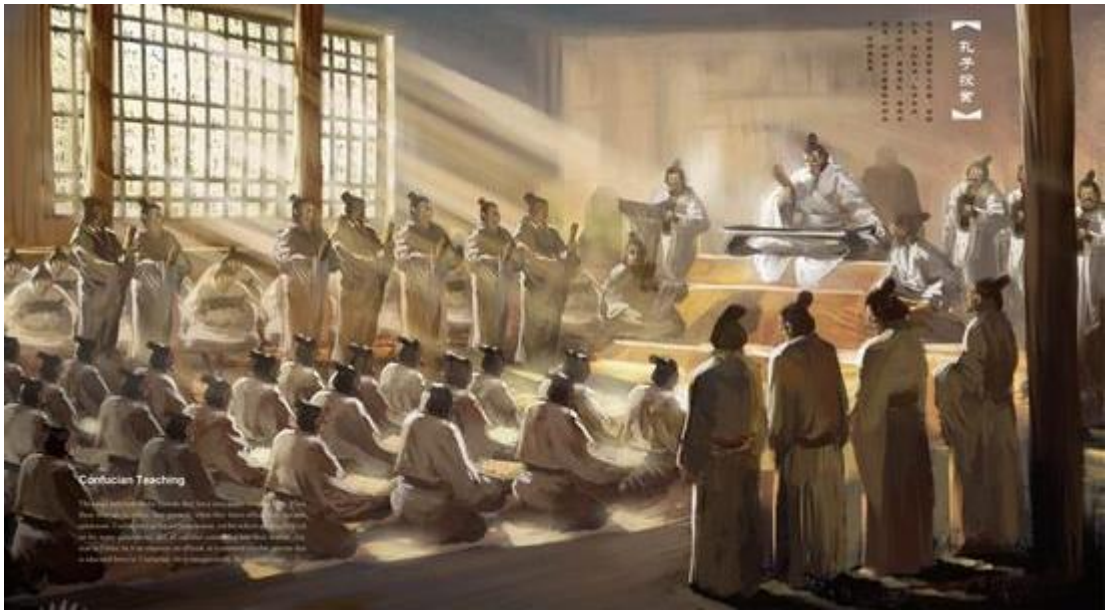
中大理學院學士班

“被誤解的科學–化學，淺談化學的功與過”

Department of Chemistry/National Central University
國立中央大學化學系
謝發坤 副教授
2-21-2017

What's Chemistry什麼是化學



子曰: 君子務本，本立而道生

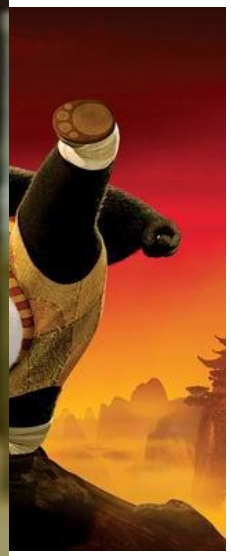
科技基本功:化學，物理，生物，數學

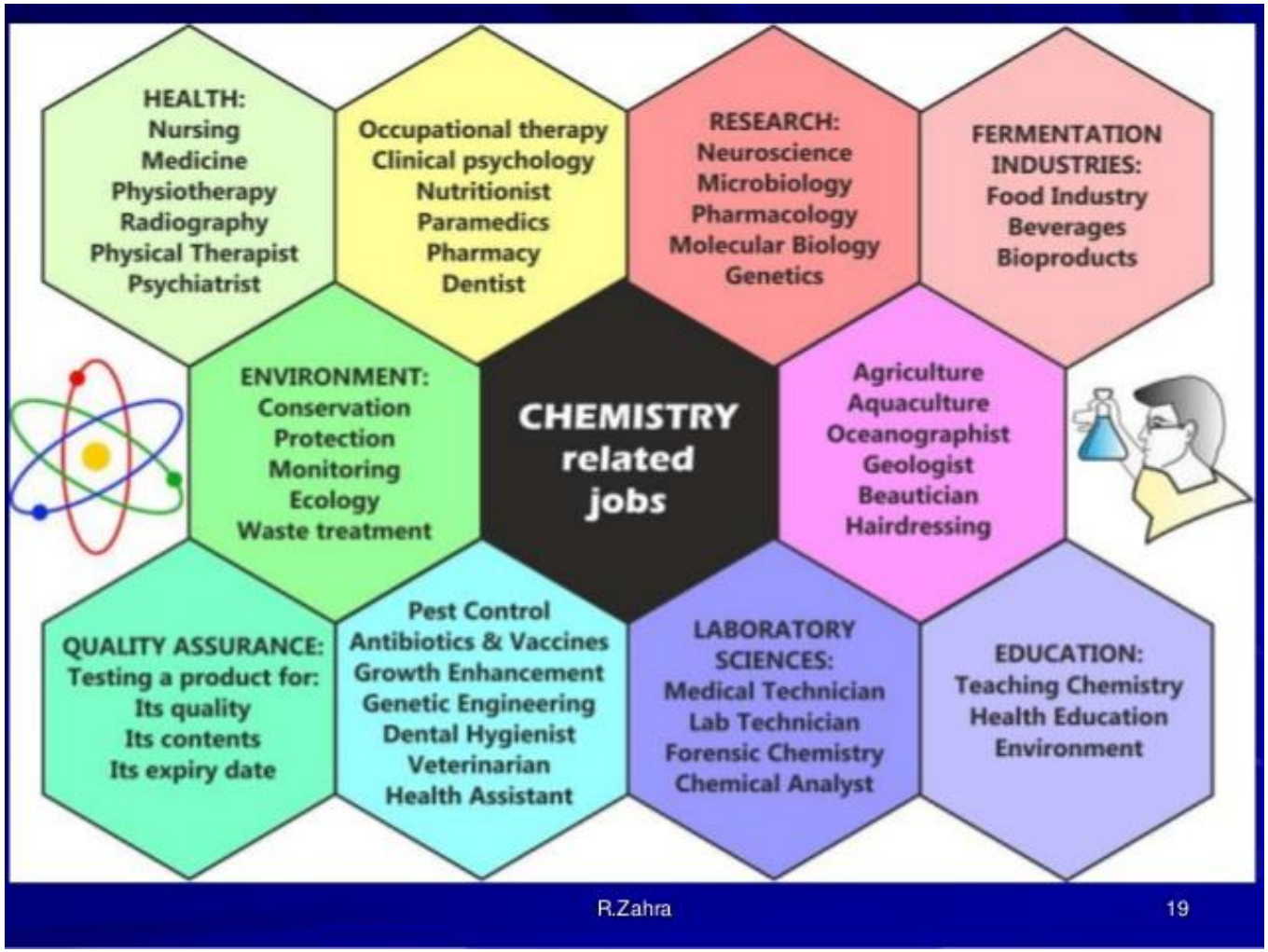
2015 WBSC Premier 12

成敗在於細微!魔鬼藏在細微處

基本功就是細微，化學是一門基本功!


PK
台灣vs日本




HEALTH:
Nursing
Medicine
Physiotherapy
Radiography
Physical Therapist
Psychiatrist
Occupational therapy
Clinical psychology
Nutritionist
Paramedics
Pharmacy
Dentist
RESEARCH:
Neuroscience
Microbiology
Pharmacology
Molecular Biology
Genetics
FERMENTATION INDUSTRIES:
Food Industry
Beverages
Bioproducts
ENVIRONMENT:
Conservation
Protection
Monitoring
Ecology
Waste treatment
CHEMISTRY related jobs
Agriculture
Aquaculture
Oceanographist
Geologist
Beautician
Hairdressing
QUALITY ASSURANCE:
Testing a product for:
Its quality
Its contents
Its expiry date
Pest Control
Antibiotics & Vaccines
Growth Enhancement
Genetic Engineering
Dental Hygienist
Veterinarian
Health Assistant
LABORATORY SCIENCES:
Medical Technician
Lab Technician
Forensic Chemistry
Chemical Analyst
EDUCATION:
Teaching Chemistry
Health Education
Environment
R.Zahra
19

Nobel Prize-Medicine

Year	Counrty	Name	
1991	德國	厄溫·內爾	「發現細胞中單離子通道的功能」
1992	瑞士 美國	埃德蒙·費希爾（Edmond H. Fischer）	「發現的可逆的蛋白質磷酸化作用是一種生物調節機制」
	美國	埃德溫·克雷布斯（Edwin Gerhard Krebs	
1993	英國	理察·羅伯茨爵士 Sir Richard John Roberts	「發現斷裂基因」
1994	美國	艾爾佛列·古曼·吉爾曼 Alfred Goodman Gilman	「發現G蛋白及其在細胞中的訊息傳遞作用」
	美國	馬丁·羅德貝爾 Martin Rodbell	
1995	德國	克里斯汀·紐斯林-沃爾哈德（Christiane Nüsslein-Volhard	「發現早期胚胎發育中的遺傳調控機理」
1996	澳洲	彼得·杜赫提 Peter C. Doherty	「發現細胞介導的免疫防禦特性」
1997	美國	史坦利·布魯希納 Stanley B. Prusiner	「發現普里昂蛋白——傳染的一種新的生物學原理」
1998	美國	羅伯·佛契哥德（Robert Francis Furchgott，	「發現在心血管系統中起信號分子作用的一氧化氮」
	美國	費瑞·慕拉德 Ferid Murad	
2001	英國	理察·蒂莫希 Sir Richard Timothy	「發現細胞周期的關鍵調節因子」
	英國	保羅·納斯爵士，FRS（Sir Paul Nurse，	
2003	美國	保羅·克里斯琴·勞特伯 Paul Christian Lauterbur	「在核磁共振成像方面的發現」
2007	美國	馬里奧·卡佩奇 Mario Capecchi	「在利用胚胎幹細胞引入特異性基因修飾的原理上的發現」
	美國	奧利弗·史密斯 Oliver Smithies	
2009	美國 澳洲	伊莉莎白·海倫·布雷克本 Elizabeth (Liz) Helen Blackburn	
	美國	卡羅琳·維德尼·卡蘿·格萊德（Carolyn Widney "Carol" Greider	「發現端粒和端粒酶如何保護染色體」
	美國 英國	傑克·索斯塔克（Jack Szostak	
2011	法國	朱爾斯·A·霍夫曼（Jules A. Hoffmann	"他們對於先天免疫機制激活的發現"

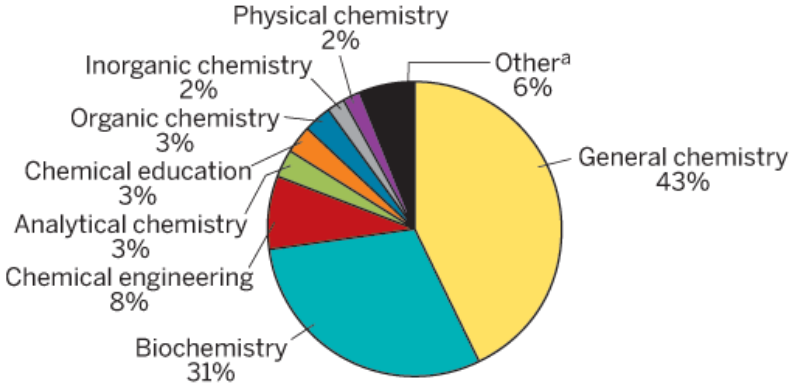
Percentage of respondents who were unemployed job seekers in 2013:

14.9

Percentage of respondents who are female:

51.2

Most respondents' highest degree was in general chemistry or biochemistry.



Respondents = 2,035

NOTE: Of the respondents who indicated both their highest degree earned and their field of highest degree, 85% earned new bachelor's degrees, 5% earned master's degrees, and 9% earned Ph.D.s. **a** Includes respondents who selected agricultural/food chemistry, environmental chemistry, forensic chemistry, materials science, medical/pharmaceutical chemistry, or polymer chemistry as field of highest degree, as well as those who opted not to select a field.

NOTE: For some respondent groups, the number of responses was small and not necessarily representative of the wider pool of chemistry graduates in a given group.

Median 2013 starting salary for inexperienced grads:

$39,560
for bachelor's

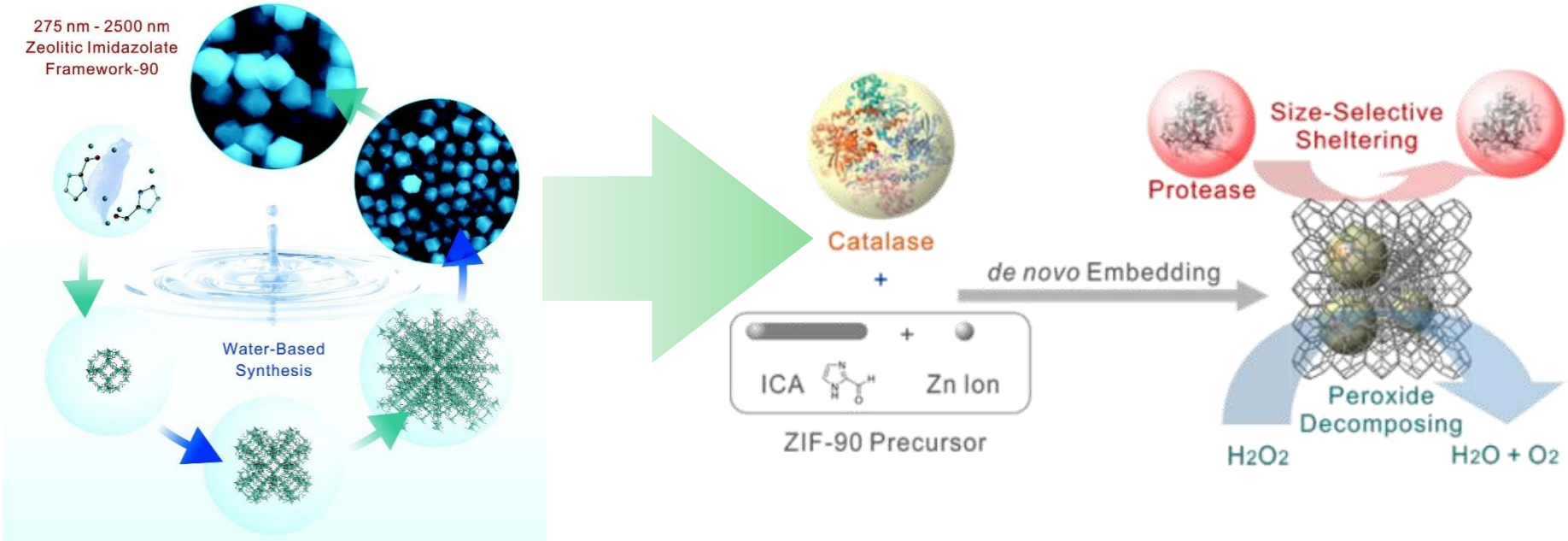
$55,000
for master's

$75,750
for Ph.D.s

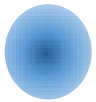
Median age of 2013 survey takers:

23	**27**	**29**
for bachelor's	for master's	for Ph.D.s

From Water-Based Synthesis to Enzyme Immobilization in Metal-organic Frameworks

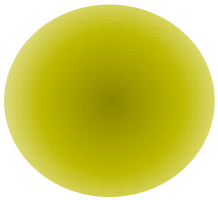


Metal-Organic Frameworks (MOFs)

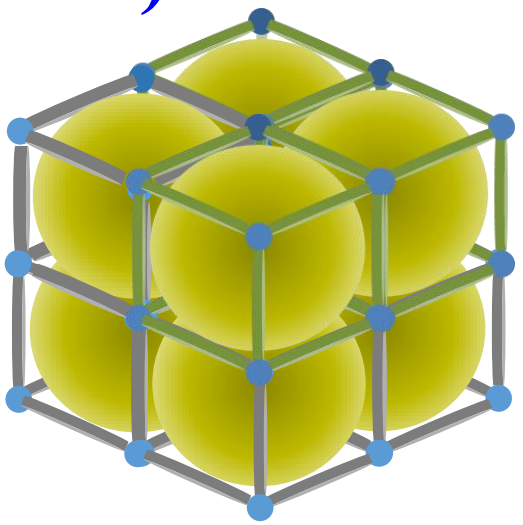


Metal Cluster

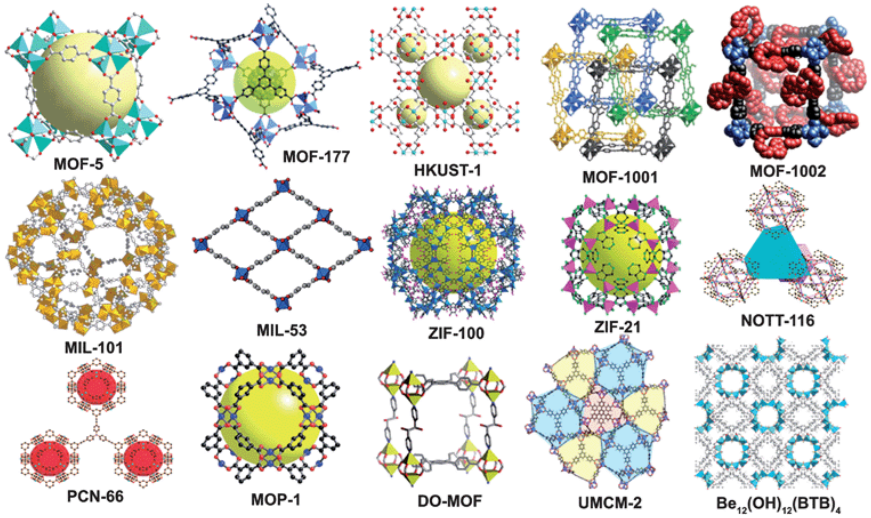
Organic ligand



Pore



- Open framework - porous and surface areas
- Designable



Porous Materials

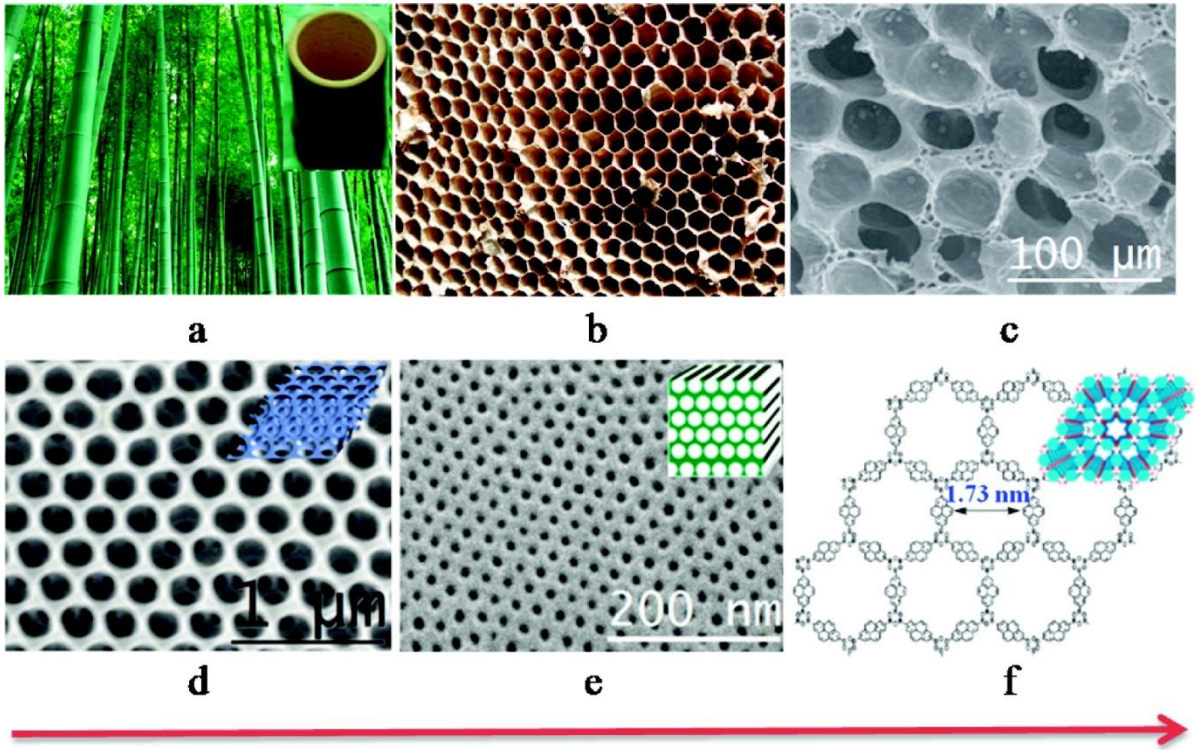


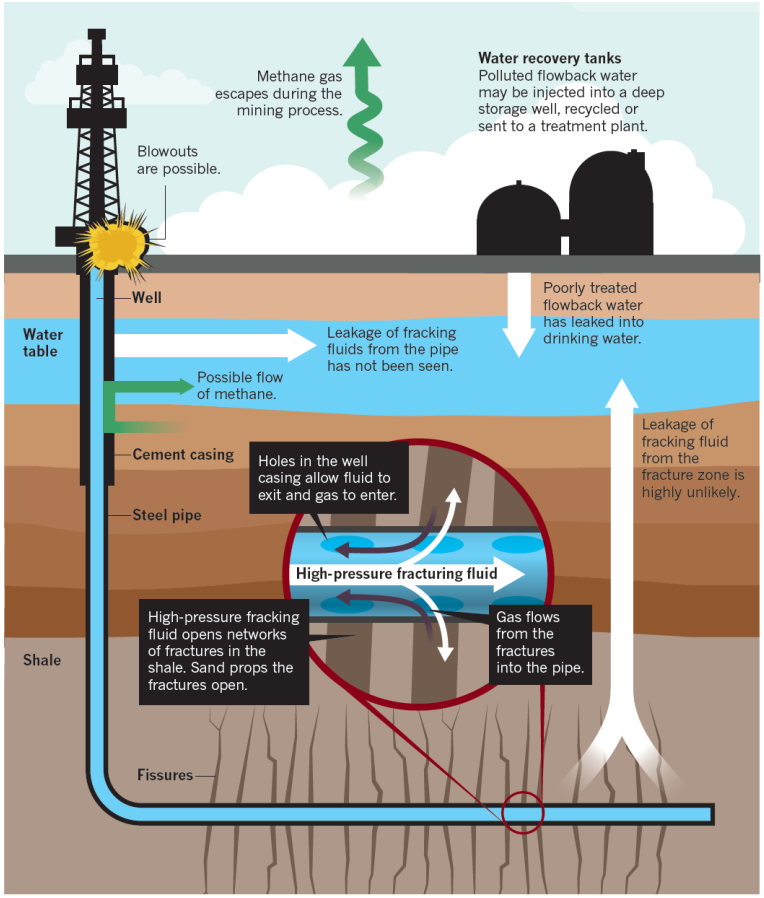
Illustration of porosity existing in nature and synthesized materials with a decreasing pore size: (a) bamboo; (b) honeycomb; (c) SEM image of alveolar tissue in mouse lung (Reprinted with permission from ref 24; Copyright 2011 Wiley-VCH); **(d)** SEM image of an ordered **macroporous** polymer from direct templating (Reprinted with permission from ref 25; Copyright 2010 American Chemical Society); **(e)** SEM image of an ordered **mesoporous** polymer from self-assembly of block copolymers (Reprinted with permission from ref 26; Copyright 2010 American Chemical Society); **(f)** structural representation of an ordered **microporous** polymer (Reprinted with permission from ref 27; Copyright 2009 Wiley-VCH).

Published in: Dingcai Wu; Fei Xu; Bin Sun; Ruowen Fu; Hongkun He; Krzysztof Matyjaszewski; *Chem. Rev.* **2012,** 112, 3959-4015.
DOI: 10.1021/cr200440z

MOFs with high surface area/thermal stability

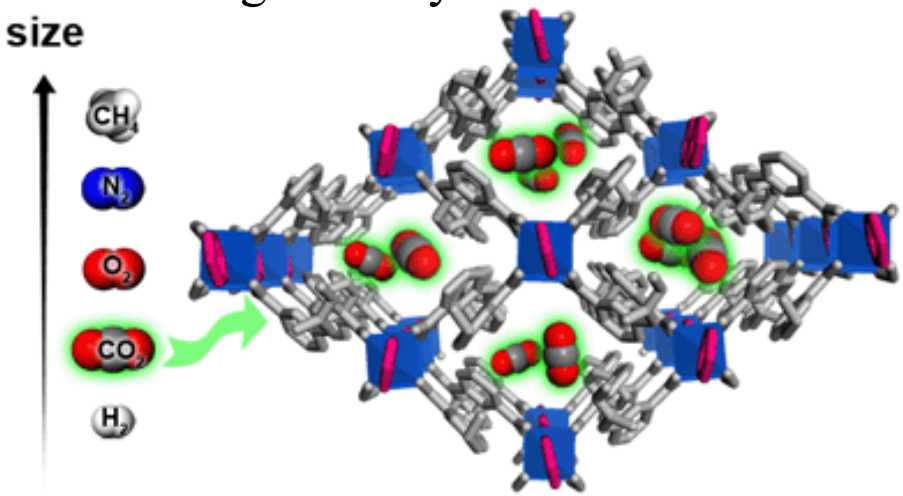
Omar M. Yaghi,* *Science*, **2013**, 341, 6149

Applications: Shale/Green House Gas Adsorption



Applications:

- Gas storage
- Gas separation
- Heterogeneous catalyst
- Drug delivery

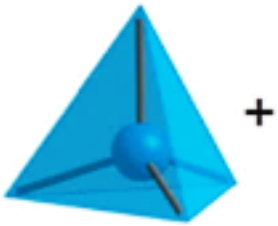


Zeolitic Imidazolate Frameworks (ZIFs)

-Subclass of MOFs

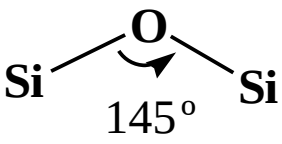
-Highly chemical and thermal stability

-Best porous material for CO_2 capitulation by physisorption



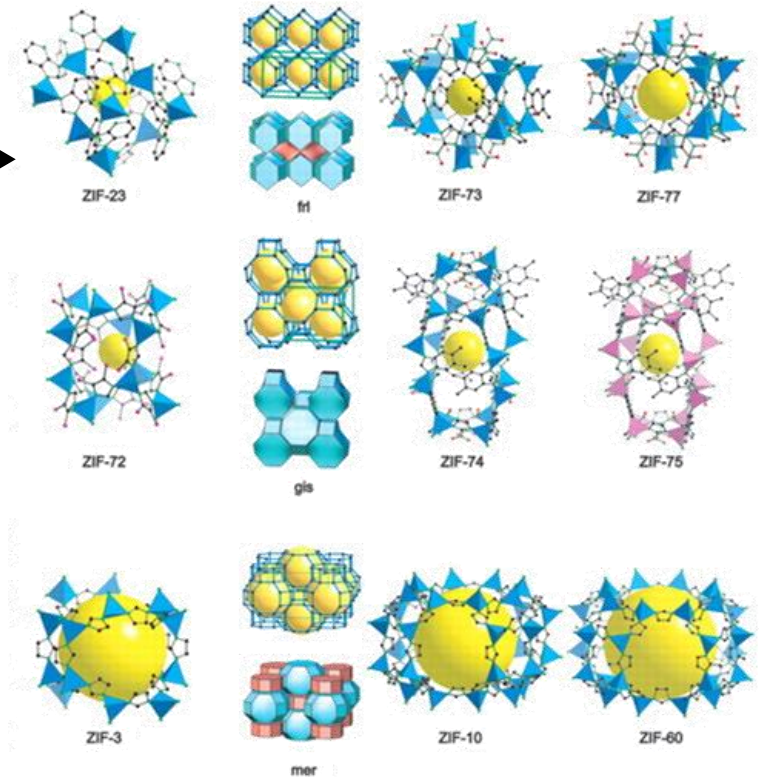
Tetrahedral metal
(e.g., Zn or Co)

Imidazolate



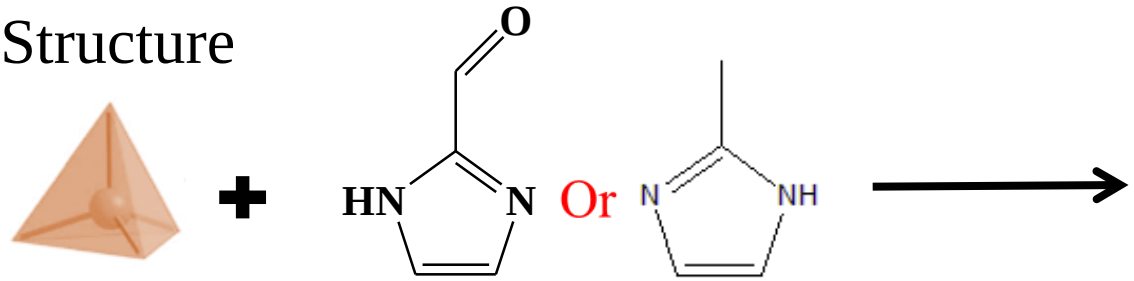
Si-O-Si

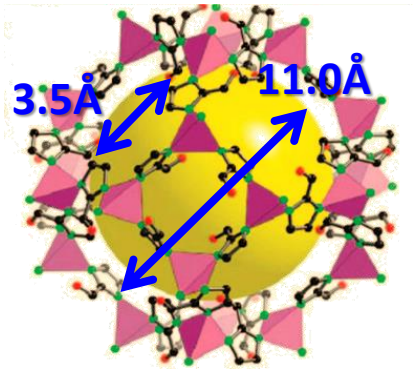
M-Im-M



Zeolitic Imidazolate Frameworks -8 & -90

- Structure

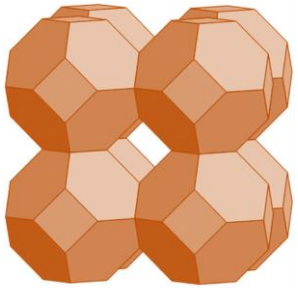




Zinc ions 2-Imidazolecarboxaldehyde

ZIF-90 Or ZIF-8

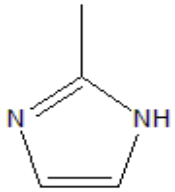
IUPAC	Pore Diameter (D)
Macroporous	> 50 nm
Mesoporous	2 ~ 50 nm
Microporous	< 2 nm



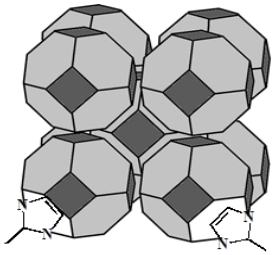
- Application:
  - Gas separation membrane

Green Chemistry: Water-based synthesis

Rapid Synthesis of ZIF-8 in Aqueous System



2-methylimidazole

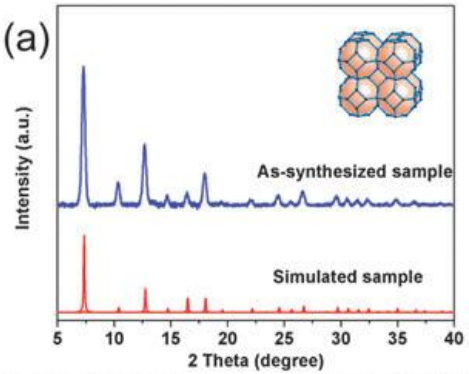


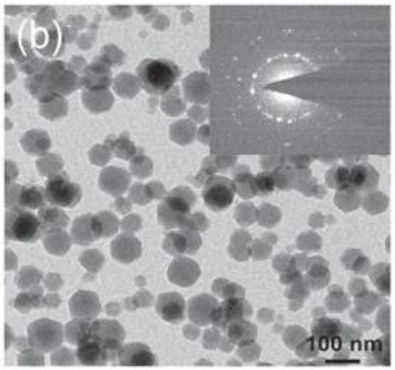
ZIF-8

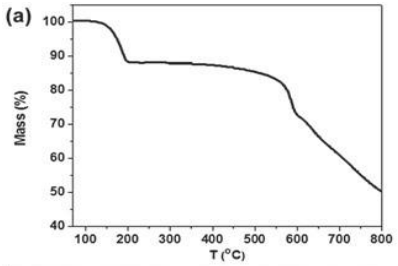
Zn^{2+} : mIm : H_2O

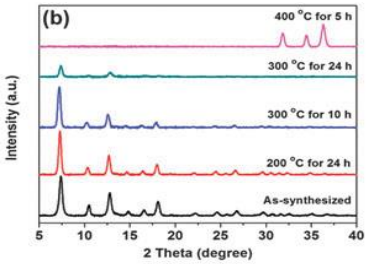
1 : 70 : 1238

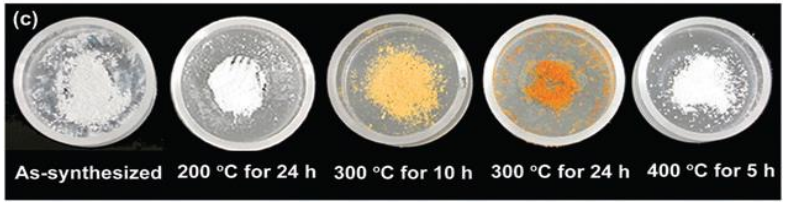
Stir ~5 min, rt

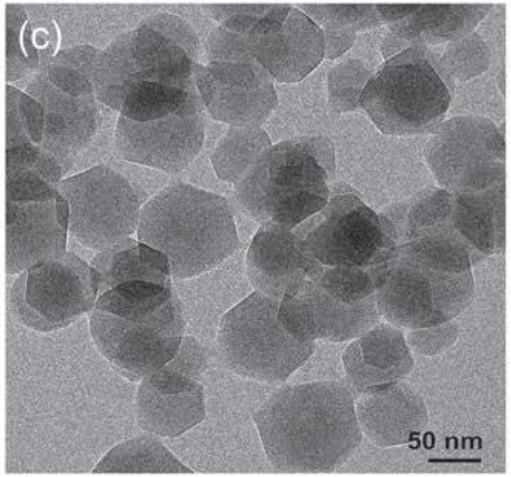


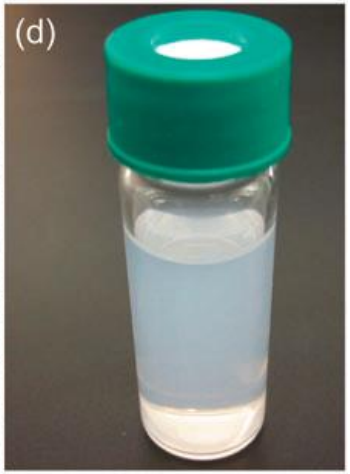






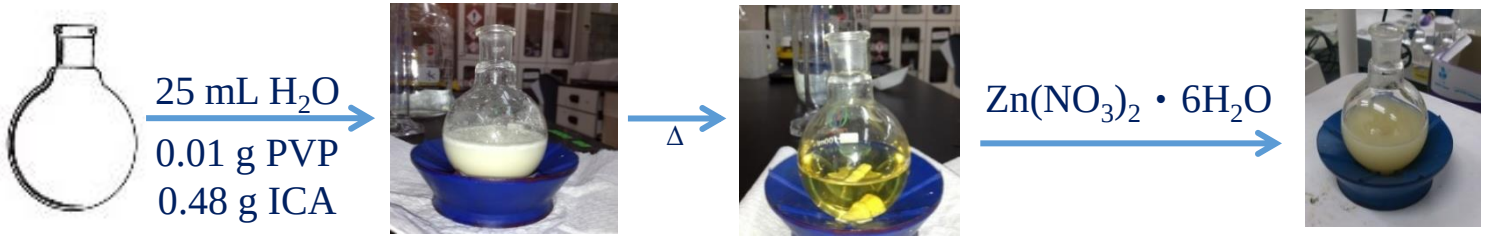






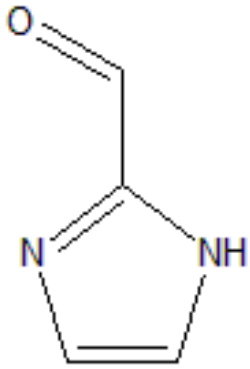
Zhiping Lai* *et al. Chem. Commun.*, **2011**, *47*, 2071–2073

Water Based Synthesis of ZIF-90

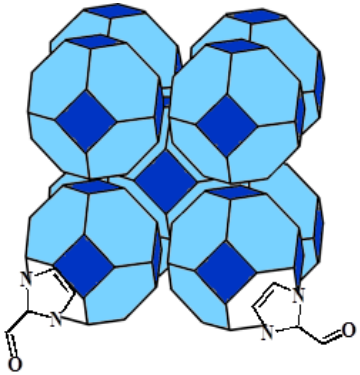


PVP ：Polyvinylpyrrolidone / ICA：Imidazole-2-carboxaldehyde

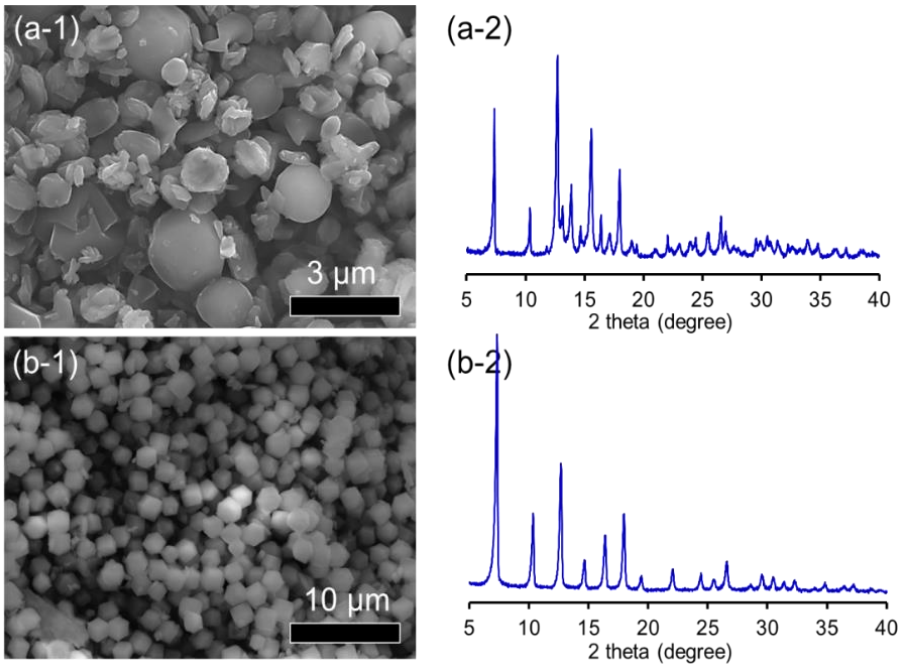
Zn^{2+} : ICA : H_2O
1 : 4 : 1244



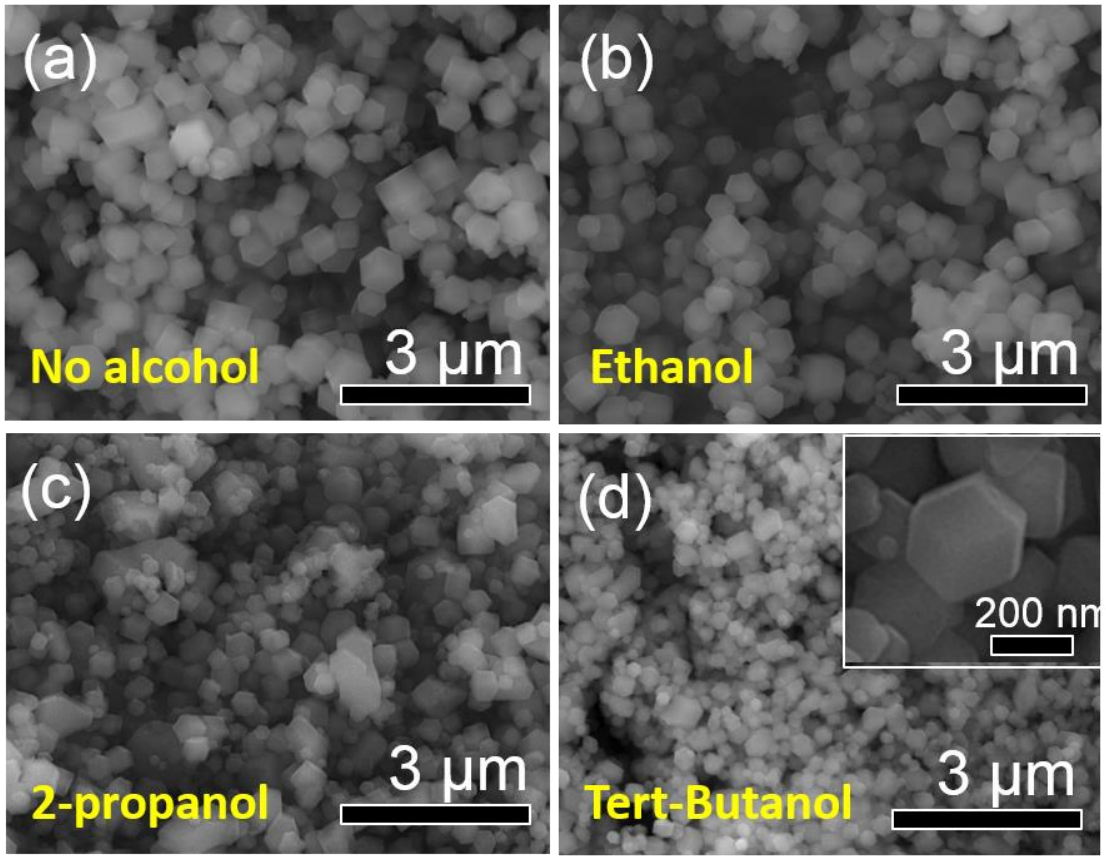
Imidazole-2-carboxaldehyde

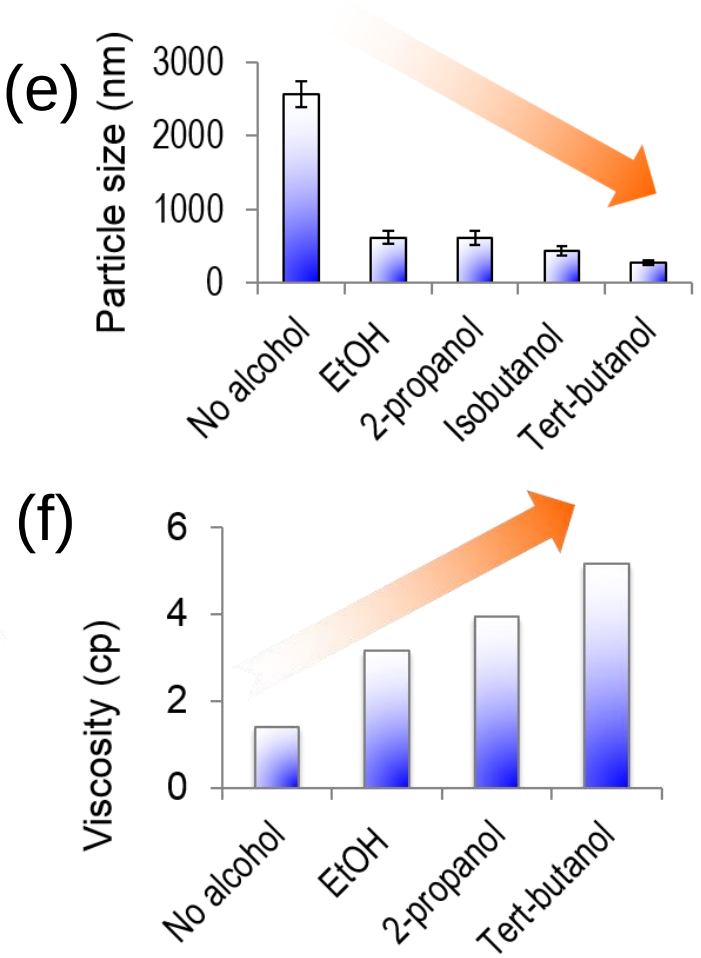


ZIF-90



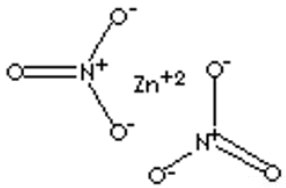
Controllable Particle Size by Viscosity Change of Synthetic System





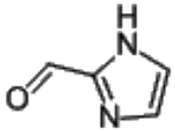
Cover Image

urnal 2013



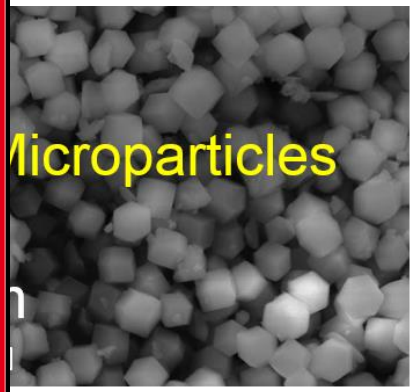
$Zn(NO_3)_2$ H_2C

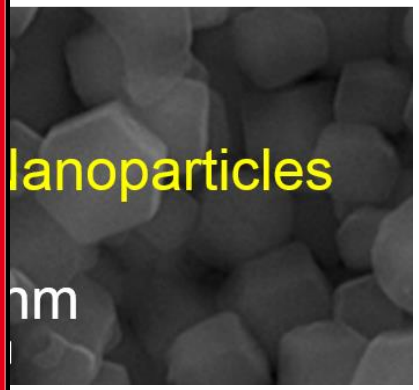
sy



ICA

Zec

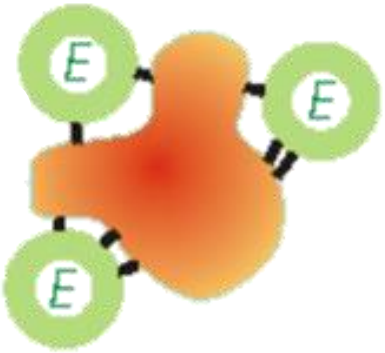




S-C Wang, Kevin Wu* **3,** 19, 11139-11142

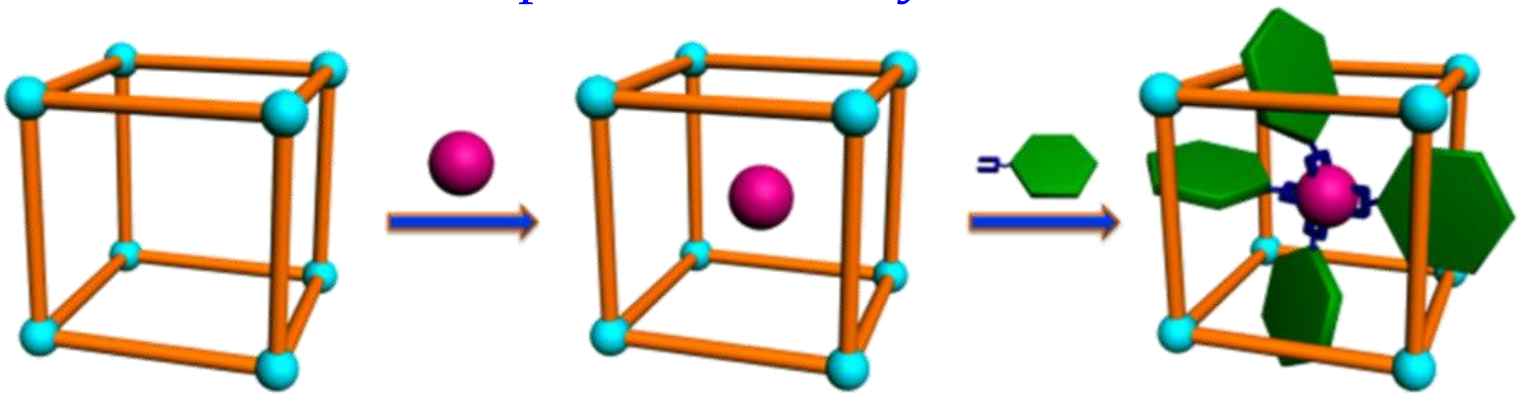
Enzyme Immobilization

A: Covalent bonding



B: Physical absorption

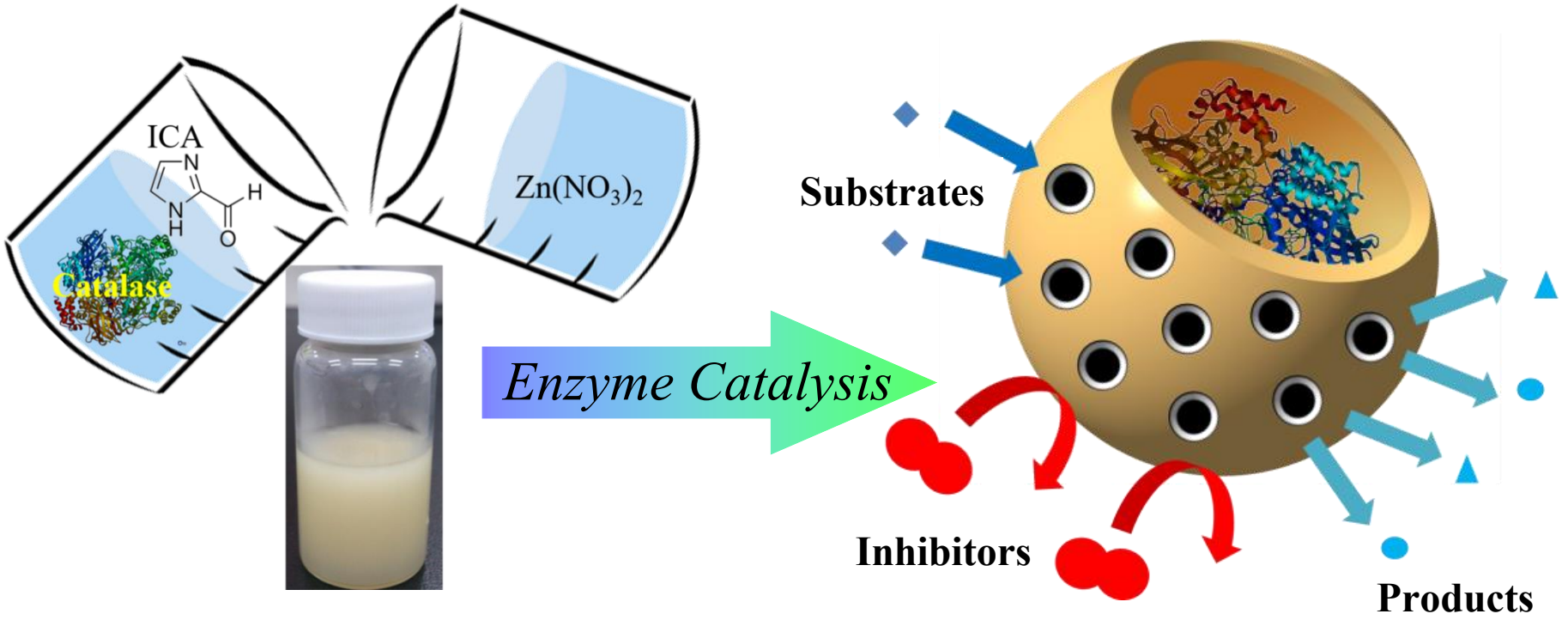
C: Ship-in-a-bottle synthesis



J. Am. Chem. Soc. **2000**, 122, 6311. ;*J. Am. Chem. Soc.* **2014**, 136, 1202.

De Novo Encapsulation and Enzyme Catalysis

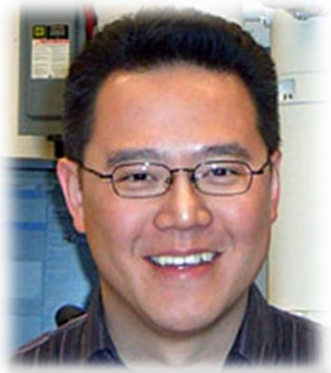
Shao-Chun Wang



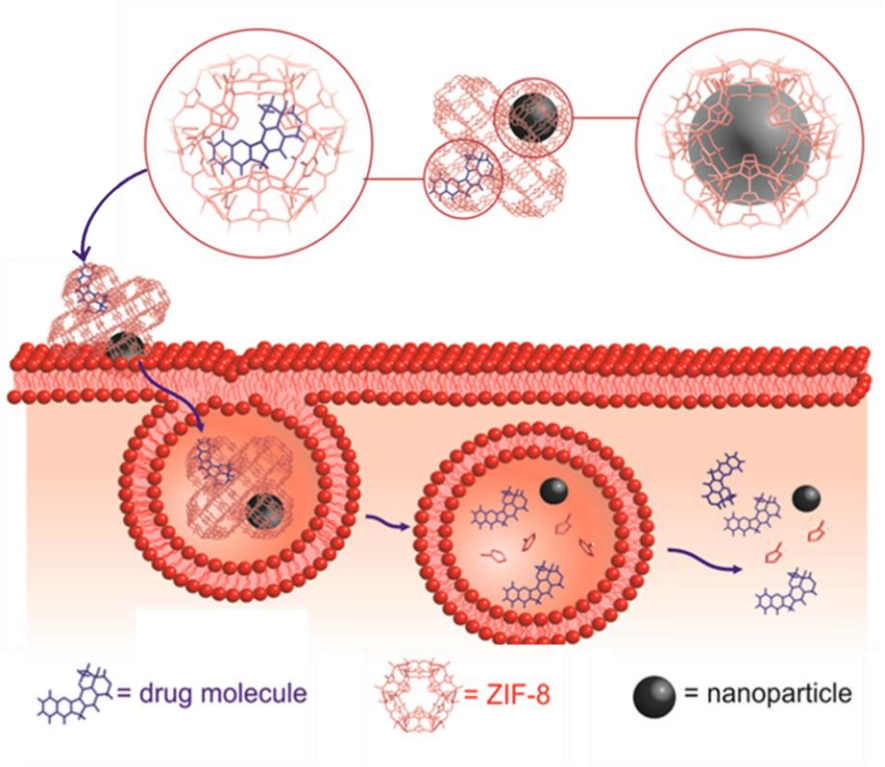
Catalase@ Zeolitic Imidazolate Framework-90

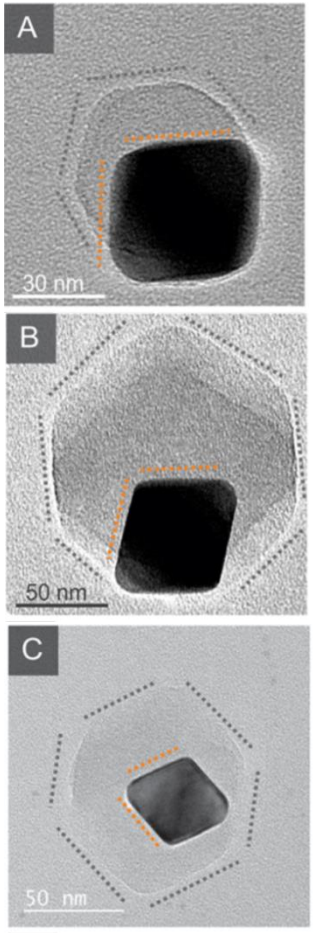
Enzyme protected and no leaching problem

Catalysis: Metal@ZIF-8



Prof. Tsung

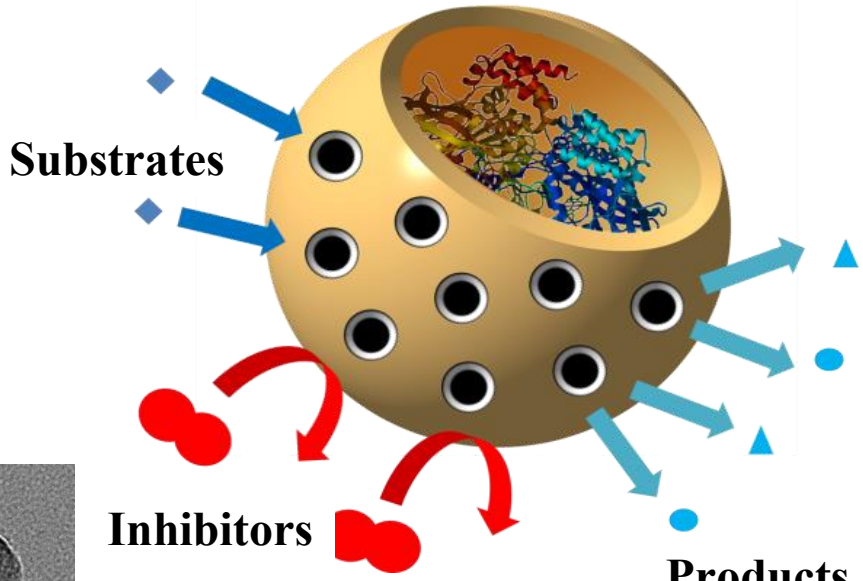


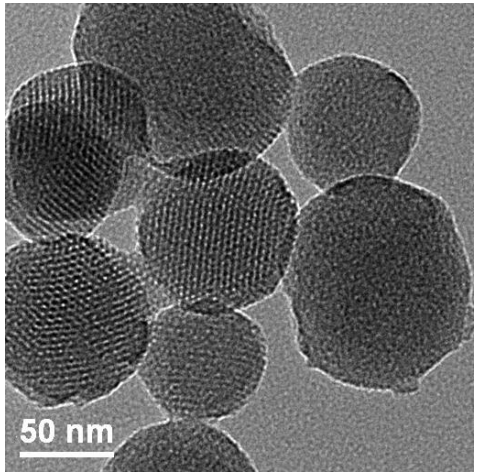


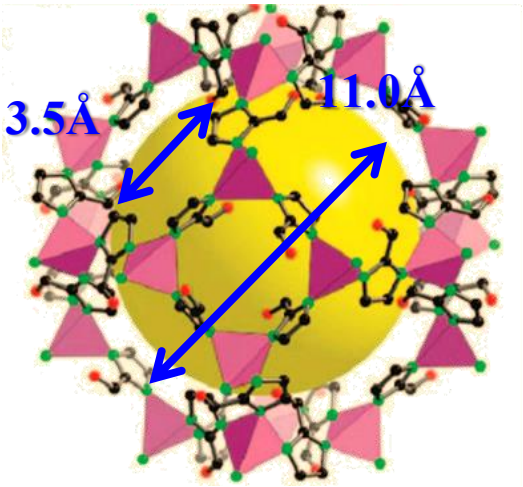
Chia-Kuang Tsung*, ACS *Nano*, **2014**, *8*, 2812–2819

Chia-Kuang Tsung*, *J. Am. Chem. Soc.* **2014**, *136*, 10561−10564

Biocatalysis: Enzyme@ZIFs

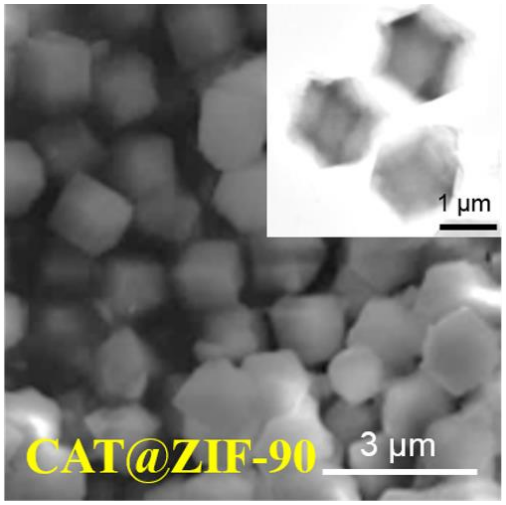


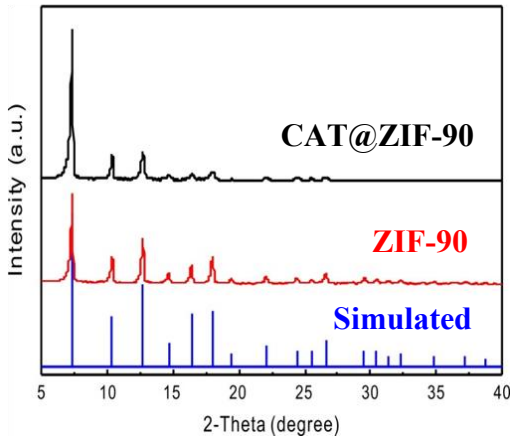


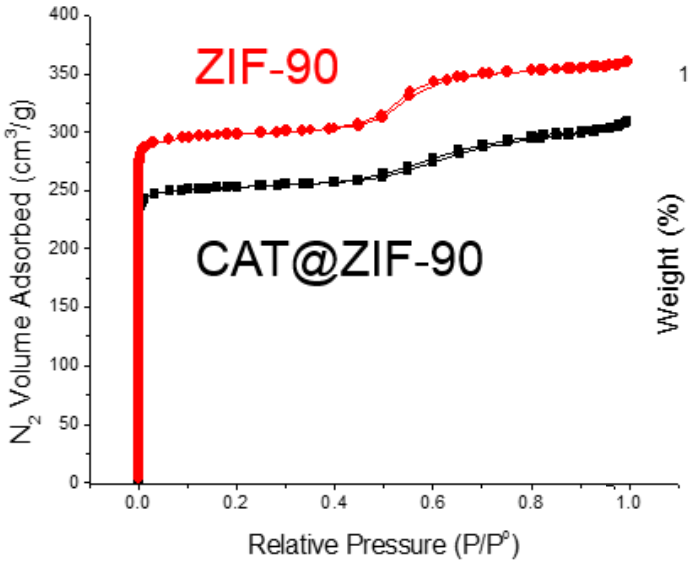


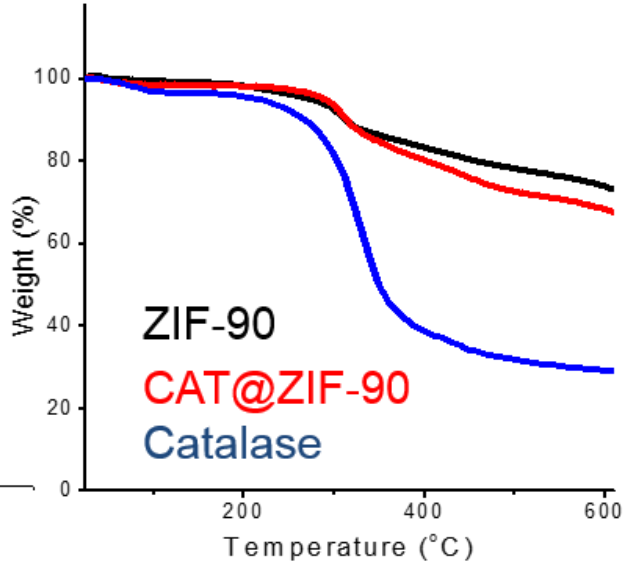
MOFs: ZIF-90; Enzyme : Catalase-hydrogen peroxide decomposed

Characterizations of CAT@ZIF-90





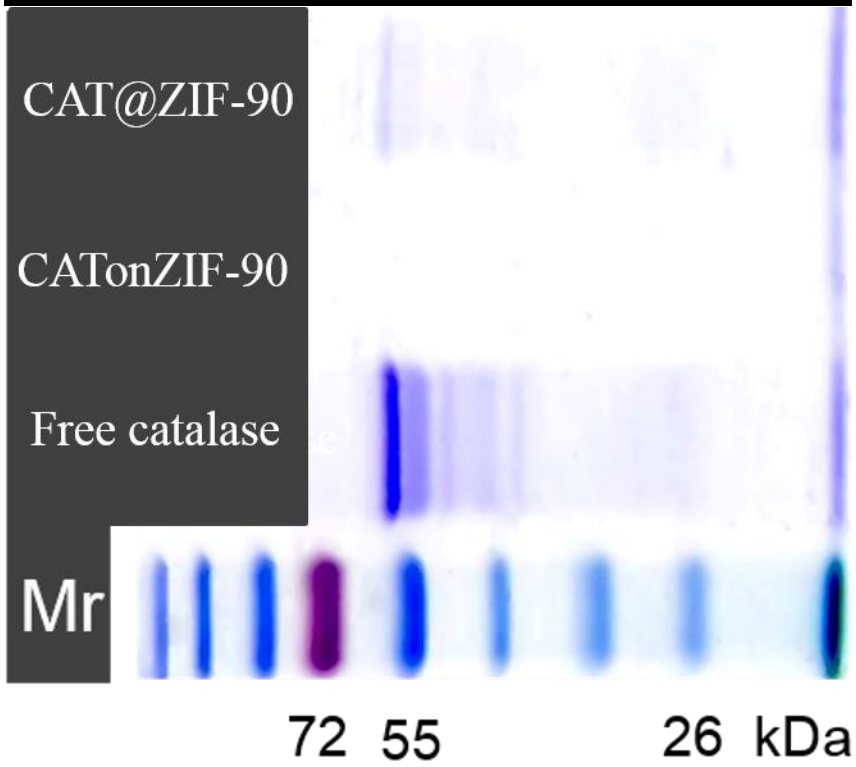




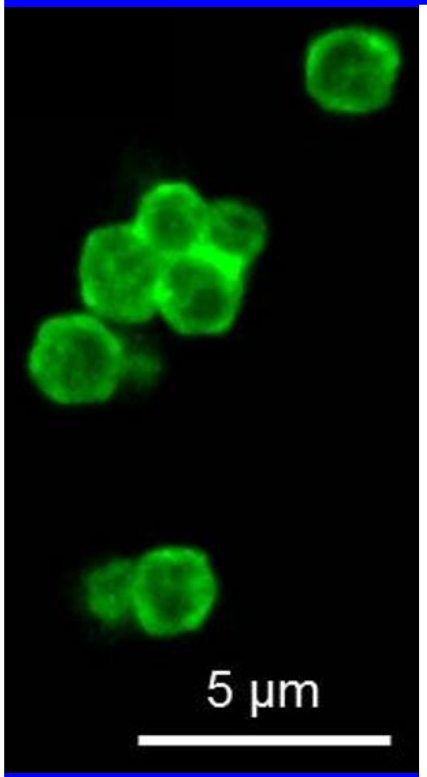
	S_L (m^2/g)	S_{BET} (m^2/g)	V_{total}(cm^3/g)	V_{micro} (cm^3/g)
ZIF-90	1309	992	0.55	0.38
CAT@ZIF-90	1111	843	0.47	0.37

Seeing embedded enzyme in ZIF-90!!?

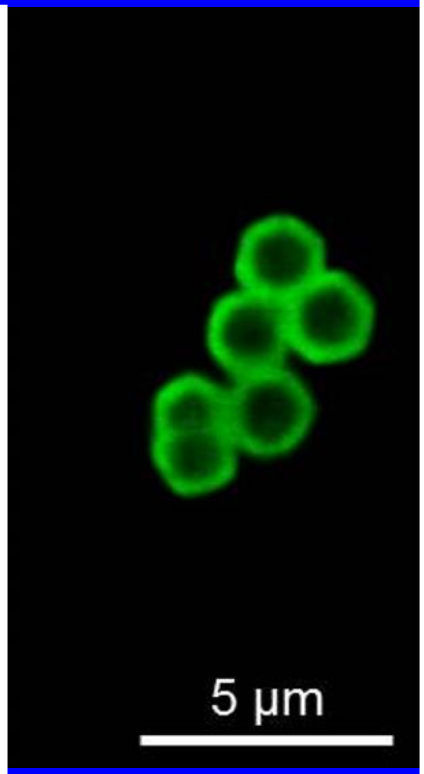
SDS-PAGE gel



Confocal microscope images

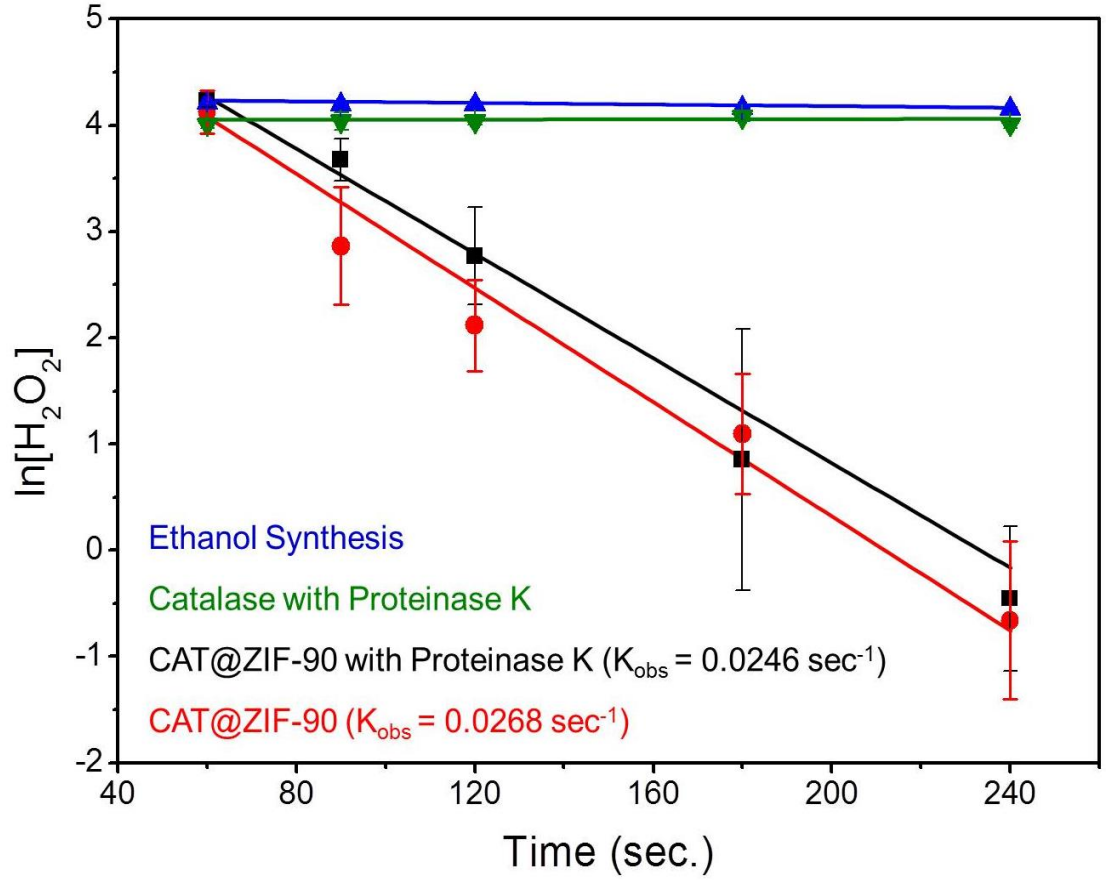


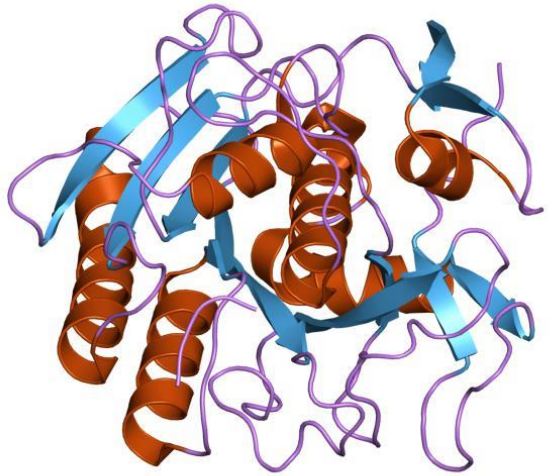
FITC-CAT@ZIF-90



FITC-CAT-on-ZIF-90

Size-Selective Sheltering of Catalase in ZIF-90





Proteanase K: 28.9 kDa

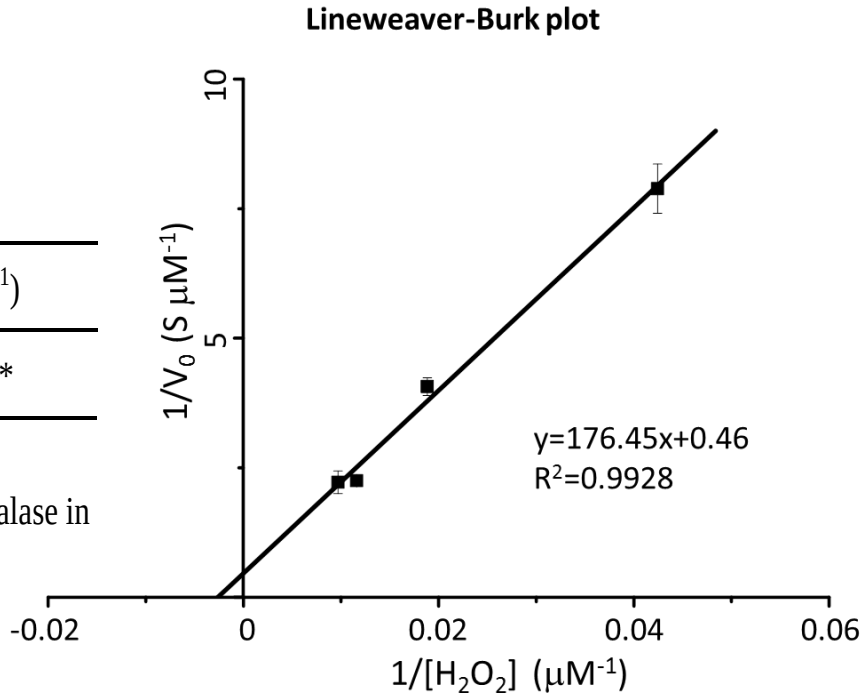
	Pore diameter (Å)
ZIF-90	4.8
CAT@ZIF-90	4.8

Size-Selective Sheltering of Catalase in ZIF-90

Table S3: The kinetic parameters on catalase in CAT@ZIF-90

	K_M (mM)	V_{max} (μM/s)	k_{cat} (s^{-1})
CAT@ZIF-90	0.38	2.17	26.06*

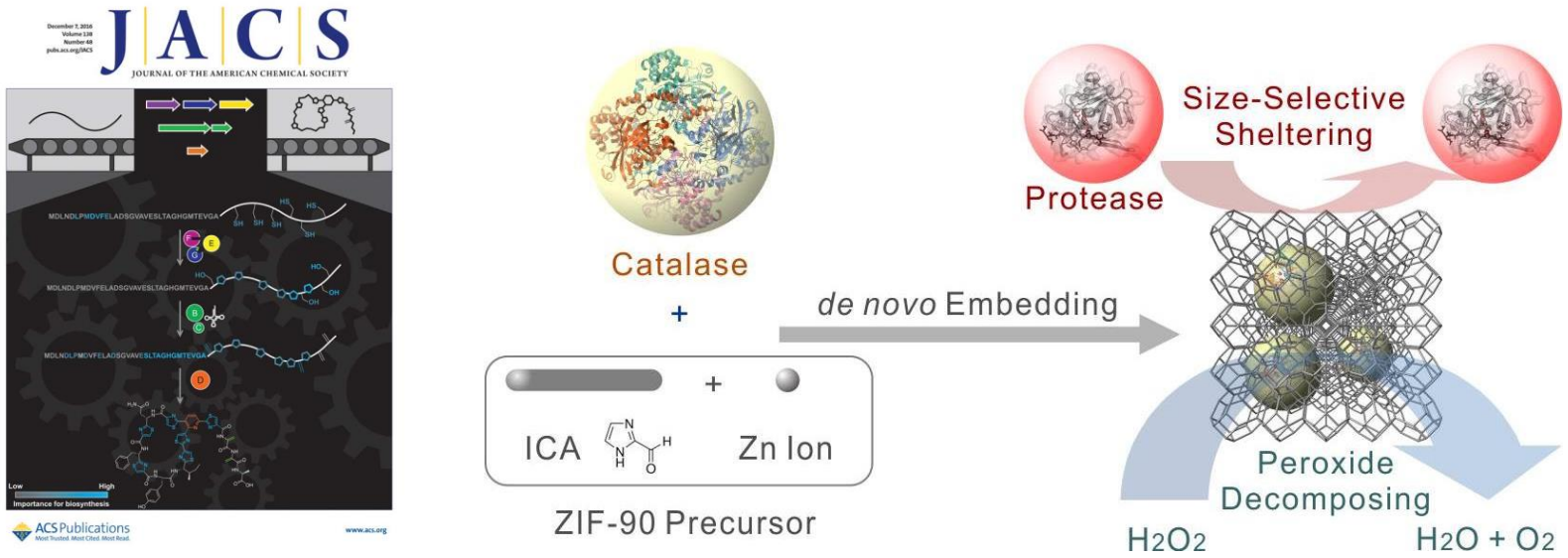
*: $[E]_T$ is calculated with approximately 5 wt. % loading efficiency of catalase in CAT@ZIF-90



Catalytic activity of catalase in different conditions

Lineweaver–Burk plot for determination the kinetic parameters on catalase in CAT@ZIF-90

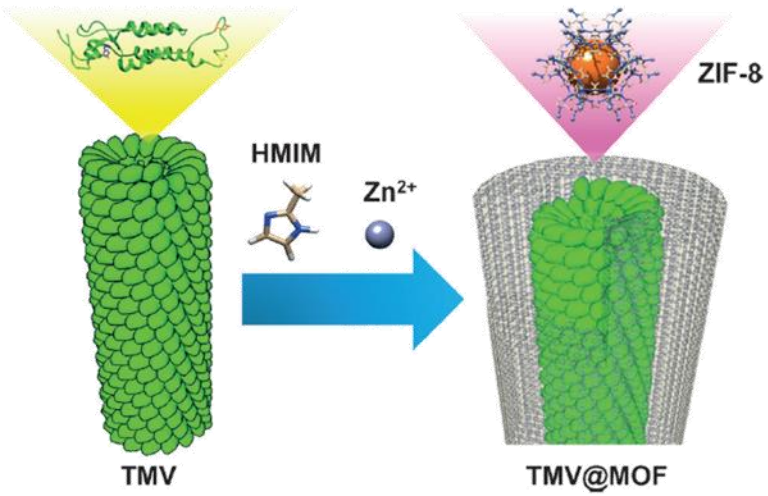
Selected by the special edition of virtual issue JACS 2016

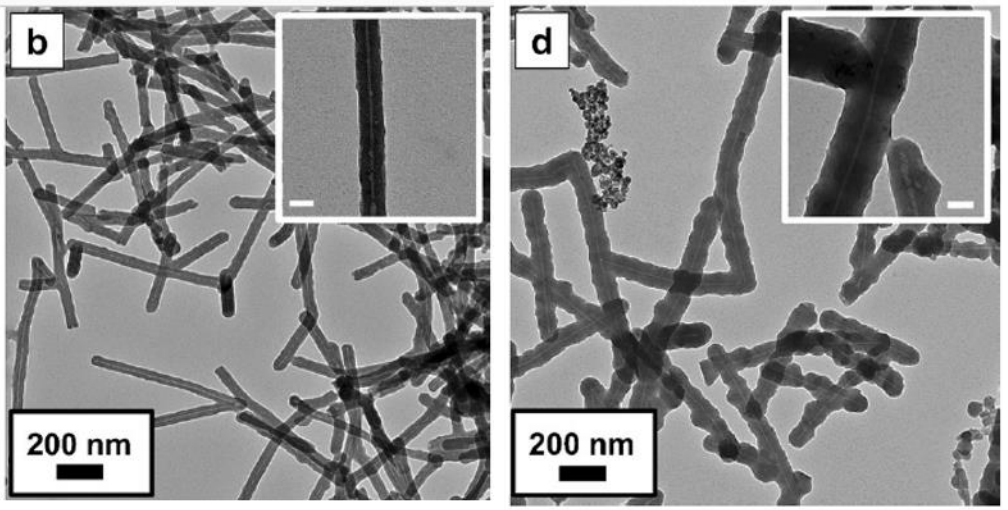


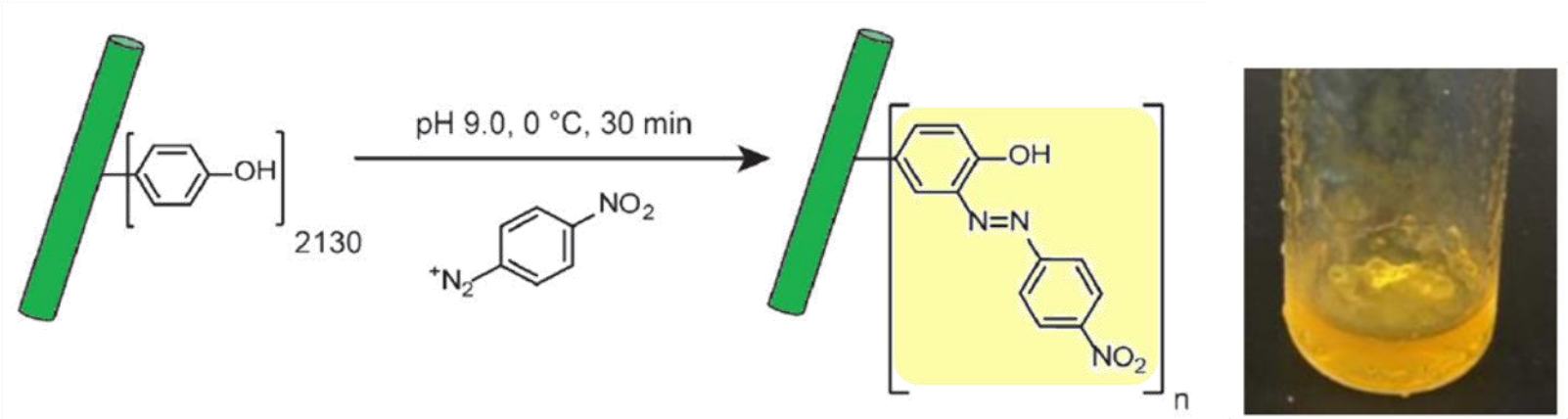
F.-K. Shieh,* S.-C. Wang, C.-I Yen, C.-C. Wu, Kevin Wu* and C.-K. Tsung* *et al.*, *J. Am. Chem. Soc.*, **2015,** 137, 4276–4279 (Citation:53)

Omar M. Yaghi.,* *J. Am. Chem. Soc.*, **2016,** 138, 15507-15509

Virus in MOF

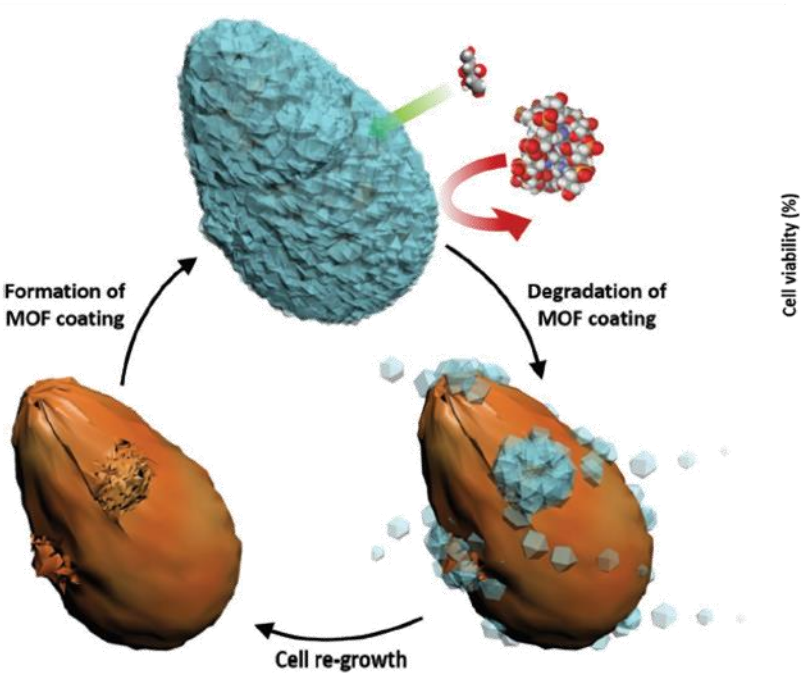


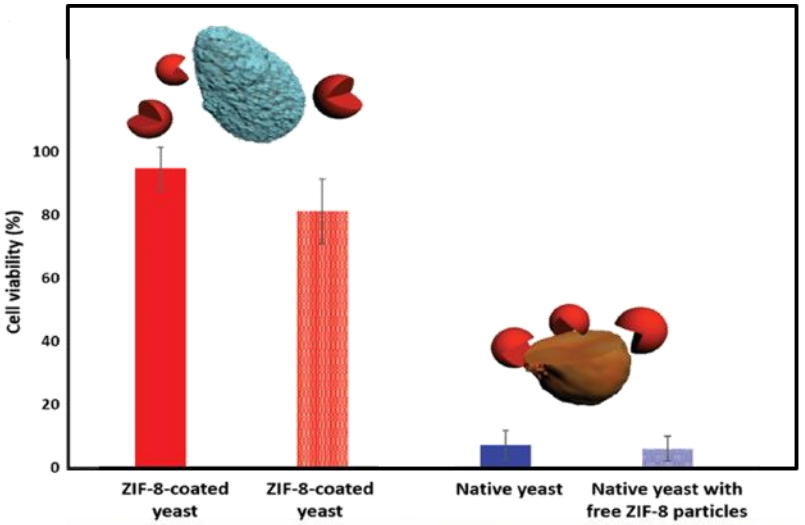


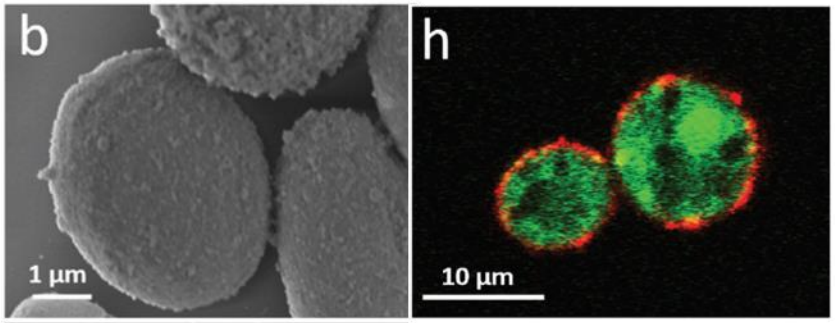


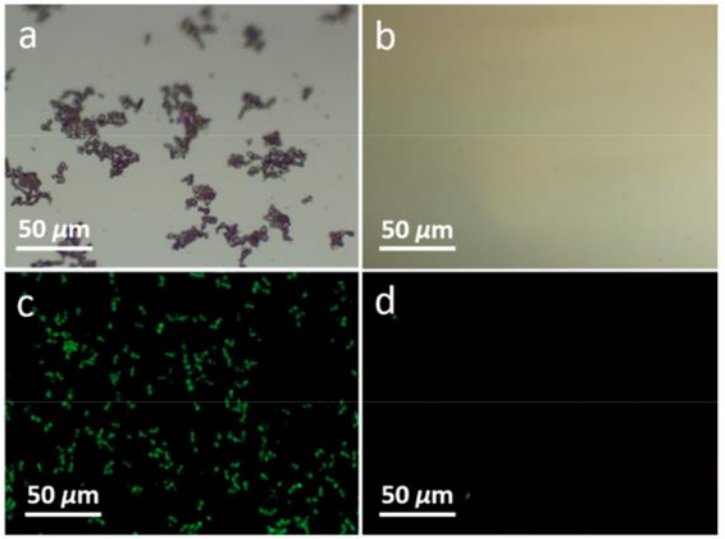
Angew. Chem. Int. Ed. 2016, 55, 1–7

Yeast wrapped by MOFs

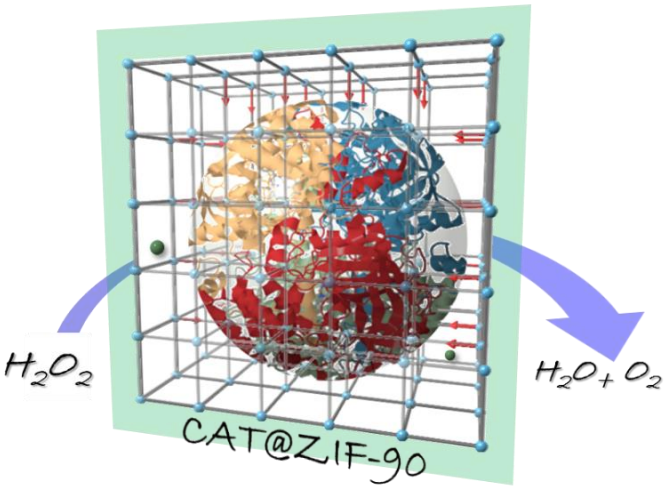


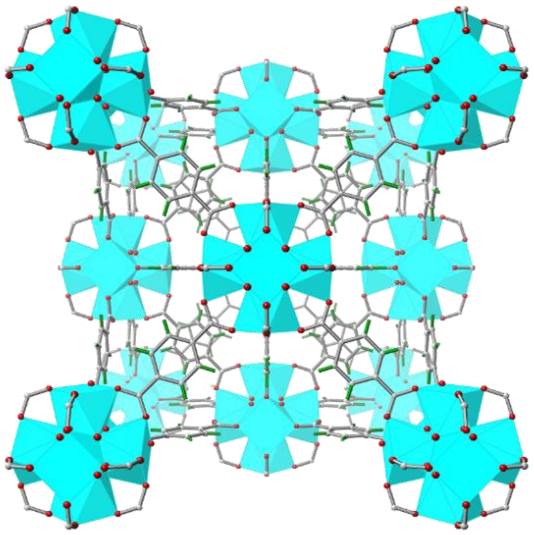






Adv. Mater. **2016**, ASAP





Enzyme-MOFs

2011

Immobilization: Physical absorption

Ma, S.* *J. Am. Chem. Soc.*, **2012**, *134*, 13188

Ma, S.* *J. Am. Chem. Soc.*, **2011**, *133*, 10382

2015

Covlent immobilization

H. C. Zhou,* *Nat. Commun.*, **2015**, 6, 5979

Controllable release

P. Falcaro,* *Nat. Commun.*, **2015**, 6, 7240

Size Shielding & Proteinase K

Fa-Kuen Shieh,* *J. Am. Chem. Soc.* **2015**, 137, 4276

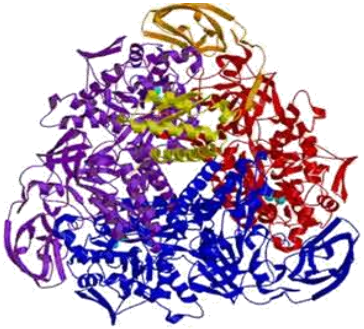
2016

Long-term stability of OPAA@MOF

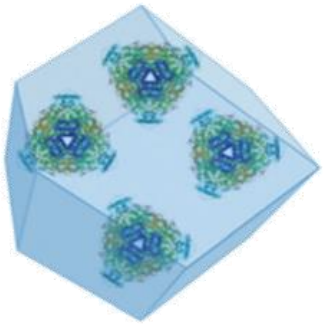
Omar. K. Farha,* *J. Am. Chem. Soc.*, **2016**, *138*, 8052

Why enzyme immobilization conquer denature?

Proteinase K



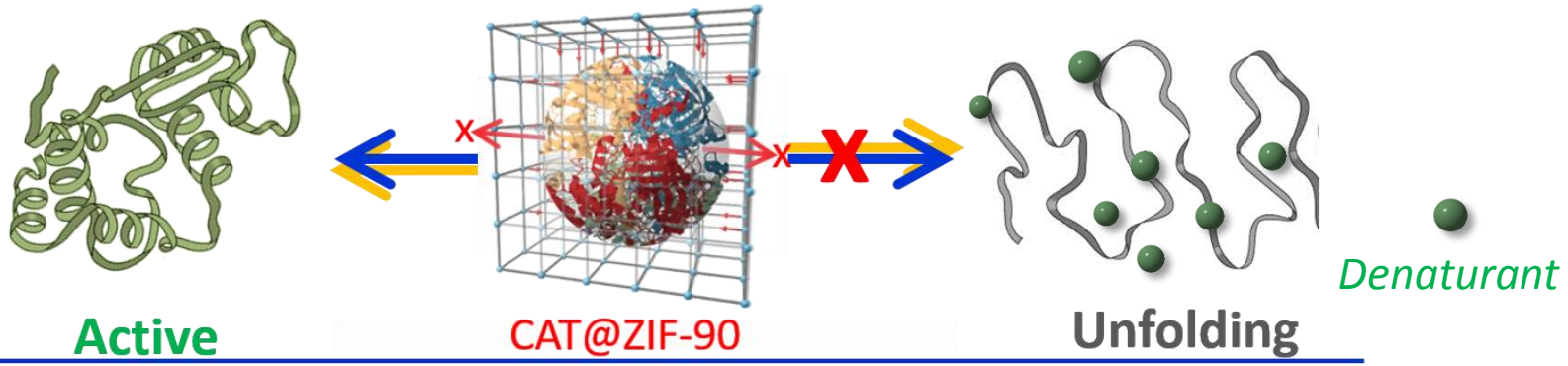
Enzyme

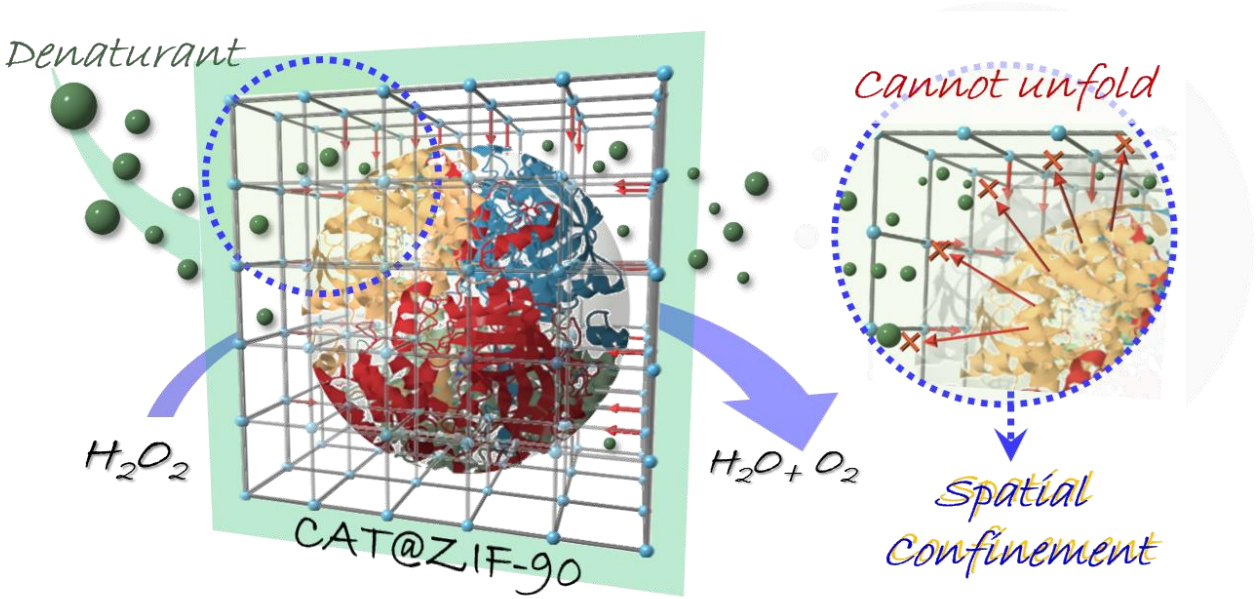


Enzyme@MOFs

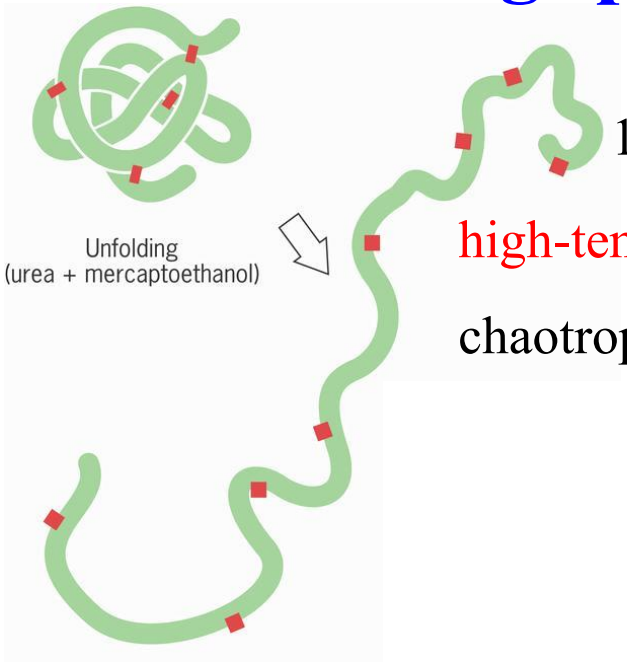
Fa-Kuen Shieh,* *et. al., J. Am. Chem. Soc.* **2015**, 137, 4276

Spatial Confinement Effect

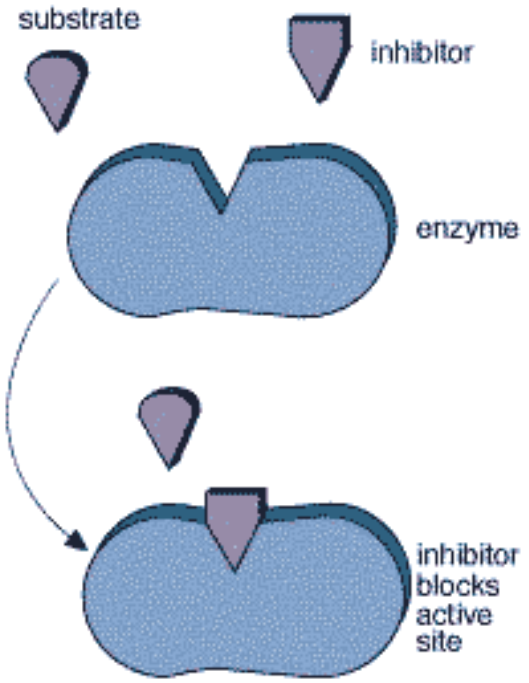




Probing spatial confinement effect



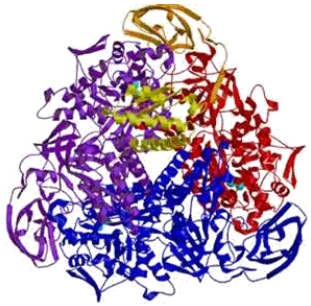
1) Enzyme denaturation by unfolding the structure: high-temperature or denaturing treatments such as **urea**-a chaotropic molecule- disrupting hydrophobic interactions.



2) Enzyme inactivation was also achieved without structural changes by blocking the active site using inhibitors.

Catalase inhibition by 3-AT

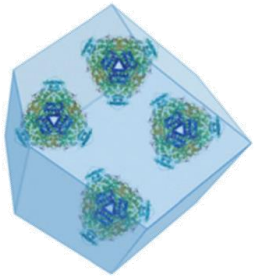
Urease@ZIF-90:



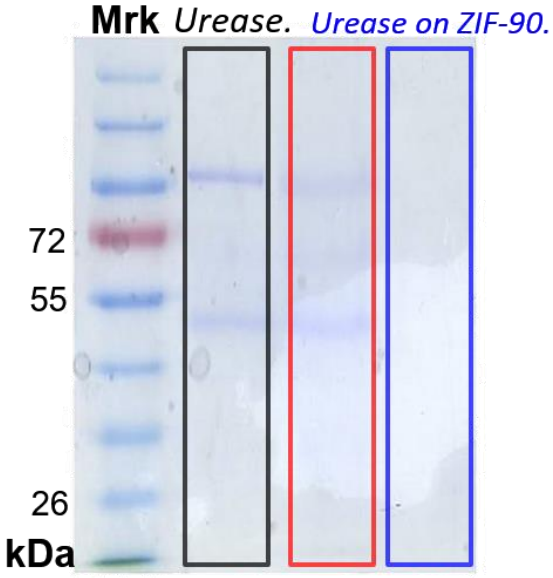
Urease

de novo approach of Urease@ZIF-90

1. Mw: 440–480 kDa
2. *Urease from Jack Bean*
3. Catalytic reaction-**Hydrolysis of Urea**



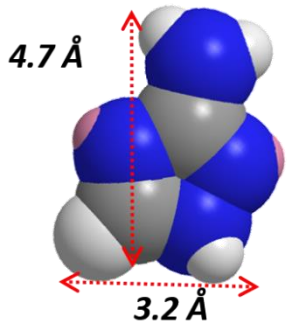
Urease@ZIF-90



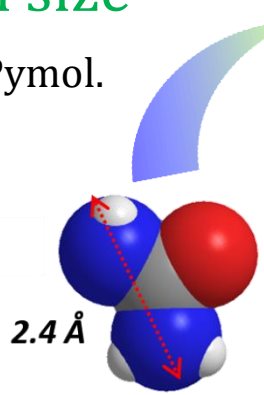
Urease@ZIF-90

Dimensional size

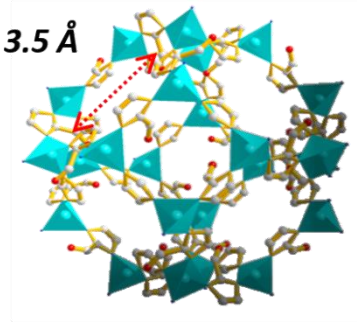
Calculated via Pymol.



3-Amino-1,2,4-triazole

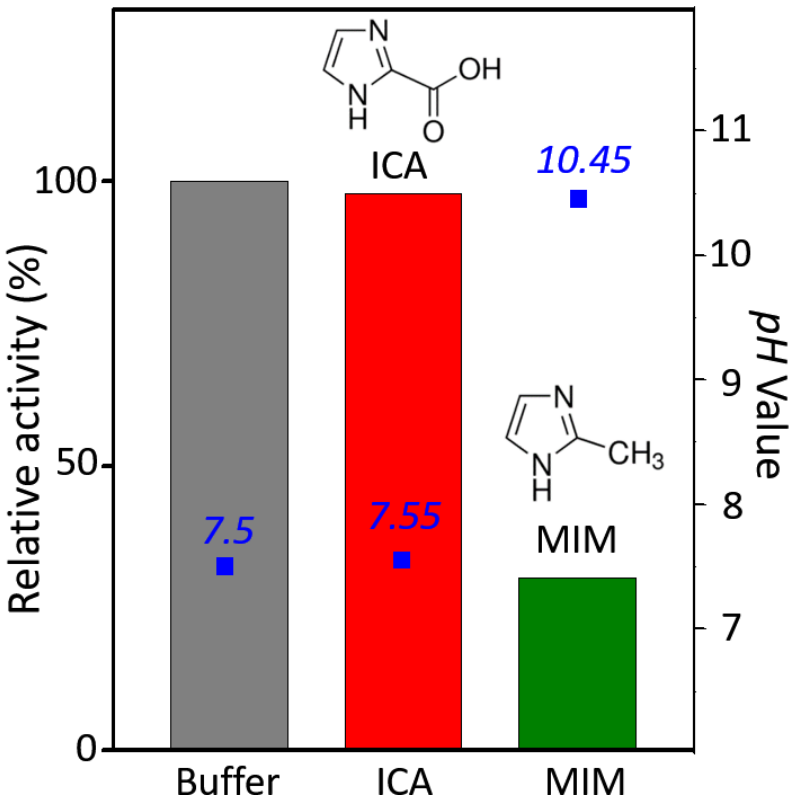


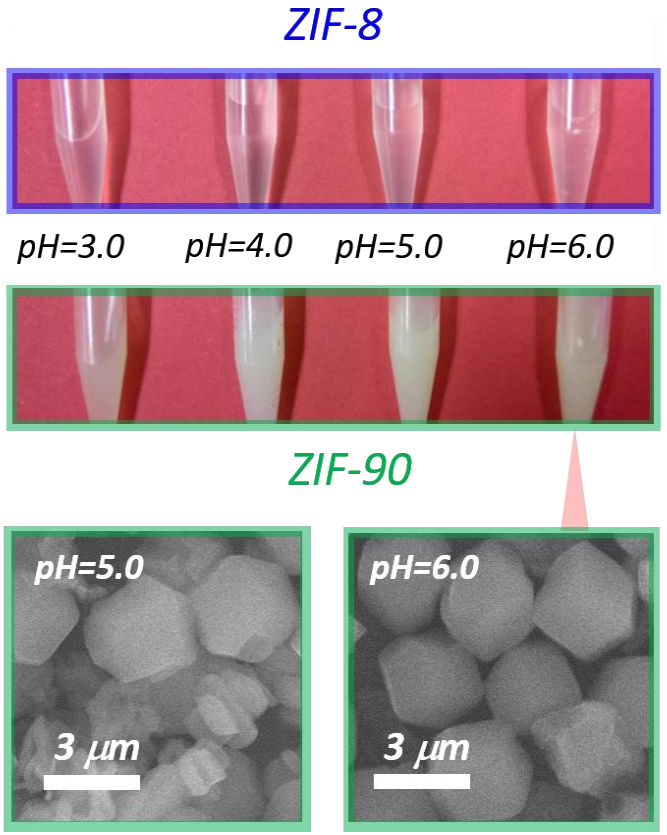
Urea



ZIF-90

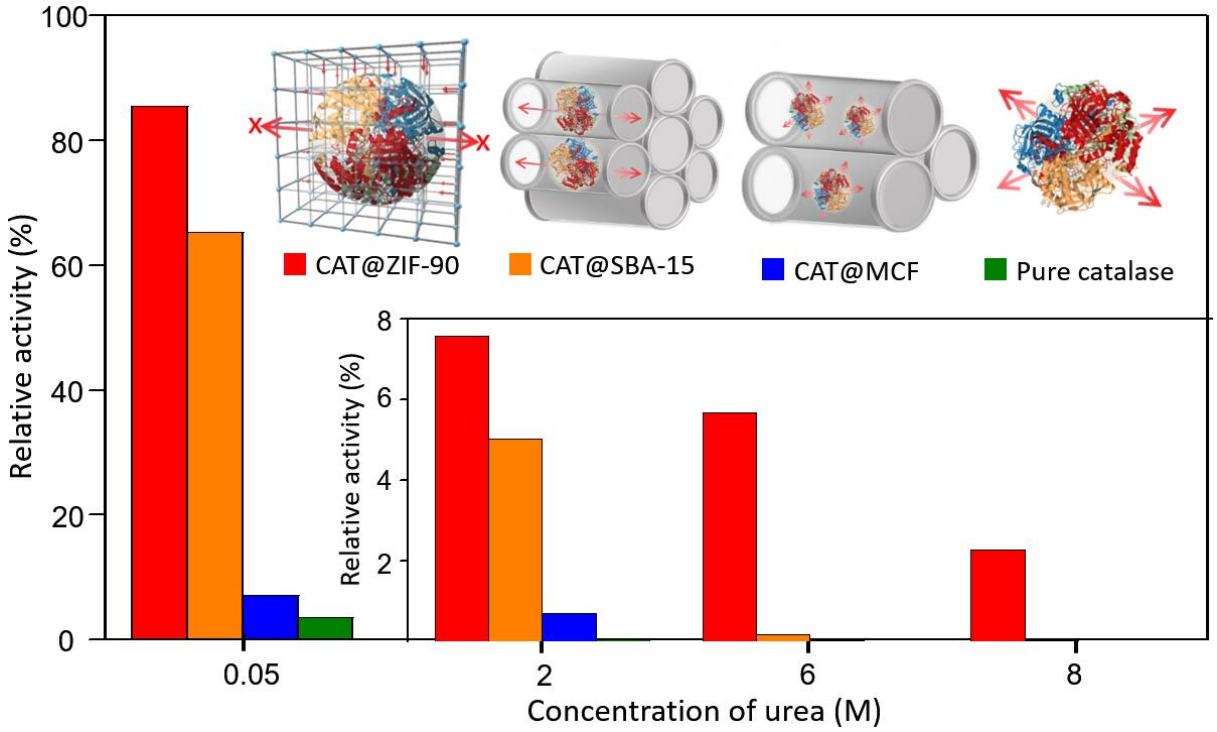
ZIF-90 selected for demonstrating hypothesis

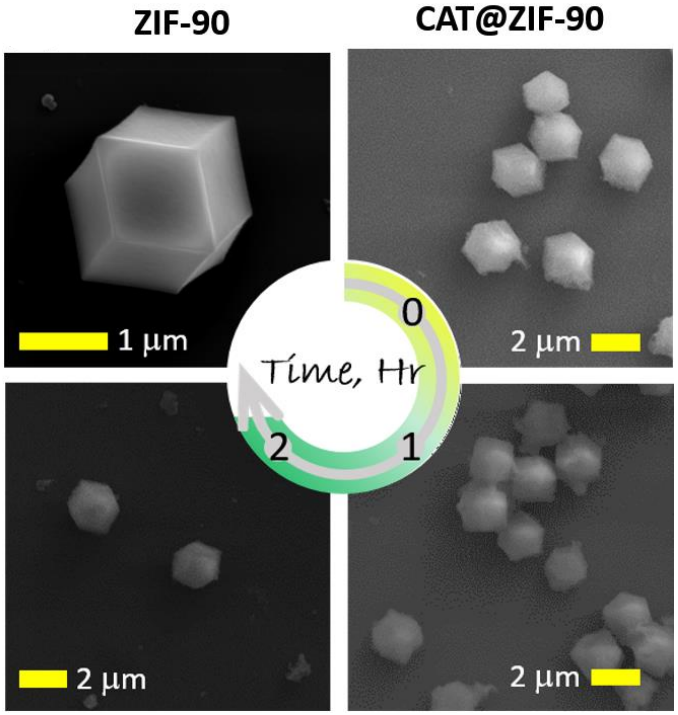




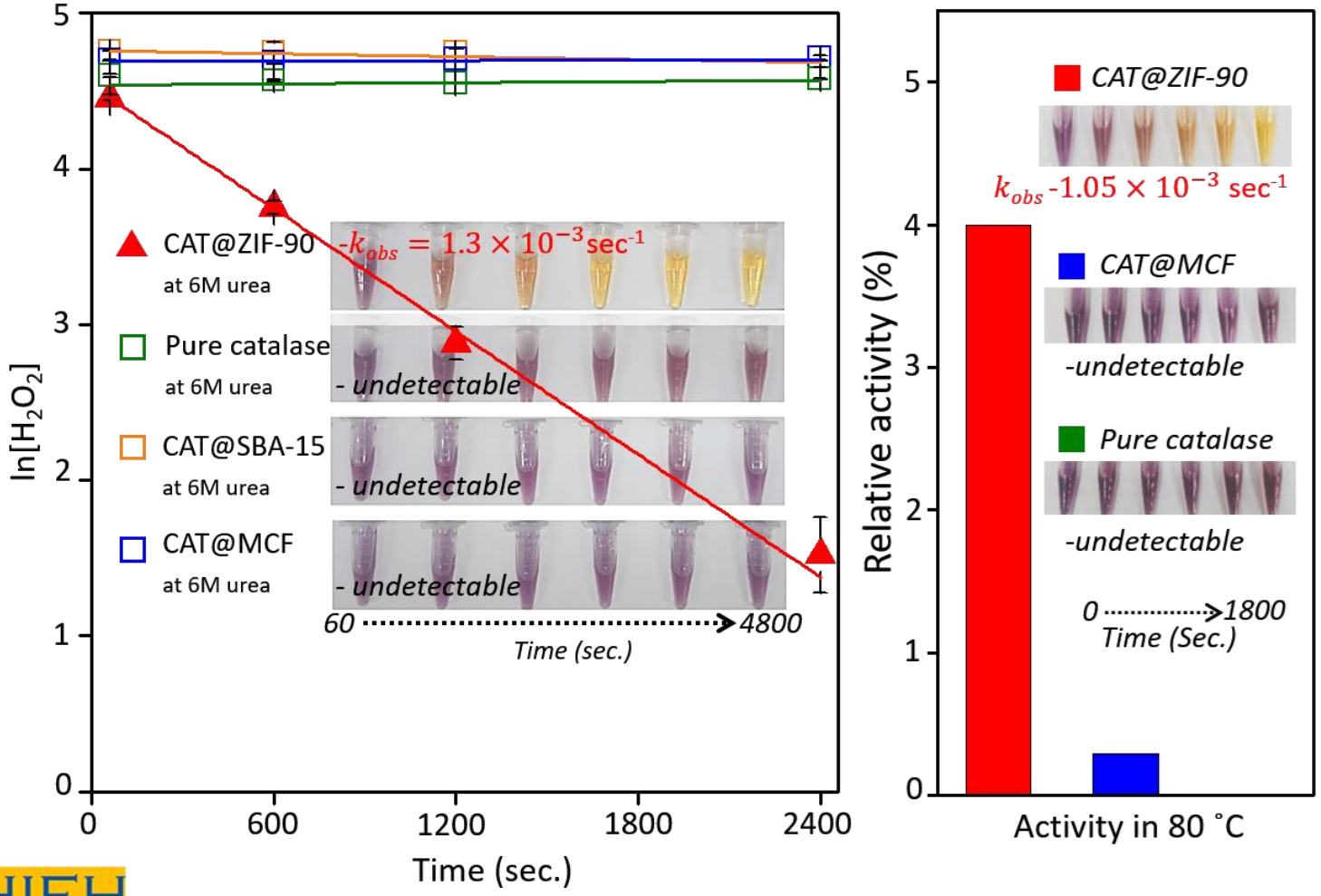
****50mM Citric buffer

Relative activity of CAT@ZIF-90 under urea

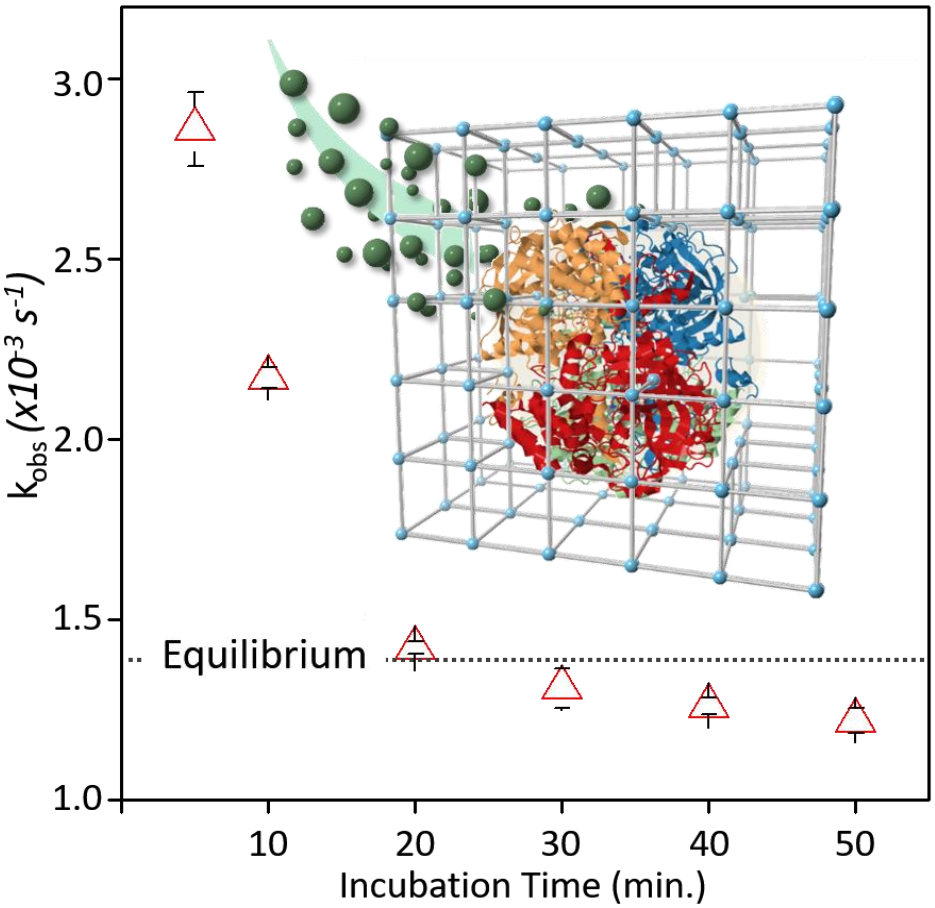


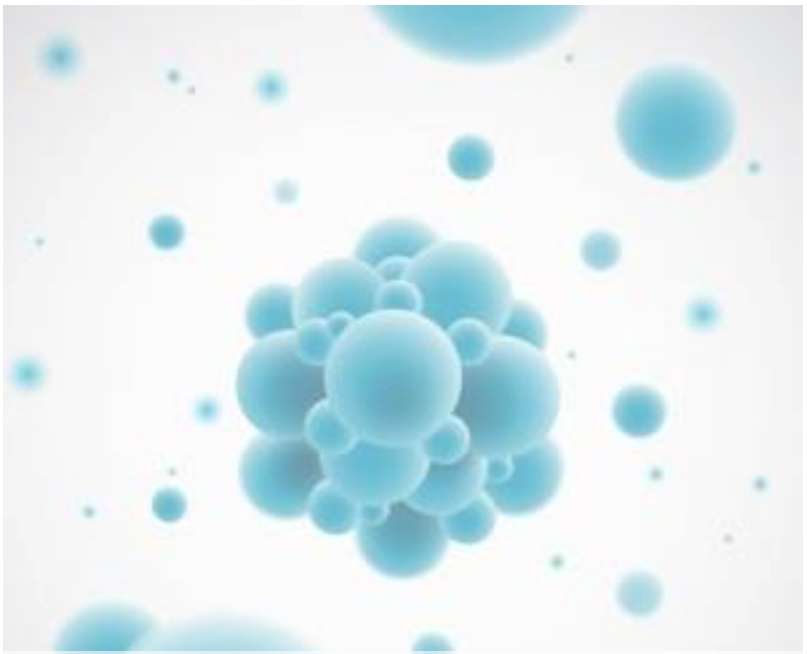


Kinetic decomposition of H_2O_2 under denatured conditions



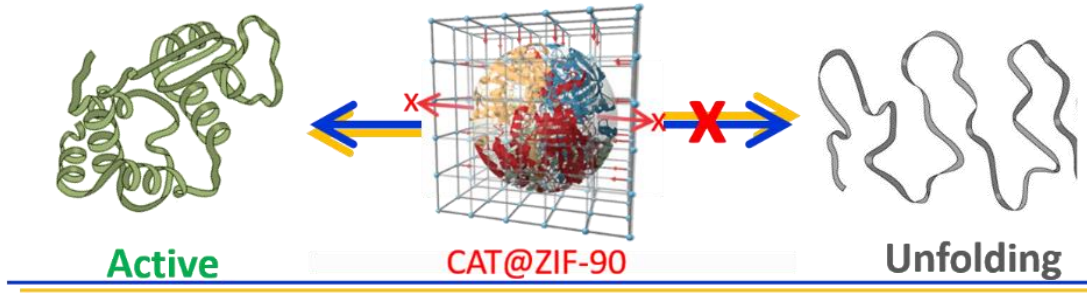
Local concentration reached equilibrium



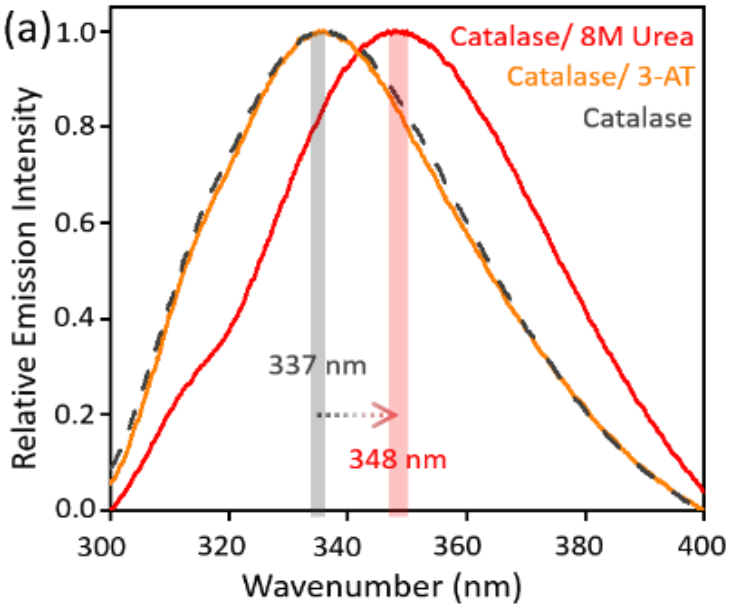


Biological Functional Capability k_{obs} reached constant after 30 min Incubation

Unfolding enzyme



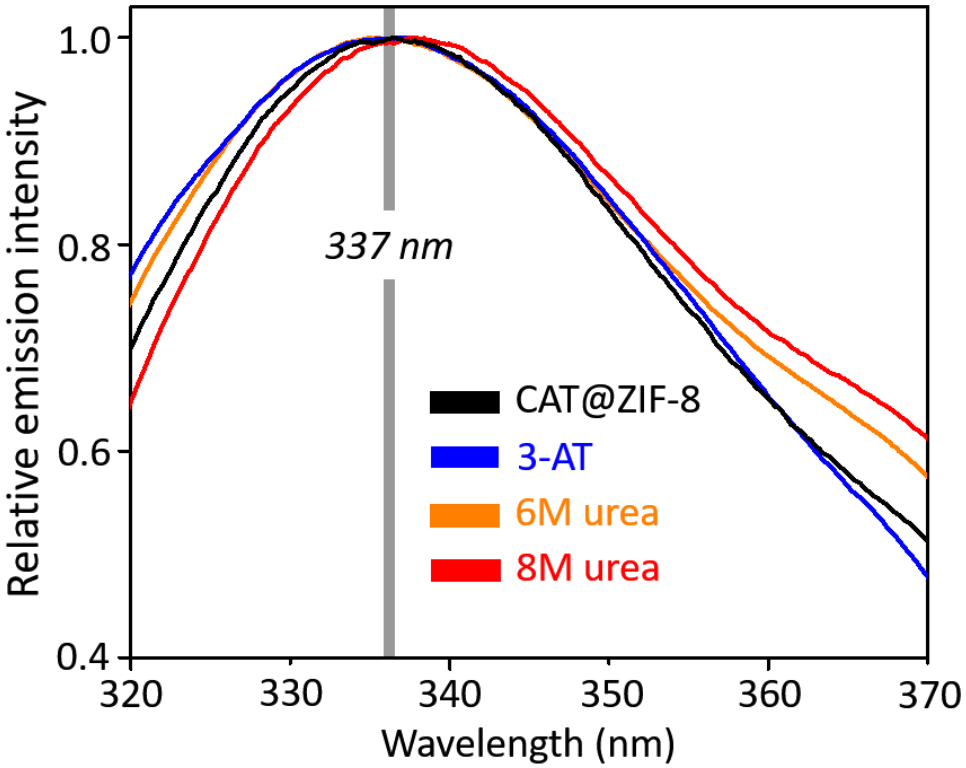
Fluorescence spectra using wavelength$_{excitation}$ as 280 nm

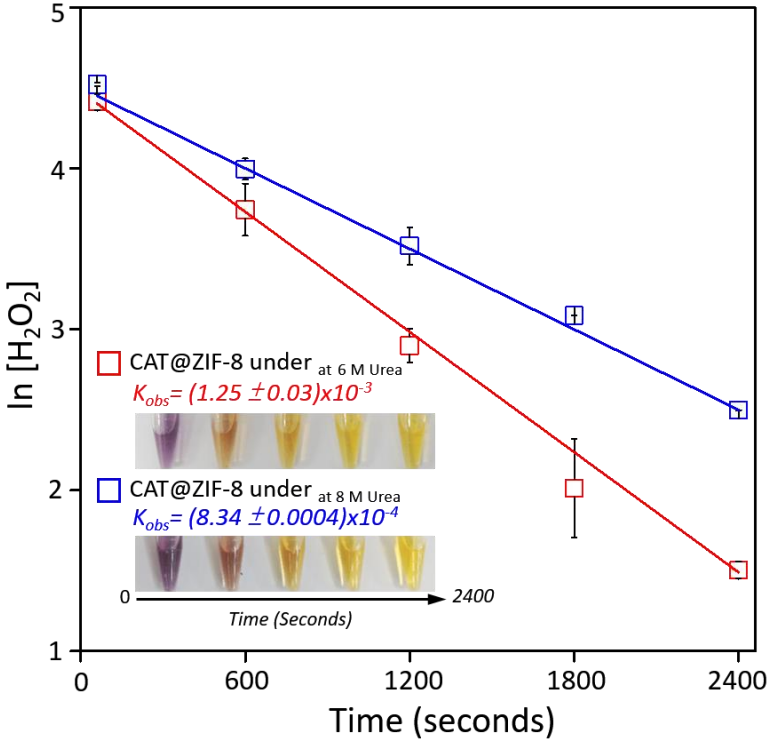


J. Am. Chem. Soc., **1975**, 97, 4131–4133

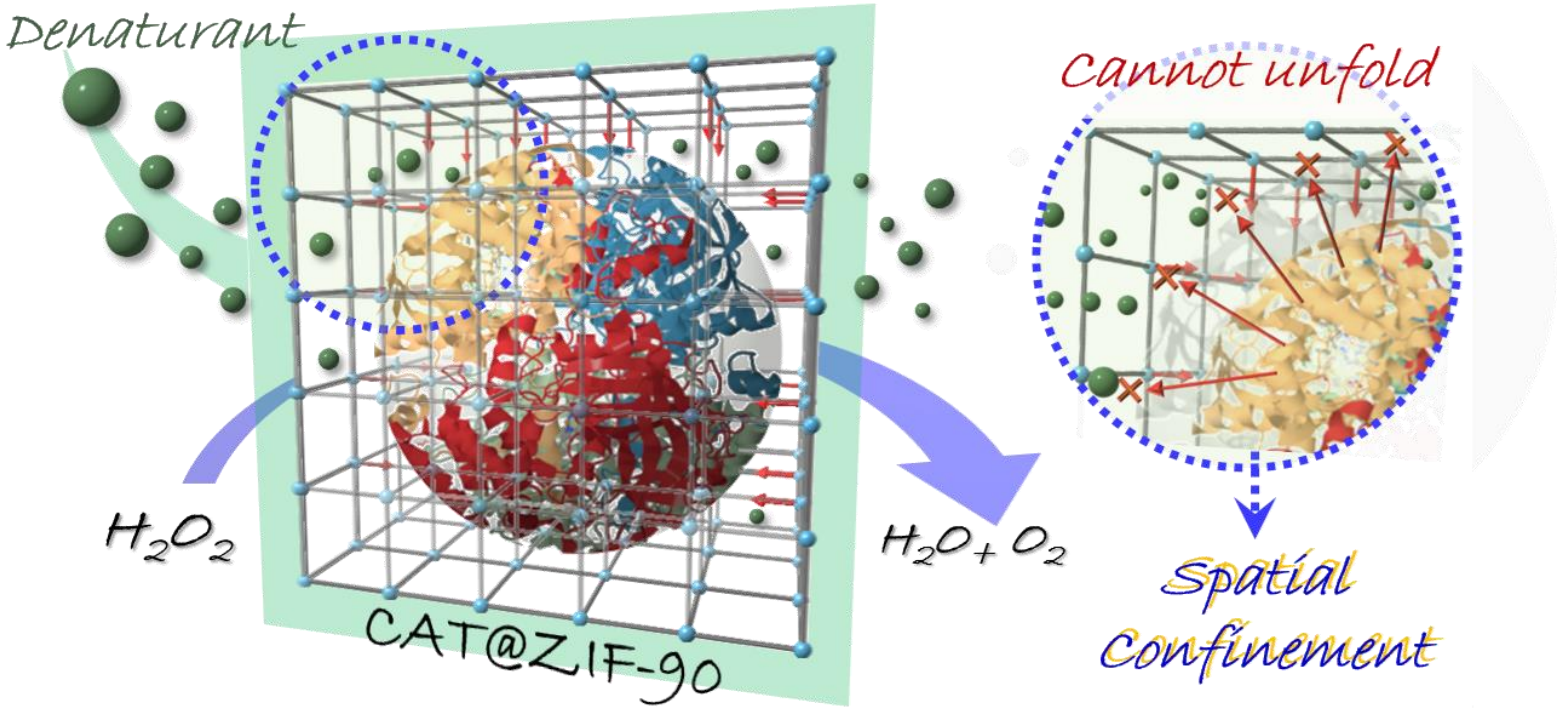
Fluorescence Spectra:

CAT@ZIF-8 under 3-AT and urea





Spatial Confinement Effect in Metal-Organic Frameworks Conquers Enzyme Unfolding: Boosting the Biological Stability of Catalase@ZIF-90 in Urea

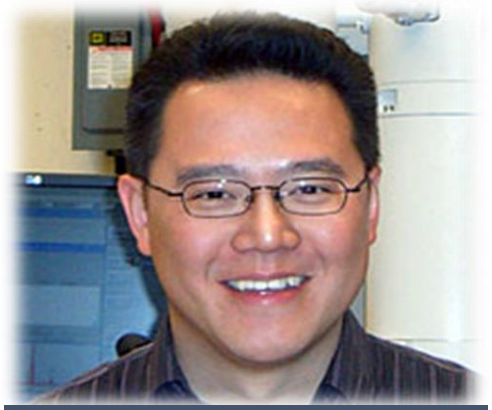


Ready to Submit


Long way to go ……..

Acknowledgements

Collaboration Group



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Nat. Taiwan Univ.

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National Central University

Publication Contributions

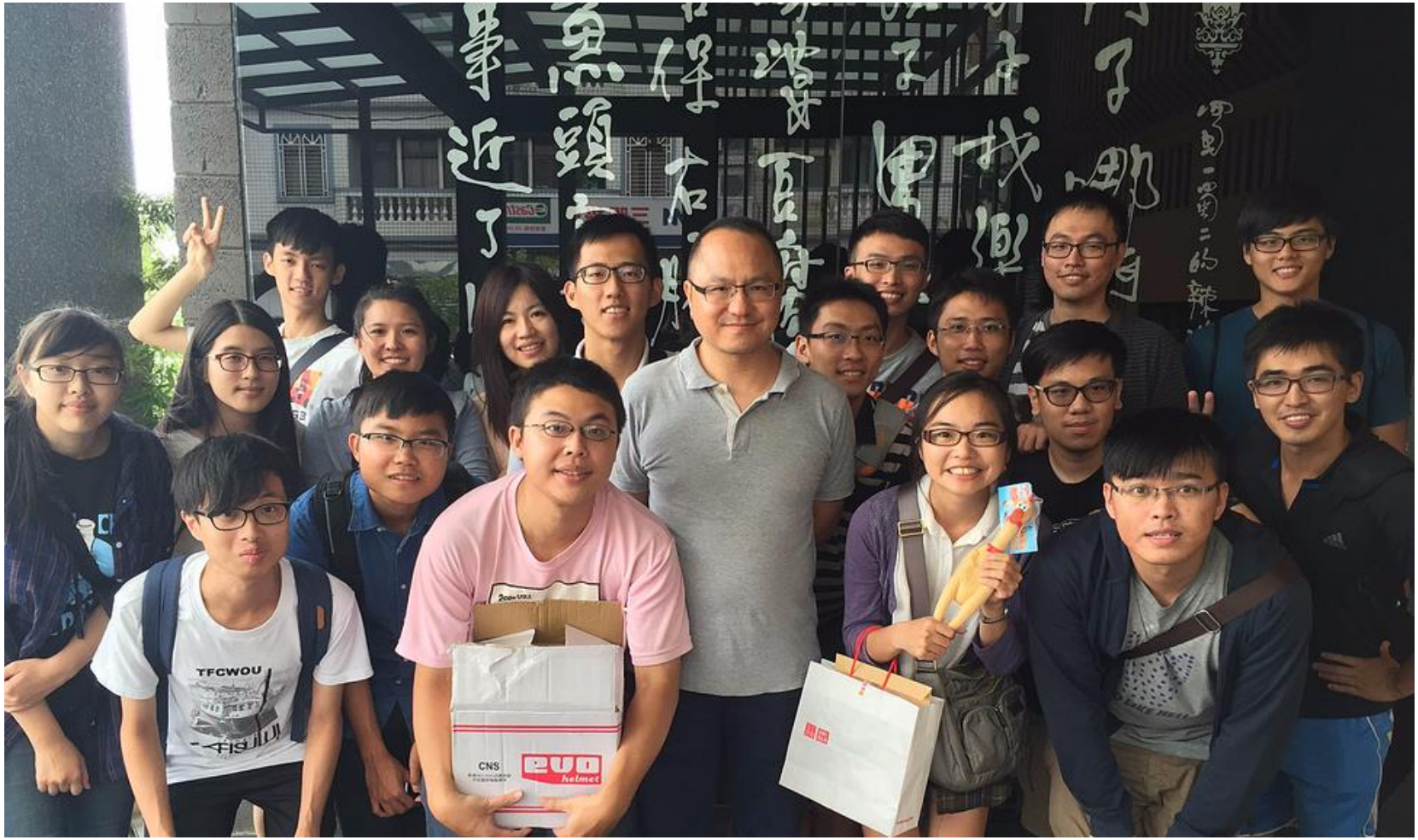
JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

CHEMISTRY A European Journal

王劭群/NCTU　顏嘉儀/NTHU　吳哲偉/NCU　羅煒勝/NCU

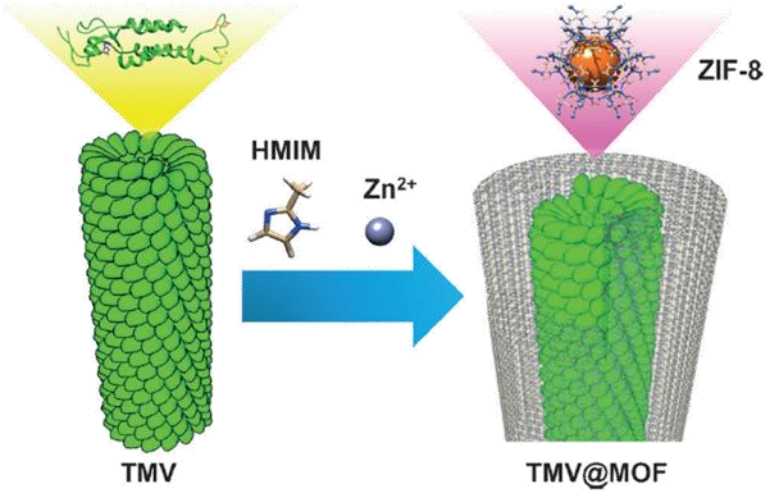
吳征戰/NCU　廖富祥/NCCU　許育慎/NCU

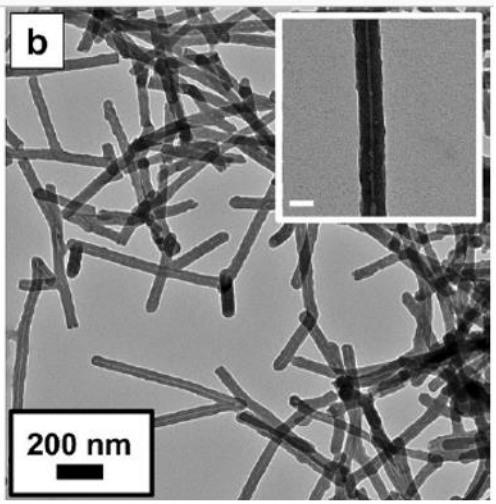
Group Photo

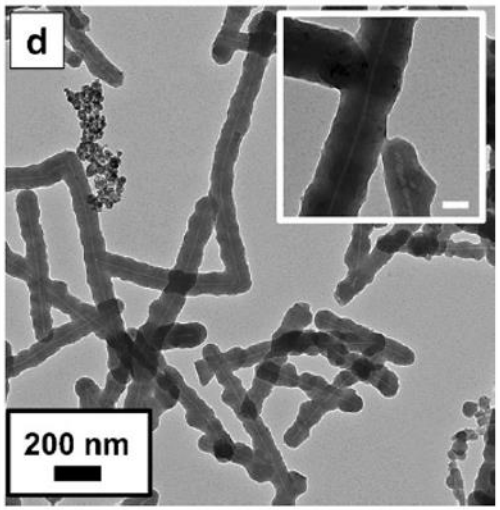


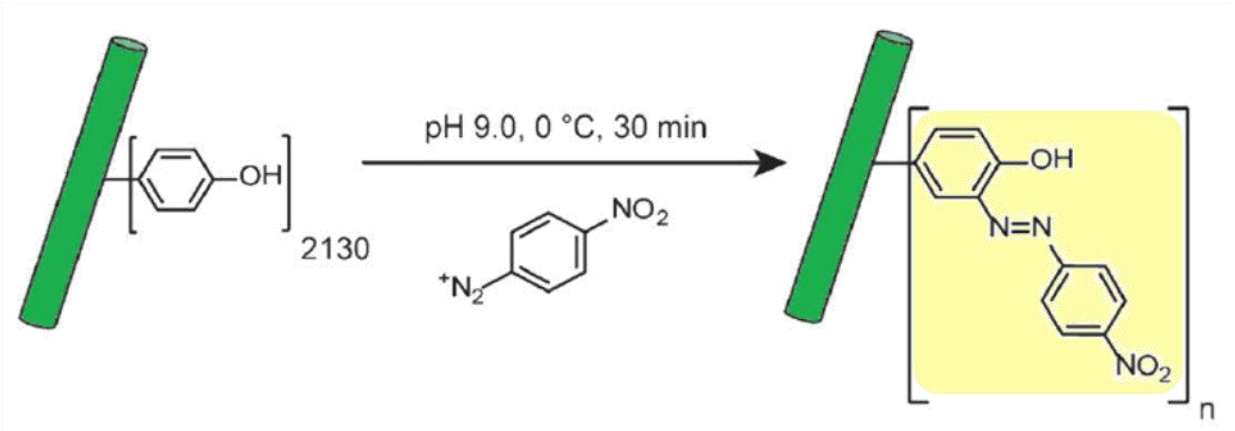
Thank you for Attention !!

Virus in MOF









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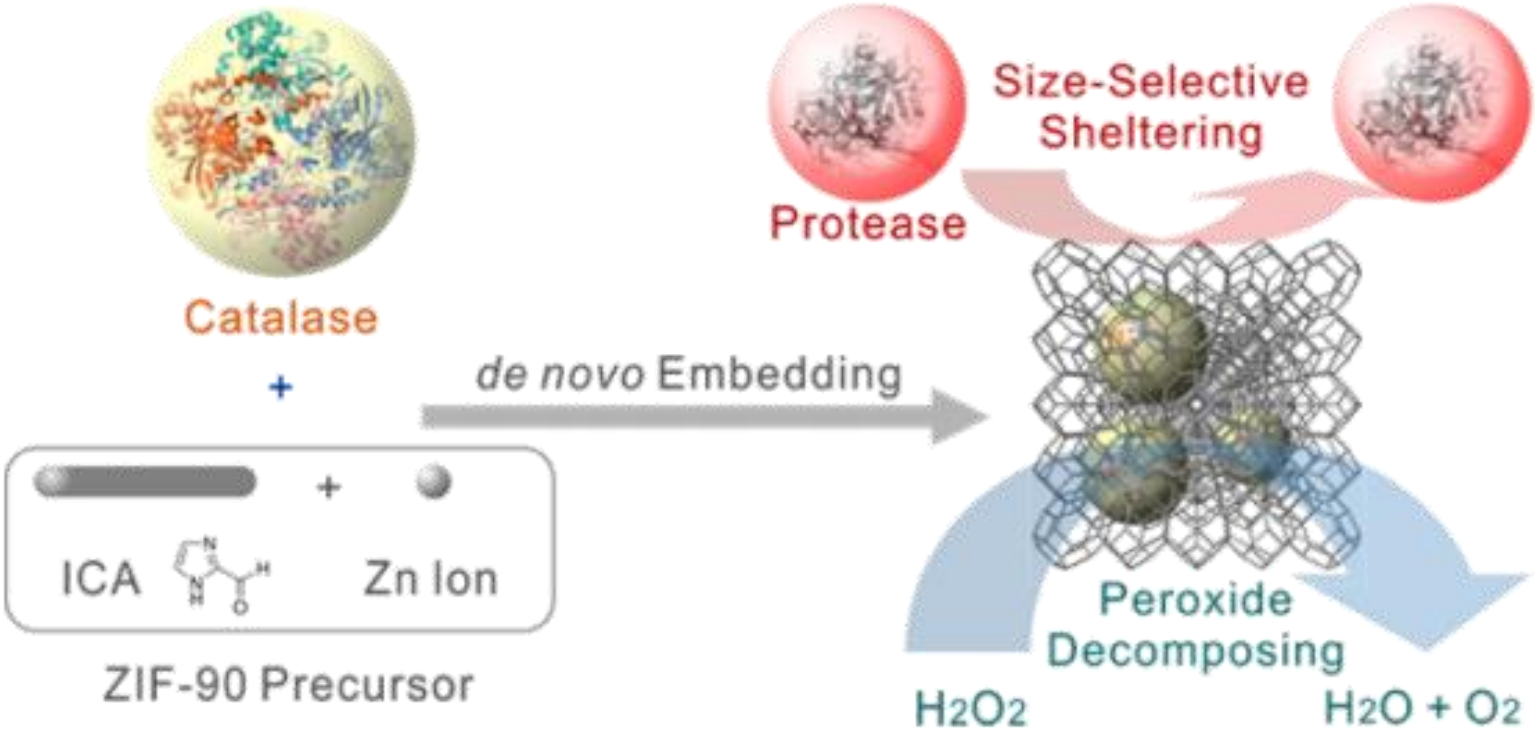

Fa-Kuen Shieh,* *et. al., J. Am. Chem. Soc.* **2015**, 137, 4276