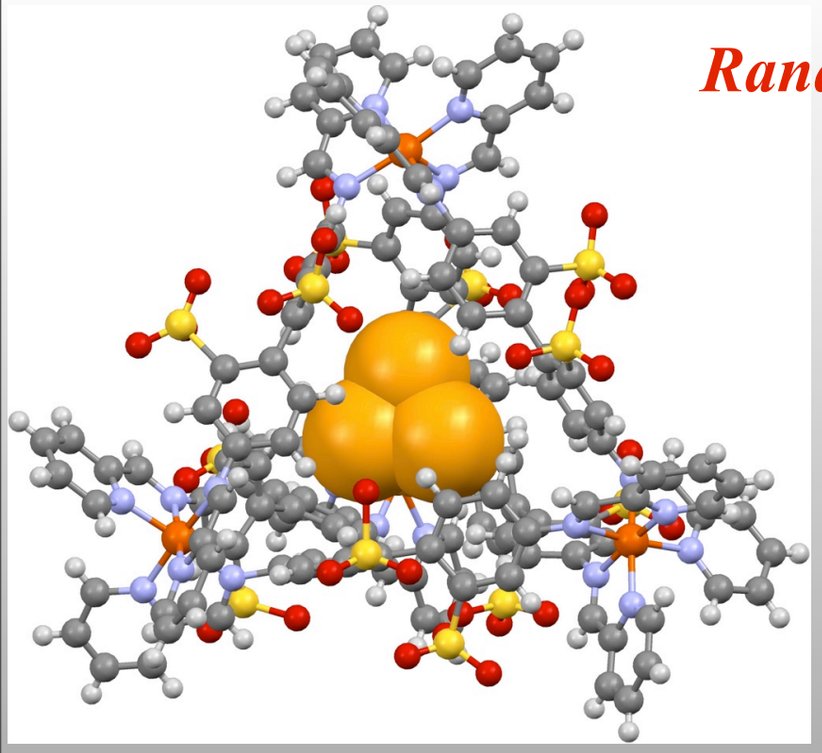
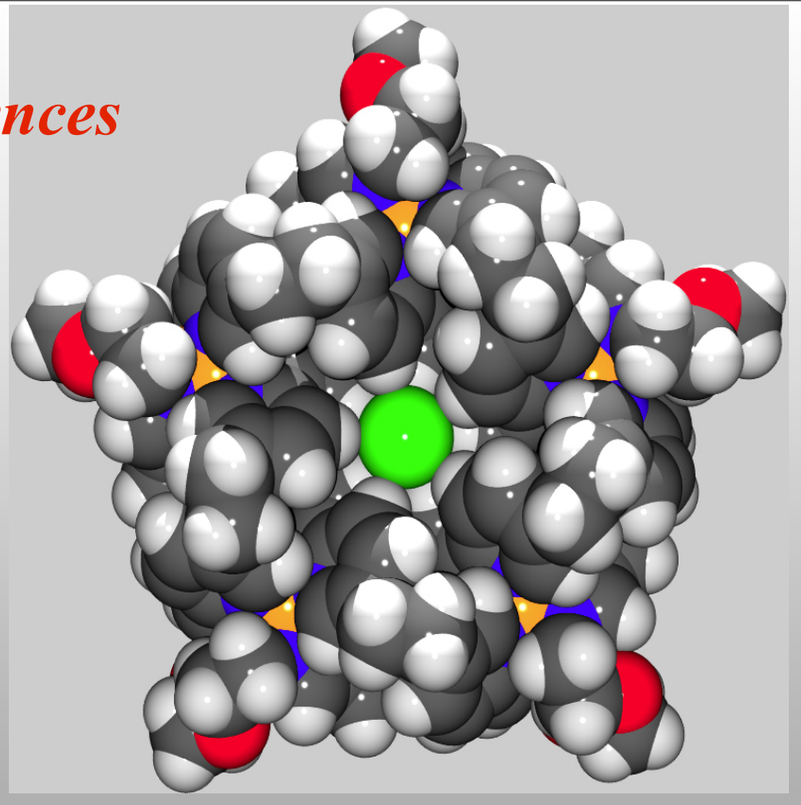
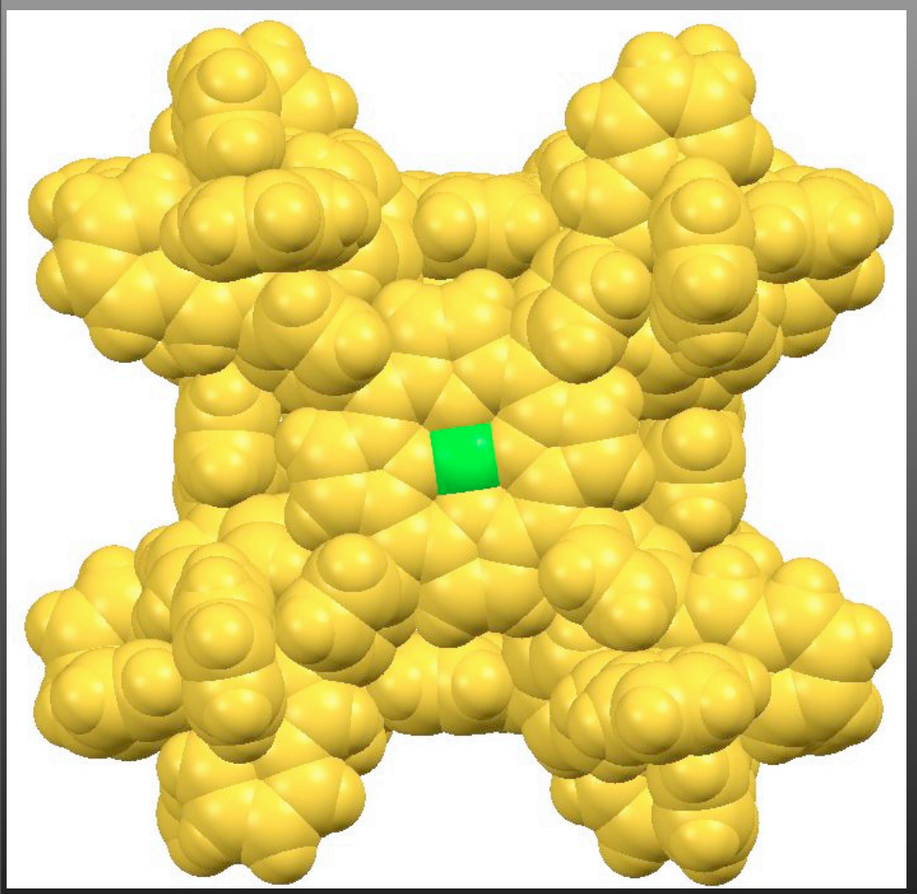


Randomness and order in the exact sciences

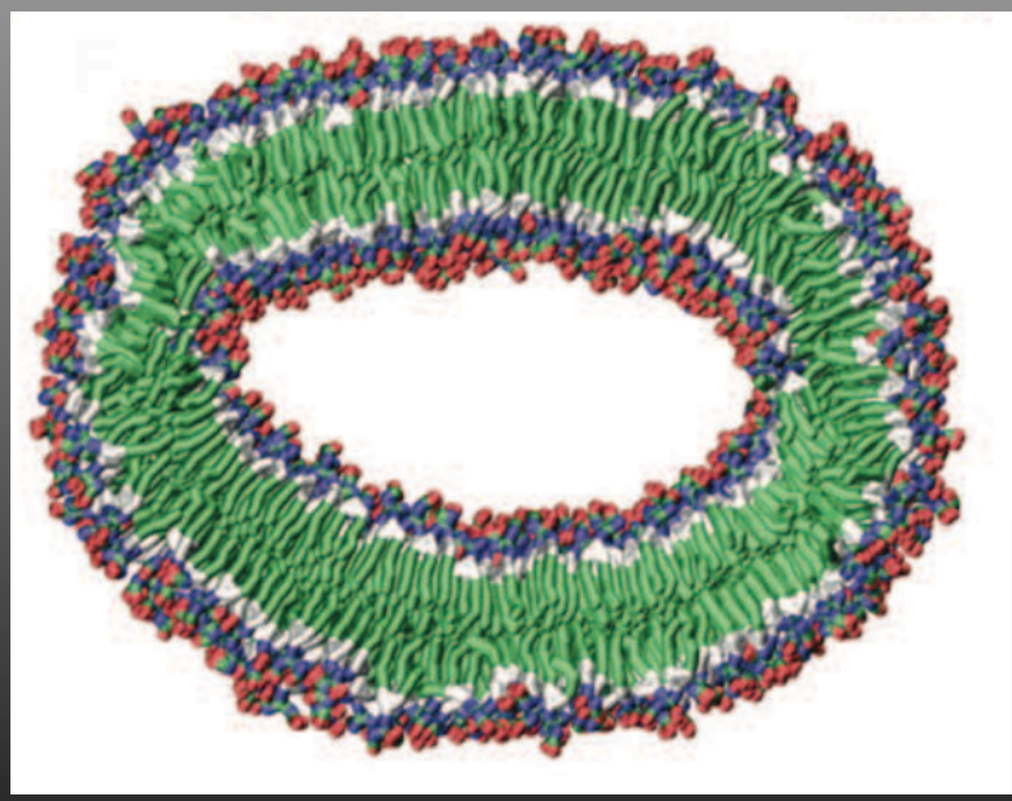
175th Anniversary Symposium
Finnish Society of Sciences and Letters
Helsinki, Finland
3rd September, 2013



Molecular Self-Assembly of Nano-sized (Functional) Supramolecules



Kari Rissanen
Department of Chemistry
Nanoscience Center
UNIVERSITY OF JYVÄSKYLÄ

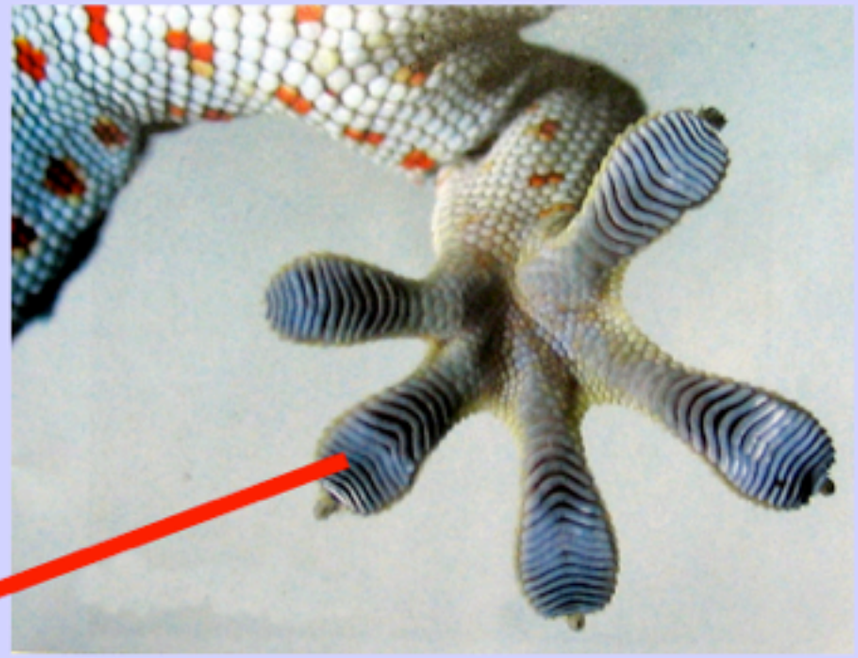


Function:

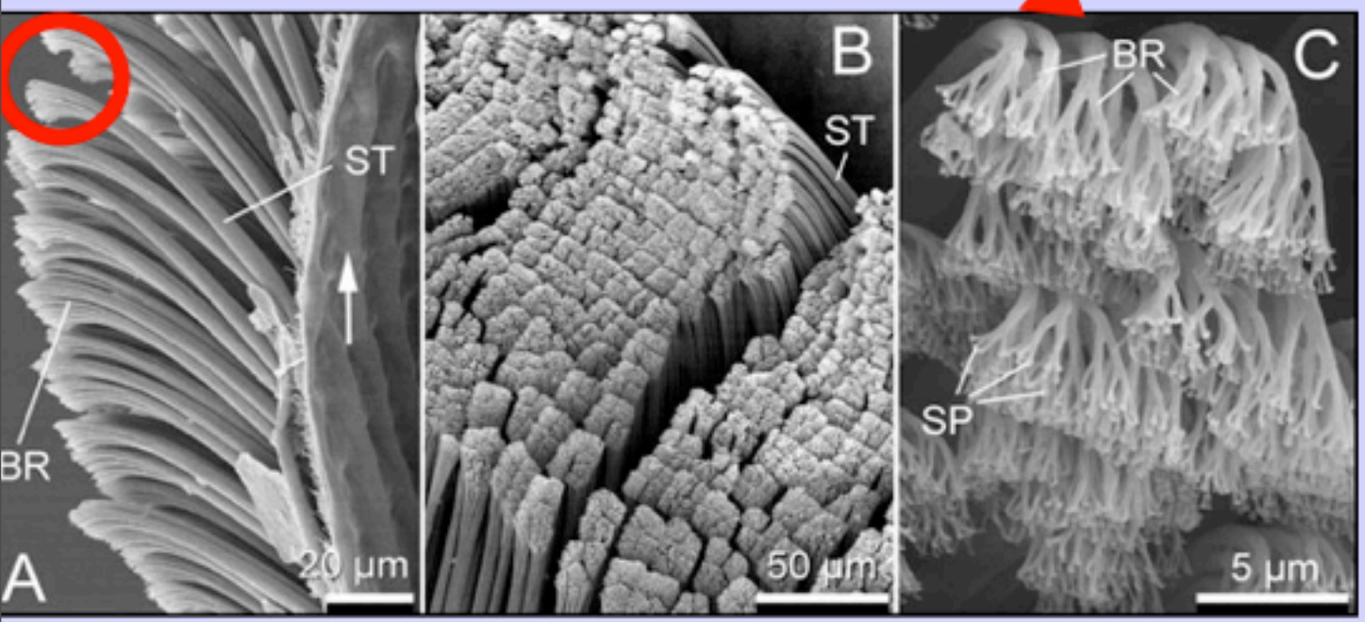
Geckos Climb by the (1 Billion) Hairs of Their Toes

Larger bodyweight of animal:
more and smaller hairs necessary

A single hair can lift an ant,
1 million a little child



Hairs with multiple (1000-fold) split ends;
van der Waals-forces disappear by changing the angle of the hairs



***Acccumulation* of functional arms**
leads to new properties
(amplification of effects)

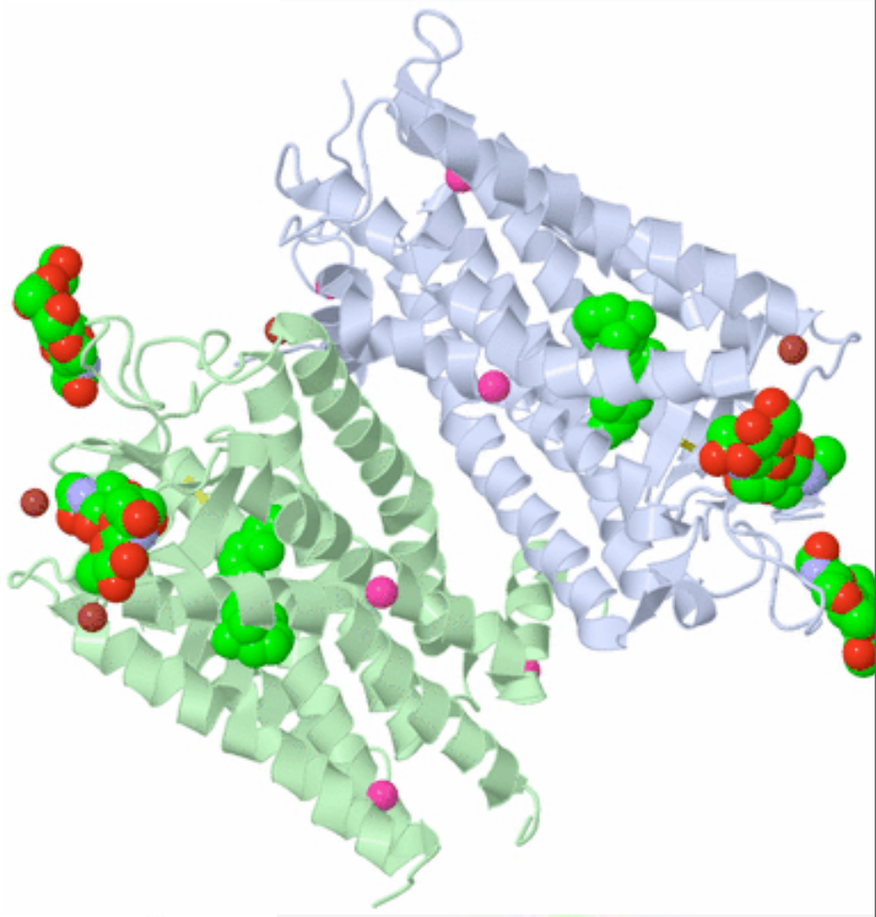
E. Pennisi, *Science* **2000**, *288*, 717–718;
K. Hien, Laborjournal *1-2*/**2004**, 32-34;
K.Autumn, R. Full, GEO Magazin 10/00

Nanotechnology by animals → **new glue?**
climing robots?

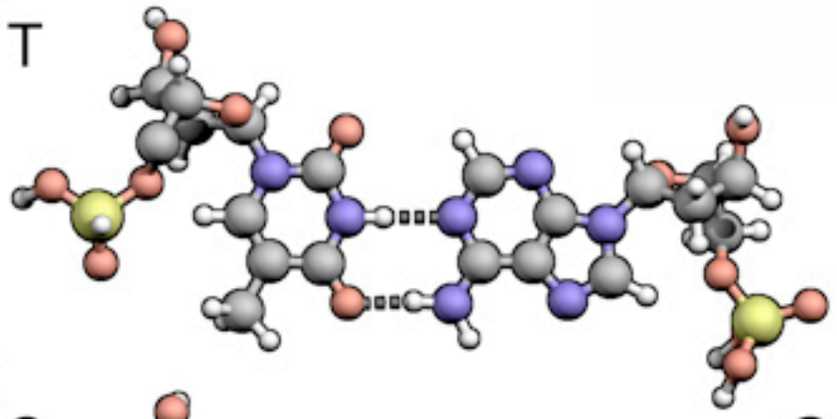
Minor groove

Major groove

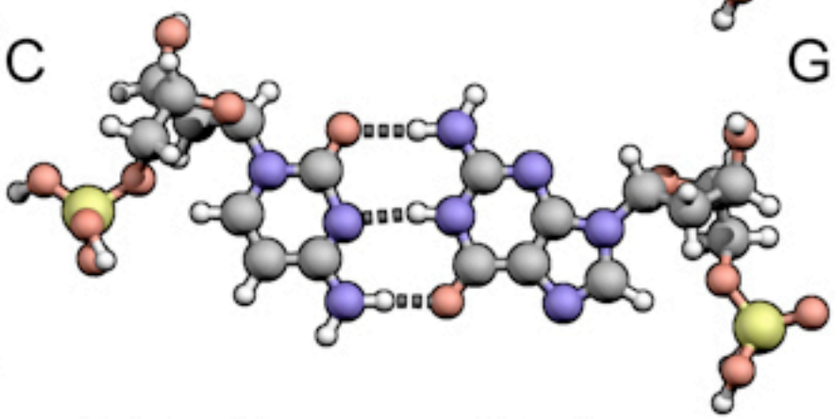
Hydrogen
Oxygen
Nitrogen
Carbon
Phosphorus



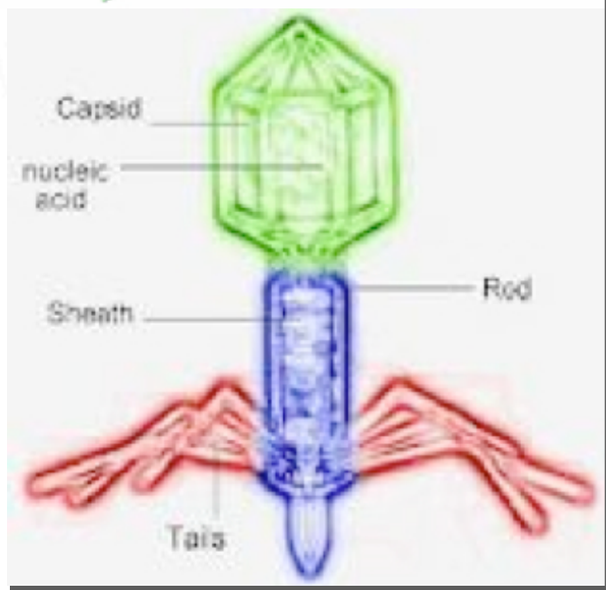
T



C G



Pyrimidines Purines



http://oscarbonilla.com/2011/04/radiation/

Non-covalent intermolecular interactions

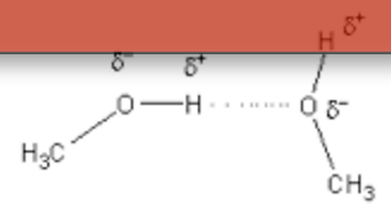
”CLASSICAL”

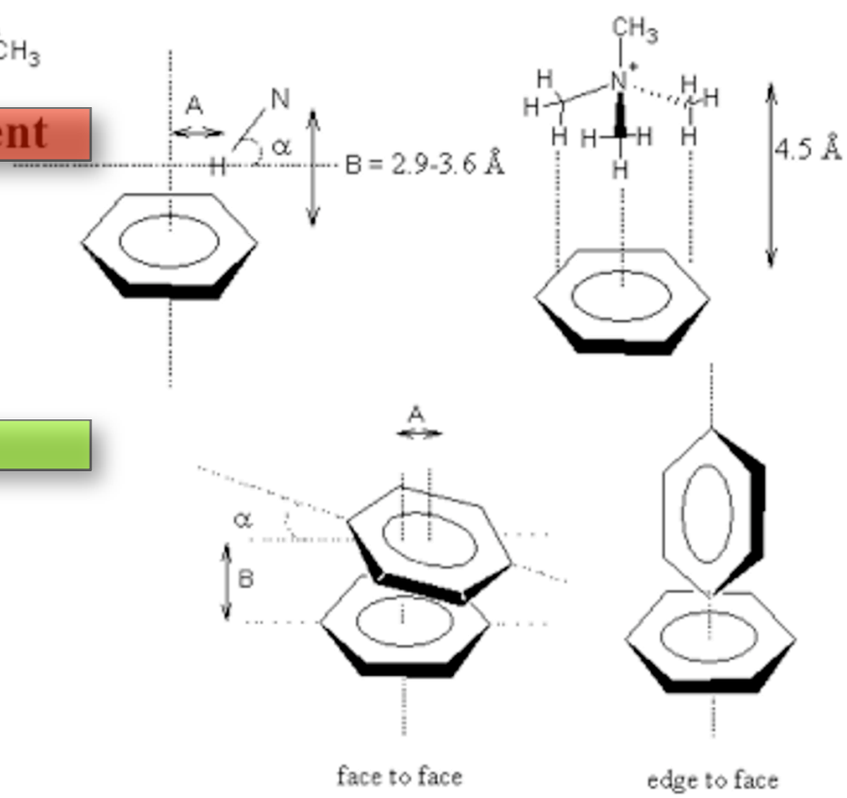
ION .... ION INTERACTIONS:	**ca. 200 - 300 kJ/mol**
ION .... DIPOLE INTERACTIONS:	**ca. 50 - 200 kJ/mol**
DIPOLE .... DIPOLE INTERACTIONS:	**ca. 5 - 50 kJ/mol**
HYDROGEN BONDING, STRONG:	**ca. 60 - 120 kJ/mol**
MODERATE:	**ca. 14 - 60 kJ/mol**
WEAK:	**< 14 kJ/mol**
CATION ... π	**ca. 5 - 80**
π... π	**ca. 1 - 50**
VAN DER WAALS	**< 5**
HYDROPHOBIC	**depends on solvent environment**

”NEW”

ANION ... π	**??**
C-H ... π	**weak**
HALOGEN BONDING	**as H-bonding**
C-H ... anion	**weak**

D	A	D --- A distance [Å]
F-H	F-	2.3
Ph-O-H	H_2O	2.5 – 2.7
H-O-H	Cl-	3.3
C-H	O=C	3.0-3.8
C-H	Br-	3.2– 3.9
C-H	O-H	3.0 -3.4
C-H	Ph	3.2 – 3.8





G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond In Structural Chemistry and Biology*, Oxford Science publications, 1999.

E.A. Meyer, R.K Castellano and F. Diedrich, *Angew.Chem.Int.Ed.*, **42** (2003) 1210 – 1250.

Steed, Turner and Wallace, Core Concepts in Supramolecular and Nanochemistry, John Wiley & Sons (2007).

Dendrimersomes

(Self-assembly of Janus Dendrimers)

Dendrimers

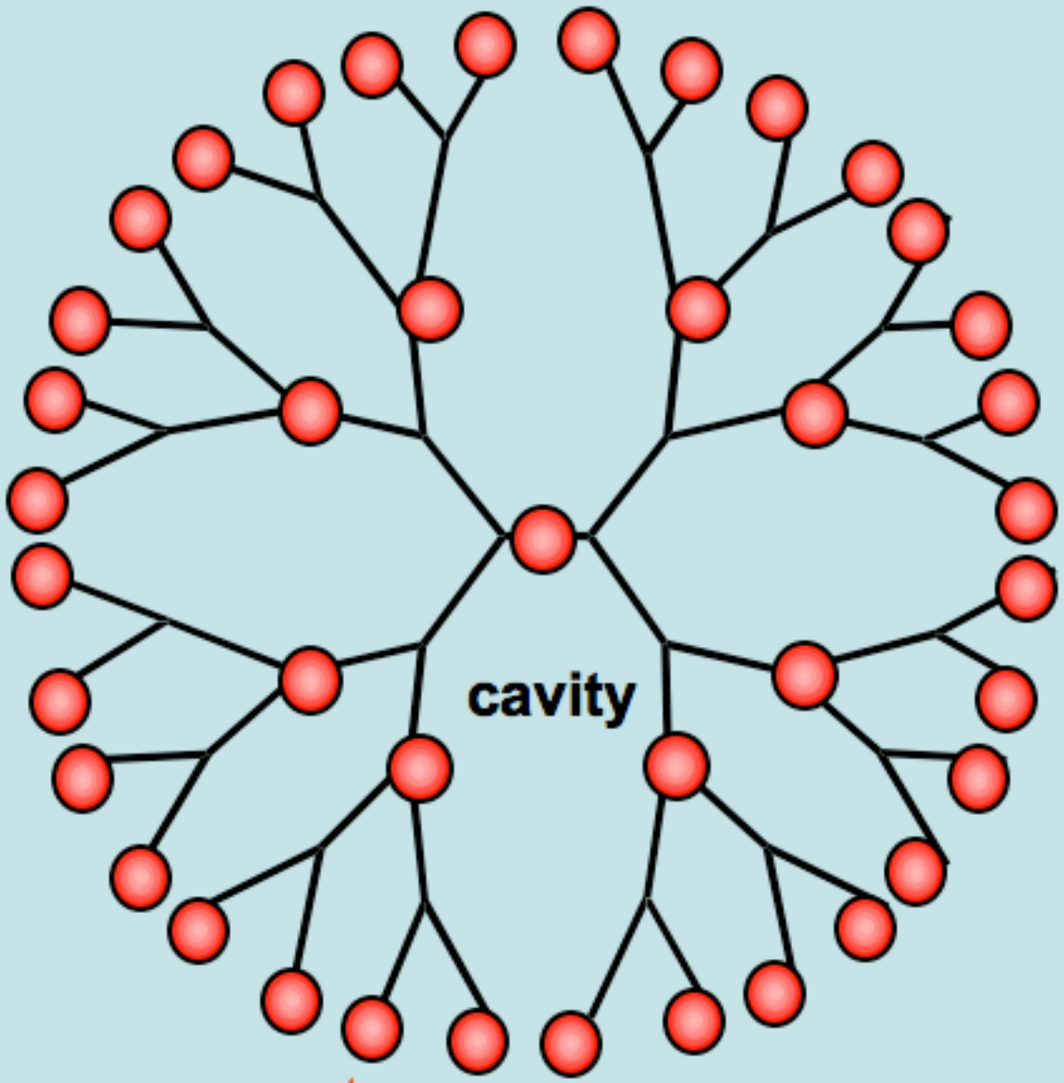
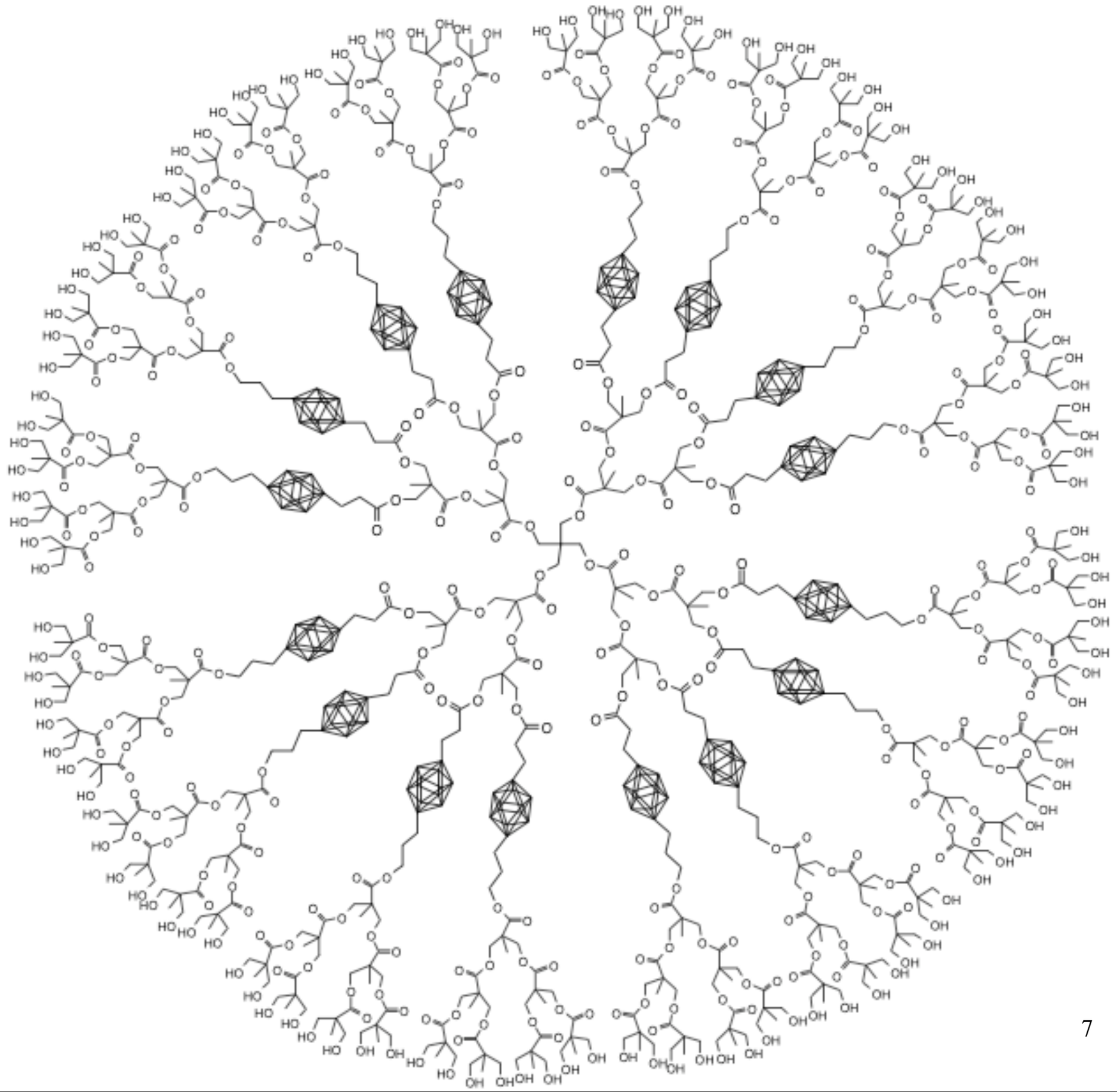
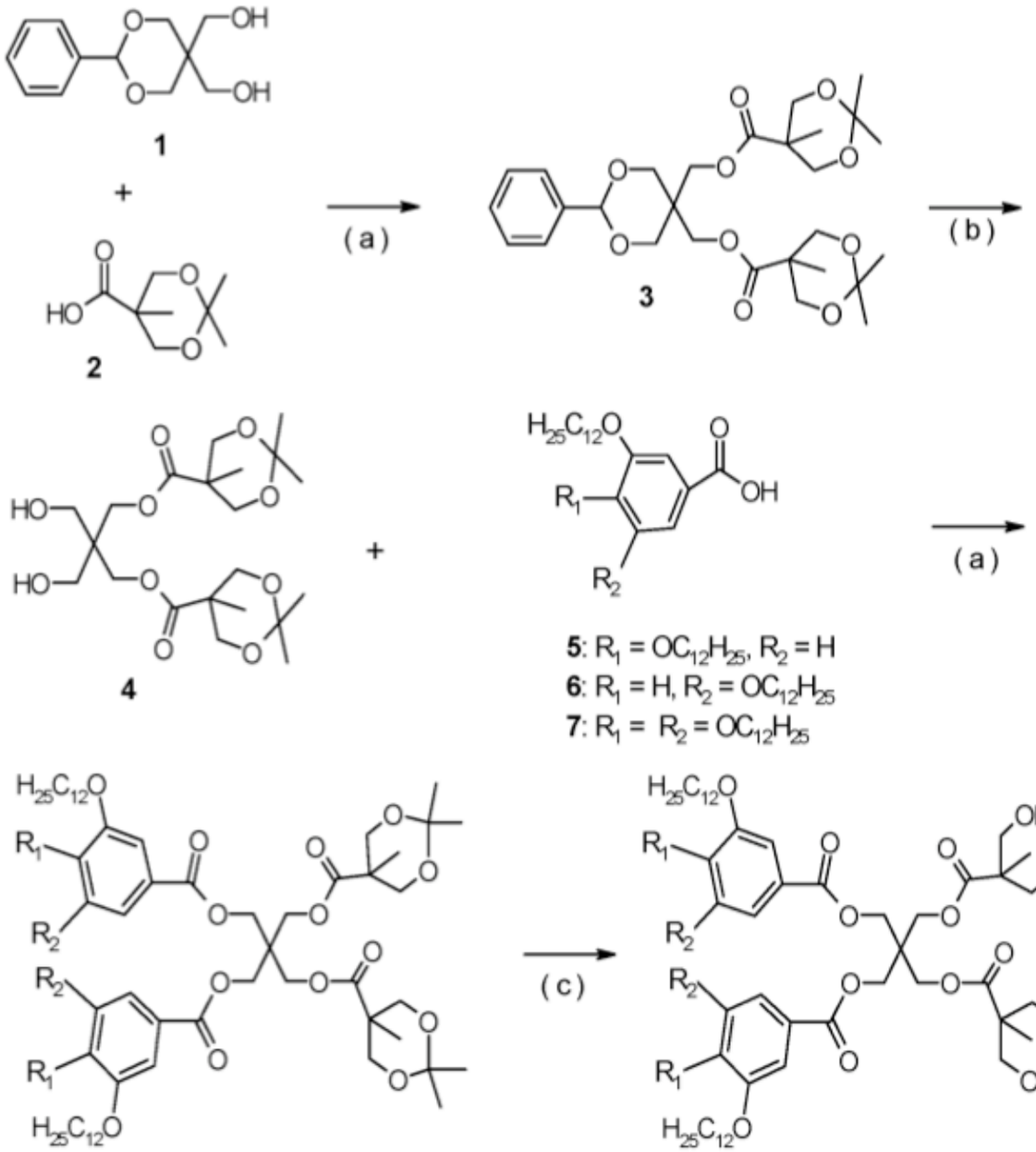


photo and/or redox active units

tree-like structure



Scheme 1. Synthesis of First-Generation Dendrimers[a]



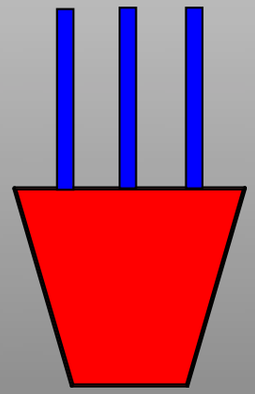
[a] Reagents and conditions: (a) DCC, DPTS, CH_2Cl_2, rt, 20 h; (b) H_2, Pd/C, THF−EtOAc, 6 h; (c) THF−HCl (6 M), rt, 3 h.

We have demonstrated that a protection−deprotection scheme in combination with a divergent−convergent−divergent method is a very efficient route to novel bis-functionalized dendritic multiester molecules with two faces, viz. Janus. Using this facile modular synthetic method, we have combined nonpolar aromatic monodendrons with the aliphatic highly branched multiester molecules. Work toward higher generation bisfunctionalized Janus dendrimers and research on their thermal, self-assembling, and liquid crystalline properties are currently in progress in our laboratory.

Ropponen, Nummelin, Rissanen, *Org. Lett.* **2004**, 2495.

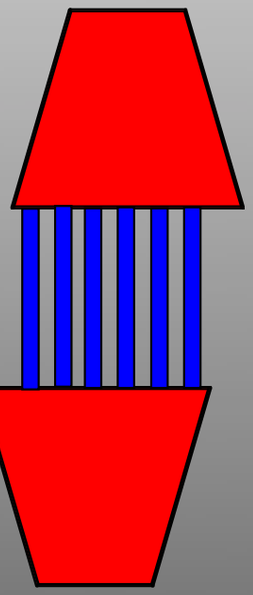
Janus dendrimer

Non-polar part

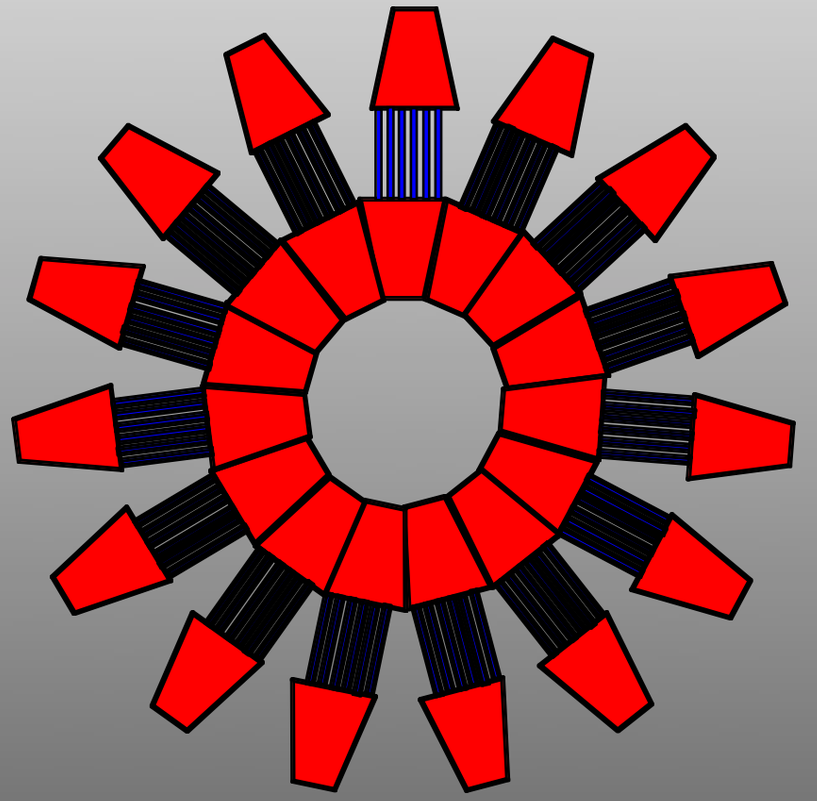


Polar part

Self-assembly

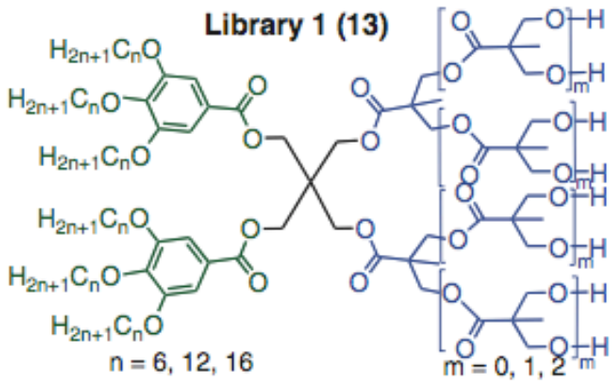


Self-assembly

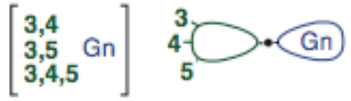


Bilayered dendrimersome

Library 1 (13)

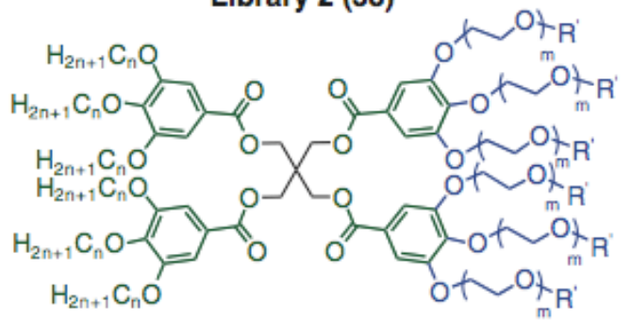


(3,4,5)12G1-PE-BMPA-Gn-(OH)$_y$

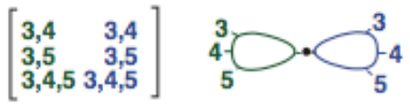


Substitution pattern - generation

Library 2 (58)

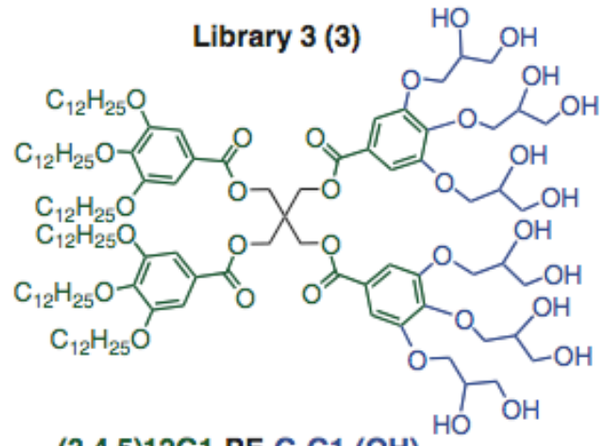


(3,4,5)12G1-PE-(3,4,5)-mEO-G1-(OCH$_3$)$_y$
(3,4,5)12G1-PE-(3,4,5)-mEO-G1-(OH)$_y$

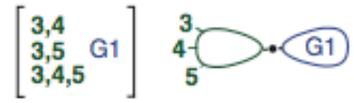


Substitution pattern - combinations

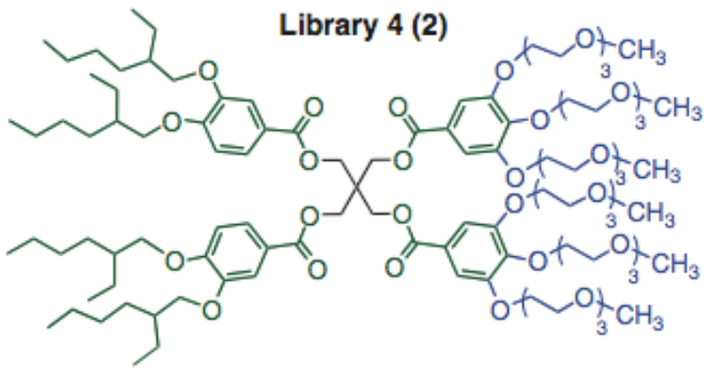
Library 3 (3)



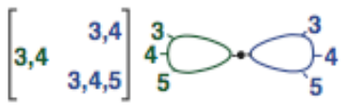
(3,4,5)12G1-PE-G-G1-(OH)$_{12}$



Library 4 (2)

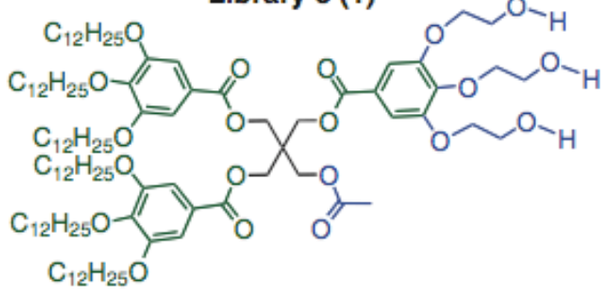


(3,4,5)2Ethyl8-G1-PE-(3,4,5)-mEO-G1-(OCH$_3$)$_y$



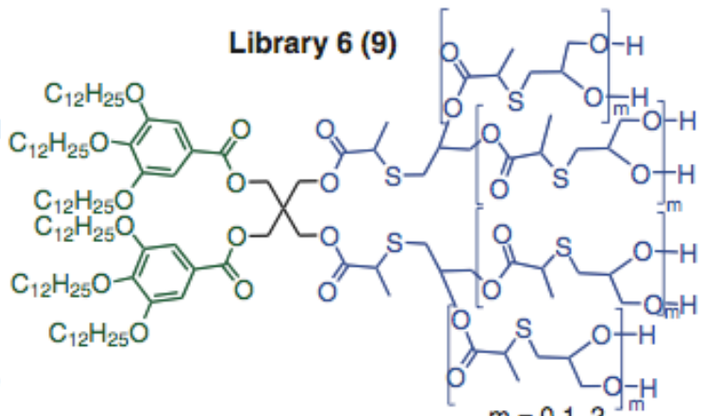
Substitution pattern - combinations

Library 5 (1)

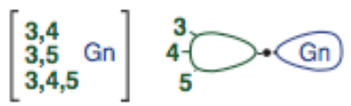


(3,4,5)12G1-PE-(3,4,5)$_1$-mEO-G1-(OH)$_y$

Library 6 (9)

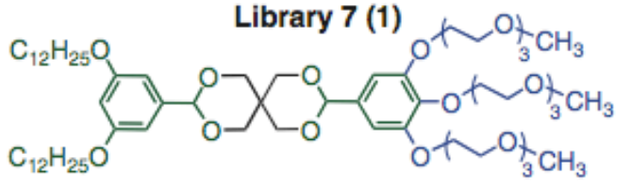


(3,4,5)12G1 PE-TP-Gn-(OH)$_y$



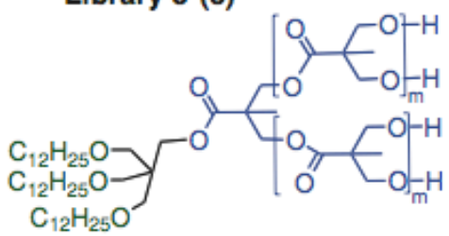
Substitution pattern - generation

Library 7 (1)

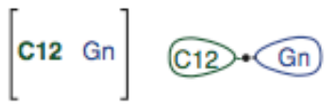


(3,5)12G1-dAc-(3,4,5)-mEO-G1-(OCH$_3$)$_y$

Library 8 (3)

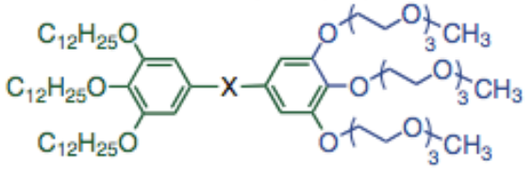


tris12-PE-BMPA-Gn-(OH)$_y$

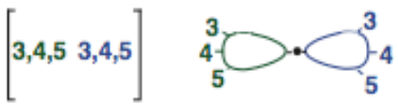


Substitution pattern - generation

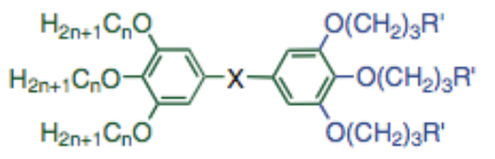
Library 9 (10)



(3,4,5)12G1-BnE-(3,4,5)-3EO-G1-(OCH$_3$)$_y$
(3,4,5)12G1-PhA-(3,4,5)-3EO-G1-(OCH$_3$)$_y$

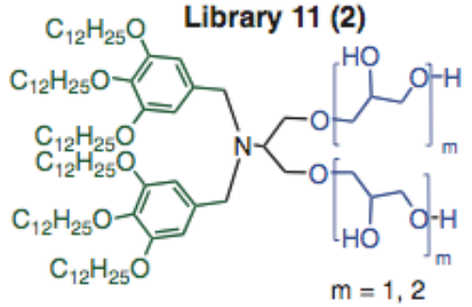


Library 10 (6)

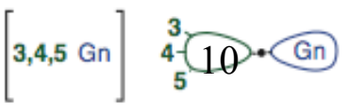


(3,4,5)12G1-BnA-(3,4,5)3-G1-(NHBoc)$_3$
(3,4,5)12G1-BnA-(3,4,5)3-G1-($\overset{\oplus}{N}H_3Cl^{\ominus}$)$_3$
(3,4,5)12G1-PhA-(3,4,5)3-G1-(NHBoc)$_3$
(3,4,5)12G1-PhA-(3,4,5)3-G1-($\overset{\oplus}{N}H_3Cl^{\ominus}$)$_3$

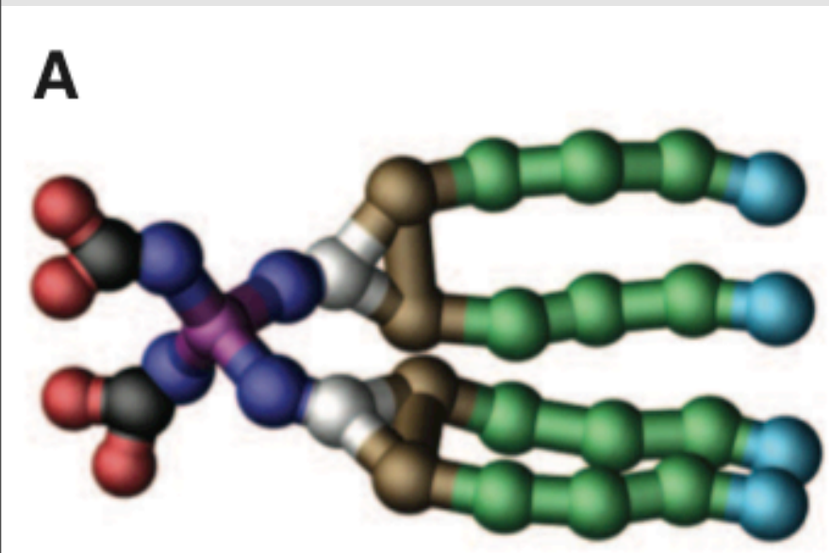
Library 11 (2)

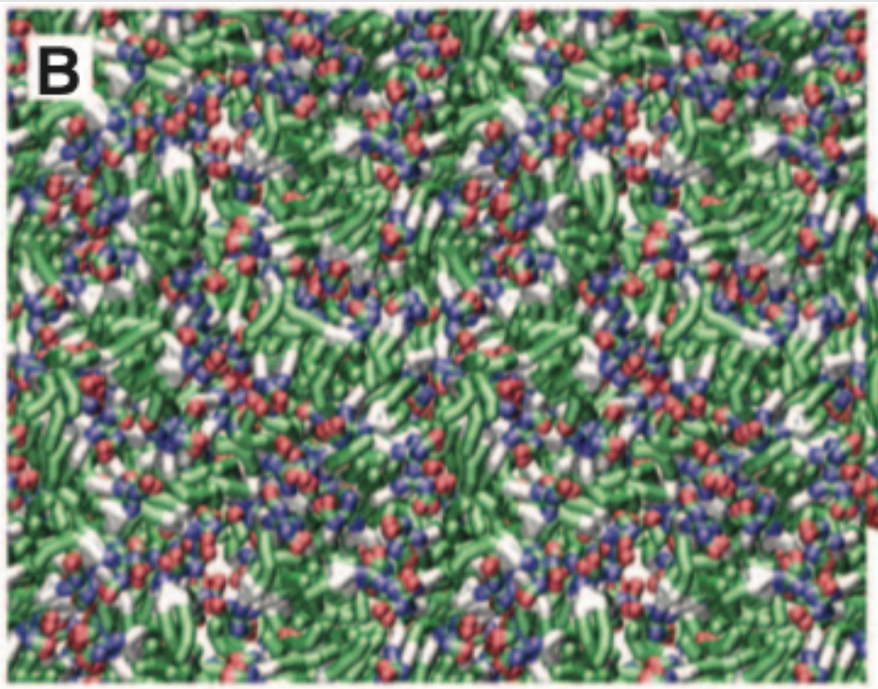


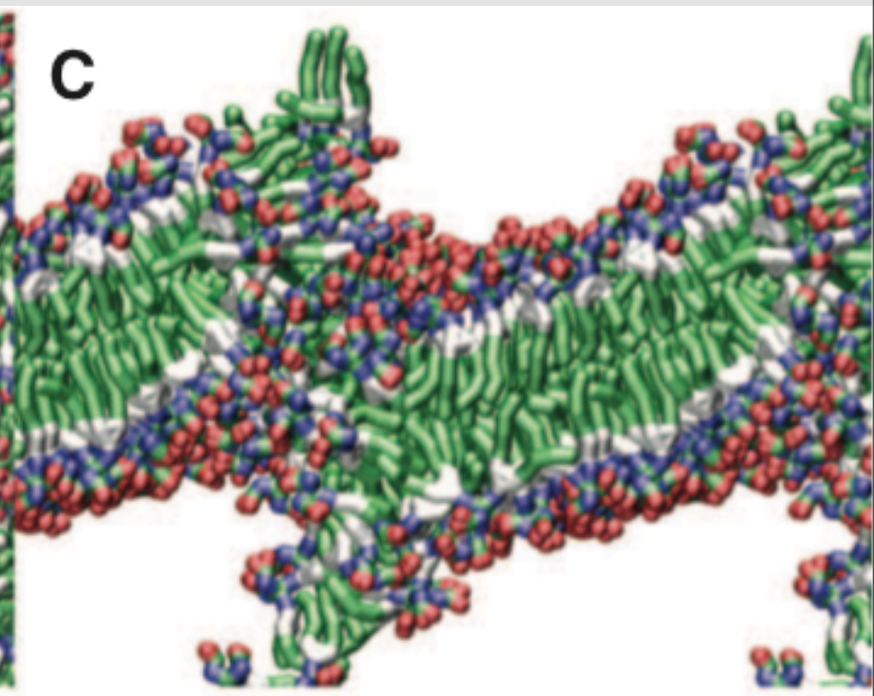
(3,4,5)12G1-APD-G-Gn-(OH)$_y$

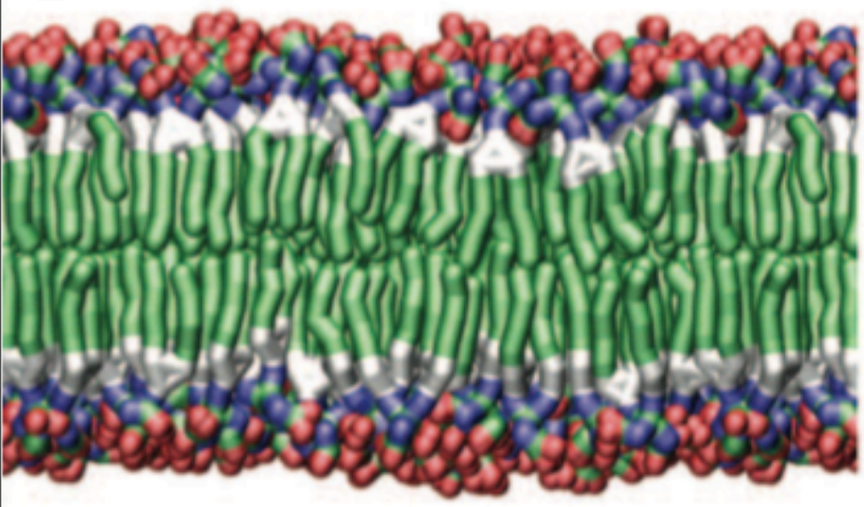


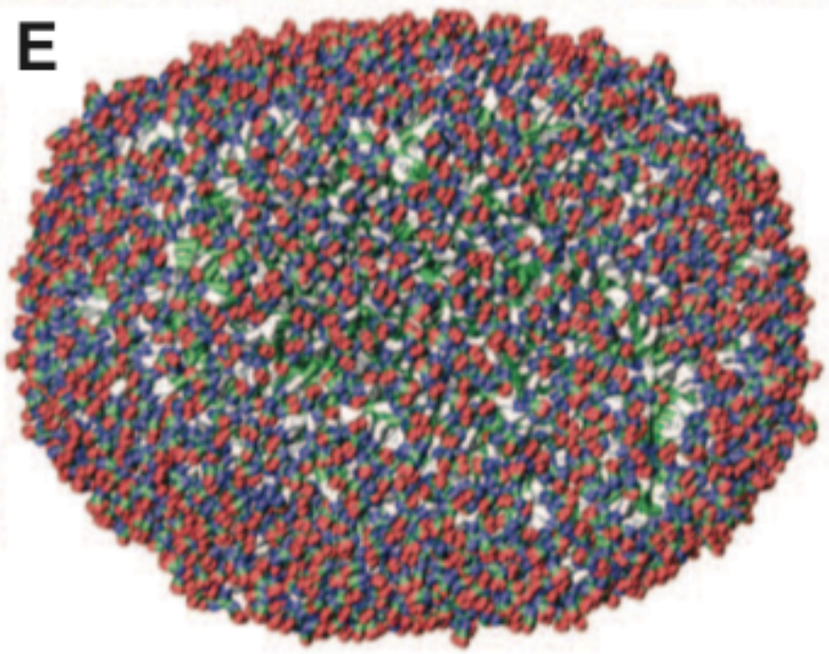
Substitution pattern - generation

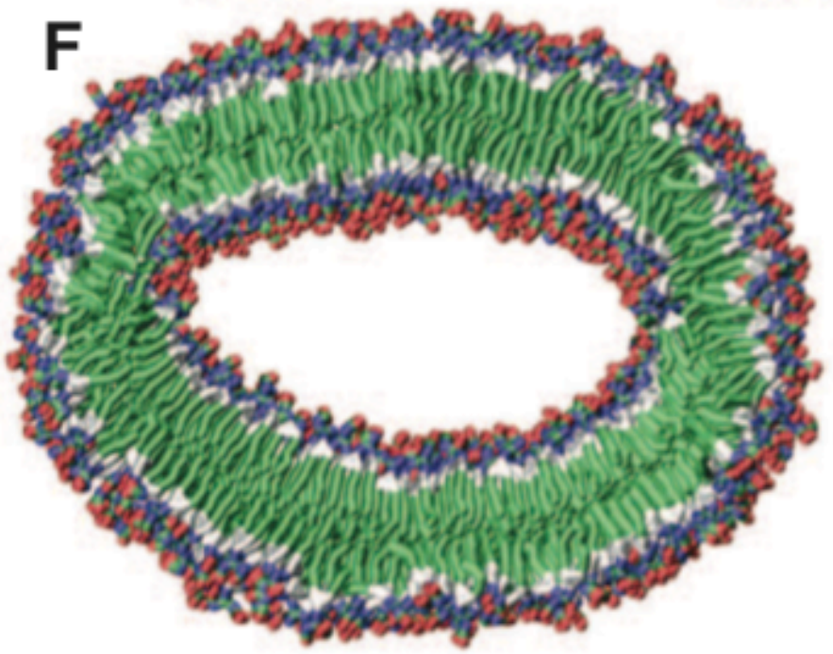

A

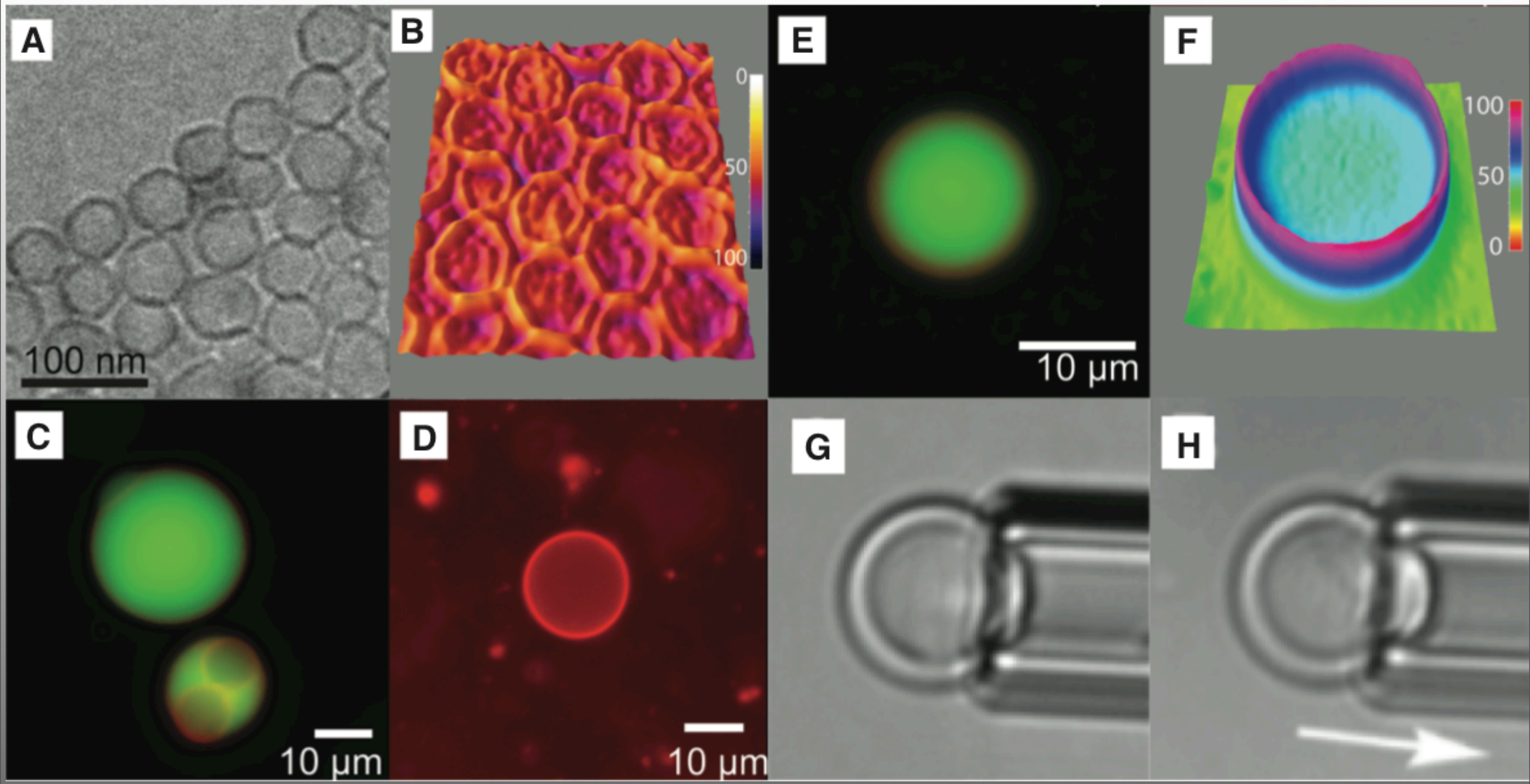

B


C


D


E


F

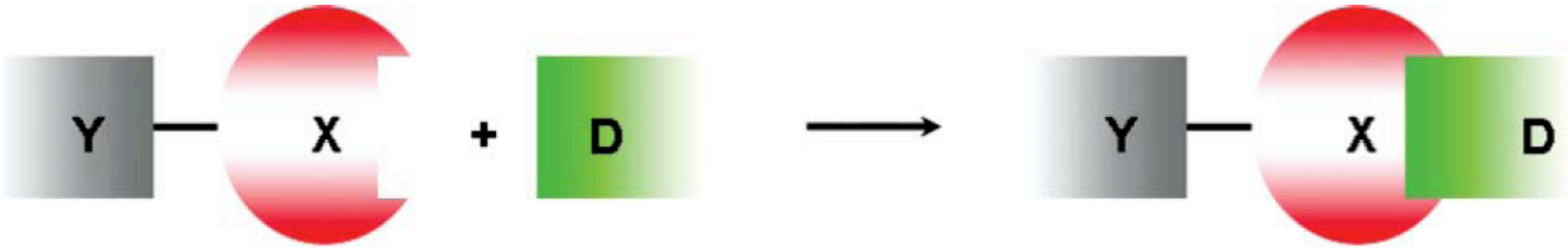


Percec, Wilson, Leowanawat, Wilson, Hughes, Kaucher, Hammer, Levine, Kim, Bates, Davis, Lodge, Klein, DeVane, Aqad, Rosen, Argintaru, Sienkowska, Rissanen, Nummelin, Ropponen, *Science*, *328*, **2010**, 1009.

Scientific breakthrough of year 2010,
Chemical and Engineering News (Dec 20, 2010 Vol.88, no. 51 pp. 13-17)

HALOGEN BONDING

The long lost brother of hydrogen bonding!



D = N, O, S, Se, Cl, Br, I…
I⁻, Br⁻, Cl⁻, F⁻…

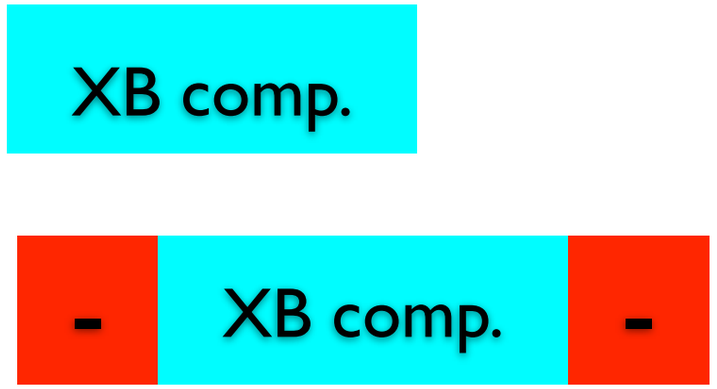
X = I, Br, Cl

Y = C, N, halogen, etc.

Metrangolo, Resnati, *Chem.Eur. J.*, **2001**, 7, 2511.
Rissanen, *CrystEngComm*, **2008**, 10, 1107.
Brammer, Espallargas, Libri, *CrystEngComm*, **2008**, 10, 1712.
R. W. Troff, T. Mäkelä, F. Topić, A. Valkonen, K. Raatikainen and K. Rissanen, *Eur. J. Org. Chem.* (2013), 1617 - 1637.
G. R. Desiraju, P. S. Ho, L. Kloo, A. C. Legon, R. Marquardt, P. Metrangolo, P. A. Politzer, G. Resnati and K Rissanen, Definition of the Halogen Bond, *Pure Appl. Chem.* (2013), 1711 - 1713.

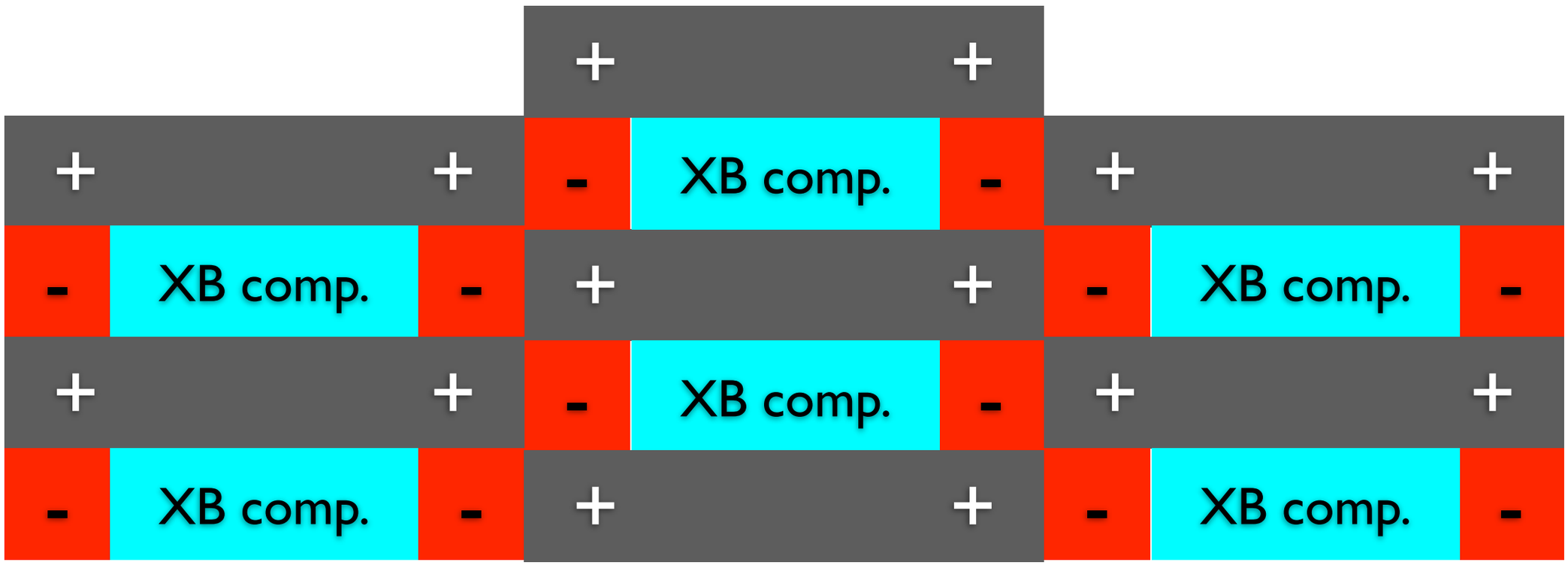
Supramolecular separation using nano-sized cavities via halogen bonding

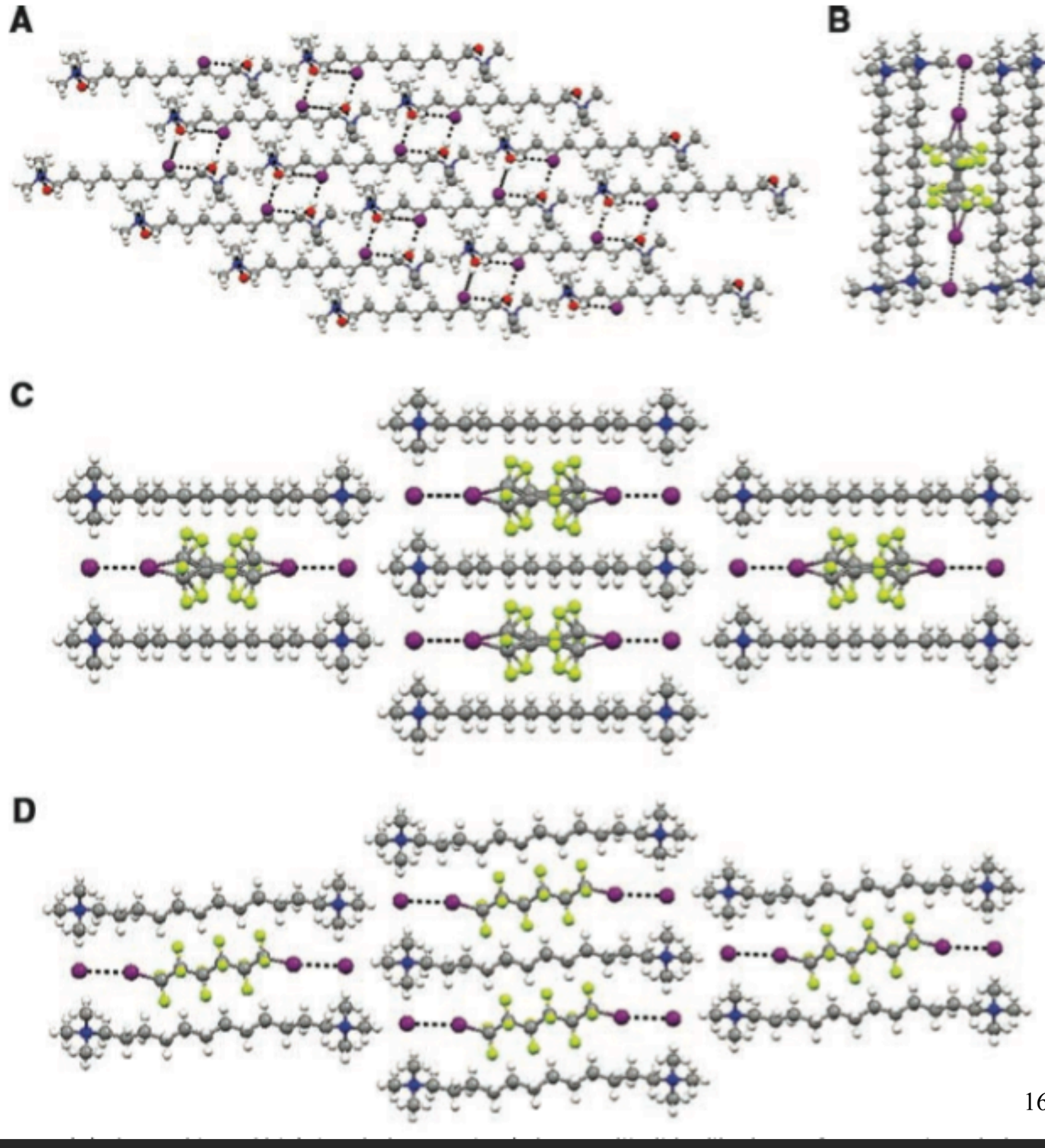
Crystallization

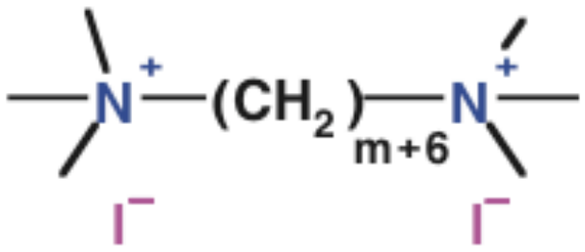


Halogen bonded dianion

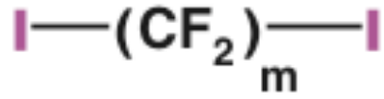
Only when the size of the dianion match the distance of the positive charges the system will work!!




A
B
C
D



1

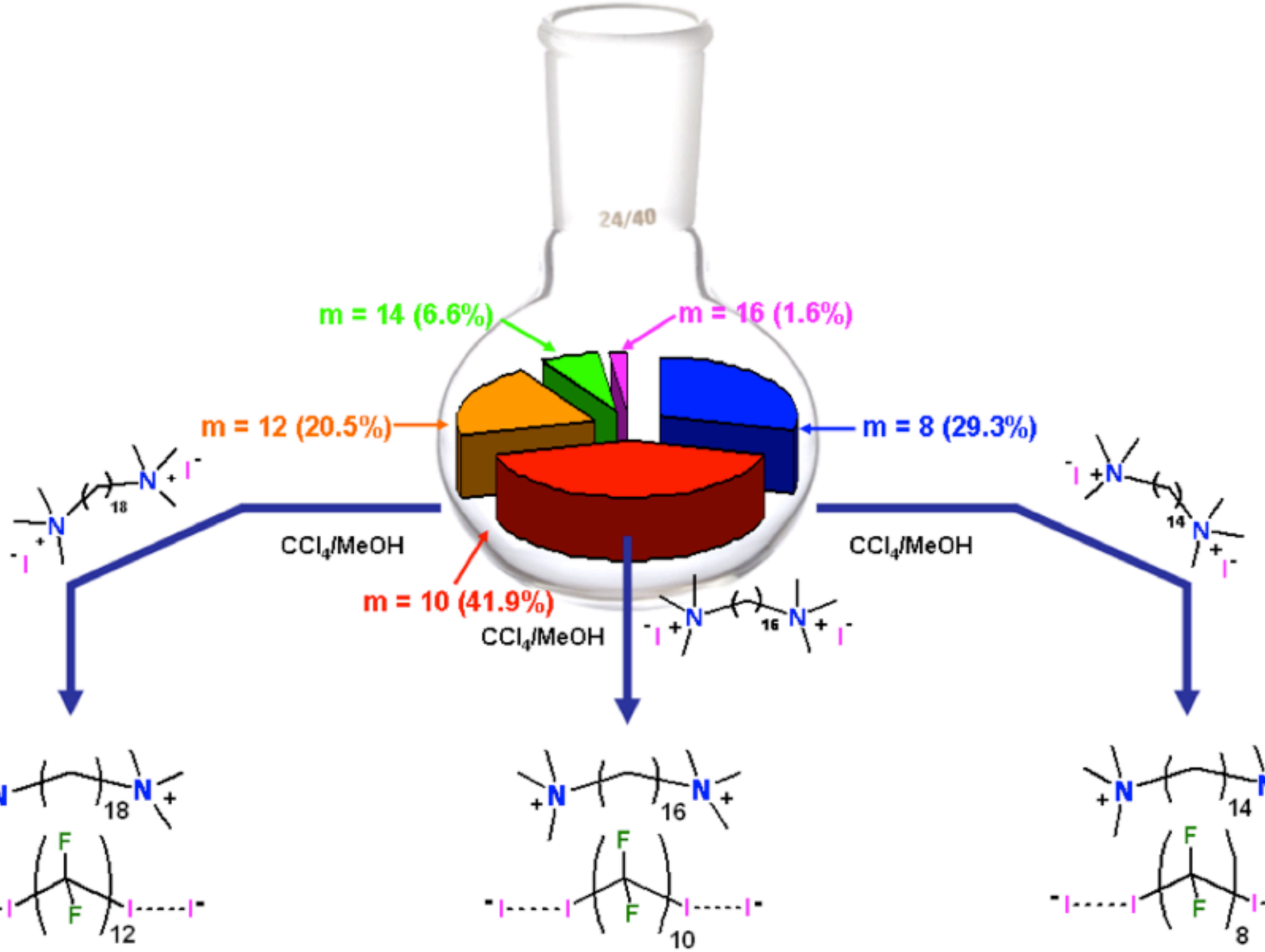


2

Adduct 1 • 2

1, 2	a	b	c	d	e	f
m	2	4	6	8	10	12

Adduct	Distance A ⟷ $^{+}N(CH_2)_{m+6}N^{+}$ (Å)	Distance B ⟷ $I^{-}\cdots I(CF_2)_mI\cdots I^{-}$ (Å)		Δ (B - A) (Å)	Distance $I^{-}\cdots I$ (Å)	Angle $I^{-}\cdots I\text{-}C$ (°)
1a • 2a	11.290(14)	12.056(5)	MATCH	0.766	3.478(2)	167.8(4)
1b • 2b	13.628(12)	14.483(4)	MATCH	0.855	3.4517(11)	166.0(4)
1c • 2c	16.395(11)	17.083(5)	MATCH	0.688	3.4627(11)	167.5(2)
1b • 2d	13.62(4)	18.797(4)	MISMATCH	5.177	3.357(3), 3.410(2)	173.3(7), 176.1(6)
1a • 2b	10.527(8)	14.104(3)	MISMATCH	3.577	3.3514(9)	174.7(4)



P. Metrangolo, Y. Carcenac, M. Lahtinen, T. Pilati, K. Rissanen, A. Vij and G. Resnati, *Science* 323 **2009**, 1461 – 1464.

Metal Ion Based Self-assembly

(Cube, Knot, Tetrahedron and Sphere)

The Cube (38 components)

6

M-TAPP

M = H_2, Ni^{2+}, Zn^{2+}

24

8 $Fe(OTf)_2$

DMF

C_4-symmetric

6

M-L

M = H_2, Ni^{2+}, Zn^{2+}

O-symmetric

C_3-axis

$[Fe_8(M\text{-}L)_6]$•16OTf

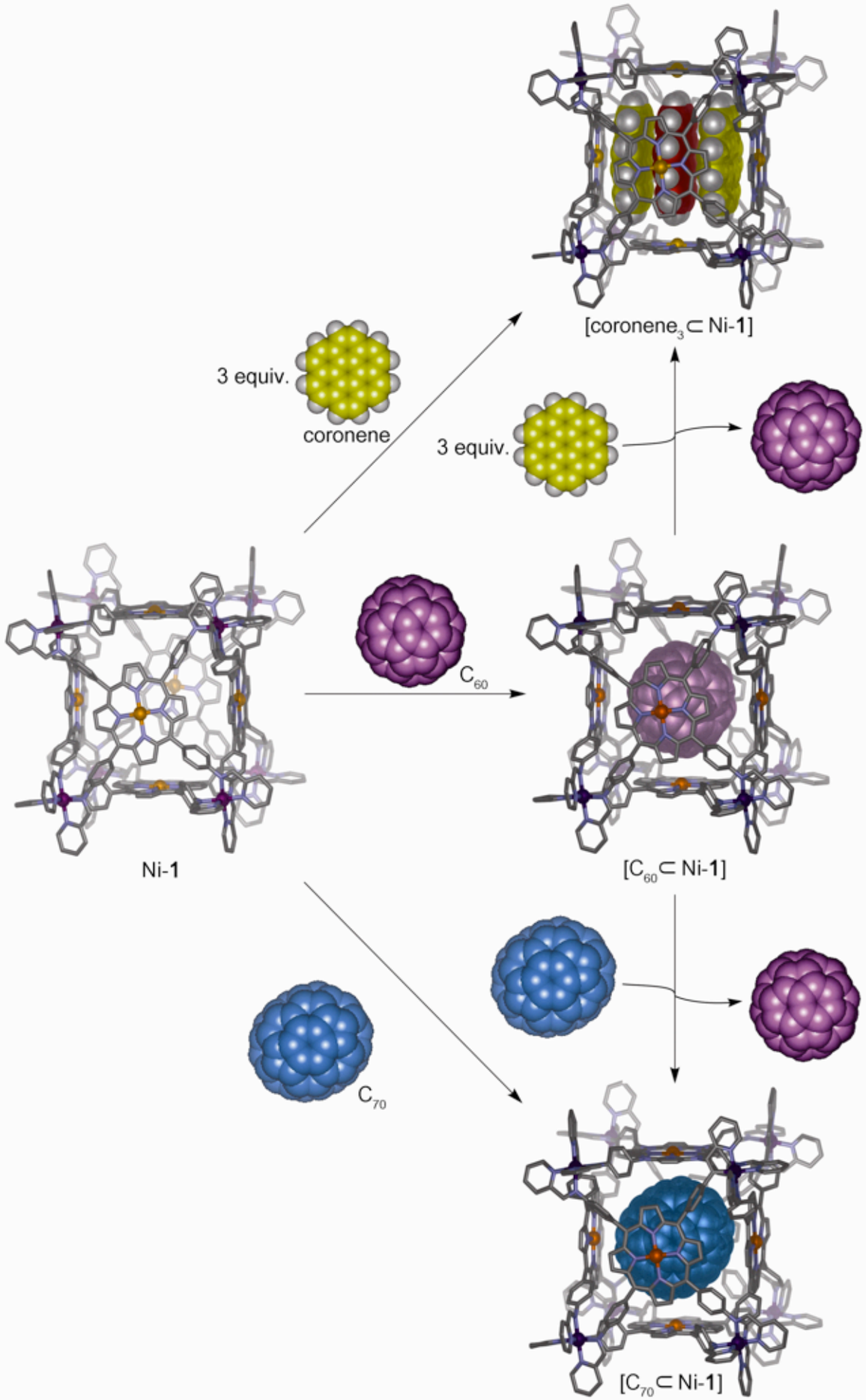
=

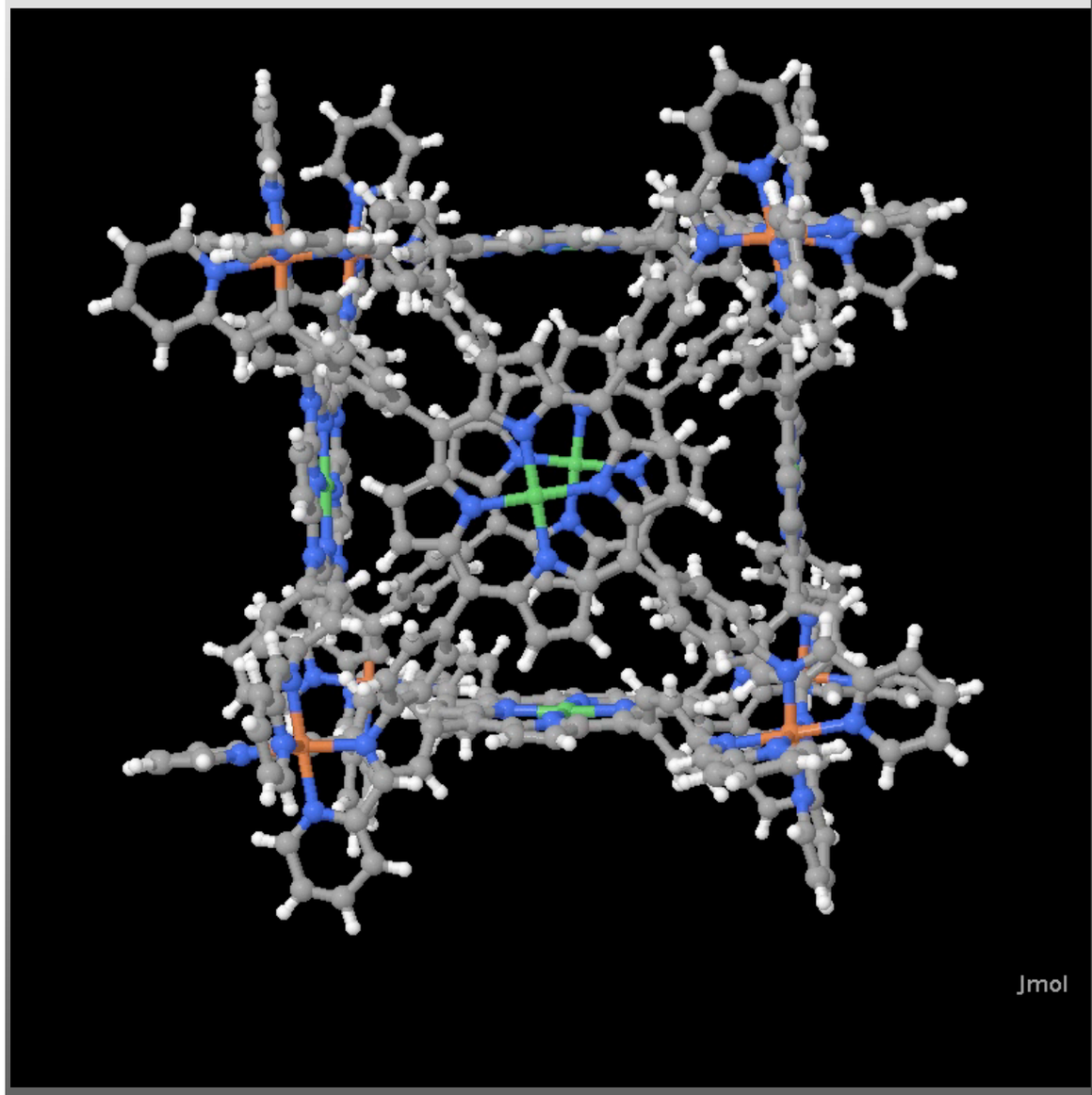
M-**1**

a

b

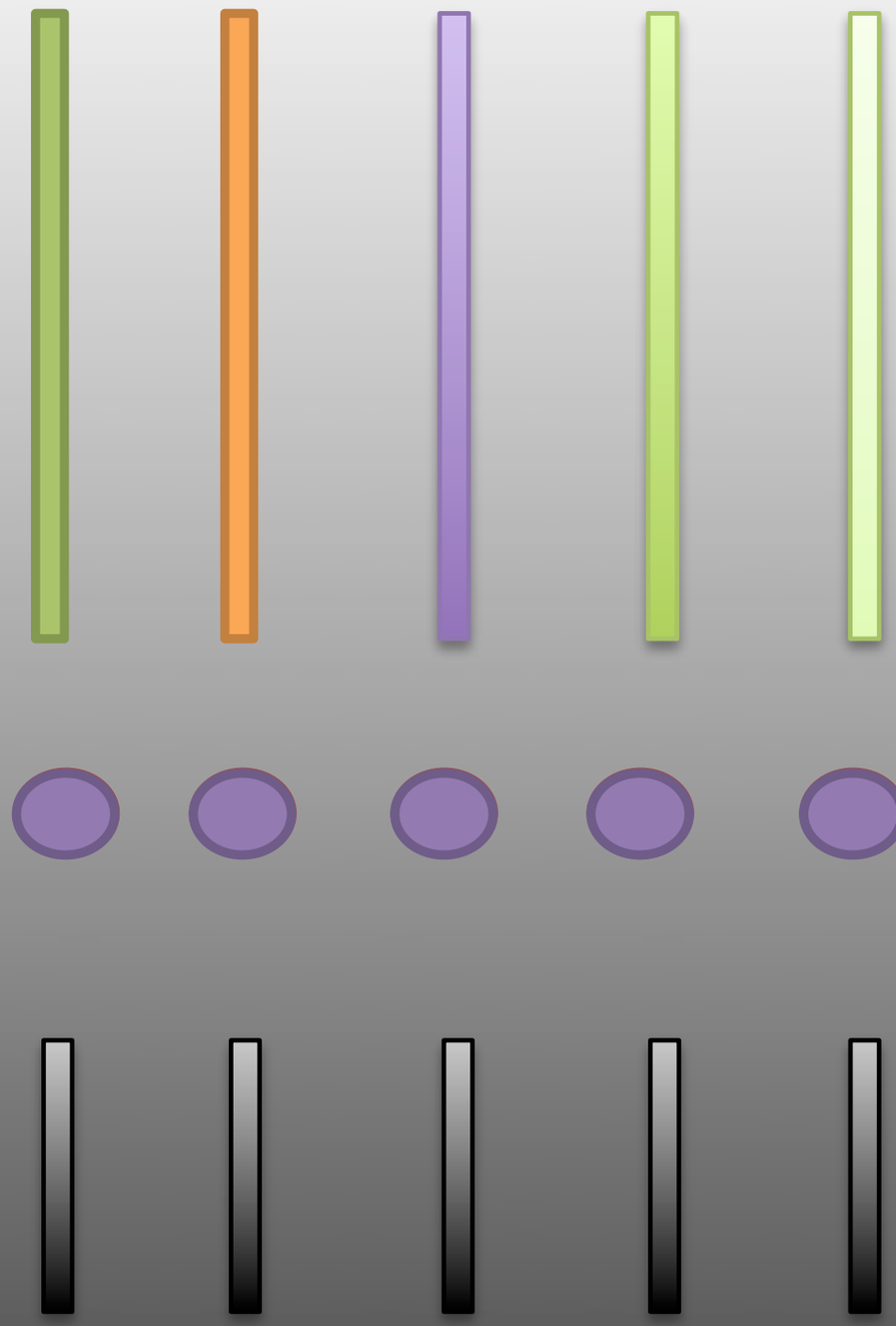
c



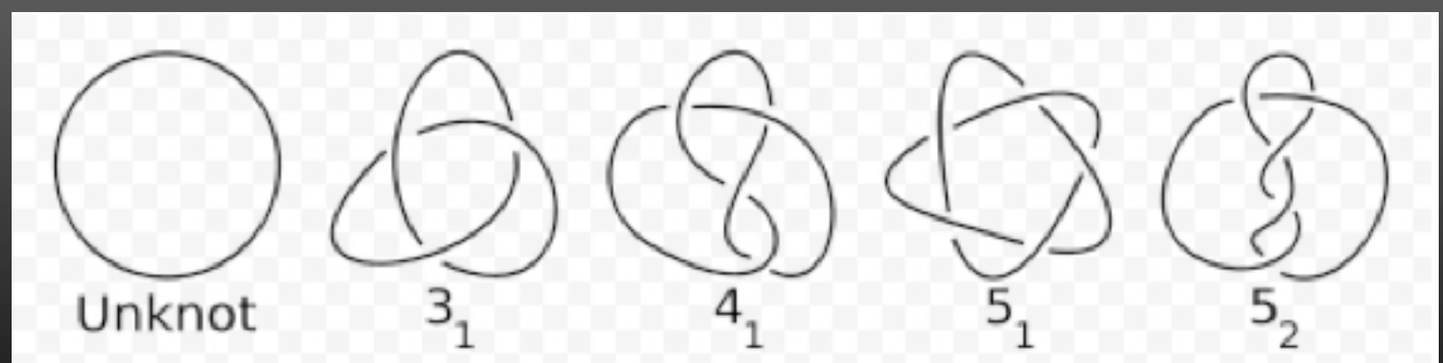


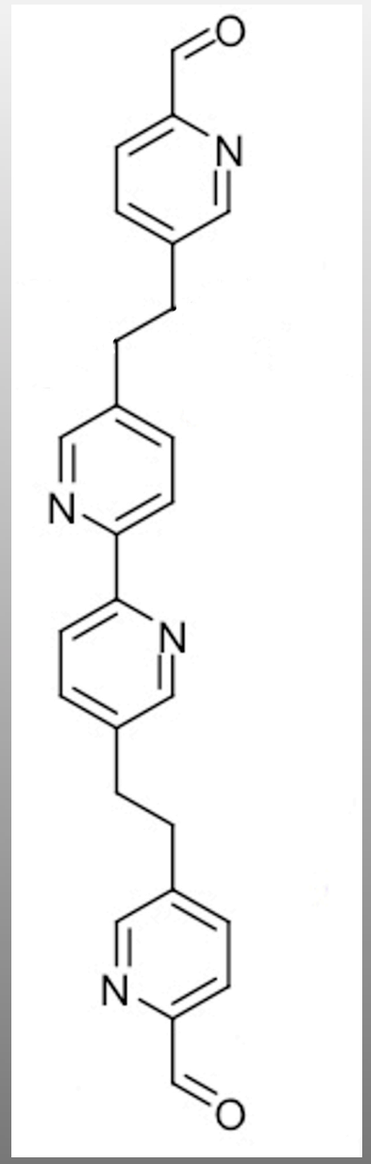
W. Meng, B. Breiner, K. Rissanen,
J. D. Thoburn, J. K. Clegg, J. R. Nitschke,
Angew. Chem. Int. Ed. (2011), 3479 - 3483
C&EN **89** (2011), 41 - 42.

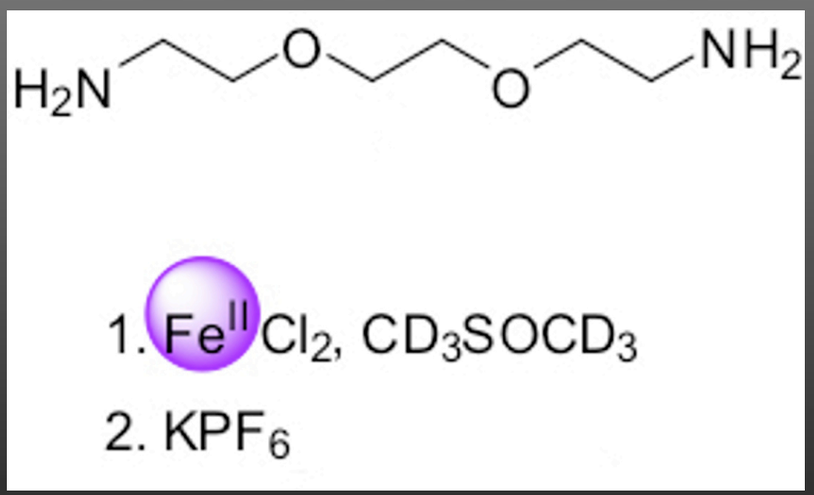
The Knot (15 components)

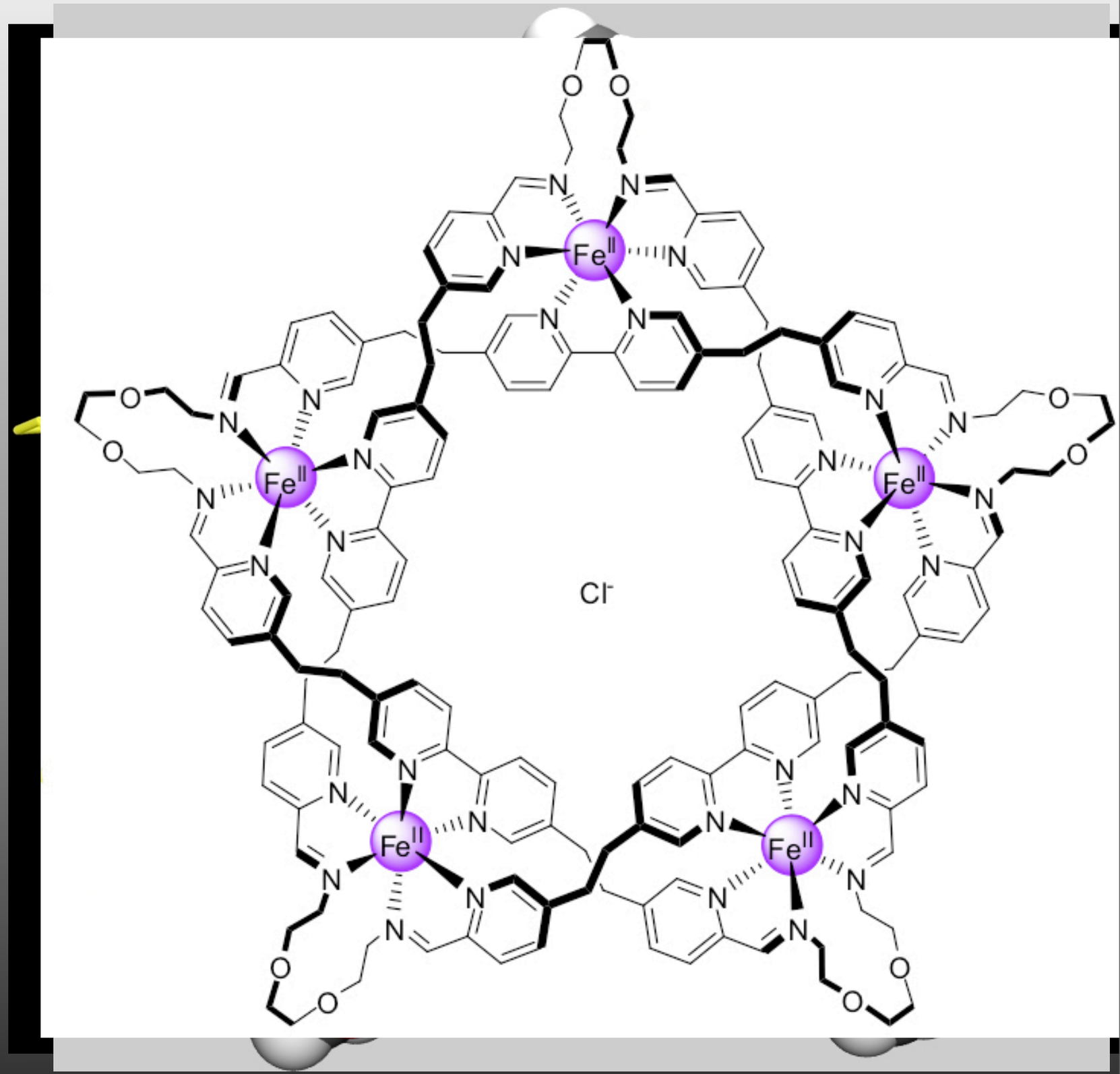


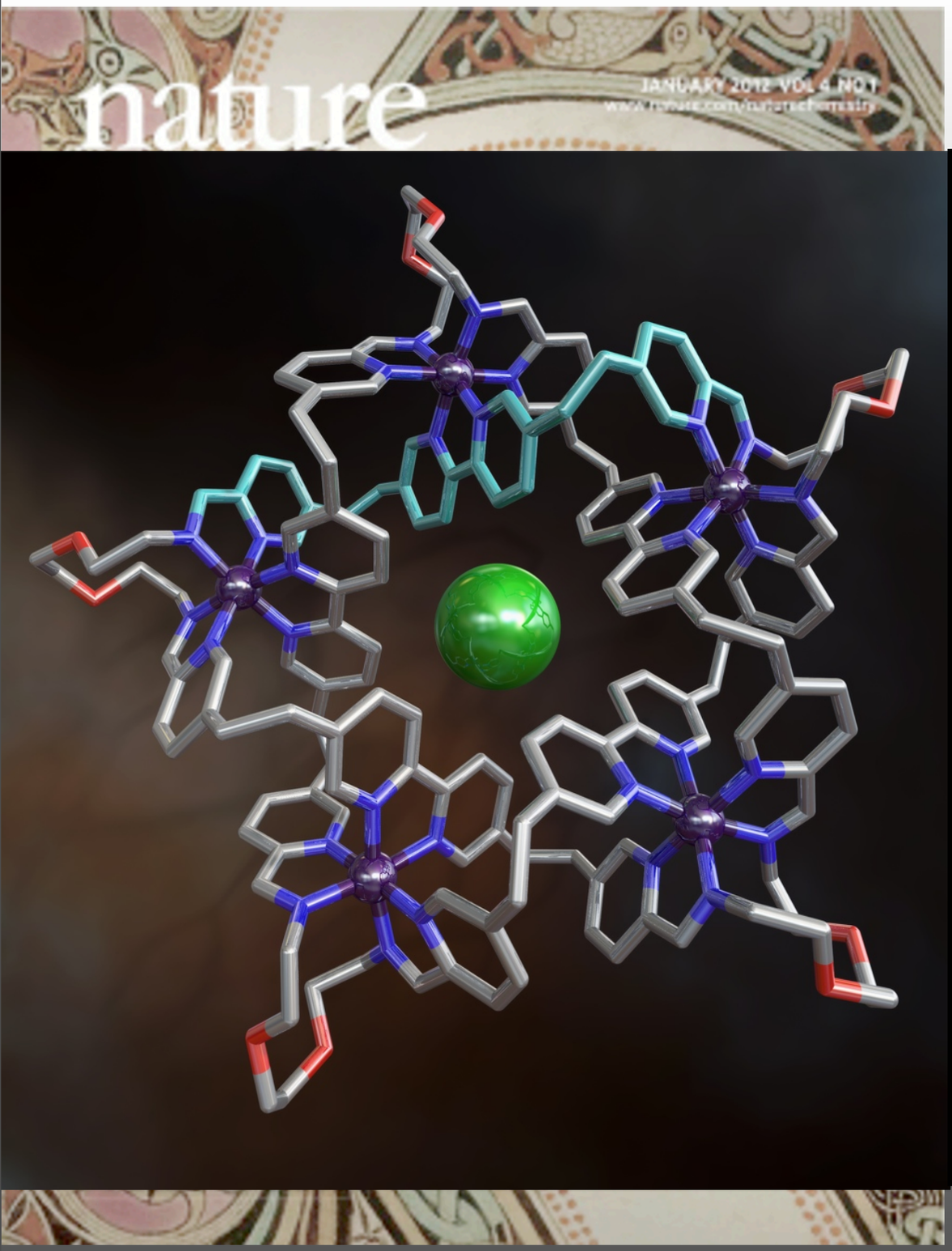

Nothing

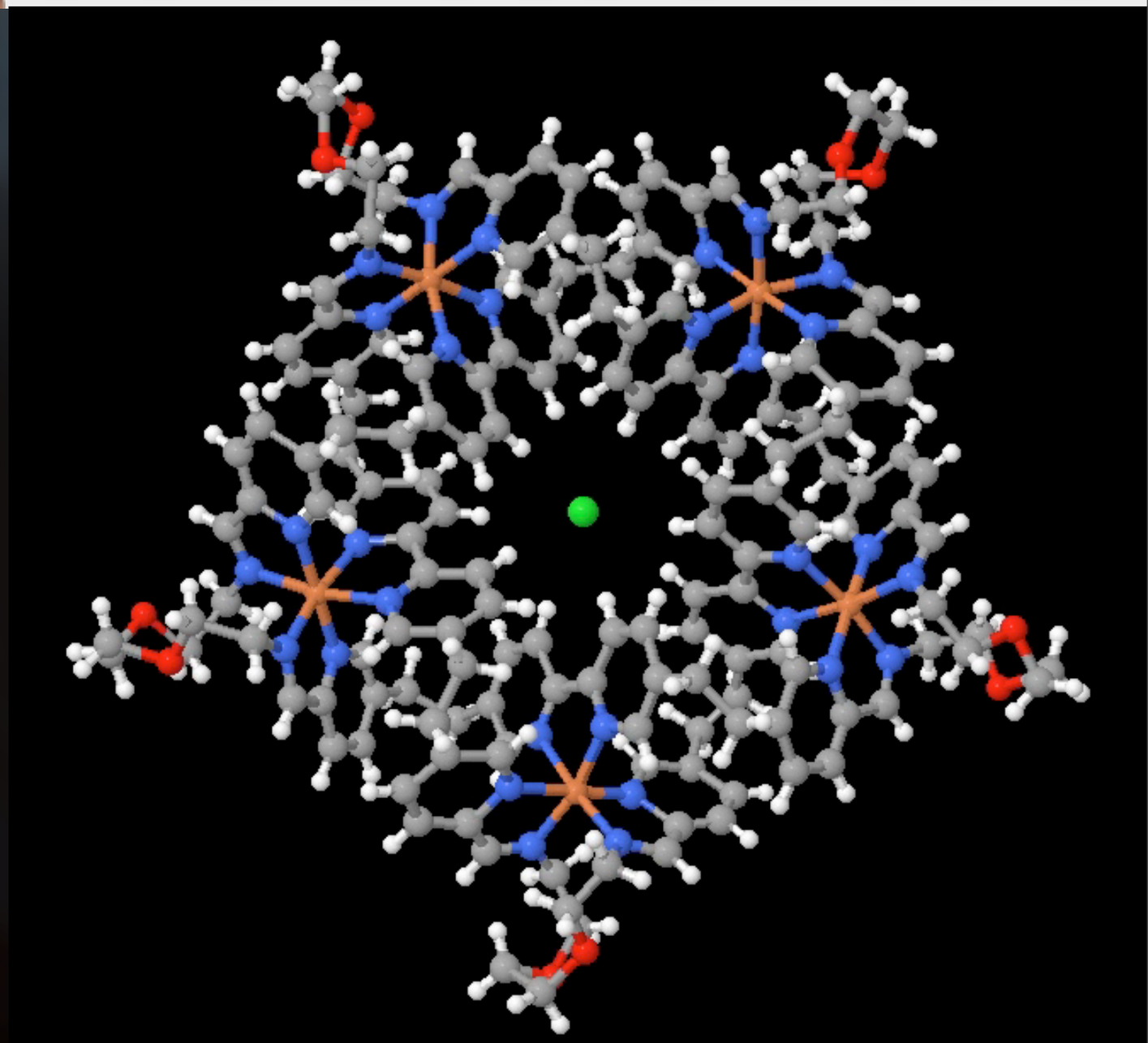

Unknot
3 1
4 1
5 1
5 2




H_2N
O
O
NH_2
1. $Fe^{II}Cl_2$, CD_3SOCD_3
2. KPF_6


Fe^{II}
Cl^-

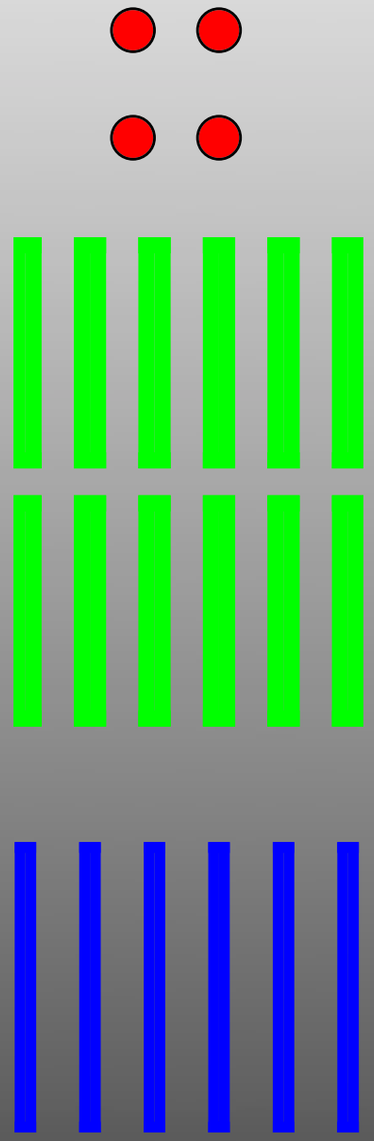




J.-F. Ayme, J. E. Beves, D. A. Leigh, R. T. McBurney, K. Rissanen ja D. Schultz, *Nature Chemistry* (2012), 15 - 20.
J.-F. Ayme, J. E. Beves, D. A. Leigh, R. T. McBurney, K. Rissanen ja D. Schultz, *J.Am. Chem. Soc.* (2012), 9488 - 9497.

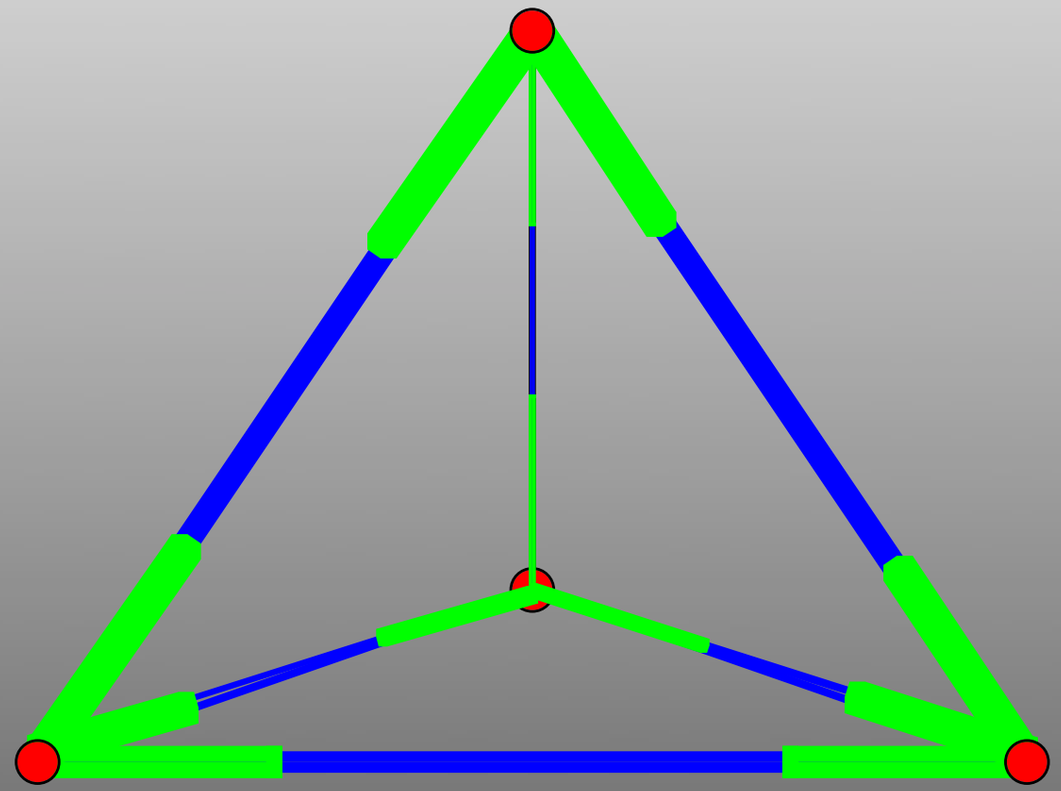
Fire within a tetrahedron

(Metal-ion assisted self-assembly in water, 22 components)



Self-
assembly

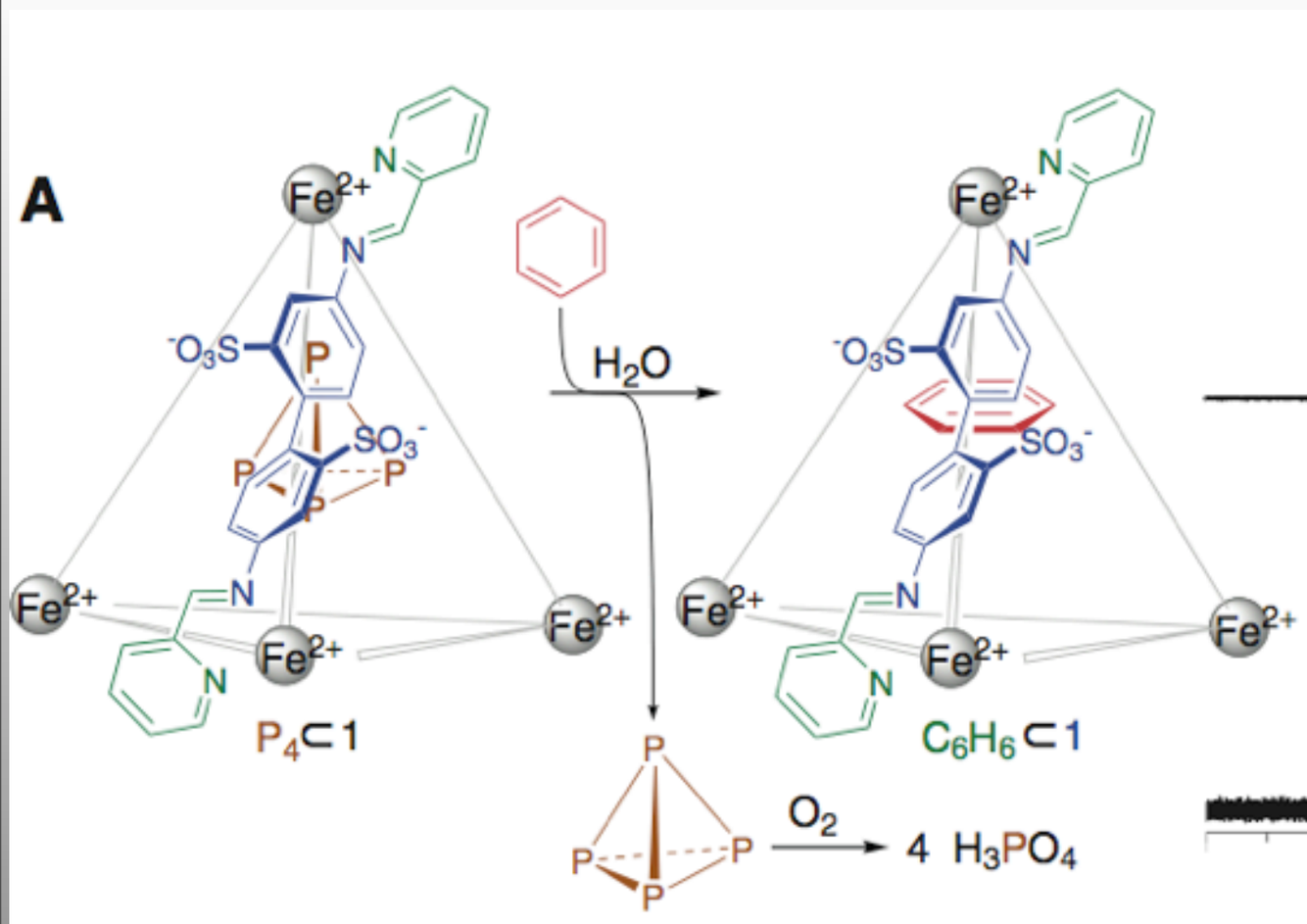
Water

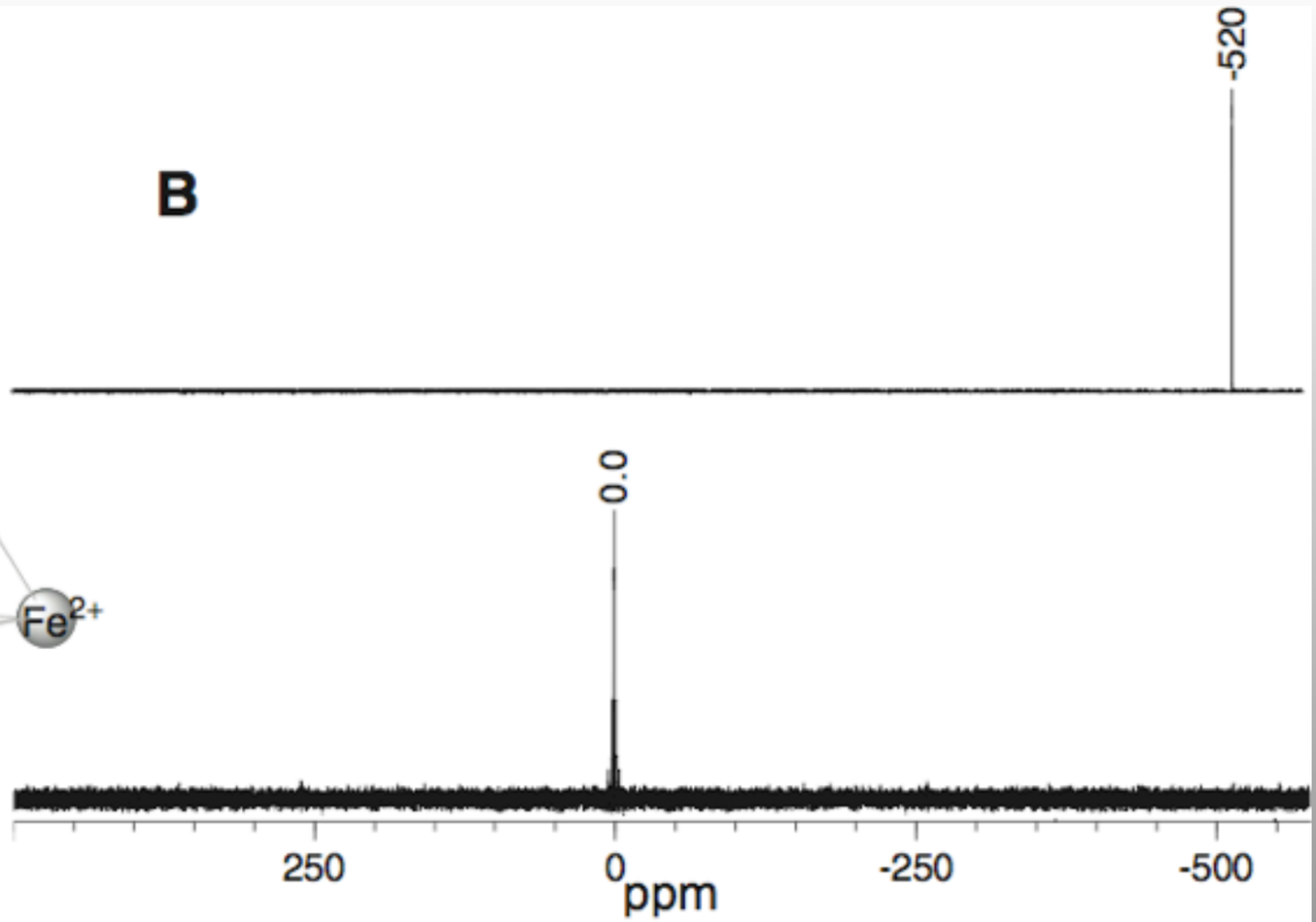


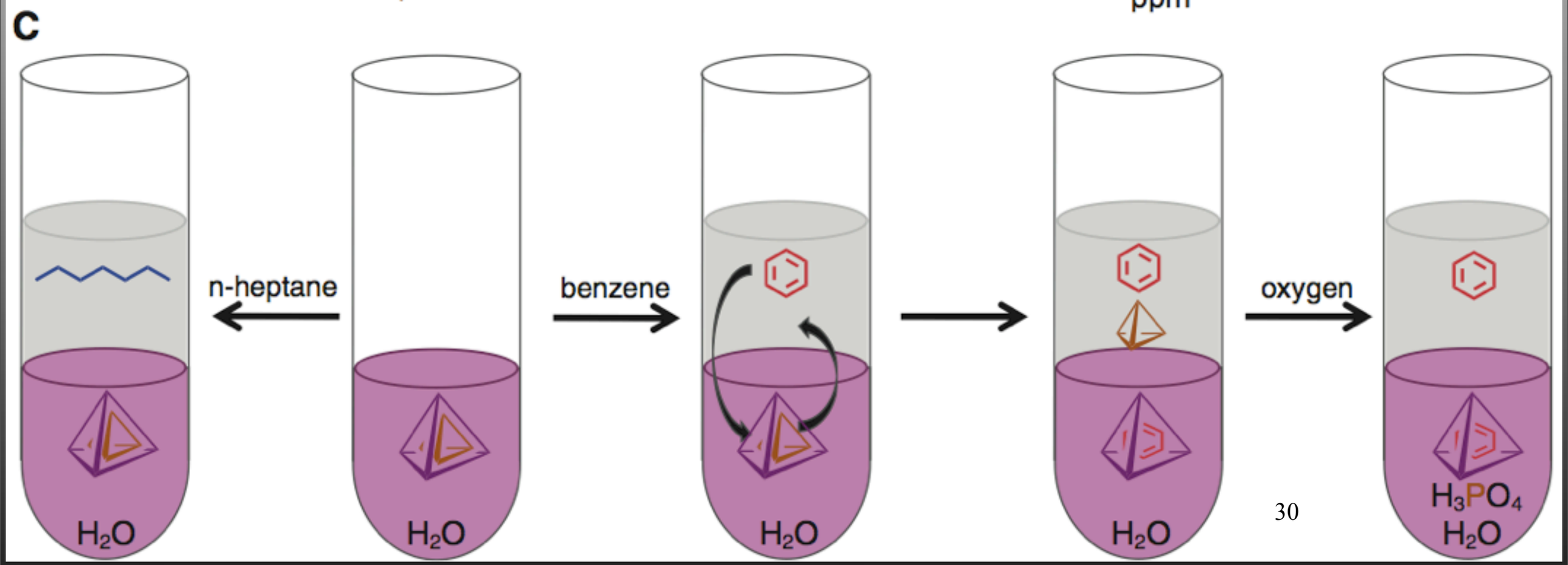
Tetrahedron

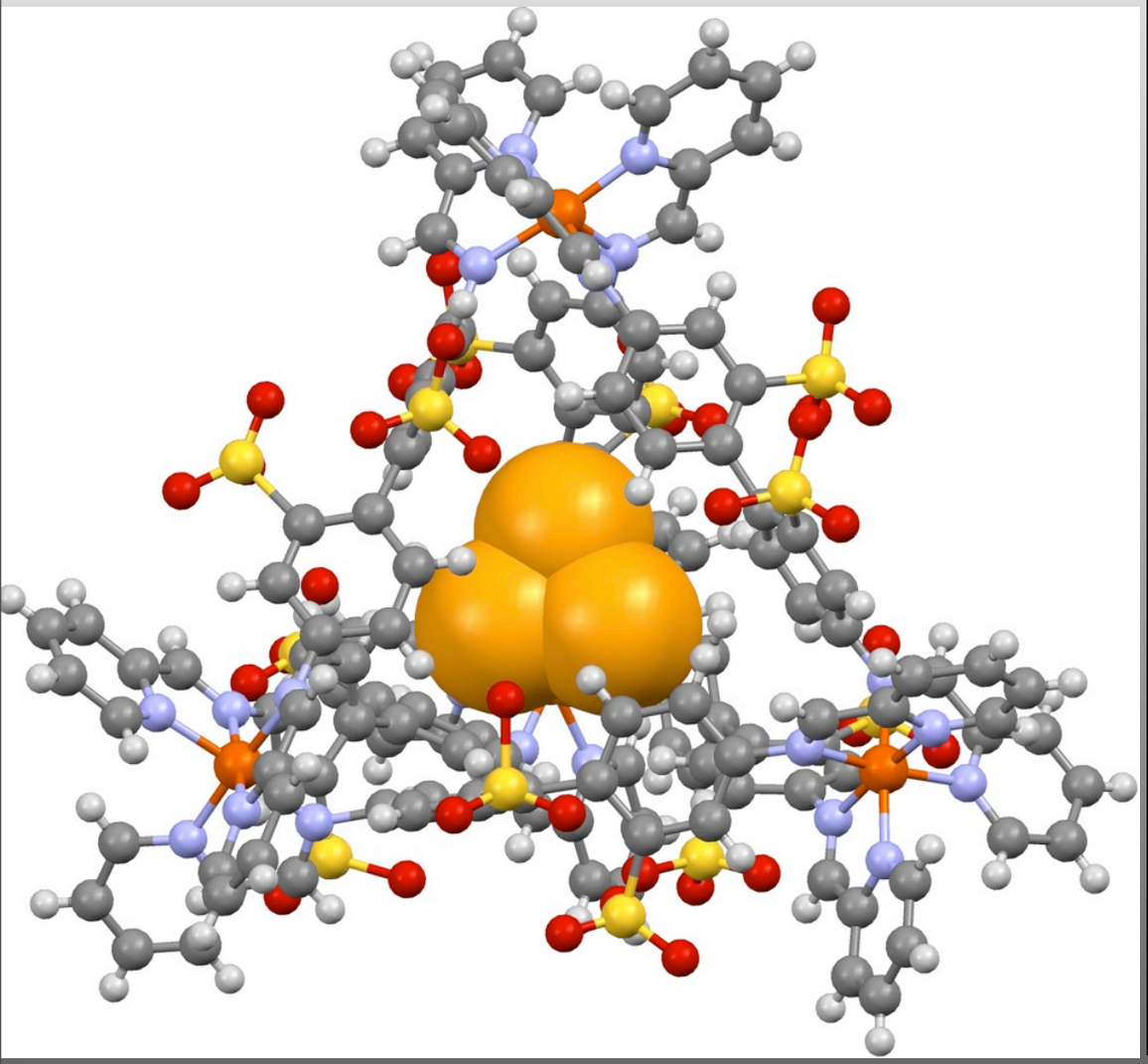
White phorphorus, *viz.* P4, spontaneously ignites when taken out from water

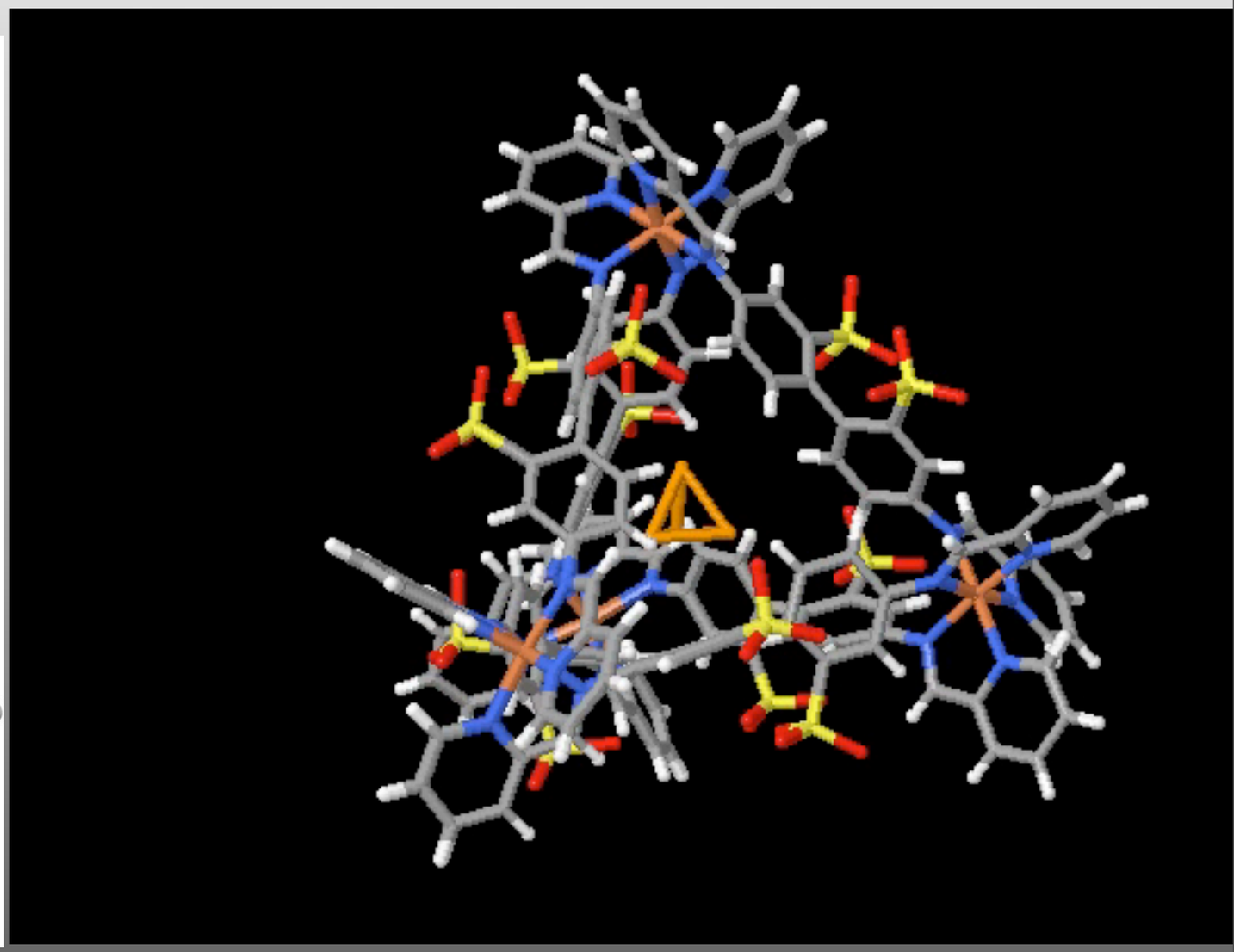
Elementary Productions: White Phosphorus
http://www.youtube.com/watch?v=Oke8GinWDG8


A
Fe2+
N
-O3S
P
SO3-
P4⊂1
H2O
C6H6⊂1
O2
4 H3PO4

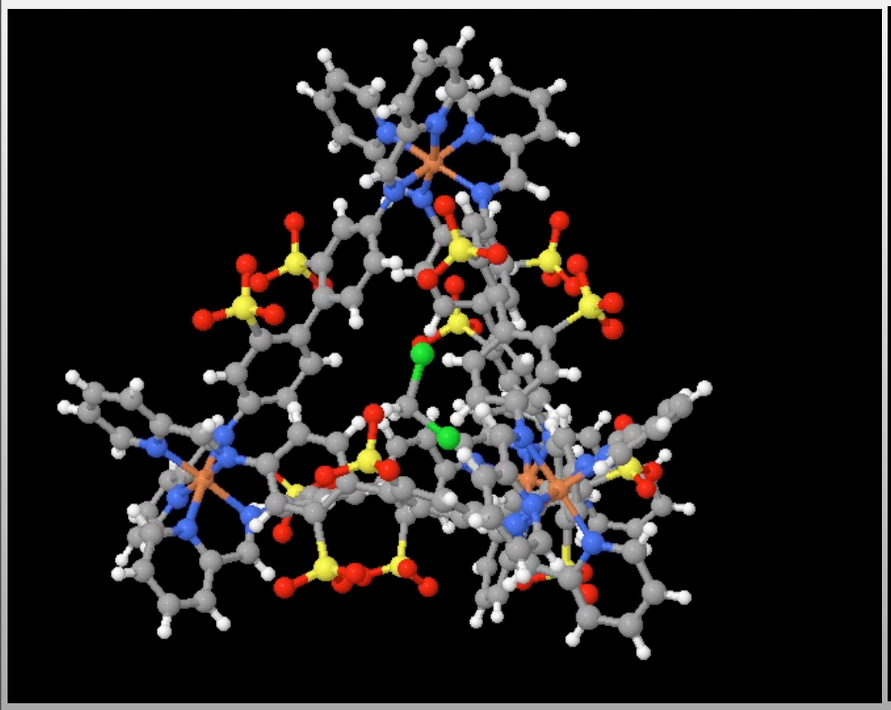
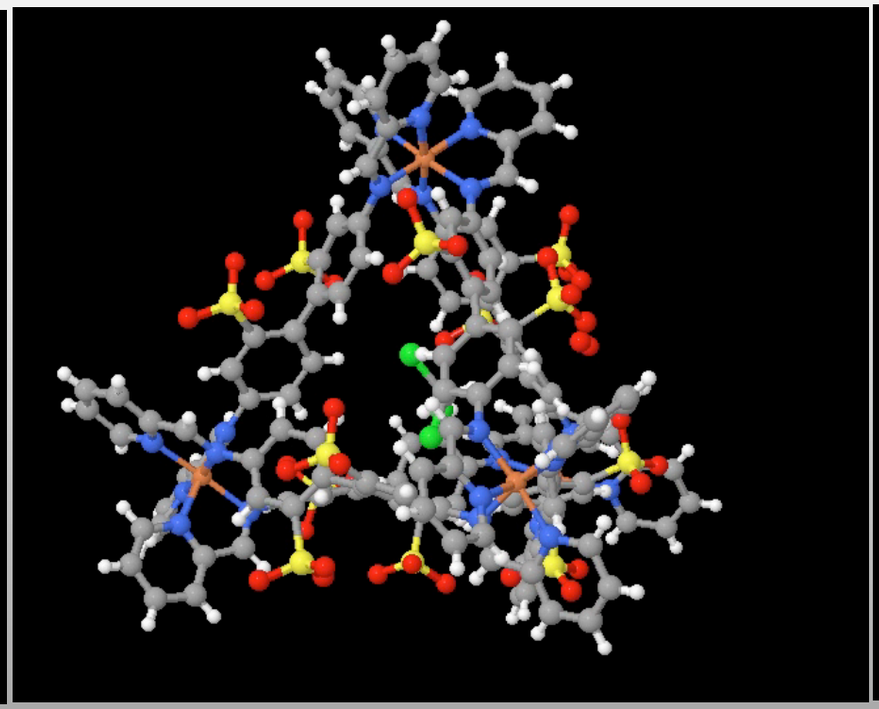
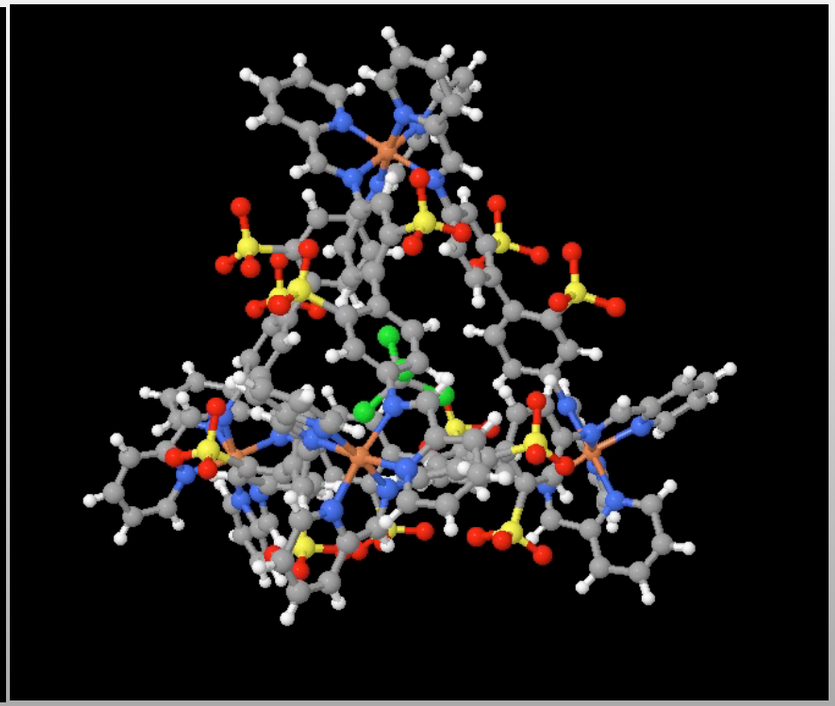
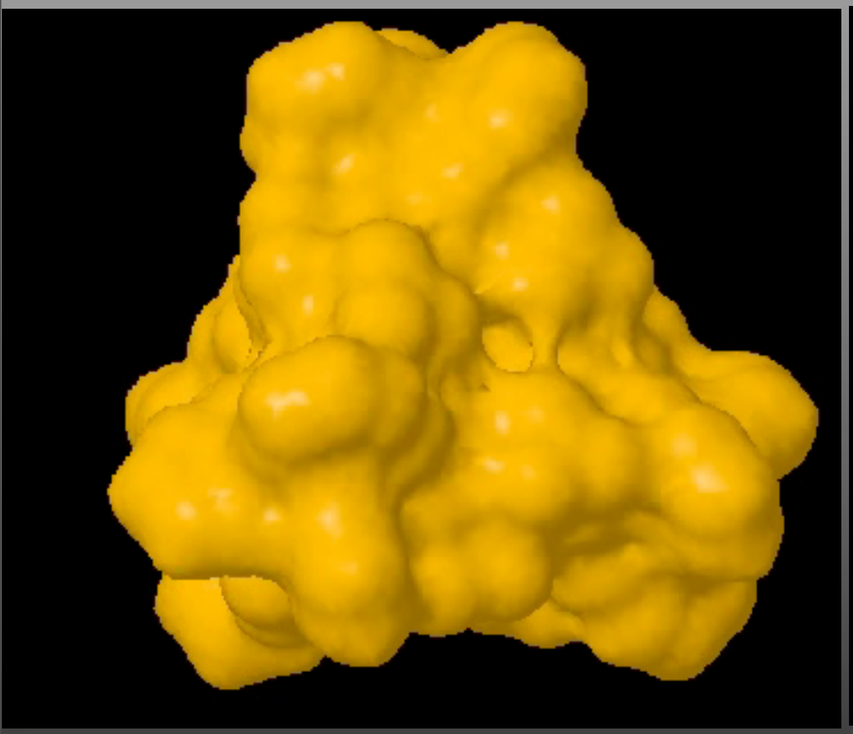
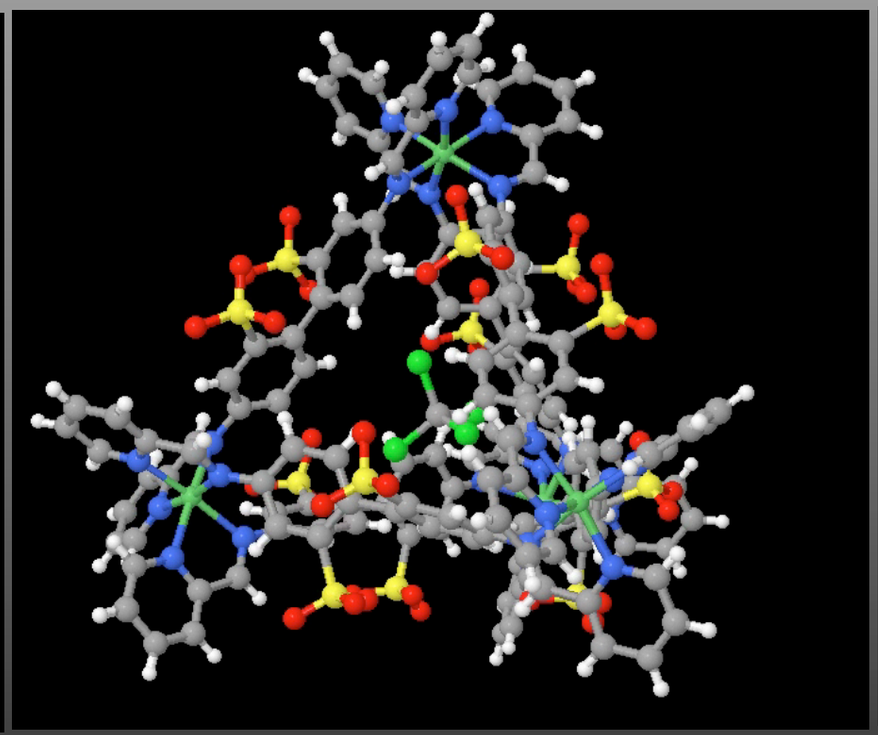
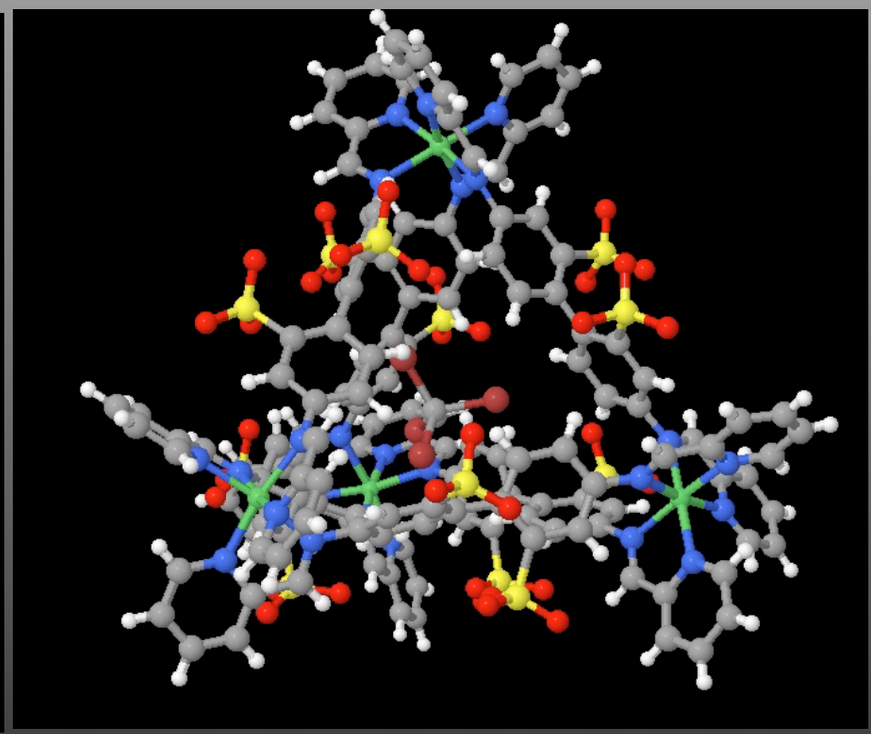

B
-520
0.0
250
0
ppm
-250
-500


C
n-heptane
benzene
oxygen
H2O
H3PO4



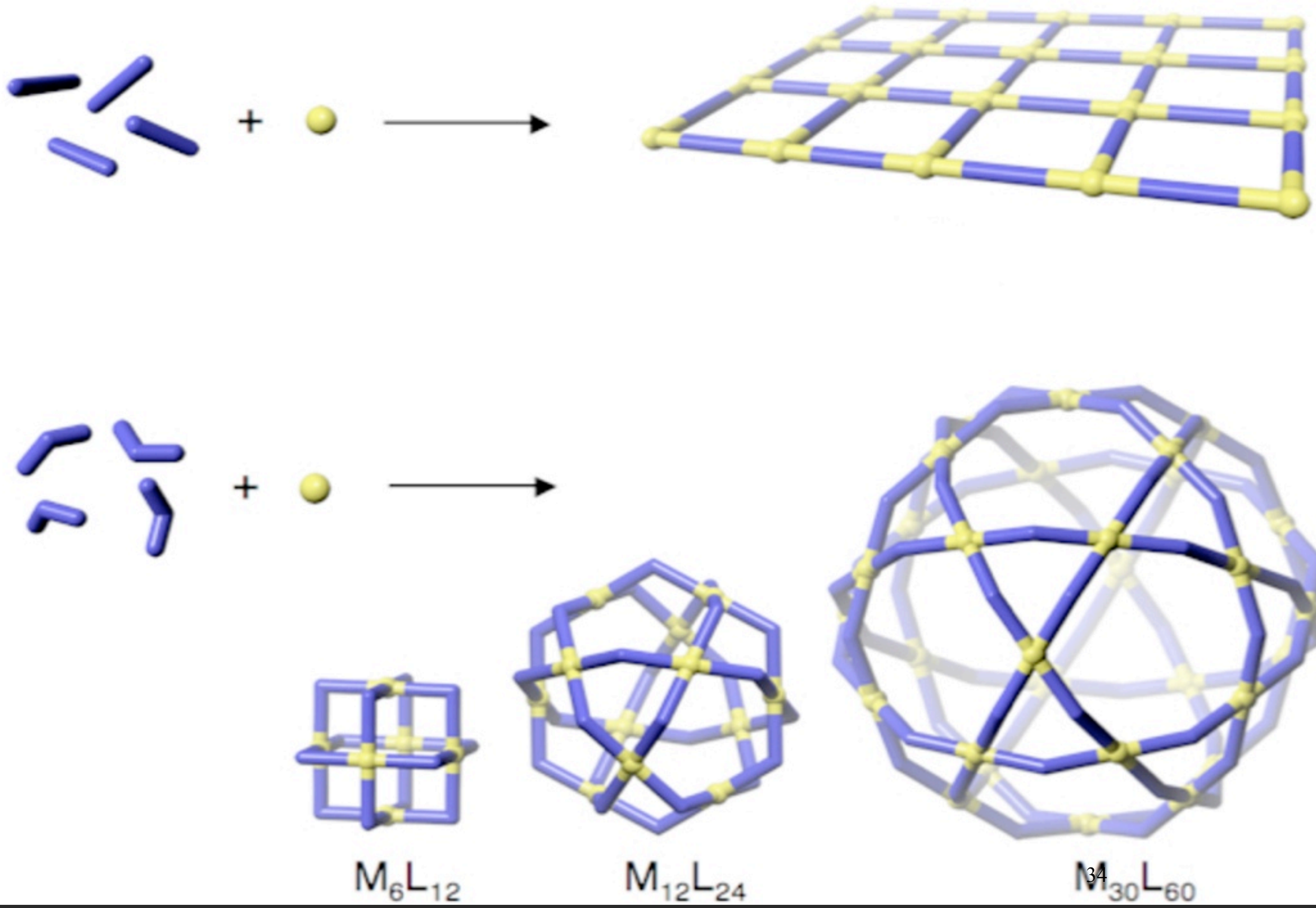


P. Mal, B. Breiner, K. Rissanen and J.R. Nitschke, *Science* (2009), 324, 1697.

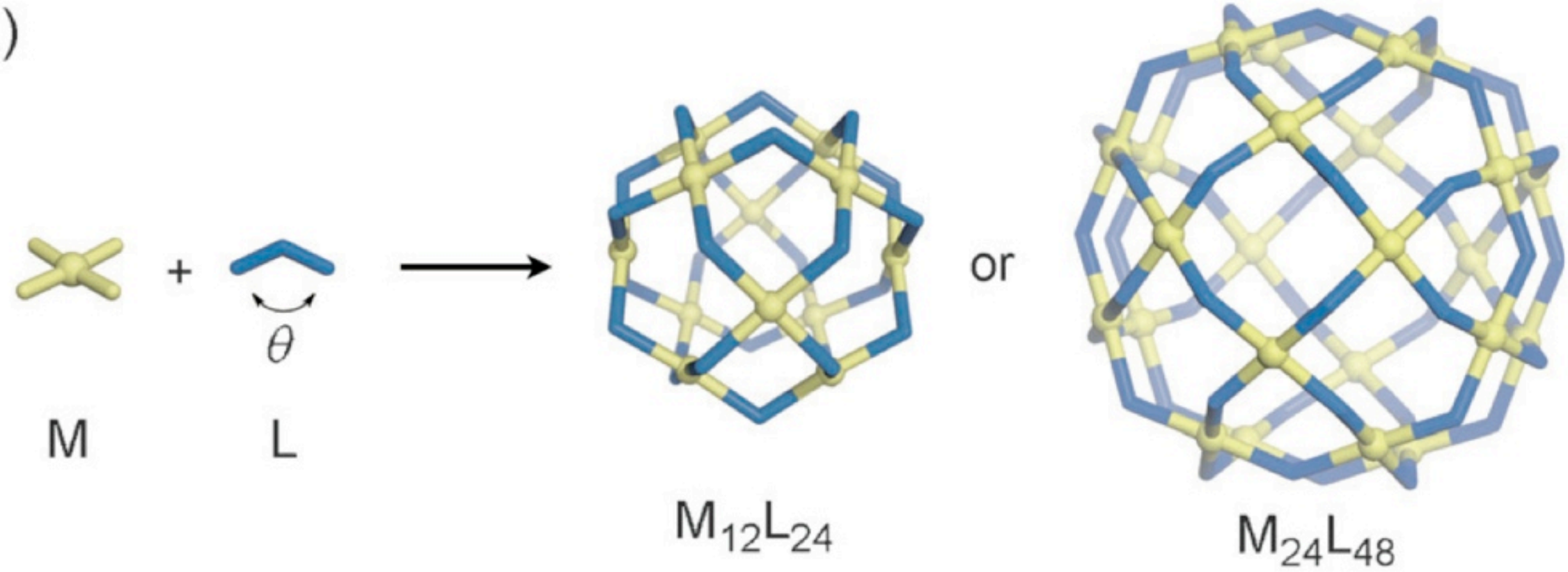







T. K. Ronson, C. Giri, N. K. Beyeh, A. Minkkinen, F. Topić, J. J. Holstein, K. Rissanen and J. R. Nitschke, *Chem. Eur. J.* 19 (2013), 3374 - 3382.

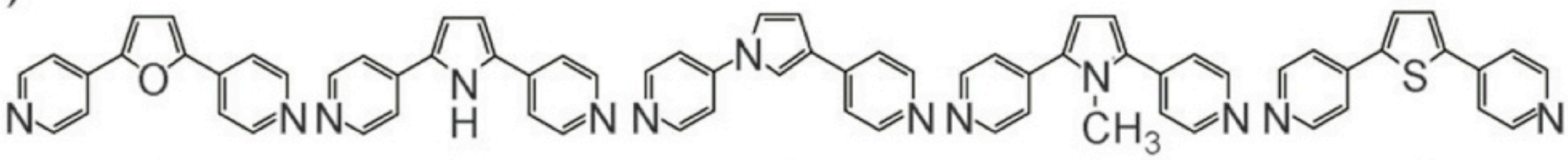
Giant Molecular Spheres (72 components)


M_6L_{12}
$M_{12}L_{24}$
$M_{30}L_{60}$

a)

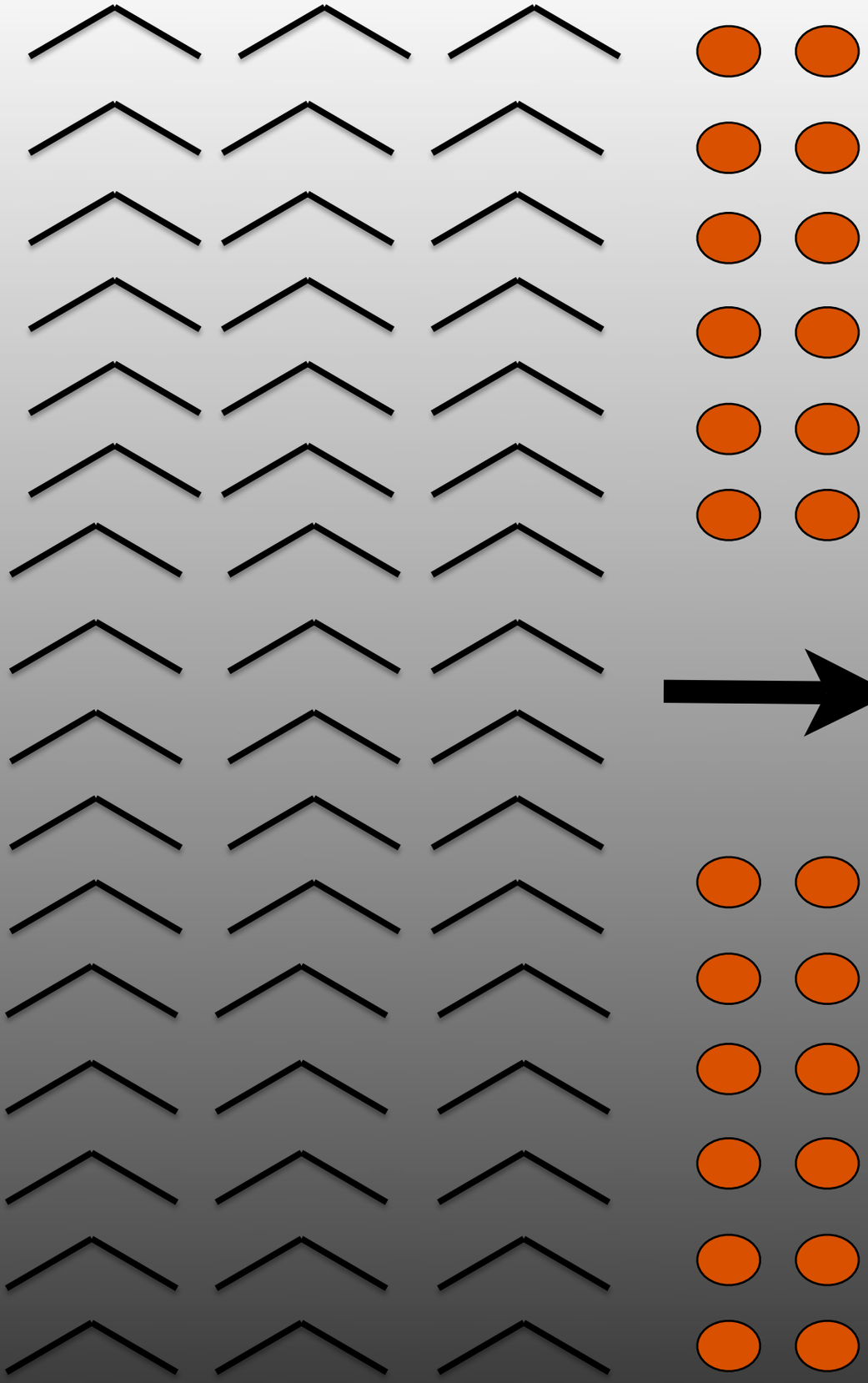


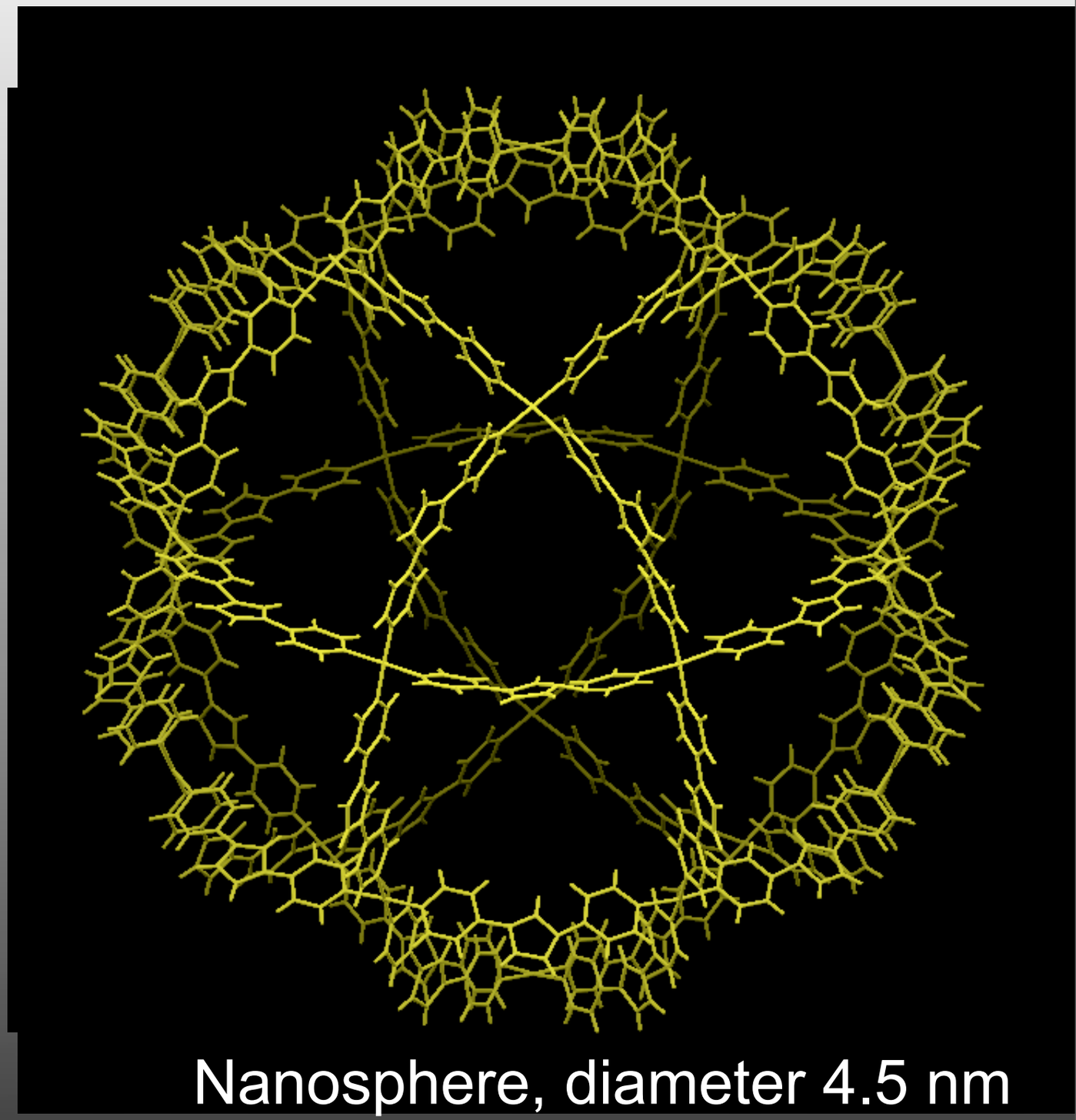
b)



1 $\theta = 127°$ **2** $\theta = 135°$ **3** $\theta = 143°$ **4** $\theta = 147°$ **5** $\theta = 149°$

127 ← $M_{12}L_{24}$ → 131 134 ← $M_{24}L_{48}$ → 149





Nanosphere, diameter 4.5 nm

J. Bunzen, J. Iwasa, P. Bonakdarzadeh, E. Numase, K. Rissanen, S. Sato and M. Fujita, *Angew. Chem.* **124** (2012), 3161 - 3163.

DEPARTMENT OF CHEMISTRY

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F. Bates, M. Fujita, D. Hammer, M. Klein, M. Lahtinen, T. Lodge, J. Nitschke, V. Percec, P. Metrangolo, G. Resnati, S. Sato

J. Beves, N.K. Beyeh, P. Bonakdarzadeh, B. Breiner, J. Bunzen, J. K. Clegg, N. Kuuloja, P. Mal, W. Meng, S. Nummelin, J. Ropponen, D. Schulz, J. D. Thoburn, T. Tuuttila

THANK YOU very much for your kind attention!