Rapid Removal of Organic Micropollutants from Water using a Porous Cyclodextrin Polymer

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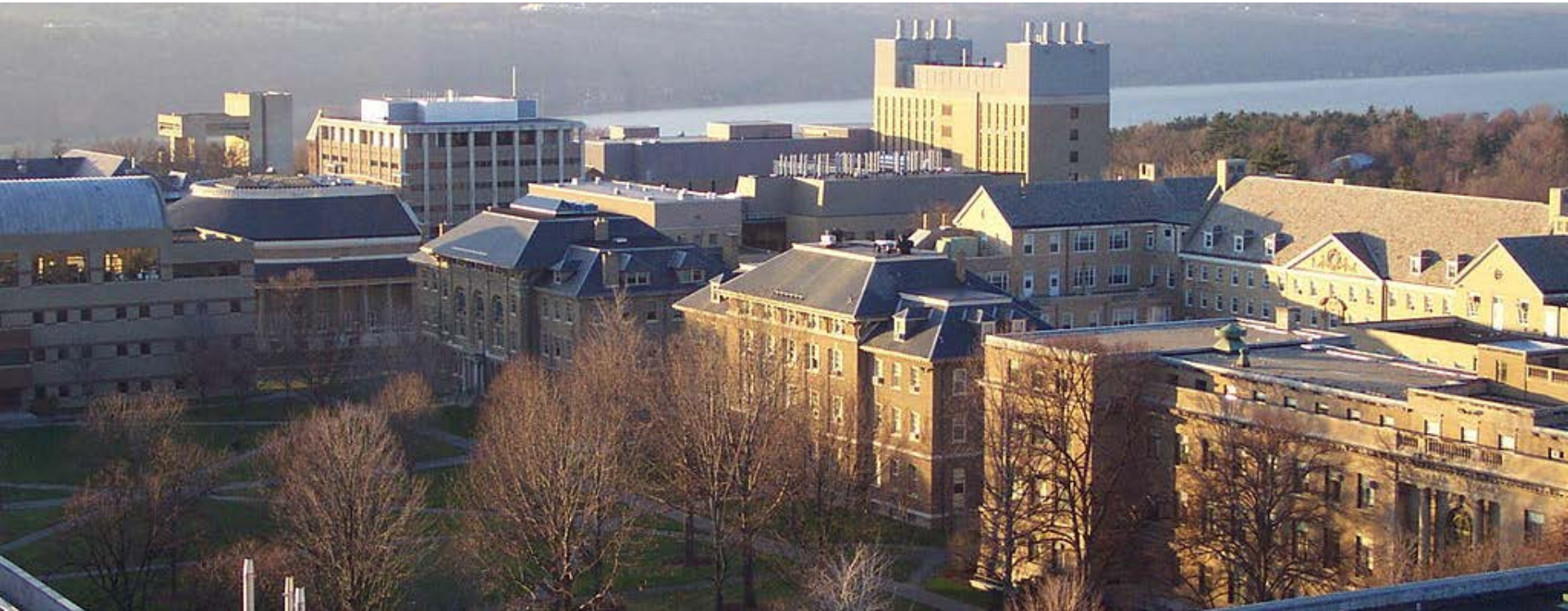
Environmental Chemistry Laboratory
March 16, 2016



Diary: 6:00 am – 9:00 am

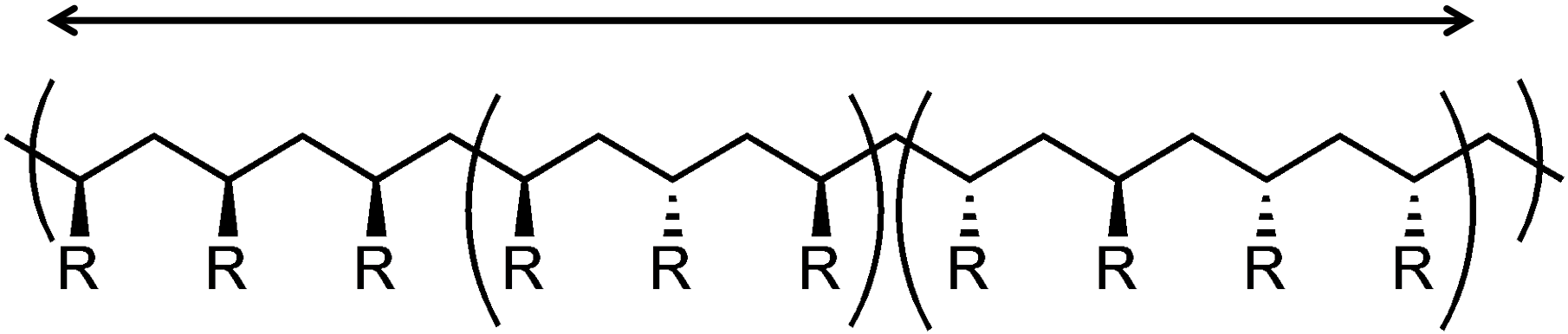
The Polymer Age

Polymer production by volume passed iron in 1970s

60% of industrial chemists work on polymers in some form.

The most versatile class of materials on earth?

Chain Length

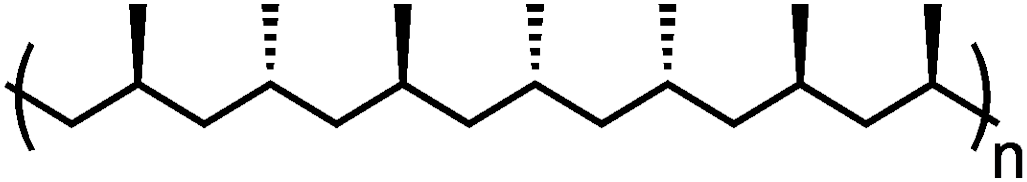


Identity of “R” = type of polymer

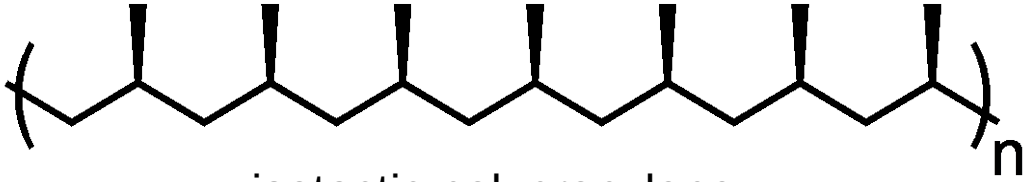
Relative positions of “R”

Structure-based Design

Stereochemistry: How are bonds oriented in space?



atactic polypropylene

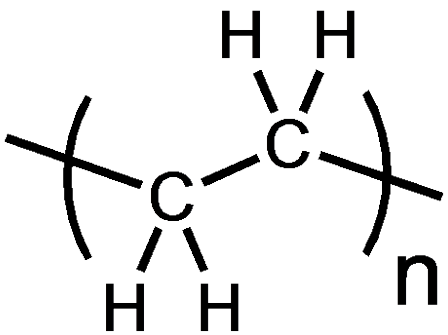


isotactic polypropylene

50 million tons produced annually

Structure-based Design

Polymer Architecture: What shape is a macromolecule?



Polyethylene
80,000,000 tons / year

very high molecular weight
very low branching

Science & Society Picture Library

high molecular weight
low branching

Wikimedia commons

low molecular weight
significant branching

Jonathan Youngblood

You Gotta Have Ma

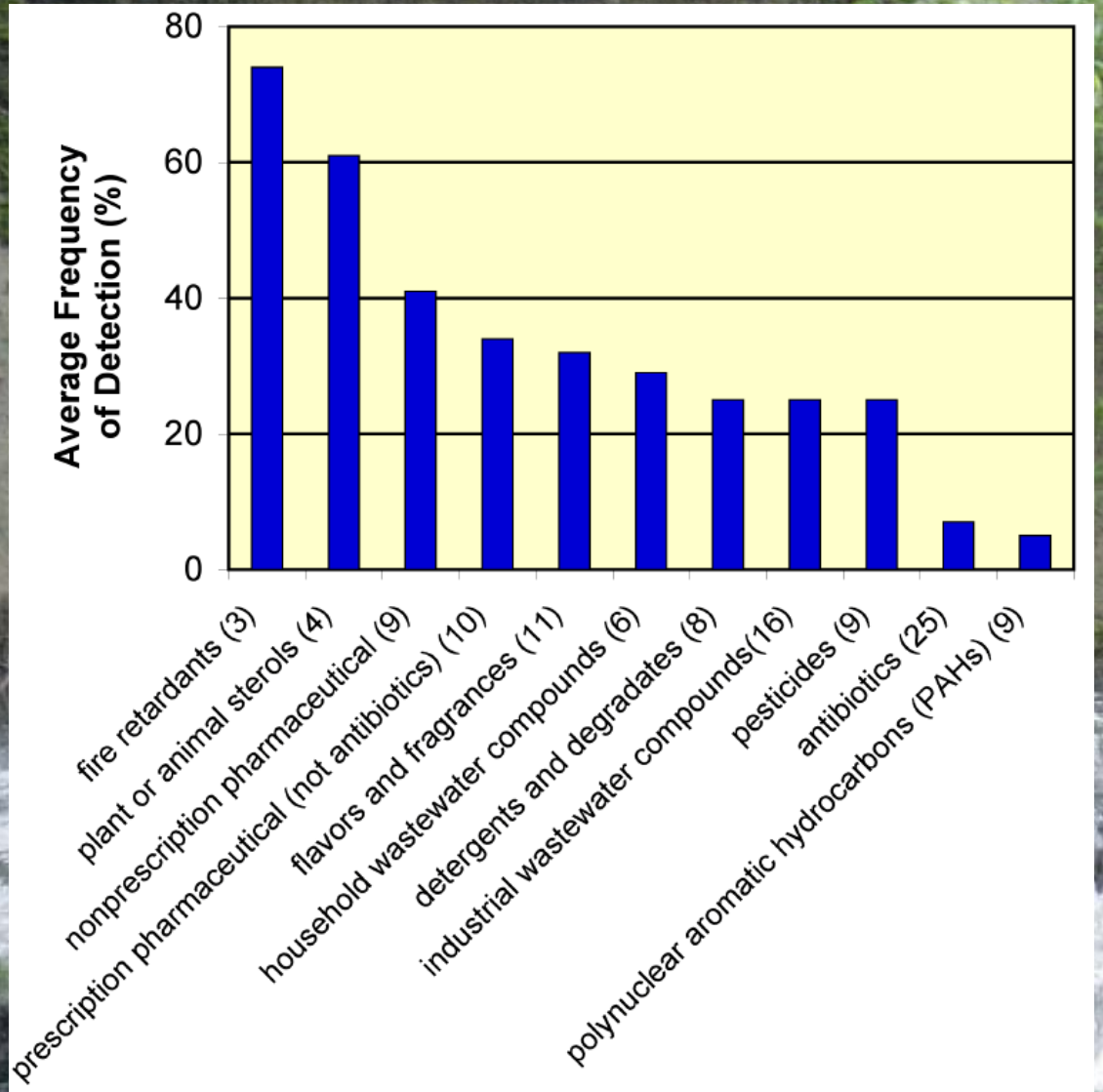
間

THE MUSIC IS NOT IN THE NOTES, BUT IN THE SILENCE BETWEEN.

—Wolfgang Amadeus Mozart

Empty Space Creates Opportunity

Discharge from a wastewater treatment plant on Four Mile Creek, Iowa
http://toxics.usgs.gov/highlights/tracing_wastewater.html



Glassmyer *et al. Environ. Sci. Technol.*, **2005**, *39*, 5157.

Frustrated Packing

Design Criteria

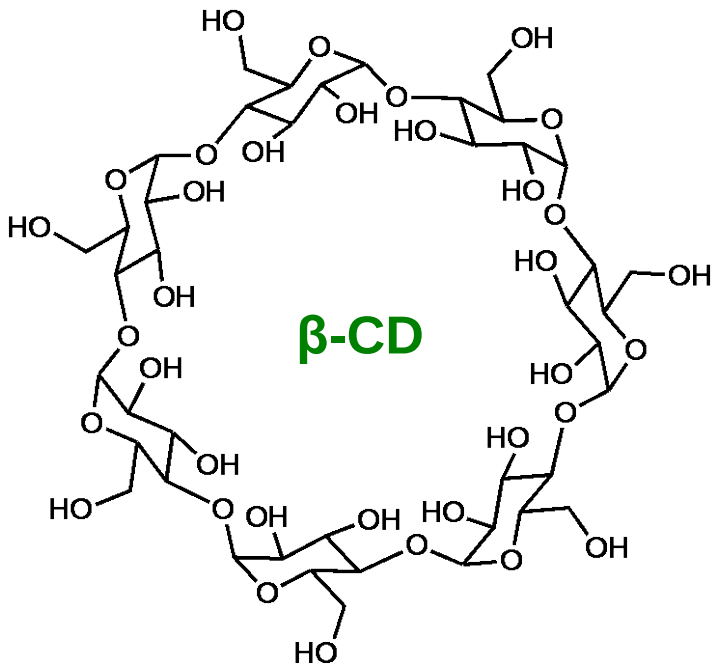
Rigid building blocks…

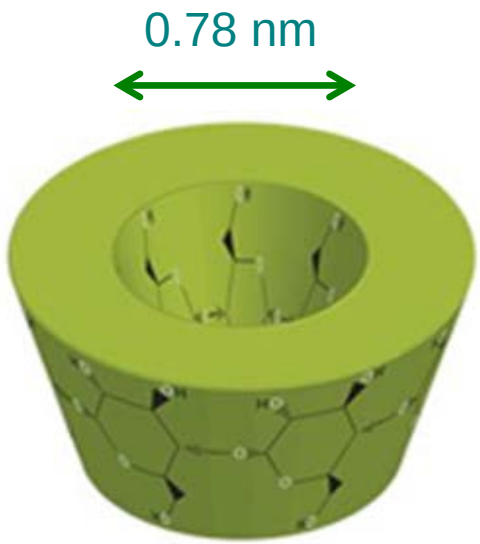
…or contain voids or non-complementary shapes

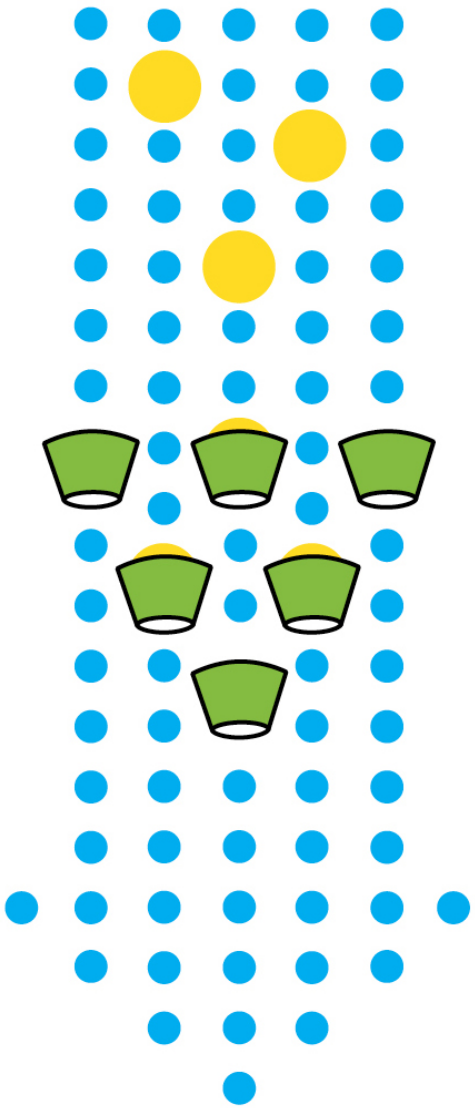
Irreversible reactions

Little or no reorganization of the final structure

Cyclodextrin Primer







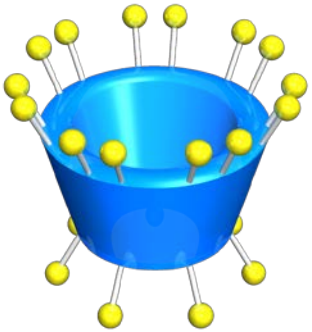
Macrocycle of glucose produced from corn starch

Used in drug formulations and personal care products

Hydrophobic groups bind within the interior cavity

Capable of sequestering both metal ions and organic pollutants from water

Crosslinked CD Polymer Synthesis



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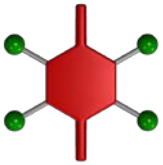
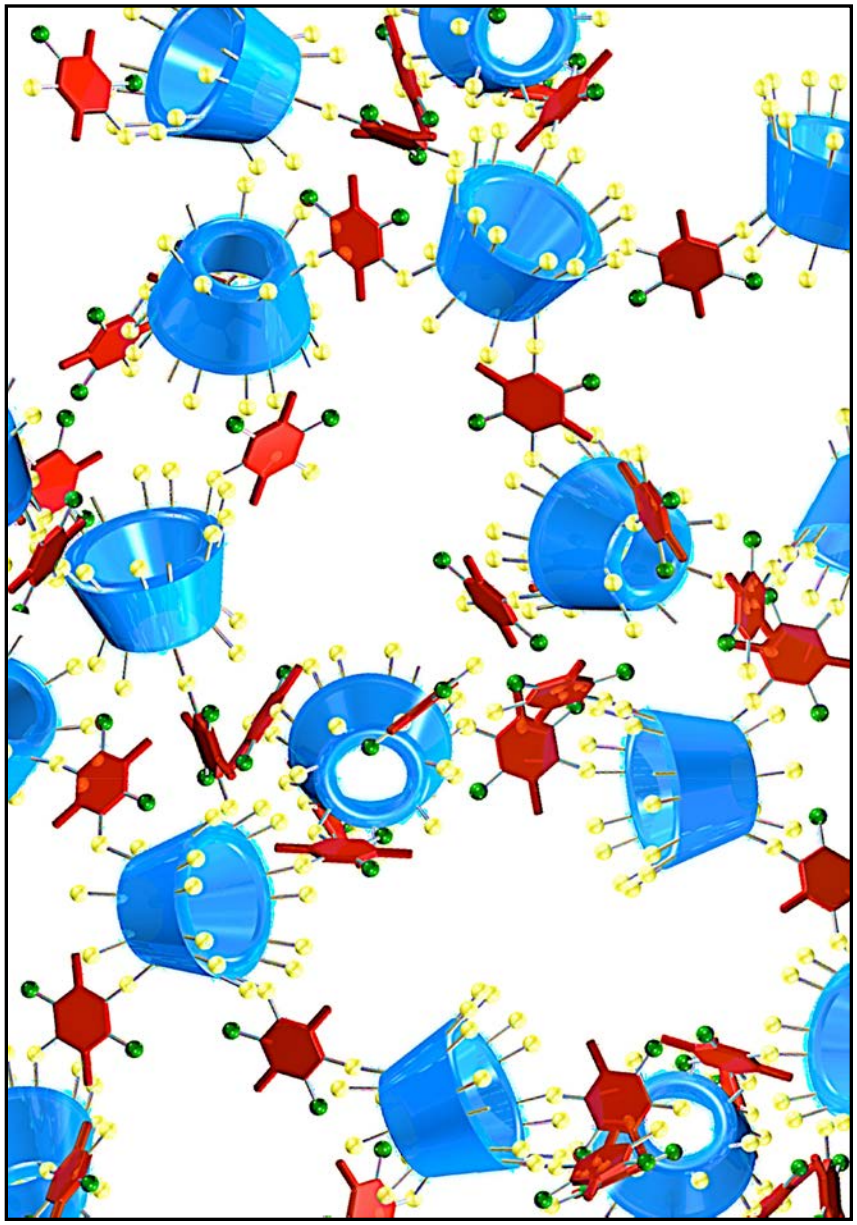
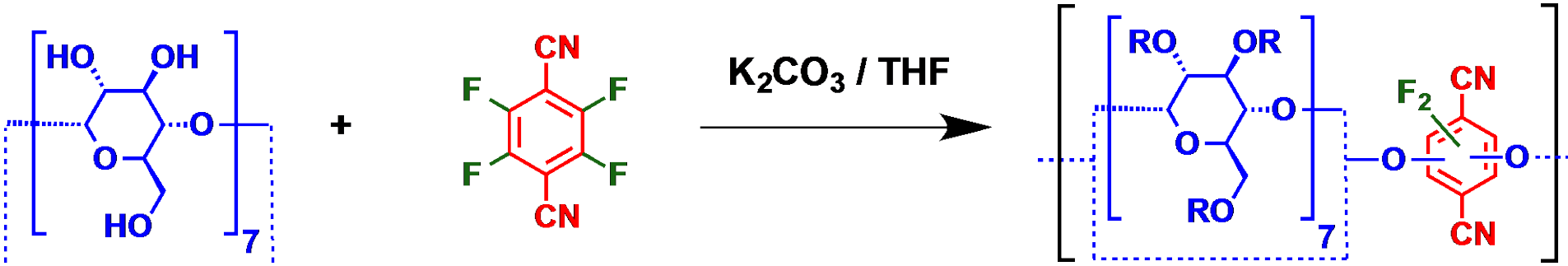




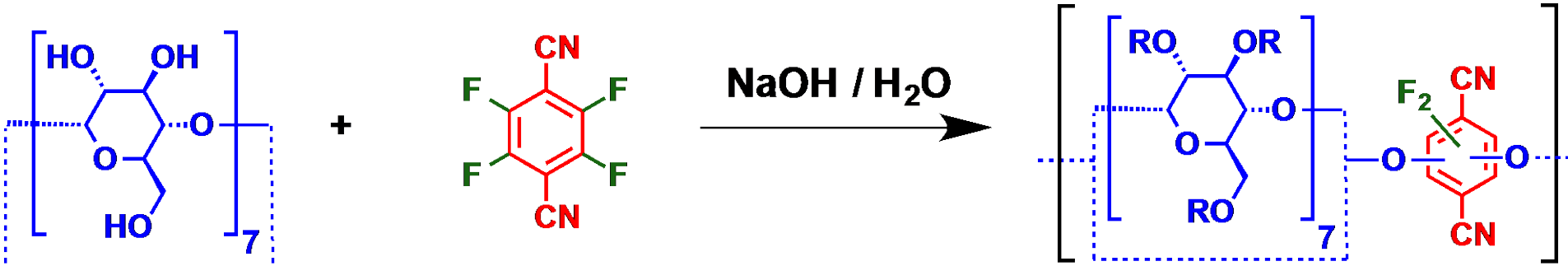
Crosslinked CD Polymer Synthesis



P-CDP

S_{BET} = 263 m^2/g

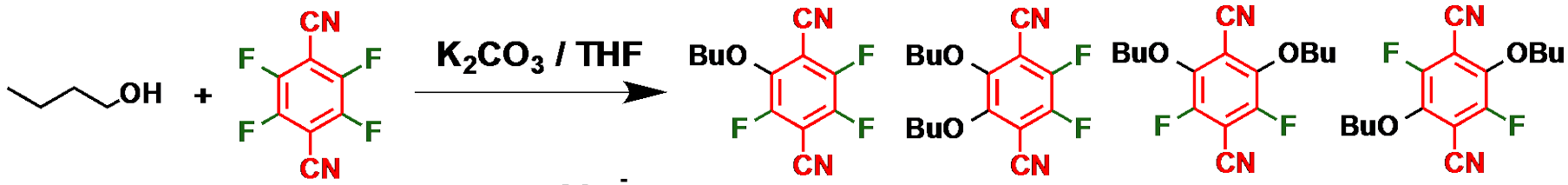
	P-CDP	NP-CDP
β-CD : TFP	1 : 6.1	1 : 3.5
Substitution (TFP)	2.1	2.2



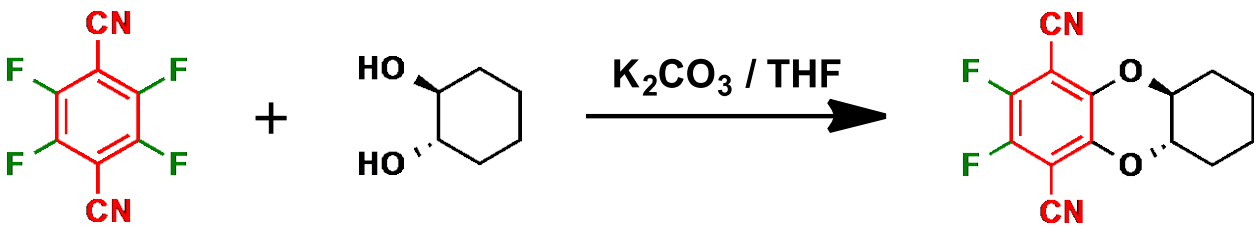
NP-CDP

S_{BET} = 6 m^2/g

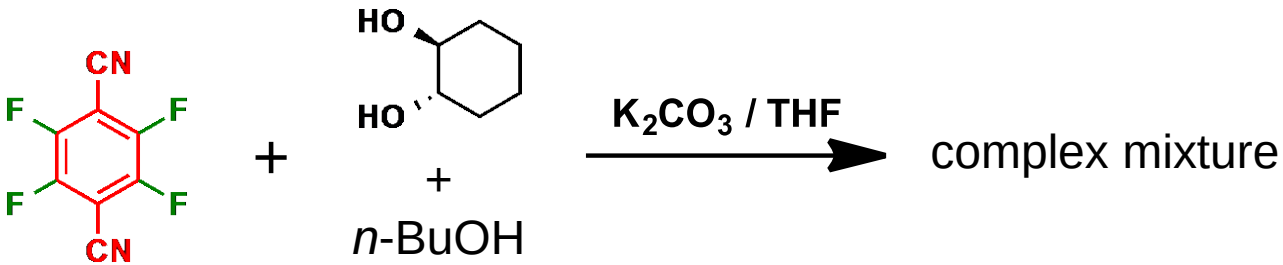
Model Reactions



equiv BuOH	mono	1,2-di	1,3-di	1,4-di
2.3	65%	4%	10%	21%
4.0	24%	8%	23%	45%



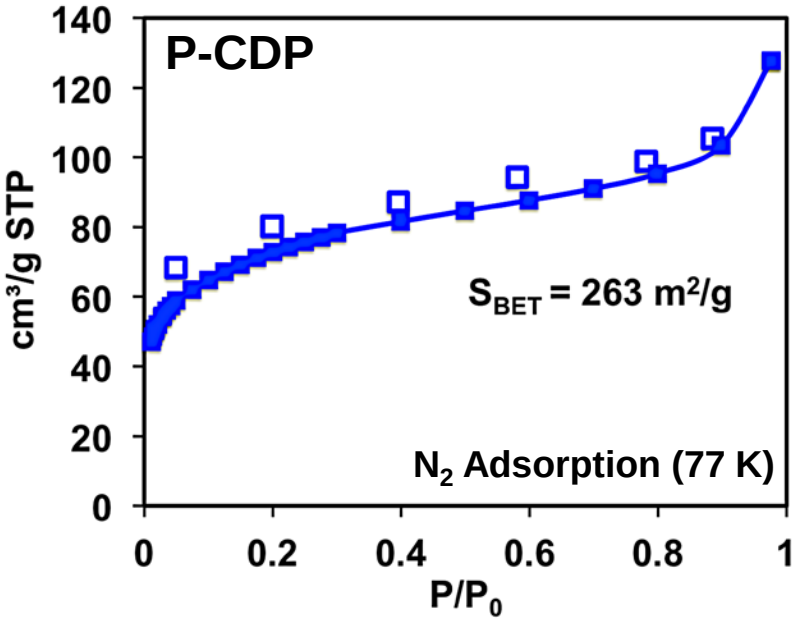
P-CDP and NP-CDP are linked mostly through disubstituted terephthalonitriles

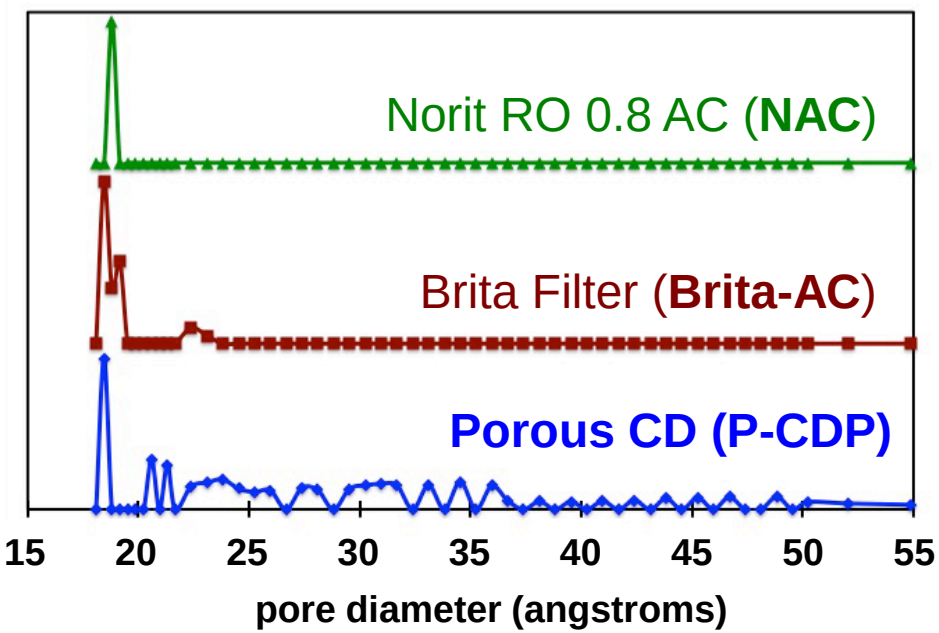


Unclear if 2 –OH groups are capped or connected

Linkages in polymer will be determined by SS NMR.

Surface Area / Porosity Comparison





Cyclodextrin Polymers

Epichlorohydrin (EPI-CDP)	<10 m²/g
Non-porous CD (NP-CDP)	<10 m²/g
Porous CD (P-CDP)	**263 m²/g**

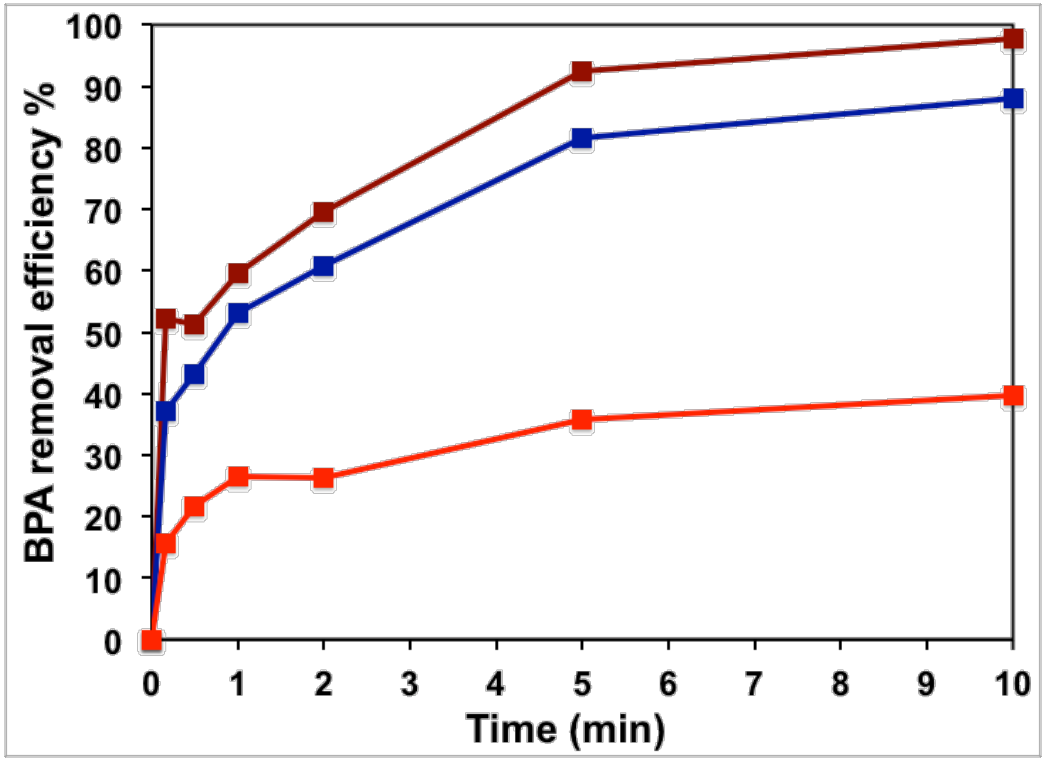
Activated Carbons

Brita Filter (Brita-AC)	502 m²/g
Granulated AC (GAC)	612 m²/g
Norit RO 0.8 AC (NAC)	**984 m²/g**

mass = ~1 g

geometric area: ~0.01 m²

Bisphenol A Uptake



Adsorbent	BPA k_{obs} (g mg^{-1} min^{-1})
Brita AC	0.009
GAC	0.05
NAC	0.09

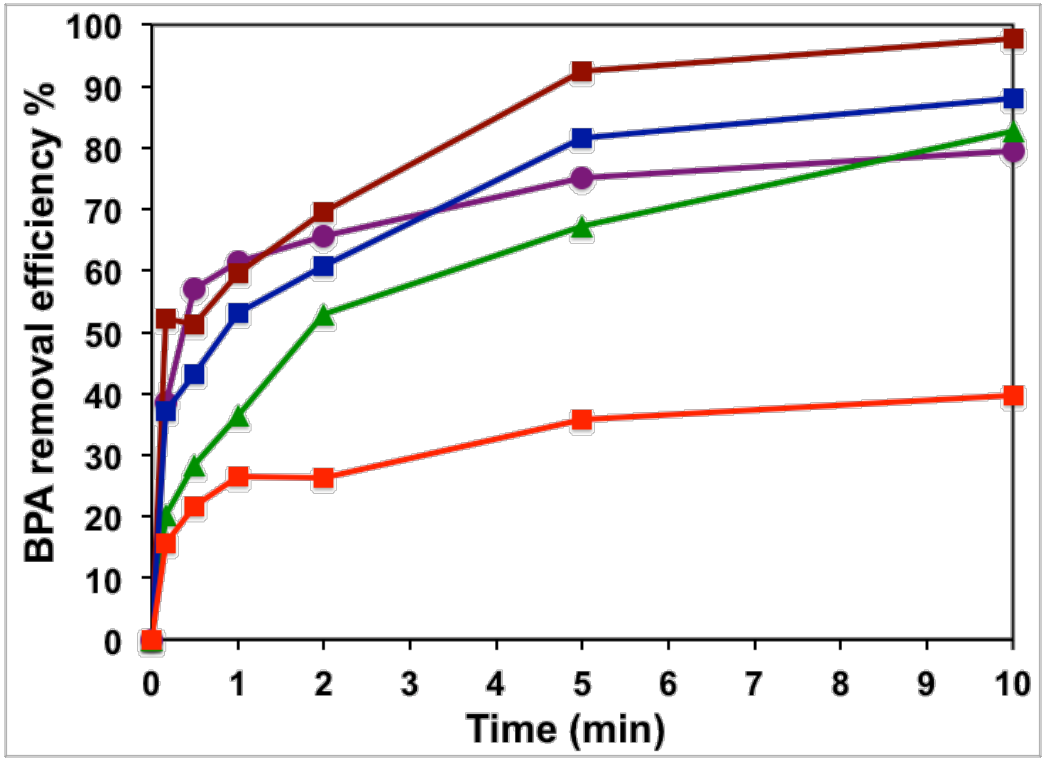
2nd Order Binding Model

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_{obs} q_e^2}$$

k_{obs}: Figure of merit for how quickly an adsorbant establishes equilibrium

2nd order binding model: Y. S. Ho; G. McKay *Process Biochem.* **1999**, *34*, 451–465.

Bisphenol A Uptake



Adsorbent	BPA k_{obs} (g mg^{-1} min^{-1})
Brita AC	0.009
GAC	0.05
NAC	0.09
EPI-CDP	0.03
NP-CDP	0.1

2nd Order Binding Model

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_{obs} q_e^2}$$

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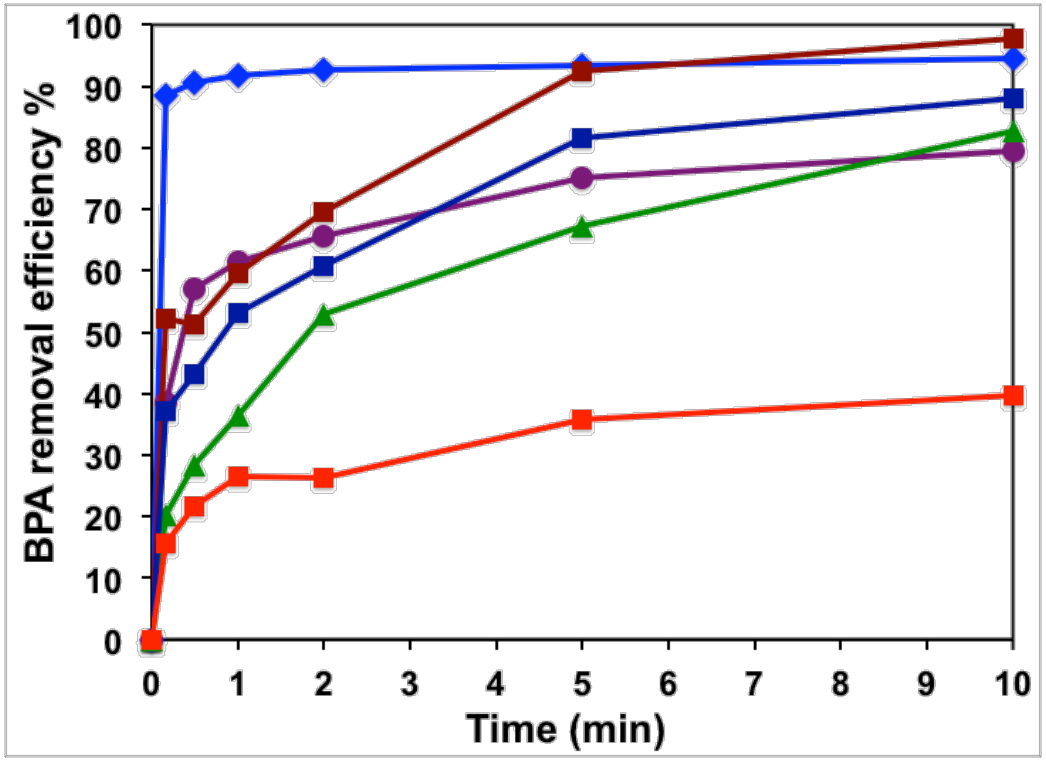


Adsorbent	BPA k_{obs} (g mg^{-1} min^{-1})
Brita AC	0.009
GAC	0.05
NAC	0.09
EPI-CDP	0.03
NP-CDP	0.1
P-CDP	1.5

2nd Order Binding Model

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_{obs} q_e^2}$$

k_{obs}: Figure of merit for how quickly an adsorbant establishes equilibrium

2nd order binding model: Y. S. Ho; G. McKay *Process Biochem.* **1999**, *34*, 451–465.

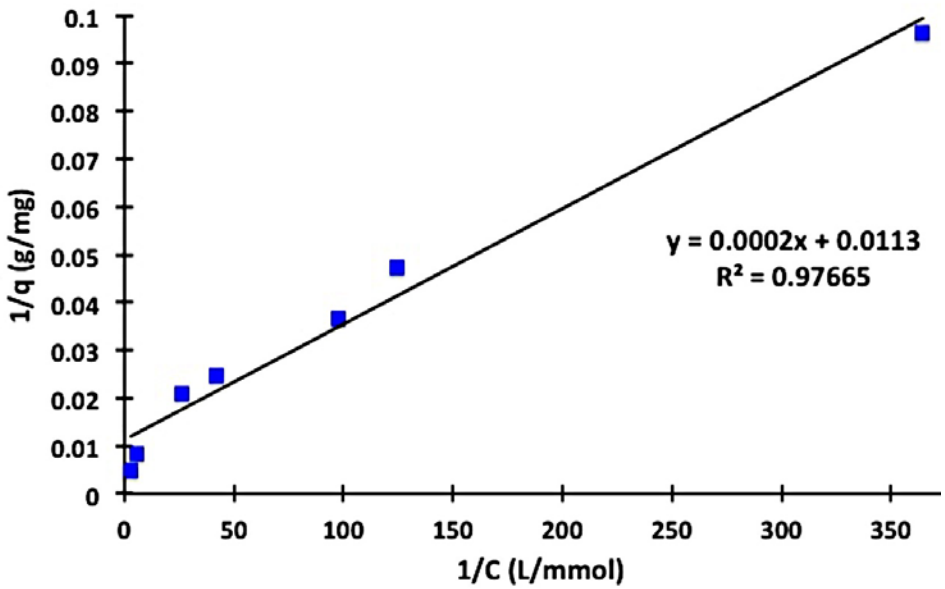
Thermodynamics of BPA Binding

Langmuir Model of Adsorption

$$\frac{1}{Q_t} = \frac{1}{Q_{max}} + \frac{1}{Q_{max} \cdot K} \frac{1}{C}$$

Q_t: mg/g adsorbed
Q_{max}: mg/g maximum adsorption capacity

Prog. Polym. Sci. **2013**, *38*, 344
J. Incl. Phenom. Macrocycl. Chem. **2004**, *50*, 115



$K = 56\,000\ M^{-1}$

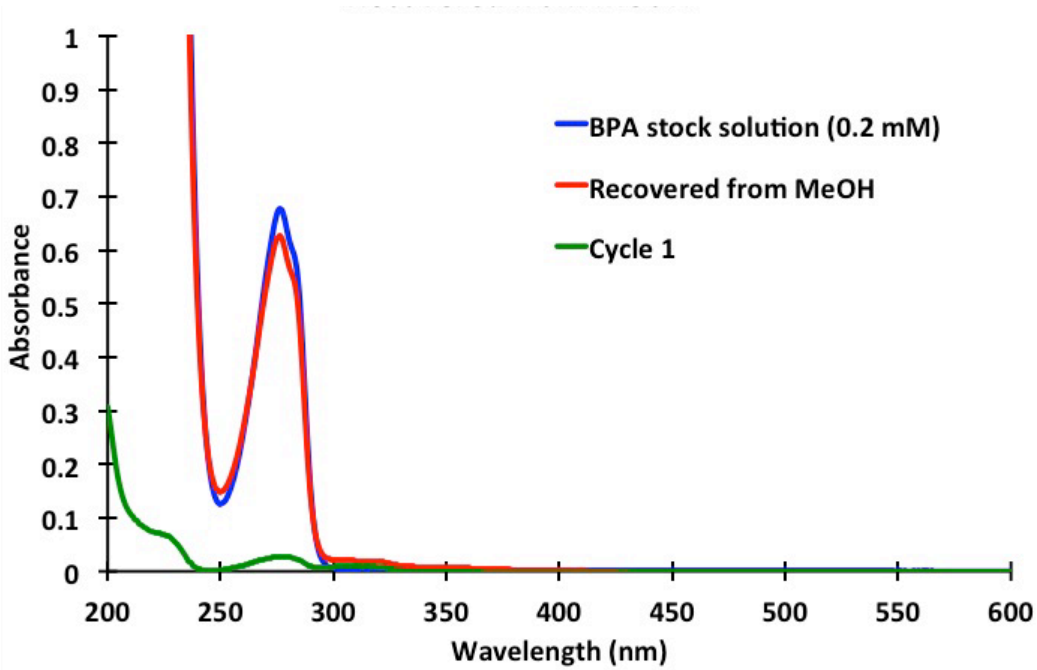
$Q_{max} = 88$ mg/g

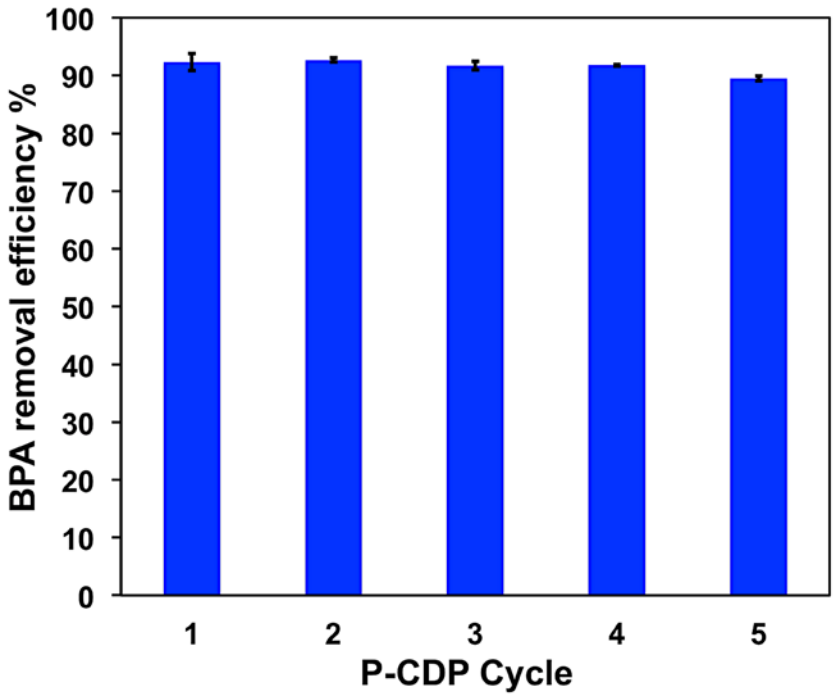
Literature: highest 84 mg/g

1:1 complex of CD/BPA

0.38 mM BPA to 0.37 mM CD

Regenerating the Polymer





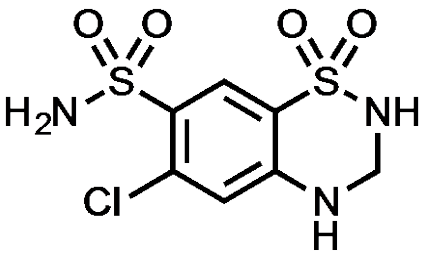
BPA recovered by washing P-CDP with alcohol solvents at room temperature

Spent activated carbon is usually re-activated at 500-900 °C with loss of performance

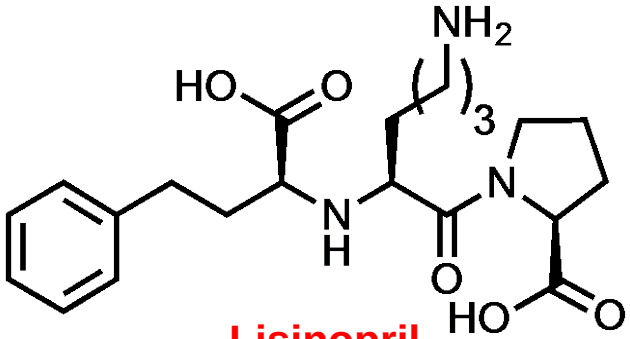
Emerging Organic Micropollutants

Survey of 50 the largest wastewater treatment plants in the United States (each 15,000,000–660,000,000 gallons / day)

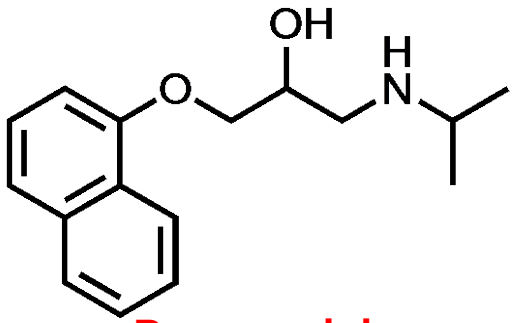
These plants process 6B gallons / day from 46M people (17% of US wastewater)



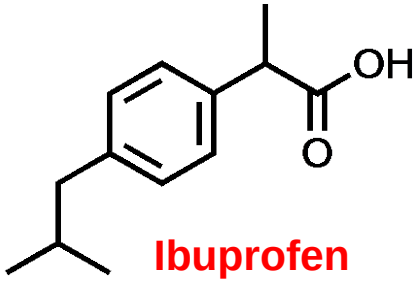
Hydrochlorothiazide
Hypertension
50 / 50
Max 2.80 µg/L



Lisinopril
Hypertension
23 / 49
Max 3.30 µg/L

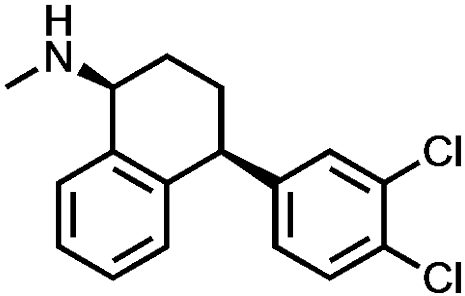


Propranolol
Hypertension
44 / 50
Max 260 ng/L = 65 % C_{plasma}



Ibuprofen
Anti-inflammatory
23 / 50
Max 4.20 µg/L

Not a threat to humans at these concentrations BUT ecological effects are unknown

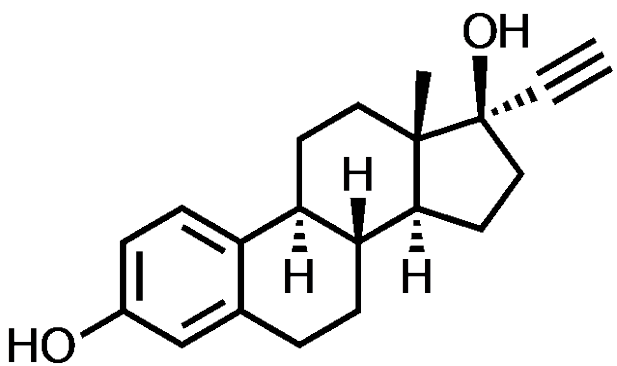


Sertraline
Depression
32 / 50
Max 71 ng/L = 70 % C_{plasma}

Kostich, M. S.; Batt, A. L.; Lazorchak, J. M. *Environ. Pollut.* **2014**, *184*, 354.

Ecological Concern for Bioactive Compounds

Ethinyl estradiol (EE2)
Contraception



5 ng/L over 3 years

Experimental Lake Area

Ontario, Canada

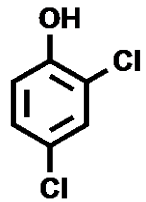
Fathead Minnow: Male Feminization

Photo: Rankin1958 on http://tinyurl.com/ou2mwel (CC by 3.0)

K. A. Kidd, P. J. Blanchfield, K. H. Mills, V. P. Palace, R. E. Evans, J. M. Lazorchak, R. W. Flick *PNAS* **2007**, *104*, 8897.

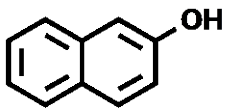
Other pollutants

Aromatic Models / Industrial intermediates



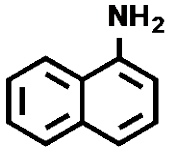
2,4-Dichlorophenol

Carcinogen



2-Naphthol

Model for Naphthols

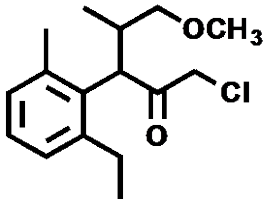


1-Naphthyl amine

Carcinogen

Model for Naphthyl amine pollutants

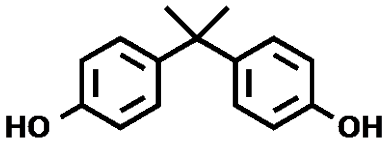
Agriculture



Metolachlor

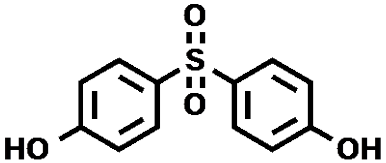
Leading pesticide

Plastic Industry



Bisphenol A

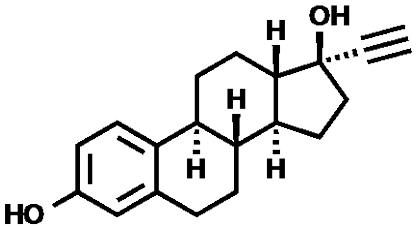
Endocrine disruptor



Bisphenol S

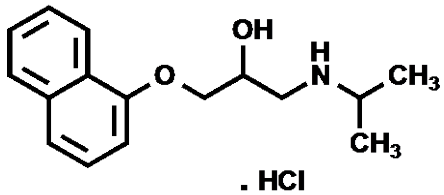
Endocrine disruptor

Medical



Ethinyl estradiol

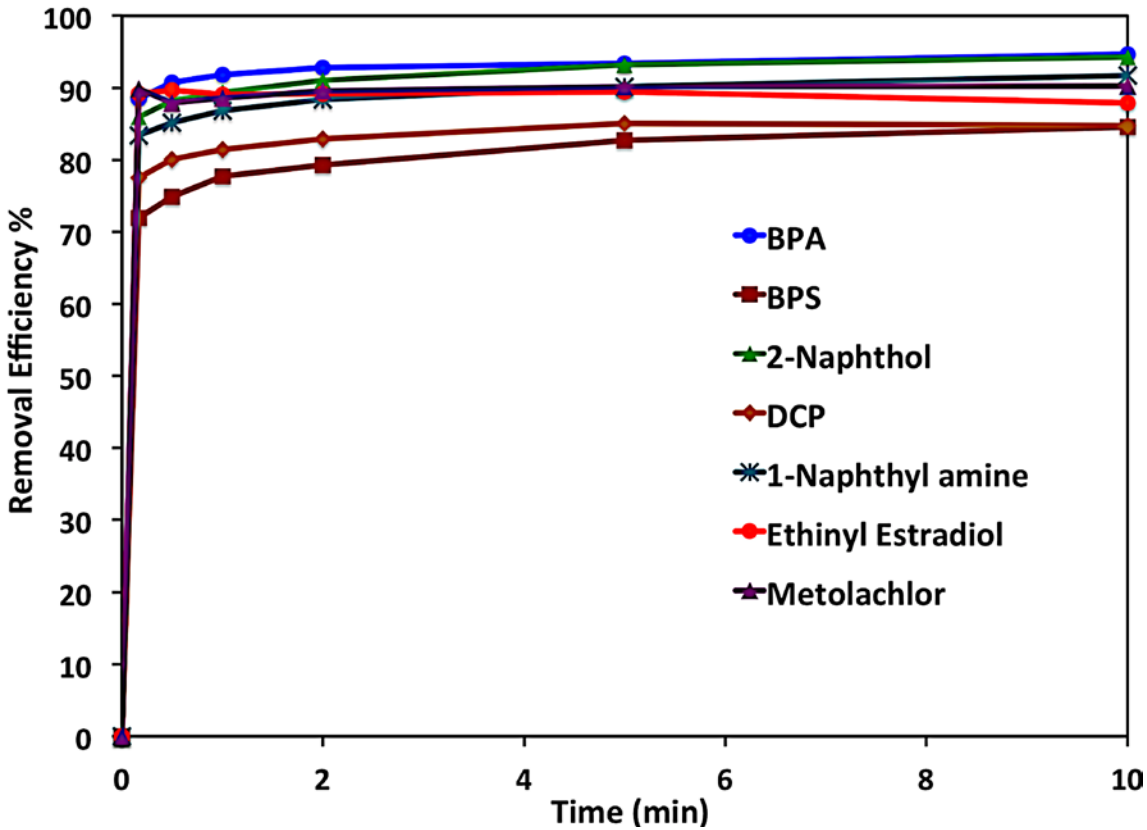
Birth control medication



Propranolol hydrochloride

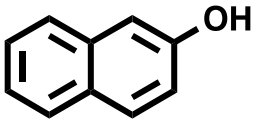
Blood pressure medication

Time-dependent Removal



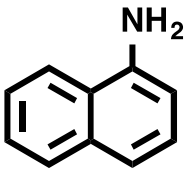
	BPA	BPS	Metolachlor	Ethinyl Estradiol	1-Naphthyl amine	2-Naphthol	2,4-DCP
k_{obs} (mg g^{-1} min^{-1})	1.5	0.6	3.0	20	1.8	1.9	2.3
% uptake at eq	95	85	92	89	92	91	85

Lower Concentration / Pollutant Mixture



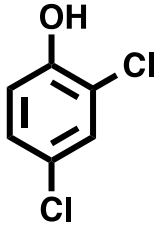
2-Naphthol

25 µg/L



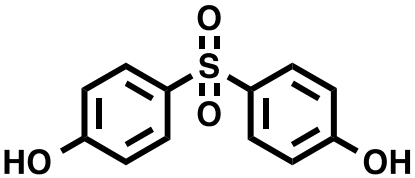
1-Naphthyl amine

5 µg/L



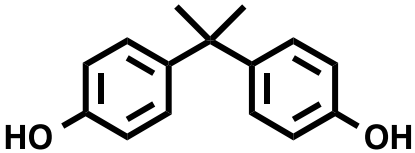
2,4-Dichlorophenol

2.5 µg/L



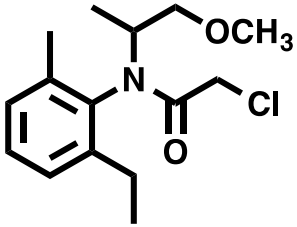
Bisphenol S

5 µg/L



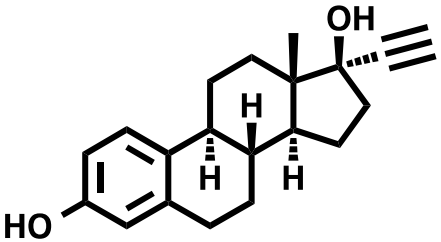
Bisphenol A

100 µg/L



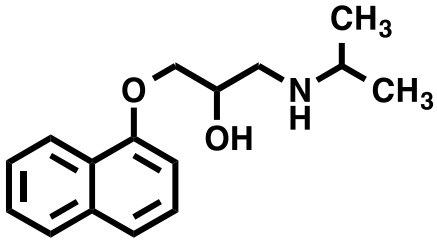
Metolachlor

10 µg/L



Ethinyl estradiol

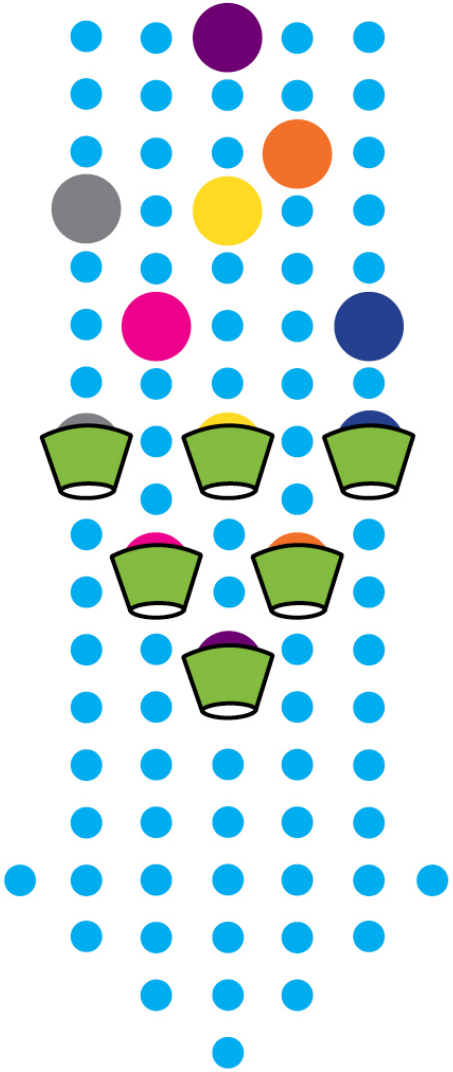
50 µg/L

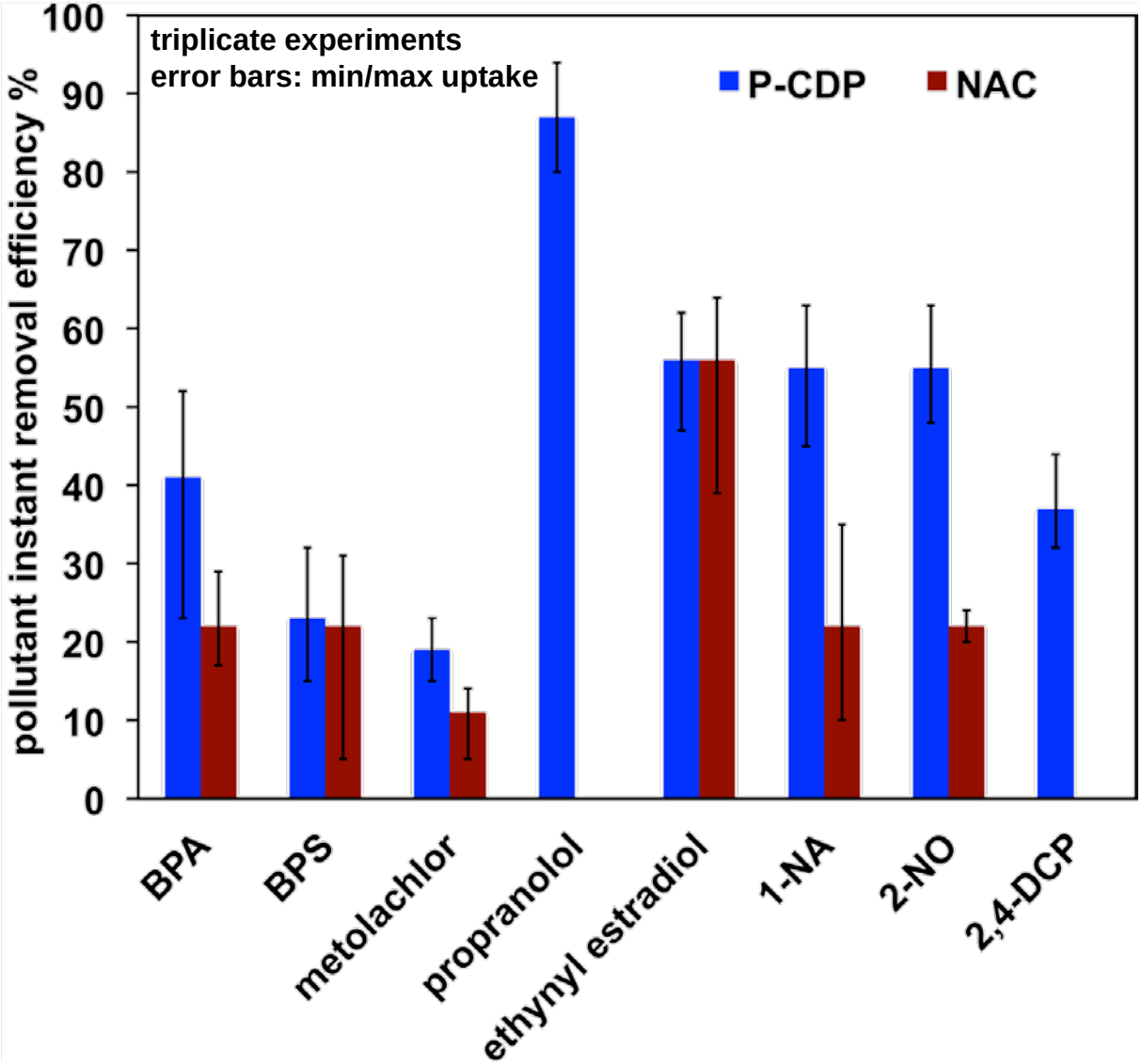


Propranolol hydrochloride

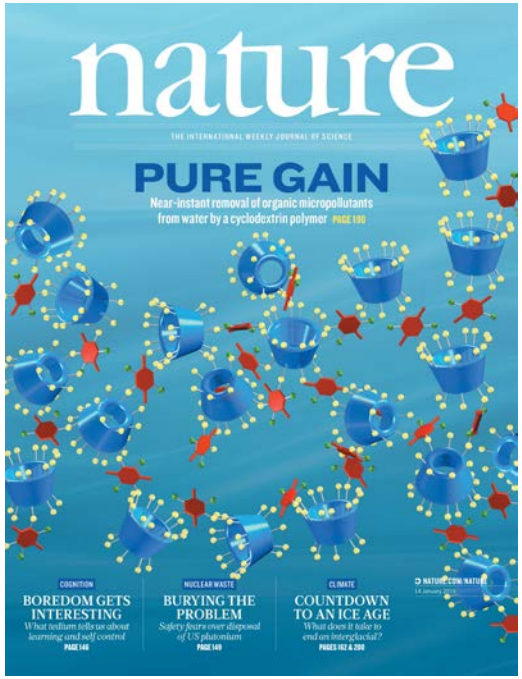
100 µg/L

Instant Uptake of a Pollutant Mixture

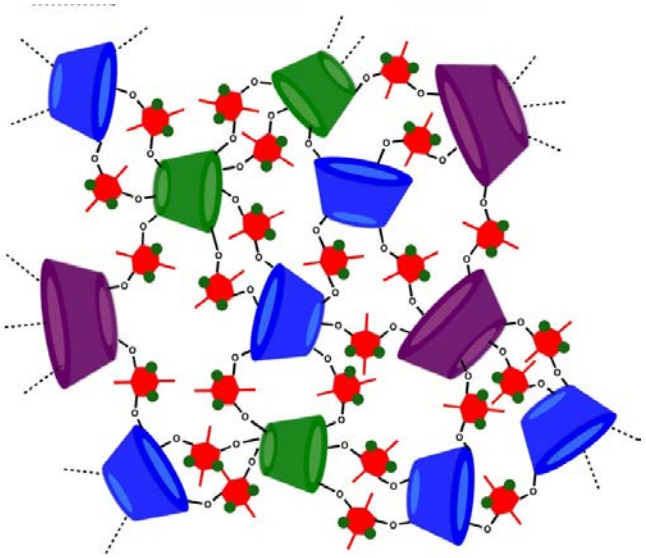




Ongoing and Future Work



CycloPure Inc.



Structural Variation

Mixtures of CDs
Alternative crosslinkers
Varied Functional Forms

U.S. Patent Application No. 62/149,975

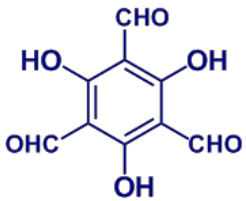
A. Alsbaiee, B. J. Smith, L. Xiao, Y. Ling, D. E. Helbling, W. R. Dichtel, “Rapid Removal of Organic Contaminants from Water by a Porous β-Cyclodextrin Polymer” *Nature*, **2016**, *529*, 190.

How can we *design* free space?

?

FedEx

Covalent Organic Frameworks



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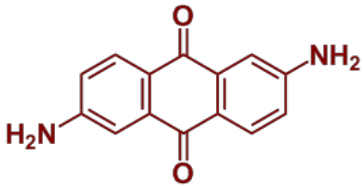

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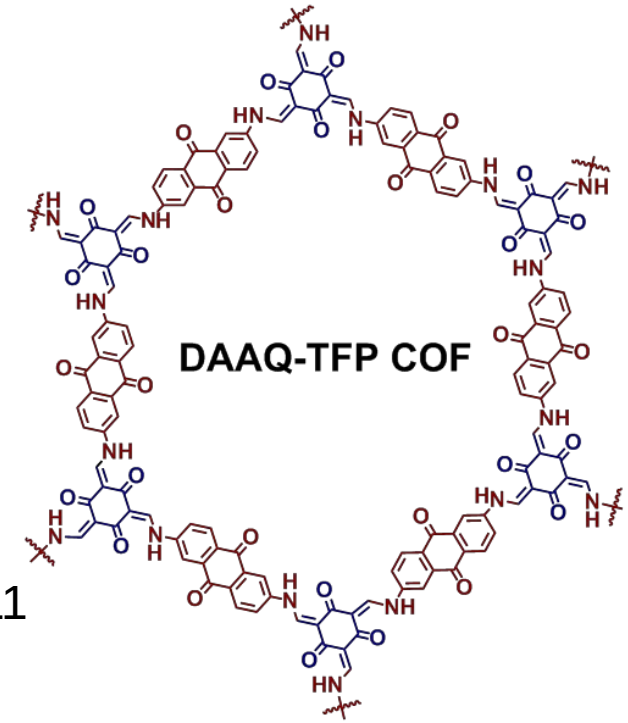
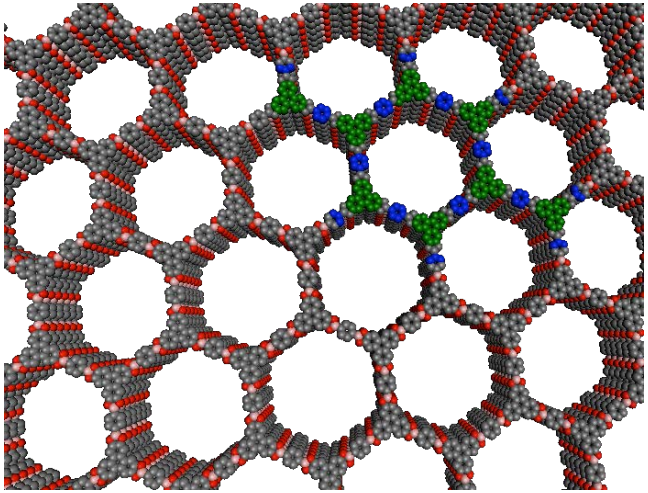


Predictable solid-state structure

Near-eclipsed stacking of 2-D sheets

LBNL Seminar: Tues 3/1, 11a, Bulding 67, Room 3111
Chemistry Special Seminar: TBD



Need for Explosive Detection

1993 Mumbai bombings (13 explosions using RDX)

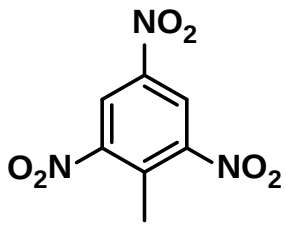
2009 failed airline bombing plot (PETN was not detected)

Failed 2000 plot to bomb LAX airport (using 2 bottles containing RDX)

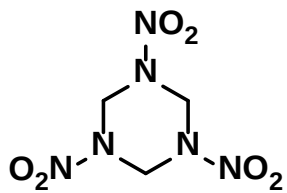
There are an estimated **100 million landmines** buried around the world and **one person is injured or killed by a landmine every 22 minutes**.

Challenges: Low Volatility Explosives

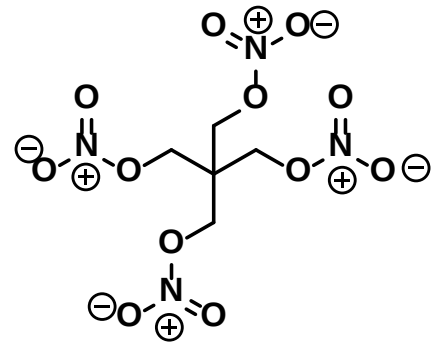
TNT

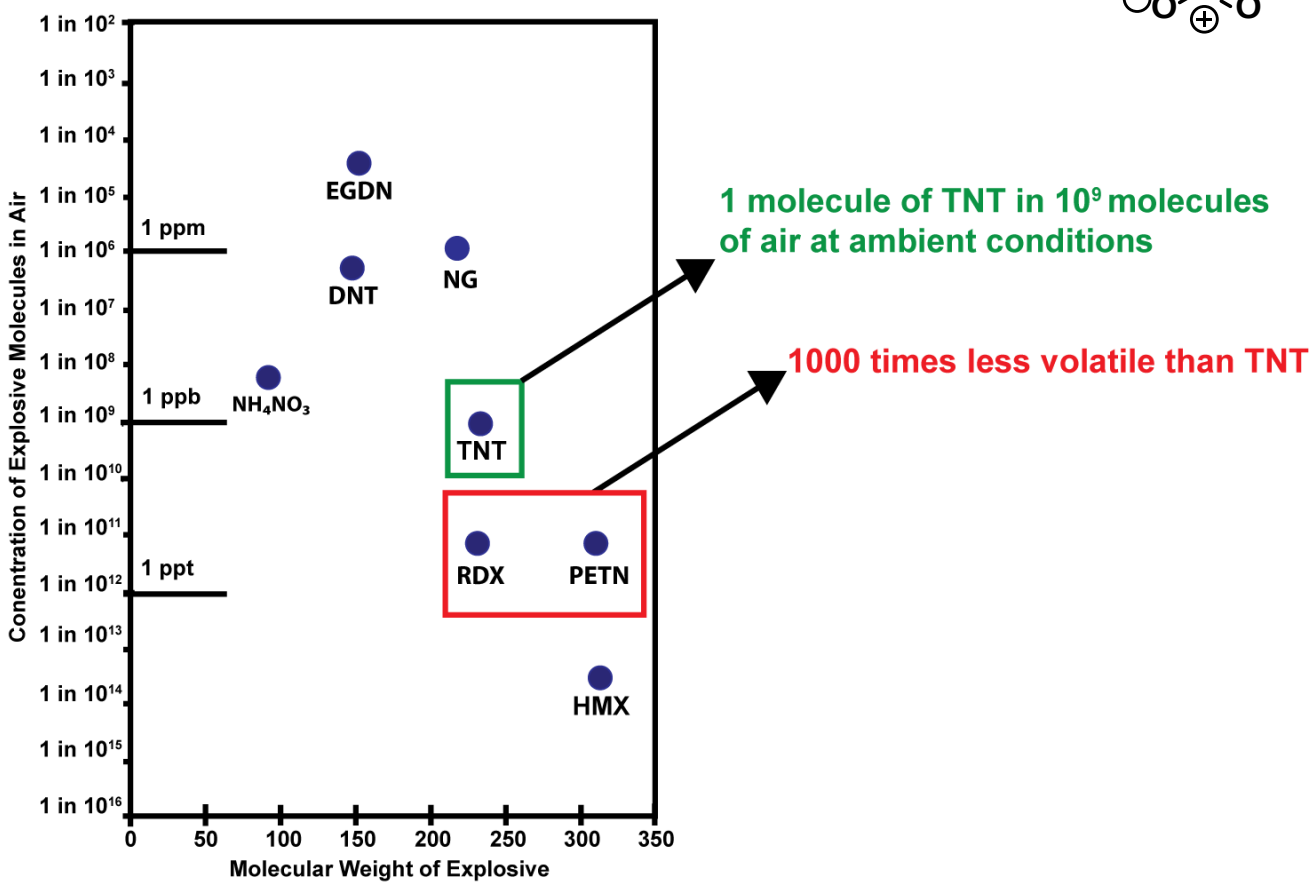


RDX



PETN

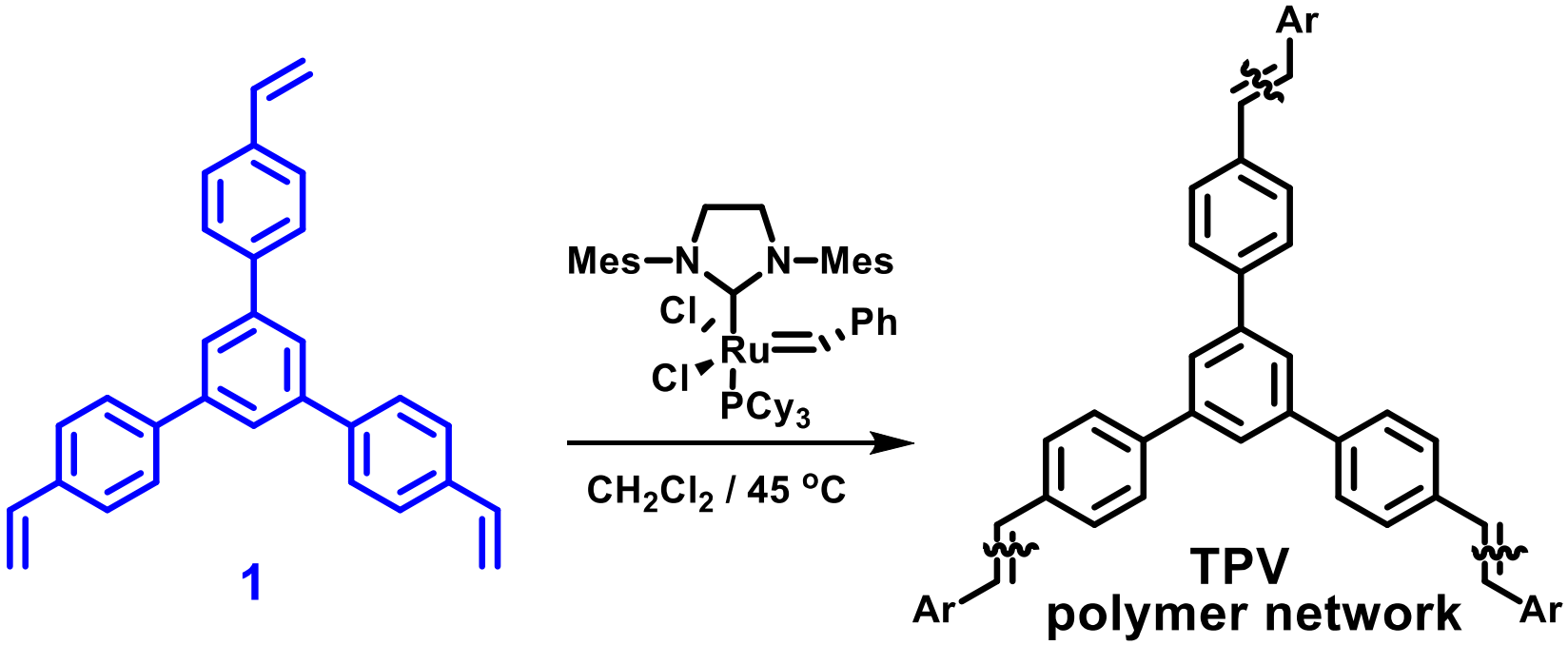




The current system can detect TNT from the vapor phase. The aim is to detect RDX and PETN which are 1000 times less volatile than TNT.

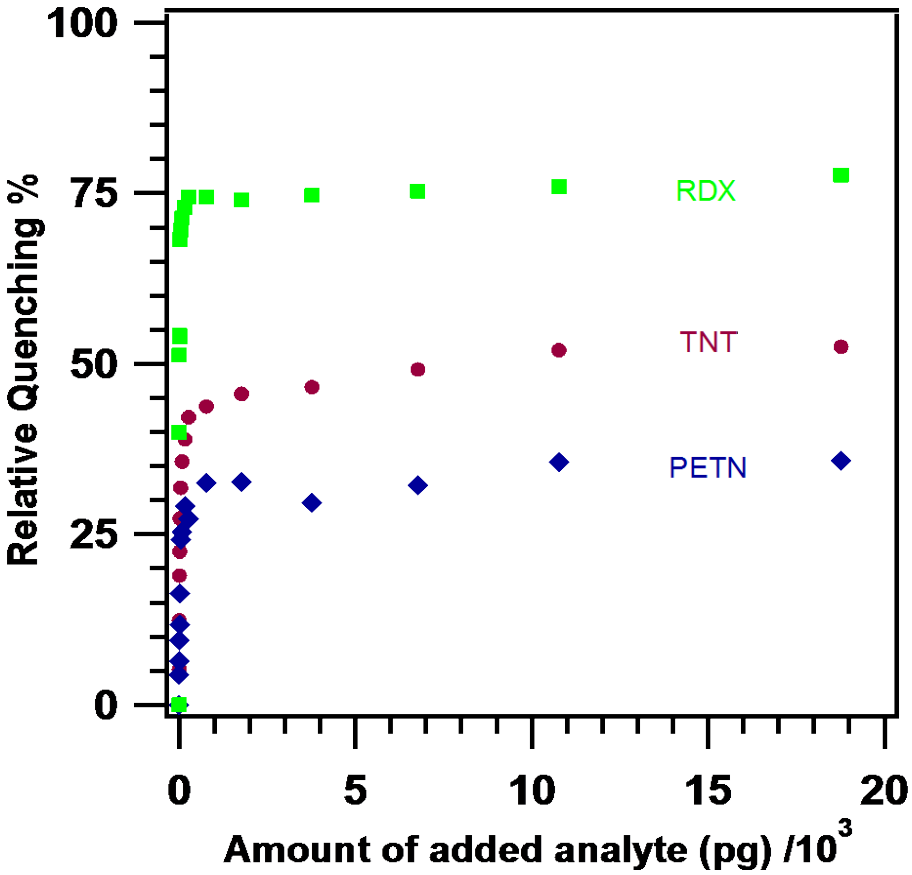
http://www.dtic.mil
Department of Defense, USA

Polymer Network for Explosives Detection

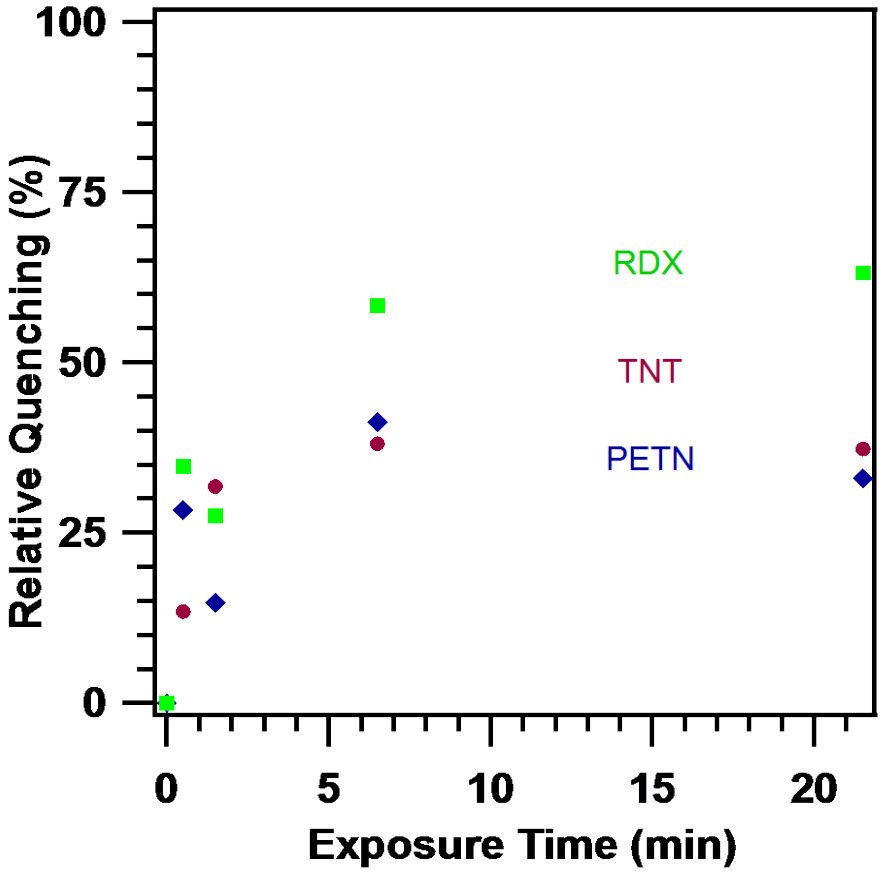


Response to Explosives

Introduced as a solution

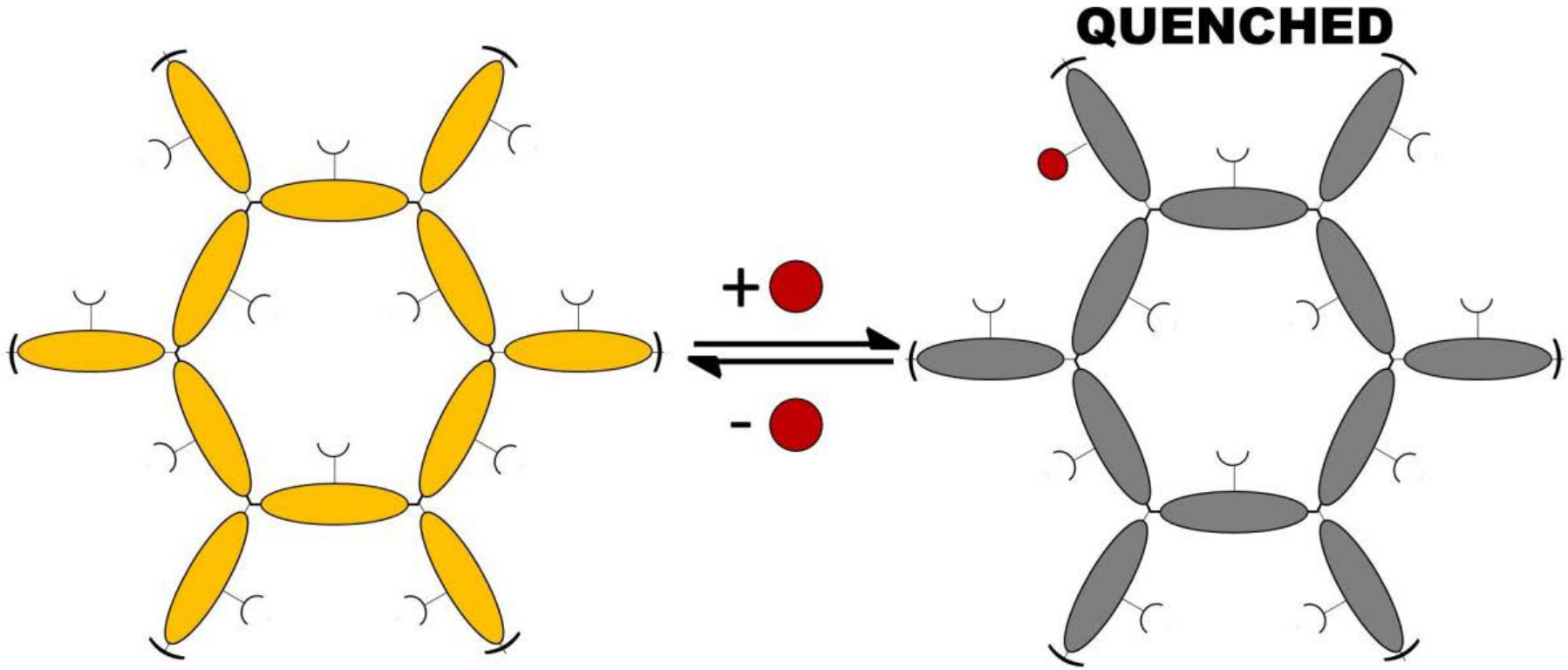


Introduced as vapor



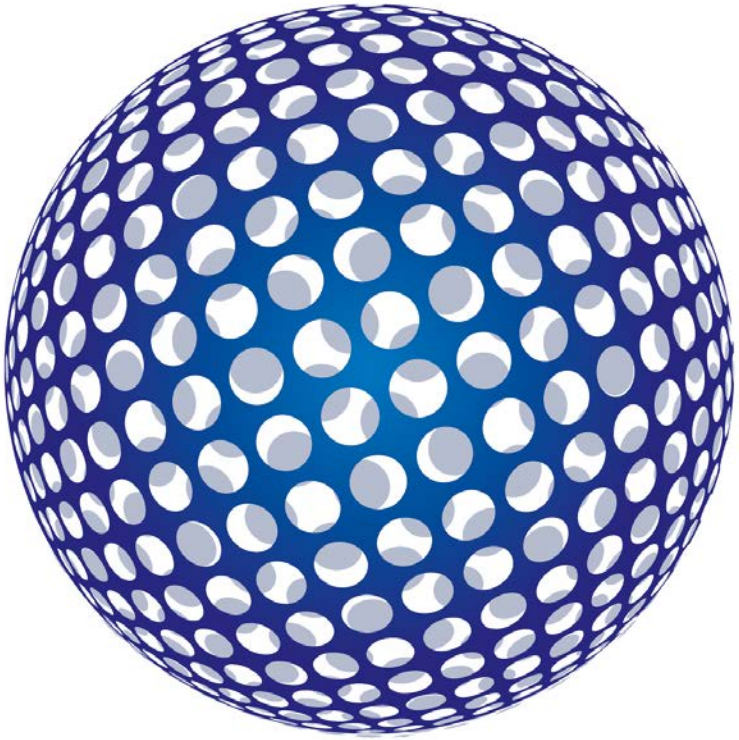
all explosives cause appreciable quenching in vapor phase

Signal Amplification



Proposed Systems**: high surface area, **maximum sensitivity

The Spectacular Properties of Porous Polymers



We realize outstanding and useful properties and functions by designing pores at the size scale of molecules and ions

Collaborators and Funding

Prof. Damian Helbling
Environmental Engineering
Cornell University

NSF

Center for Sustainable Polymers

Department of Energy United States of America

ACS PRF

Atkinson Center for a Sustainable Future

Cornell University Founded A.D. 1865

MacArthur Foundation

NYSTAR

Science to Shape the Future of the Army — Army Research Office 1951

Alfred P. Sloan Foundation 1934

Arnold and Mabel Beckman Foundation

The Camille & Henry Dreyfus Foundation, Inc.

NRI

ACS

Dichtel Research Group

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