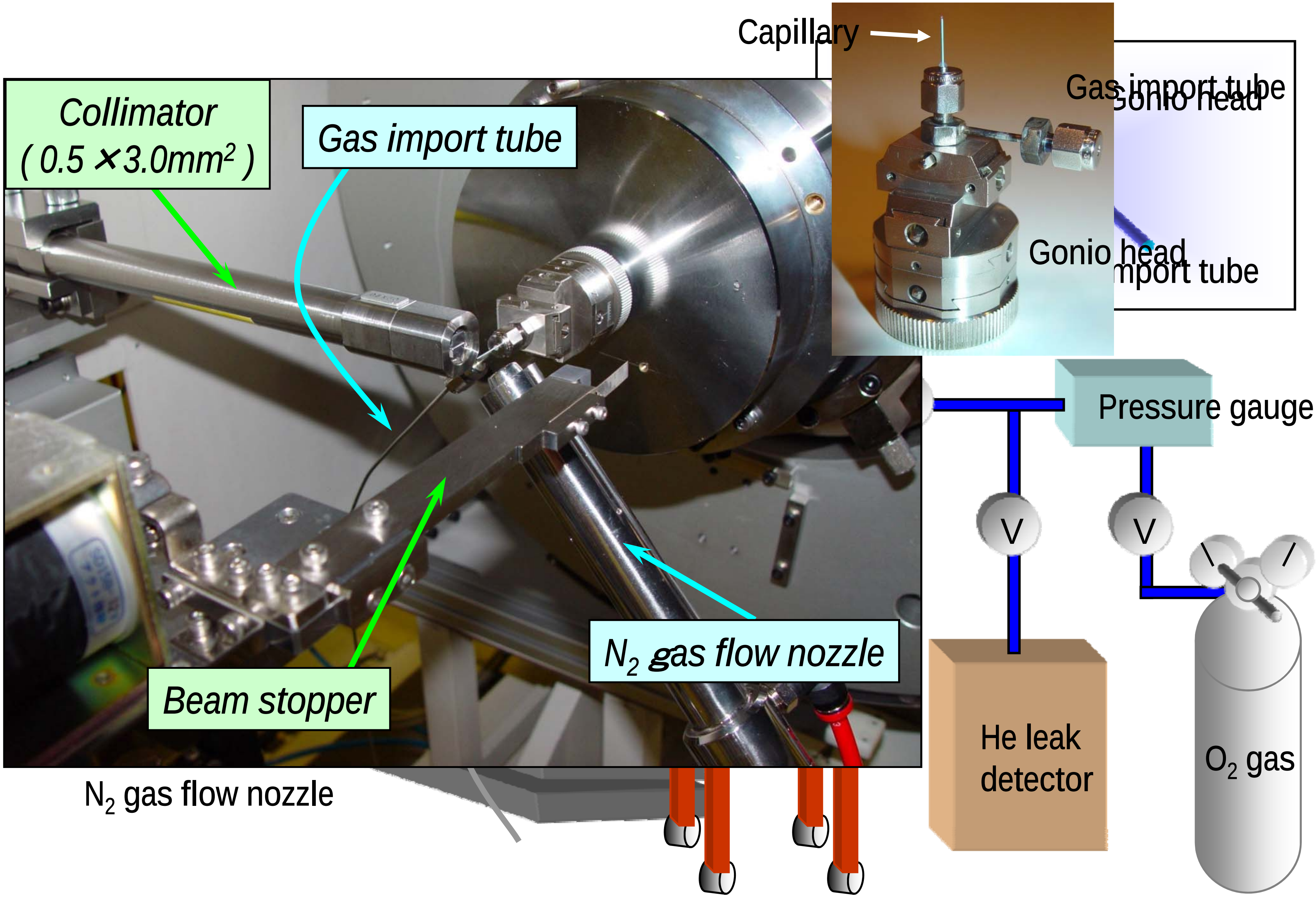
Isosteric heat of adsorption (CO_2)	
CPL-1	-34 KJ/mol
Silicalite-I	-20 KJ/mol
AC	-25 KJ/mol

The Large Debye-Scherrer Camera at SPring-8 BL02B2



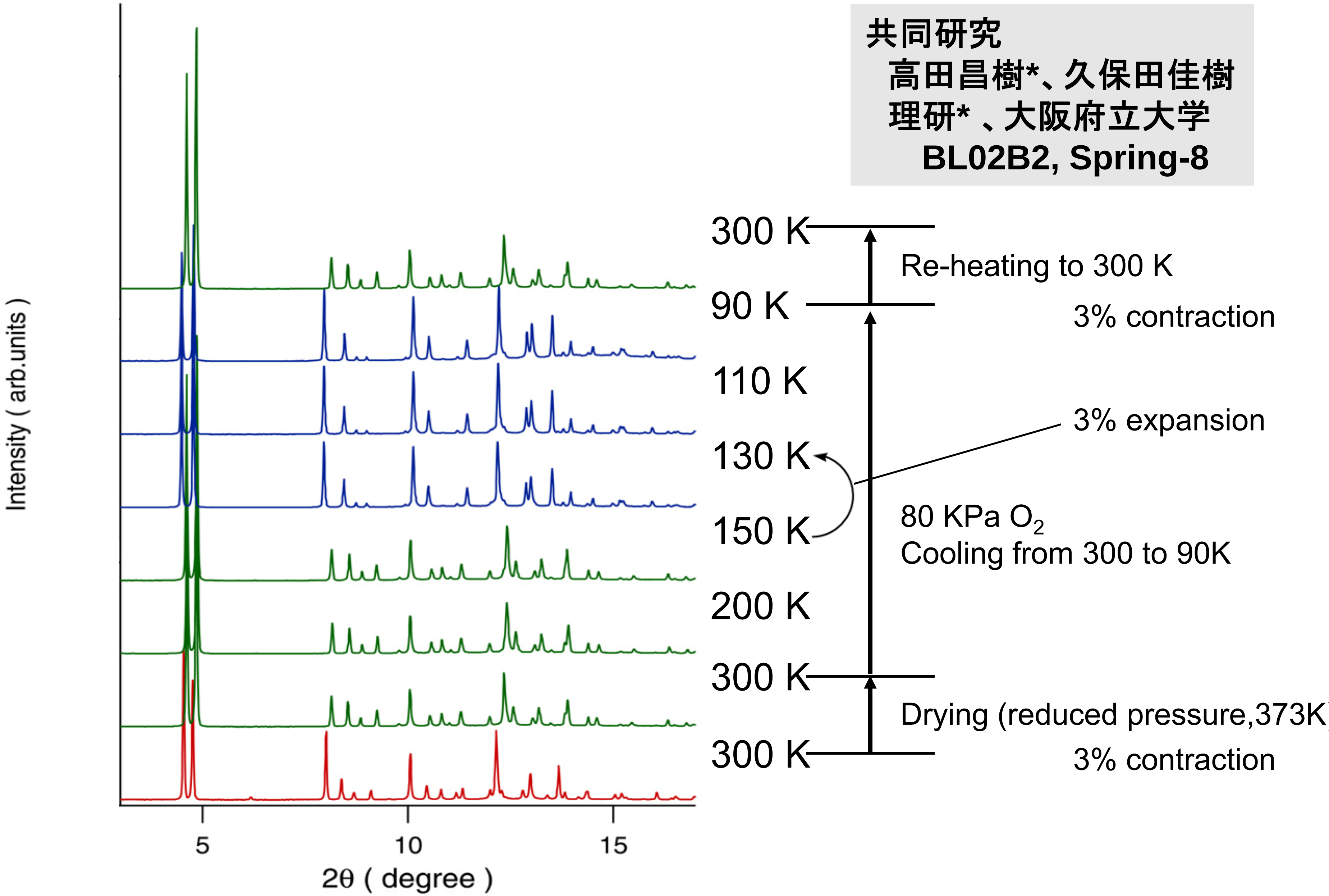


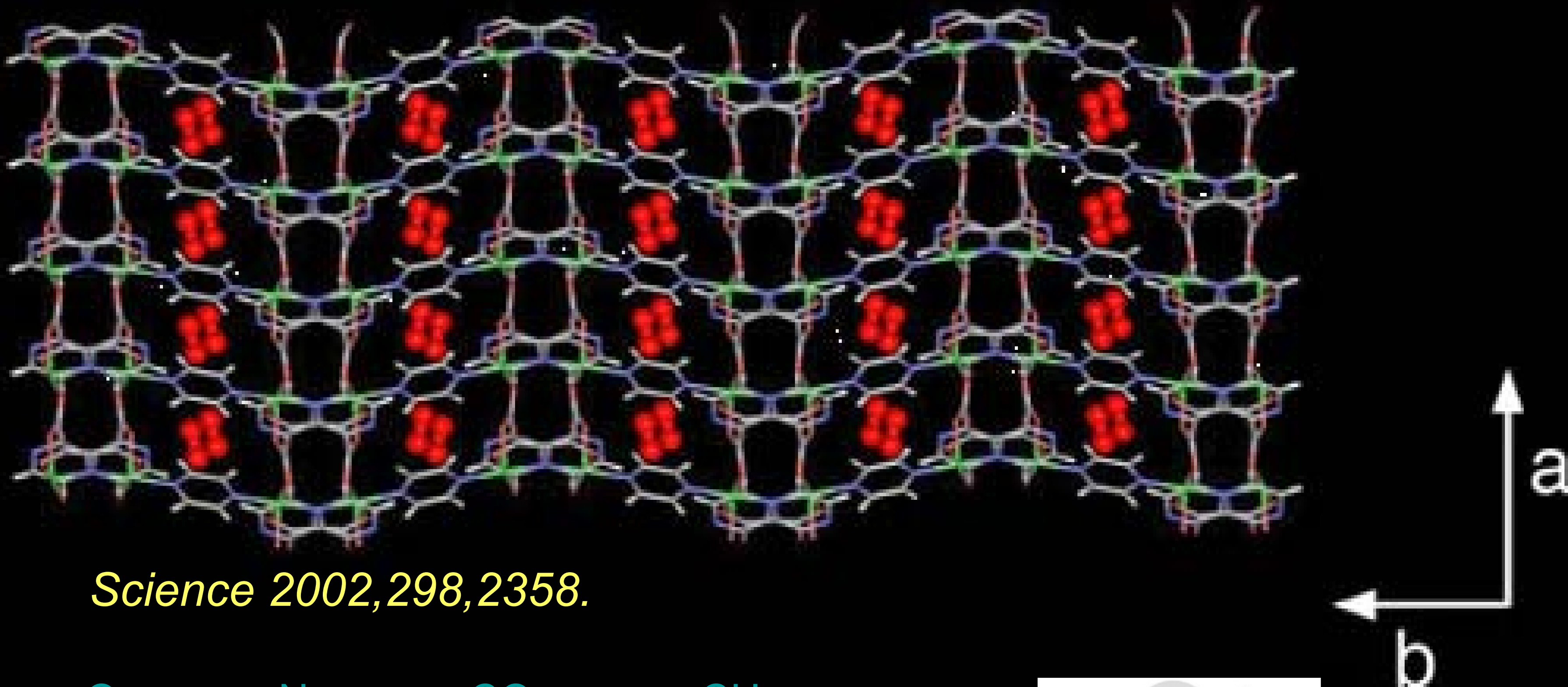
Schematic view of gas import system at BL02B2



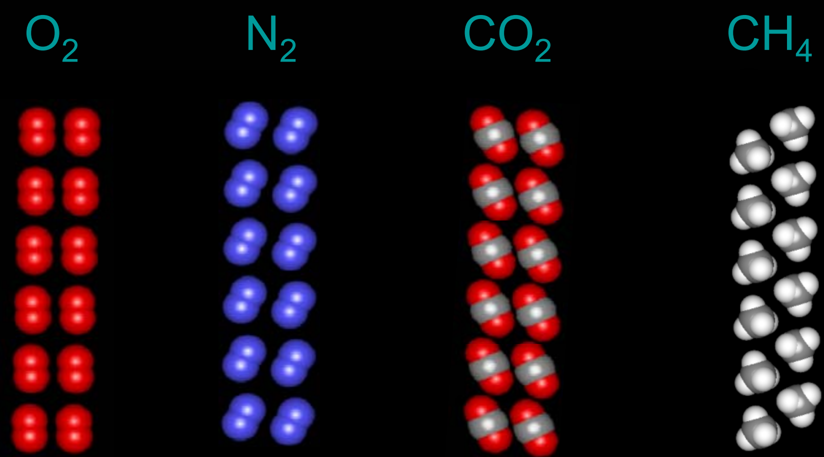
XRPD Patterns of CPL-1 in 80 KPa O_2 Gas

共同研究
高田昌樹*、久保田佳樹
理研* 、大阪府立大学
BL02B2, Spring-8





Science 2002,298,2358.

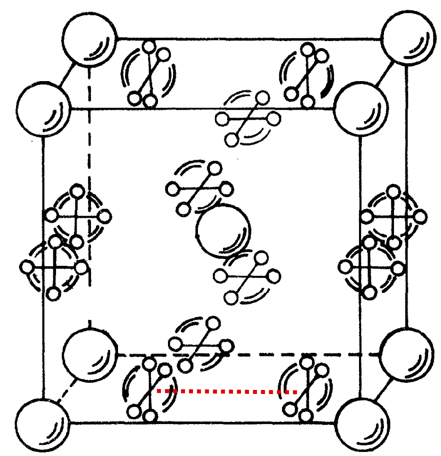


J.Phys.Chem.B,2005,109,23378.

Angew.Chem.Int.Ed.2005,44,2920.

Structures of Bulk Solid O_2 under Atmospheric Pressure

$\gamma-O_2$



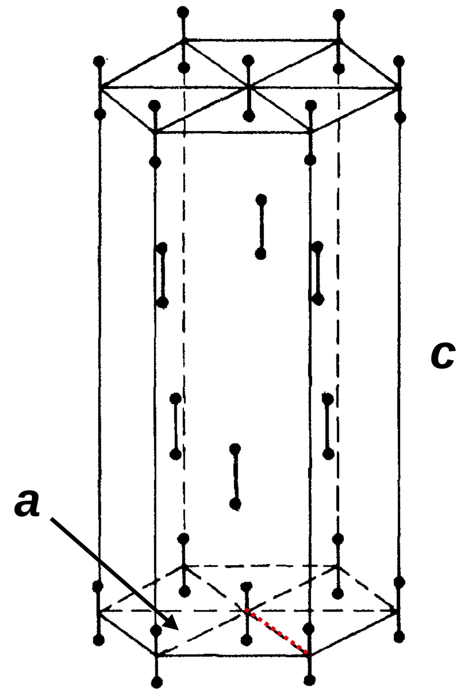
54.4 > T > 43.8 K

Pm3n

a = 6.78 Å

O-O 3.39 Å

$\beta-O_2$

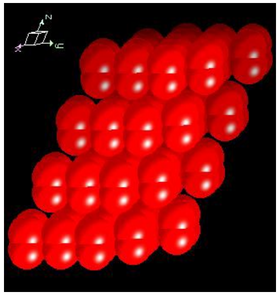


43.8 > T > 24 K

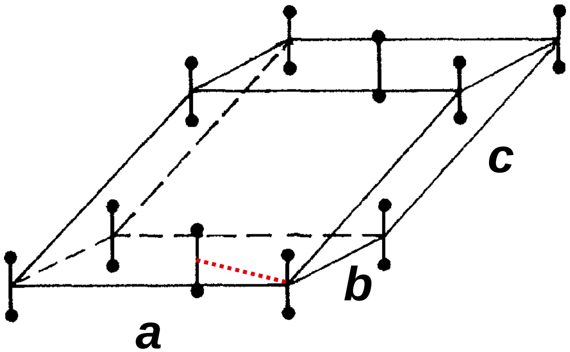
R$\bar{3}$m

a = 3.30 Å
c = 11.26 Å

O-O 3.30 Å



$\alpha-O_2$

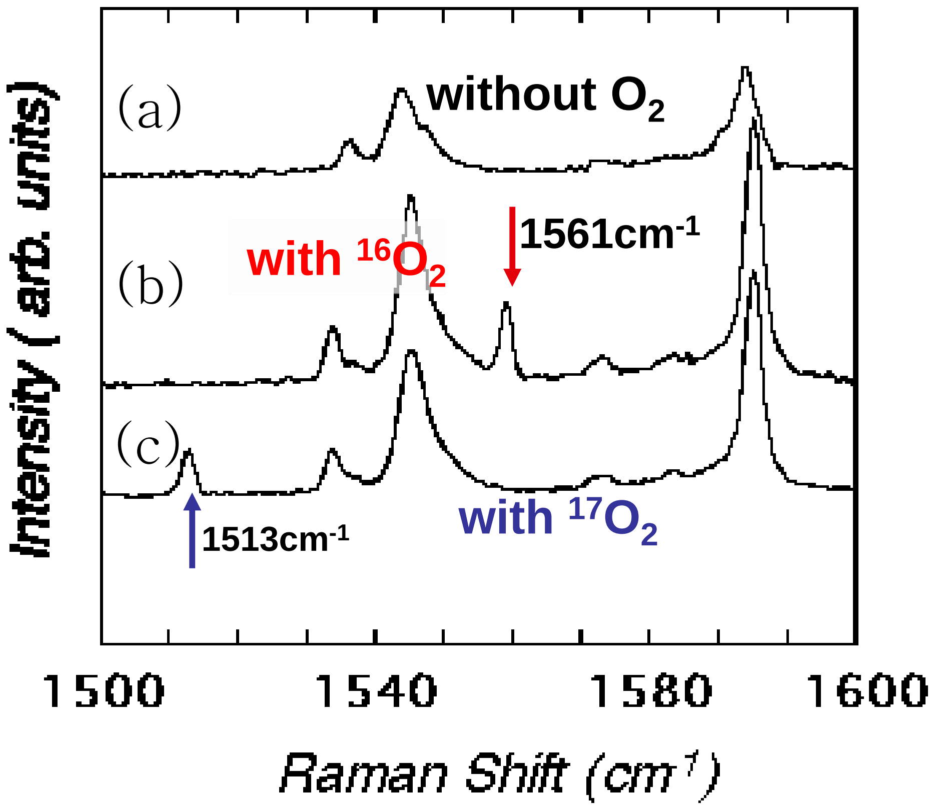


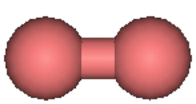
24 K >T

C2/m

a = 5.403 Å **O-O 3.200 Å**
b = 3.429 Å
c = 5.086 Å
β = 132.53 °

In situ Raman Spectrum of CPL-1 at 80 KPa of O_2





Band frequency at 2 GPa

1561 cm^{-1}

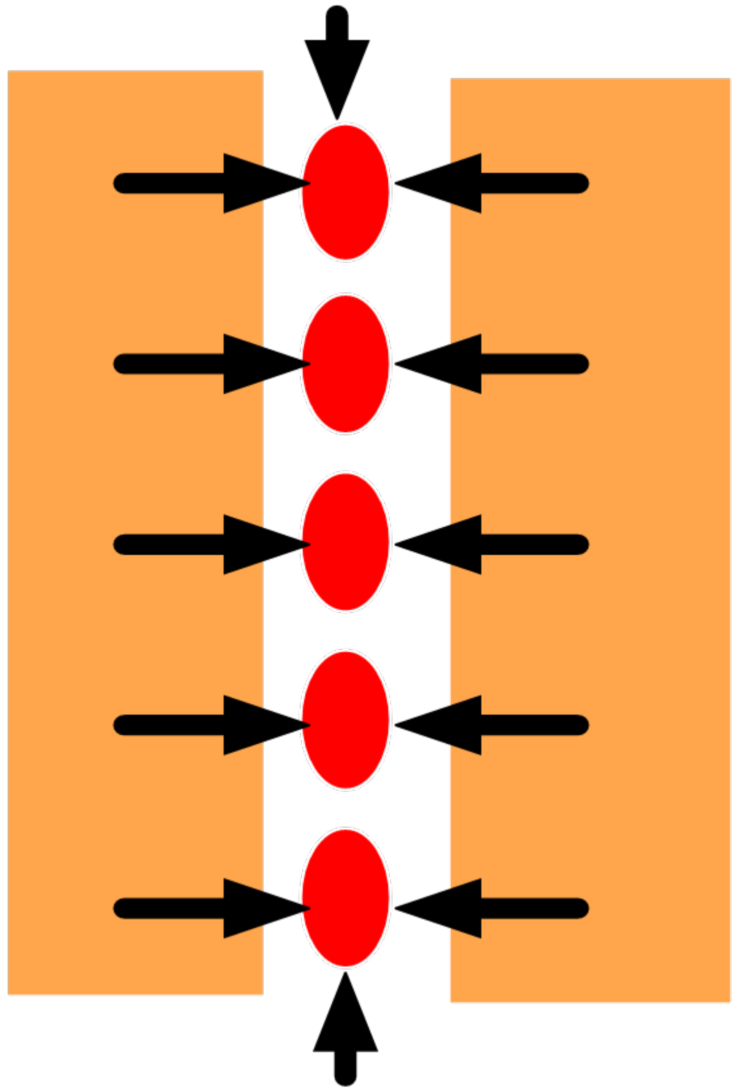
1552 cm^{-1} at 0.1 MPa

	T (K)	*Raman Shift (cm^{-1})*
Gas	145	1553.2 ± 0.5
Liquid	80	1552.0 ± 0.5
γ-solid	45	1552.0 ± 0.5
β-solid	40	1552.0 ± 0.5
α-solid	20	1552.0 ± 0.5

J.Chem.Phys,81,3,1192(1985)

酸素分子が受ける圧力？

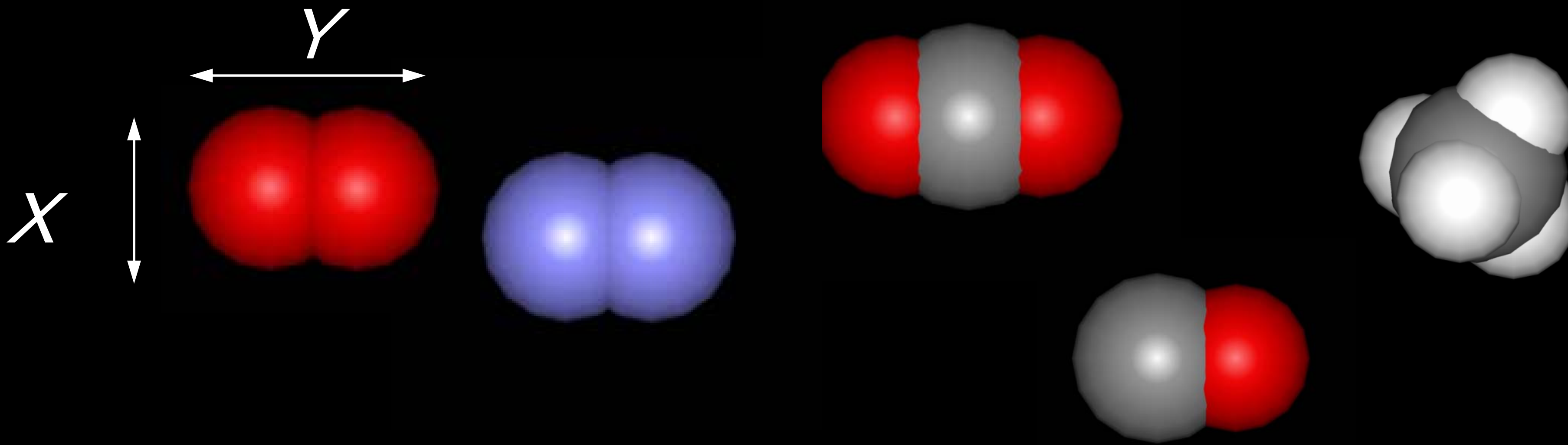
チャンネルの
壁が分子を
拘束する力



外から全く圧力
をかける必要はない

2万気圧

Molecular Size

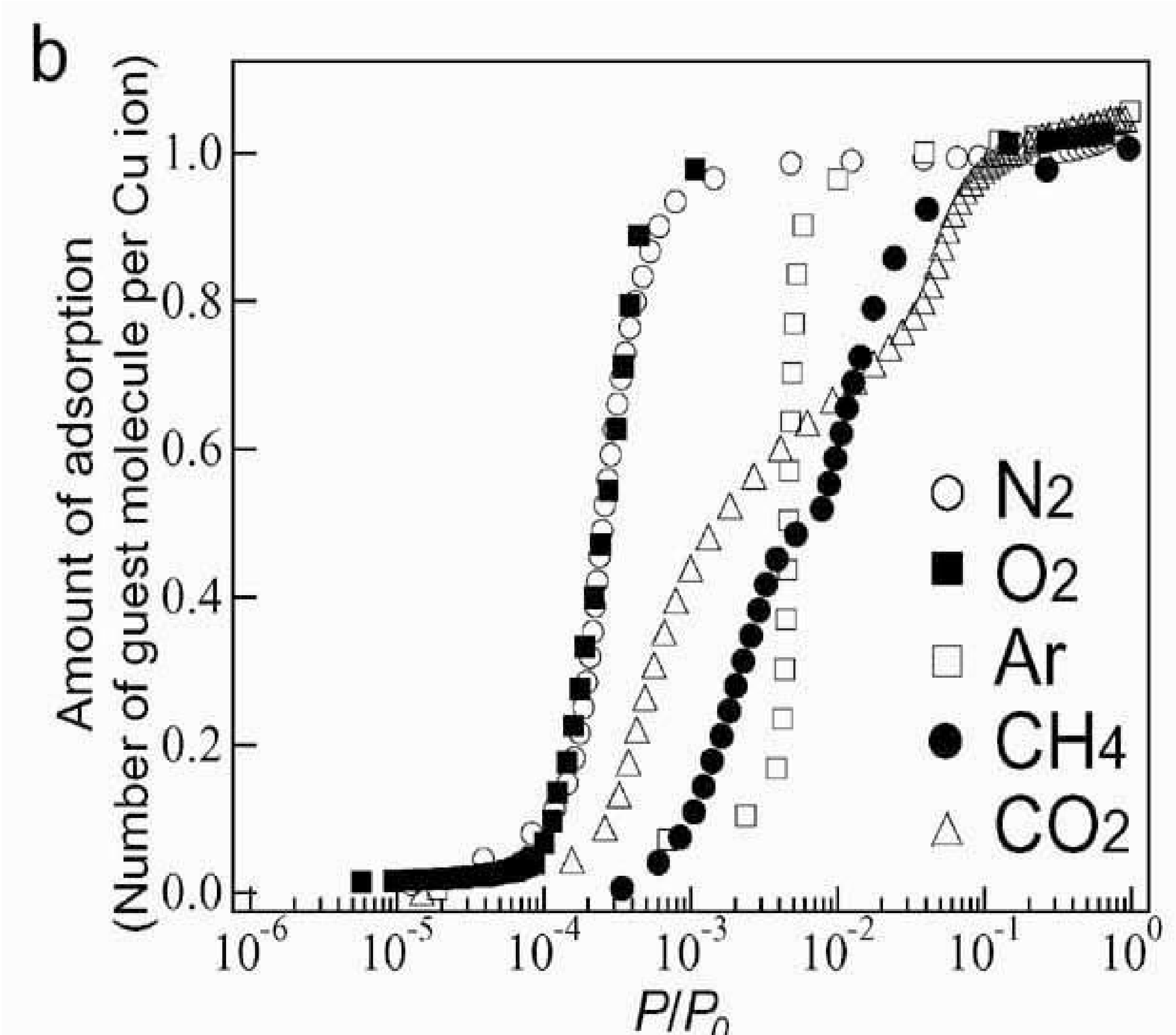


	O_2	N_2	CO_2	CO	CH_4
X (Å)	2.985	3.054	3.339	3.339	3.942
Y (Å)	4.052	4.046	5.361	4.182	3.942

Webster, C. E., *et al. J. Am. Chem. Soc.* **1998**

Isotherms

Low pressure region



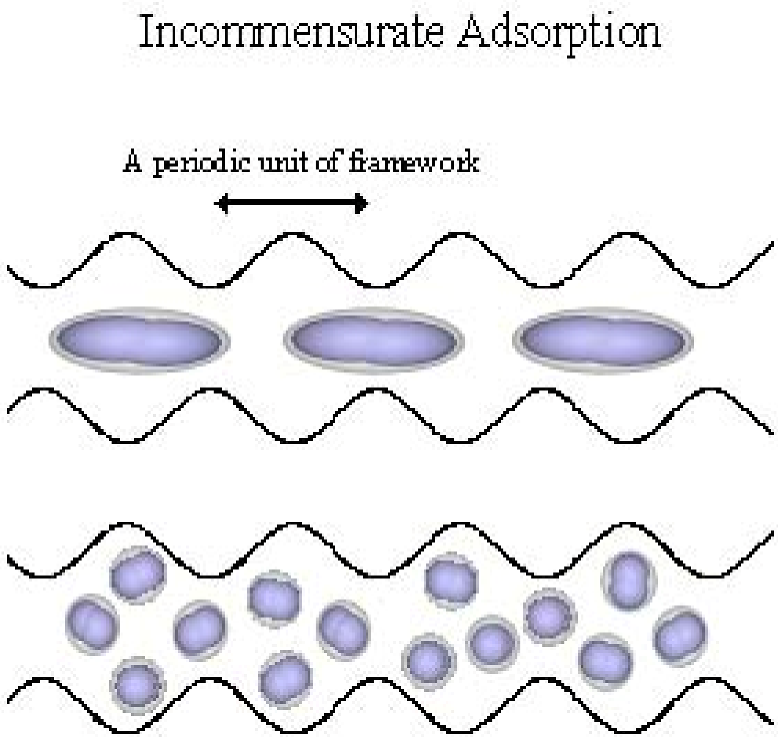
Intermolecular Distances of Confined Guest Molecules (d_{obs}) and Lennard-Jones Potential Minimum (d_{min})

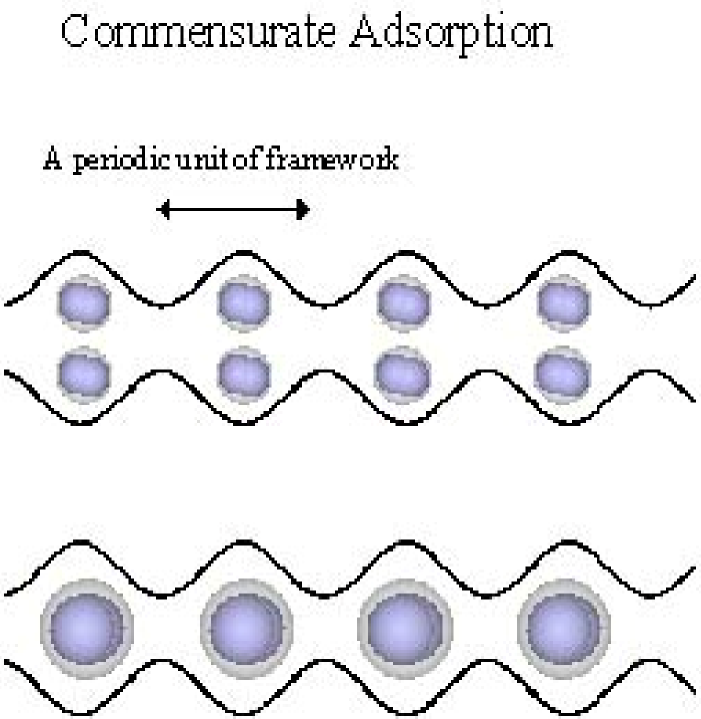
		N_2	O_2	Ar	CH_4
d_{obs}	(Å)	3.33(2)	3.28(4)	3.60(1)	3.70(1)
d_{min}	(Å)	3.67	3.66	3.79	4.18

Density of Confined and Bulk Liquid Phase of N_2, O_2, CO_2, Ar and CH_4

	N_2	O_2	CO_2	Ar	CH_4
d (g/cm^3)	1.11	1.27	1.74	1.58	0.63
d_{liquid} (g/cm^3)	0.808	1.14	1.56*	1.78	0.716

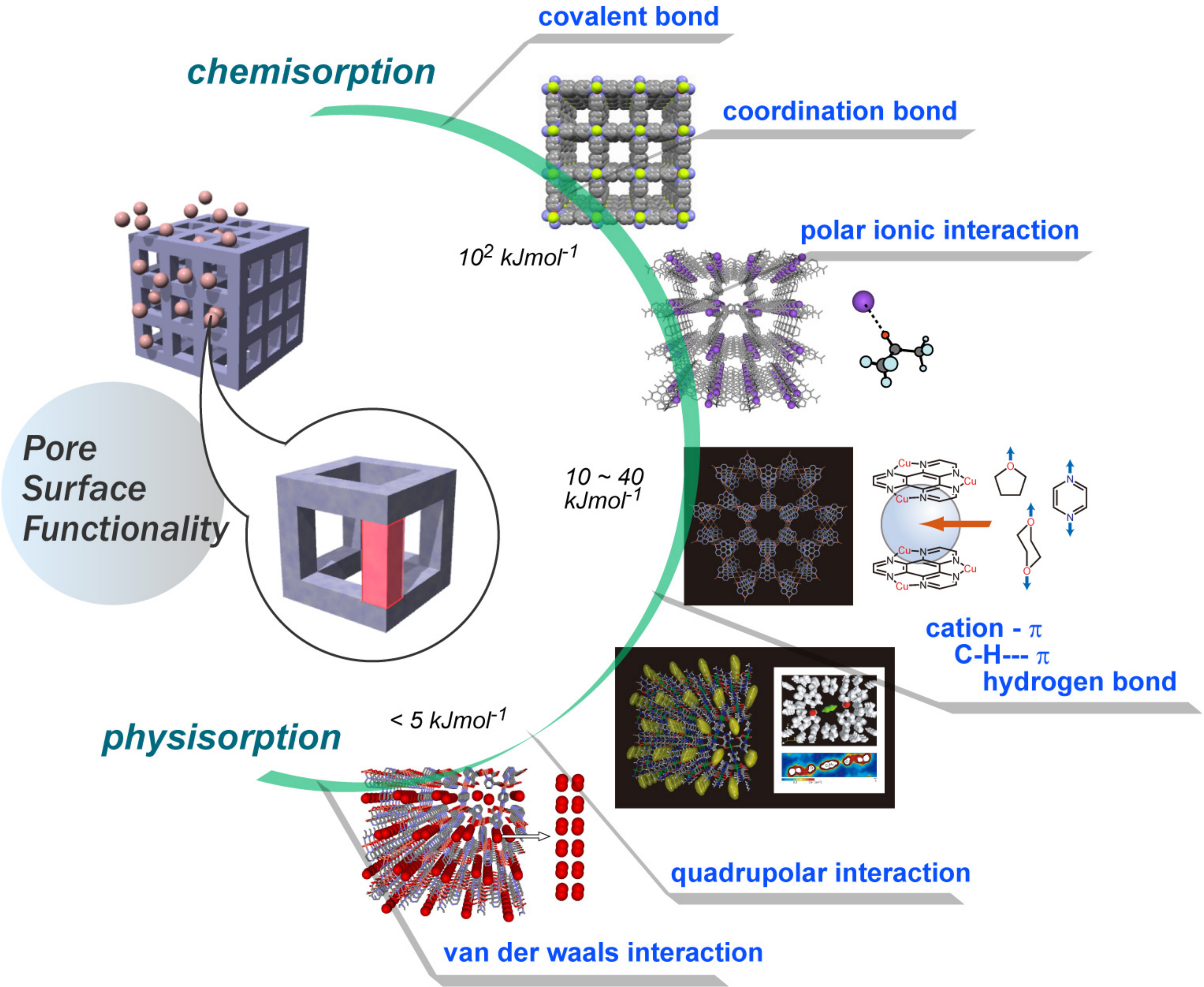
*density of solid CO_2 at 193 K

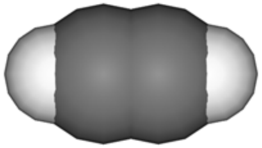

Incommensurate Adsorption
A periodic unit of framework


Commensurate Adsorption
A periodic unit of framework

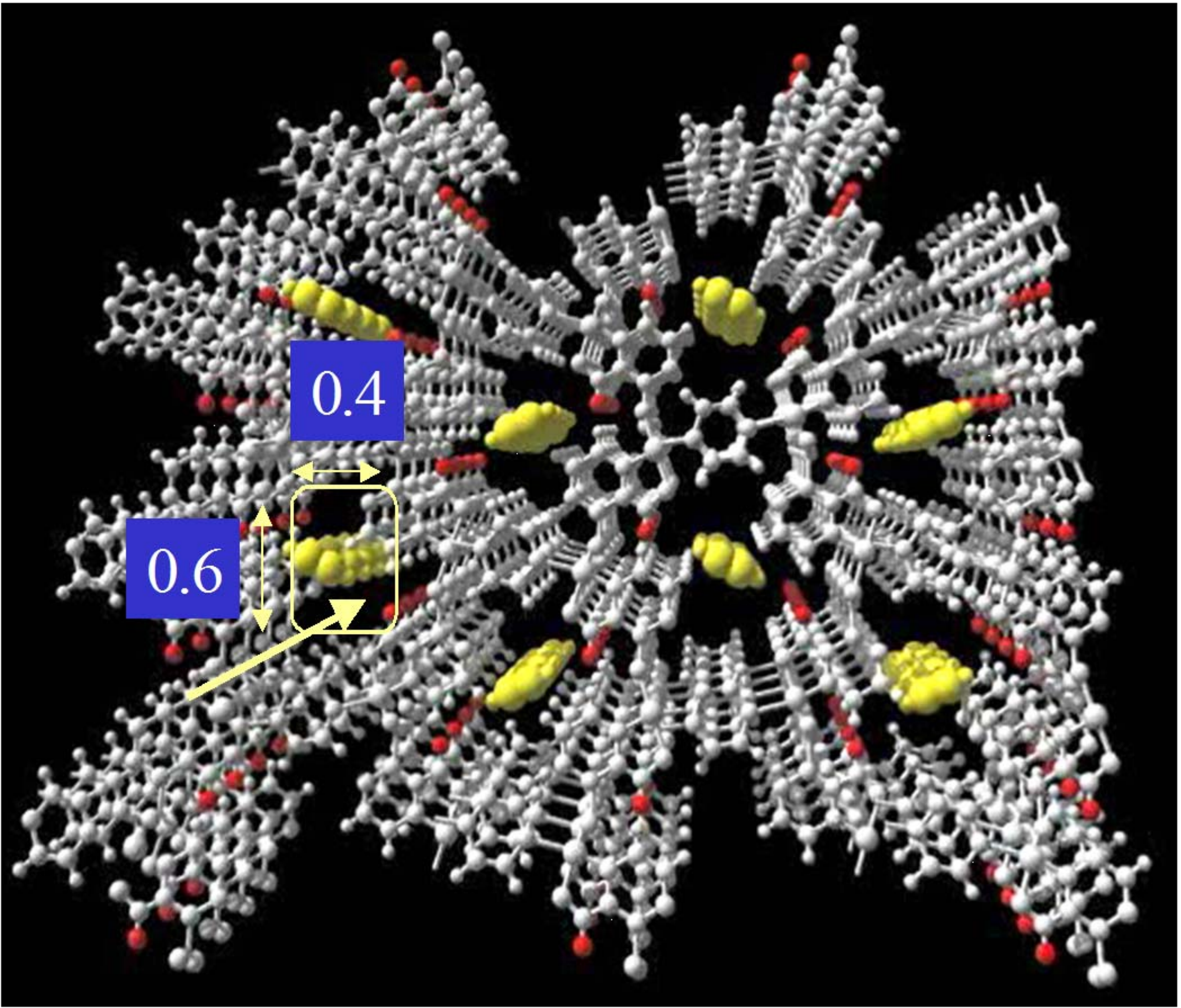
Ar, CH_4

O_2, N_2

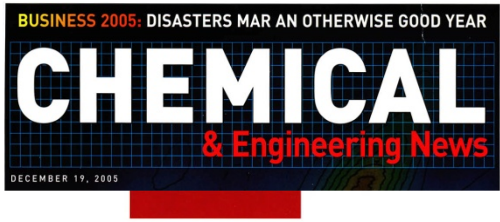

covalent bond
chemisorption
coordination bond
polar ionic interaction
10^2 kJmol^-1
Pore
Surface
Functionality
10 ~ 40
kJmol^-1
cation - π
C-H--- π
hydrogen bond
< 5 kJmol^-1
physisorption
quadrupolar interaction
van der waals interaction



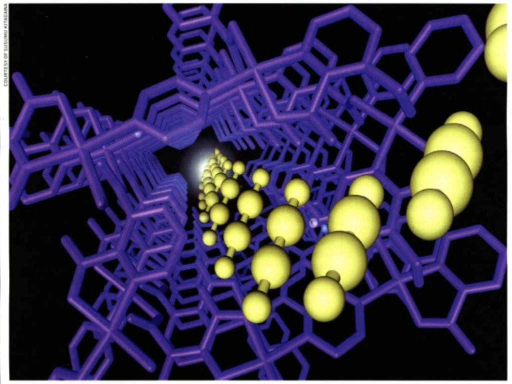
-Nature, 2005, 436, 238.
-Nature, 2005,436,187.News &Views



C & E News
Highlights 2005



COVER STORY



SAFE SQUISH A new metal-organic microporous material (purple) designed and synthesized by Kitagawa and coworkers makes it possible to store acetylene (yellow) safely at a density 200 times its normal safe compression limit. Acetylene is normally highly reactive and explodes when compressed at more than 2 atm at room temperature.

CHEMISTRY HIGHLIGHTS 2005

Key advances have been made this year in organic and inorganic chemistry, biochemistry, nanotechnology, and other areas

STU BORMAN, C&EN WASHINGTON

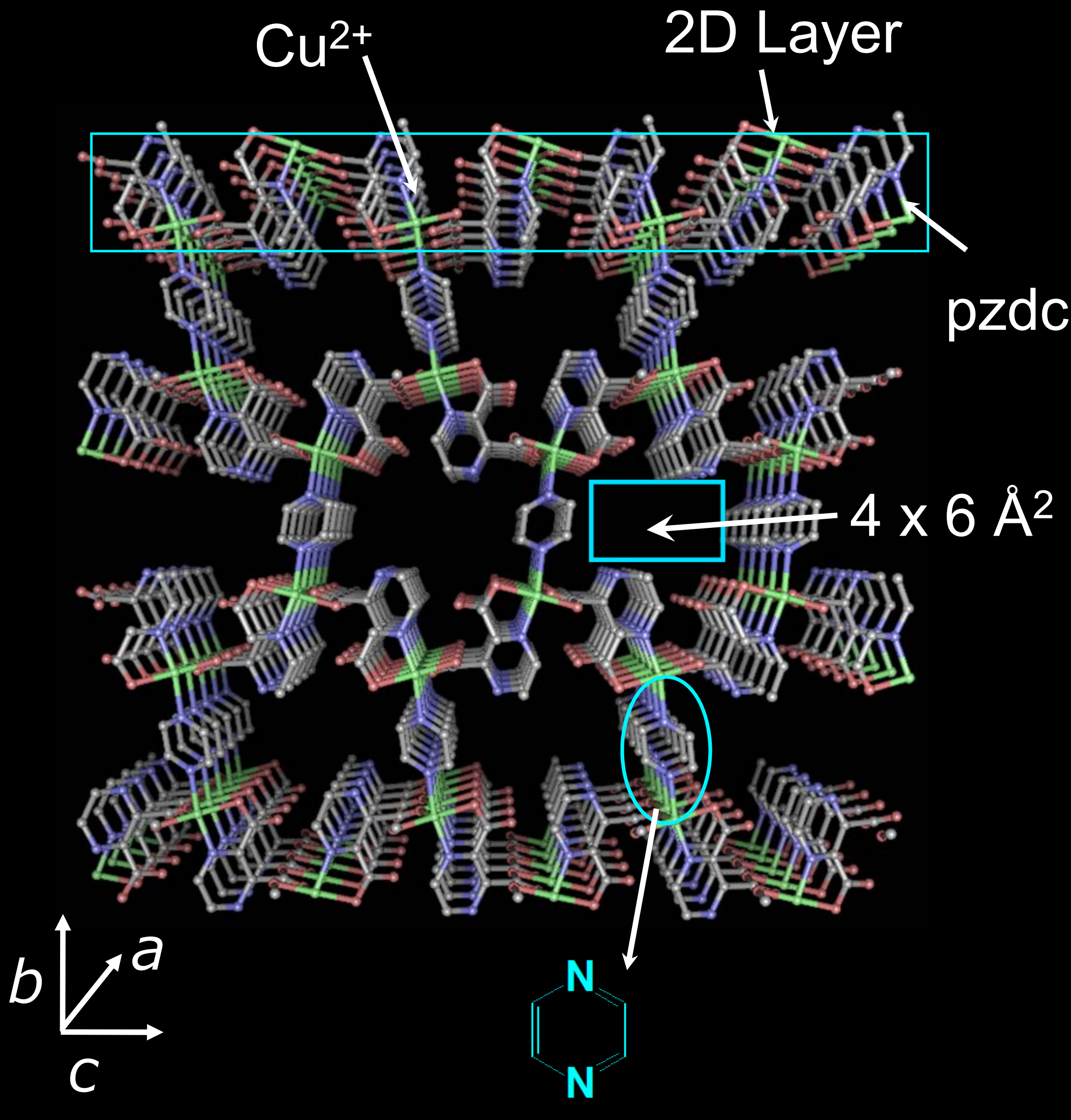
EACH YEAR, WE AT C&EN HIGHLIGHT SOME OF THE MOST significant chemical research advances that we've reported over the preceding 12 months. Like pharmaceutical chemists, we screen our library of news stories for those that seem most significant and try to ferret out the most promising hits.

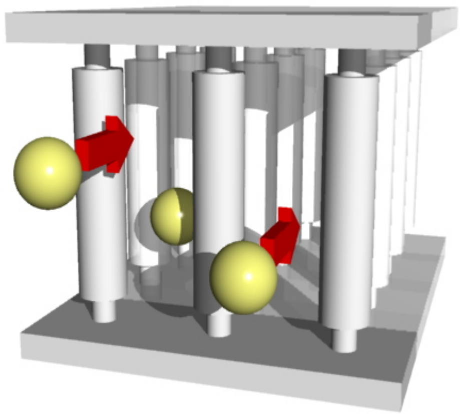
We look for long-sought or surprising breakthroughs, first-of-a-kind advances, and findings that are likely to have long-lasting influence. For 2005, we've identified 24 developments that we believe meet these criteria.

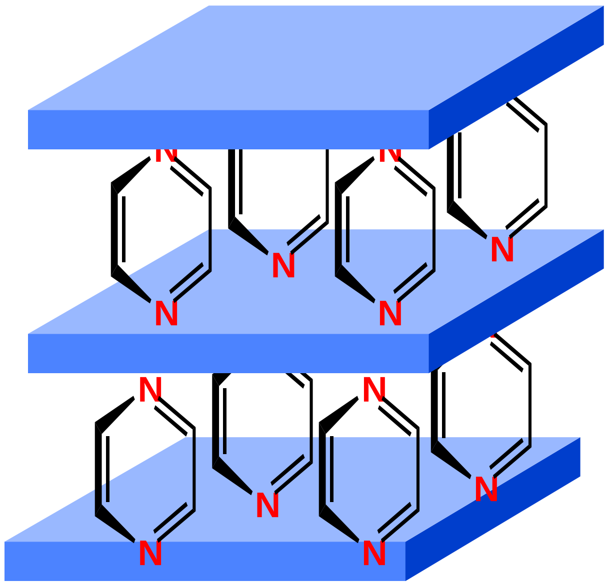
The advances range all over the various chemical disciplines, from organic chemistry to molecular biology, from structural biology to inorganic chemistry, and from nanotechnology to physical chemistry. Our list helps bring into focus the extraordinary and inspiring level of accomplishment achieved by the chemistry research enterprise.

This year, **organic chemistry** was thrust into the limelight by the Nobel Prize in Chemistry, which honored a powerful class of catalytic organic reactions. The prize was awarded to three chemists who developed olefin metathesis: Yves Chauvin of the French Petroleum Institute, Rueil-Malmaison, France; Robert H. Grubbs of Califor-

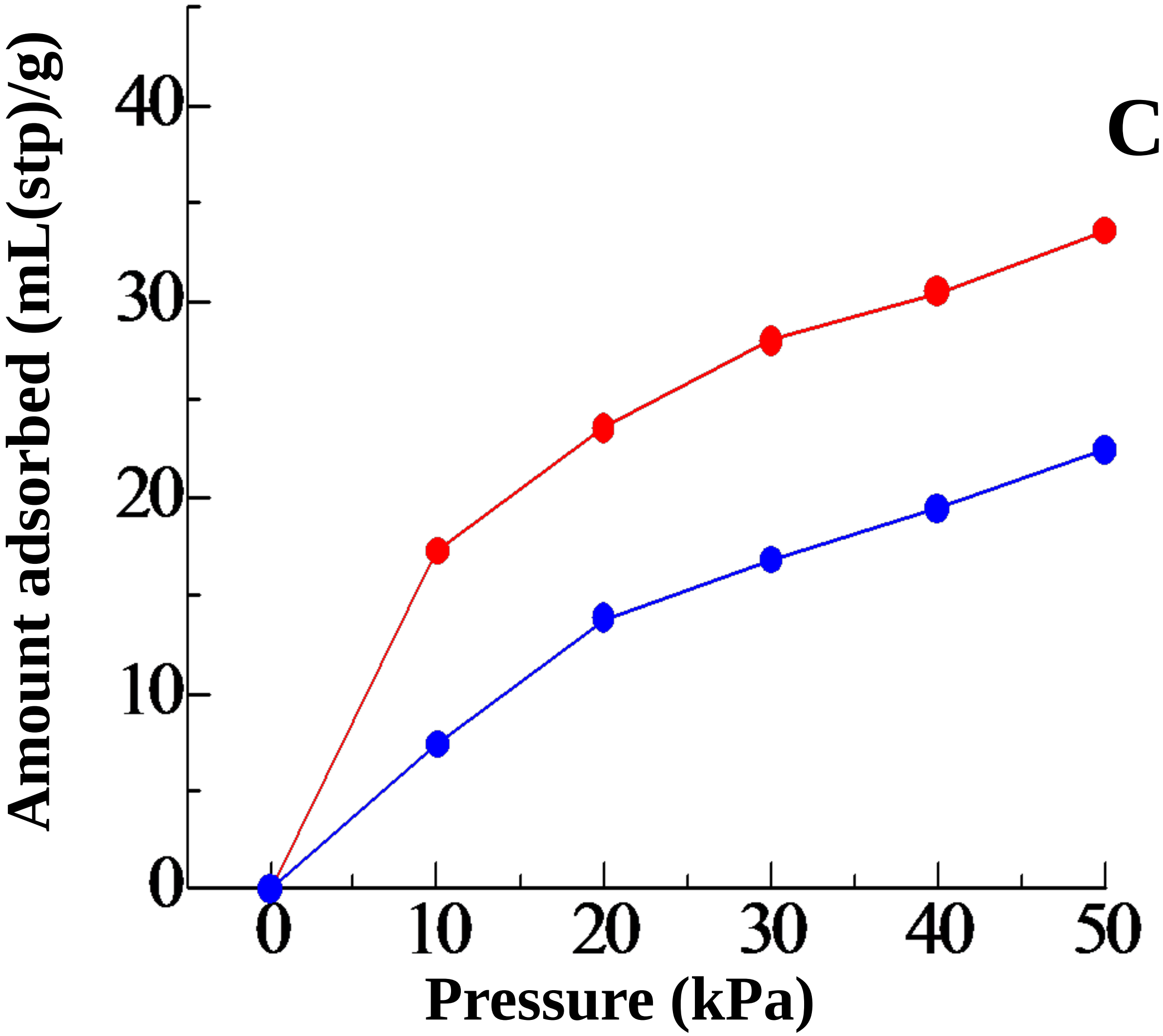
3-D Structure of [$Cu_2(pzdc)_2(pyz)$] (CPL



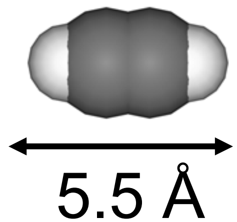




Adsorption Isotherms at 303 K on Activated Carbon Fiber

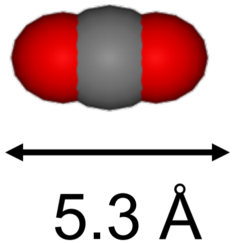


C_2H_2



b.p. 189.2 (K)

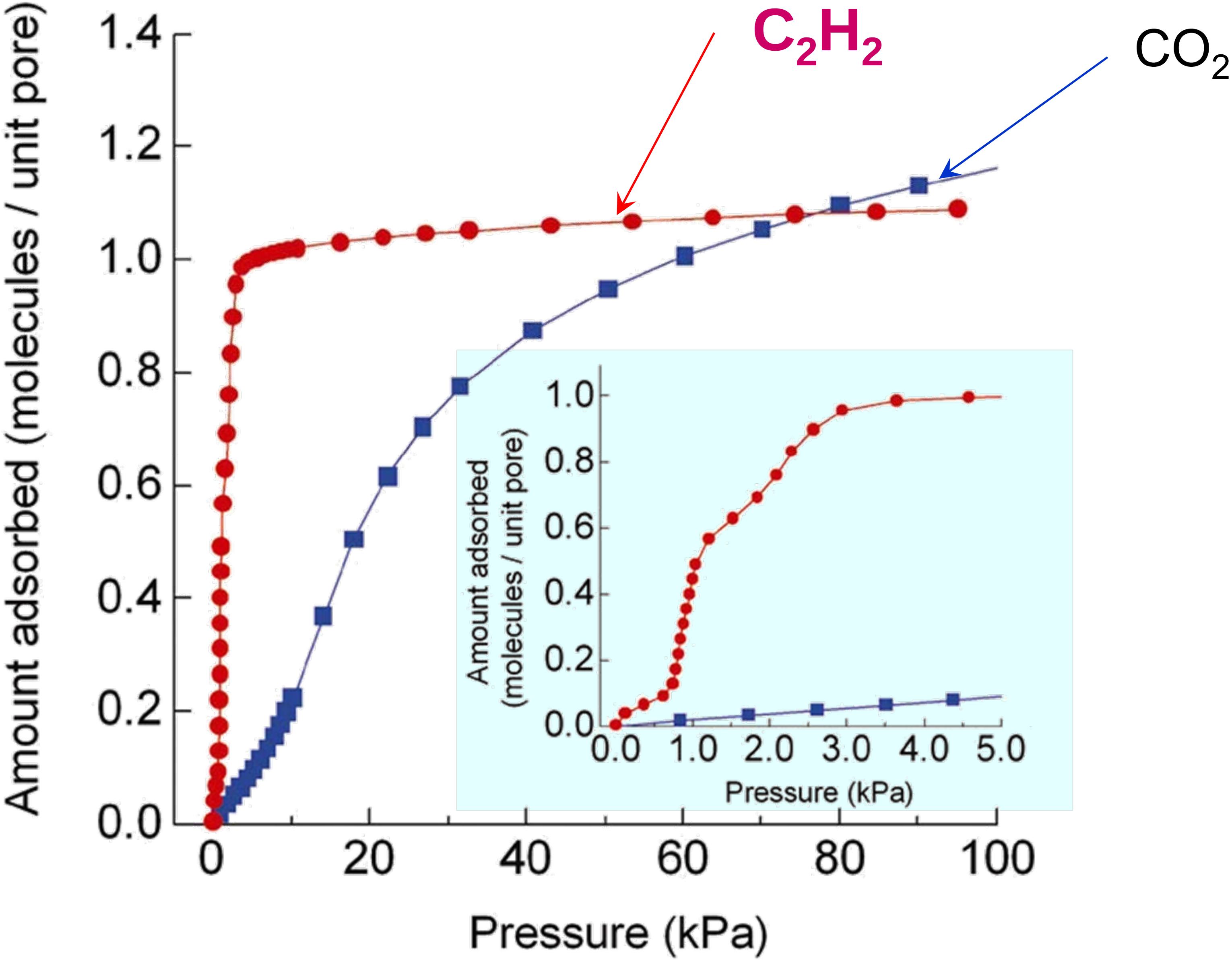
CO_2



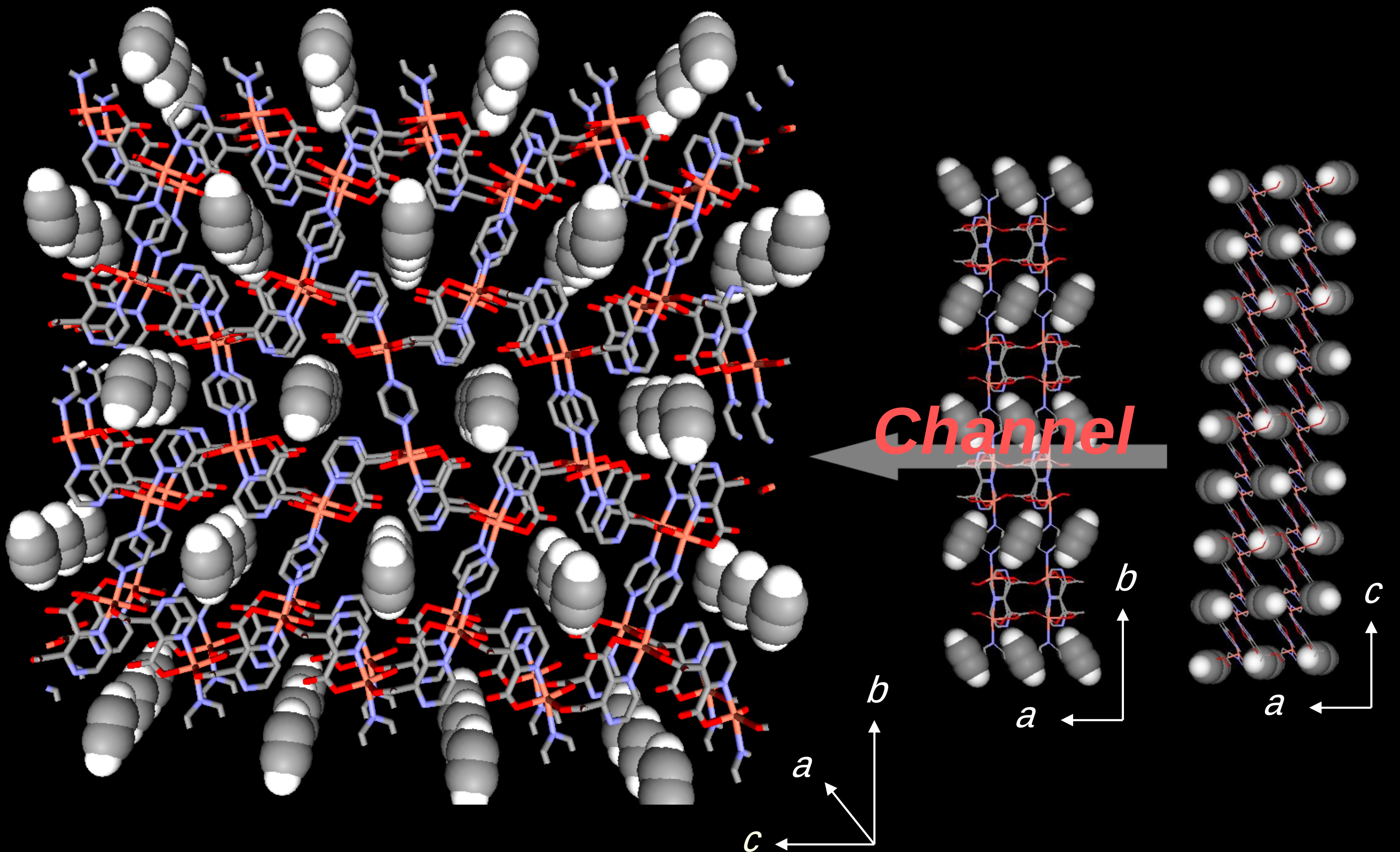
b.p. 194.7 (K)

Thomas, ***Langmuir* (1999)**

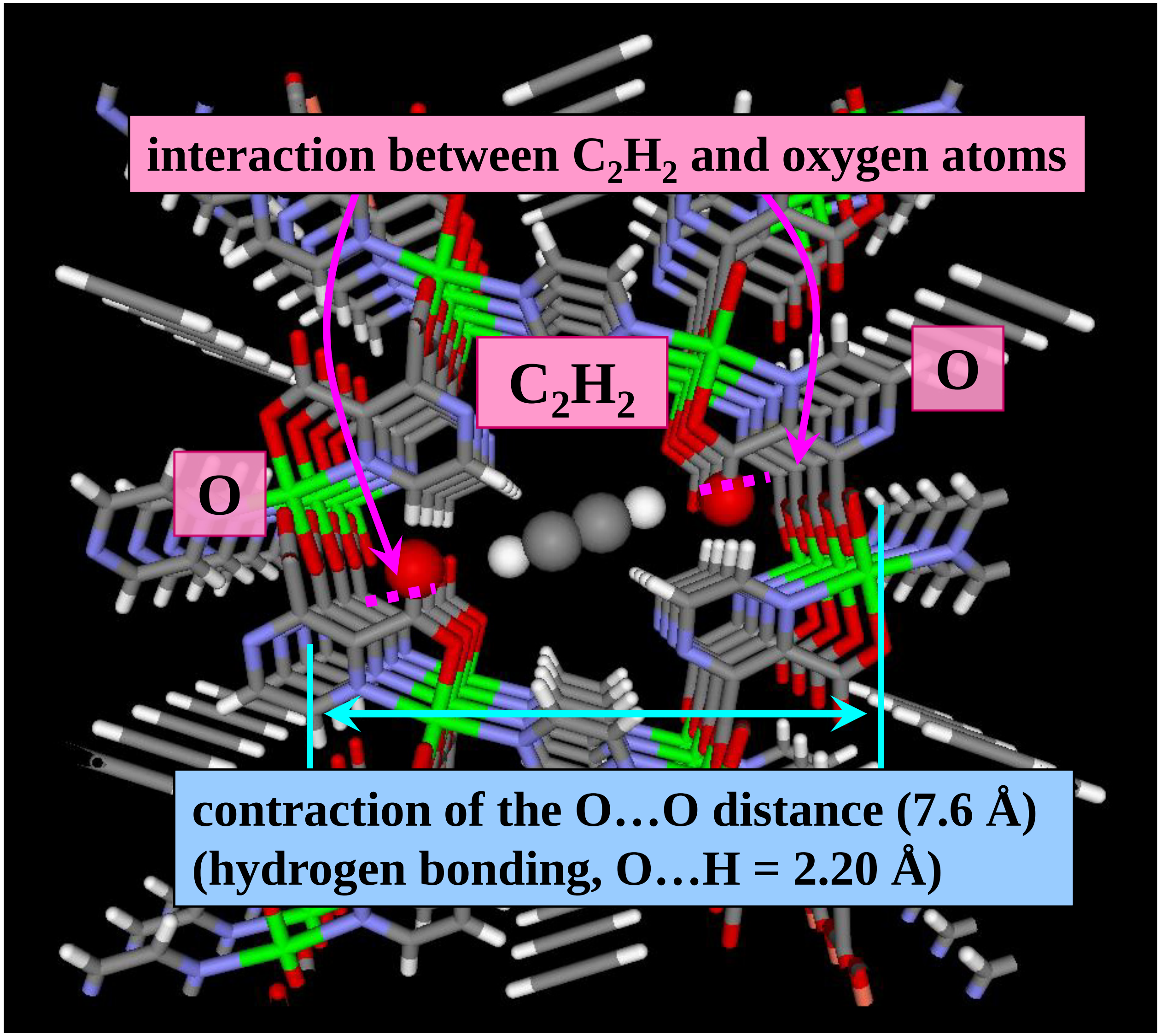
Adsorption isotherm of C_2H_2 & CO_2 in CPL-1



Crystal Structure of CPL-1 with Acetylene at 170K

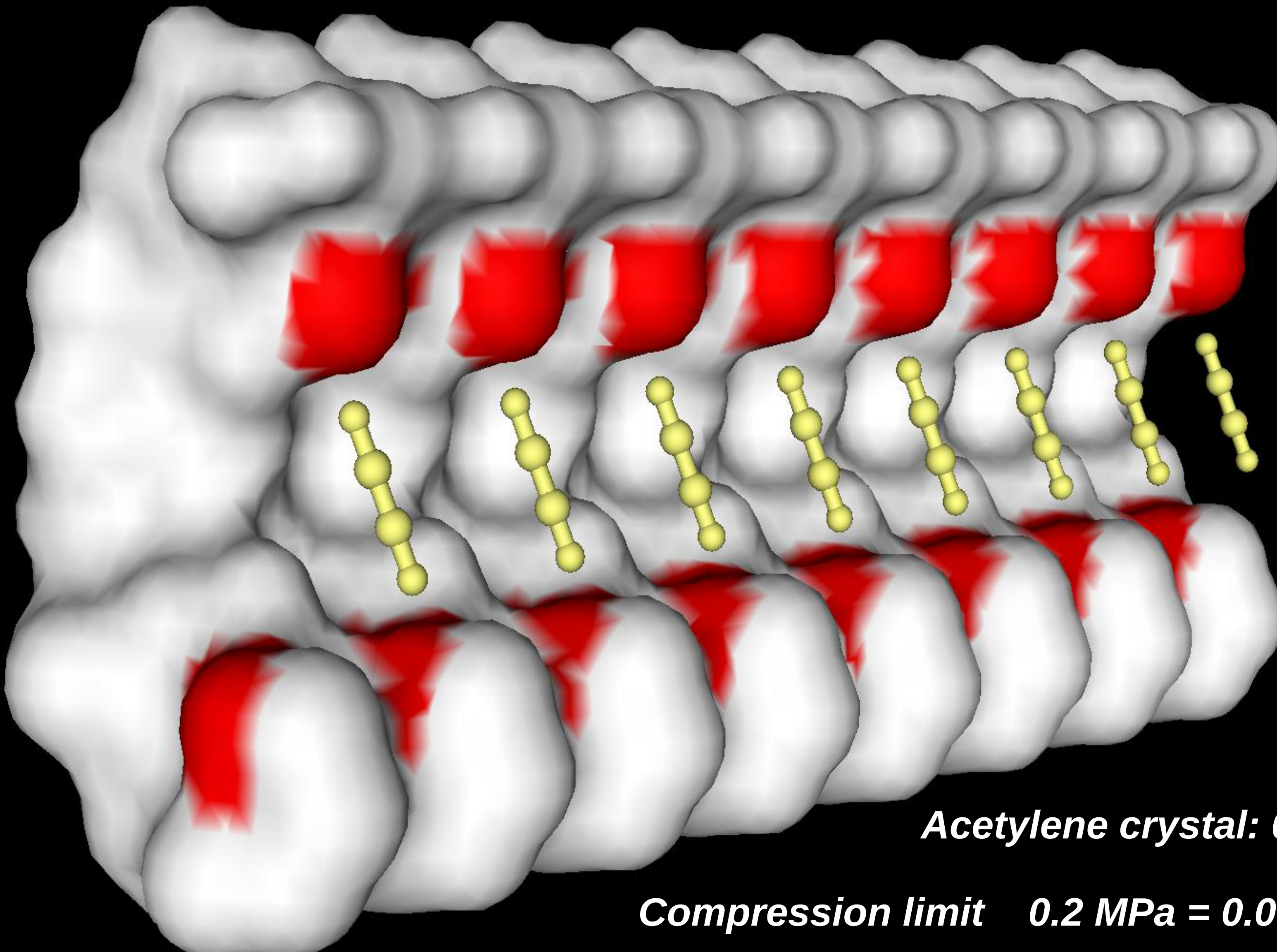


acetylene molecule incarcerated in a porous framework



micropore volume
99.7 Å^3 / unit pore

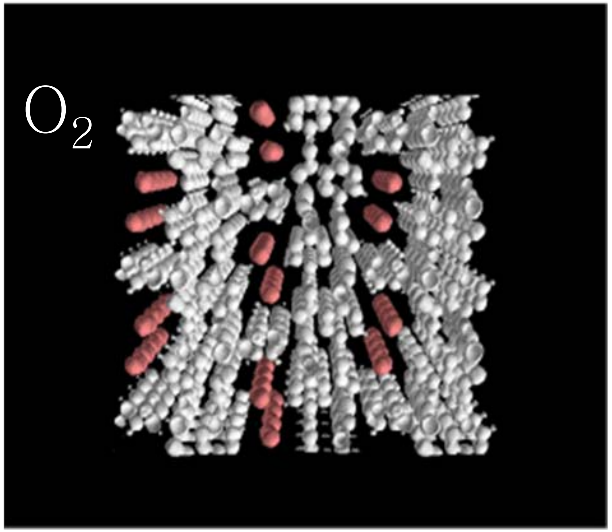
density (C_2H_2) = 0.44 g / cm^3



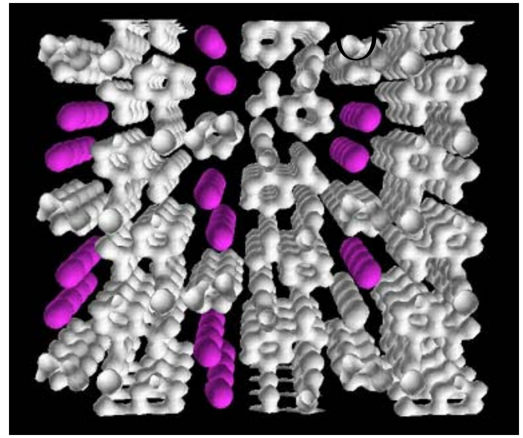
Acetylene crystal: 0.75 g / cm^3

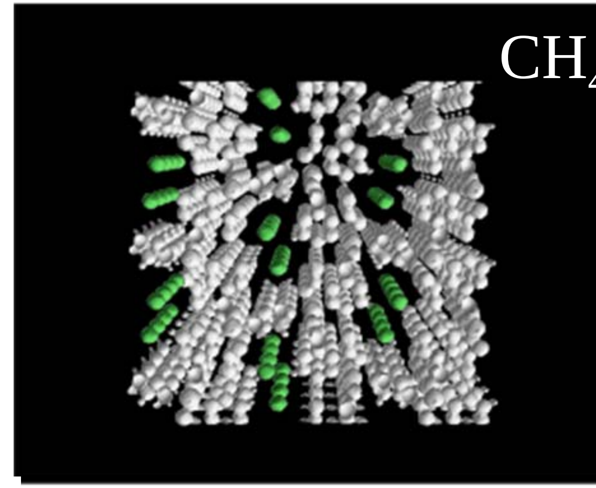
Compression limit 0.2 MPa = 0.0021 g / cm^3

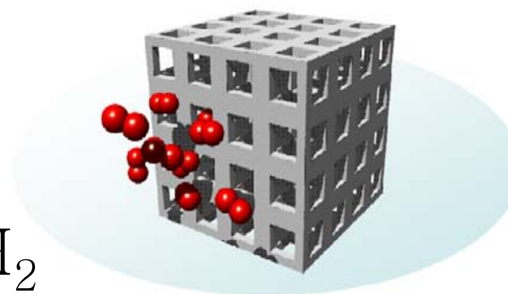
Comfinement of gas molecules



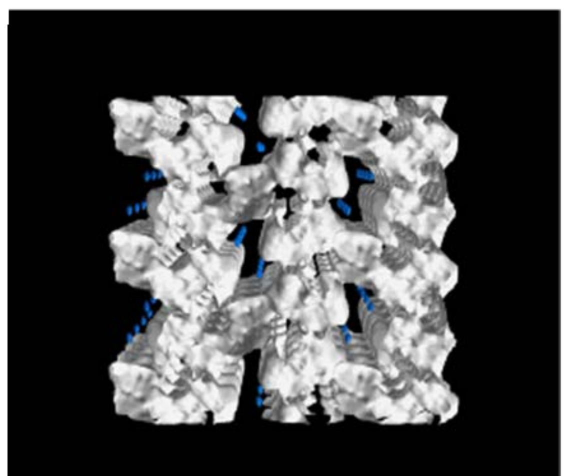
N

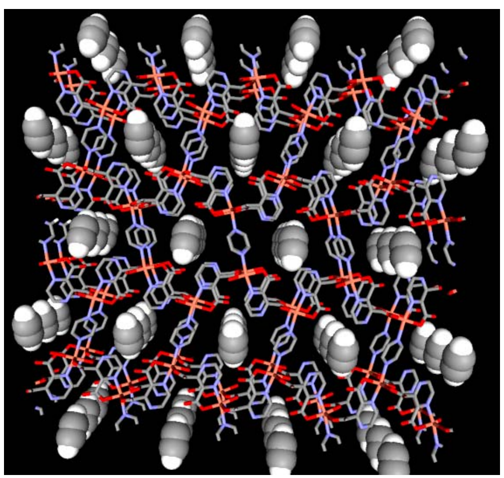






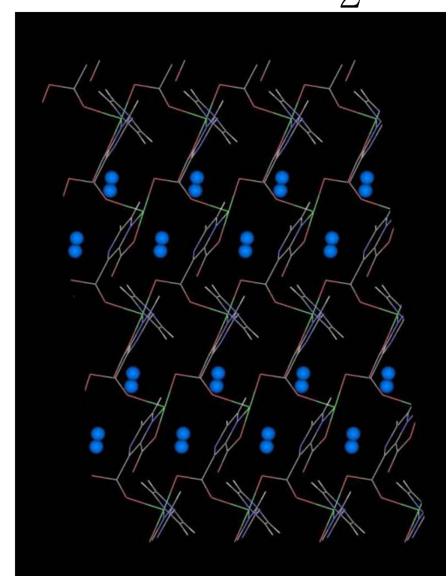
H_2

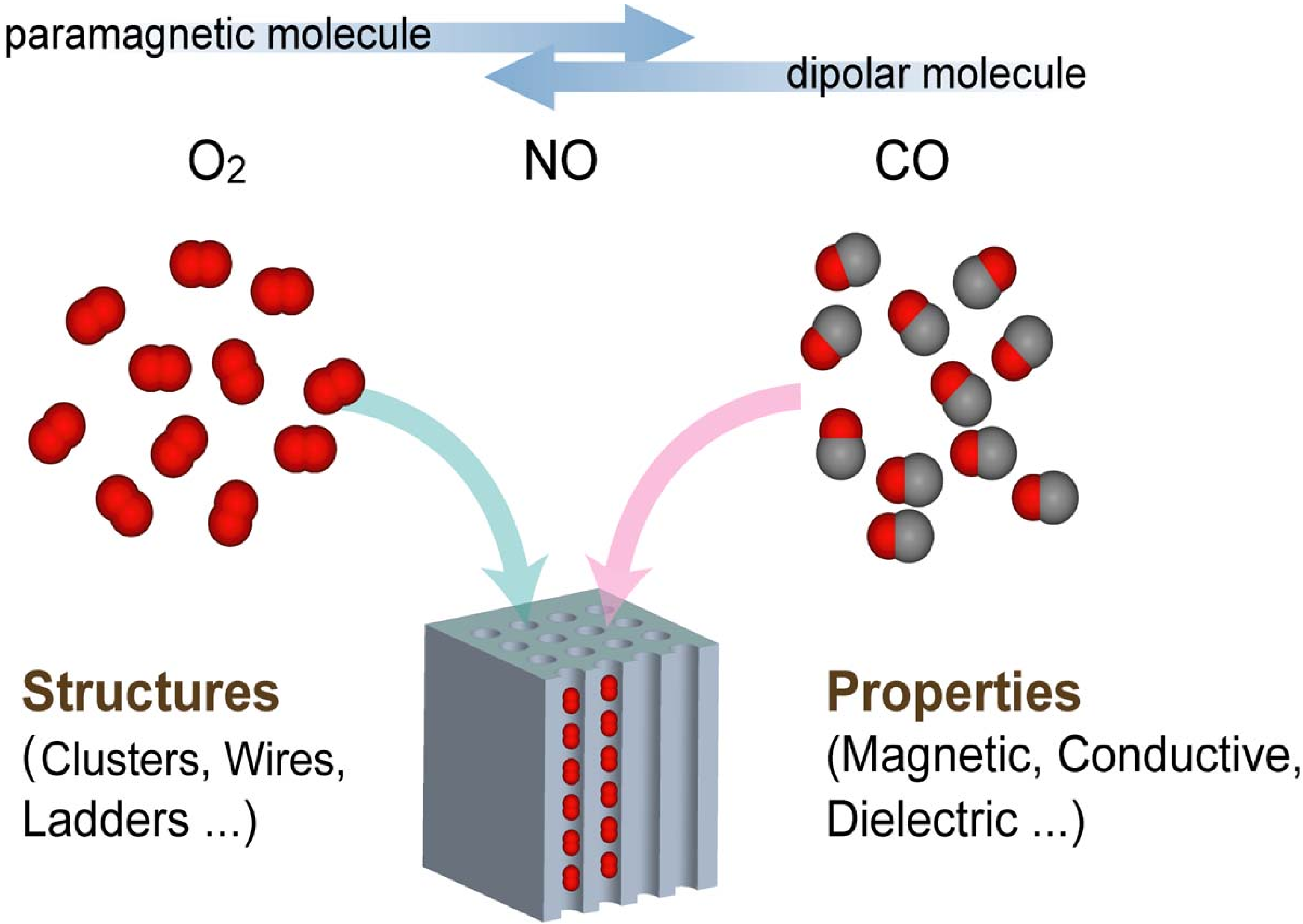




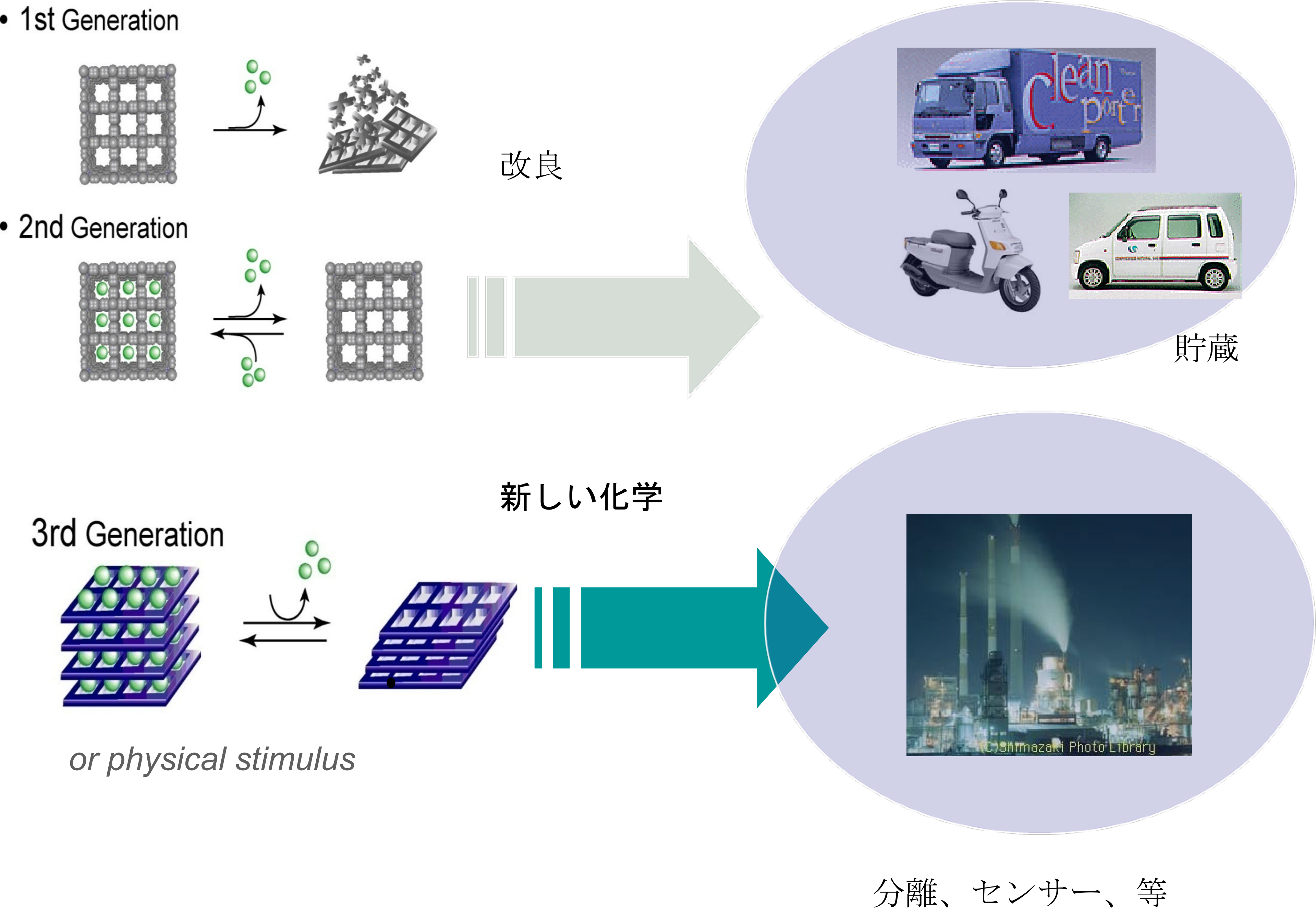
C_2H_2

N_2





Nature, 2006, 444,584. News & Views


1st Generation
改良
2nd Generation
貯蔵
新しい化学
3rd Generation
or physical stimulus
(C)Shimazaki Photo Library
分離、センサー、等

Separation

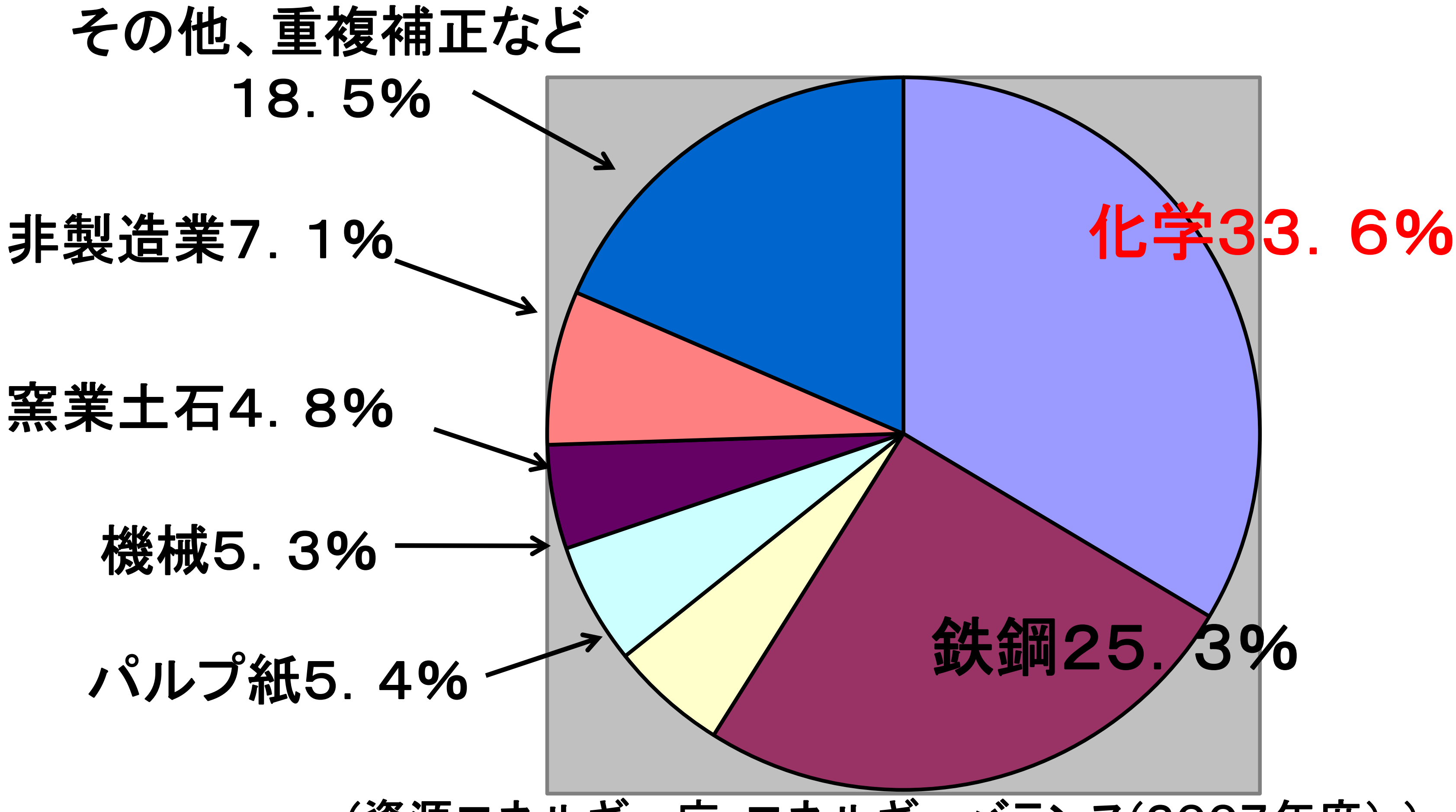
蒸留塔
A Pipestill at Fawley

N_2 ガスセパレーター
Activated Carbon
KURARAY CHEMICAL CO,. LTD

H_2O&CO_2 除去装置
Activated Alumina &
Molecular Sieve
PSB Industries Inc.

分離膜
MF1-Type Zeolite
©NGK INSULATOR. LTD.

全産業のエネルギー消費割合



（資源エネルギー庁；エネルギーバランス(2007年度））

エネルギー消費

１．化学産業のエネルギー消費

全産業分野の約３４％（２位鉄鋼）

（資源エネルギー庁；エネルギーバランス(2007年度））

２．蒸留操作（分離・精製）

１の約４０％

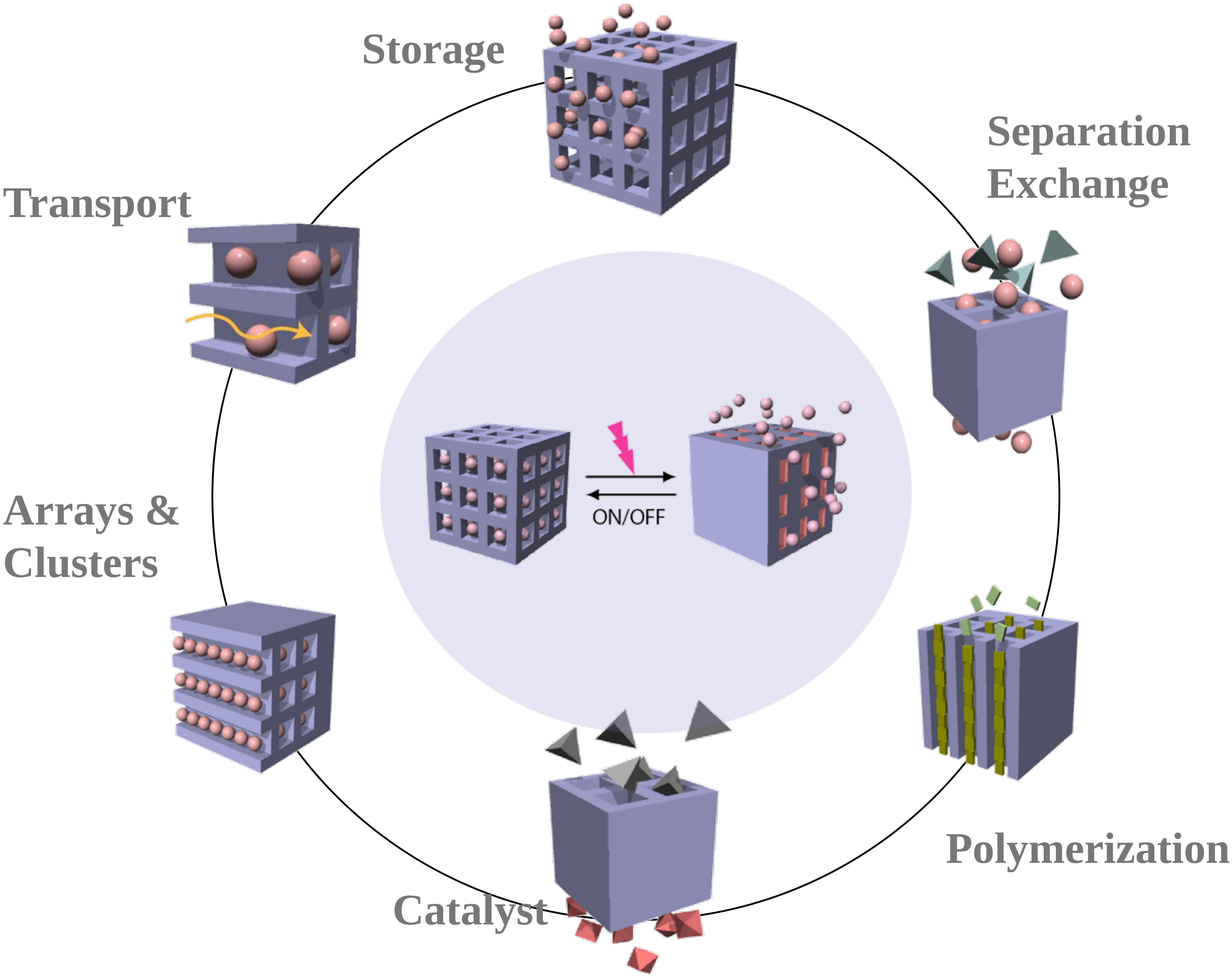
（科学技術動向、2009年2月号）

３．石油化学産業（製品）

１の約５３％

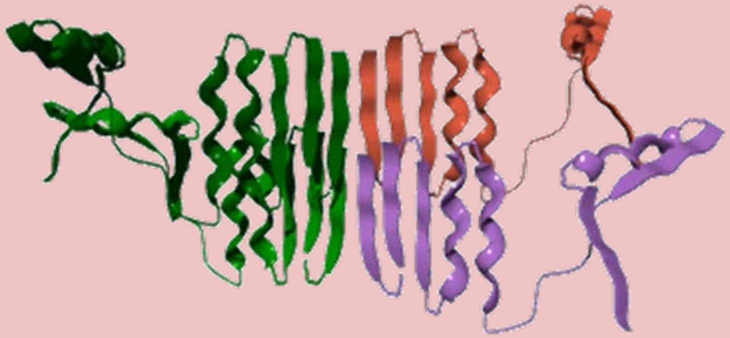
（資源エネルギー庁；エネルギーバランス(2006年度））

３の約１／３はエチレンプラントで消費


Storage
Separation
Exchange
Transport
ON/OFF
Arrays &
Clusters
Polymerization
Catalyst

The symbiotic unification of “softness” and “regularity”

Soft Materials

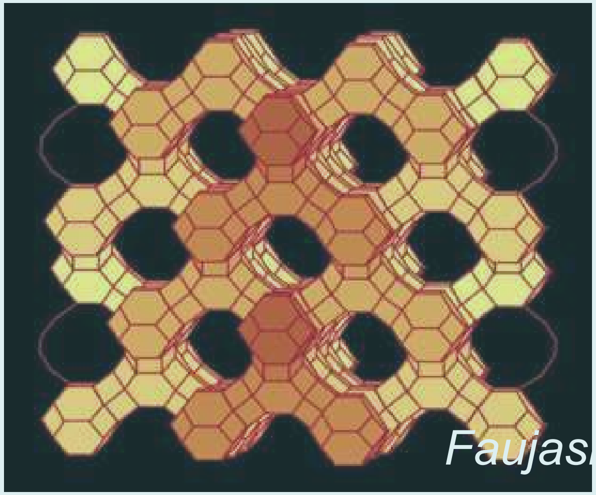


Proteins
Organic Polymers

softness

?

Inorganic Porous Materials



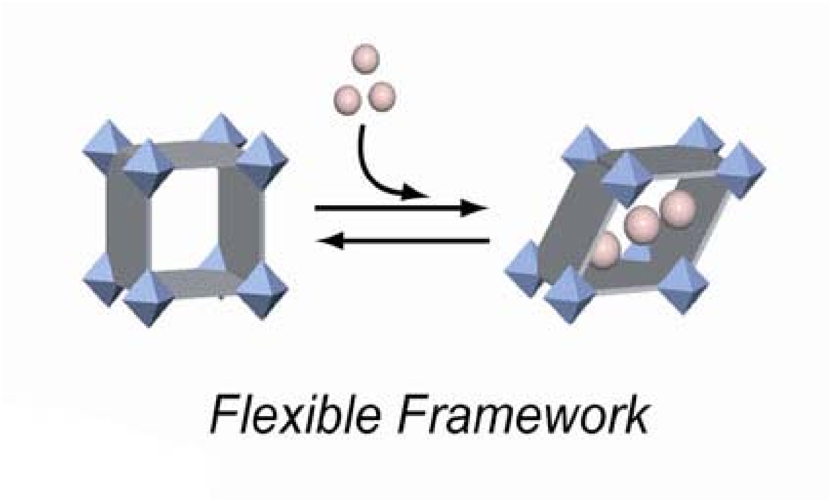
Zeolites

regularity

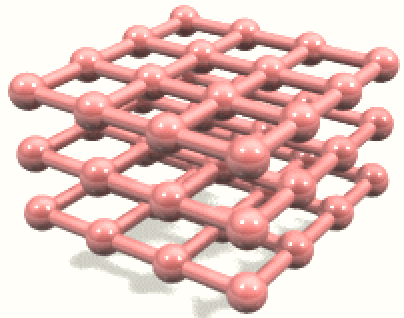
Soft Porous Crystals (SPCs)

Definition

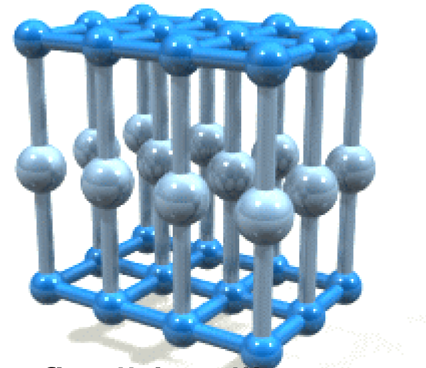
1. *Single crystals: Long Range Regularity*
2. *Transformable foms: One crystal form to others*
3. *Porous frameworks*



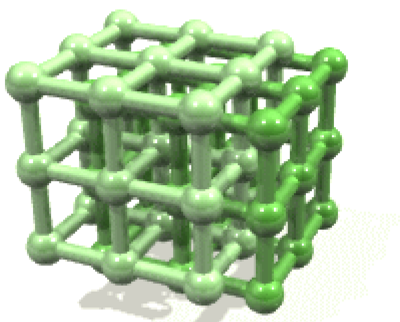
Motifs for Soft Porous Crystals



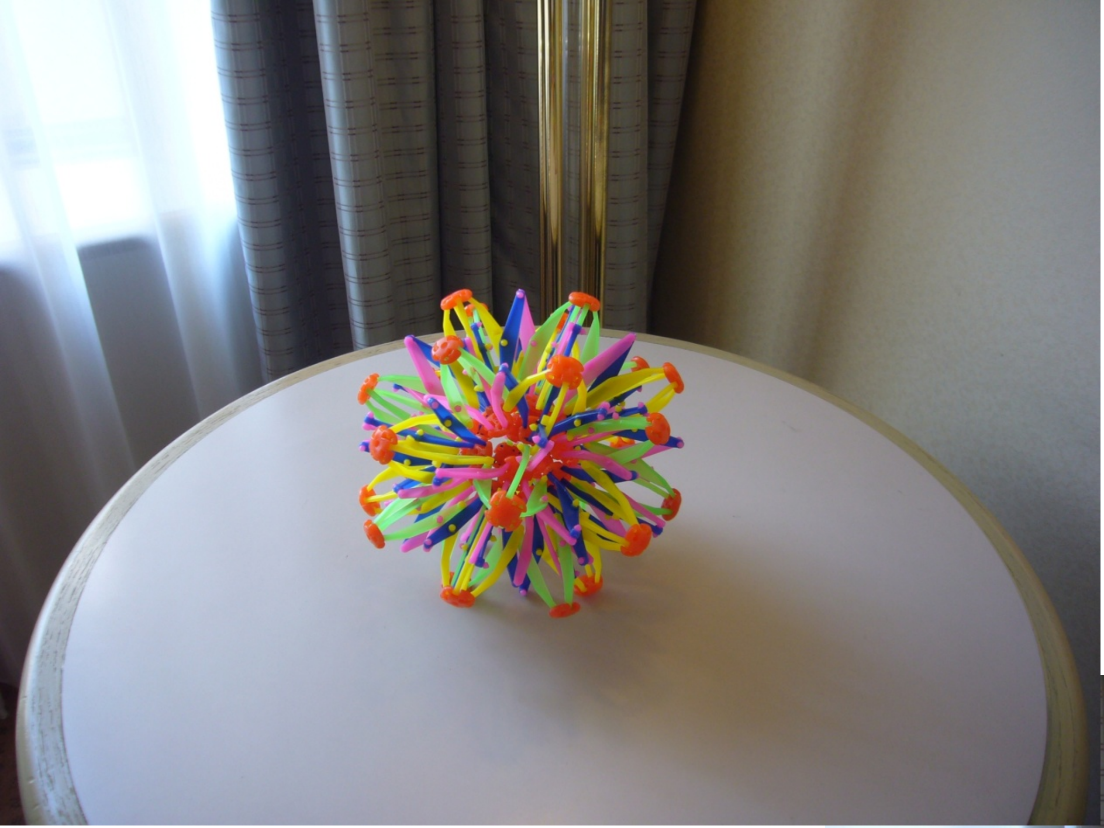
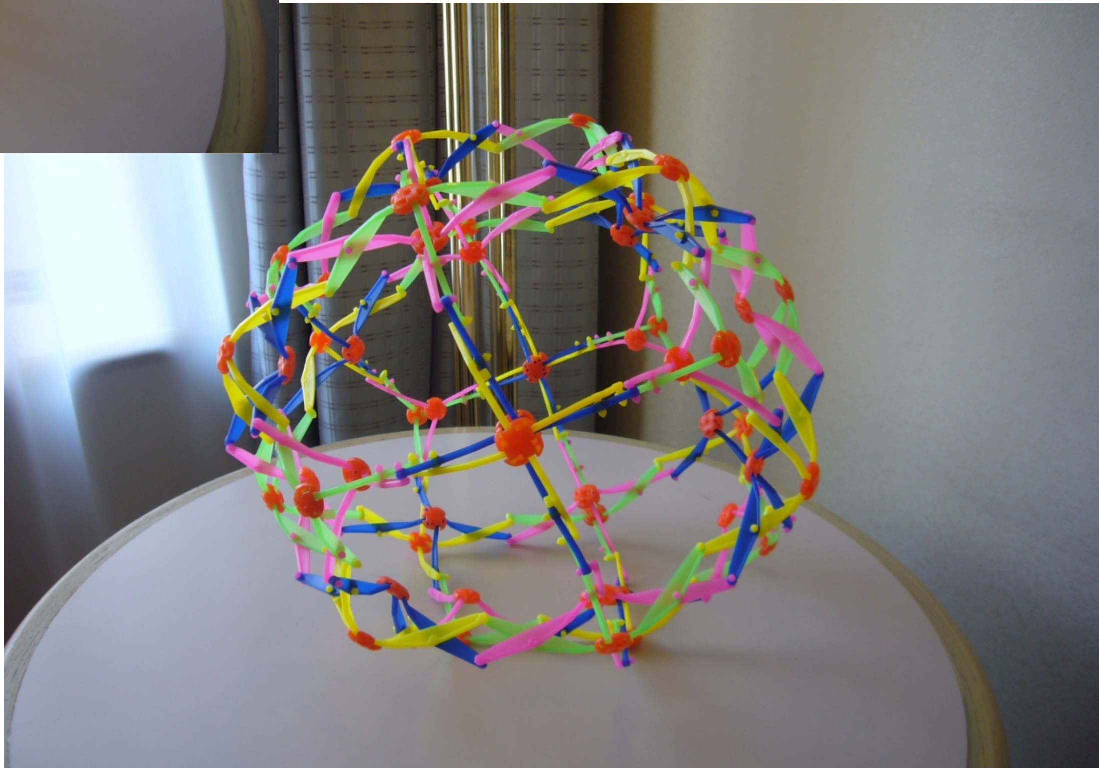
stacked layers

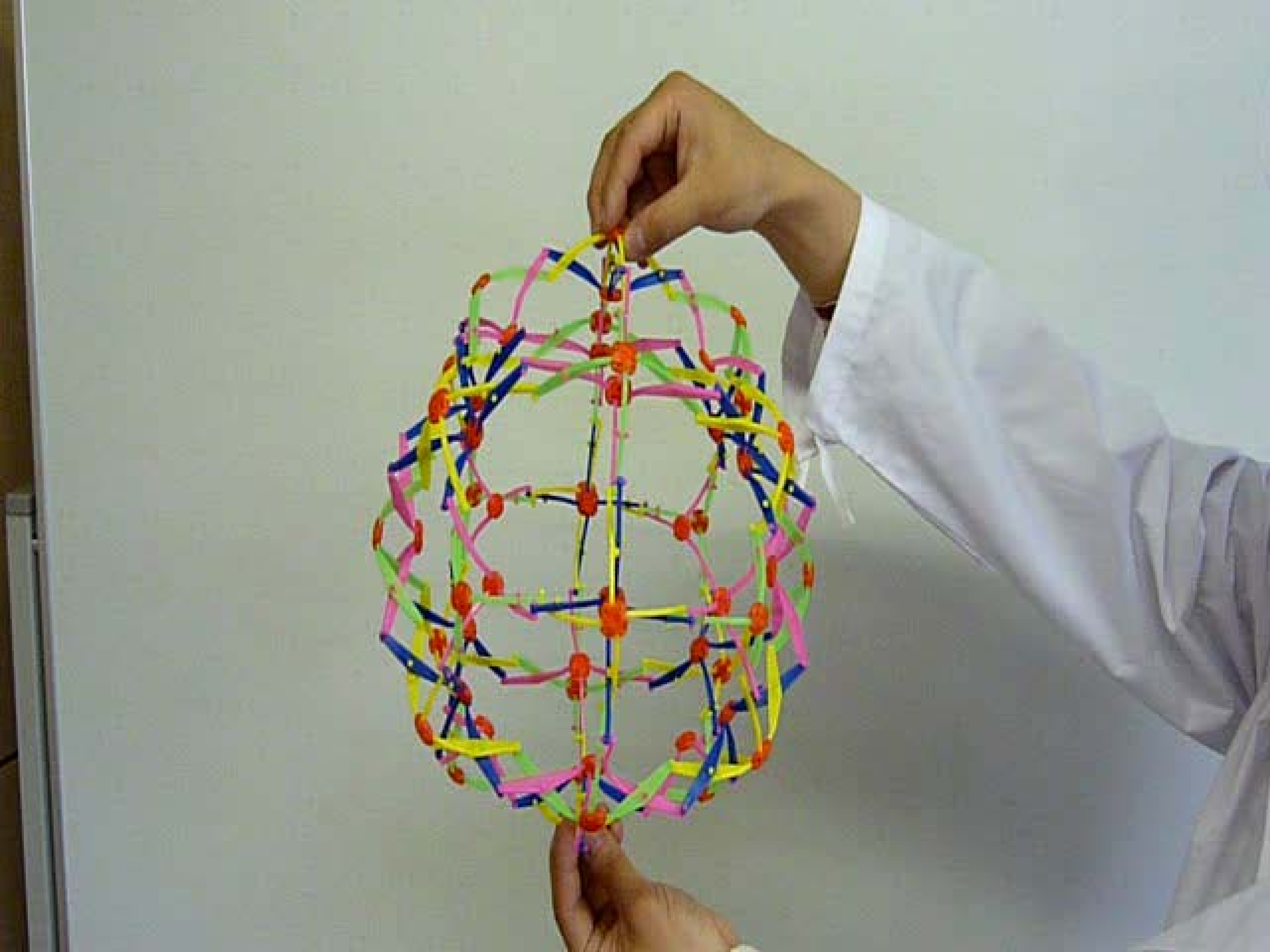


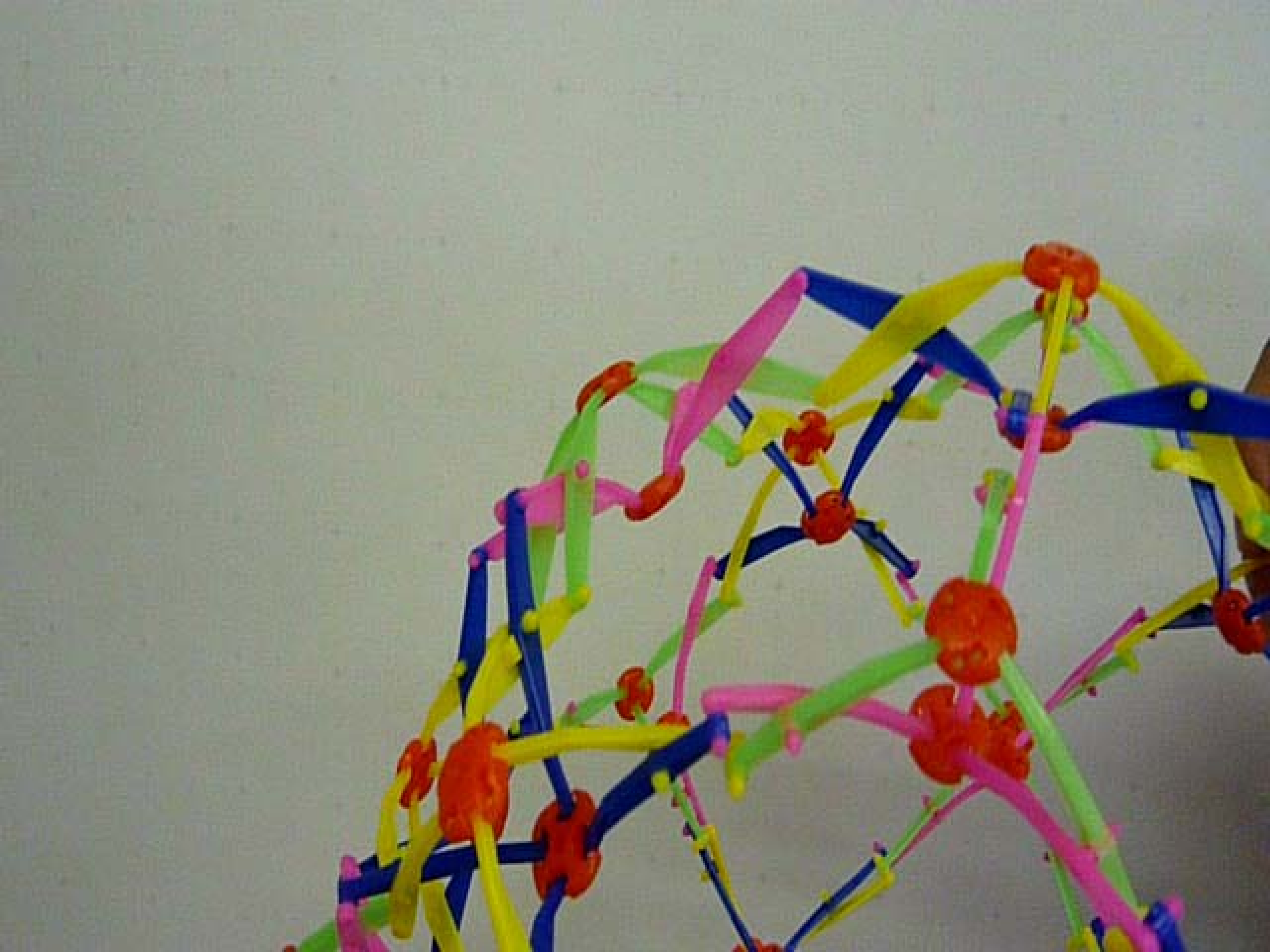
flexible pillars



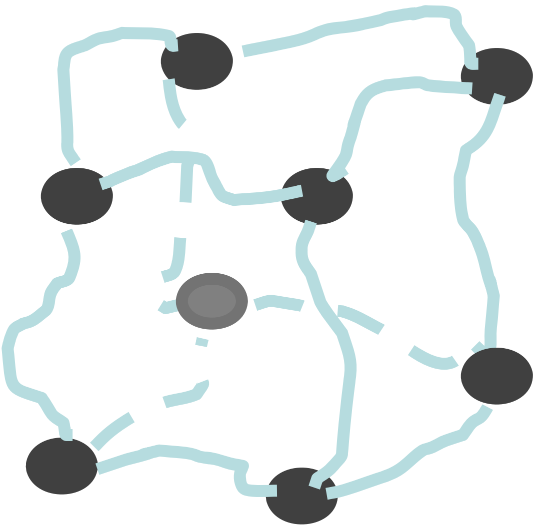
interpenetration





Flexible building units are pinned at the corners.



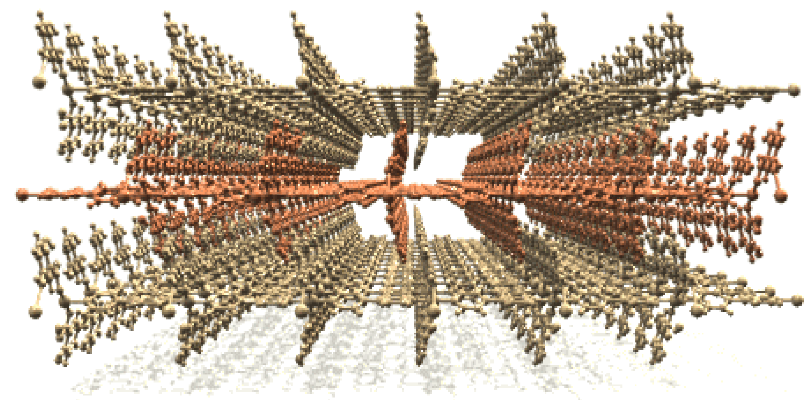
Coordination bond

Degree of freedom to some extent

-organic parts + inorganic parts

-regularity

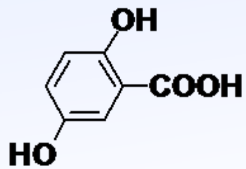
(π–π stacking) cushion pillar



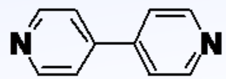
interdigitation

Angew.Chem.Int.Ed.2003,42,428.

Synthesis of π-stacked pillared layer structure

$Cu(CH_3COO)_2\cdot H_2O$ + 

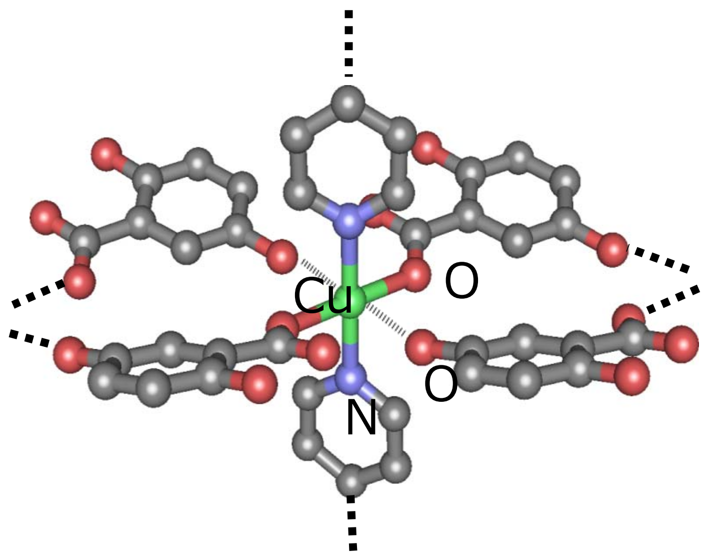
Hdhbc

\+ 

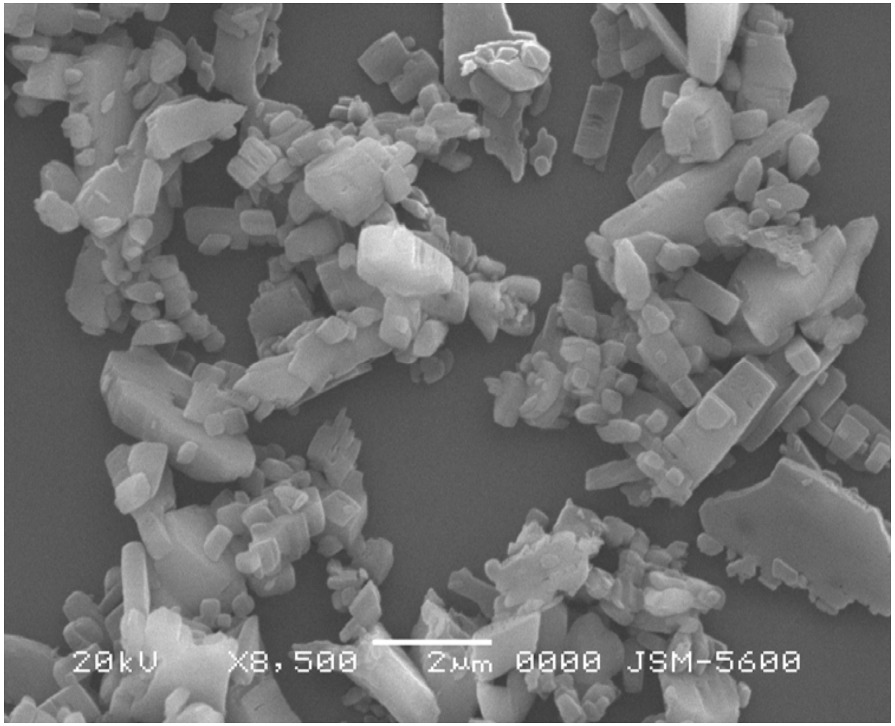
bpy

→ $\{[Cu_2(dhbc)_2(bpy)]\cdot H_2O$

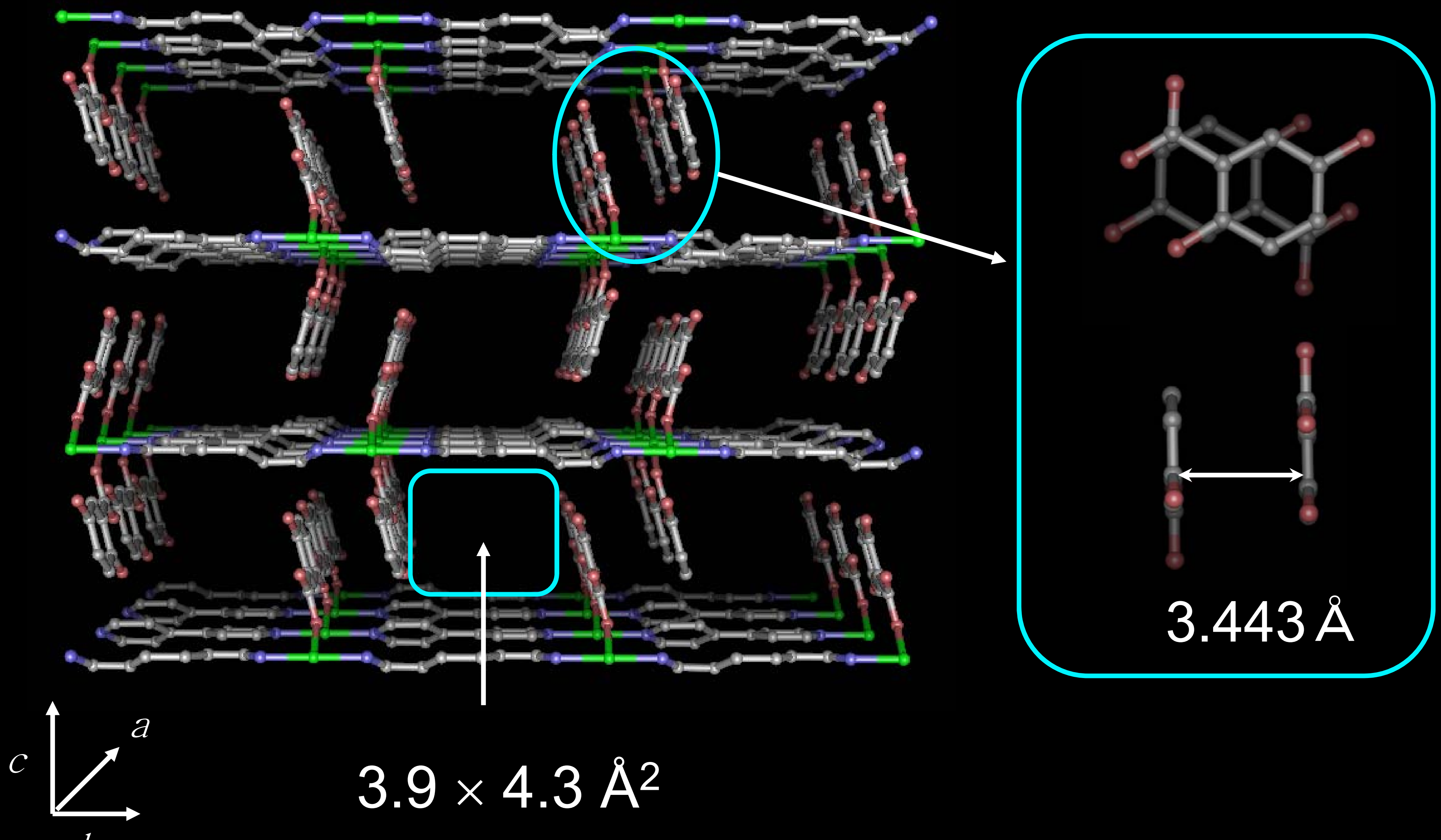
green crystal



Monoclinic, P2/c (#13)
a=8.167(4), b=11.094(8) Å,
c=15.863(2) Å β=99.703(4),
V=1416(1) Å^3, Z=2
R=0.065, Rw=0.103



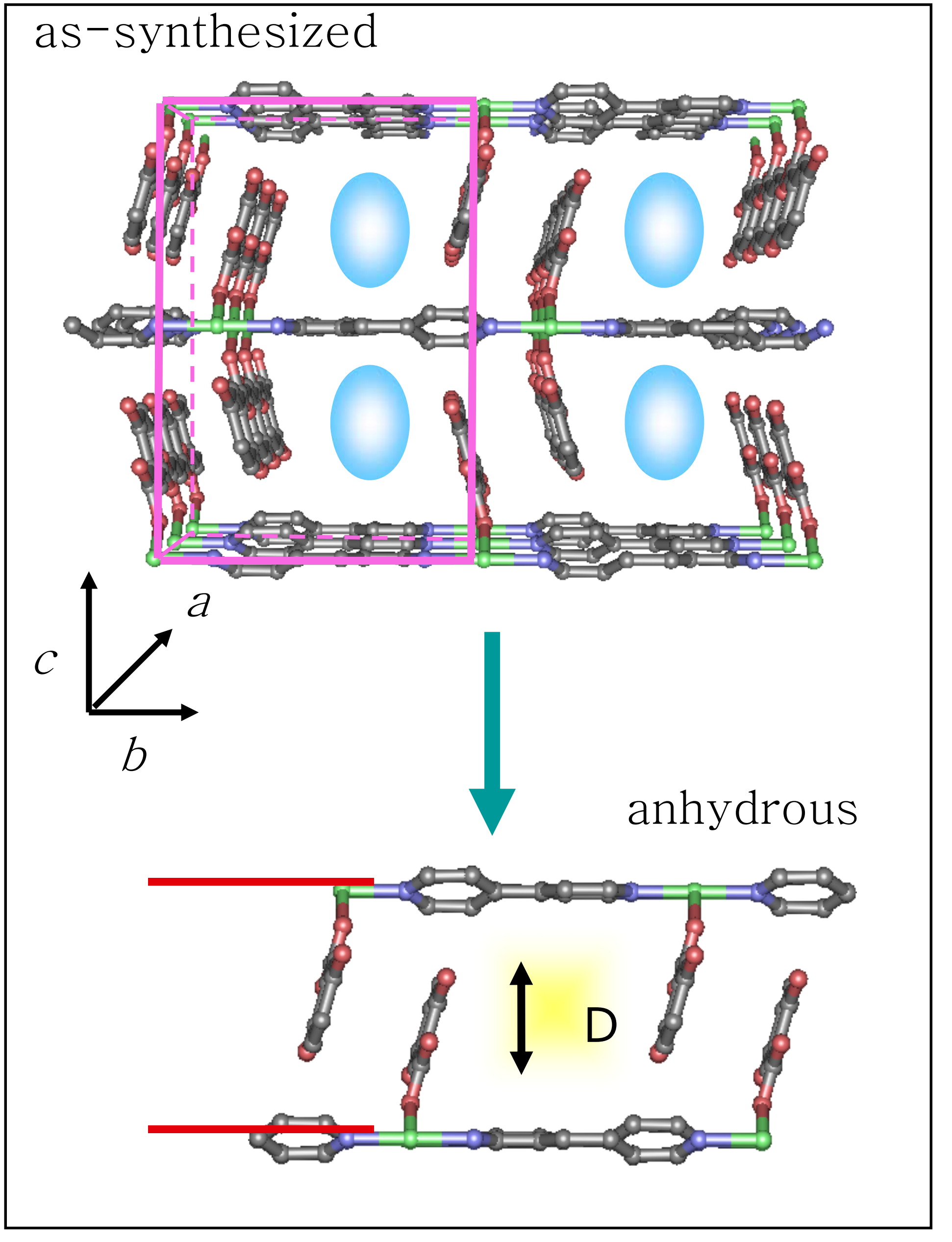
Channel Structure of [$Cu_2(dhbc)_2bpy]_n$



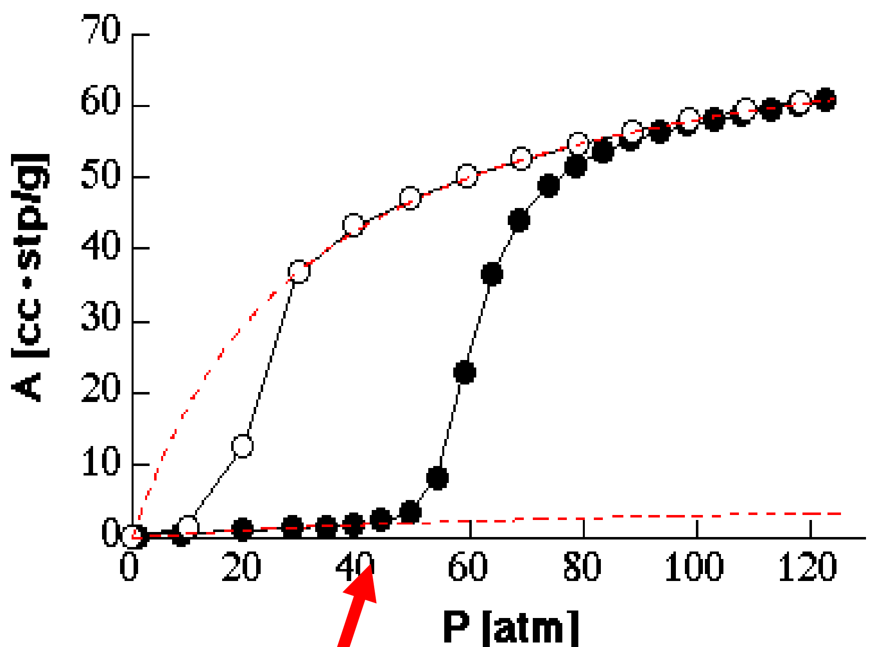
Cell Parameters

	CPL-p1	CPL-p1'
a /Å	8.167(4)	8.119(4)
b /Å	11.094(8)	11.991(6)
c /Å	15.863(2) →	11.17(1)
β / deg	99.703(4)	106.27(2)
D /Å	4.3 →	2.0
V /$Å^3$	1416(1)	1033(1)
ρ/g·cm^{-3}	1.22	1.67

27 %　の体積変化

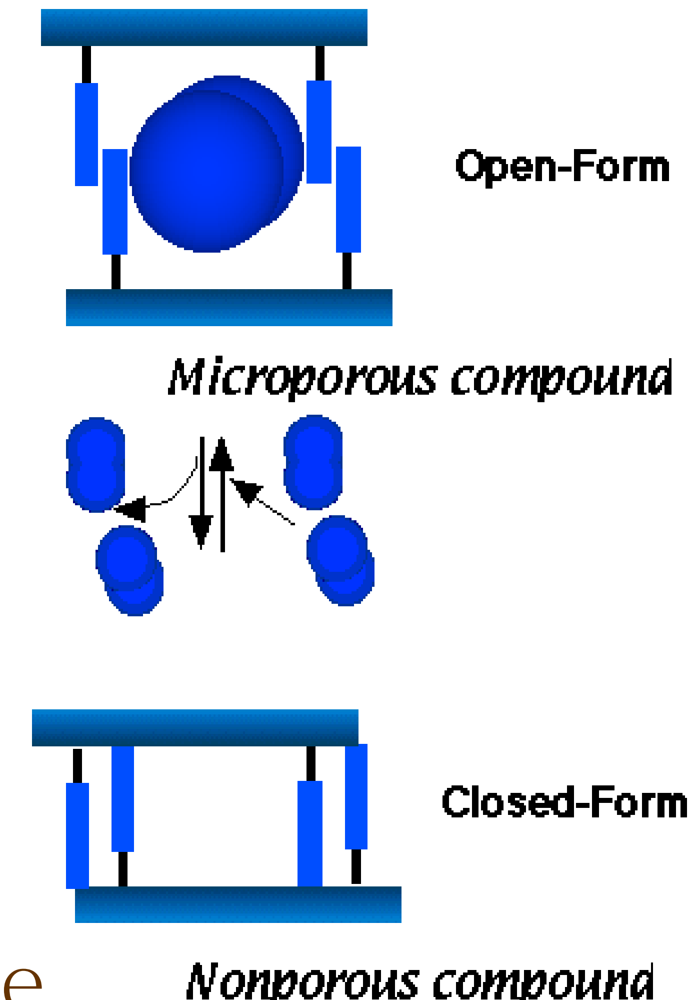


Nitrogen Adsorption Isotherm



Nitorgen Sorption Isotherm at 298K

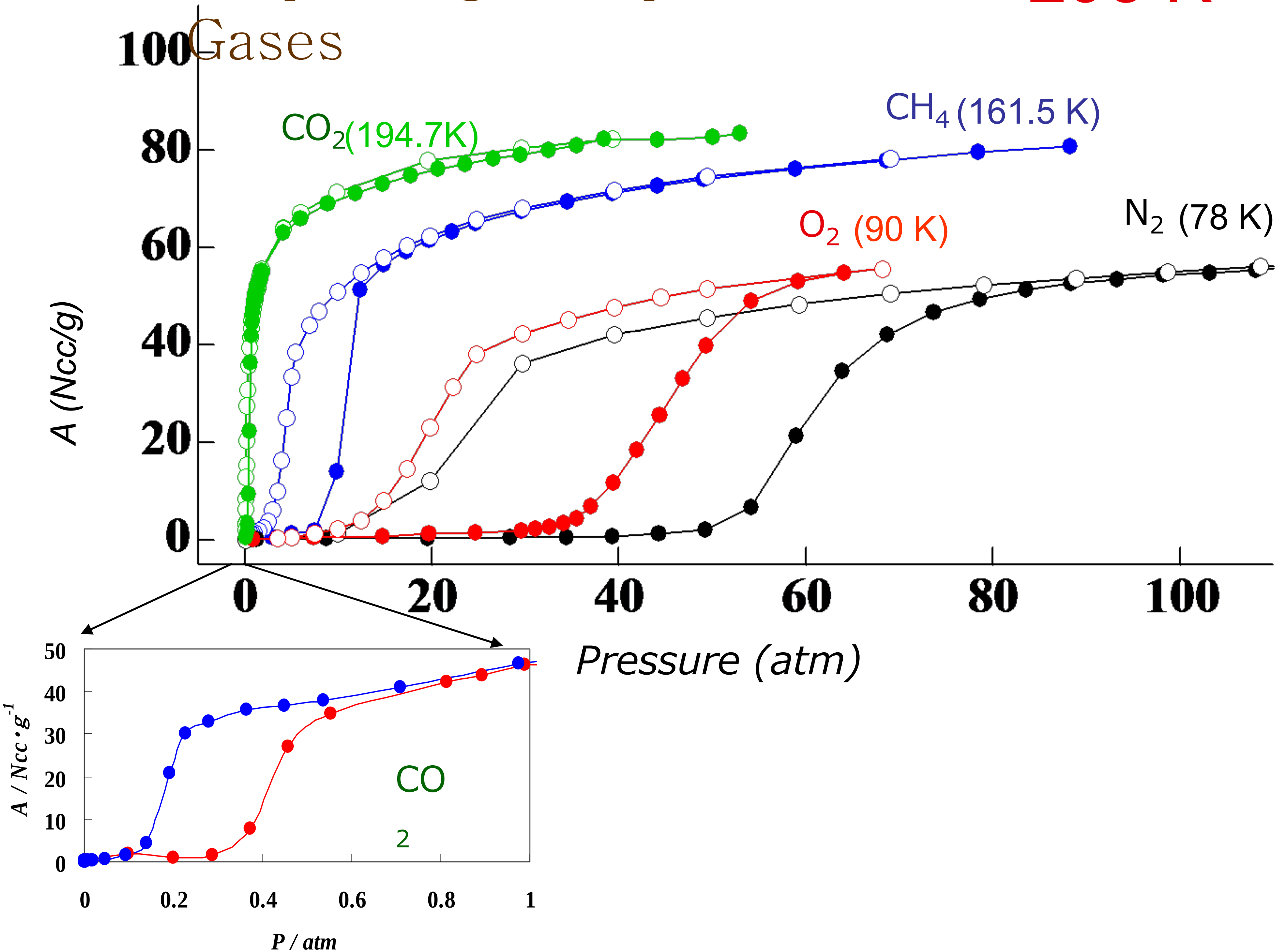
Gate-opening Pressure

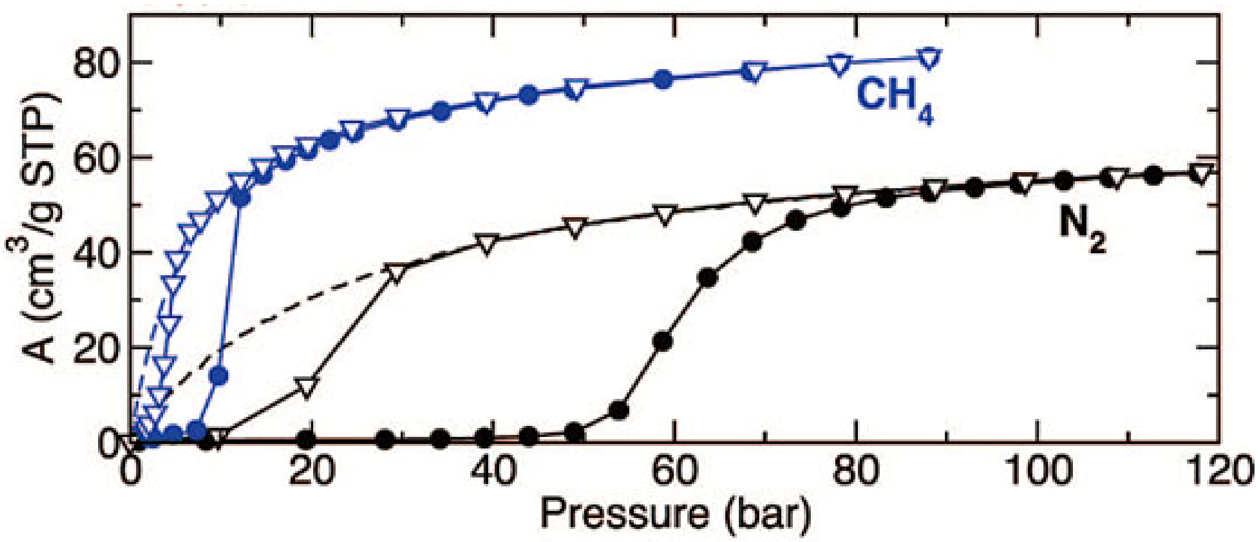


集積化錯体のガス吸着(イメージ

Responding to Supercritical Gases

298 K





ΔF_{host} = ΔFopen form – ΔFclosed form

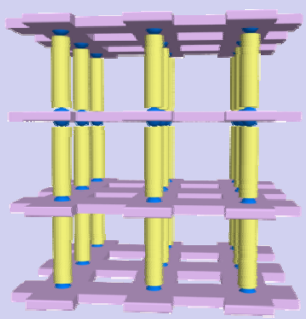
= *4 - 5* kJ/mol

adsorbate	gate-opening	gate-closing	calculated ΔF_{host}
N_2	30 bar	49 bar	3.3 − 4.5 kJ/mol
CH_4	7 bar	12 bar	3.6 − 5.1 kJ/mol
O_2	25 bar	37 bar	3.4 − 4.3 kJ/mol
CO_2	<2 bar	<2 bar	<6 kJ/mol

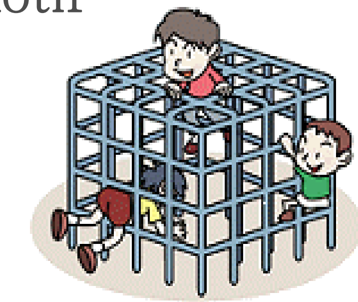
F.-X. Coudert, C.Mellot-Draznieks, *J.Am.Chem.Soc. 2008, 130 ,14294.*

JAST

(Jungle-gym Analogue STructure)

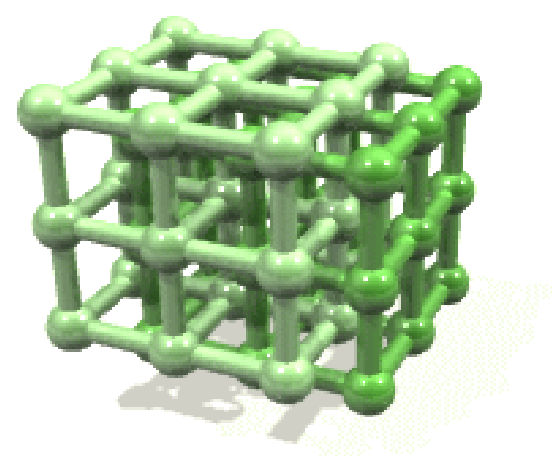


3D motif

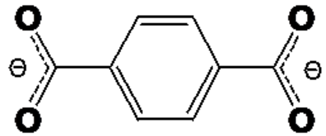


Jungle gym

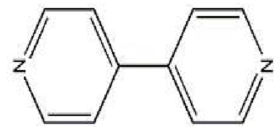
Interpenetration!



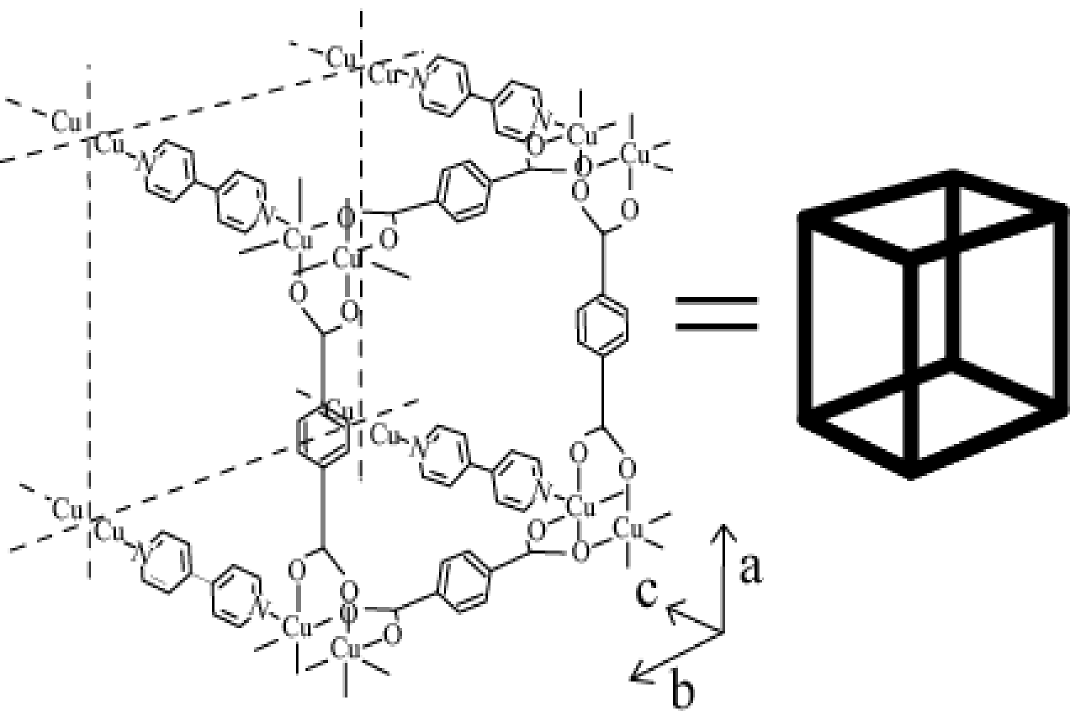
[$Cu_2(bdc)_2(4,4'\text{-bpy})$]

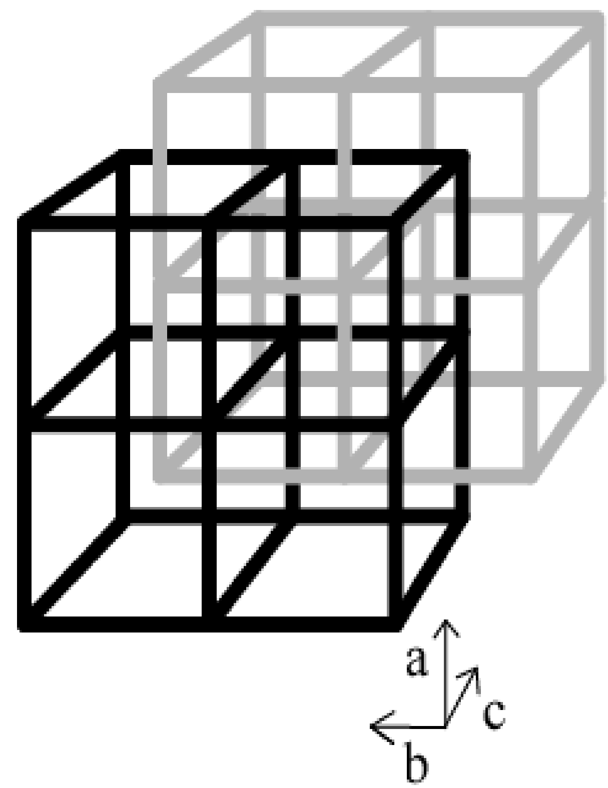


bdc



4,4'-bpy

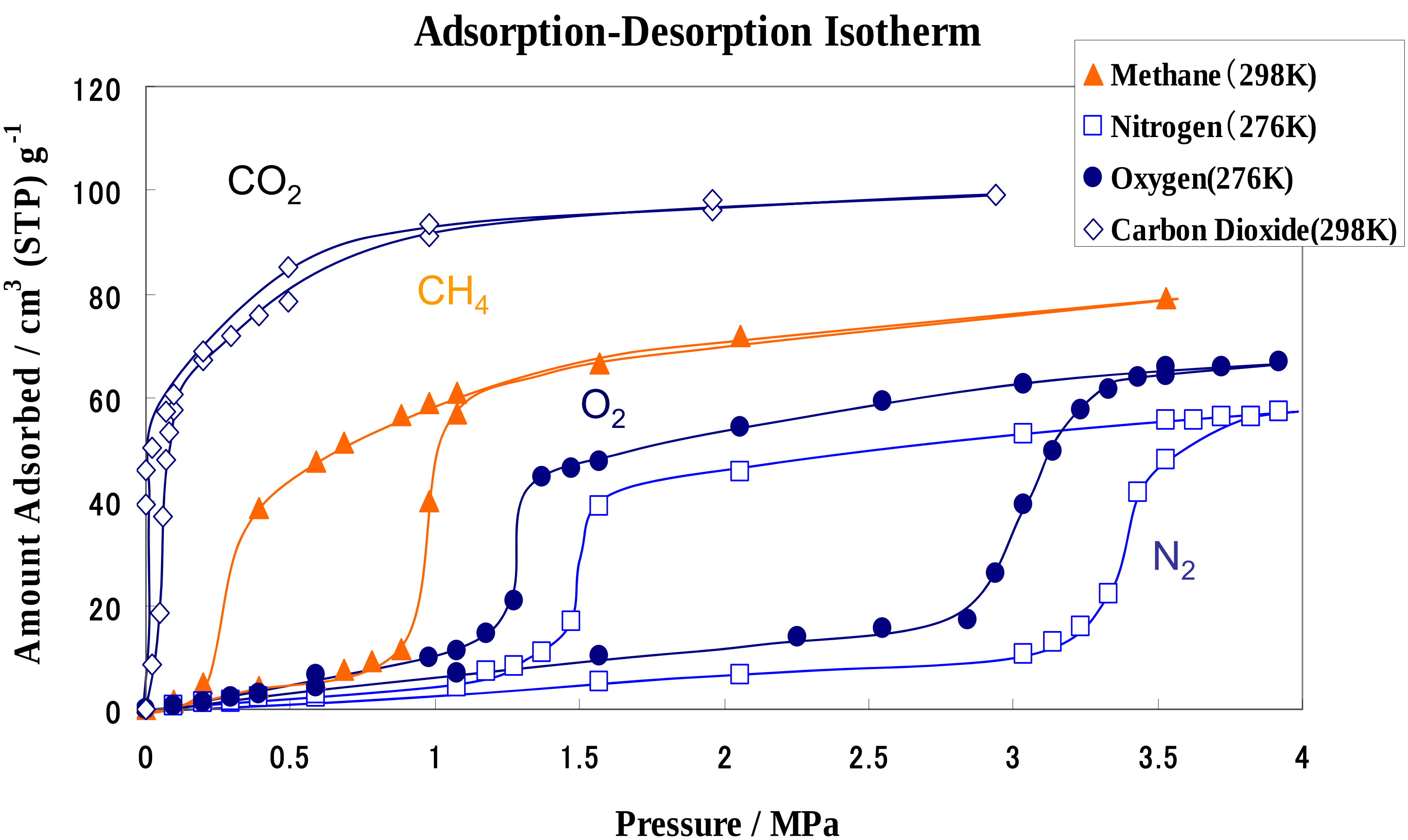


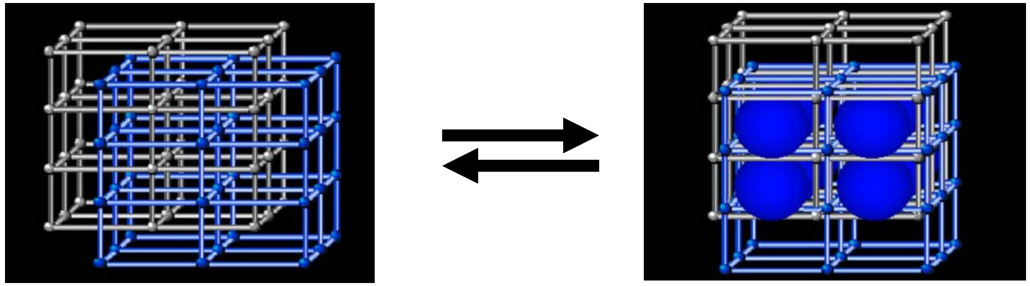


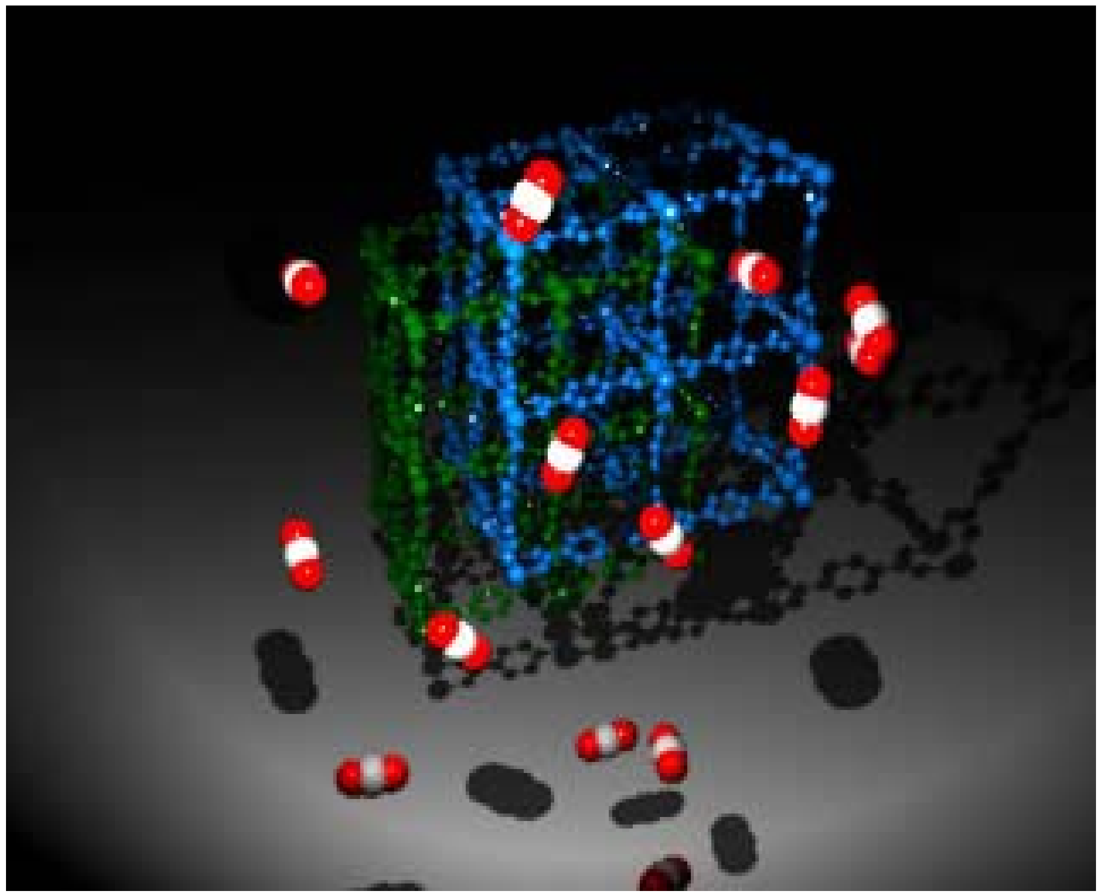
Seki, Phys*. Chem. Chem. Phys.*, **2002**, 4, 1968 . CH_4

*Kitagawa, Angew.Chem.Int.Ed.***2003***,42,428. N_2,O_2, CO_2*

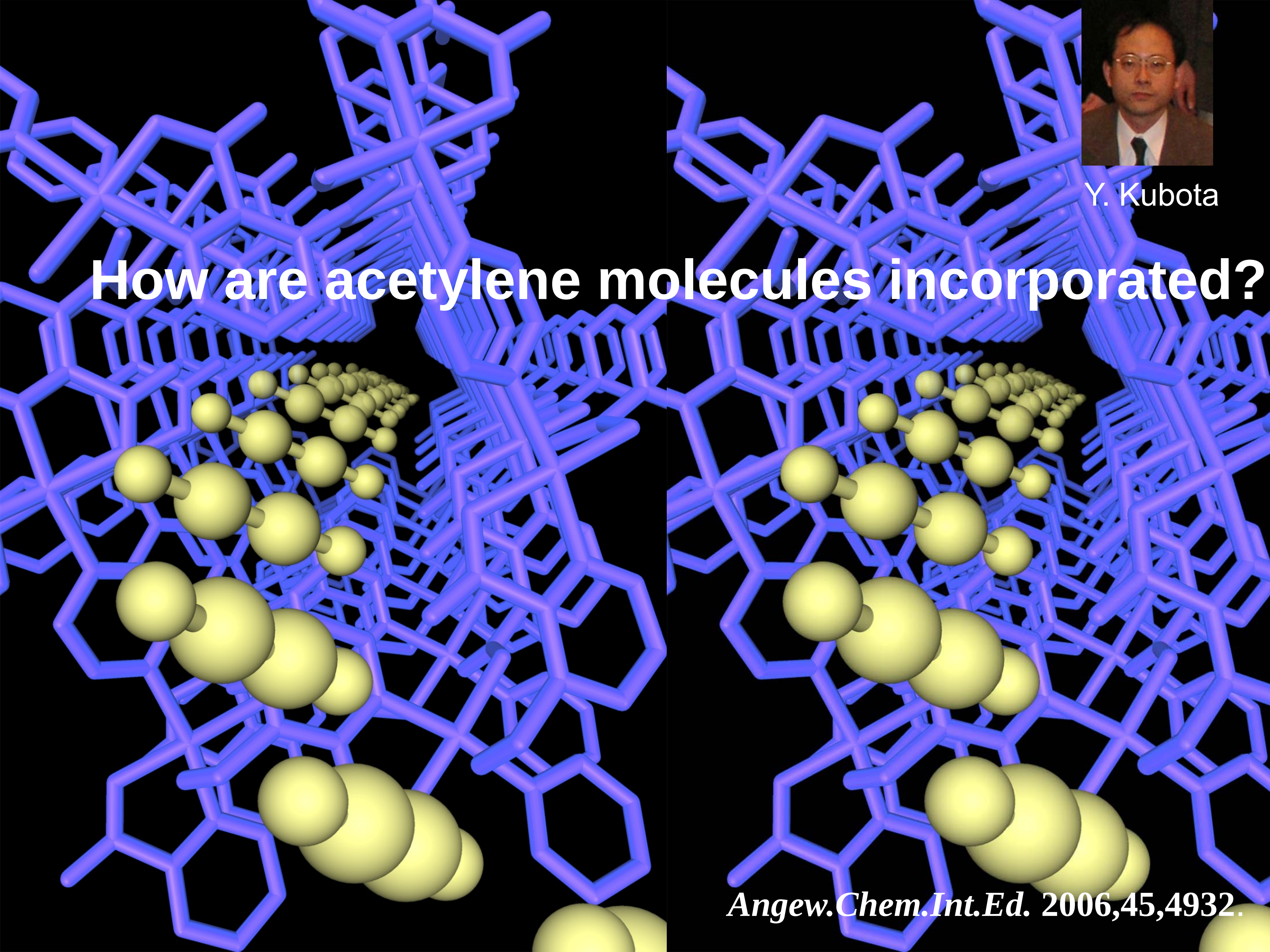
Supporting Information in *Angew.Chem.Int.Ed.* **2003**, *42*, 428.





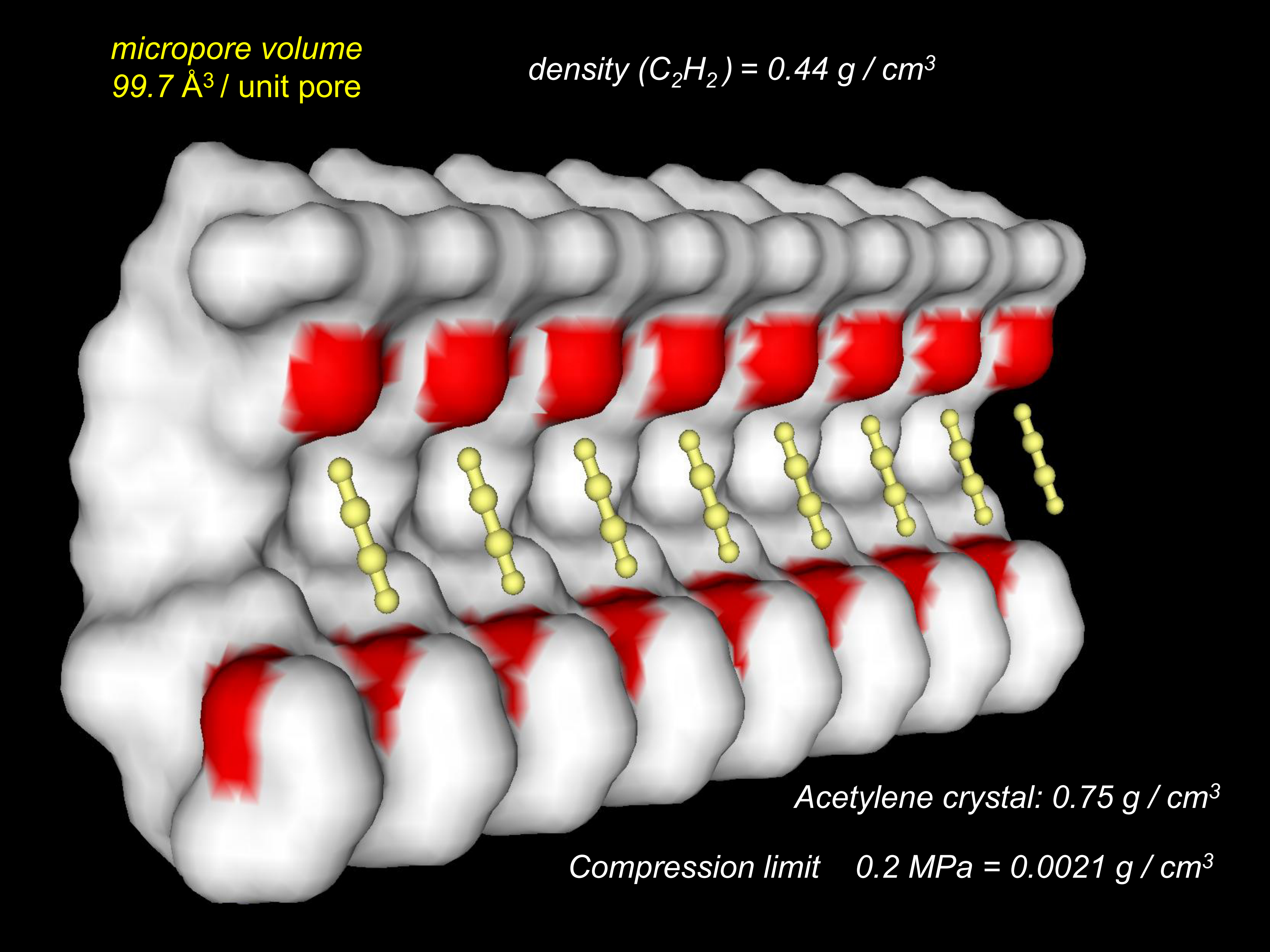


How are acetylene molecules incorporated?

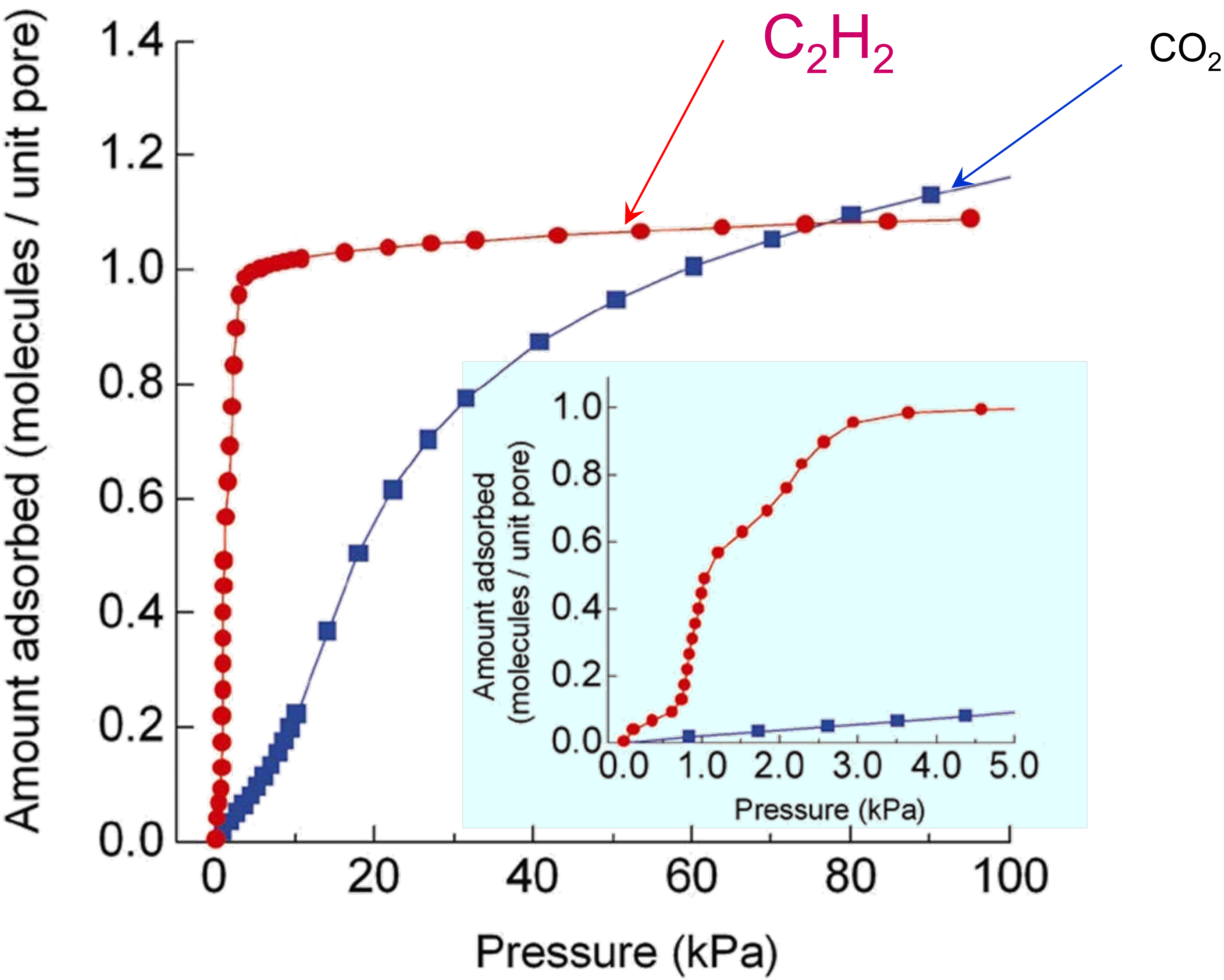


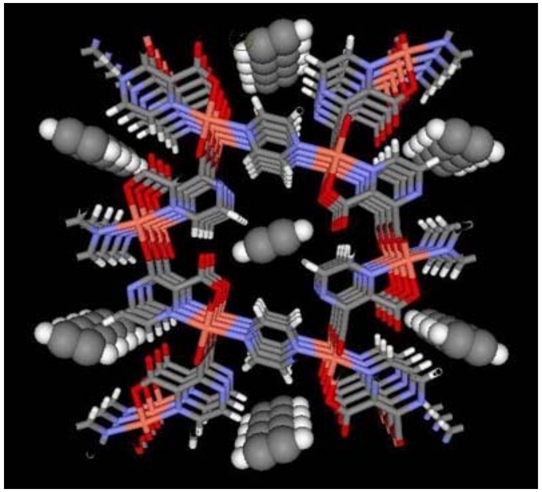
Y. Kubota

Angew.Chem.Int.Ed. **2006,45,4932**.


micropore volume
99.7 Å3 / unit pore
density (C2H2) = 0.44 g / cm3
Acetylene crystal: 0.75 g / cm3
Compression limit 0.2 MPa = 0.0021 g / cm3

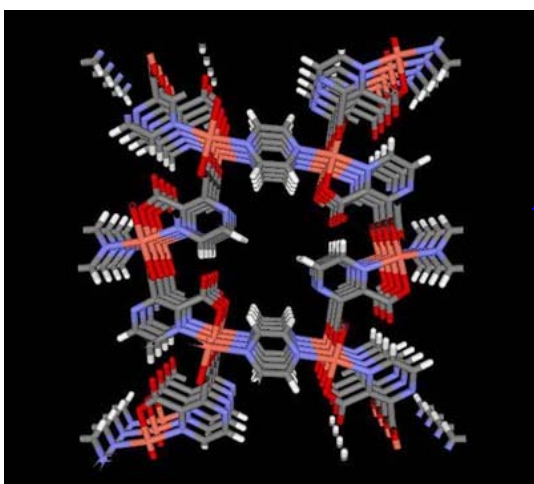
Adsorption isotherm of C_2H_2 & CO_2 in CPL-1

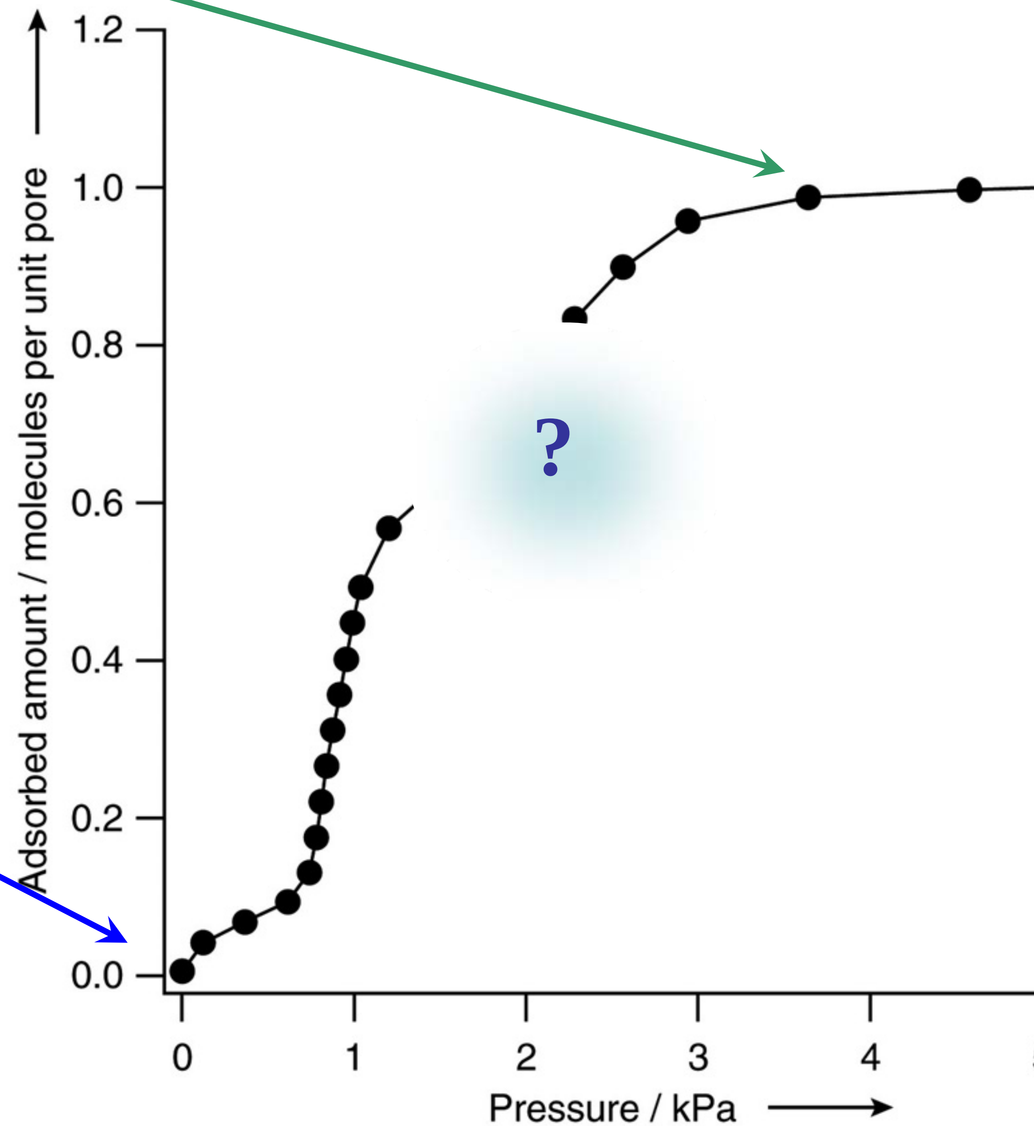




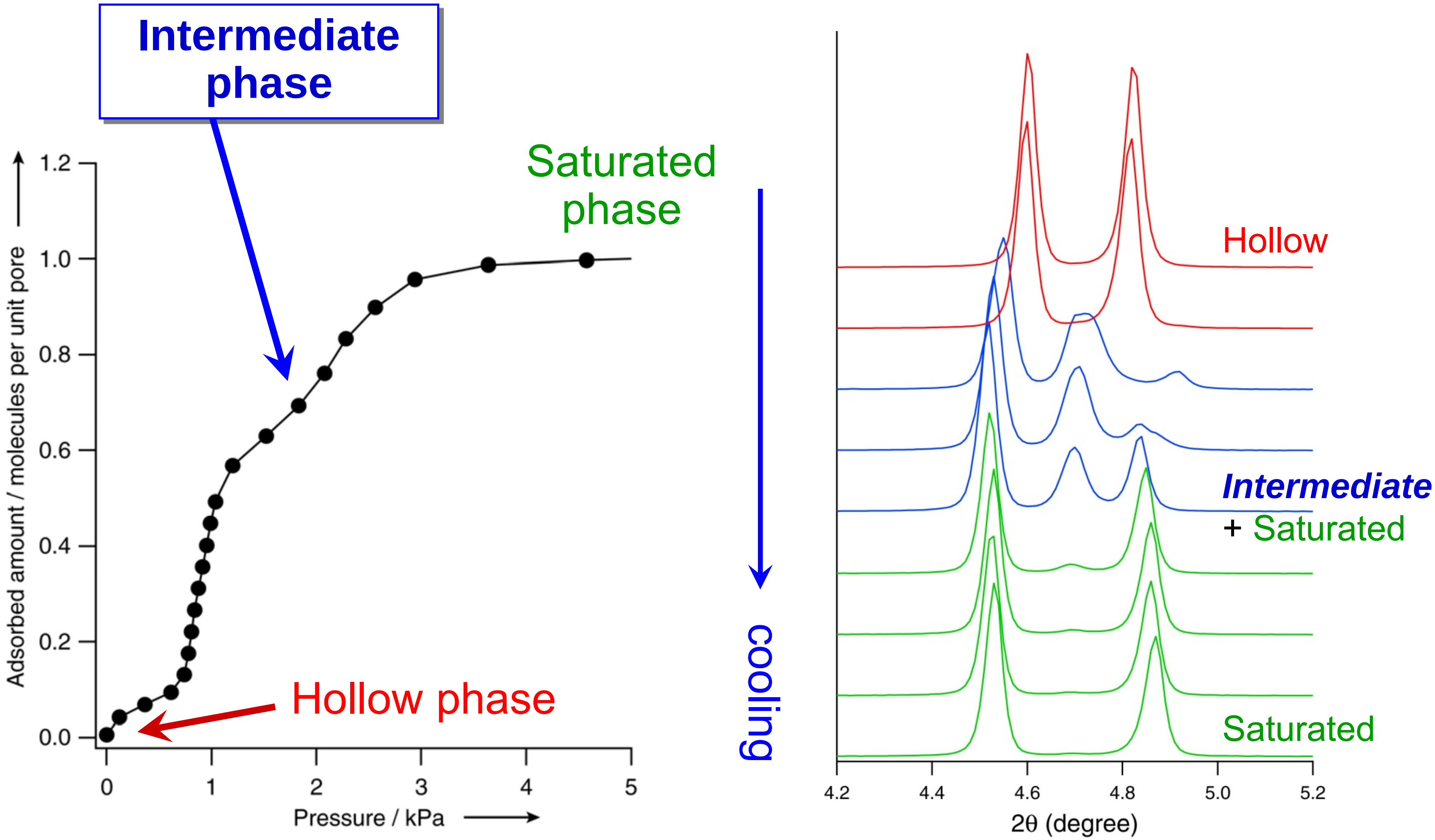
Saturated phase

Hollow phase





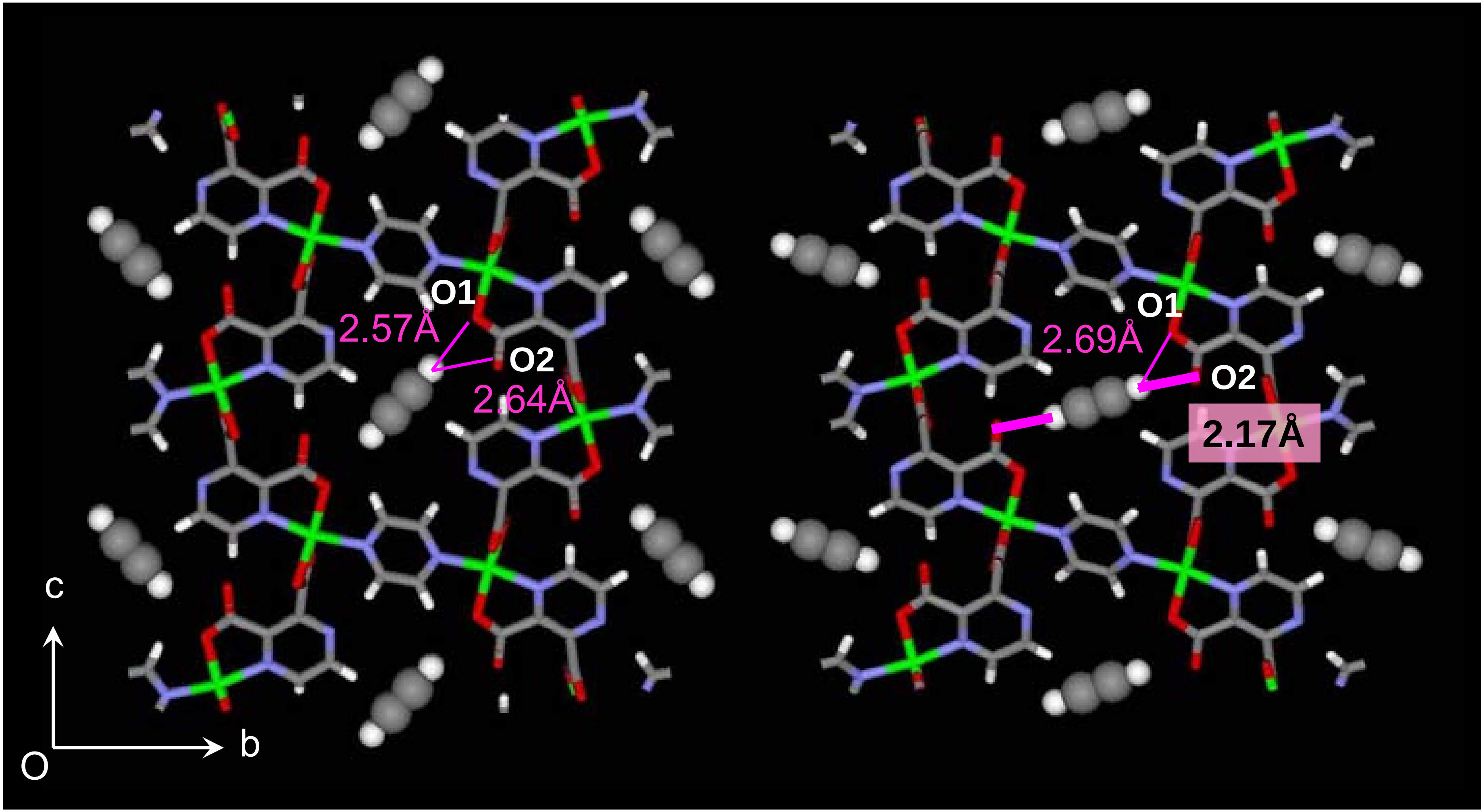
In-situ synchrotron powder diffraction patterns of CPL-1 with C_2H_2 gas at 10 kPa



Angew.Chem.Int.Ed. 2006,45,4932.

Crystal structure of phase M & S of CPL-1 with C_2H_2

Intermediate adsorbed phase M **Saturated adsorbed phase S**

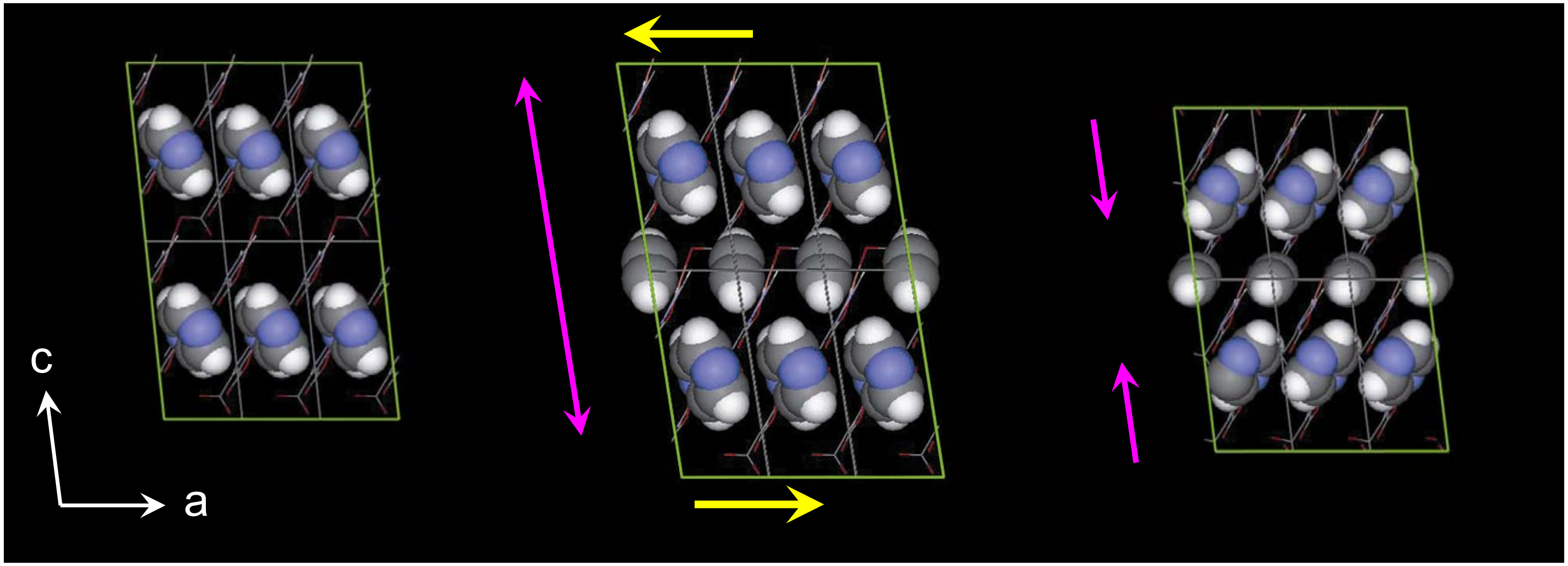


van der Waals radii H (1.2 Å) + O (1.4 Å) = 2.6 Å

acetylene **carboxylate**

Crystal structures of CPL-1 with adsorption of C_2H_2

Hollow phase I 0 % | **Intermediate phase M** ~70 % | **Saturated phase S** 100 %



Nanochannel direction →

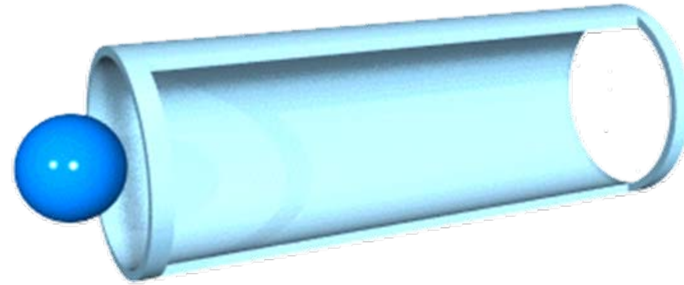
*V*cell [Å^3] 1019.25(5) $\xrightarrow{\text{expand}}$ 1063.03(6) $\xrightarrow{\text{contract}}$ 1036.18(3)

Orientation of pillar pyrazine-ring is dramatically changing

Angew.Chem.Int.Ed. 2006,45,4932.

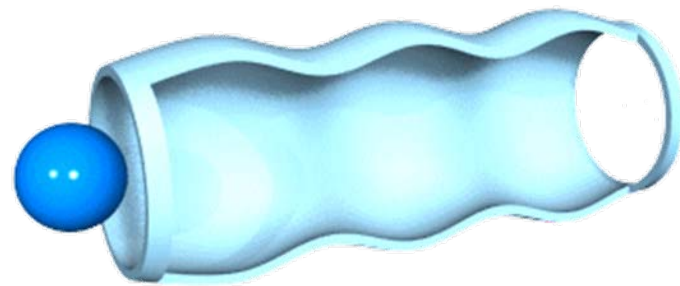
Classical Channel

static, smooth, simple



Advanced Channel

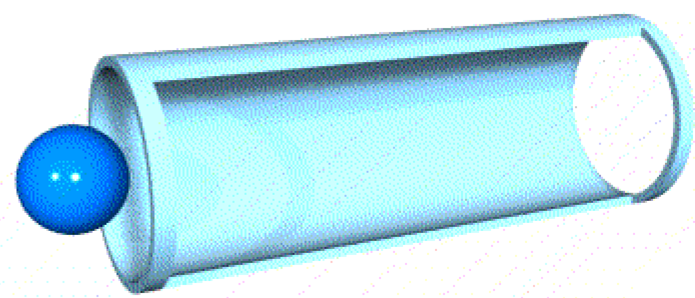
static, corrugated

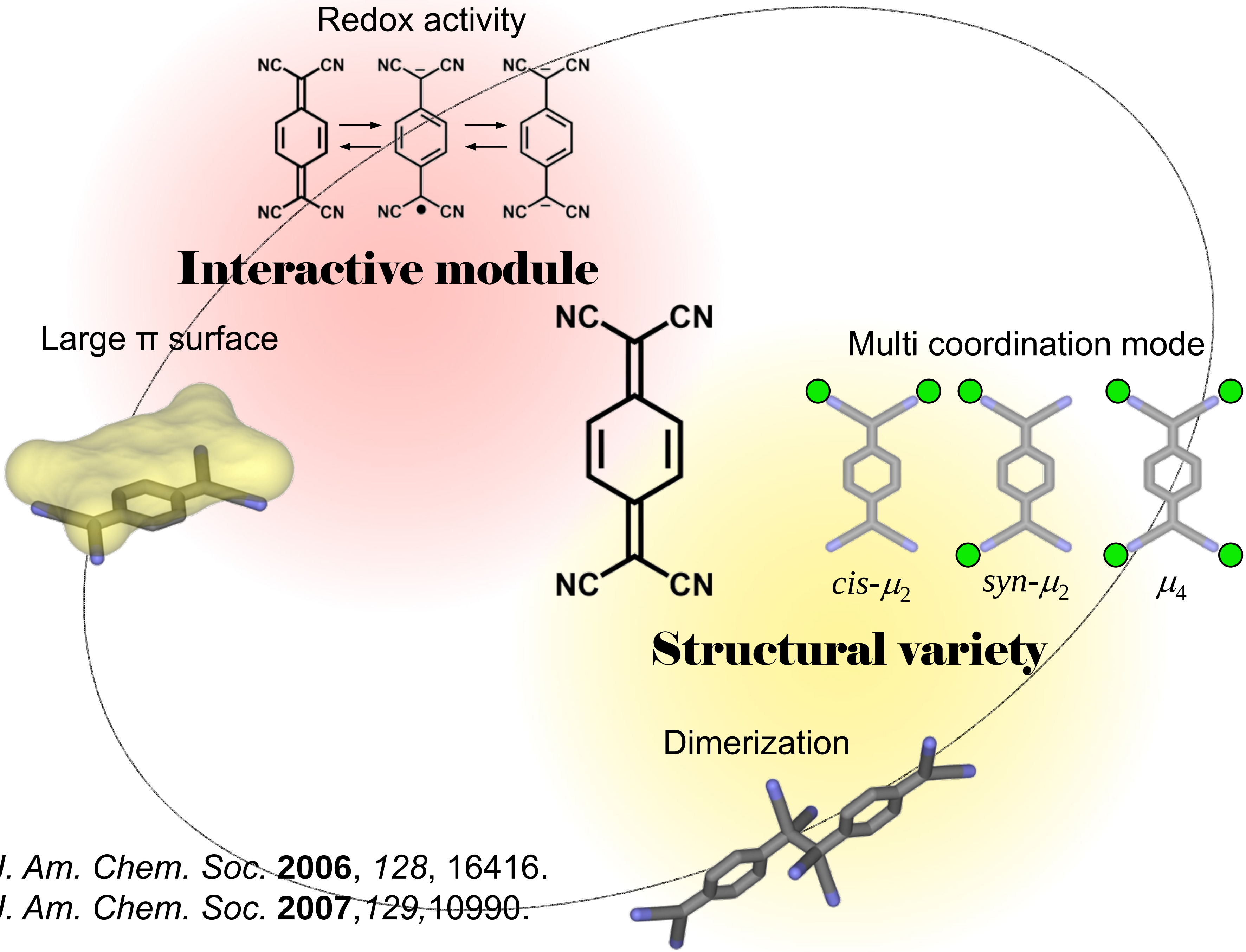


Evolving Channel

dynamic, functionalized

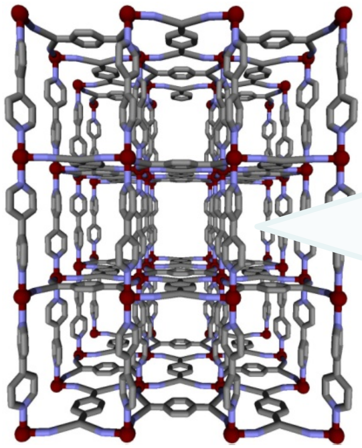
protein, enzyme



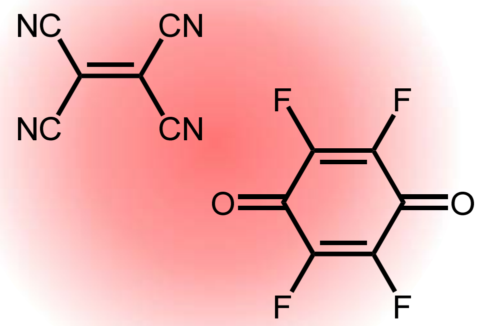


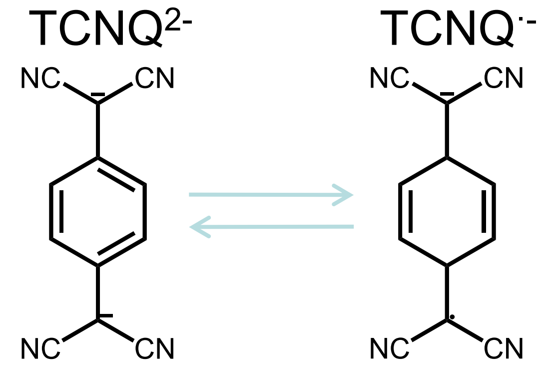
J. Am. Chem. Soc. **2006**, *128*, 16416.
J. Am. Chem. Soc. **2007**,*129*,10990.

Future work

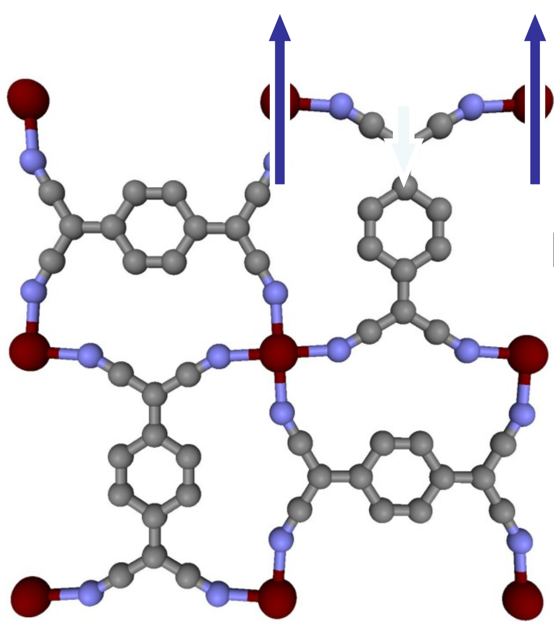


Electron acceptors



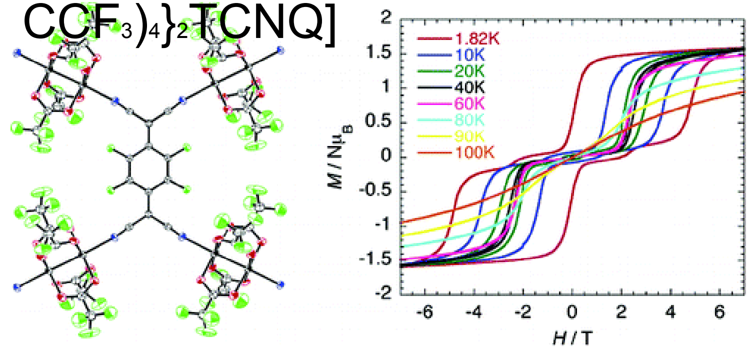


radical anion

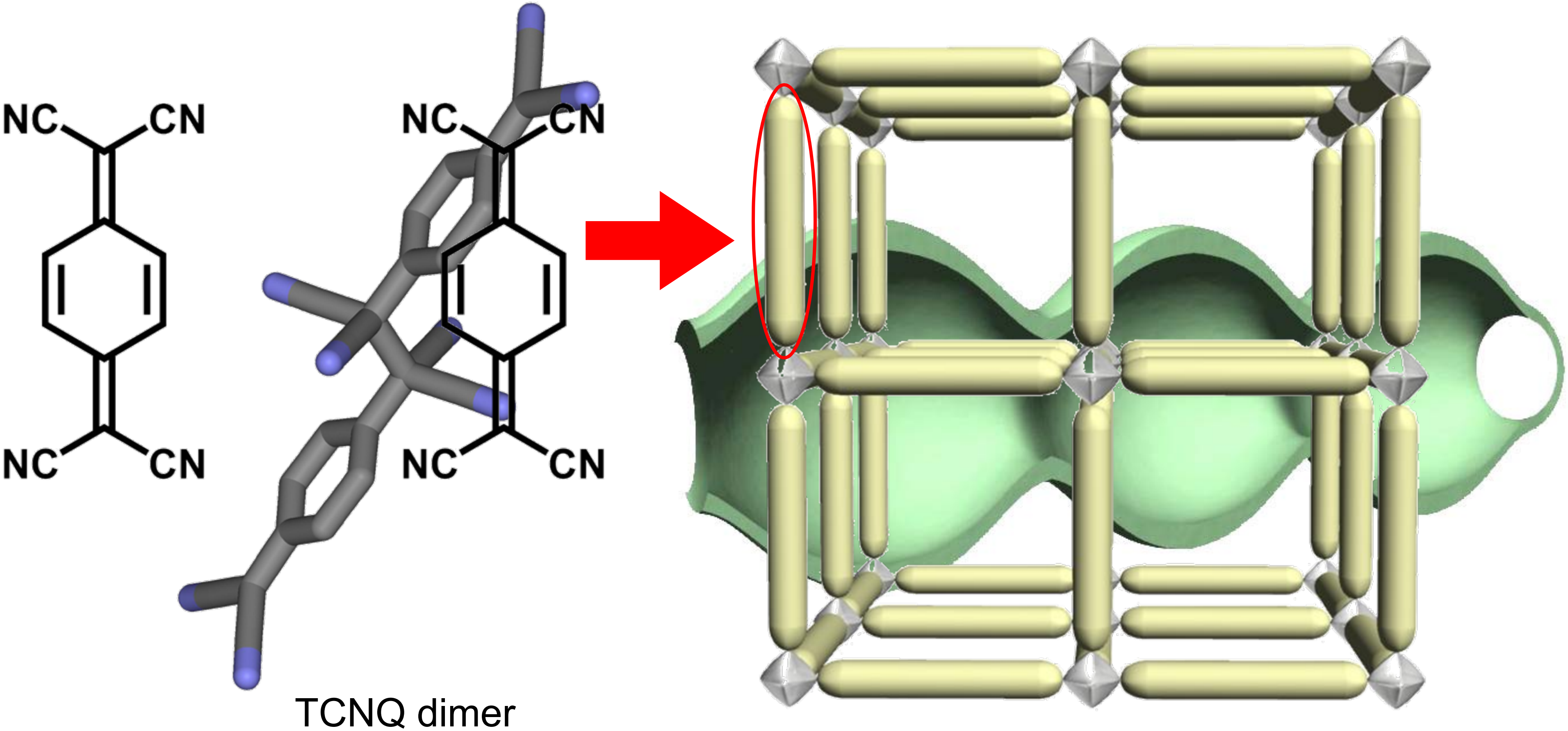


New electronic and/or magnetic properties induced by host-guest CT interaction

[{$Ru_2(O_2CCF_3)_4$}$_2$TCNQ]

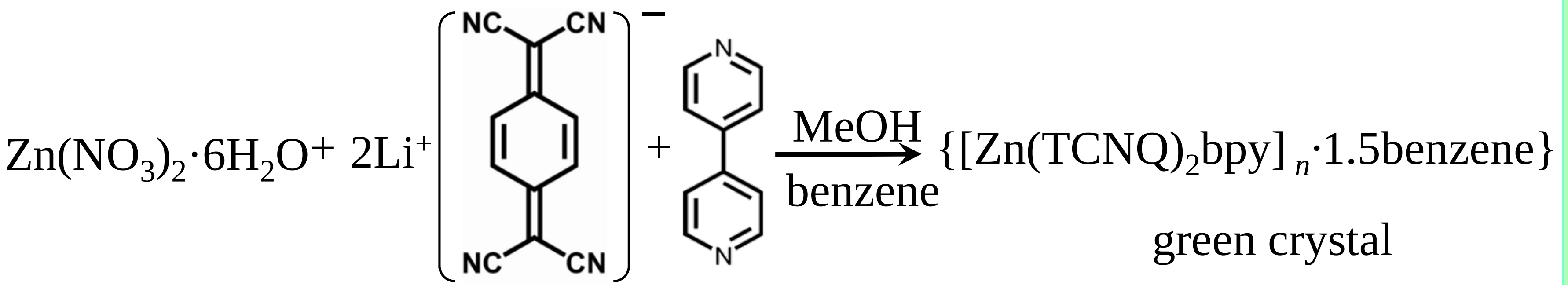


J. Am. Chem. Soc., **2006**, *128*, 11358



Property and Function of Flexible Undulating Channel

J. Am. Chem. Soc. **2006**, *128*, 16416.
J. Am. Chem. Soc. **2007**,*129,*10990.



Crystal data

orthorhombic (*Pccm*)

a = 11.361(5) Å

b = 12.645(6) Å

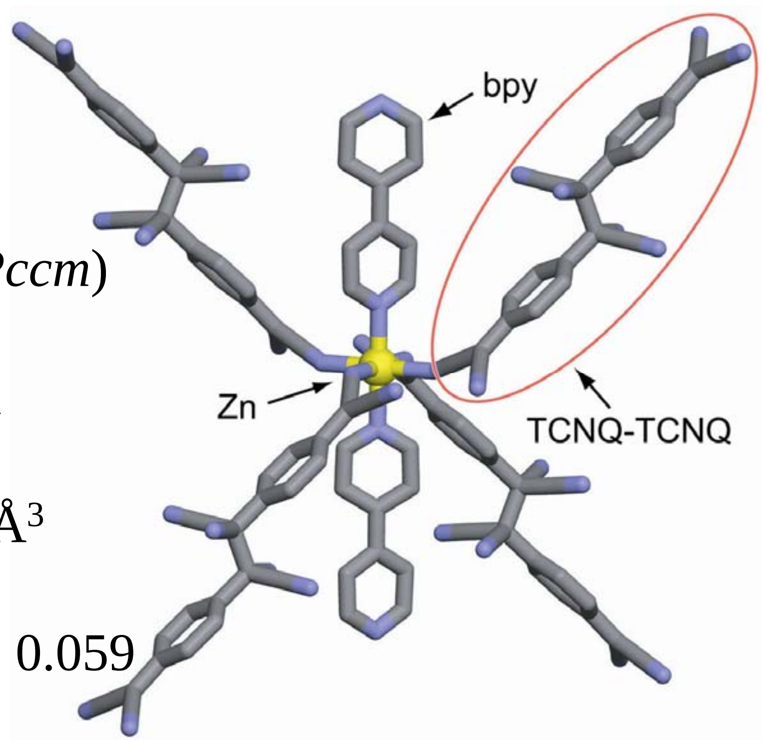
c = 14.775(7) Å

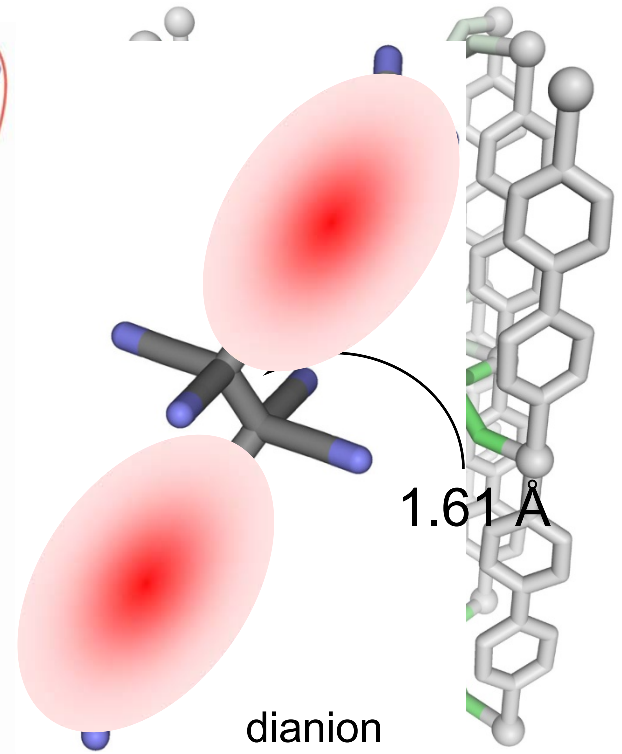
V = 2122.2(18) Å^3

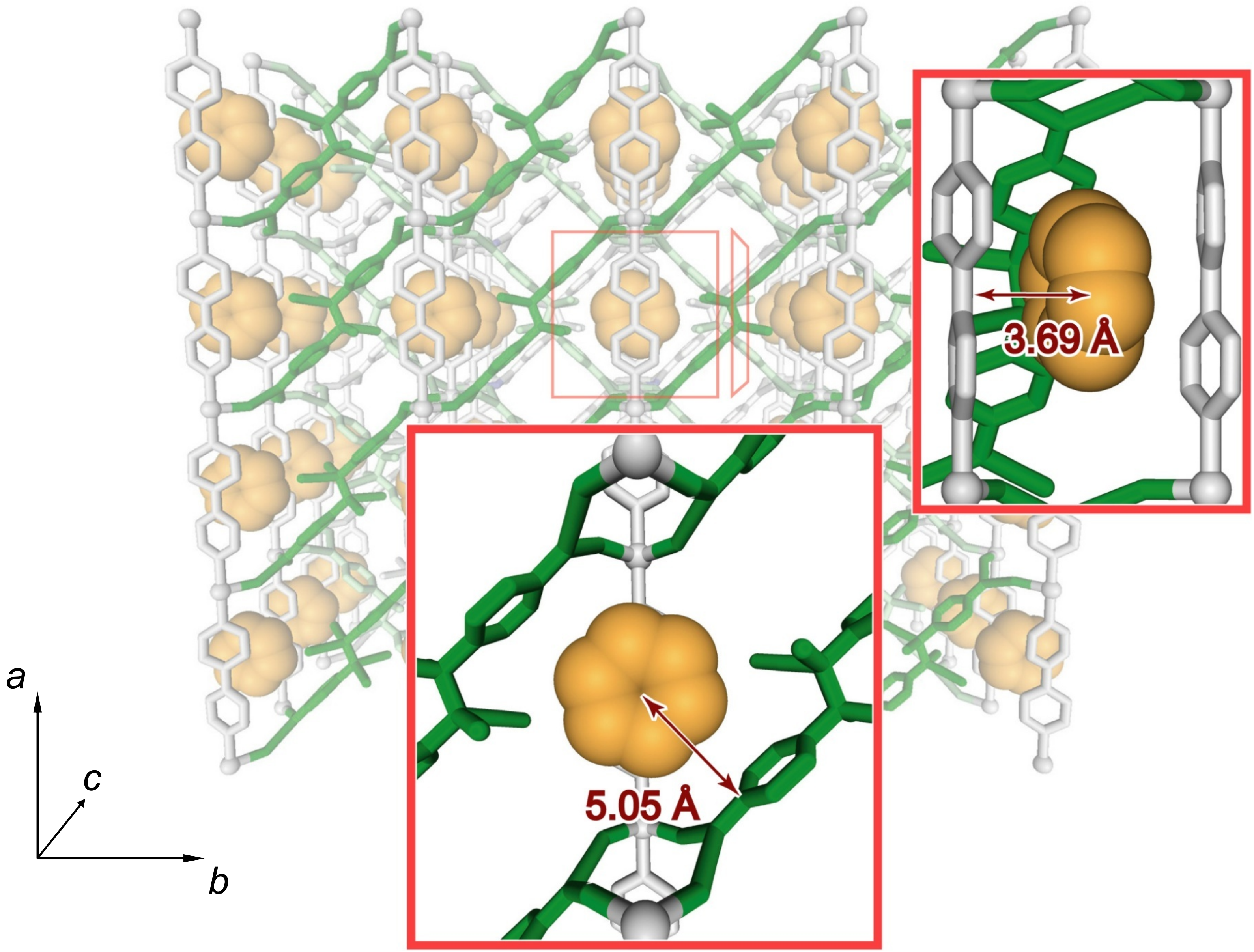
Z = 2

$R1$ = 0.059, R_w = 0.059

GOF = 1.082



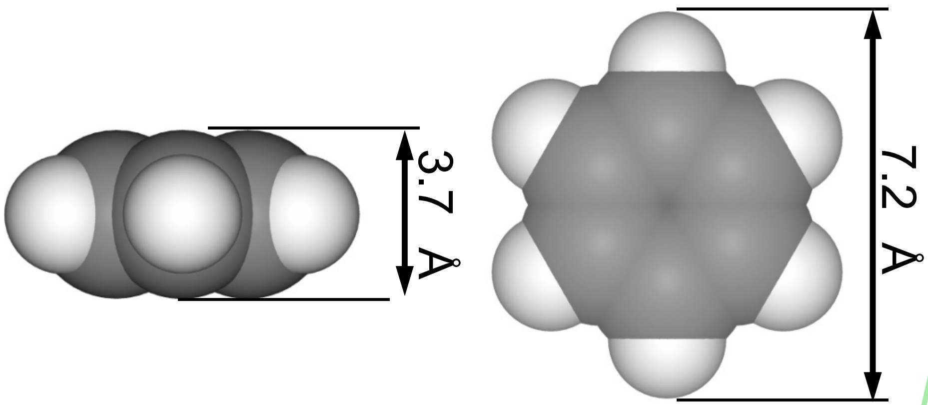



3.69 Å
5.05 Å
a
c
b

Properties of benzene and cyclohexane

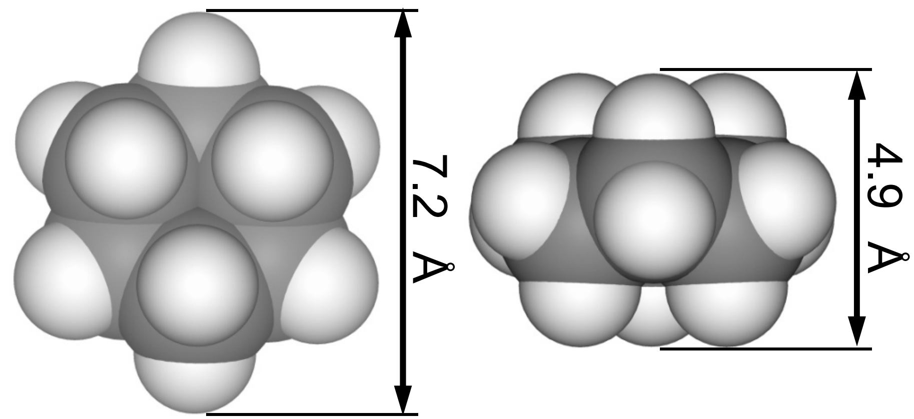
benzene C_6H_6

bp 80.10 °C



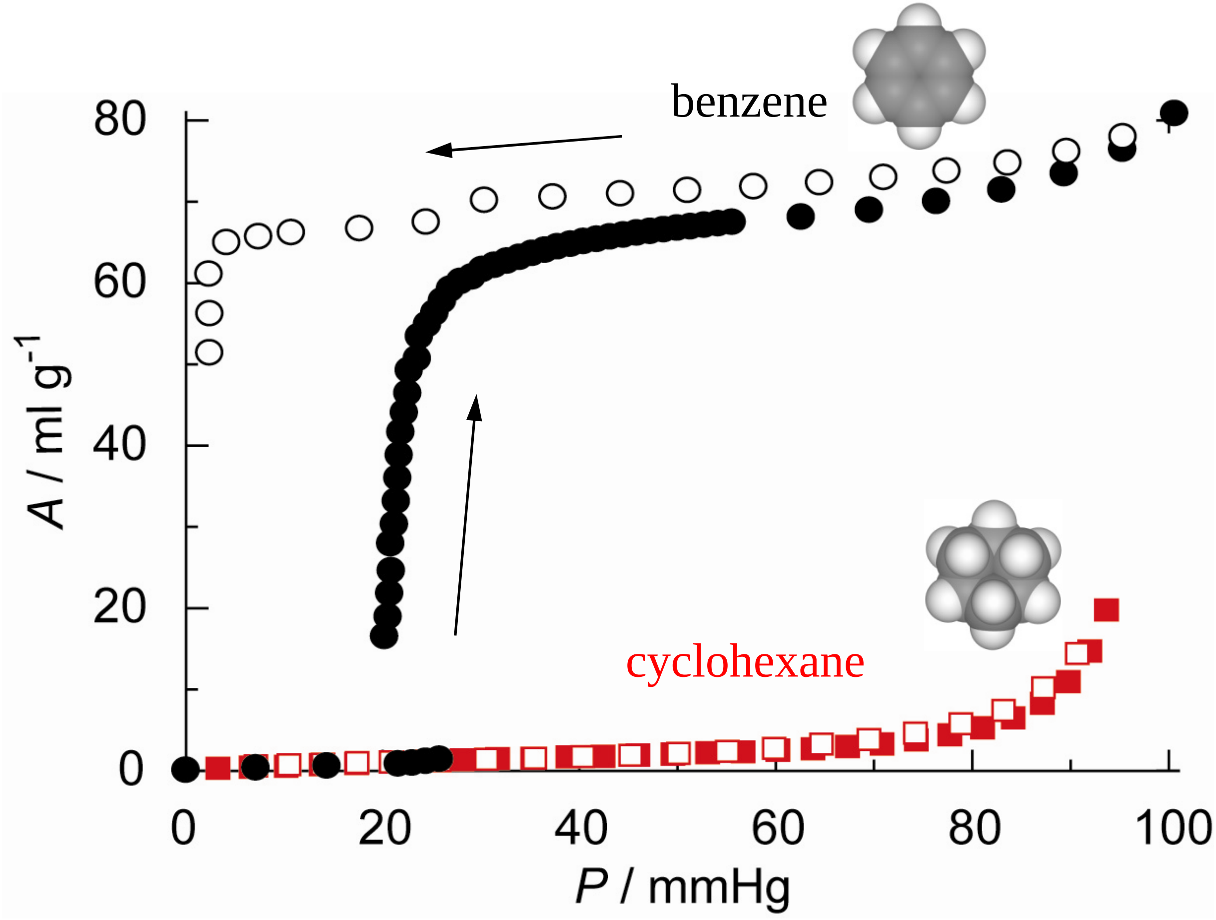
cyclohexane C_6H_{12}

bp 80.74 °C



azeotropic mixture → difficulty in separation

selective adsorption



Structural transformation on guest sorption

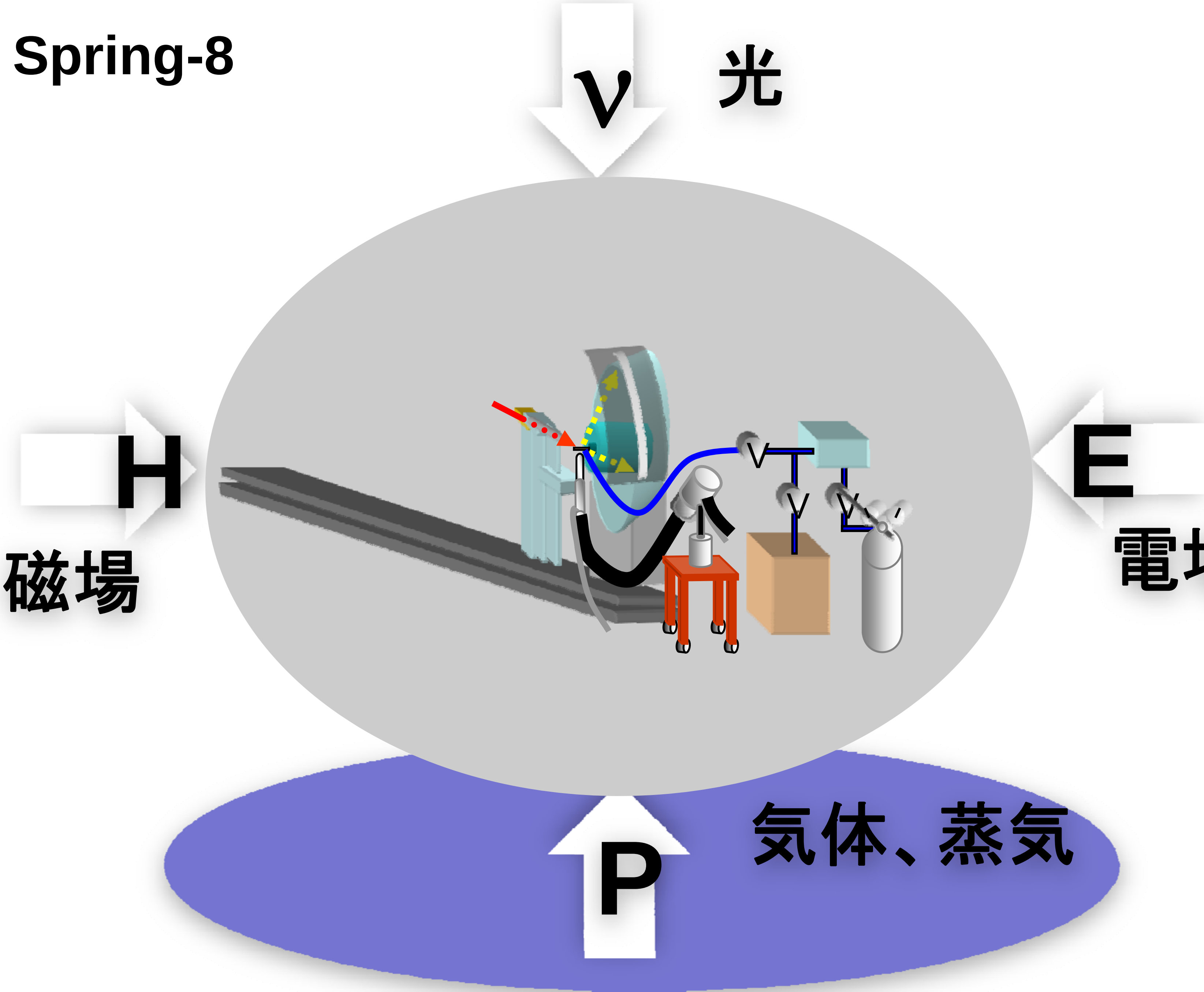
物理、化学機能

・誘電
・磁場
・光

＋

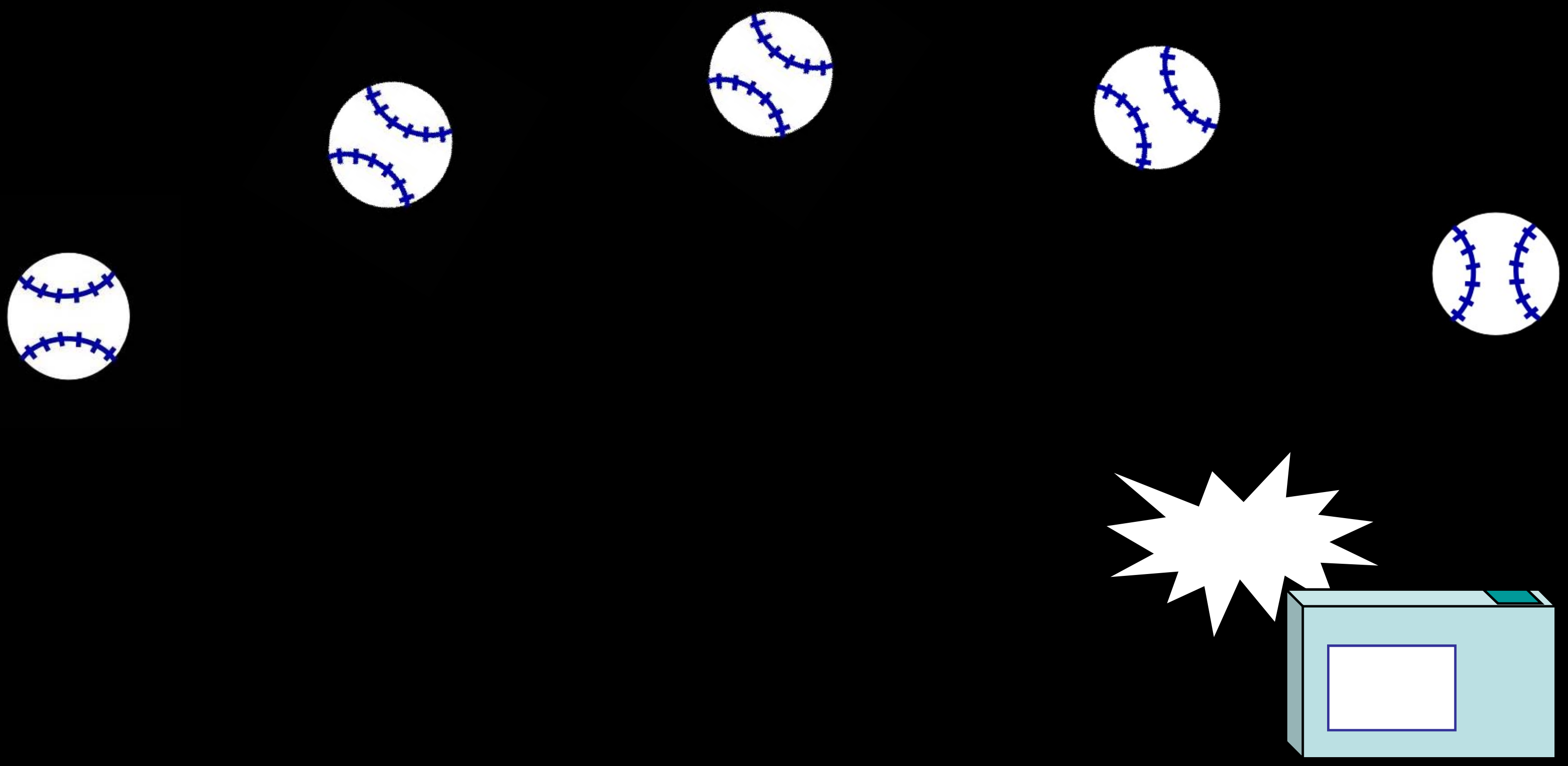
化学環境
・気体（O_2, H_2,…)
・蒸気

＜もともとの機能＞　＋　＜化学的環境＞

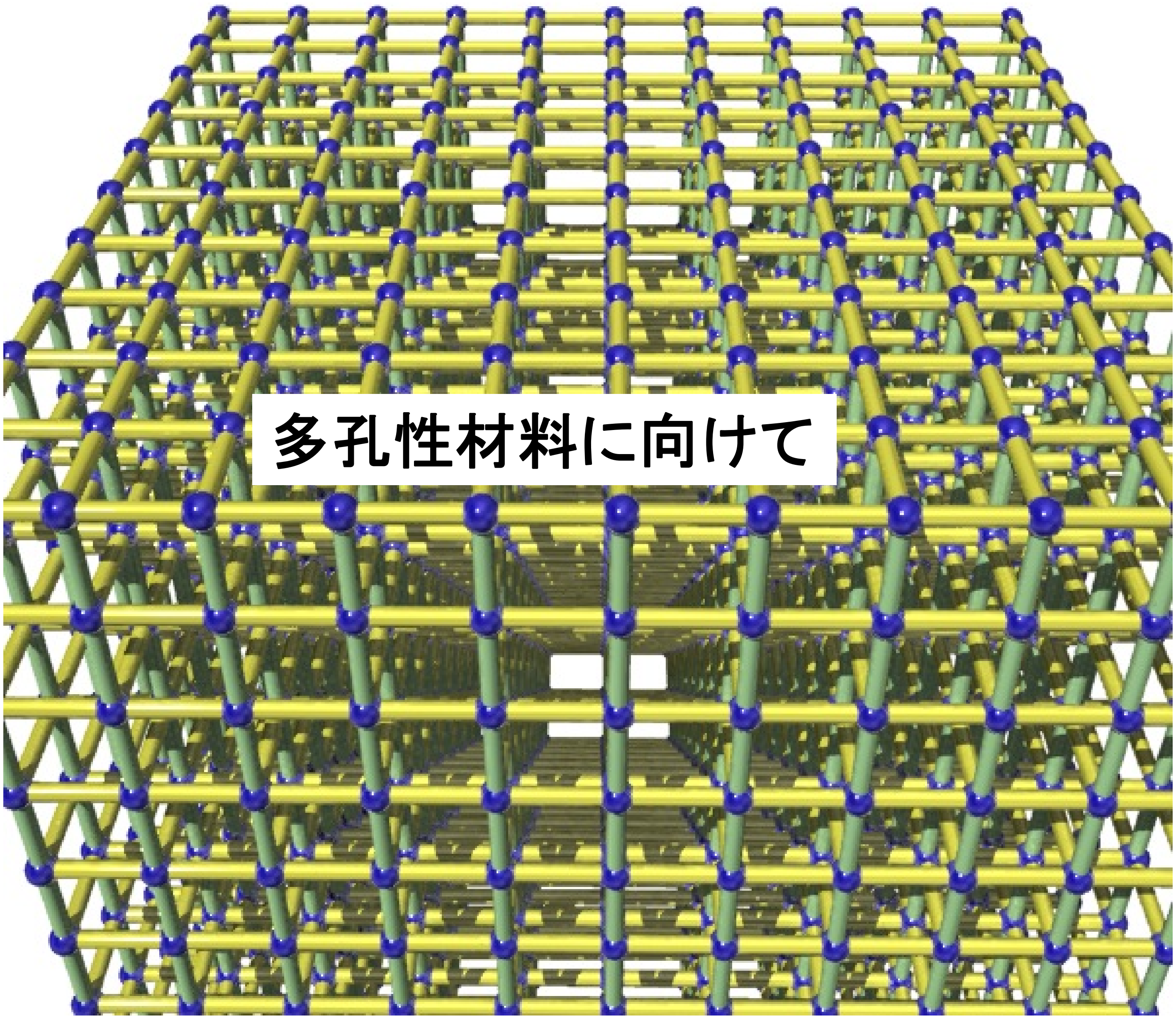

Spring-8
ν
光
H
磁場
E
電場
P
気体、蒸気

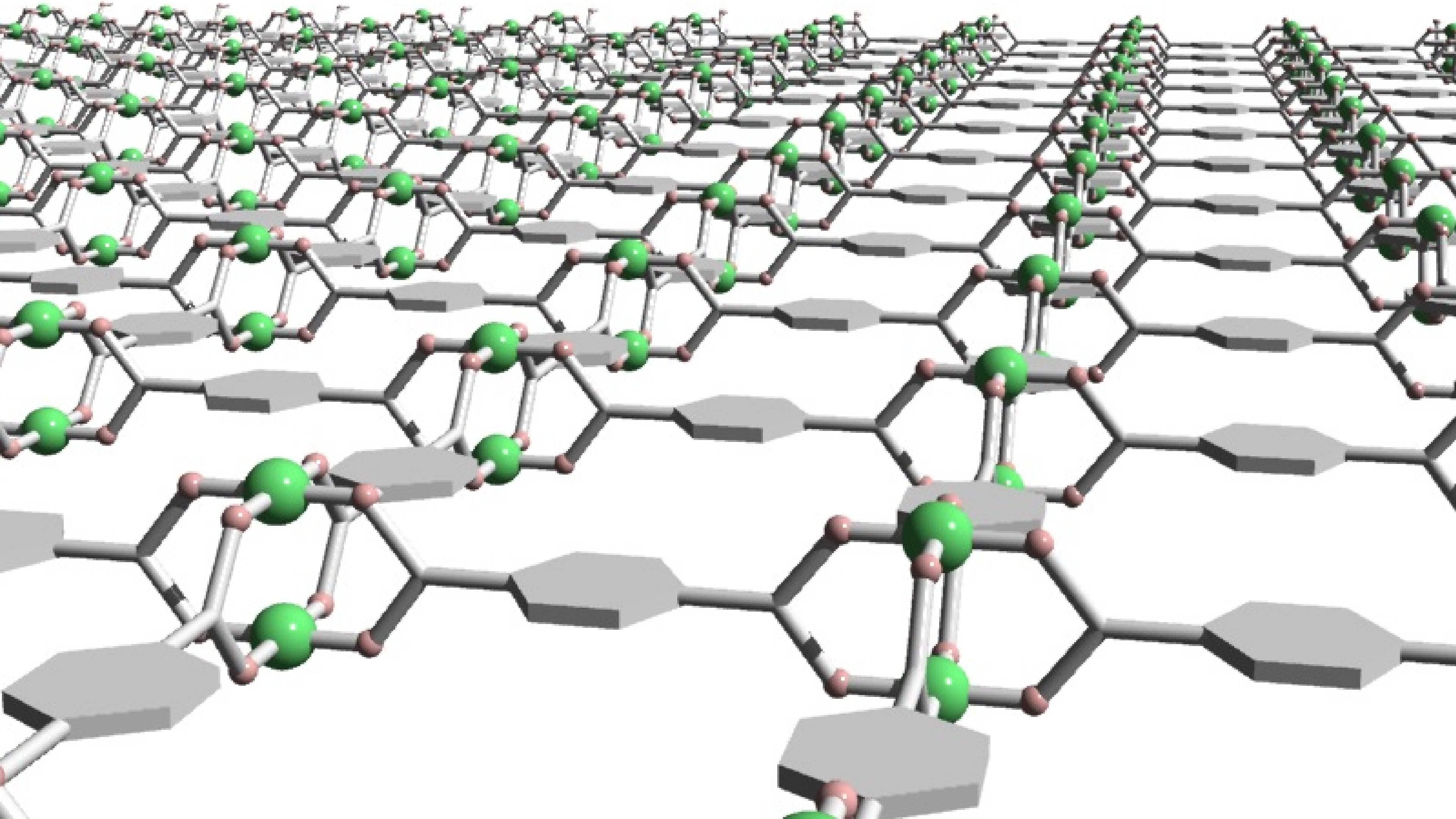
時間分解測定法概念

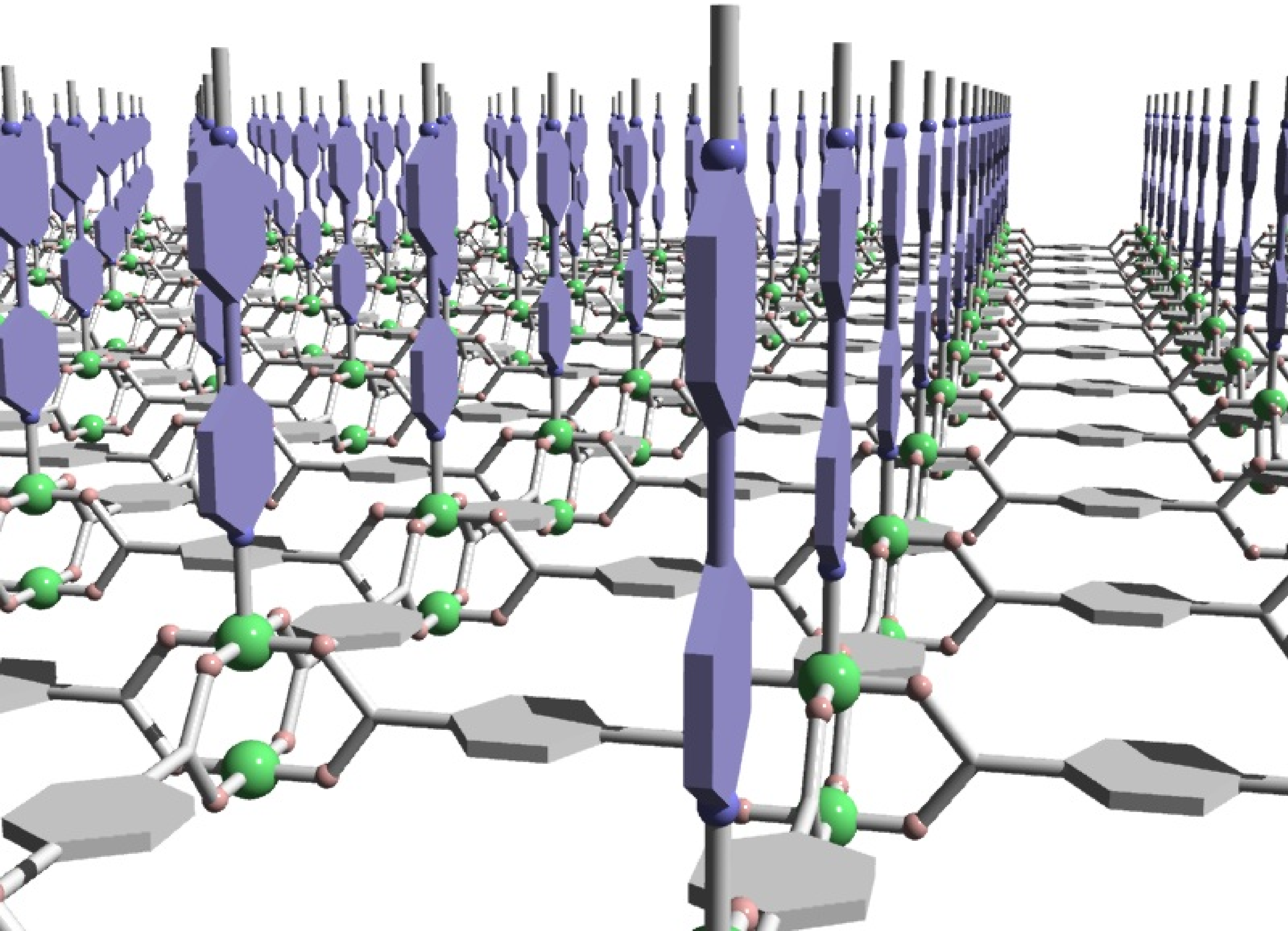
- 超短パルスX線光源を使ったストロボ撮影 -

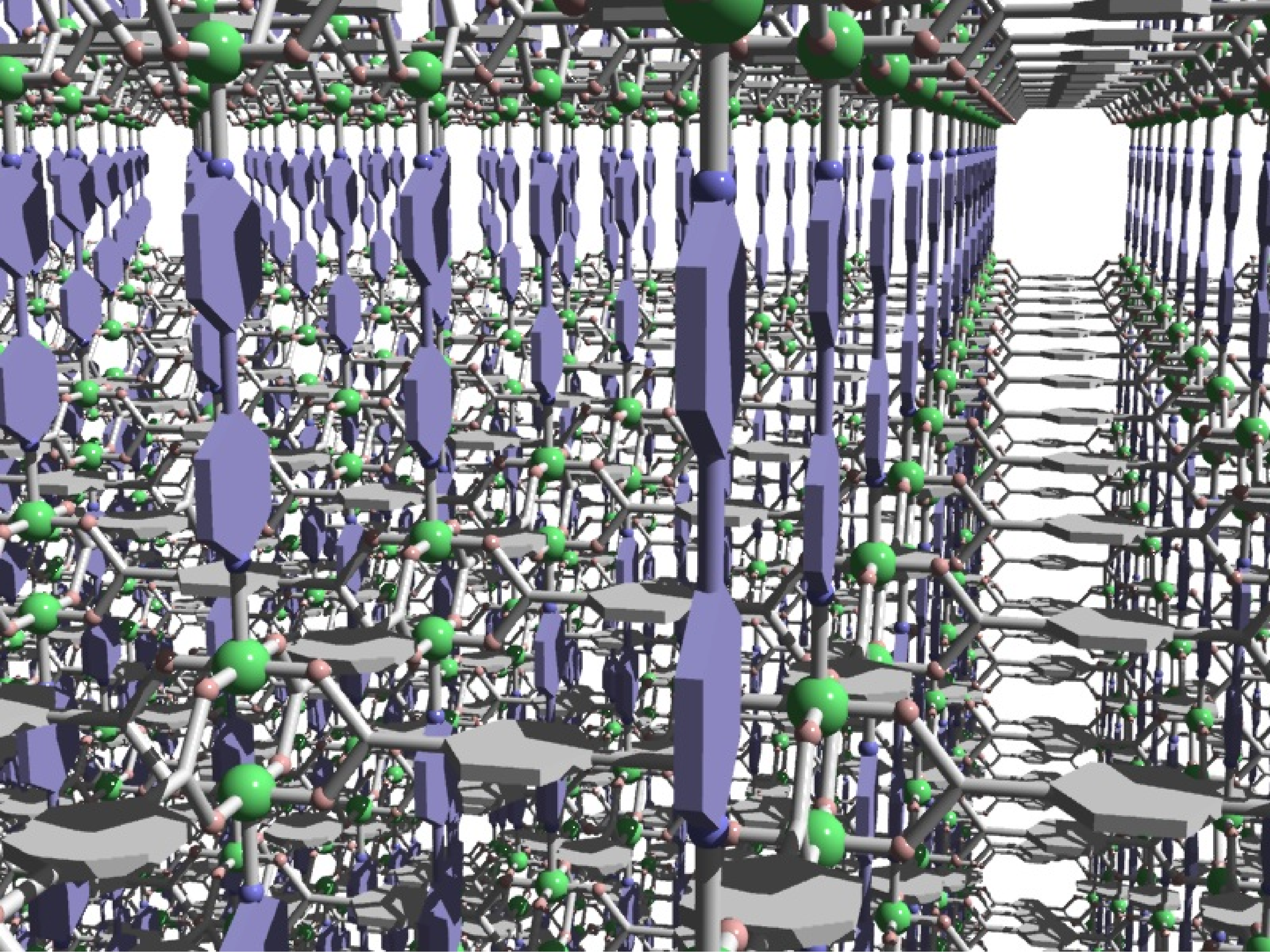


→ フェムト秒・ナノスケールの世界へ
（10^{-15}秒）（10^{-9}メートル）


多孔性材料に向けて

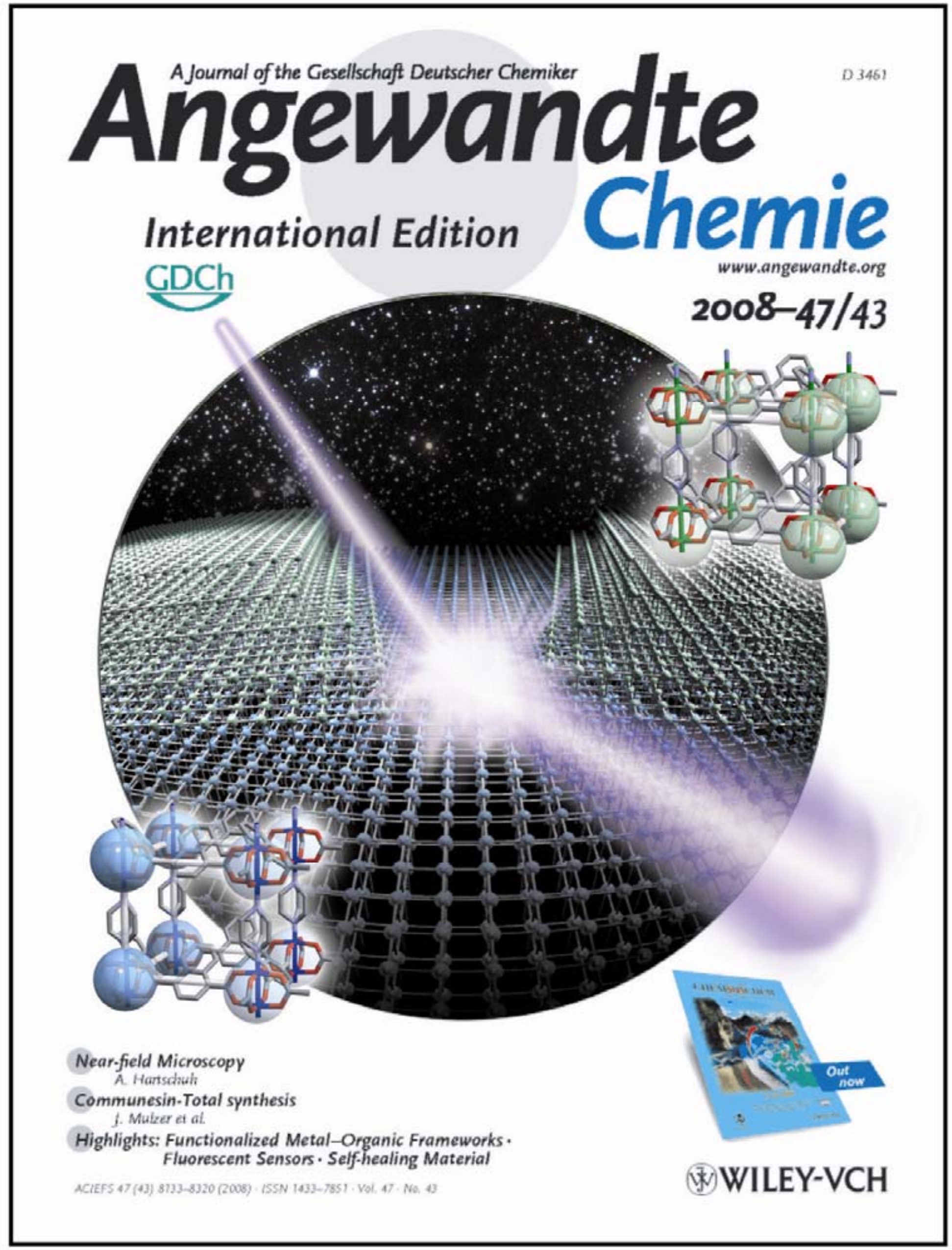






New dimension!

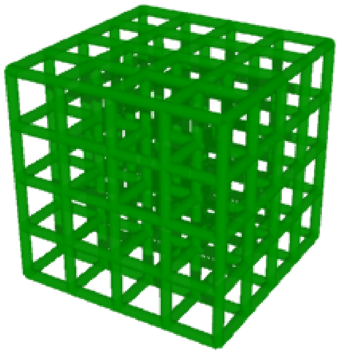
PCP on PCP (MOF on MOF)



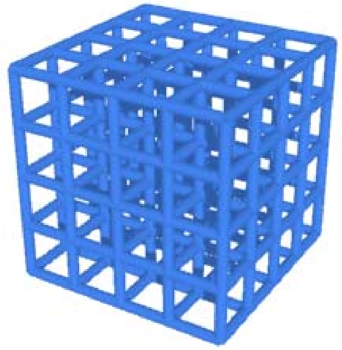
共同研究:坂田修身 (JASRI)
BL13XU in the SPring-8

Angew.Chem.Int.Ed. 2009, 48,1766.

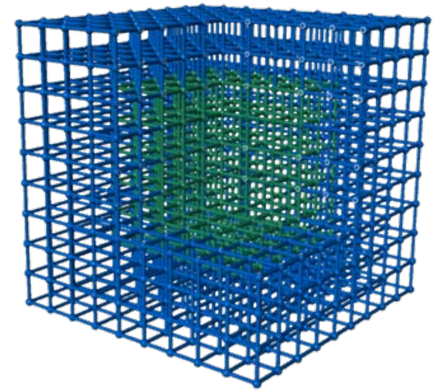
Core/shell type crystal



Core Crystal



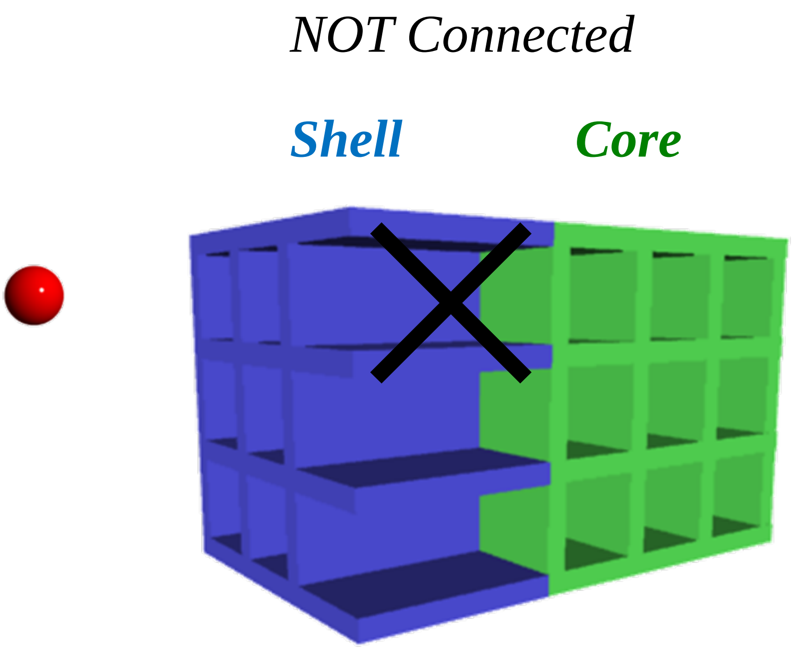
Shell Crystal

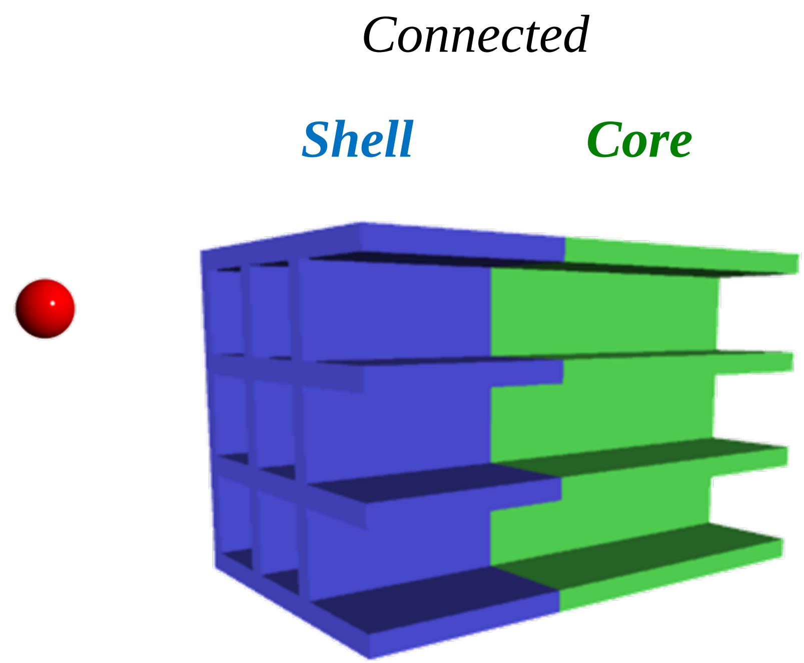


Core/Shell Crystal

Core		Shell		Core/Shell
Sorption	+	Separation	→	Storage Devices with high-separation
Catalysis	+	Response	→	Reaction vessels with high selectivity

Connection of pores



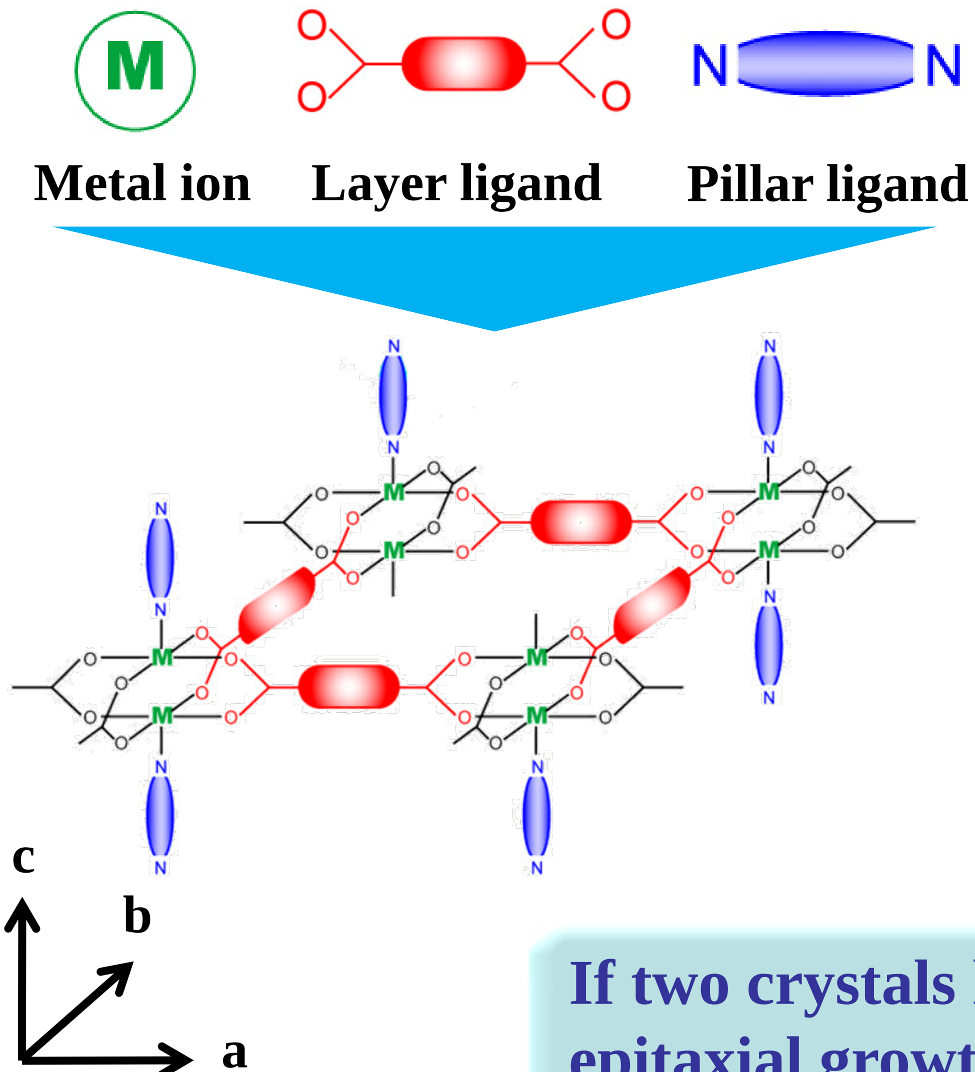


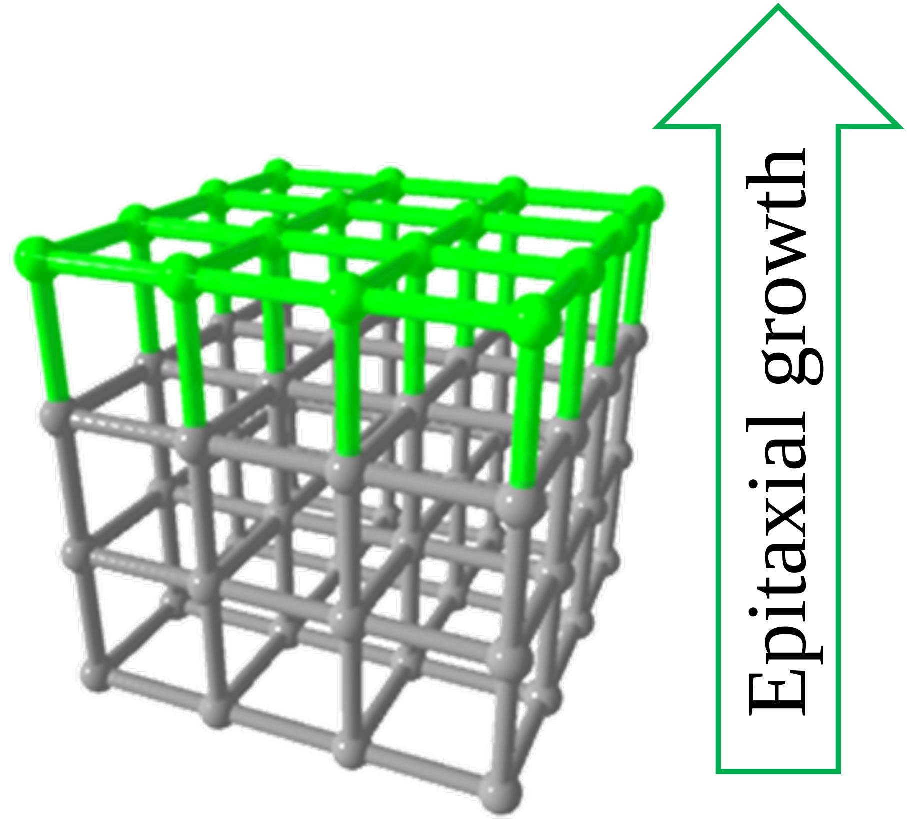
The connection of pores is essential to integrate functions

Epitaxial Growth

Tetragonal framework

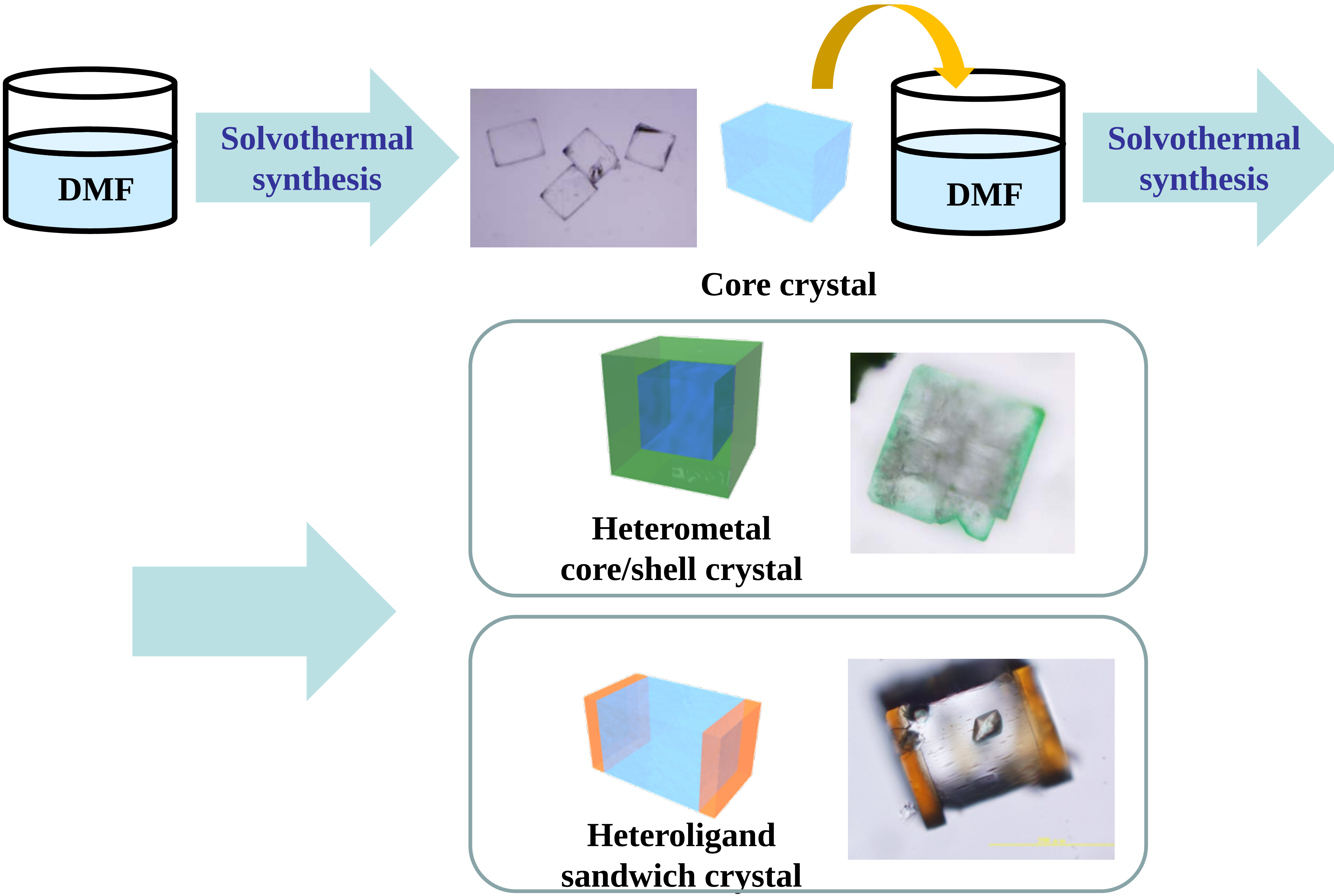
Framework components



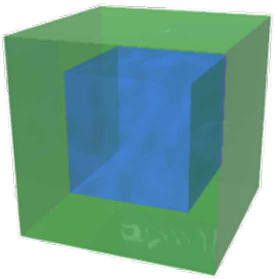


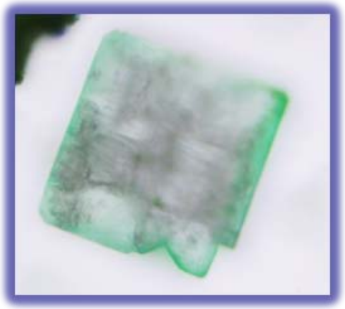
If two crystals have similar unit cell parameters, epitaxial growth can occur

Synthesis


DMF
Solvothermal synthesis
Core crystal
DMF
Solvothermal synthesis
Heterometal core/shell crystal
Heteroligand sandwich crystal

Chapter 1Heterometal core/shell crystal



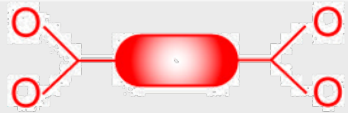
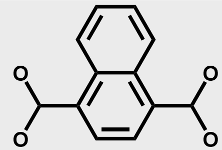
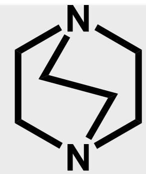
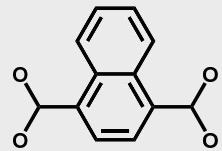
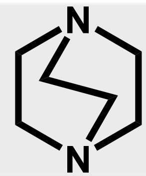


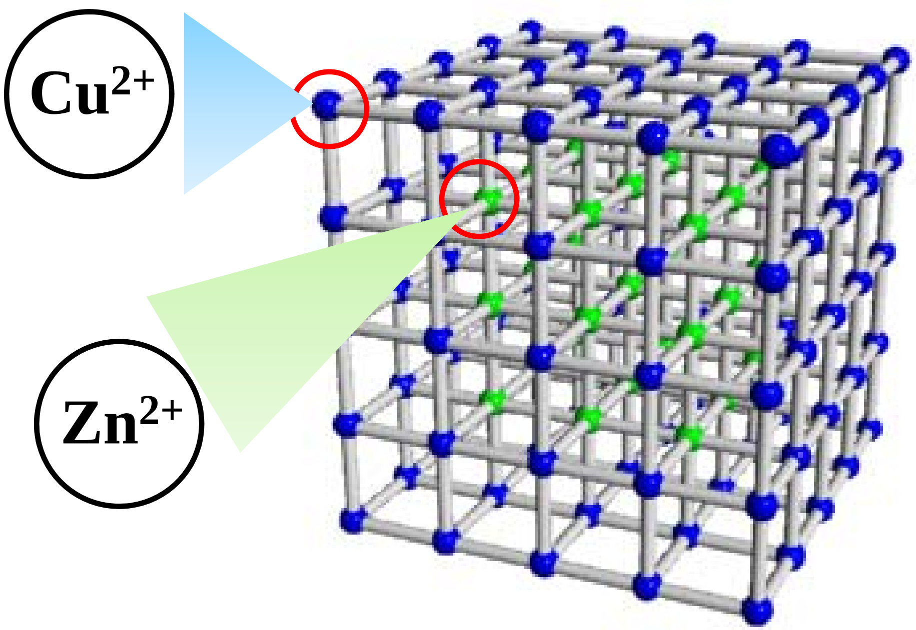
Angew. Chem. Int. Ed. 2009, *48*, 1766-1770

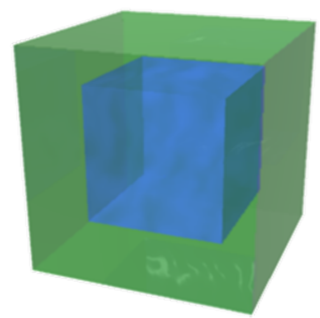
Chapter 2 Heteroligand sandwich crystal

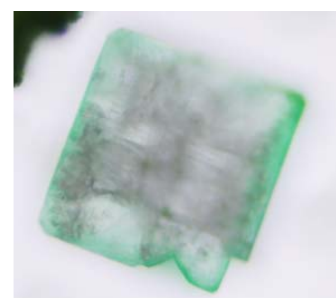
Chem. Commun. 2009, 5097-5099

Heterometal hybridization

	M			Unit cell parameters
Core crystal	Zn^{2+}			$a = b = 10.9212(6)$ $c = 9.6108(7)$
Shell crystal	Cu^{2+}			$a = b = 10.906(2)$ $c = 22.456(4)$



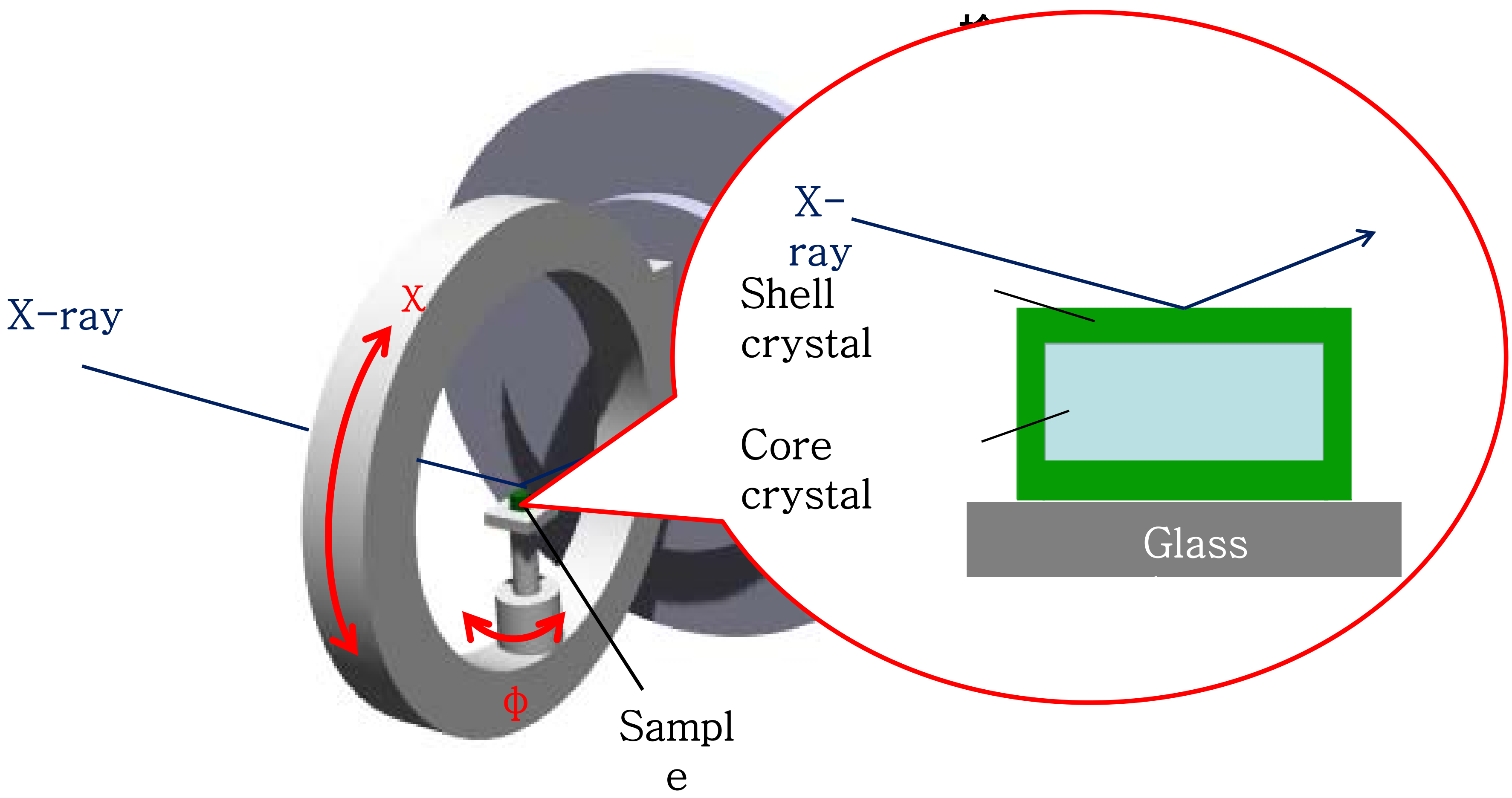




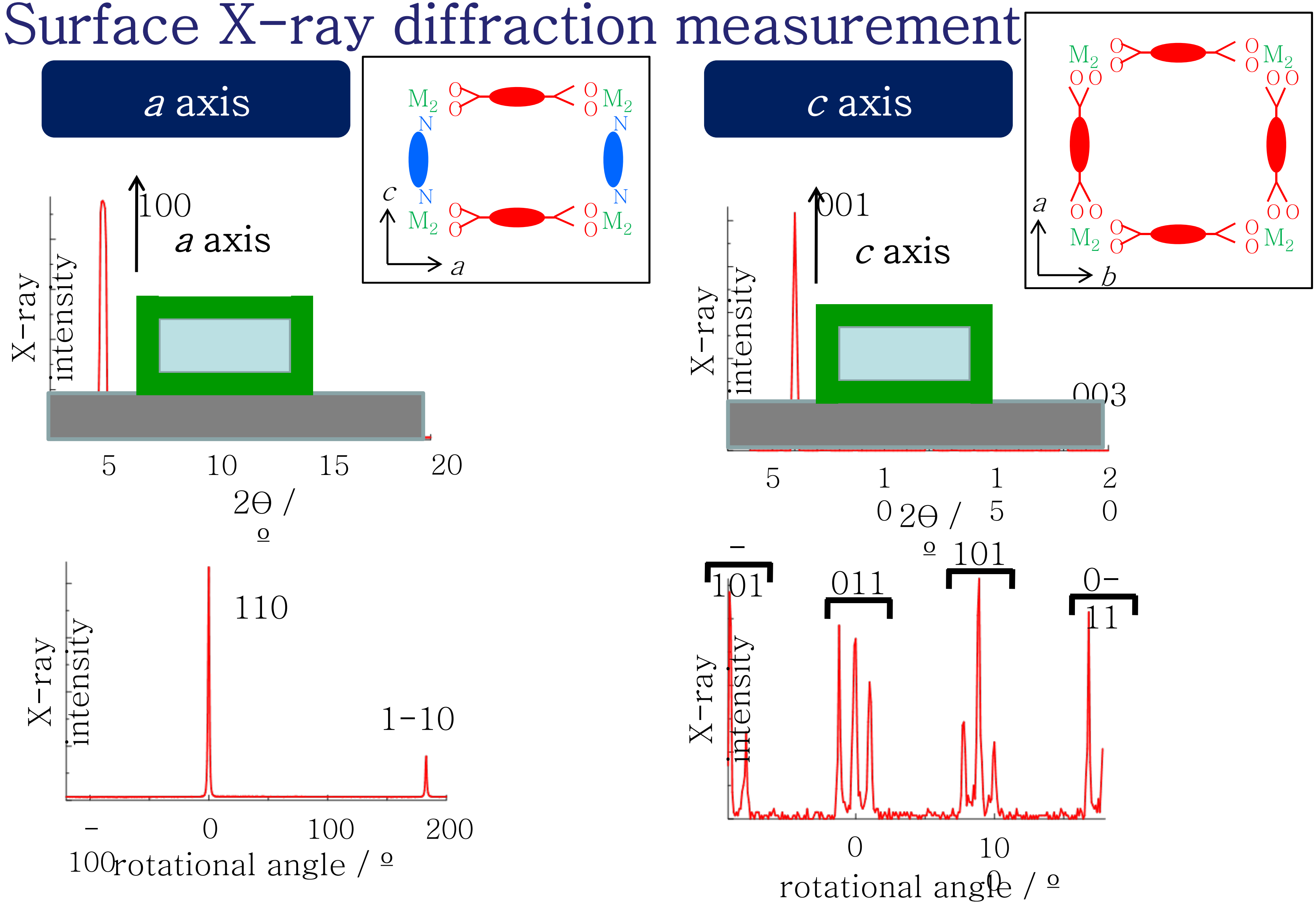
Angew.Chem.Int.Ed. 2009, 48,1766.

Shyncrotron surface X-ray measurement

BL13XU@SPring-8



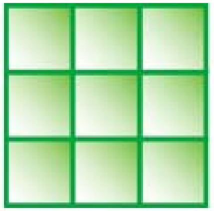
Surface X-ray diffraction measurement



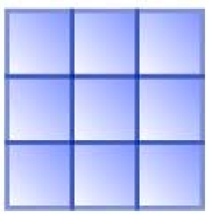
Epitaxial growth

In-plane rotational epitaxial growth

Schematic stru el

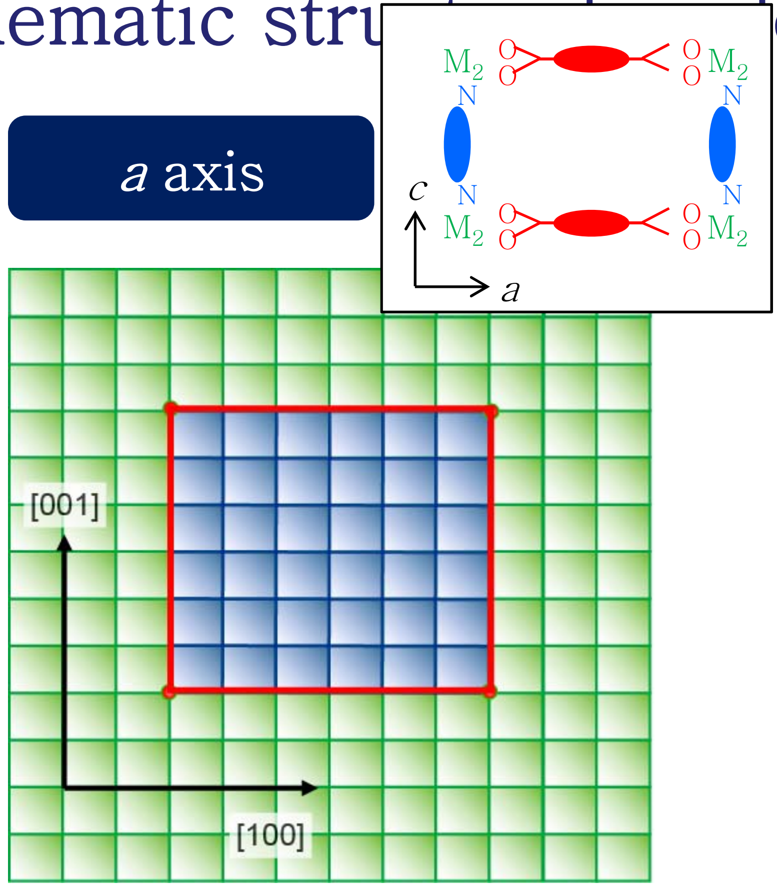


Zn framework



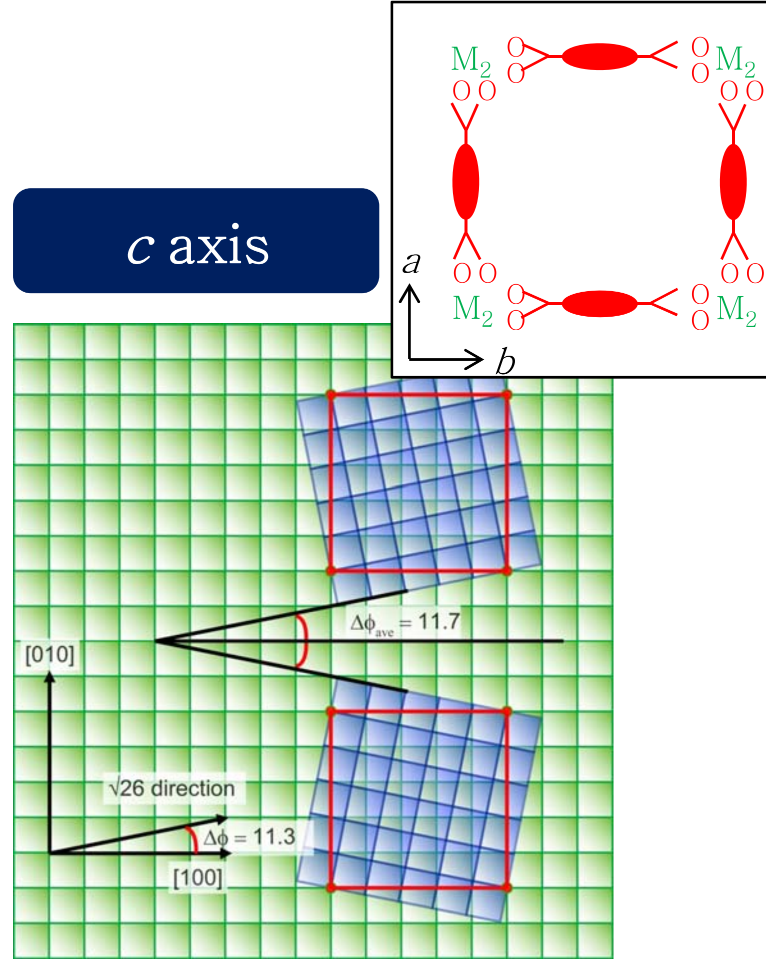
Cu framework

a axis



Epitaxial growth

c axis

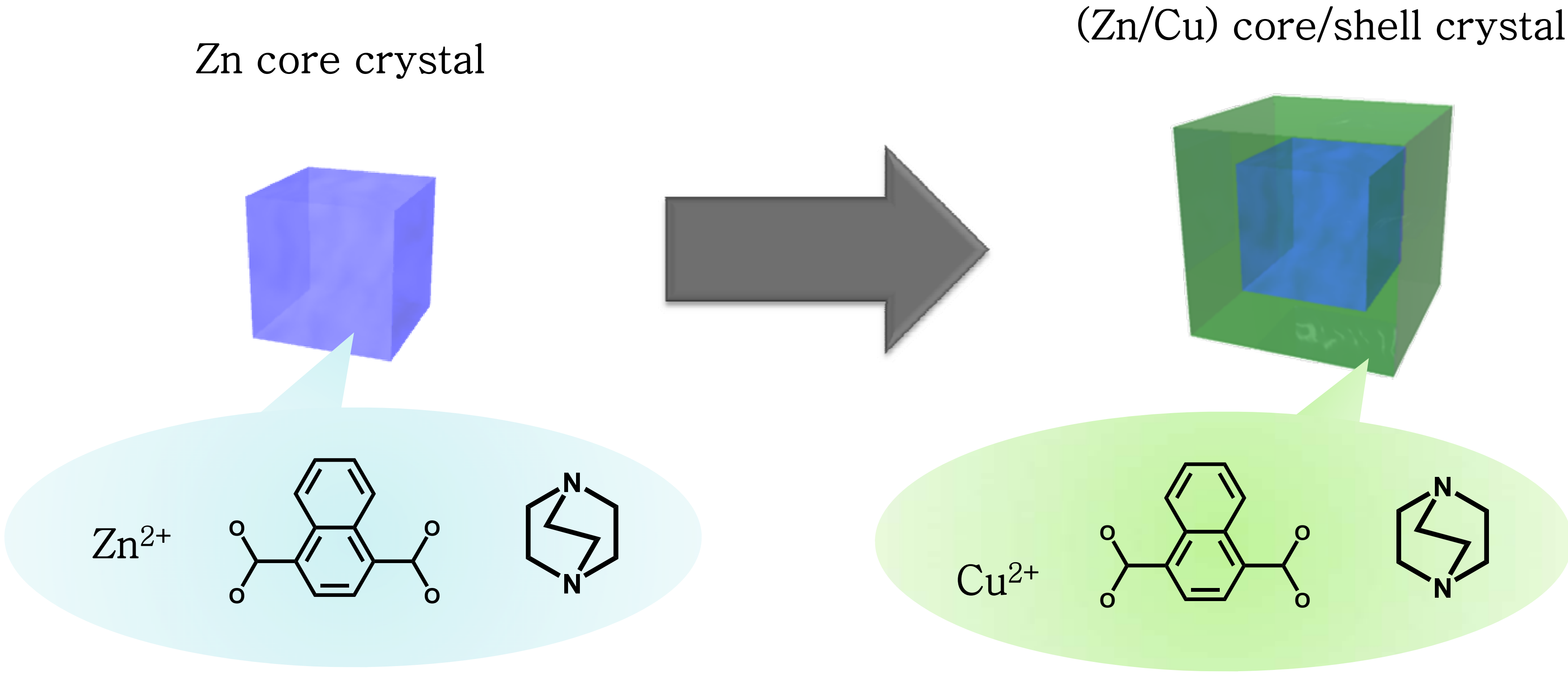


In-plane rotational

	Unit cell parameters
Zn framewor k	$a = b =$ 10.9212(6) $c =$ 9.6108(7)
Cu f	$a = b =$ 10.8190(3)

In-plane rotational epitaxial growth can compensate for the difference in the lattice constants.

Conclusion



The synthesis of the core/shell PCP crystal was successfully achieved.

The surfaces of the core PCP crystal support the growth of a single-shell crystal.

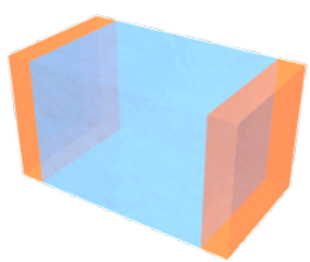
Synchrotron surface X-ray diffraction measurements unveiled the structural relationship between the core crystal and the shell crystal.

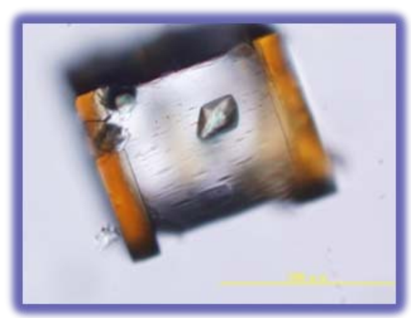
In-plane rotational epitaxial growth occurs at the (001) surface (the square lattice)

Chapter 1 Heterometal core/shell crystal

Angew. Chem. Int. Ed. 2009, *48*, 1766–1770

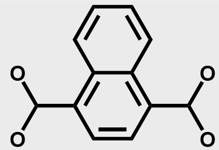
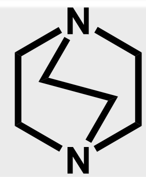
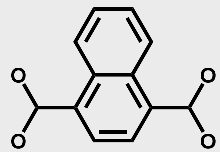
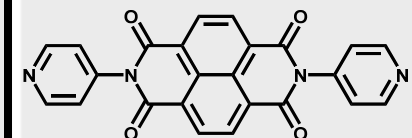
Chapter 2 Heteroligand sandwich crystal

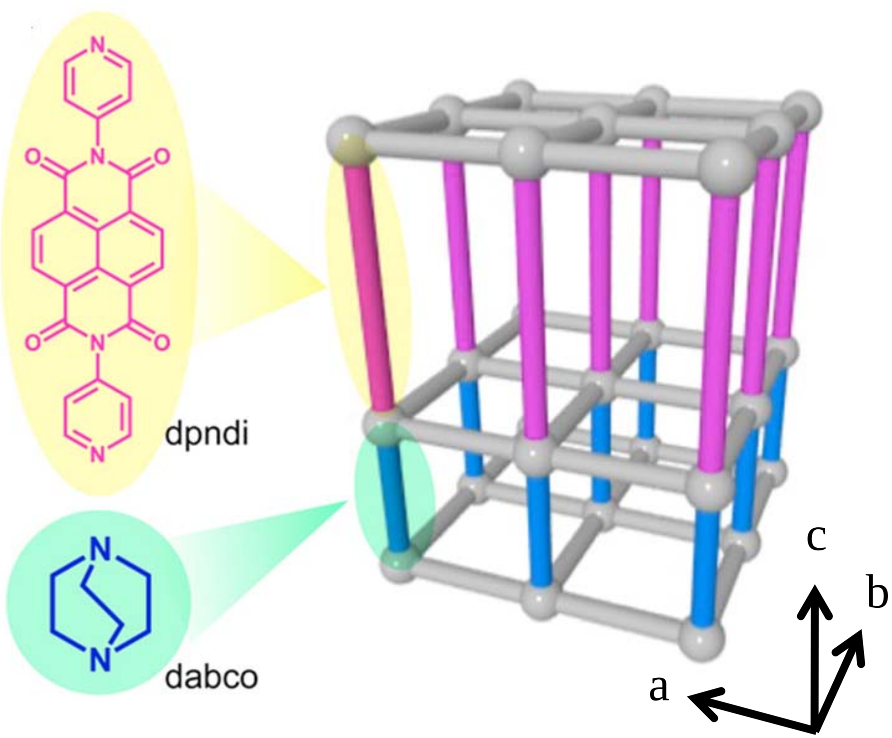


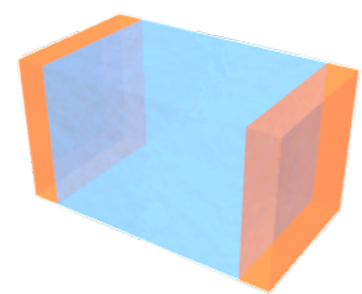


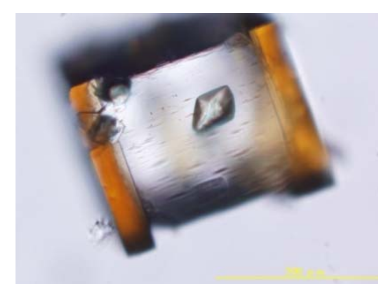
Chem. Commun. 2009, 5097–5099

Heteroligand hybridization

				Unit cell parameters
Core crystal	Zn^{2+}			*a* = *b* = 10.9212(6) ***c* = 9.6108(7)**
Shell crystal	Zn^{2+}			*a* = *b* = 10.906(2) ***c* = 22.456(4)**

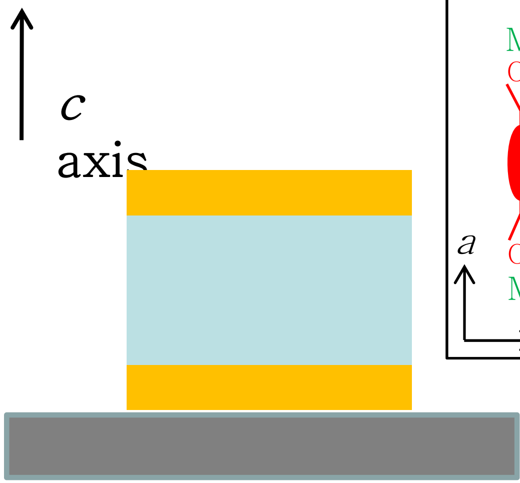


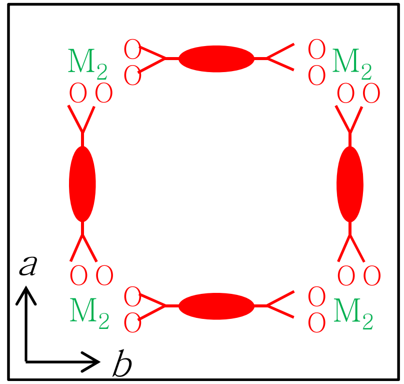


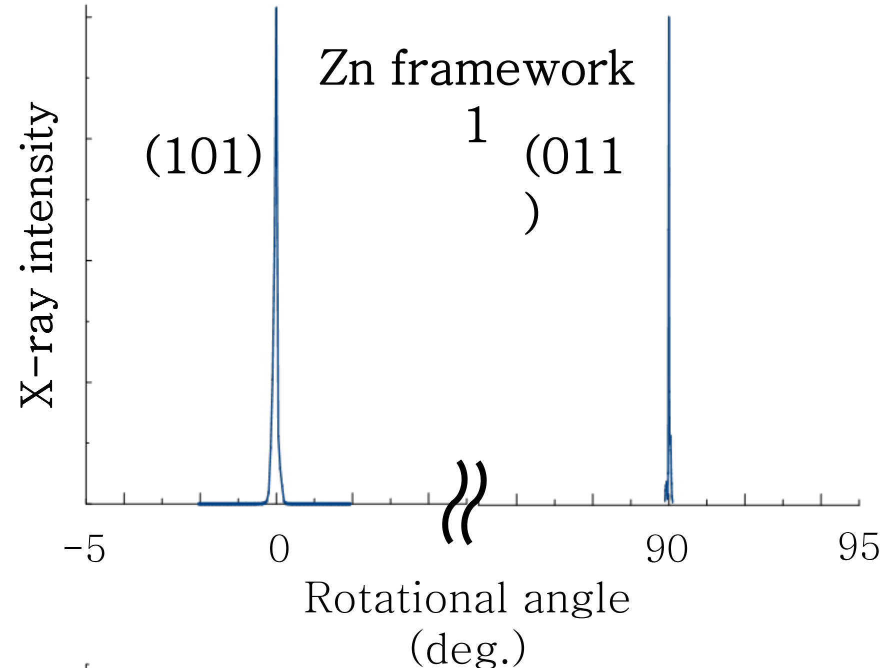


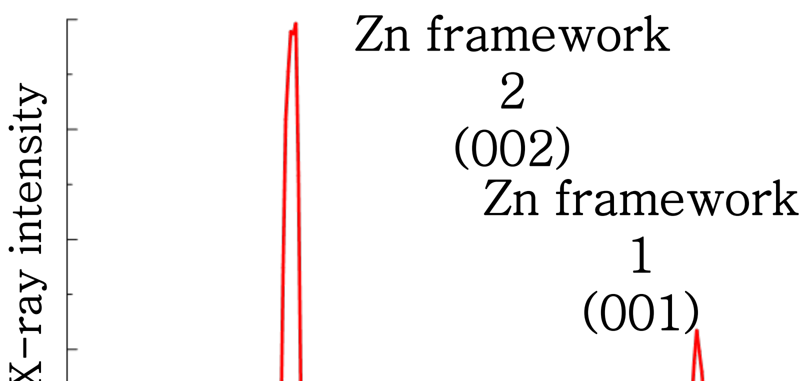
Chem. Commun. 2009, *in press*

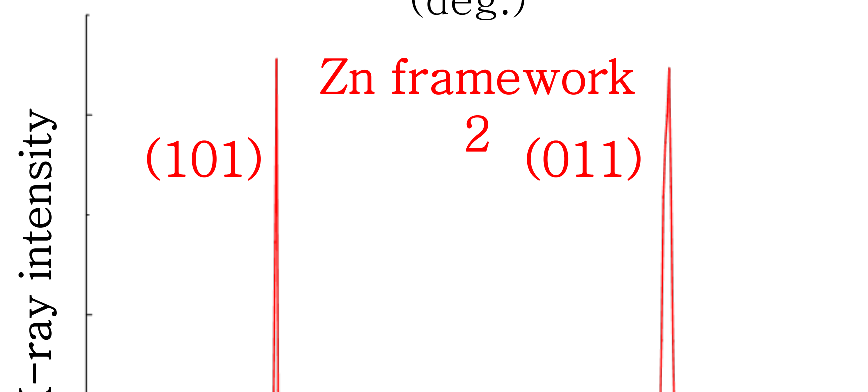
Surface X-ray diffraction measurement





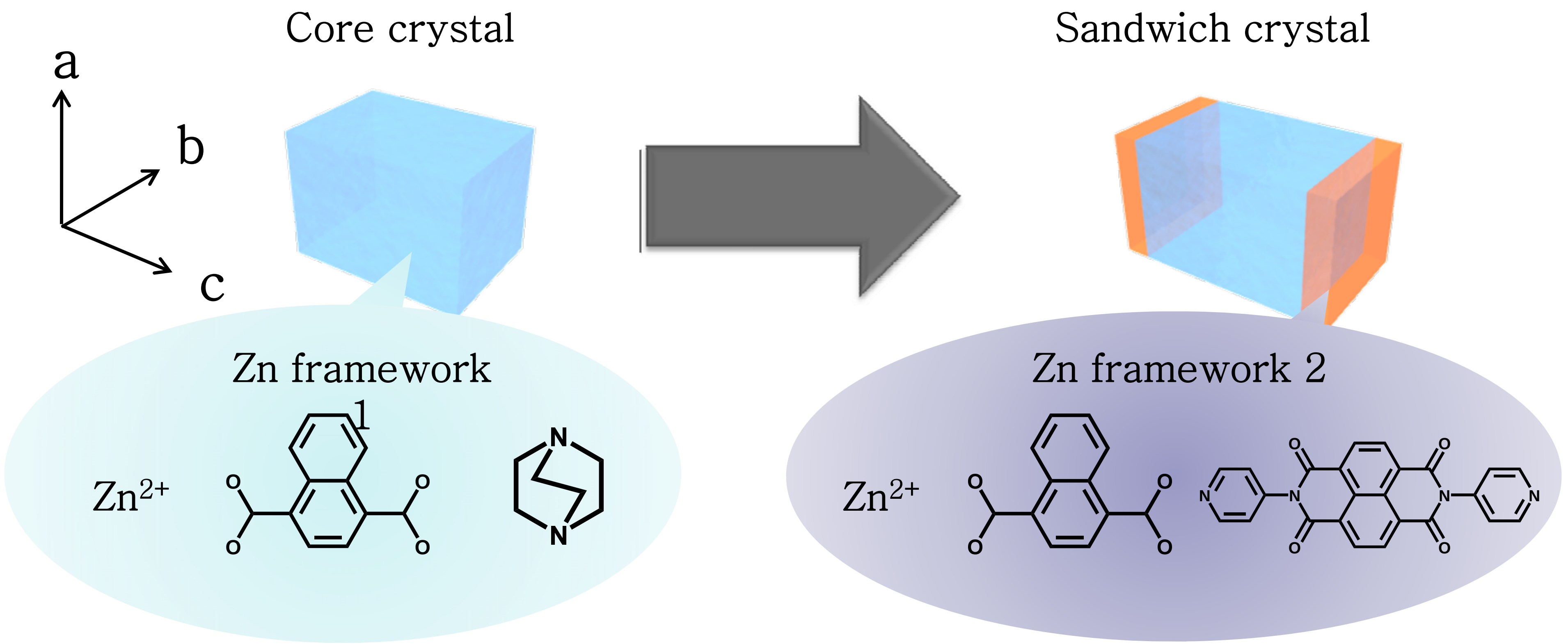






Zn framework 2 was grown along the c axis of Zn framework 1.

Conclusion

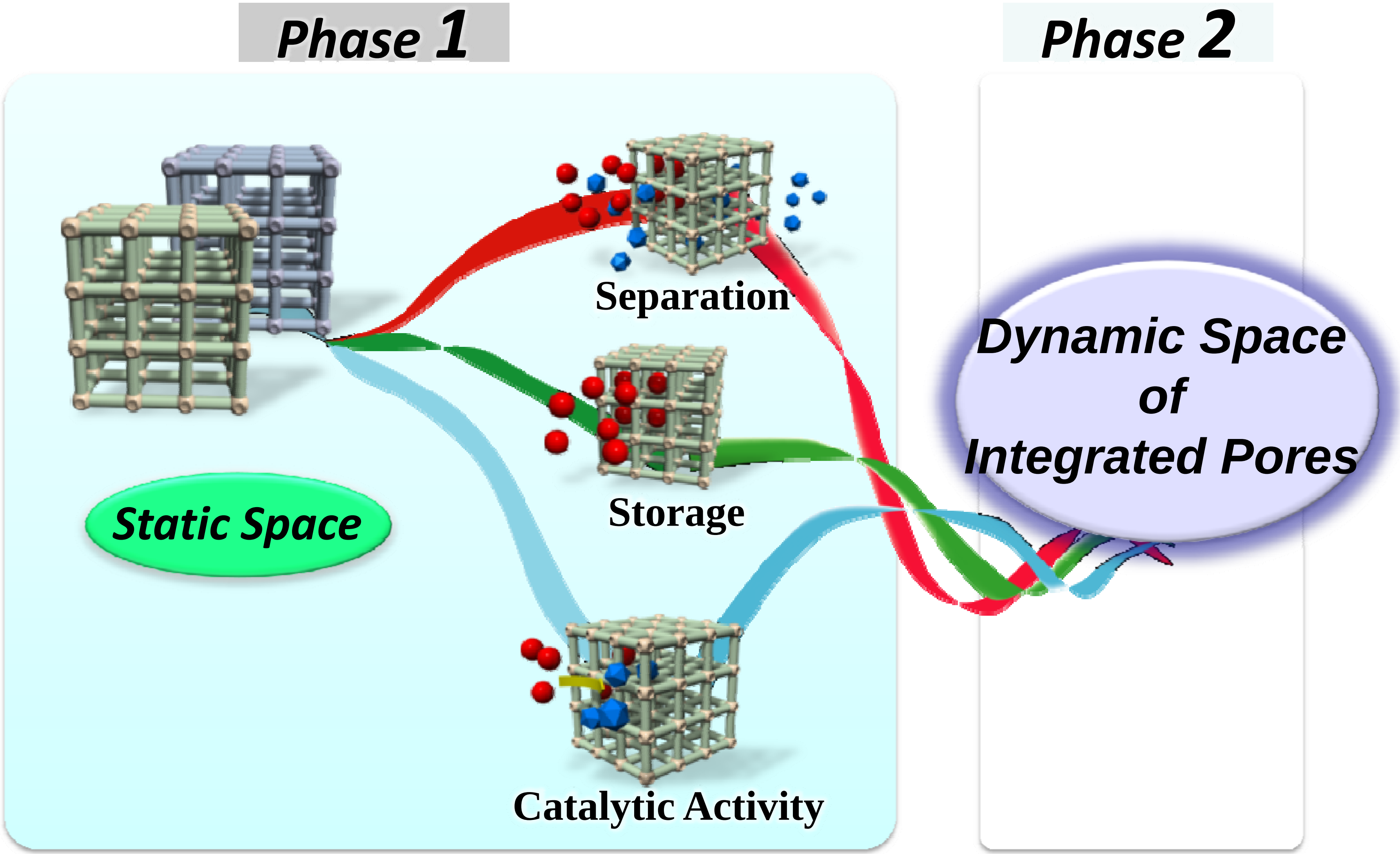


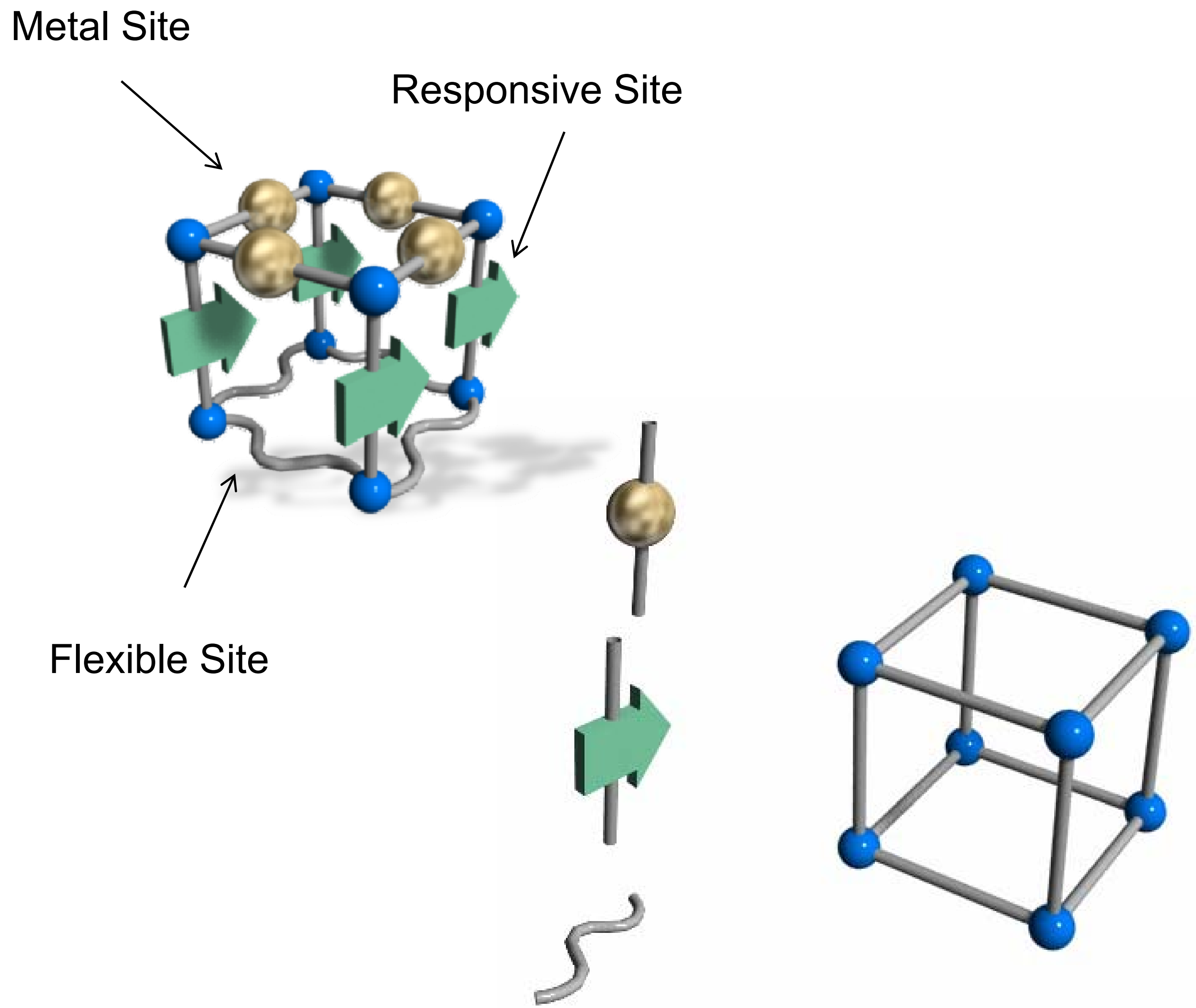
The heteroligand sandwich type PCP co-crystal has been successfully synthesized.

Face selective hybridization of PCP has been succeeded.

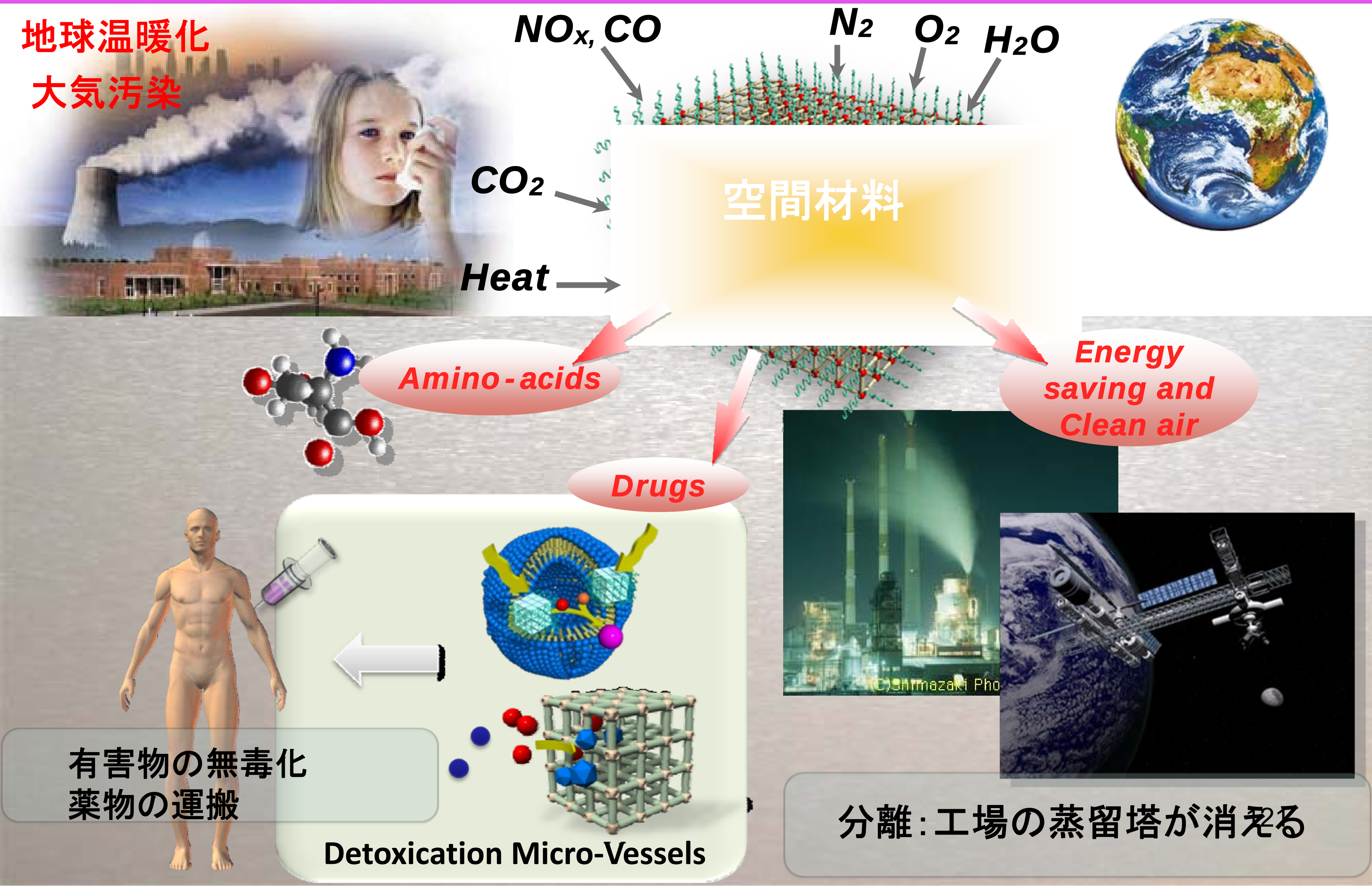
Synchrotron X-ray diffraction measurements determined the second crystal grown on the core crystal by epitaxial growth.

The next challenge is integration of the pore functions which can be responsive to the surrounding environment so-called dynamic space




Metal Site
Responsive Site
Flexible Site

ナノ空間の科学（人類の健康と地球環境に貢献する科学）



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