# High Throughput Discovery of Polymeric Hydrogen Adsorptive Materials

Andrew I. Cooper

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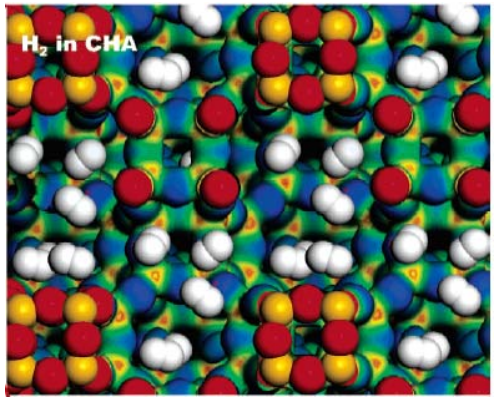
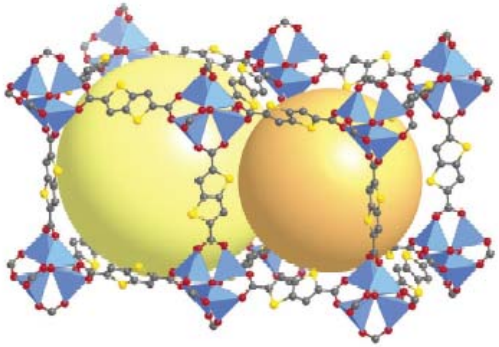
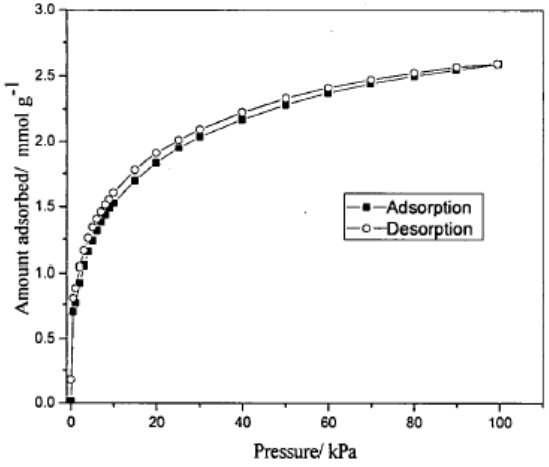
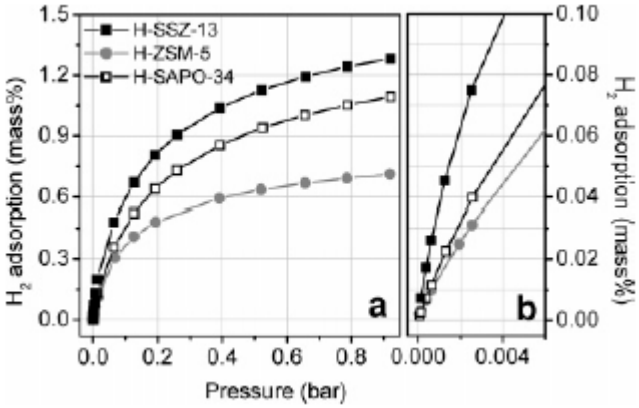
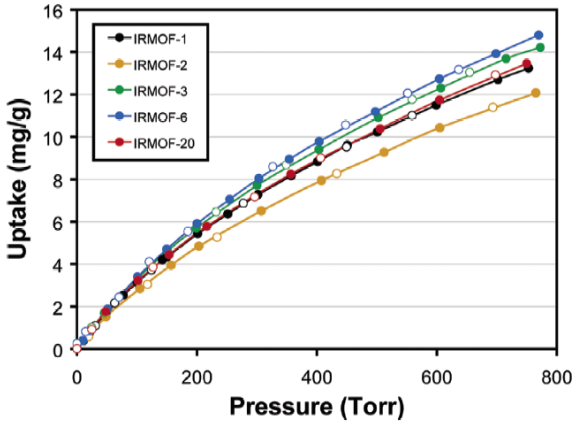
# Porous Materials for $H_2$ Physisorption






**Activated Carbon**

Zhao *et al.*
*J. Phys. Chem. B*, **2005**, *109*, 8880

**Zeolites**

Zecchina *et al.*
*J. Am. Chem. Soc.*, **2005**, *127*, 6361

**MOFs**

Rowsell & Yaghi
*J. Am. Chem. Soc.*, **2006**, *128,* 1304

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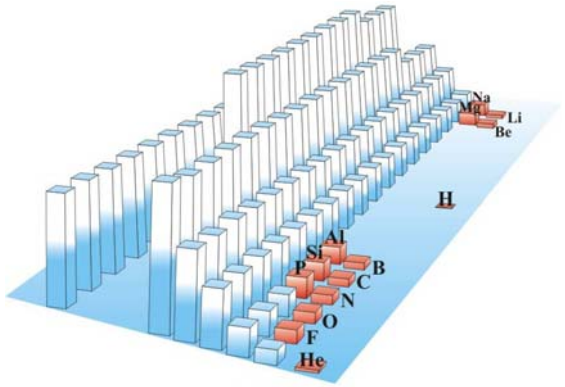
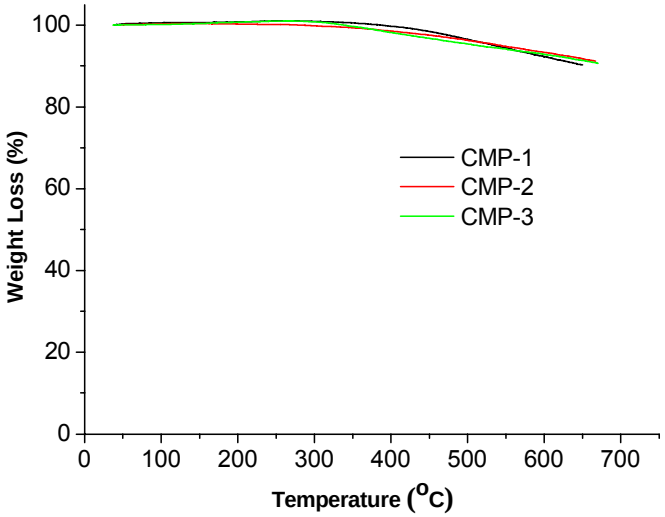
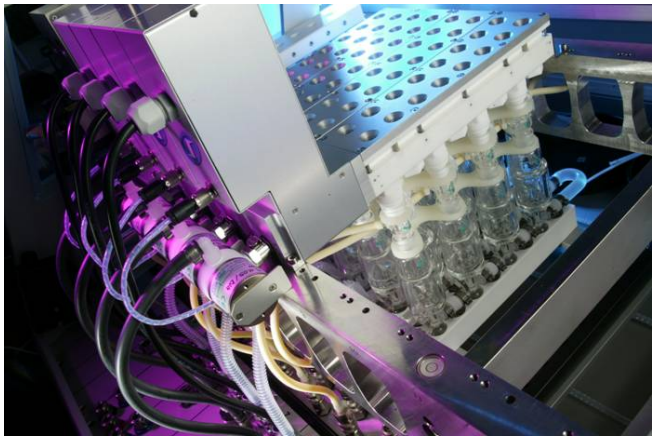
# Porous Organic Polymers for $H_2$ Storage

## Advantages and Challenges




- Based on light elements
- High thermal & chemical stability



- Synthetic versatility
- Scalable synthesis

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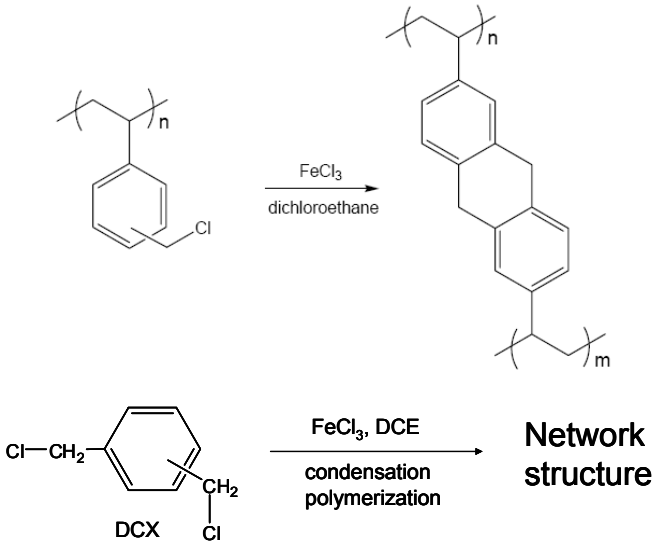
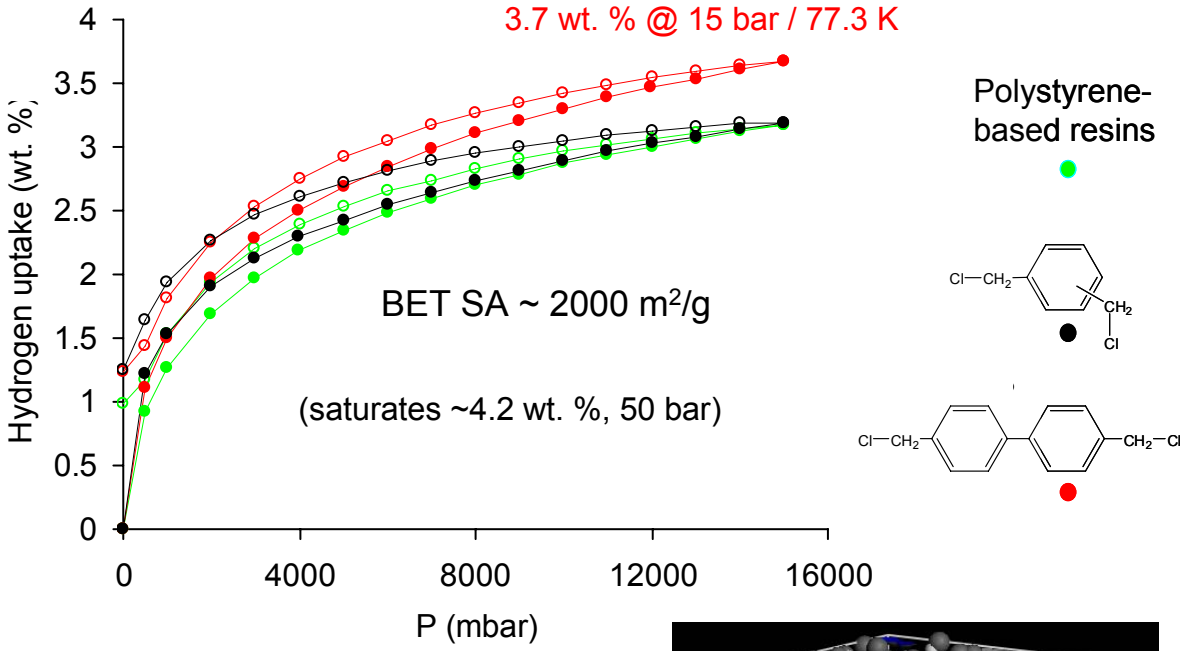
# Hypercrosslinked Polymers

*Chem. Commun.*, **2006**, 2670; *Chem. Mater.*, **2007**, 19, 2034
*J. Phys. Chem. C*, **2008**, *in press*

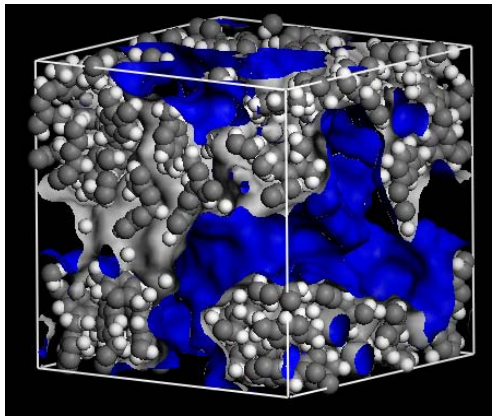



Polystyrene-based resins




- BET surface areas up to 1900 $m^2/g$
- 3.05 wt. % $H_2$ (15 bar / 77.3 K)



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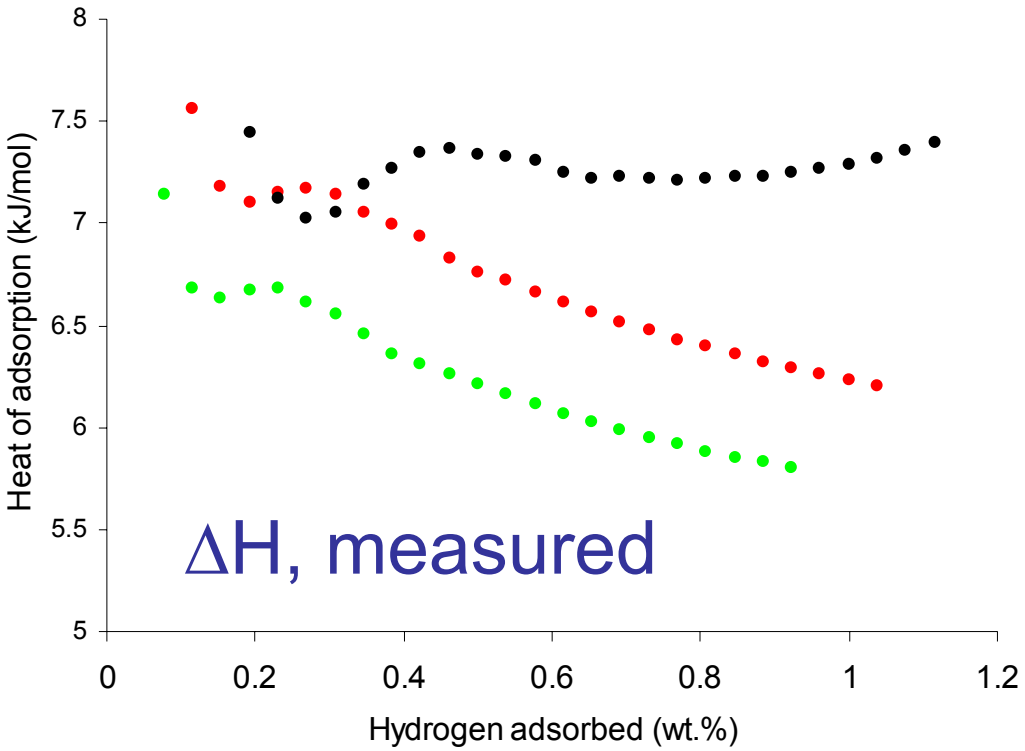
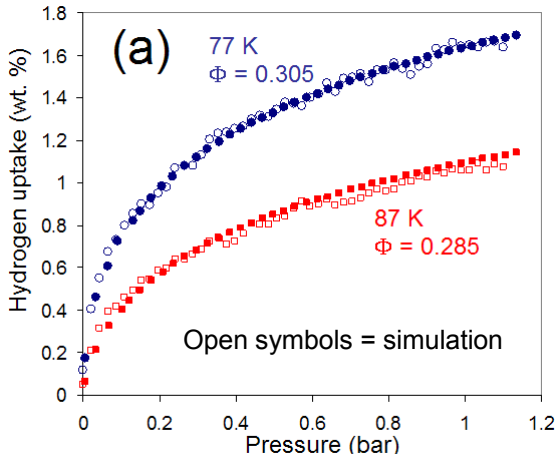
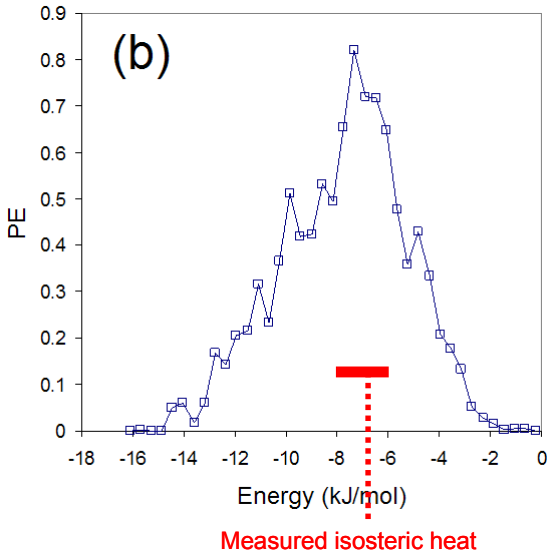
# Isosteric Heats of Sorption

*Chem. Mater.*, **2007**, 19, 2034; *J. Phys. Chem. C*, **2008**, *in press*




- Isosteric heat = –6 to – 8 kJ/mol
- Much too low for ambient T sorption

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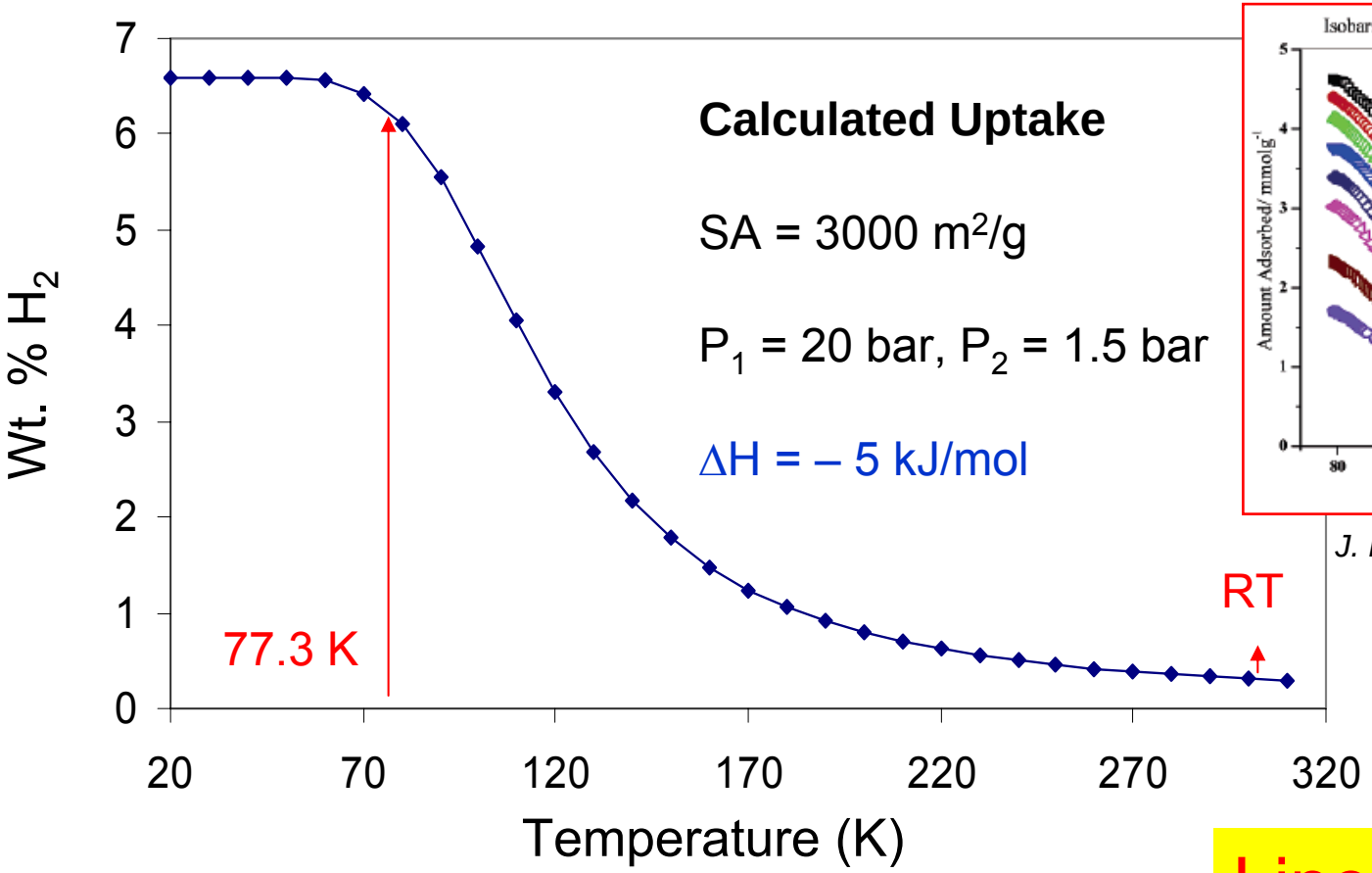
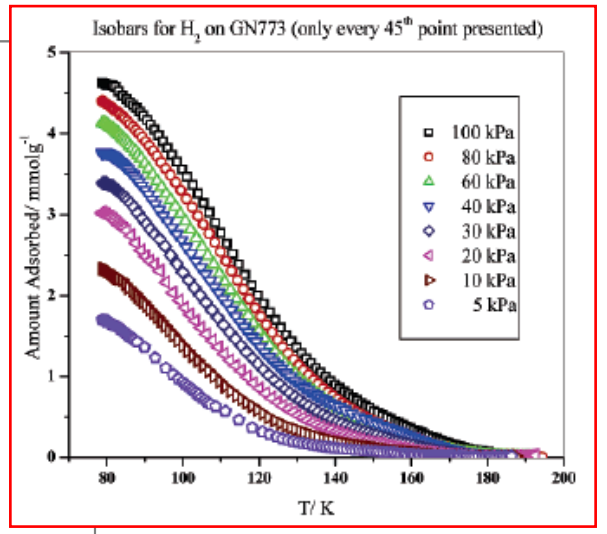
# Importance of Isosteric Heat of Sorption




*J. Phys. Chem. B*, **2005**, *109*, 8880

$$D(K,P_1,P_2) = \frac{KP_1 n_m}{1+KP_1} - \frac{KP_2 n_m}{1+KP_2}$$

$$K = (e^{\Delta S^\circ/R})(e^{-\Delta H^\circ/RT})/P_o$$

Linear in SA
Exponential in ΔH

For method see: *Langmuir* **2006,** *22,* 1688−1700

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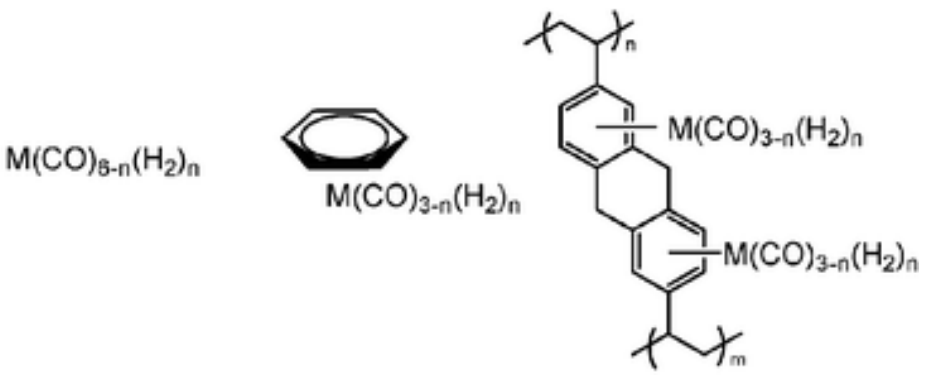
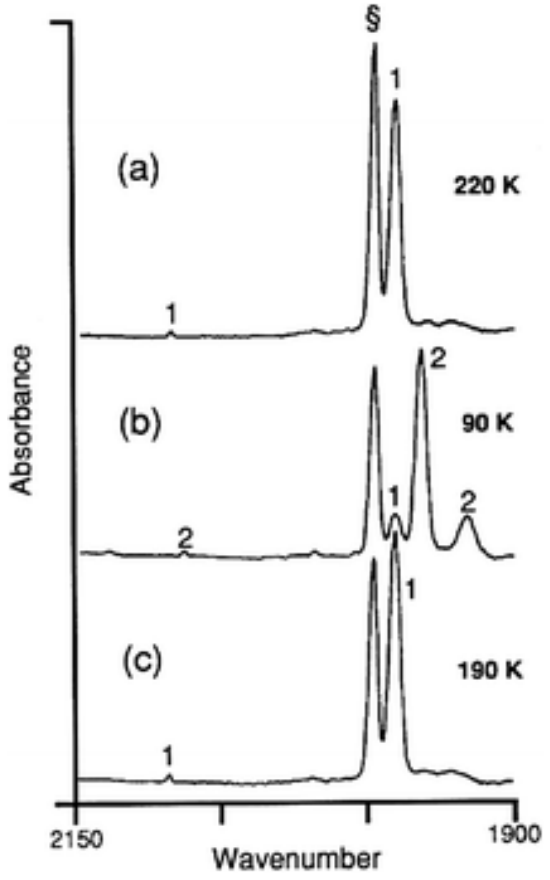
# “Designing” Higher Binding Affinities

## (i) Polymer-supported ***metal dihydrogen*** *complexes*




| | Hexacarbonyl | "Piano stool" | Polymer supported |
|---|---|---|---|
| n = 1 | 1.03 wt. % | 1.06 wt. % | 0.8 wt. % |
| n = 2 | 2.38 wt. % | 2.47 wt. % | 1.88 wt. % |




UV, +$H_2$

UV, –$H_2$

Δ, +$H_2$

- Dihydrogen complexes ~ 15–30 kJ/mol
- **2007:** UV-activated $H_2$ addition / release
- Mechanistic studies only at present
- How to make cycle reversible? Weight %?

Cooper and Poliakoff, *Chem. Commun.*, **2007**, 2965

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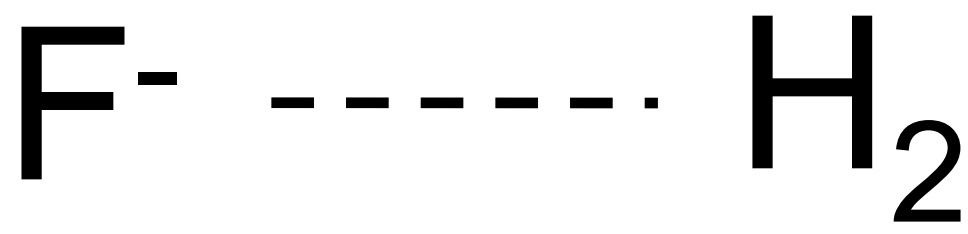
# “Designing” Higher Binding Affinities

## (ii) **Strong physisorption** – polarization of $H_2$




E ~ 24 – 26 kJ / mol

Gas phase calcn, no counter-ion

*A discouraging “upper bound”?*

*For example:* R. C. Lochan, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1357

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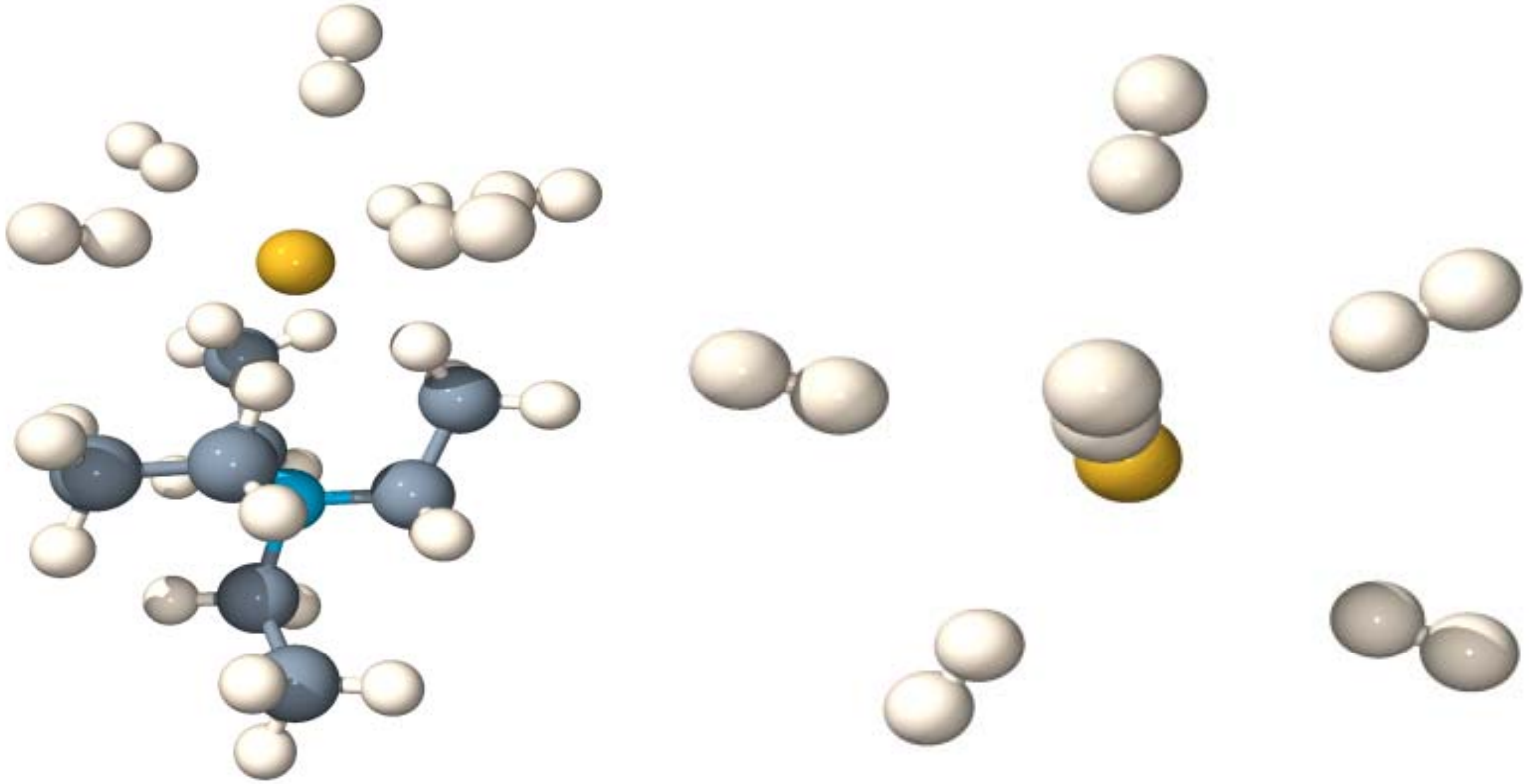
# Designing Higher Isosteric Heats

## (ii) Strong physisorption – **"naked" fluorides**



Coulombically-separated ions (delocalized cation)

Trewin *et al.*, *New J. Chem.*, **2008**, *32*, 17

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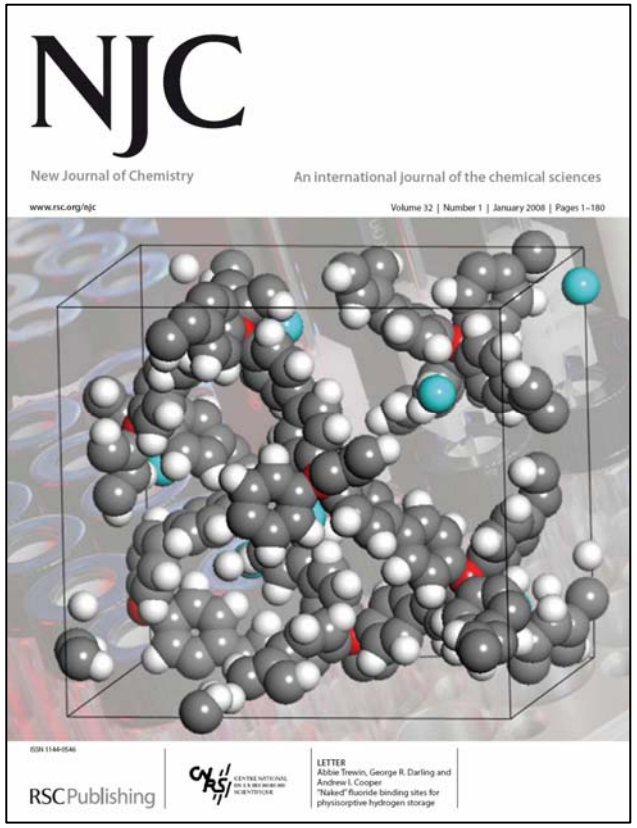
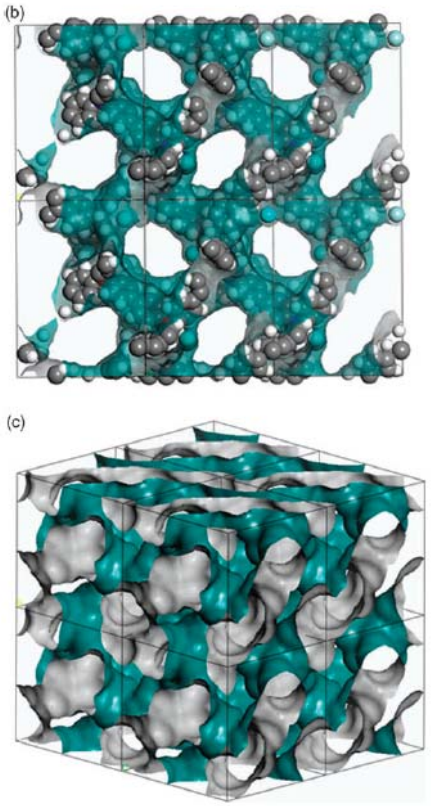
# Designing Higher Isosteric Heats

## (ii) Strong physisorption – **"naked" fluorides**




- Predict 10 – 18 kJ / mol
- How to keep halide site-isolated in extended porous structure?
- Difficult to prepare anhydrous naked $F^-$

Trewin *et al.*, *New J. Chem.*, **2008**, *32*, 17

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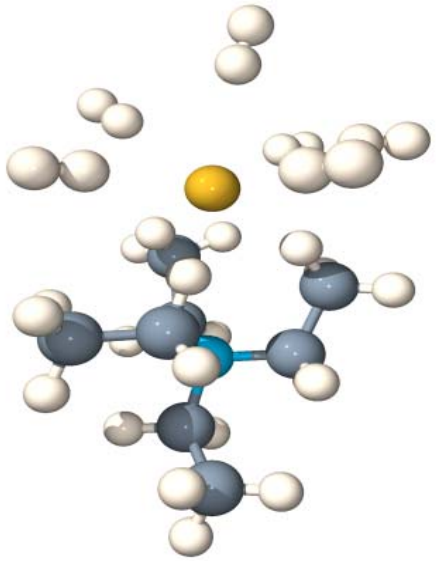
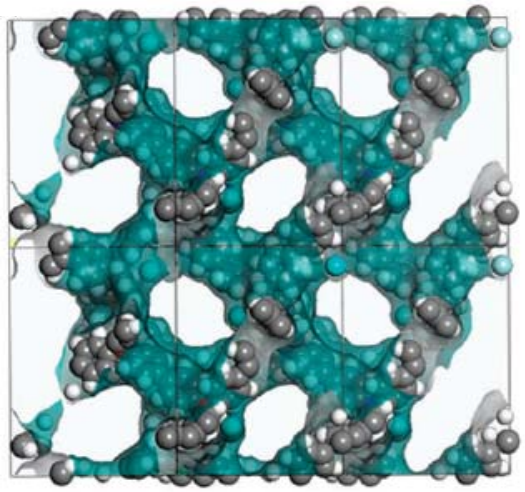
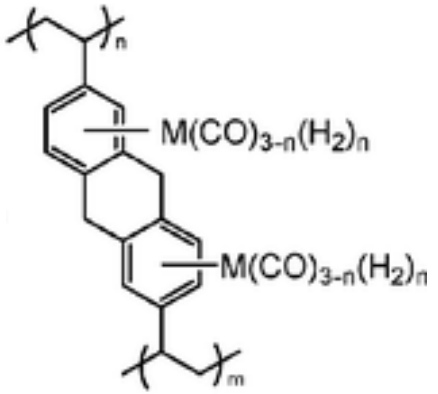
# High Throughput Approaches

- New modes of $H_2$ binding required – inherently speculative
- Need to test multiple hypotheses
- Understanding much more powerful than “screening”
- *But sometimes screening is a start….*





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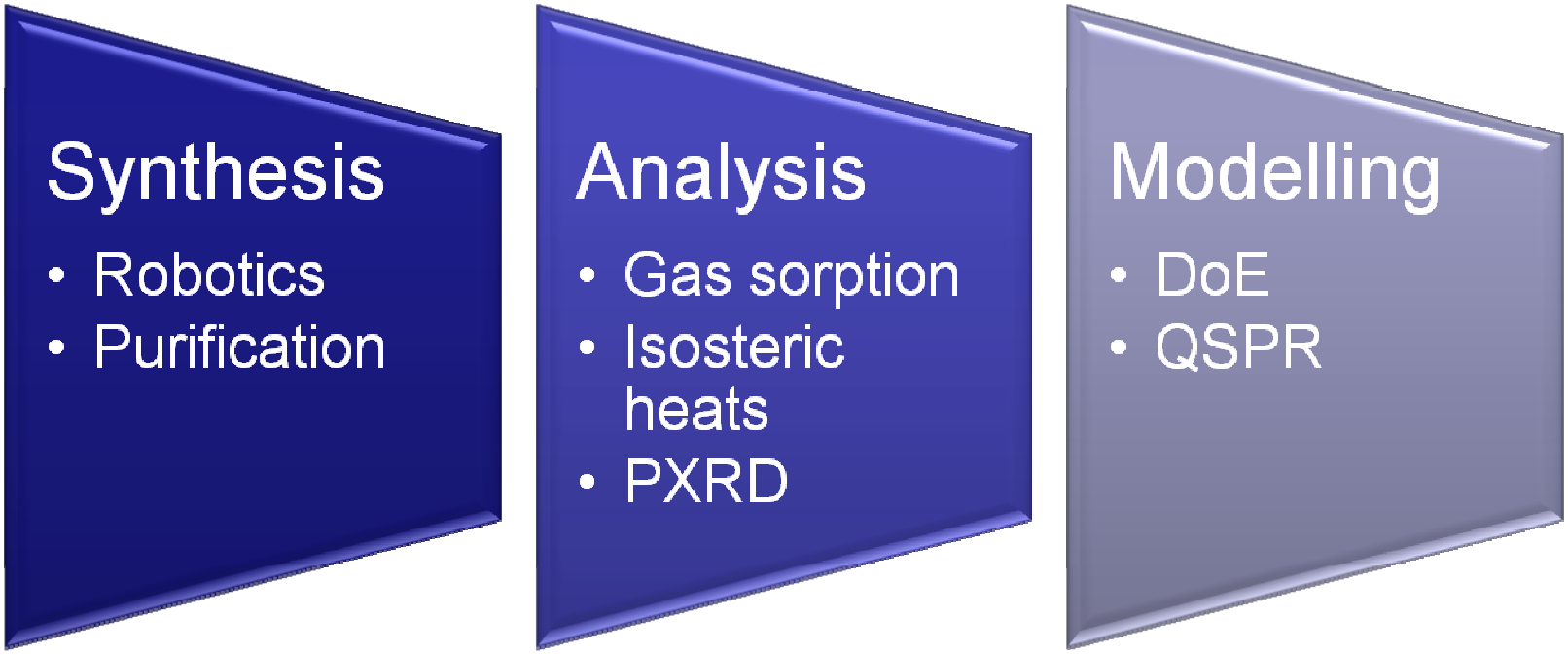
# Combinatorial Approach




48−96 purified samples / run using microwave heating or ChemSpeed robots

BET / $H_2$ / $CH_4$: 36 / day
Isosteric heat: 12 / day
PXRD / FTIR 100's per week

Umetrics MODDE 7.0
Nautilus LIMS

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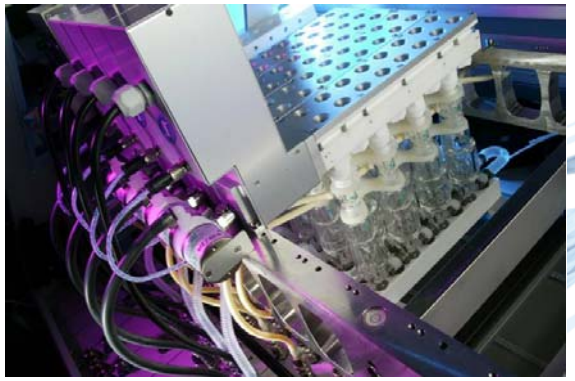
# Combinatorial Approach: Workflow



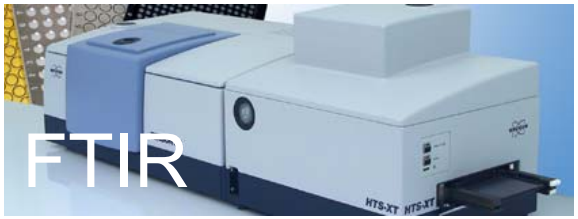
Robotics / microwaves

Gas sorption



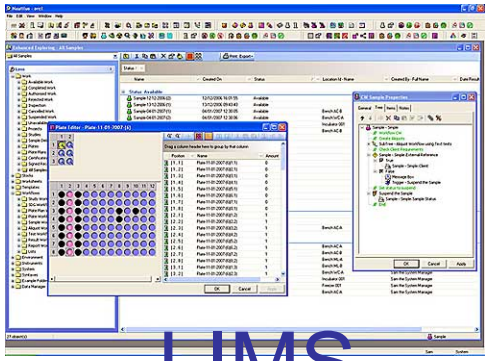
PXRD

TGA



FTIR

DSC



LIMS

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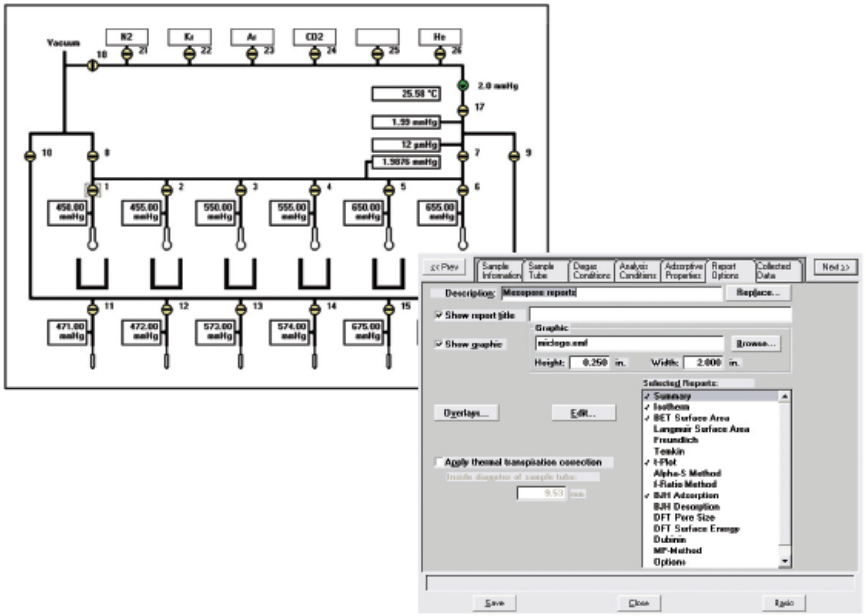
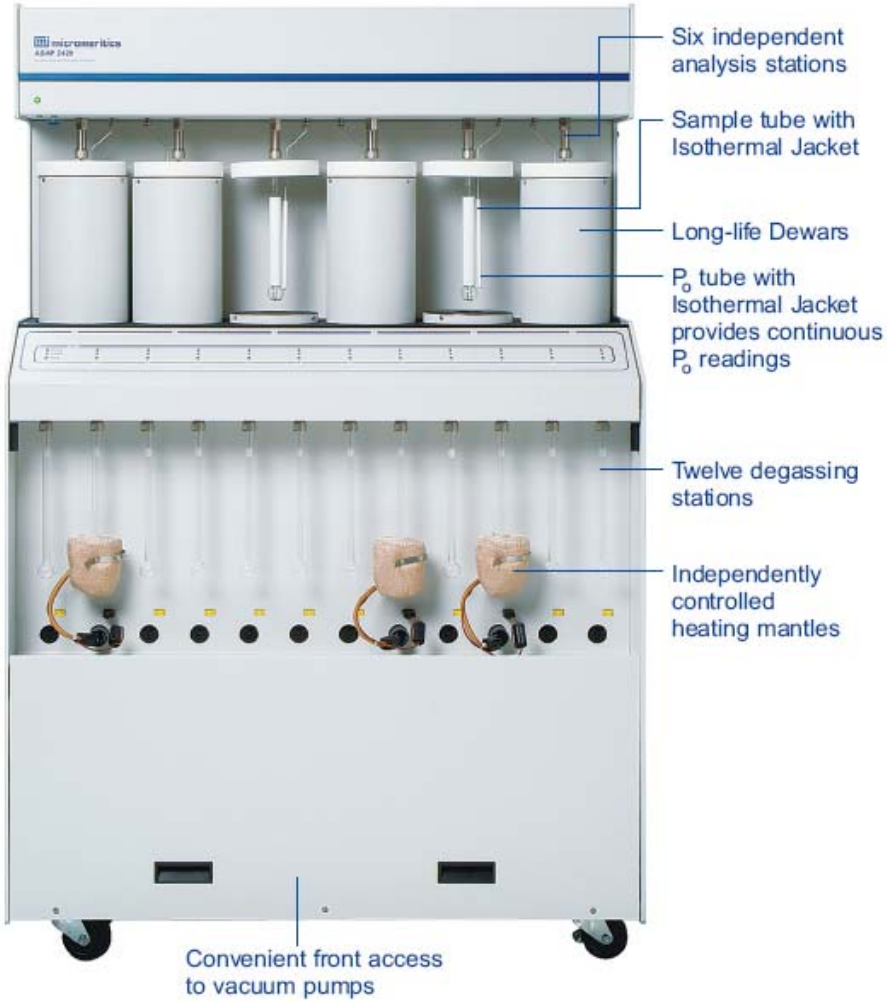
# Rapid Gas Sorption Measurements

## Micromeritics ASAP 2420 – $N_2$, $H_2$, $CH_4$, $CO_2$, Ar, etc.



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# Rapid Gas Sorption Measurements

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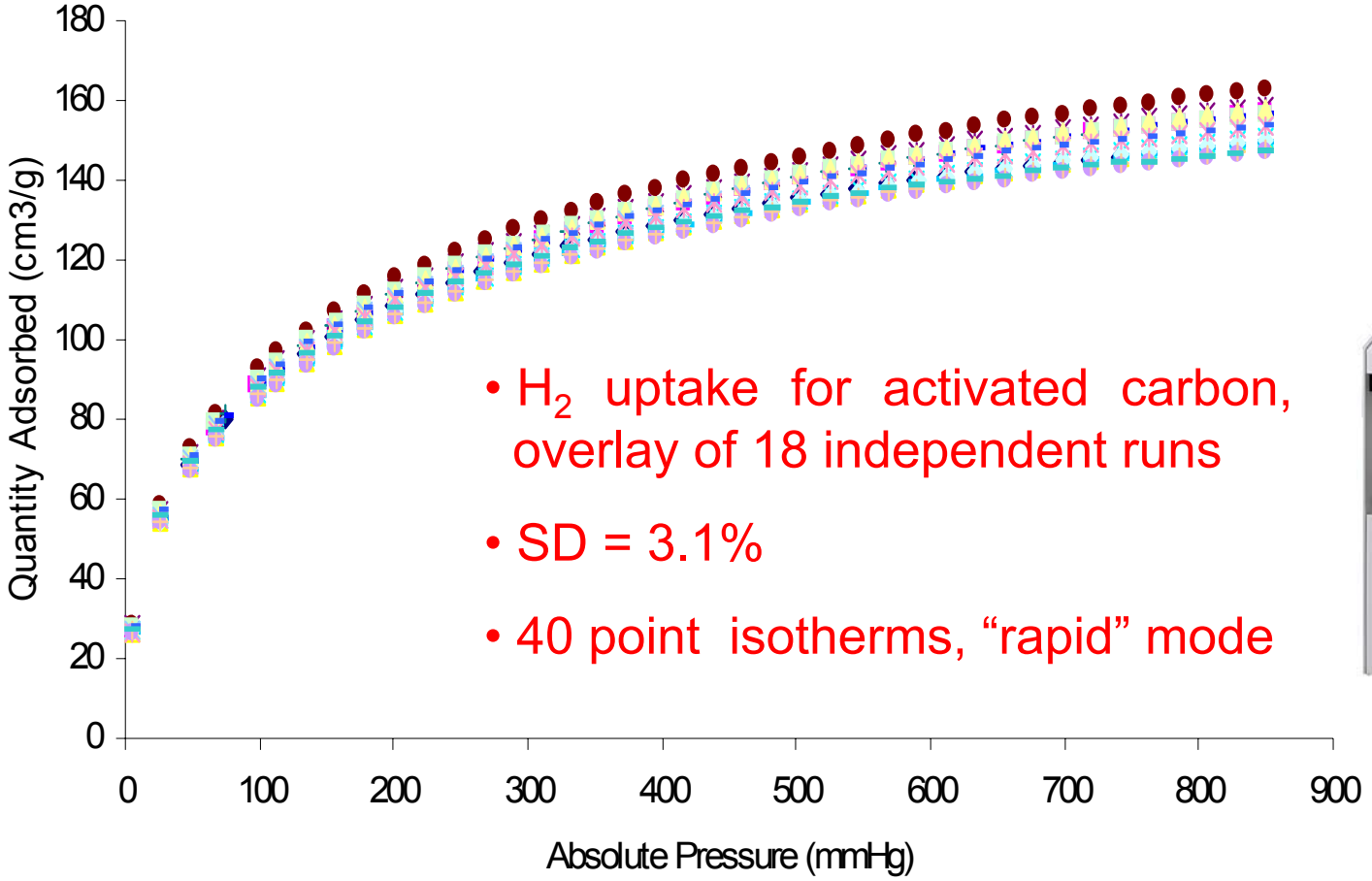


- $H_2$ uptake for activated carbon, overlay of 18 independent runs
- SD = 3.1%
- 40 point isotherms, “rapid” mode

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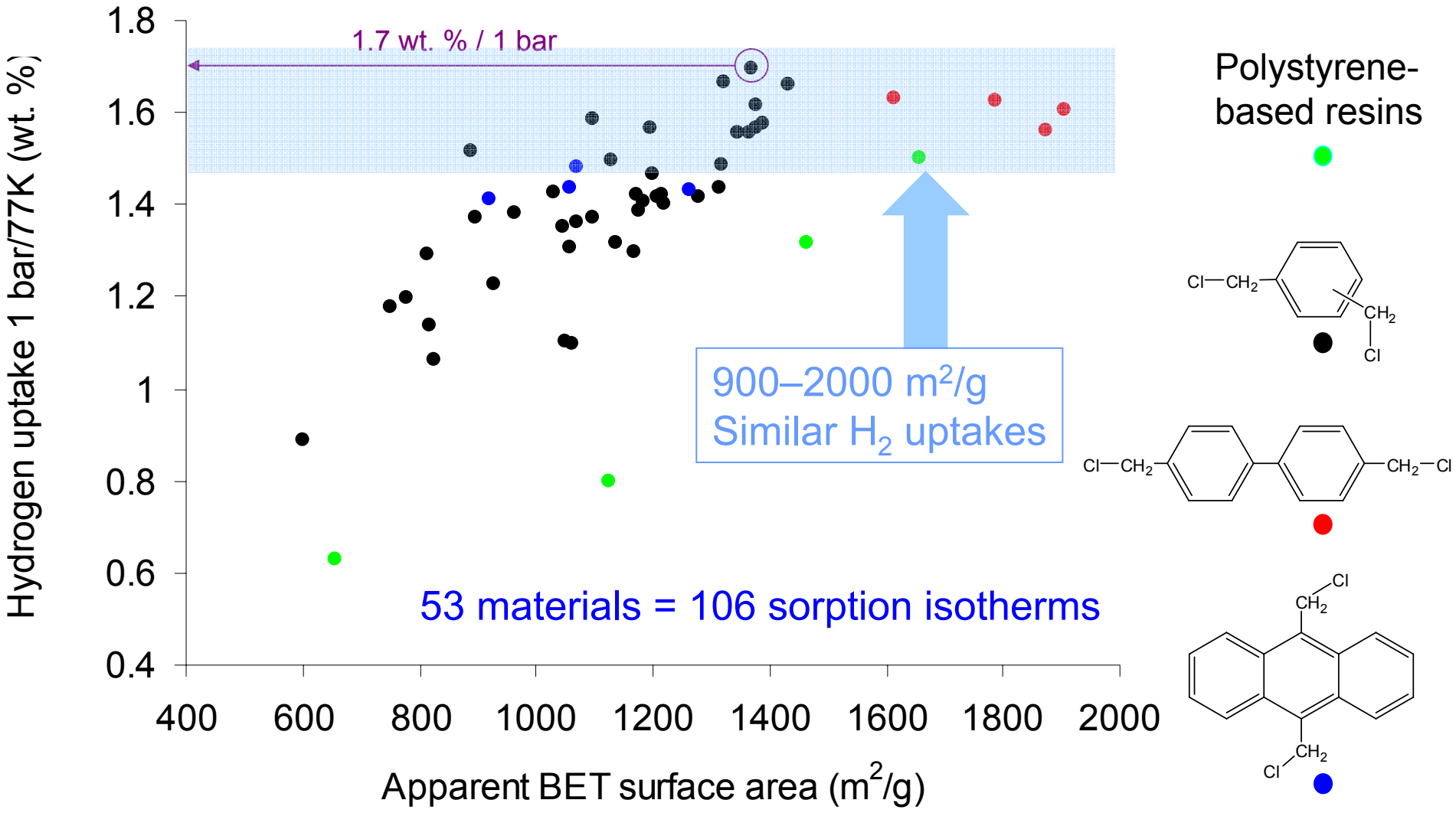
Table 1. Synthesis Conditions, Surface Areas, and Gravimetric $H_2$ Uptakes for Hypercrosslinked Polymers[a]

| | monomer (w/v %) | $FeCl_3$ (mol)[b] | $t$ (min)[c] | $o$-DCX (mol)[d] | $m$-DCX (mol)[d] | $p$-DCX (mol)[d] | BCMBP | BCMA | yield (%)[e] | BET SA ($m^2/g$)[f] | Langmuir SA ($N_2$) ($m^2/g$) | Langmuir SA ($H_2$) ($m^2/g$)[g] | $H_2$ uptake (1.13 bar/77.3K) (wt %)[h] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2.5 | 1 | 60 | 1 | 0 | 0 | | | 30 | 600 | 924 | 498 | 0.89 |
| 2 | 2.5 | 1 | 60 | 0 | 1 | 0 | | | 59 | 1097 | 1707 | 806 | 1.37 |
| 3 | 2.5 | 1 | 60 | 0 | 0 | 1 | | | 60 | 1045 | 1608 | 798 | 1.35 |
| 4 | 12.5 | 1 | 60 | 1 | 0 | 0 | | | 59 | 896 | 1393 | 781 | 1.37 |
| 5 | 12.5 | 1 | 60 | 0 | 1 | 0 | | | 64 | 1377 | 2196 | 969 | 1.61 |
| 6 | 12.5 | 1 | 60 | 0 | 0 | 1 | | | 63 | 1431 | 2281 | 999 | 1.66 |
| 7 | 2.5 | 3 | 60 | 1 | 0 | 0 | | | 55 | 777 | 1200 | 675 | 1.19 |
| 8 | 2.5 | 3 | 60 | 0 | 1 | 0 | | | 60 | 1098 | 1716 | 925 | 1.59 |
| 9 | 2.5 | 3 | 60 | 0 | 0 | 1 | | | 66 | 963 | 1455 | 801 | 1.38 |
| 10 | 2.5 | 3 | 60 | 0 | 0.5 | 0.5 | | | 63 | 1131 | 1764 | 878 | 1.50 |
| 11 | 12.5 | 3 | 60 | 1 | 0 | 0 | | | 64 | 750 | 1142 | 659 | 1.18 |
| 12 | 12.5 | 3 | 60 | 0 | 1 | 0 | | | 74 | 1279 | 2026 | 832 | 1.41 |
| 13 | 12.5 | 3 | 60 | 0 | 0 | 1 | | | 70 | 1172 | 1788 | 832 | 1.42 |
| 14 | 12.5 | 3 | 60 | 0 | 0.5 | 0.5 | | | 60 | 1220 | 1946 | 827 | 1.40 |
| 15 | 2.5 | 2 | 60 | 0 | 0 | 1 | | | 61 | 1182 | 1820 | 824 | 1.41 |
| 16 | 2.5 | 2 | 60 | 0.5 | 0.5 | 0 | | | 58 | 1317 | 2020 | 873 | 1.48 |
| 17 | 12.5 | 2 | 60 | 0.5 | 0 | 0.5 | | | 62 | 1177 | 1903 | 811 | 1.39 |
| 18 | 7.5 | 1 | 60 | 0 | 0.5 | 0.5 | | | 48 | 1313 | 2022 | 853 | 1.44 |
| 19 | 7.5 | 3 | 60 | 0 | 1 | 0 | | | 72 | 1209 | 1884 | 842 | 1.42 |
| 20 | 7.5 | 3 | 60 | 0.5 | 0 | 0.5 | | | 68 | 1069 | 1636 | 795 | 1.36 |
| 21 | 7.5 | 2 | 60 | 0.33 | 0.33 | 0.33 | | | 65 | 1347 | 2068 | 930 | 1.56 |
| 22 | 7.5 | 2 | 60 | 0.33 | 0.33 | 0.33 | | | 34 | 1032 | 1596 | 827 | 1.42 |
| 23 | 7.5 | 2 | 60 | 0.33 | 0.33 | 0.33 | | | 63 | 1137 | 1832 | 773 | 1.32 |
| 24 | 7.5 | 2 | 60 | 0.33 | 0.33 | 0.33 | | | 65 | 1058 | 1670 | 769 | 1.30 |
| 25 | 4.0 | 1 | 20 | 0 | 0 | 1 | | | 57 | 1199 | 1881 | 879 | 1.47 |
| 26 | 4.0 | 1 | 40 | 0 | 0 | 1 | | | 63 | 1324 | 2027 | 998 | 1.67 |
| 27 | 4.0 | 1 | 60 | 0 | 0 | 1 | | | 62 | 1370 | 2096 | 1013 | 1.69 (3.18) |
| 28 | 6.25 | 1 | 1080 | 0 | 0 | 1 | | | 63 | 1197 | 1833 | 924 | 1.56 |
| 29 | 12.5 | 1 | 1080 | 0 | 0 | 1 | | | 64 | 816 | 1260 | 655 | 1.14 |
| 30 | 25 | 1 | 1080 | 0 | 0 | 1 | | | 64 | 930 | 1300 | 708 | 1.23 |
| 31 | 50 | 1 | 1080 | 0 | 0 | 1 | | | 66 | 826 | 1157 | 616 | 1.06 |
| 32 | 100 | 1 | 1080 | 0 | 0 | 1 | | | 69 | 890 | 1360 | 882 | 1.52 |
| 33 | 160 | 1 | 1080 | 0 | 0 | 1 | | | 67 | 815 | 1274 | 738 | 1.29 |
| 35 | 3.75 | 0.05 | 1080 | 0 | 0 | 1 | | | 26 | 1062 | 1635 | 643 | 1.10 |
| 36 | 3.75 | 0.1 | 1080 | 0 | 0 | 1 | | | 35 | 1052 | 1621 | 651 | 1.10 |
| 37 | 3.75 | 0.2 | 1080 | 0 | 0 | 1 | | | 48 | 1169 | 1797 | 773 | 1.30 |
| 38 | 3.75 | 0.5 | 1080 | 0 | 0 | 1 | | | 60 | 1379 | 2128 | 933 | 1.56 |
| 39 | 3.75 | 1 | 1080 | 0 | 0 | 1 | | | 64 | 1391 | 2131 | 948 | 1.58 |
| 40 | 3.75 | 2 | 1080 | 0 | 0 | 1 | | | 65 | 1365 | 2098 | 932 | 1.56 |
| 41 | 3.75 | 3 | 1080 | 0 | 0 | 1 | | | 73 | 1215 | 1860 | 844 | 1.42 |
| 42 | 10.70[i] | 1 | 1080 | | | 0 | 100 | | 74 | 1874 | 2957 | 1002 | 1.56 |
| 43 | 9.93[i] | 1 | 1080 | | | 25 | 75 | | 70 | 1904 | 2992 | 1033 | 1.61 (3.68) |
| 44 | 9.07[i] | 1 | 1080 | | | 50 | 50 | | 71 | 1786 | 2756 | 1035 | 1.62 |
| 45 | 8.31[i] | 1 | 1080 | | | 75 | 25 | | 67 | 1612 | 2476 | 1014 | 1.63 |
| 46 | 11.80[i] | 1 | 1080 | | | 0 | | 100 | 55 | 921 | 1402 | 808 | 1.41 |
| 47 | 10.70[i] | 1 | 1080 | | | 25 | | 75 | 52 | 1069 | 1620 | 870 | 1.48 |
| 48 | 9.65[i] | 1 | 1080 | | | 50 | | 50 | 43 | 1057 | 1616 | 852 | 1.43 |
| 49 | 8.52[i] | 1 | 1080 | | | 75 | | 25 | 55 | 1262 | 1933 | 856 | 1.44 |

**49** polymers

**98** sorption measurements ($N_2$ and $H_2$)

# $H_2$ Uptake Versus BET Surface Area




Polystyrene-based resins







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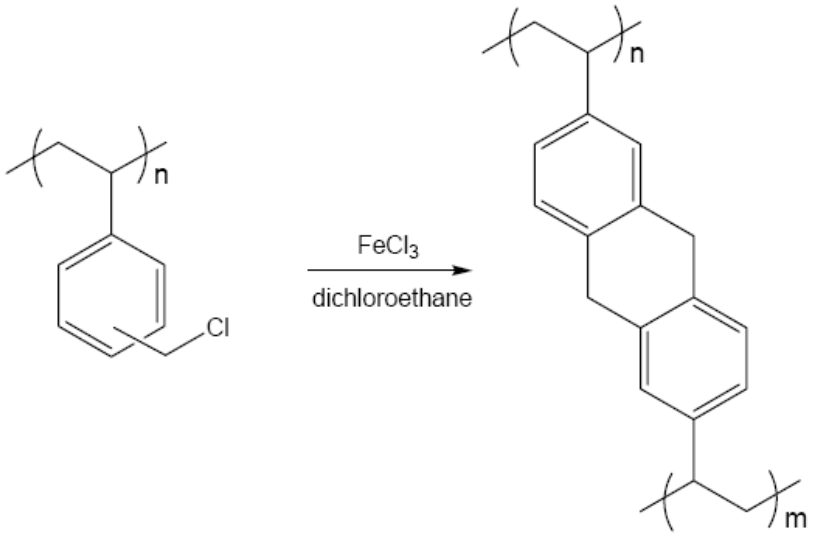
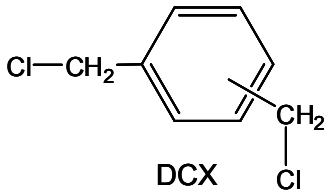
# Hypercrosslinked Polymers

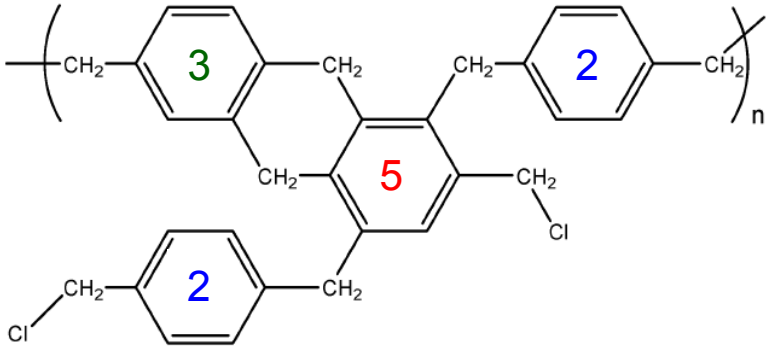
*Chem. Commun.*, **2006**, 2670; *Chem. Mater.*, **2007**, 19, 2034
*J. Phys. Chem. C*, **2008**, *in press*




FeCl$_3$, DCE
condensation polymerization

**Network structure**




- High surface areas but synthetically rather limited
- No direct synthetic control over micropore size, $SA_{BET}$, etc.

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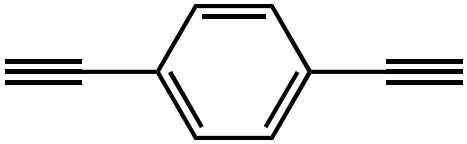
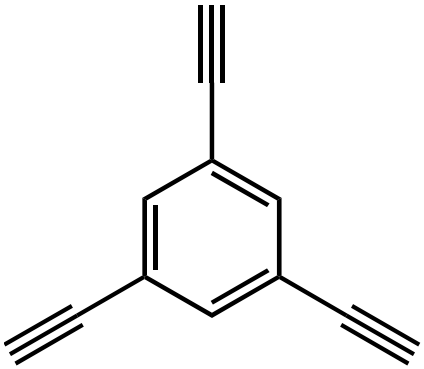
# Conjugated Microporous Polymer Networks

Jiang *et al.*, *Angew. Chem.*, 2007, *46*, 8574

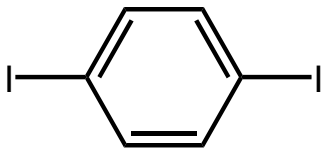
Sonagashira-Hagihara cross-coupling



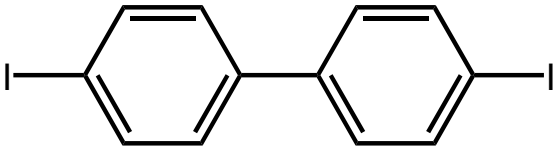
1,4-DEB



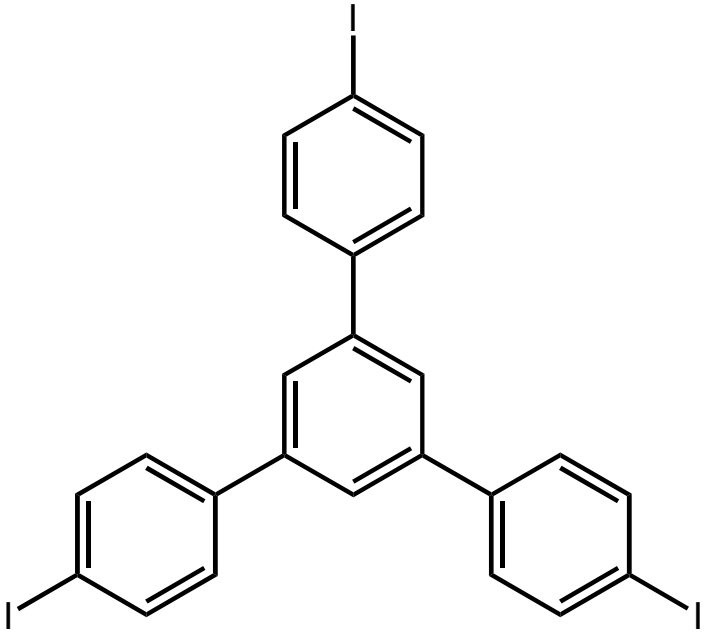
1,3,5-TEB



1,4-DIB



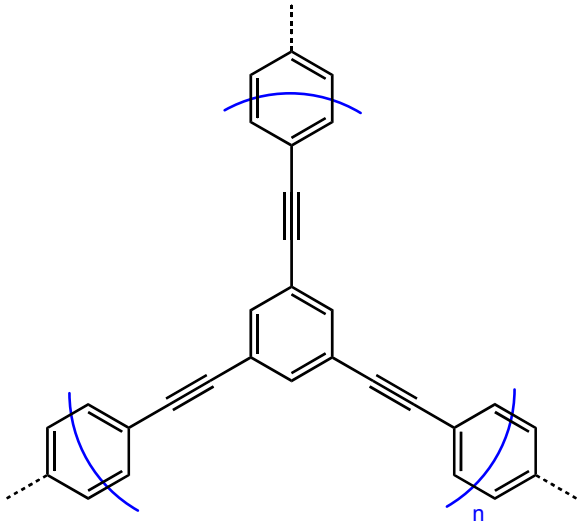
4,4'-DIBP



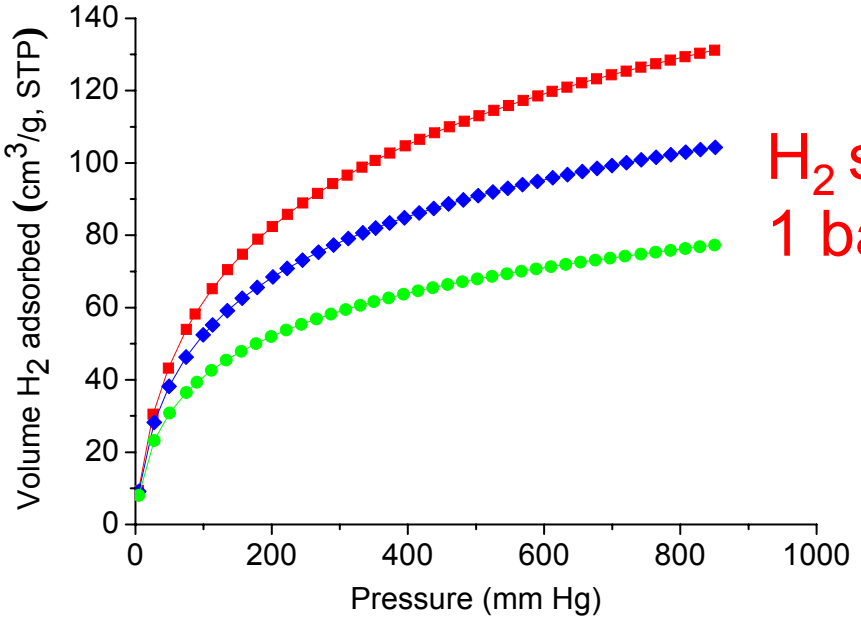
1,3,5-TIPB

# Conjugated Microporous Polymer Networks

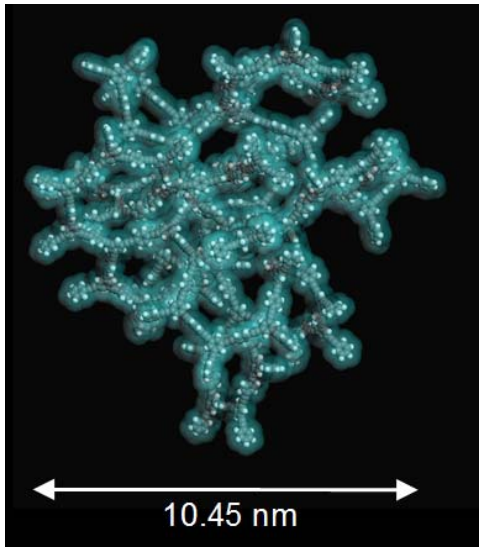
Jiang *et al.*, *Angew. Chem.*, **2007**, *46*, 8574

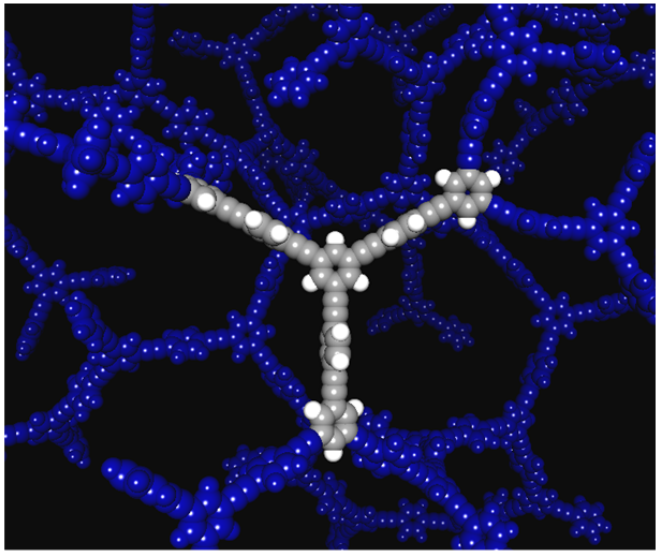



CMP-1



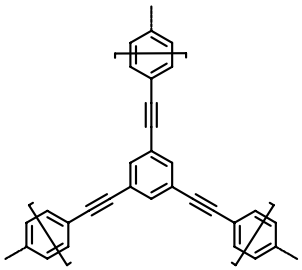

$H_2$ sorption @
1 bar / 77.3 K



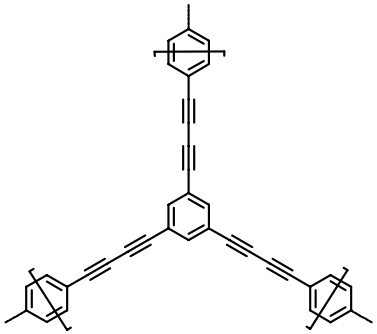
- SA's up to >1000 $m^2/g$
- Conjugated alkynes – scope for modification (*e.g.*, with metals)
- Chemically robust

# Amorphous Polymer Networks



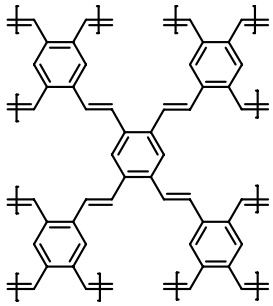
CMP-1

Microporous; $SA_{BET}$ = 834 $m^2/g$;
MPV = 0.33 $cm^3/g$; pore size ~ 1 nm[1,2]



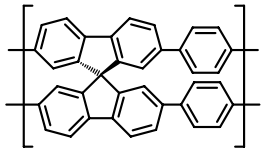
HCMP-1

Micro/mesoporous; $SA_{BET}$ = 842 $m^2/g$
$PV_{tot}$ = 1.16 $cm^3/g$; pore size ~ 1-5 nm[4]



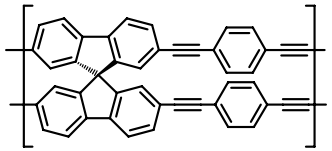
PPV network

Mesoporous; $SA_{BET}$ = 761 $m^2/g$
$PV_{tot}$ = 1.16 $cm^3/g$; pore size - 5.6 nm[6]



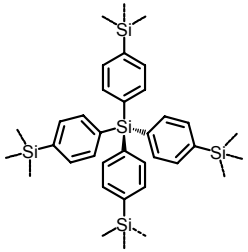
P1

Microporous; $SA_{BET}$ = 450 $m^2/g$[3]



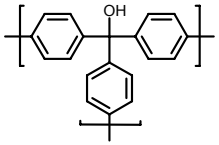
P2

Microporous; $SA_{BET}$ = 510 $m^2/g$[3]



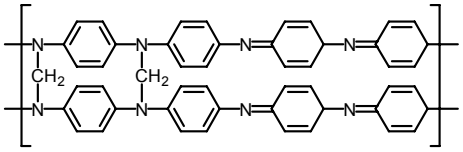

EOF-1

Microporous; $SA_{BET}$ = 780 $m^2/g$
MPV = 0.32 $cm^3/g$[5]



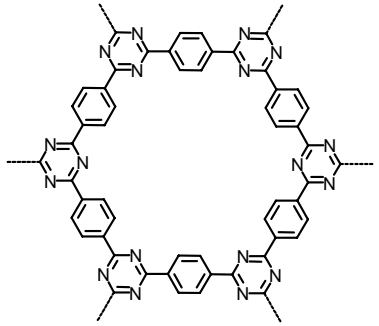

Carbinol HCP

Mesoporous; $SA_{BET}$ up to 1000 $m^2/g$[30]




Polyaniline HCP

Meso/macroporous; $SA_{BET}$ up to 632 $m^2/g$
$PV_{tot}$ = 0.94 $cm^3/g$[7]

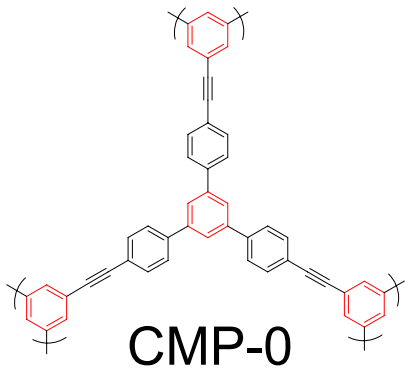


CTF-1

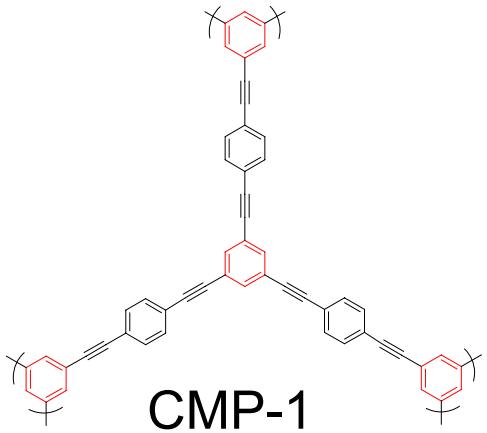
Microporous; $SA_{BET}$ = 711 $m^2/g$
$PV_{tot}$ = 0.40 $cm^3/g$; pore size ~ 1.2 nm[8]

# Conjugated Microporous Polymer Networks

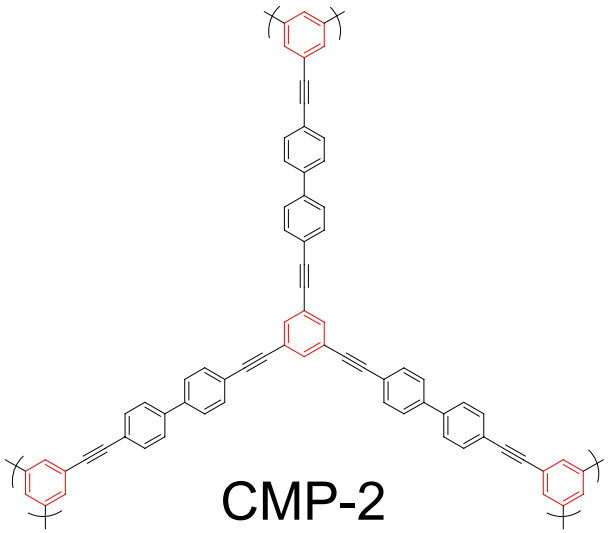
Jiang *et al.*, *Angew. Chem.*, **2007**; *JACS*, **2008**



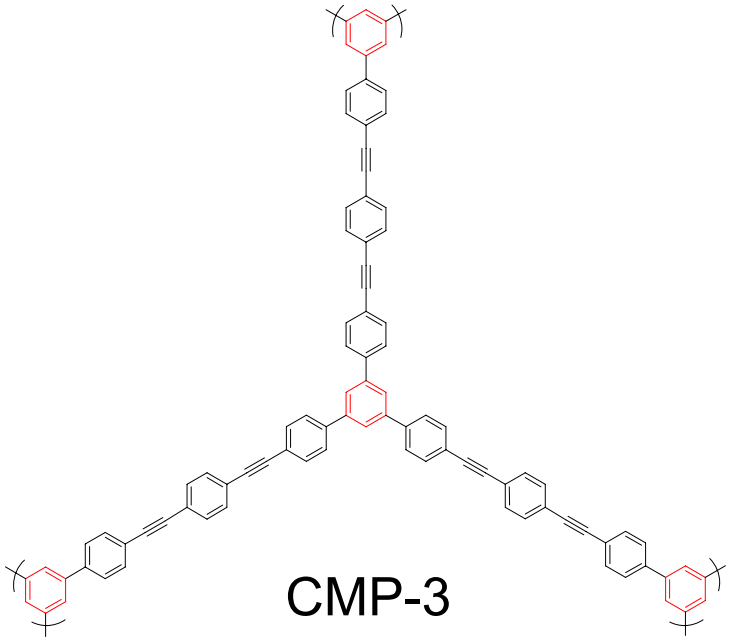
CMP-0



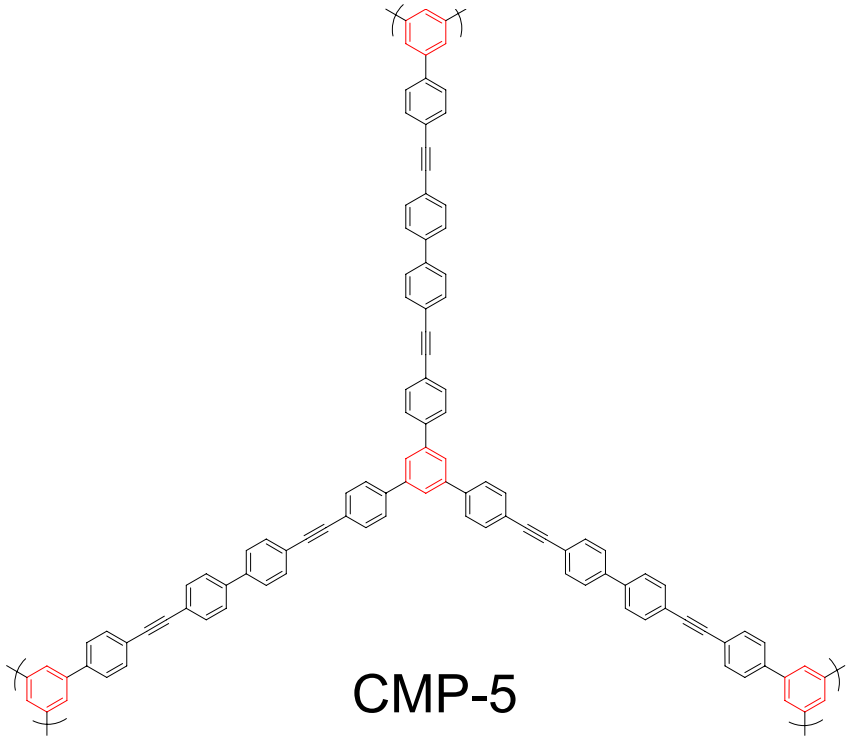
CMP-1



CMP-2



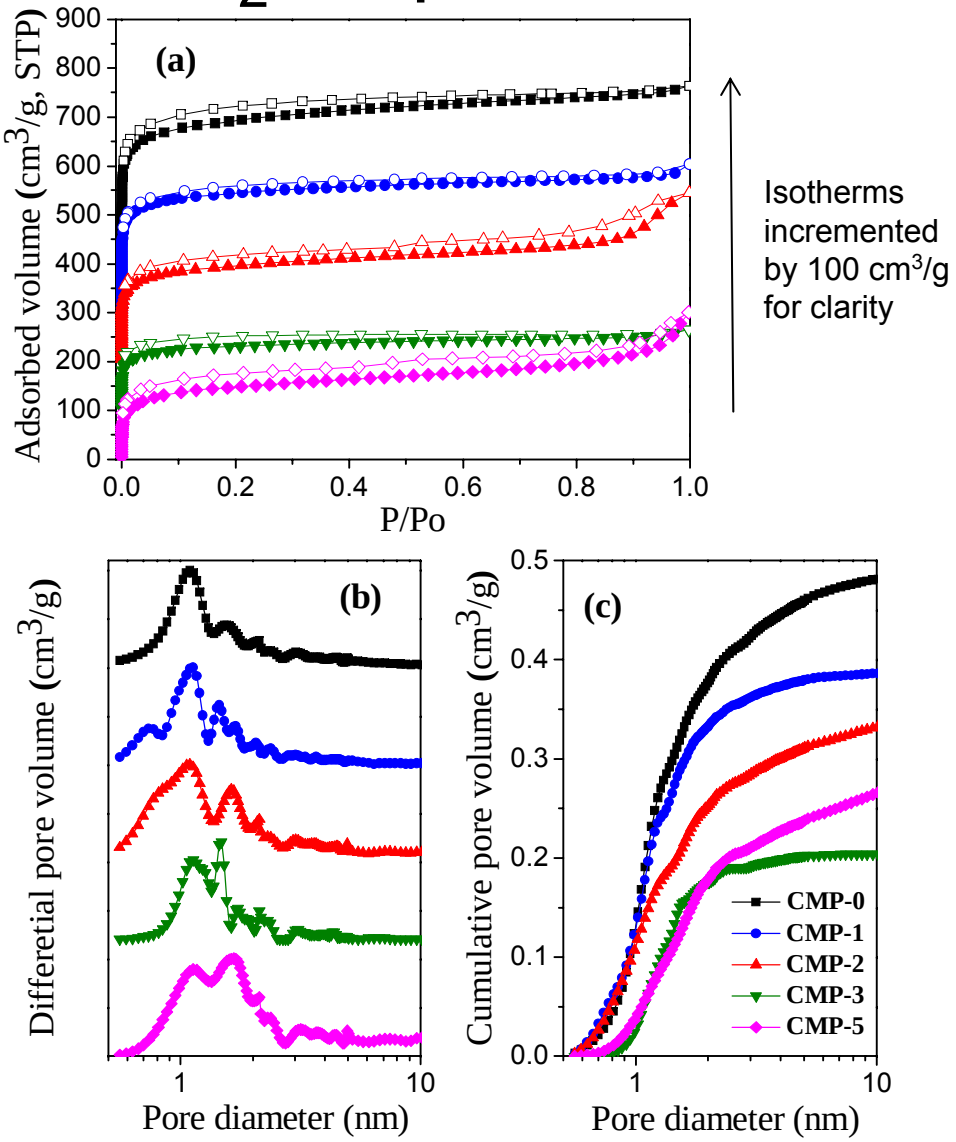
CMP-3



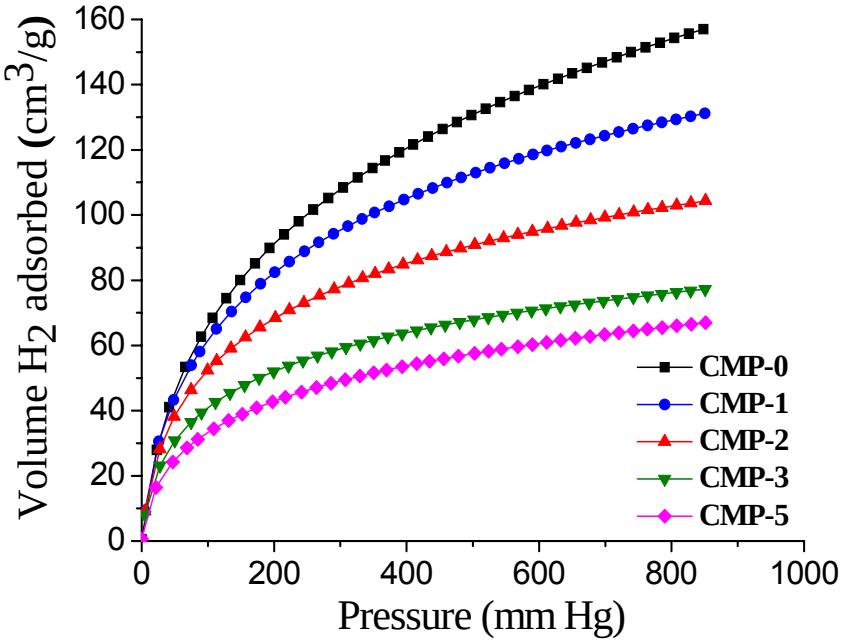
CMP-5

# Conjugated Microporous Polymer Networks

## $N_2$ sorption



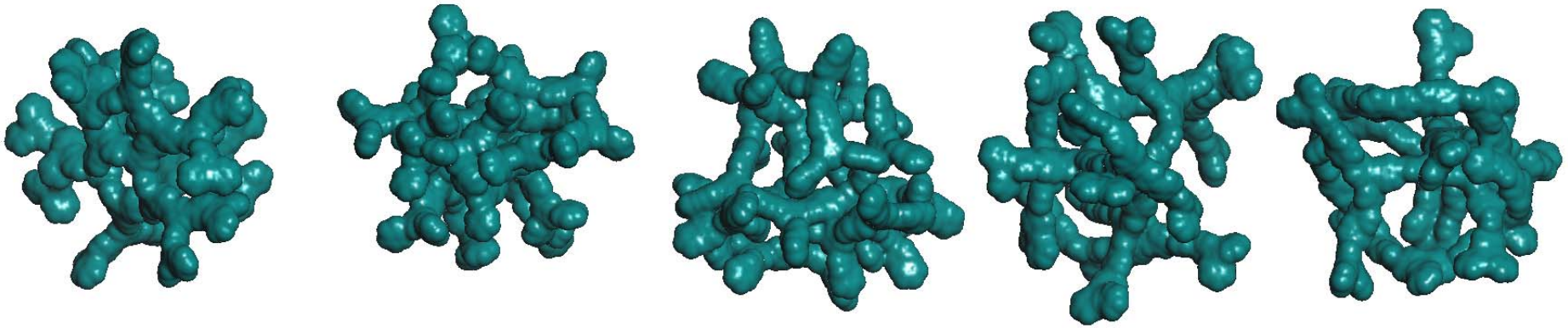

## $H_2$ sorption

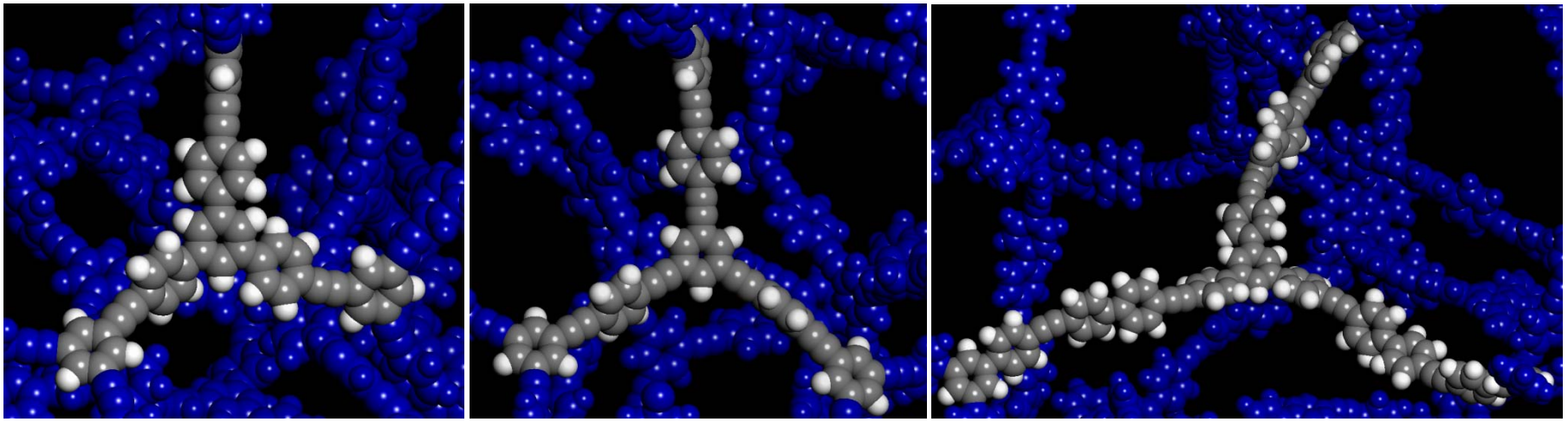



- Fine-tuning of pore size
- **Amorphous materials**

# Conjugated Microporous Polymer Networks

Jiang *et al.*, *Angew. Chem.*, **2007**, *46*, 8574





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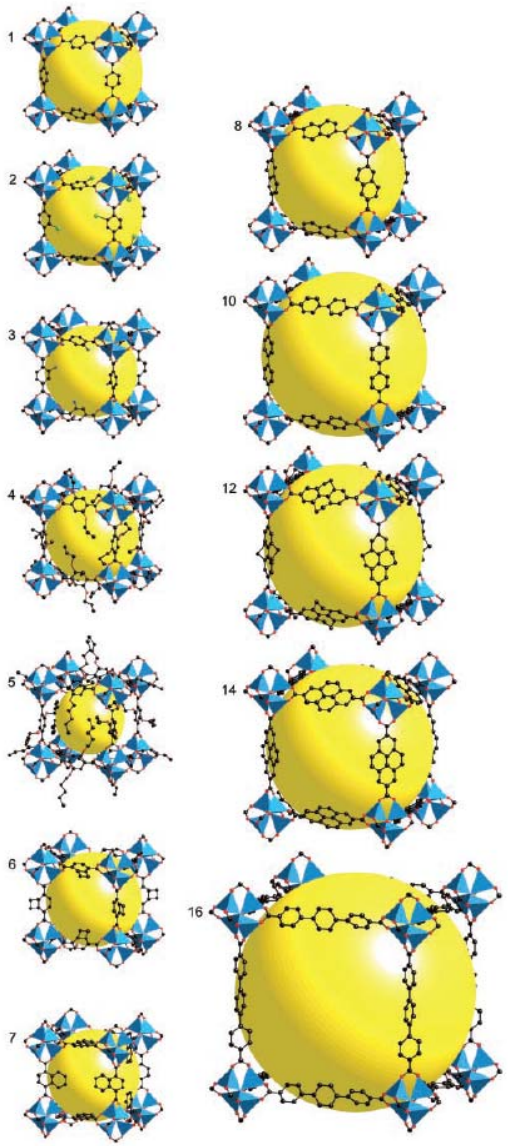
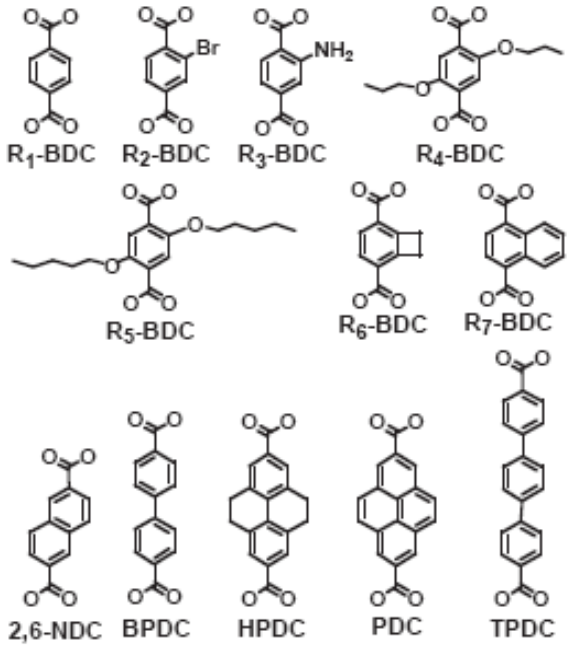
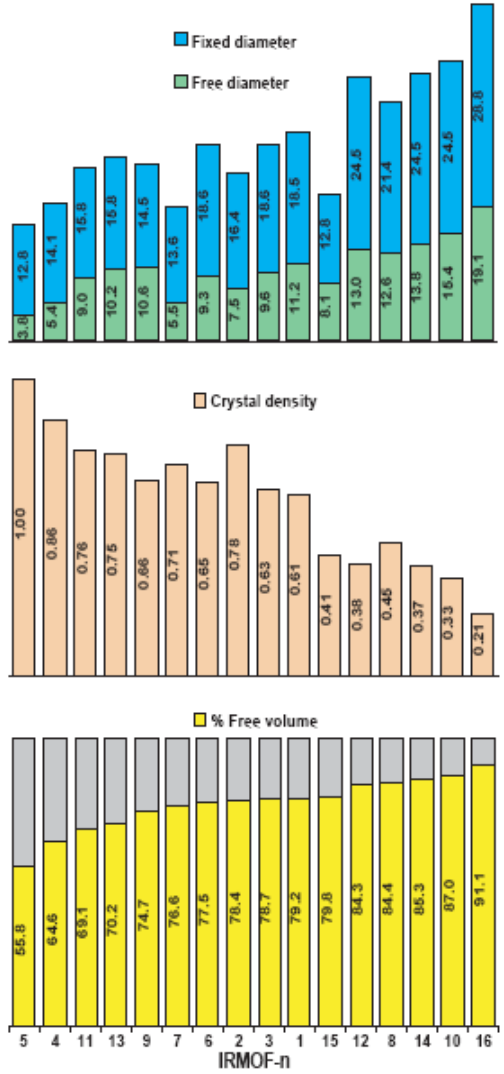
# Isoreticular Metal Organic Frameworks

Eddaoudi *et al.*, *Science*, **2002**, *295*, 469




- Tuneable properties
- Defined by biscarboxylate strut length / substituents

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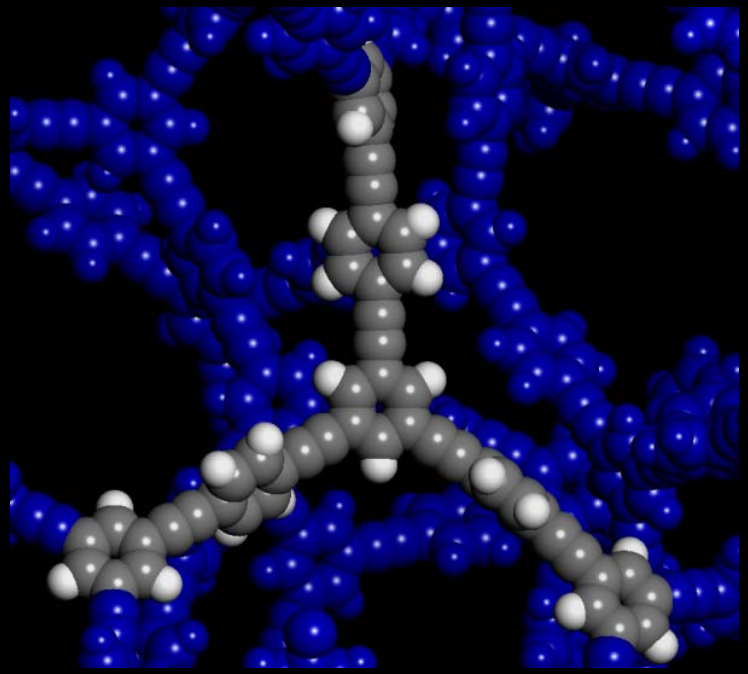
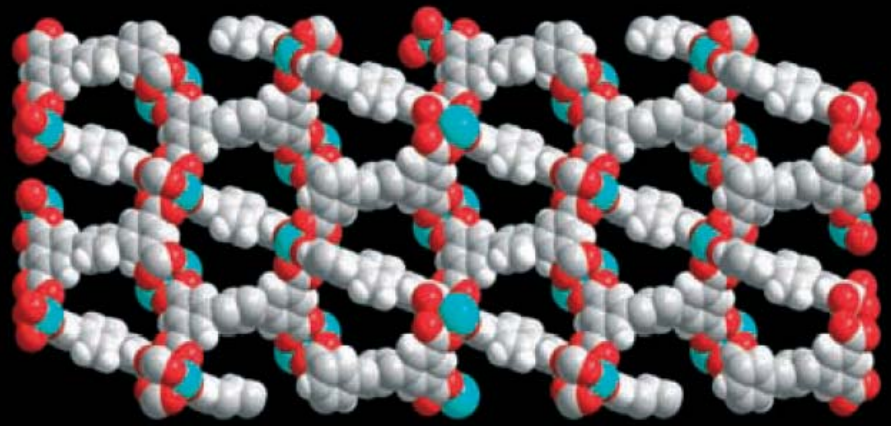
# Atomistic Simulation of Pore Structure



**Amorphous polymer**



**Crystalline MOF**

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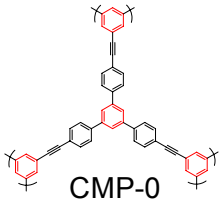
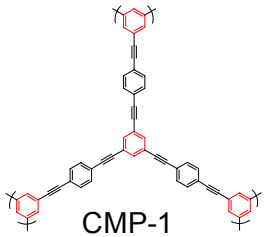
# Amorphous Polymer Networks

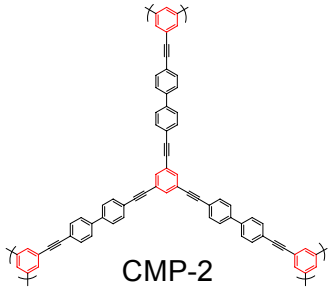
*unpublished results*



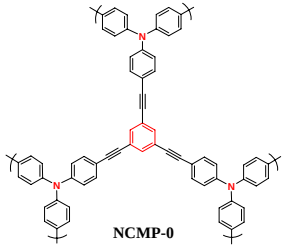
CMP-0



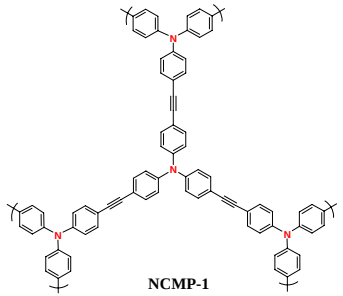
CMP-1



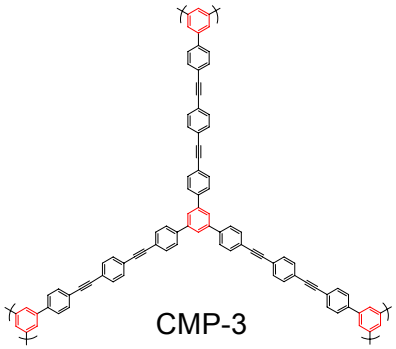
CMP-2



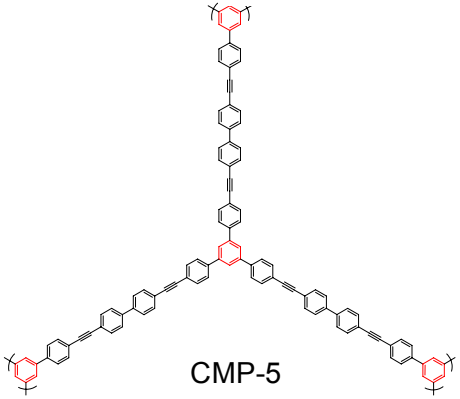
NCMP-0



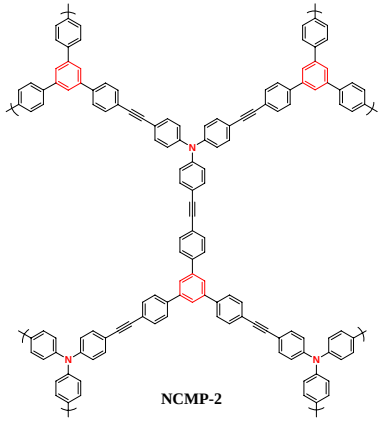
NCMP-1



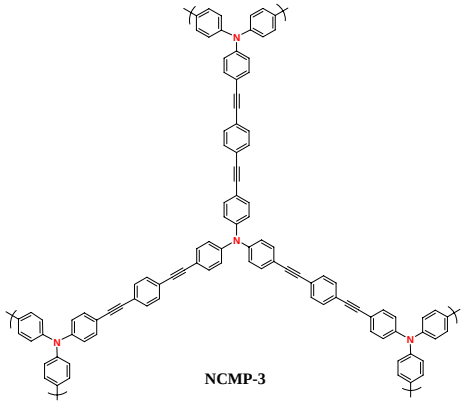
CMP-3



CMP-5

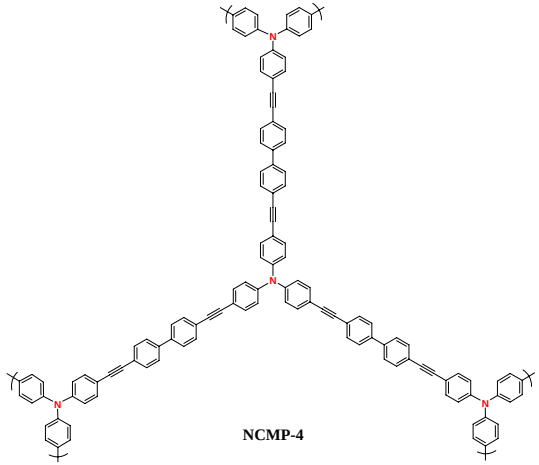


NCMP-2



NCMP-3

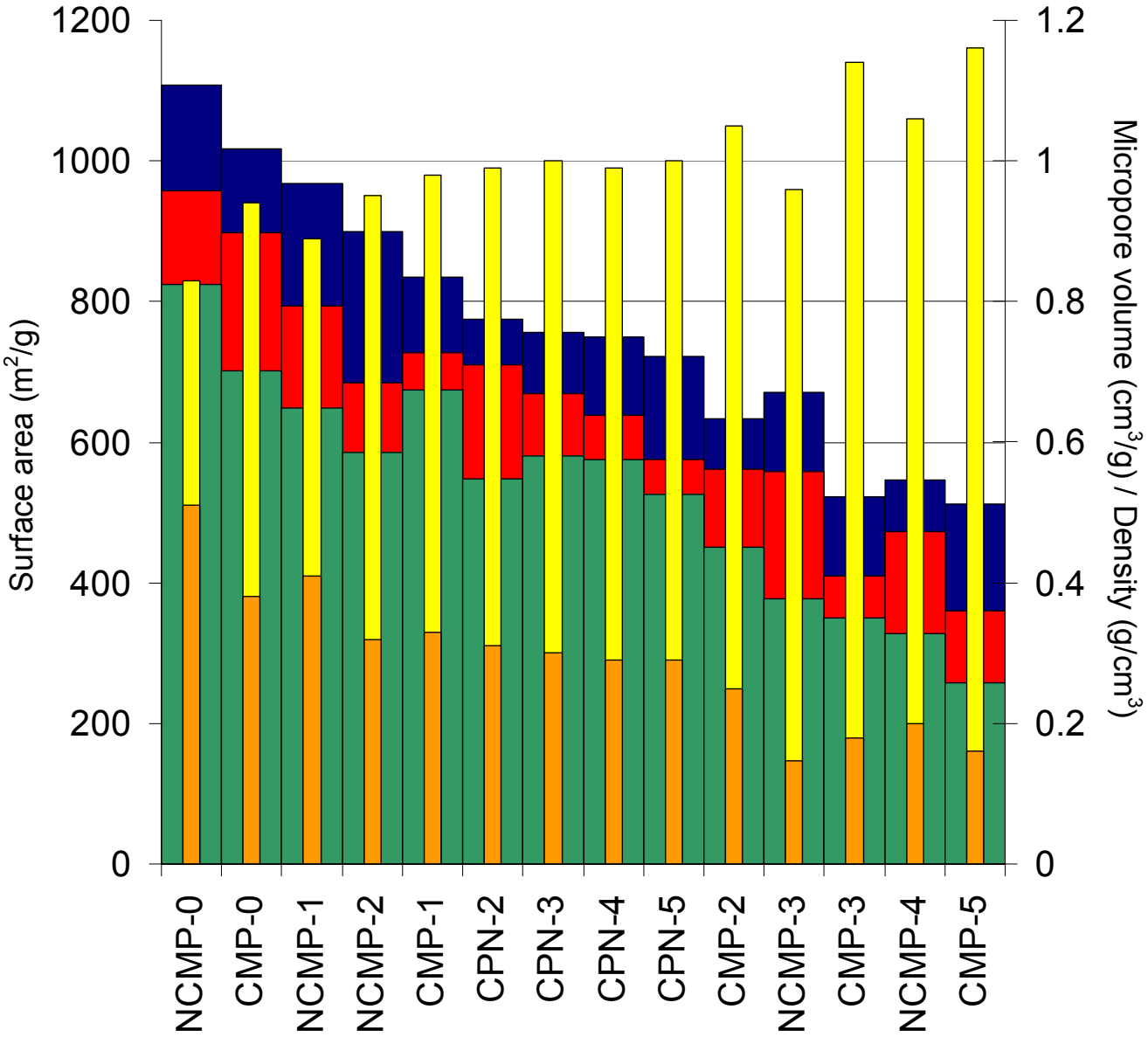
- Series of 16 homopolymers and copolymers with varying strut length



NCMP-4

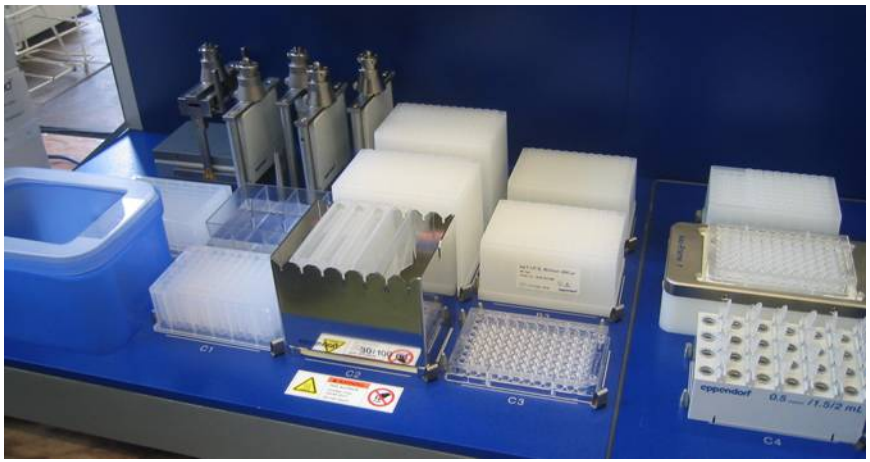
# Amorphous Polymer Networks

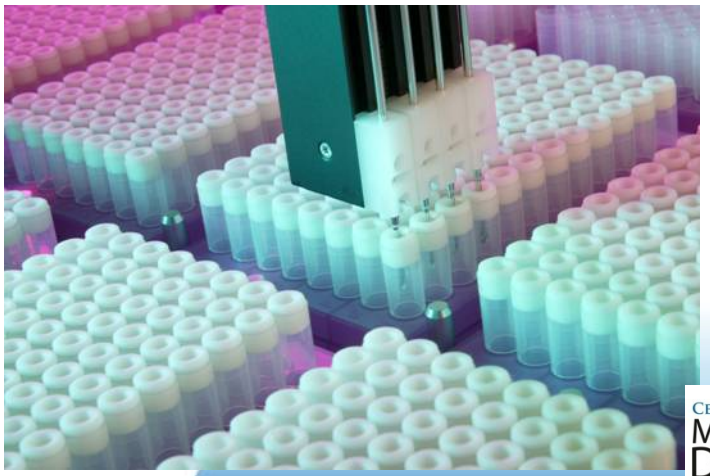
## Systematic variation of pore properties



# CENTRE FOR Materials Discovery

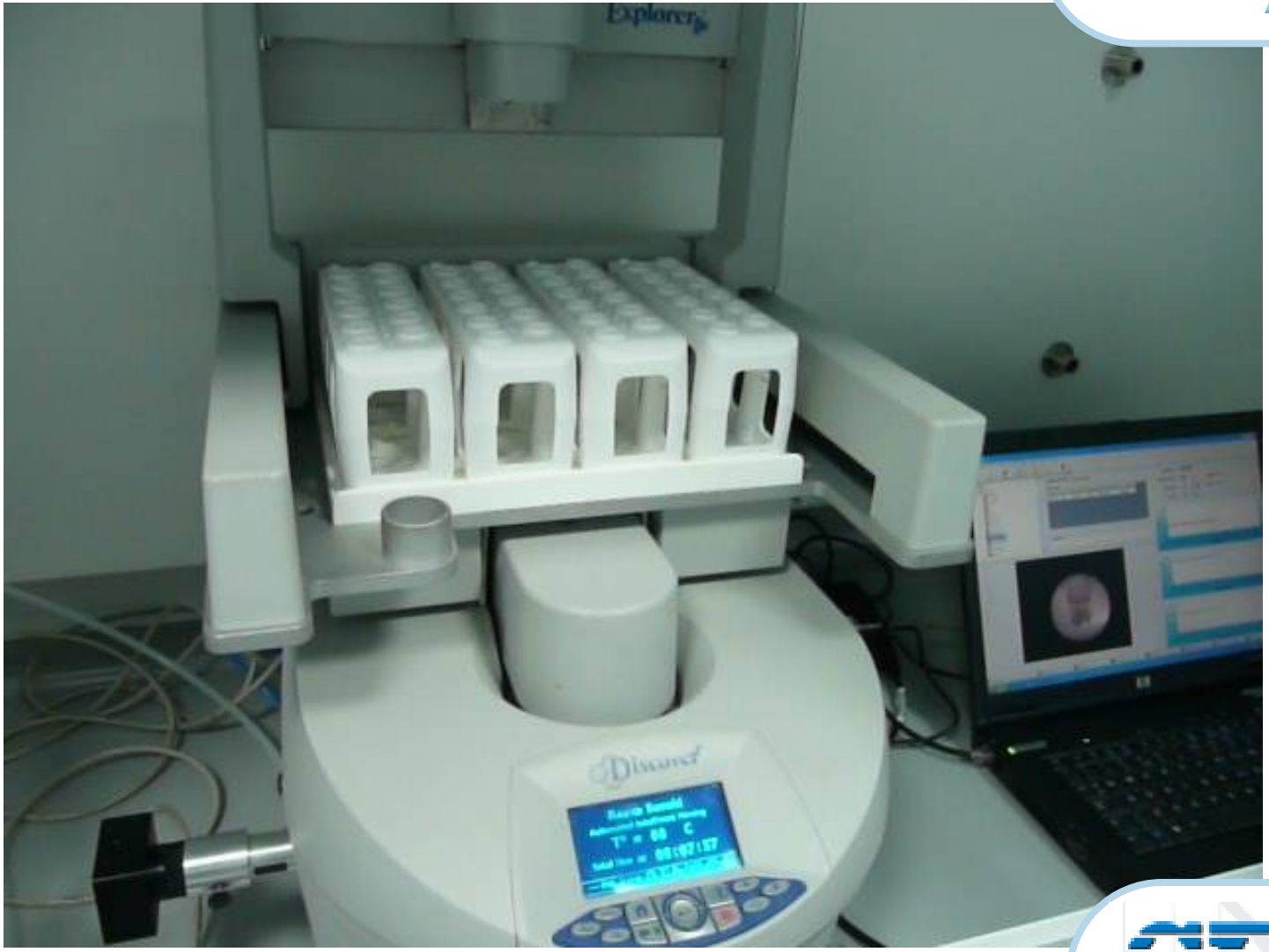
- Accelerated research via automation





CENTRE FOR Materials Discovery

# Porous Polymer Synthesis using Automated Dispensing

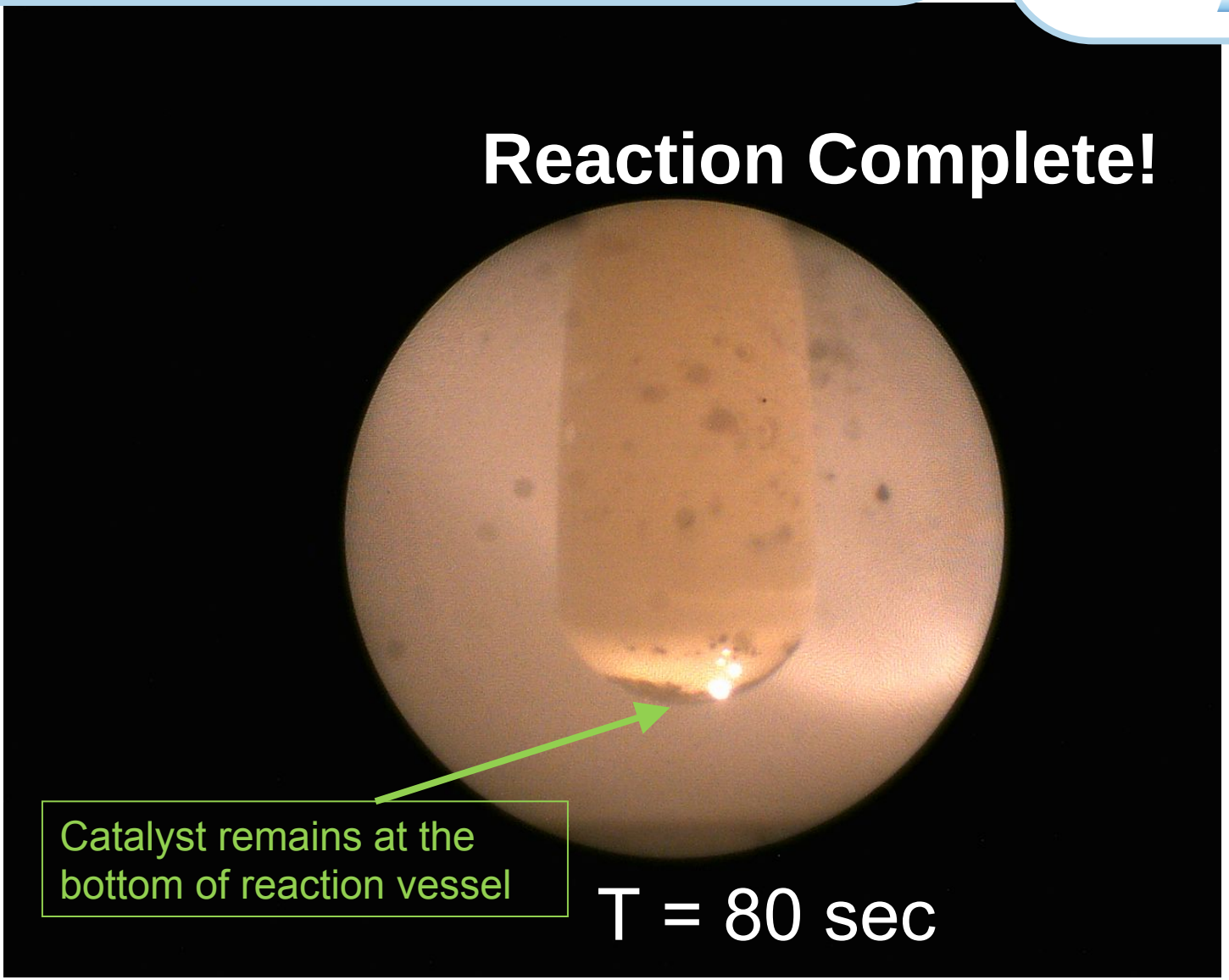


# Porous Polymer Synthesis using Automated Dispensing

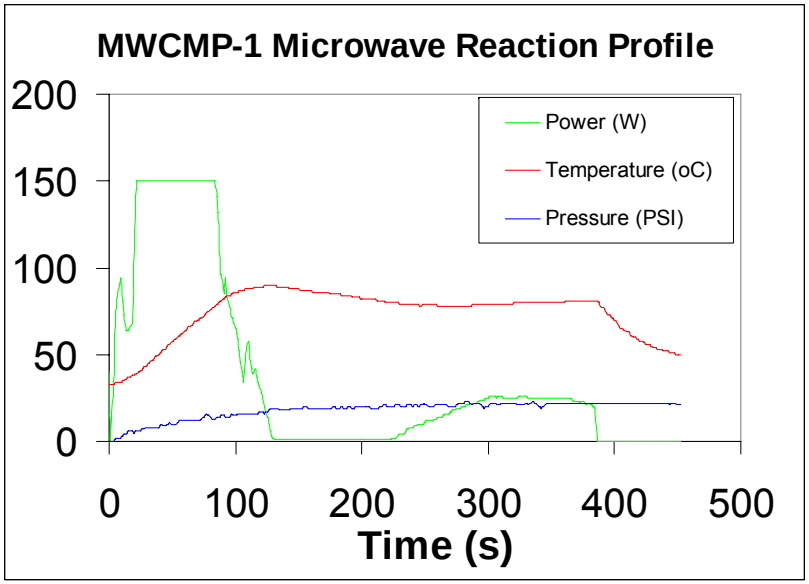
Centre for Materials Discovery

# Microwave Polymerisation of Crosslinked Ethynyl Nanoporous Polymers via Sonagashira Coupling

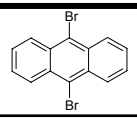
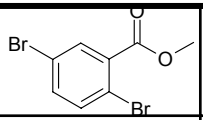
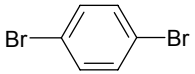
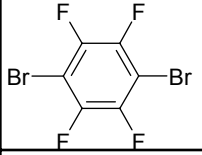
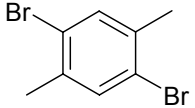
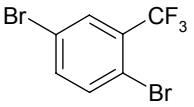
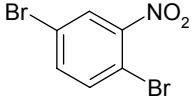
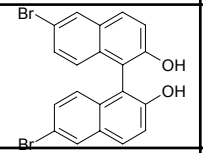
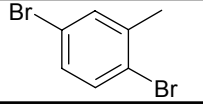
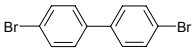
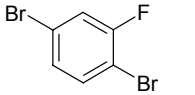
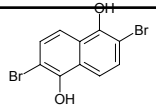
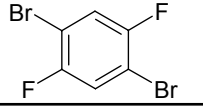
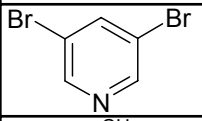
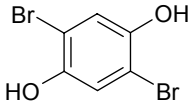
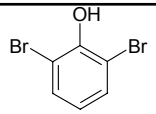
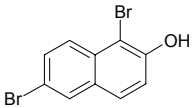
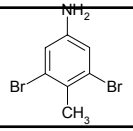
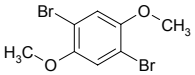
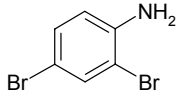
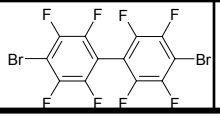
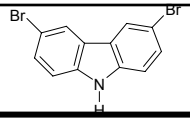
Centre for Materials Discovery



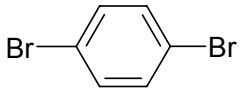
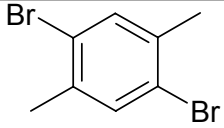
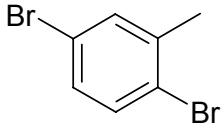
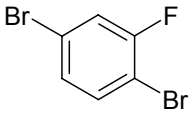
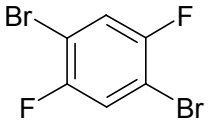
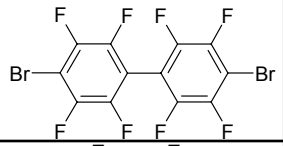
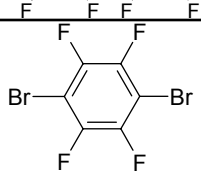
# Microwave Polymerisation of Crosslinked Ethynyl Nanoporous Polymers via Sonagashira Coupling




# Production of Nanoporous Polymer Libraries

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 9,10-dibromoanthracene |  | 182 mg<br>104 % | 14 $m^2/g$ | **12** | Methyl 2,5-dibromobenzoate |  | 150 mg<br>102 % | 519 $m^2/g$ |
| **2** | 1,4-dibromobenzene |  | 105 mg<br>98 % | 819 $m^2/g$ | **13** | 1,4-dibromotetrafluorobenzene |  | 108 mg<br>67 % | 1005 $m^2/g$ |
| **3** | 1,4-dibromo-2,5-dimethylbenzene |  | 100 mg<br>83 % | 1107 $m^2/g$ | **14** | 2,5-dibromobenzotrifluoride |  | 119 mg<br>84 % | 712 $m^2/g$ |
| **4** | 2,5-dibromonitrobenzene |  | 142 mg<br>102 % | 45 $m^2/g$ | **15** | 6,6'-dibromo-1,1'-binaphthol |  | 85 mg<br>40 % | 418 $m^2/g$ |
| **5** | 2,5-Dibromotoluene |  | 95 mg<br>82 % | 1302 $m^2/g$ | **16** | 4,4'-dibromobiphenyl |  | 140 mg<br>93 % | 185 $m^2/g$ |
| **6** | 1,4-dibromo-2-fluorobenzene |  | 112 mg<br>78 % | 1003 $m^2/g$ | **17** | 2,6-dibromo-1,5-dihydroxynaphthalene |  | 87 mg<br>56 % | 34 $m^2/g$ |
| **7** | 1,4-dibromo-2,5-difluorobenzene |  | 112 mg<br>86 % | 622 $m^2/g$ | **18** | 3,5-dibromopyridine |  | 131 mg<br>121 % | 141 $m^2/g$ |
| **8** | 2,5-dibromohydroquinone |  | 97 mg<br>77 % | 603 $m^2/g$ | **19** | 2,6-dibromophenol |  | 95 mg<br>80 % | 1136 $m^2/g$ |
| **9** | 1,6-dibromo-2-naphthol |  | 117 mg<br>86 % | 922 $m^2/g$ | **20** | 3,5-dibromo-4-methylaniline |  | None | |
| **10** | 1,4-dibromo-2,5-dimethoxybenzene |  | 98 mg<br>66 % | 883 $m^2/g$ | **21** | 2,4-dibromoaniline |  | 103 mg<br>82 % | 1024 $m^2/g$ |
| **11** | 4,4'dibromooctafluorobiphenyl |  | 150 mg<br>64 % | 873 $m^2/g$ | **22** | 3,6-dibromocarbazole |  | 135 mg<br>83 % | 601 $m^2/g$ |

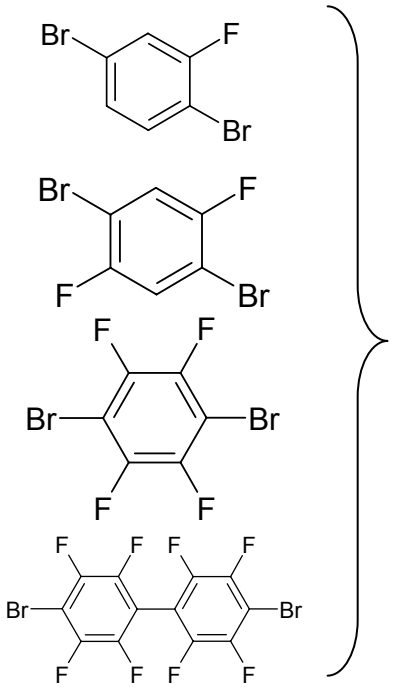
*unpublished results*

| | Dibromo monomer | $SA_{BET}$ |
|---|---|---|
| | | ***5 pt*** |
| **2** |  | 812 |
| **3** |  | 1107 |
| **5** |  | 1302 |
| **6** |  | 1003 |
| **7** |  | 622 |
| **11** |  | 873 |
| **13** |  | 1005 |

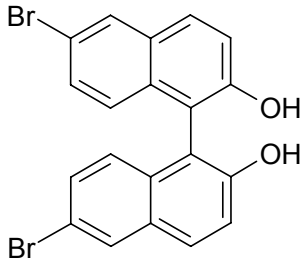
1 x $CH_3$,
60% increase
in $SA_{BET}$

*unpublished results*

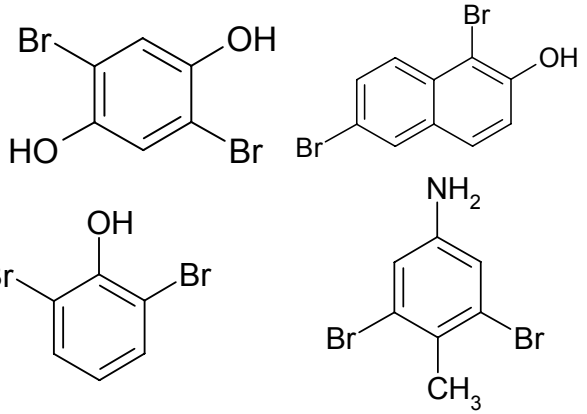
# Synthetic Elaboration and Functionality in Networks



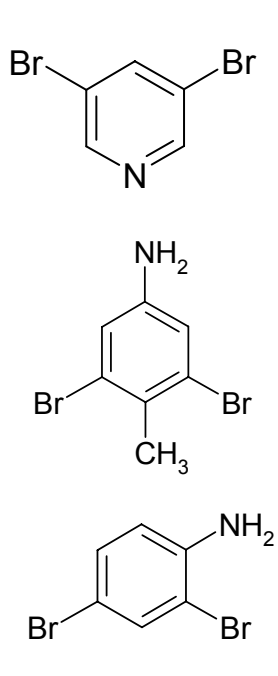

Electron-deficient linkers




Chirality



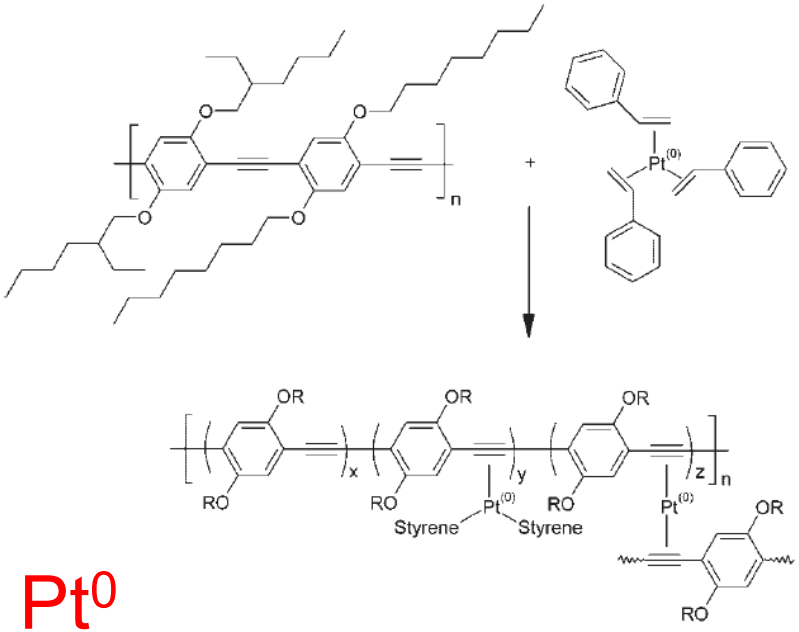

Derivatizable functional groups




Amines (*e.g.*, for $CO_2$ capture)

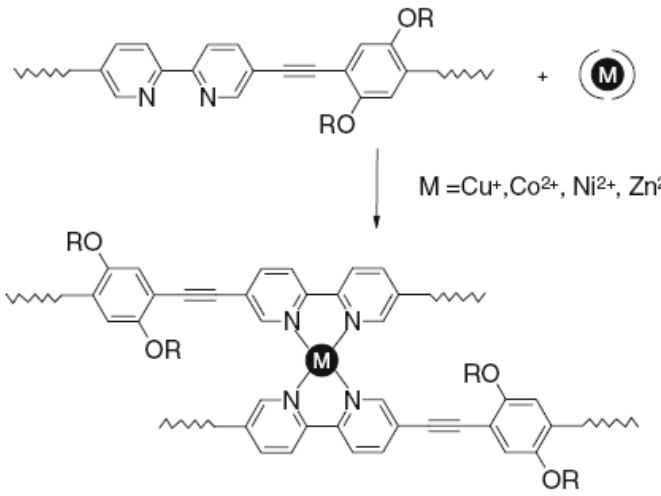
*unpublished results*

# Synthetic Elaboration and Functionality in Networks




A. Kokil, C. Huber, W. R. Caseri, C. Weder
*Macromol. Chem. Phys.* **2003**, *204*, 40–45

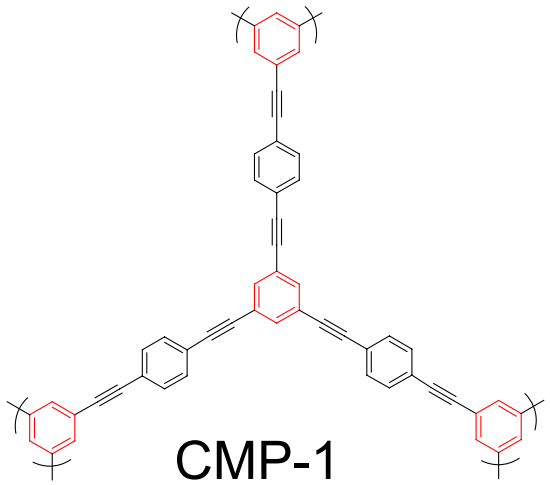
$Pt^0$




A. Kokil, P. Yao, and C. Weder, *Macromolecules* **38**, 3800 (2005).

$Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$

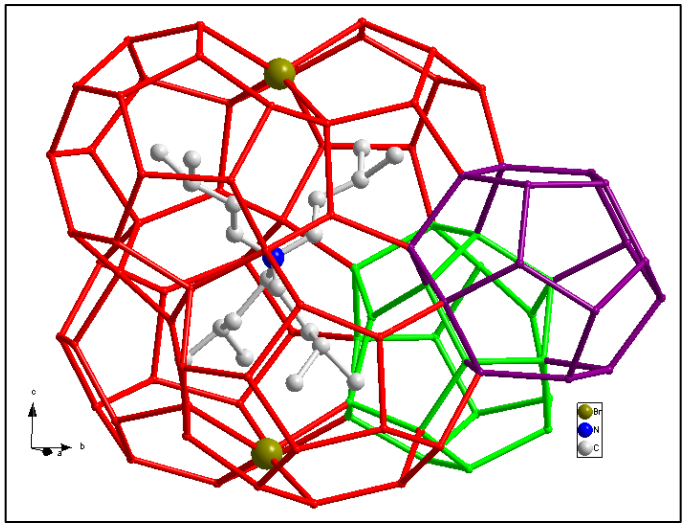
- Potential for metal incorporation
- Zero-valent metals a possibility

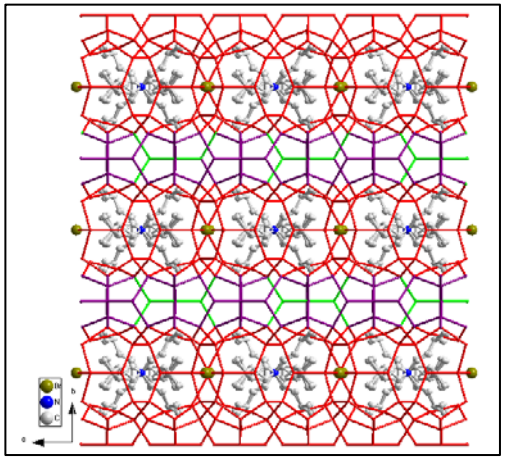


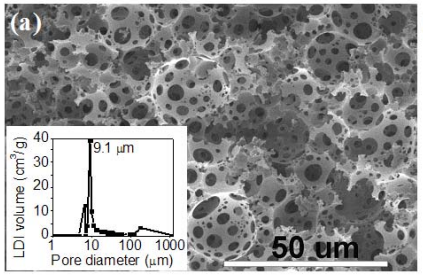
CMP-1

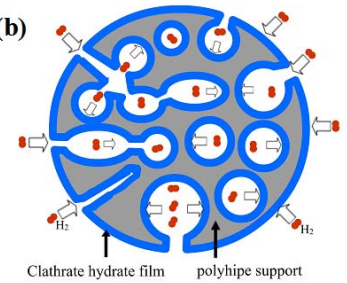
# Clathrates for Gas Storage – $H_2$ and $CH_4$

*Adv. Mater.*, **2008**, *20*, 2663; *J. Am. Chem. Soc.*, **2008**, *130*, 11608

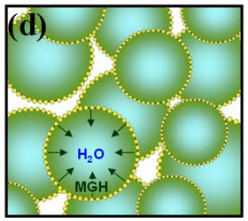


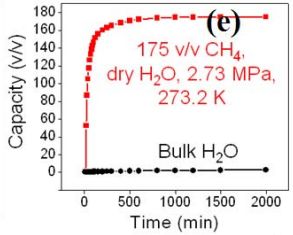


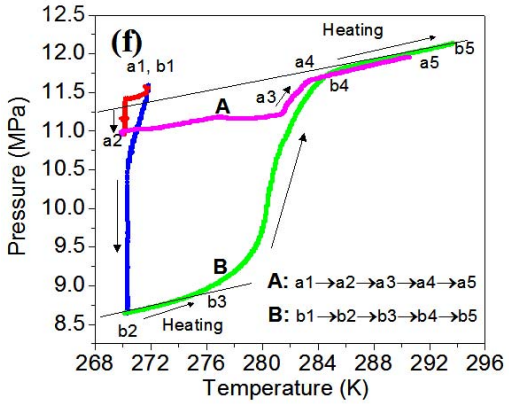






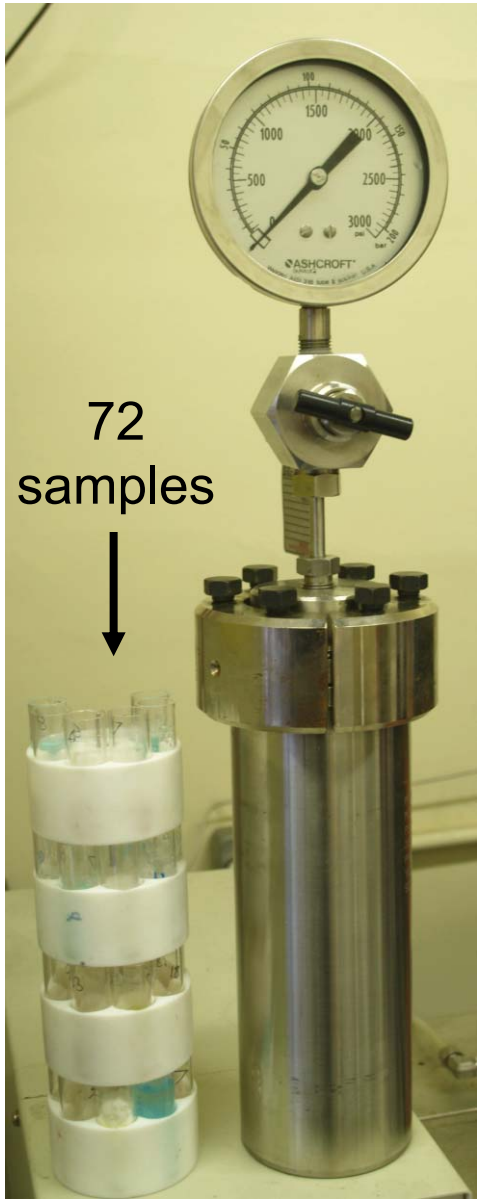



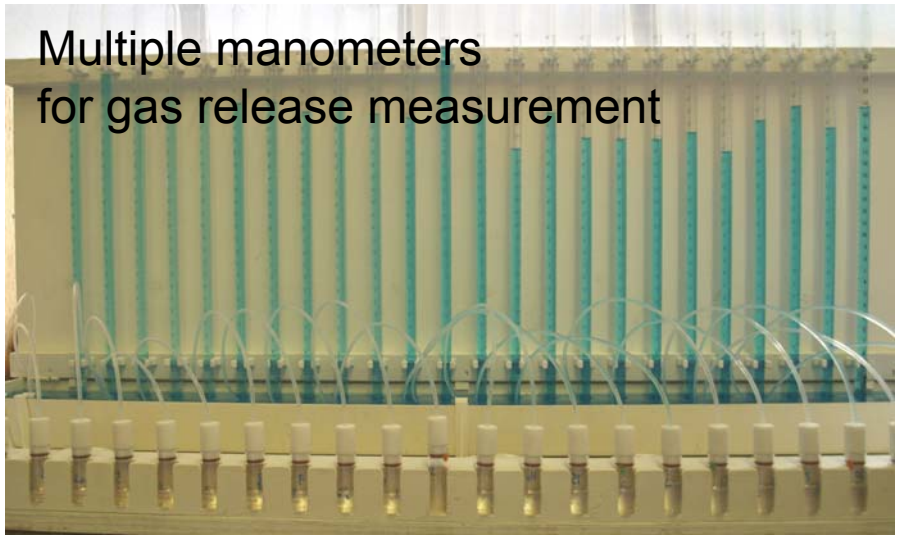



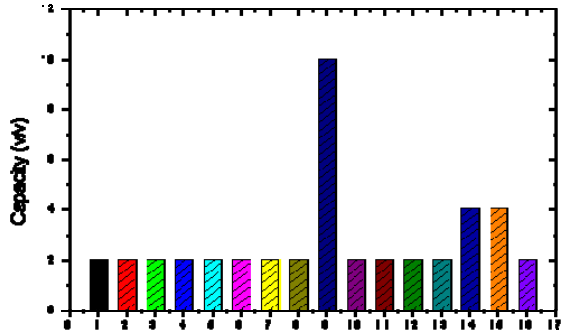


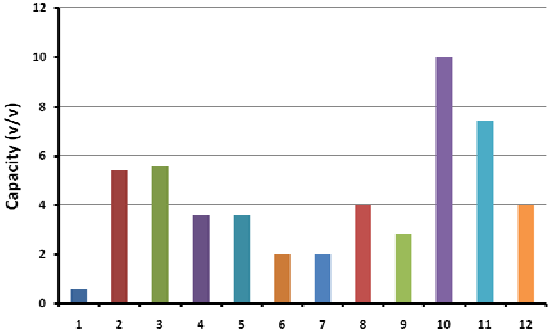
- **Goal:** storage at low pressures (1 atm), close to 298 K

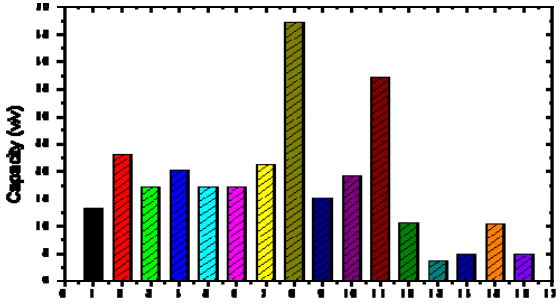
# High Throughput Discovery of Clathrates for Gas Storage

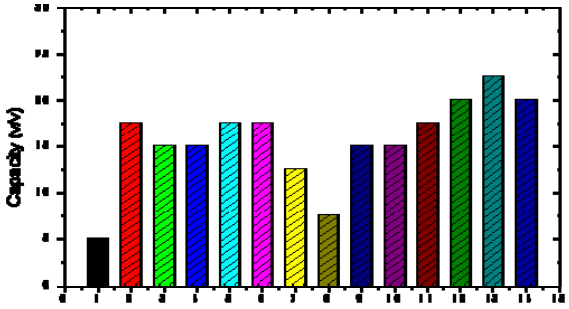


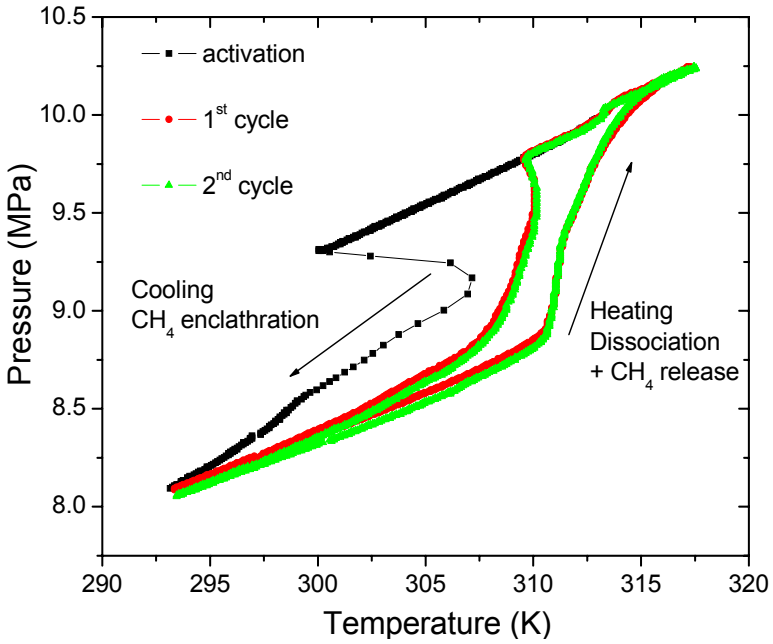



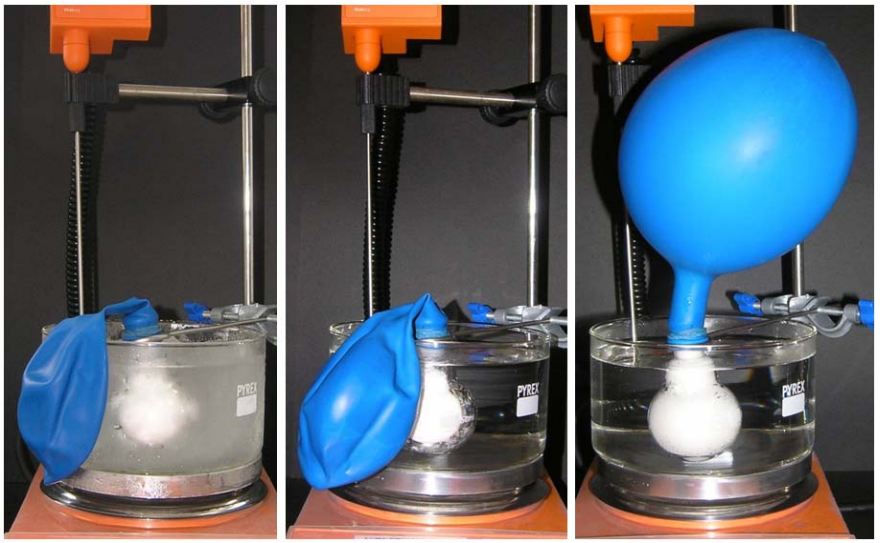



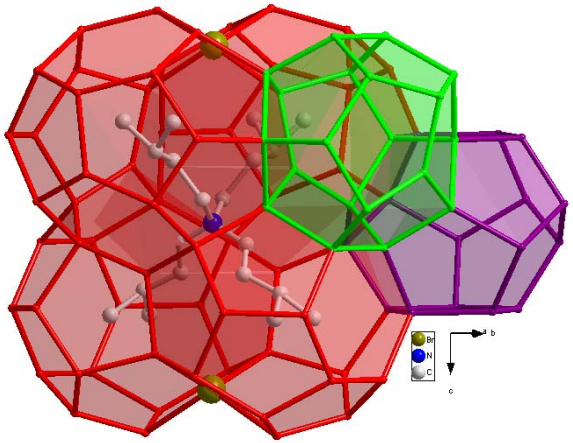



# High Throughput Discovery of Clathrates for Gas Storage



- Stores $CH_4$ at RT, releases >30 °C
- Capacity relatively low (46 v/v STP)
- 175 v/v STP possible but less stable

# Acknowledgements


**Jia-Xing Jiang** – microporous polyaryleneethynylenes

**Rob Clowes** – sorption measurements

**Hongjun Niu** – sorption measurements

**Abbie Trewin** – atomistic simulations; sorption modelling

**Ev Stöckel** – polymer synthesis and characterization

**Rob Dawson** – polymer synthesis and characterization

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**Weixing Wang** – clathrates

**Ben Carter** – clathrates

**Chris Bray** – clathrates

**Dave Adams** – clathrates

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