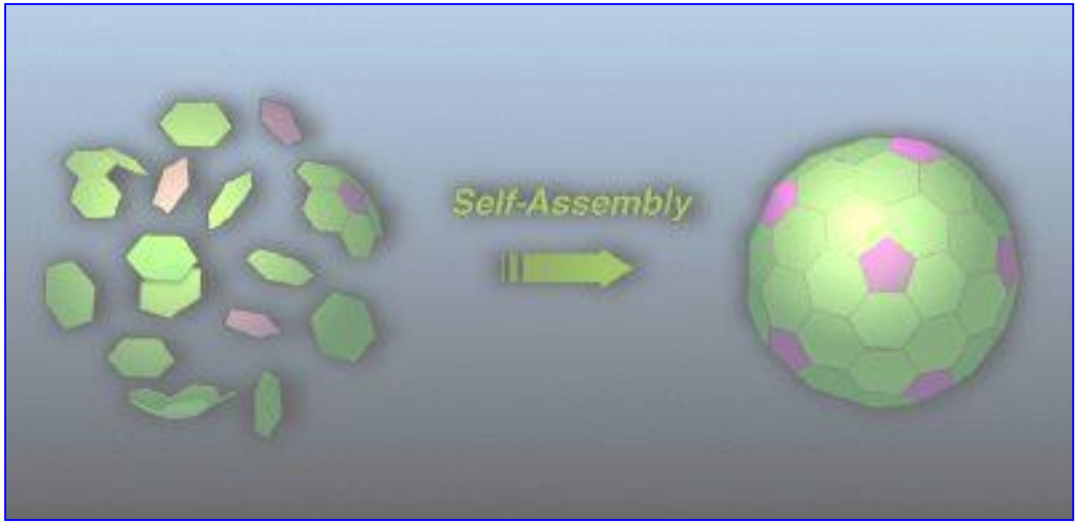
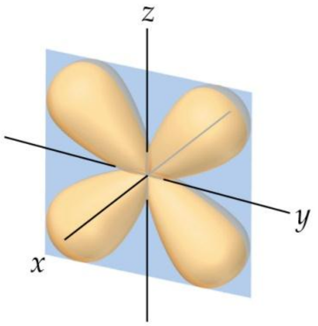
Self-Assembly

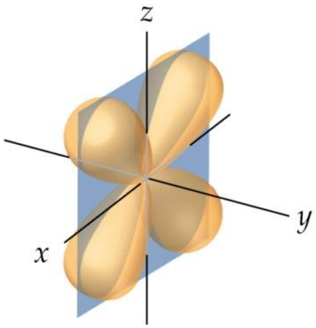
*The **spontaneous and reversible** association of molecular species to form larger, more complex supramolecular entities according to the **intrinsic information** contained in the components.*



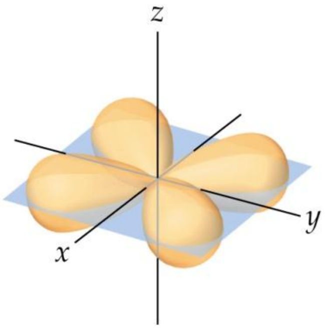
Metal-Ligand Interaction



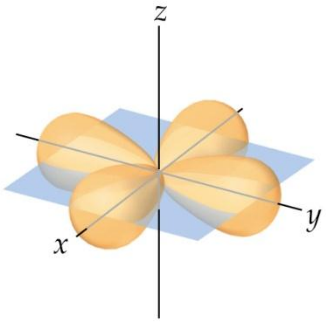
d_{yz}



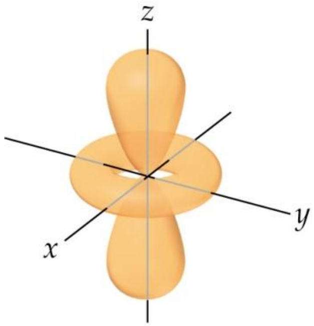
d_{xz}



d_{xy}



$d_{x^2-y^2}$



d_{z^2}

Metal as **connector** :

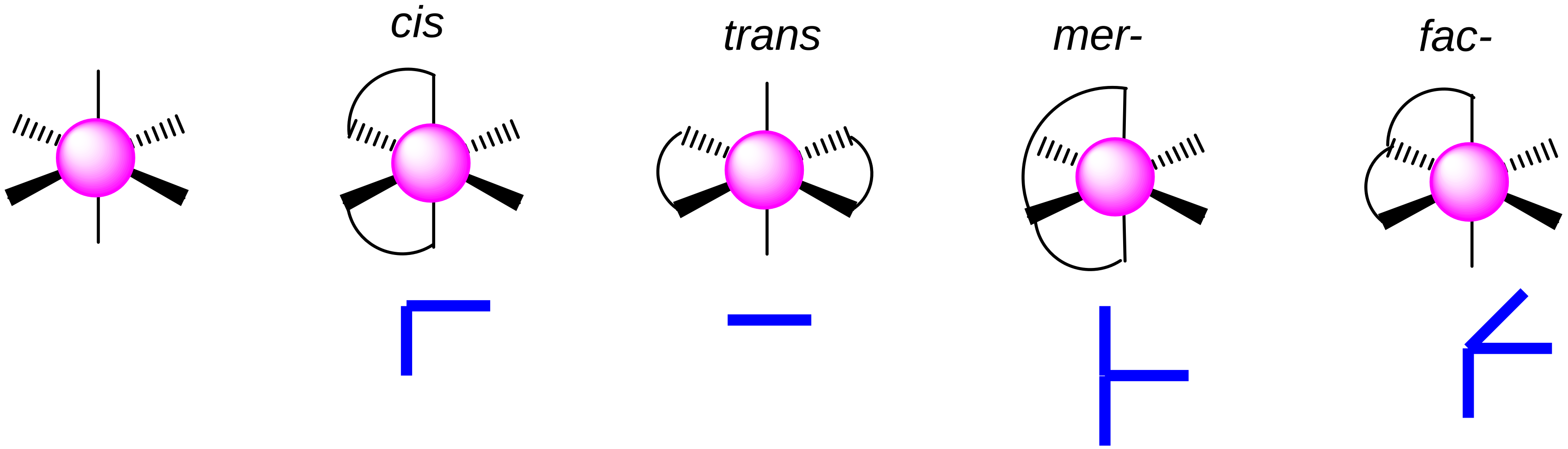
- labile M-L interaction (kinetic)
- stable compound (thermodynamic)
- highly directional with many geometries available

Metal as **functional group** :

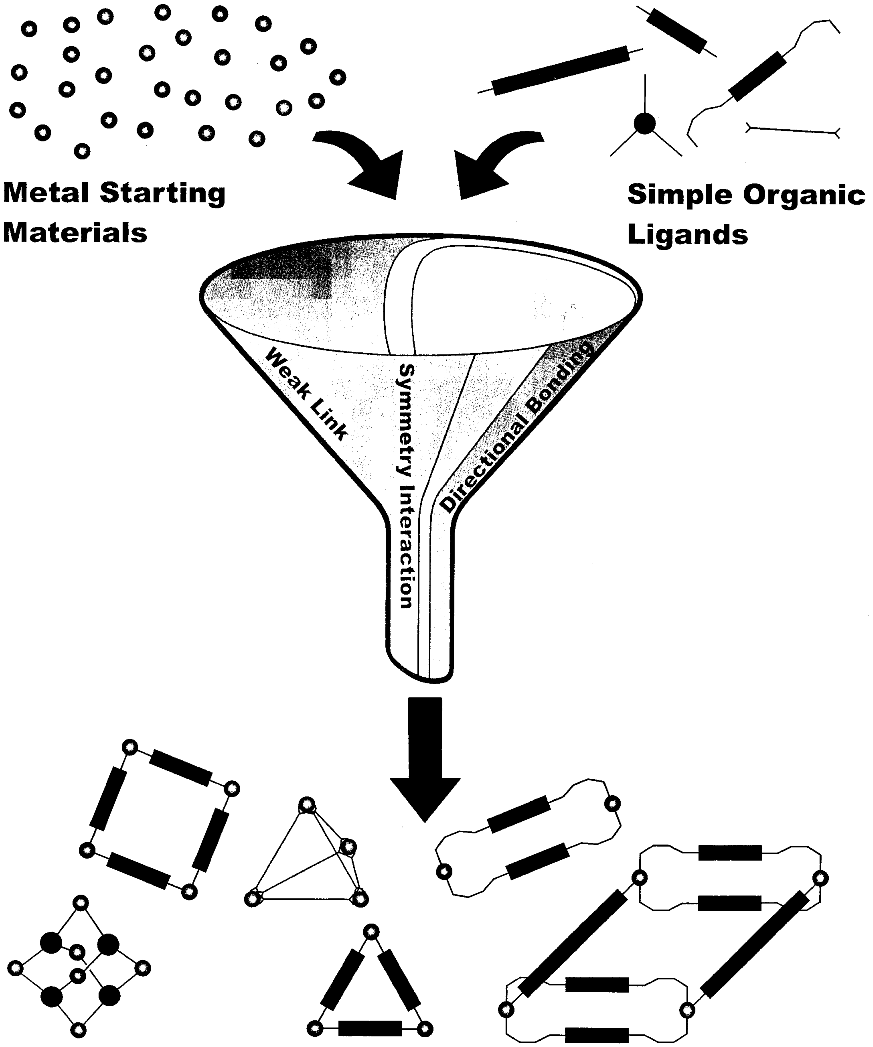
- redox active (electron transfer)
- UV-vis active (color)
- photo active (phosphorescence)
- magnetic properties

Classical metals used:

Pd(II), Pt(II), Cu(I), Cu(II), Re(I), Co(II), Fe(II), Ag(I), Zn(II), Ru(II)…

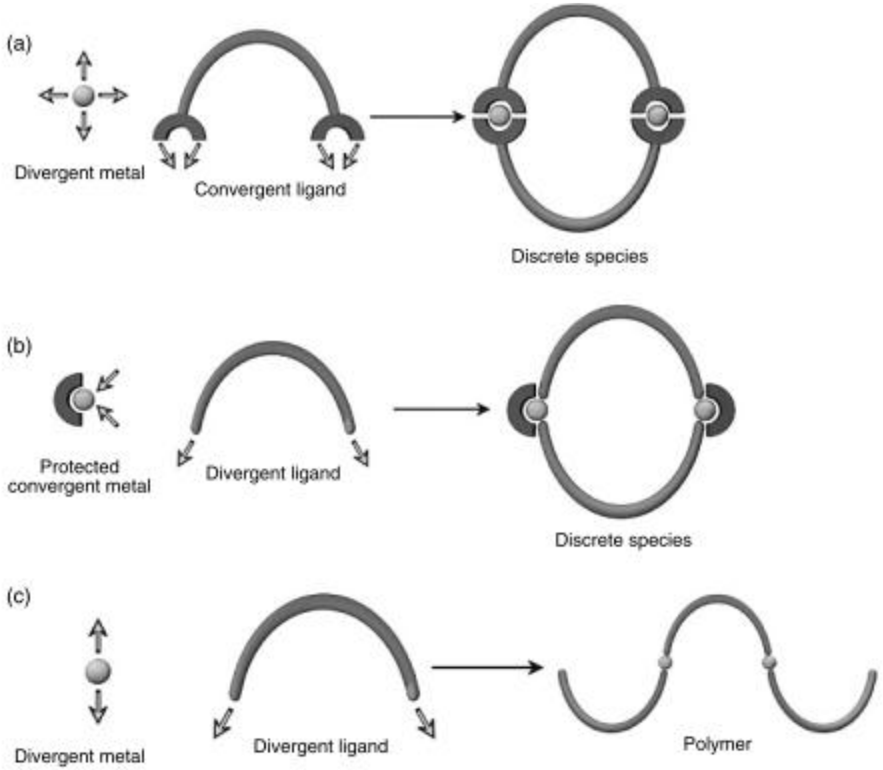


Supramolecular Coordination Chemistry



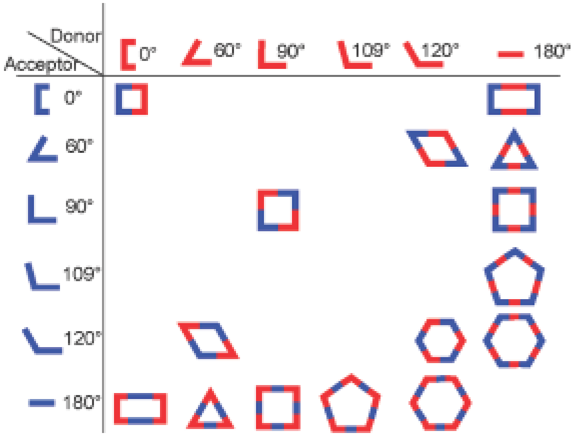
Metal Starting Materials

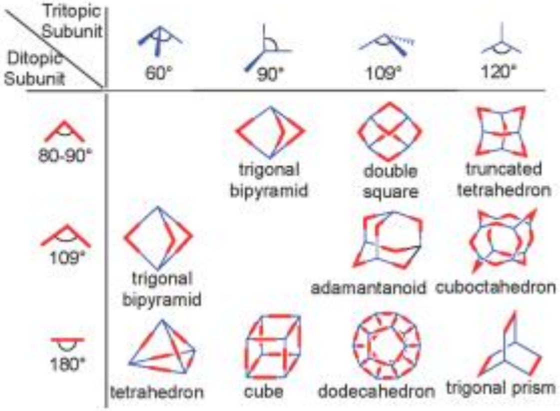
Simple Organic Ligands


(a)
Divergent metal
Convergent ligand
Discrete species
(b)
Protected convergent metal
Divergent ligand
Discrete species
(c)
Divergent metal
Divergent ligand
Polymer

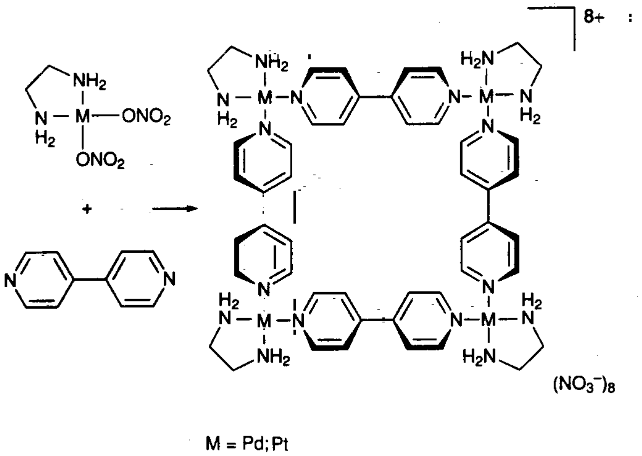
Directonal Bonding Approach

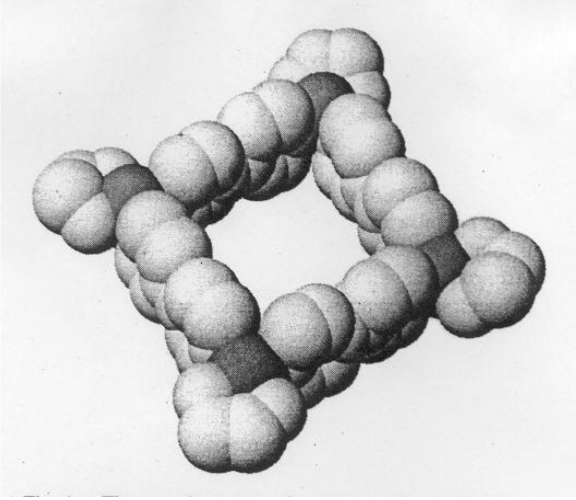
M = bb acido, **L** = bb basico, definiti secondo il numero e geometria relativa dei siti acidi e basici





Specie poligonali 2D





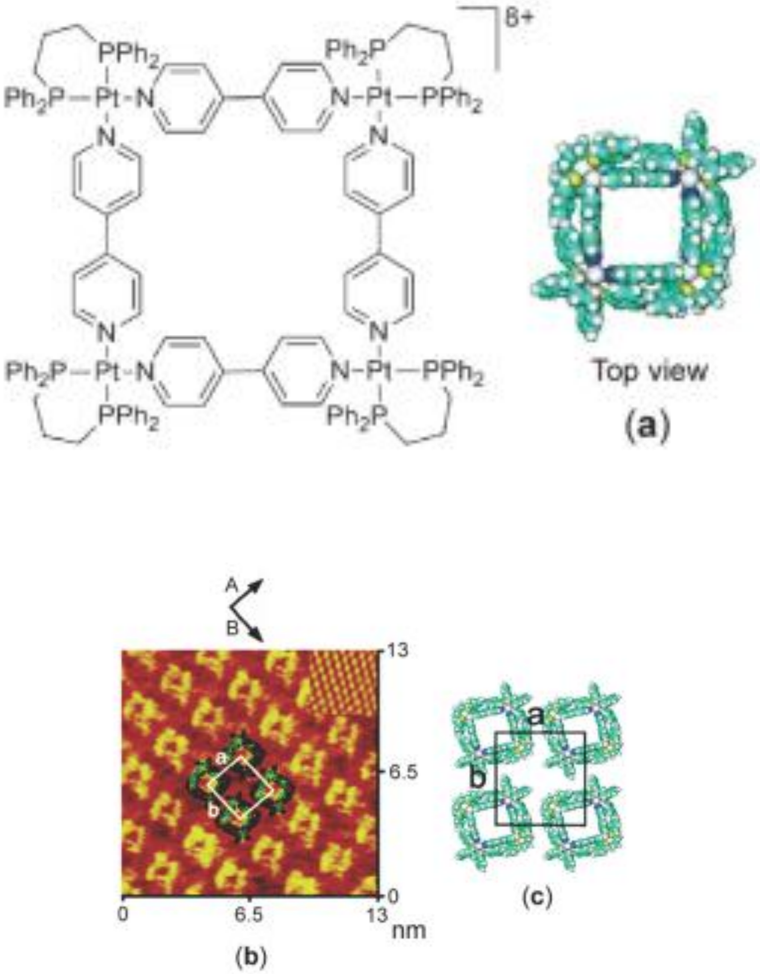
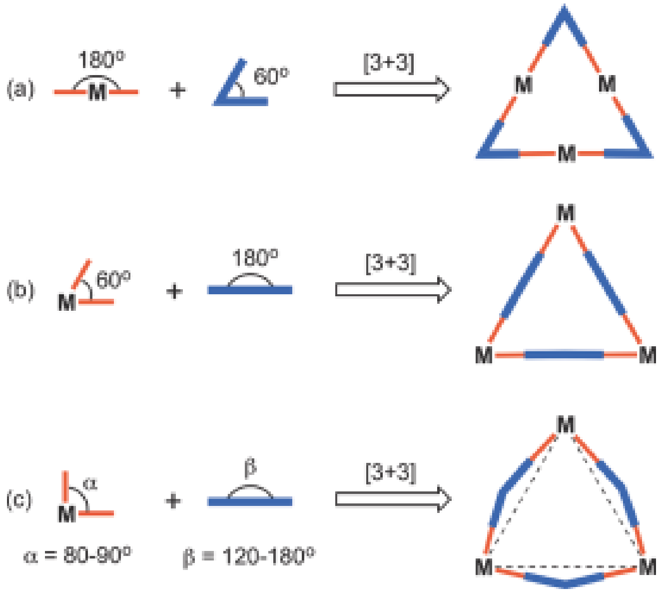
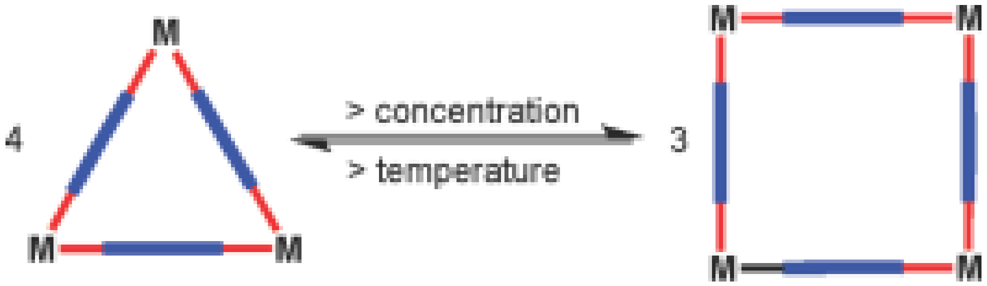


Figure 41. (a) Space-filling model of molecular square [Pt(dppp)(4,4′-bipyridine)]$_4$(PF$_6$)$_8$, (b) high-resolution STM images of the adlayer of square on Au(111), and (c) structural model of the adlayer.

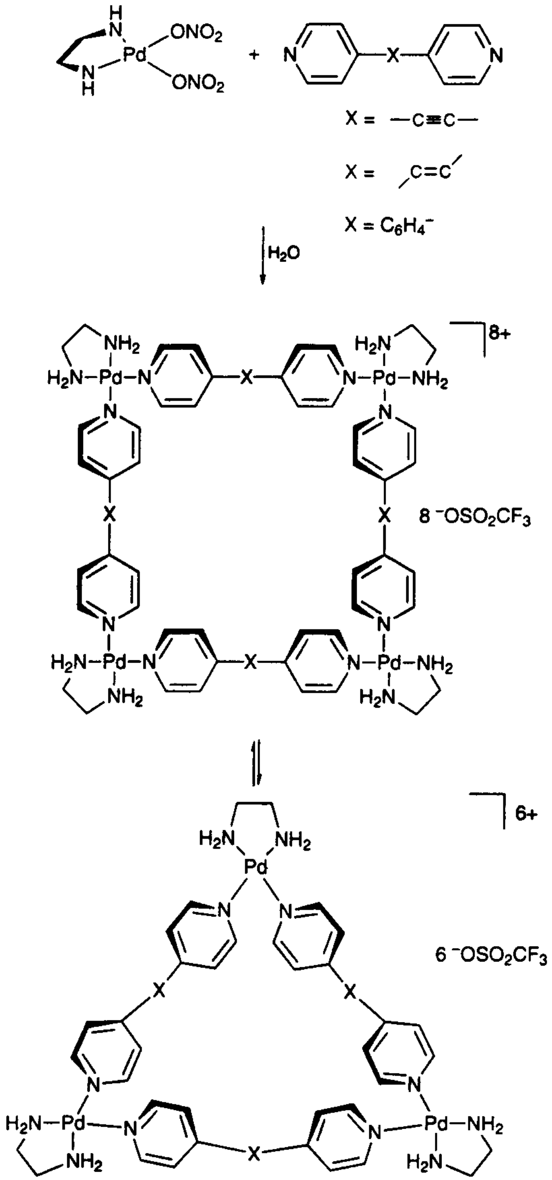
Triangoli Molecolari

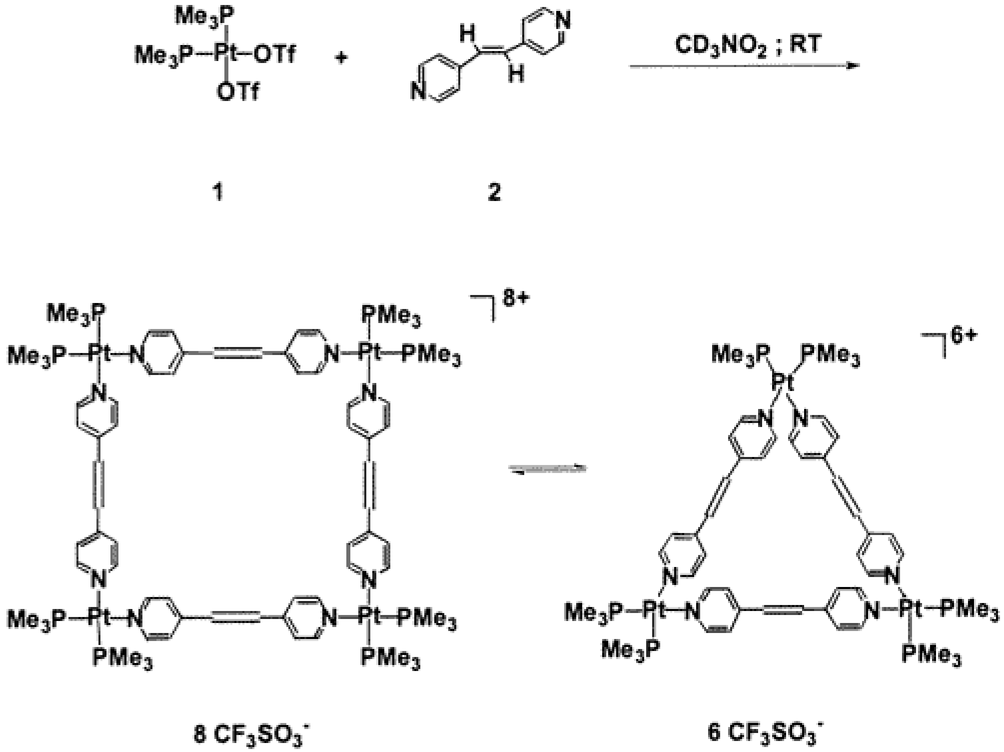


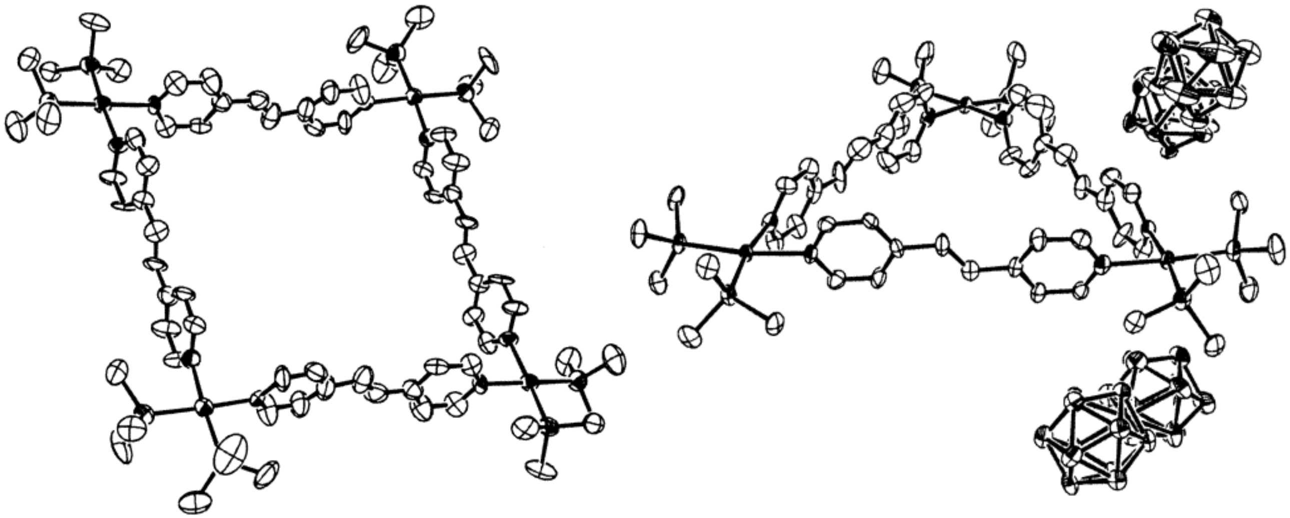


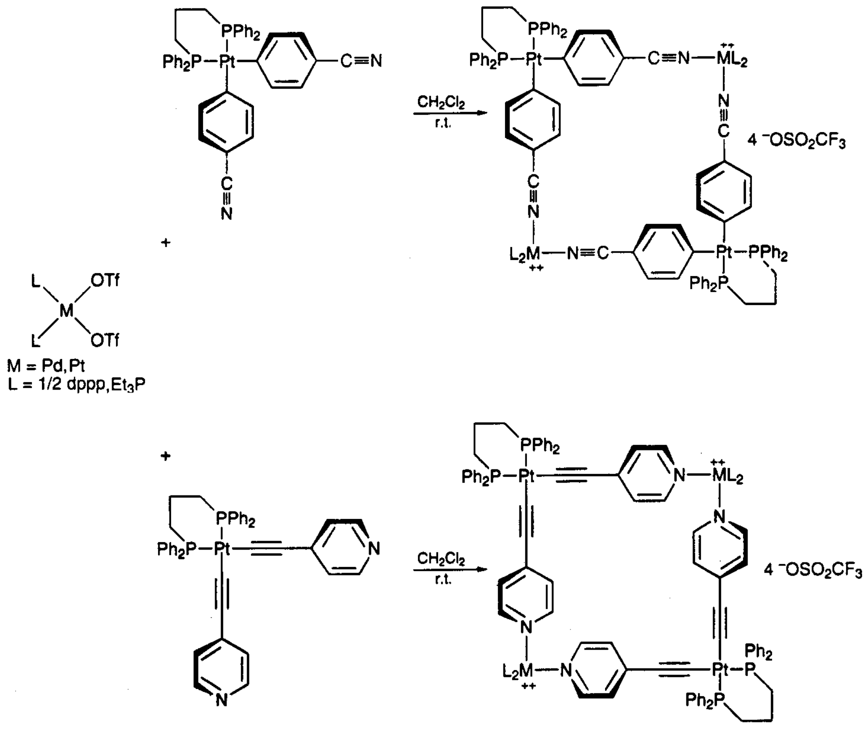
Square = Triangle endothermic $\Delta H < 0$
ΔS < ΔS < 0

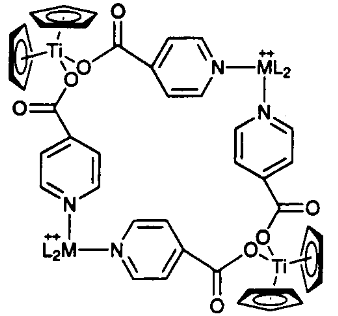
Solvent
Concentration
Temperature


ONO2
ONO2
Pd
+
X = —C≡C—
X = C=C
X = C6H4
H2O
8+
8 ⁻OSO2CF3
6+
6 ⁻OSO2CF3

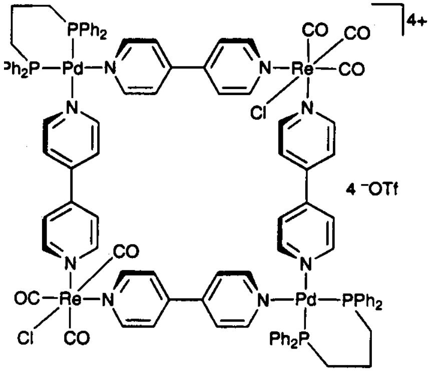

Me$_3$P
Me$_3$P—Pt—OTf
OTf
+
H
N
H
N
CD$_3$NO$_2$; RT
1
2
8+
6+
Me$_3$P
PMe$_3$
Pt
N
8 CF$_3$SO$_3^-$
6 CF$_3$SO$_3^-$

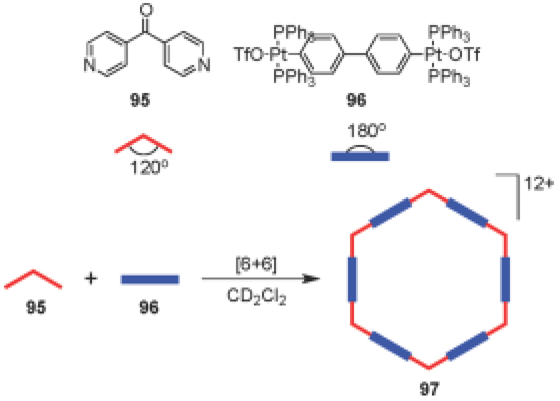


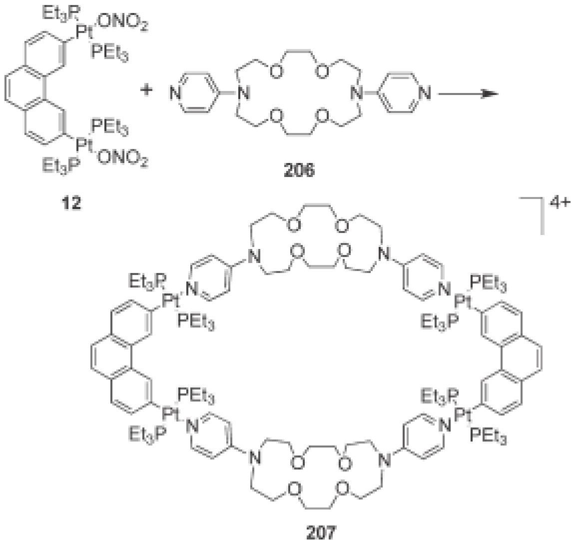


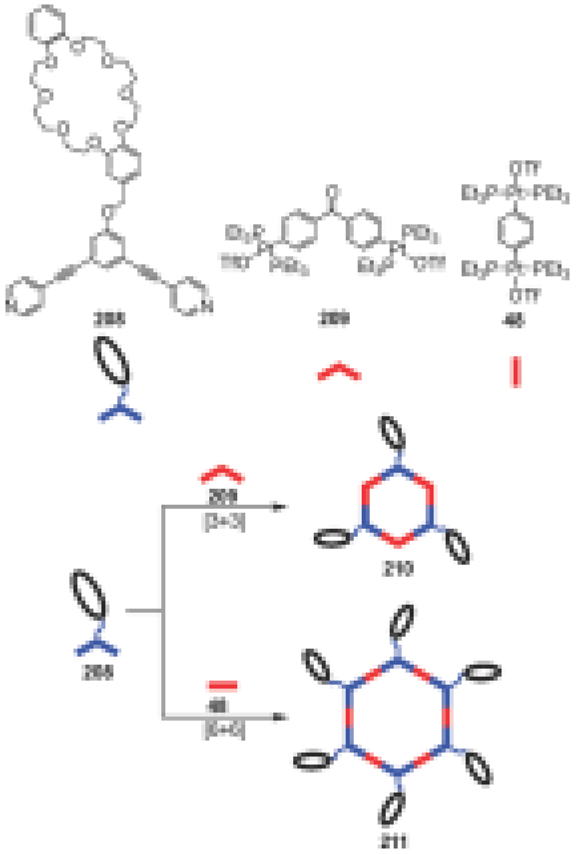


M = Pd, Pt, L = 1/2 dppp, Et$_3$P



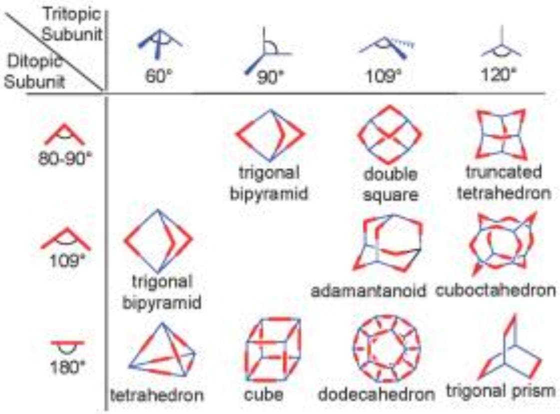

95
96
TfO-Pt
PPh3
Pt-OTf
120°
180°
12+
95
96
[6+6]
CD2Cl2
97


Et3P
Pt
ONO2
PEt3
12
206
4+
207

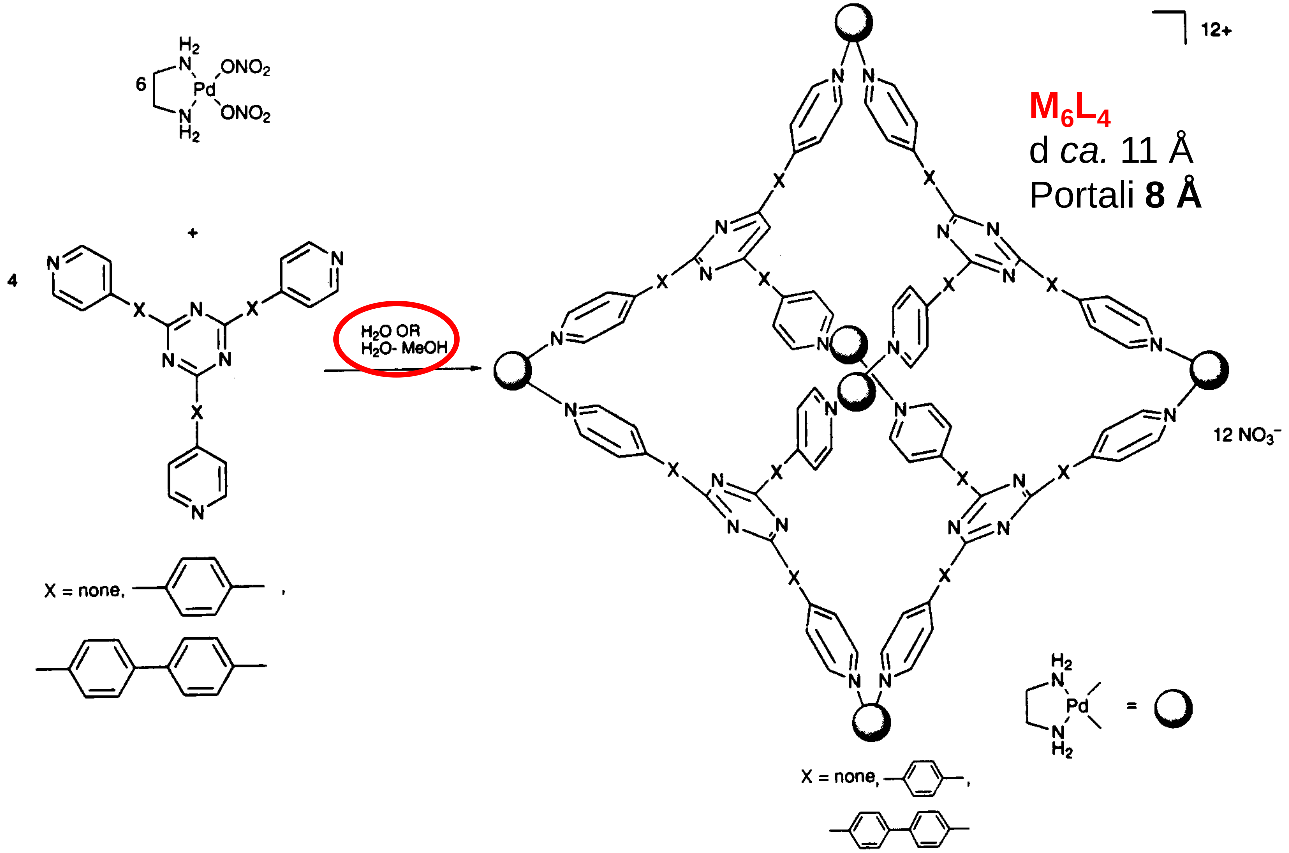

208
209
48
209
[3+3]
210
208
48
[6+6]
211

Directonal Bonding Approach

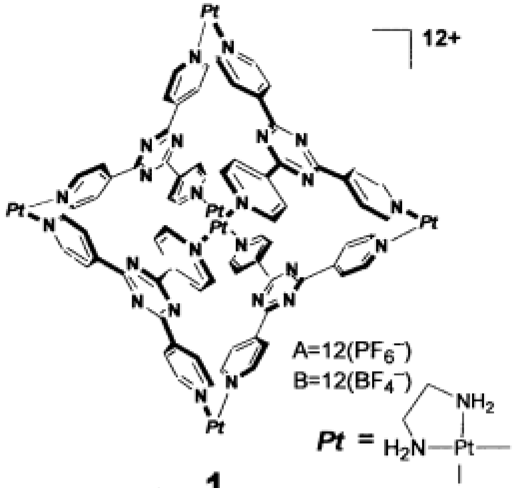
M = bb acido, **L** = bb basico, definiti secondo il numero e geometria relativa dei siti acidi e basici



Gabbie Molecolari



M$_6$L$_4$
d *ca.* 11 Å
Portali **8 Å**



1

a: $(C_{84}H_{96}N_{36}Pt_6)^{12+}\cdot 12(PF_6^-)$
FW. 4519.98

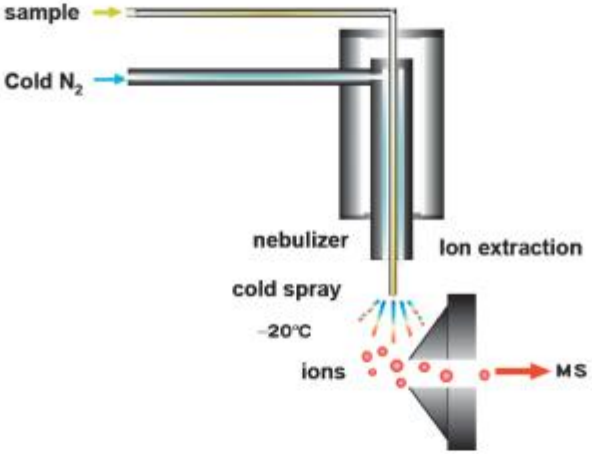


Fig. 1. Schematic illustration of the cold spray.

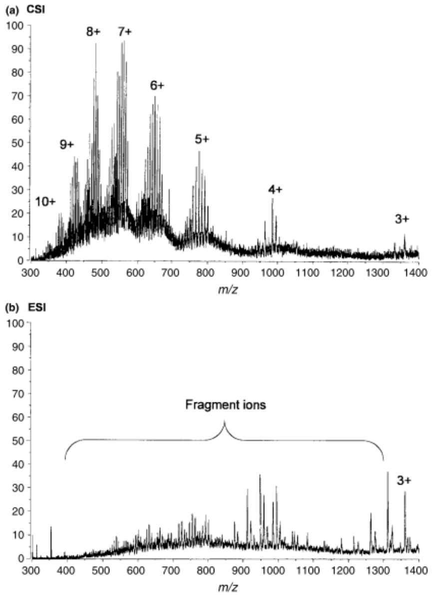
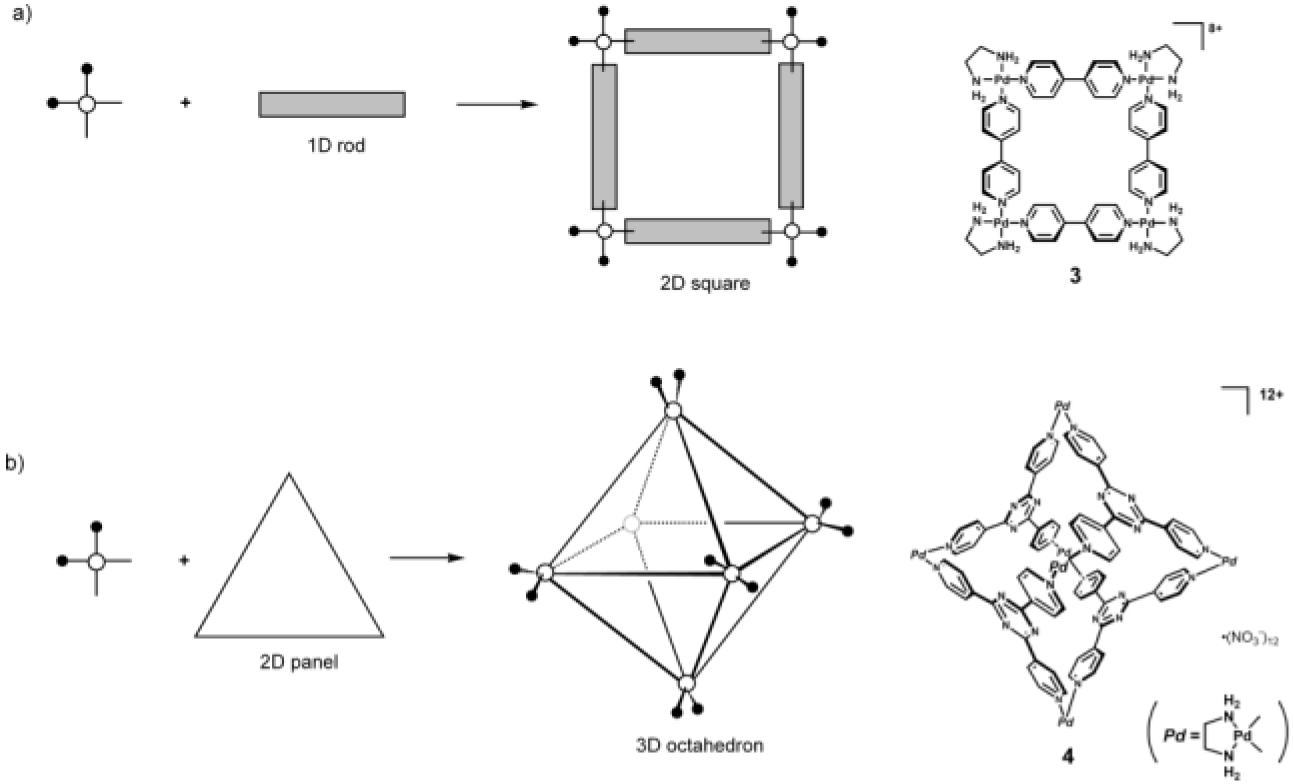
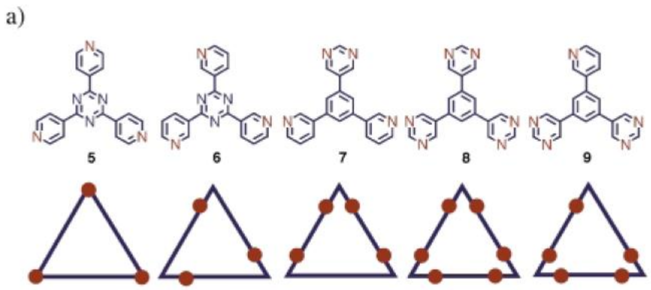
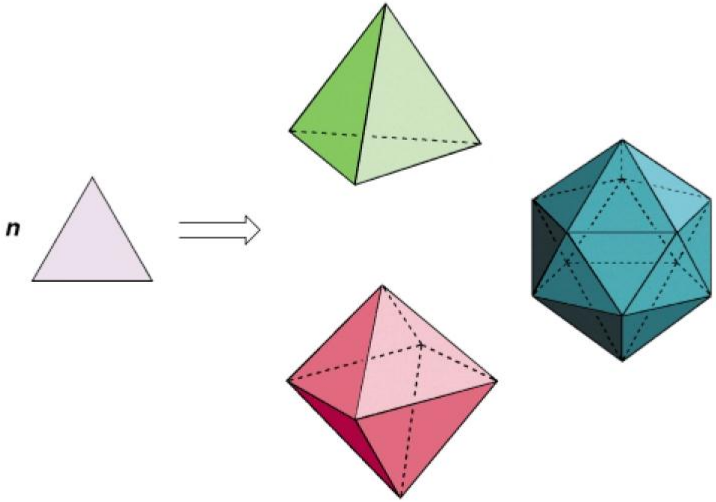


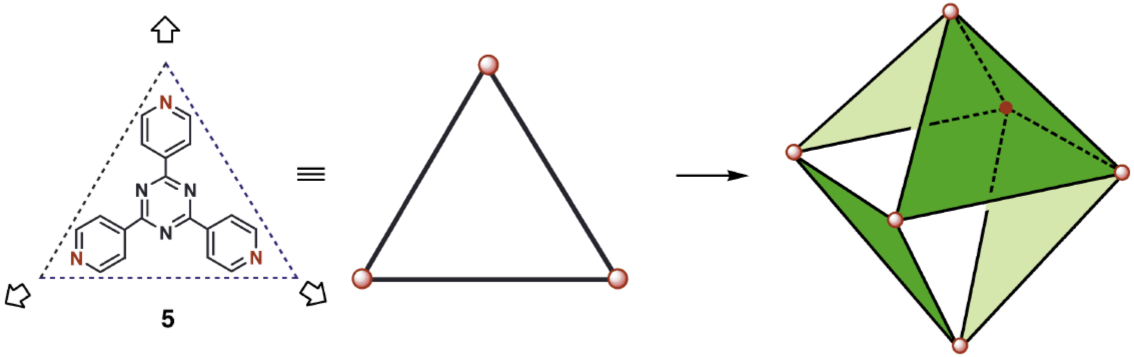
Figure 3. Comparison of (a) CSI and (b) ESI mass spectra of **1a**. Reprinted from Ref. 2 with permission from Elsevier.

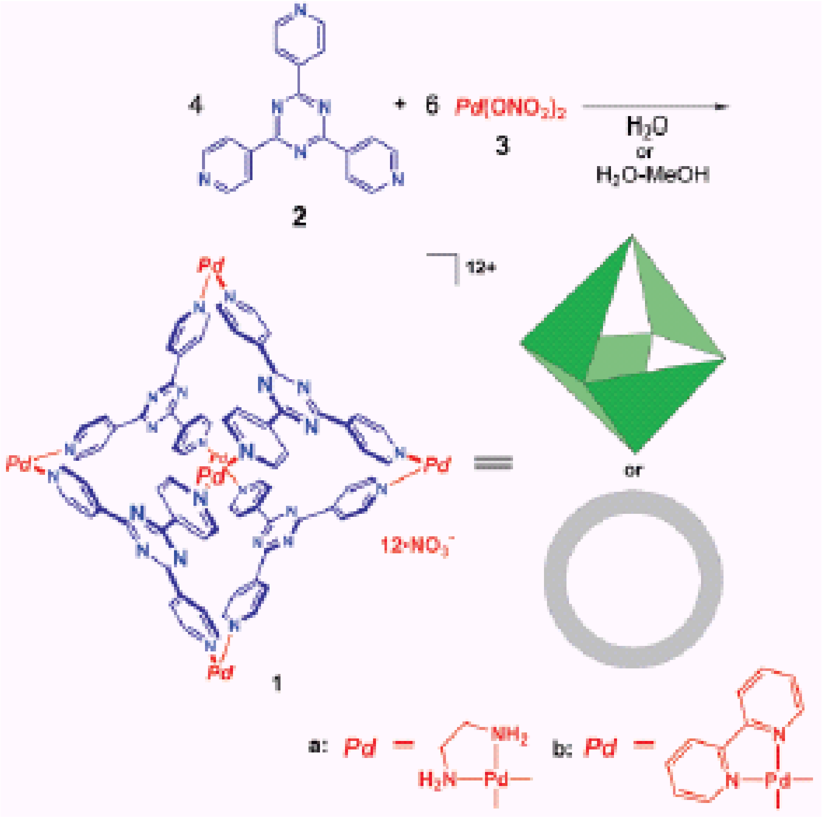
a)
+
1D rod
2D square
8+
3
b)
+
2D panel
3D octahedron
12+
•(NO3⁻)12
4
Pd =

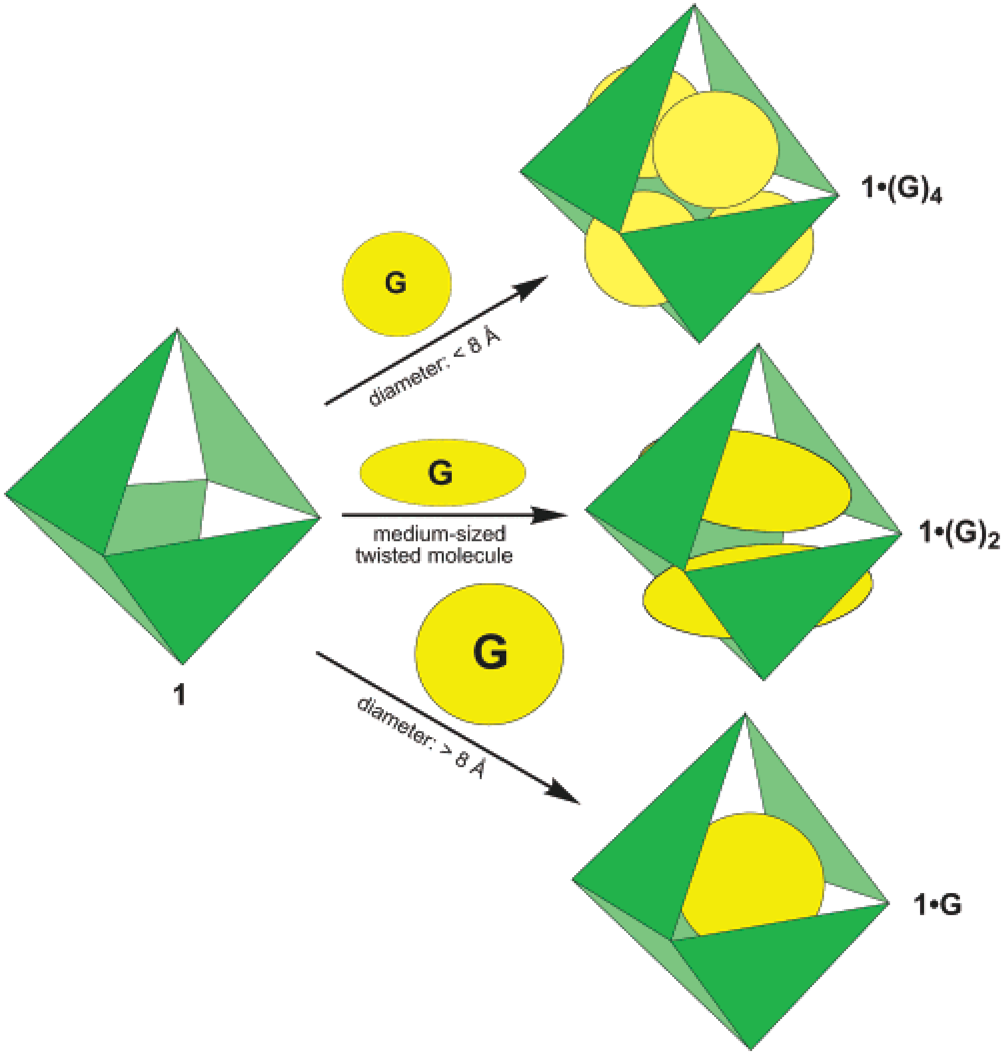
Molecular Paneling








4
+ 6
Pd(ONO2)2
3
H2O
or
H2O-MeOH
2
12+
Pd
12·NO3⁻
1
=
or
a: Pd =
NH2
H2N—Pd—
b: Pd =
N—Pd—
N


1
G
diameter: < 8 Å
1•(G)4
G
medium-sized
twisted molecule
1•(G)2
G
diameter: > 8 Å
1•G

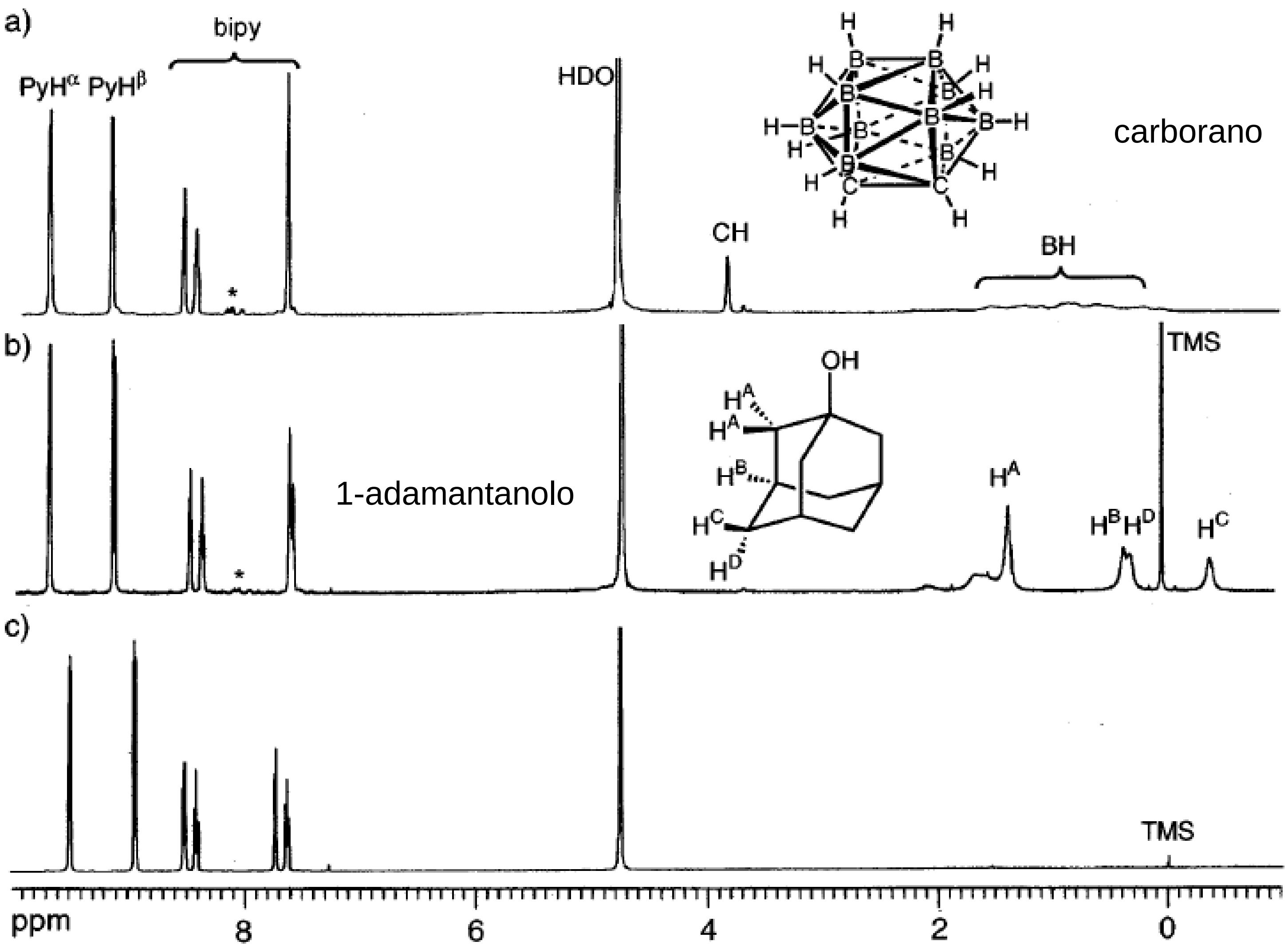
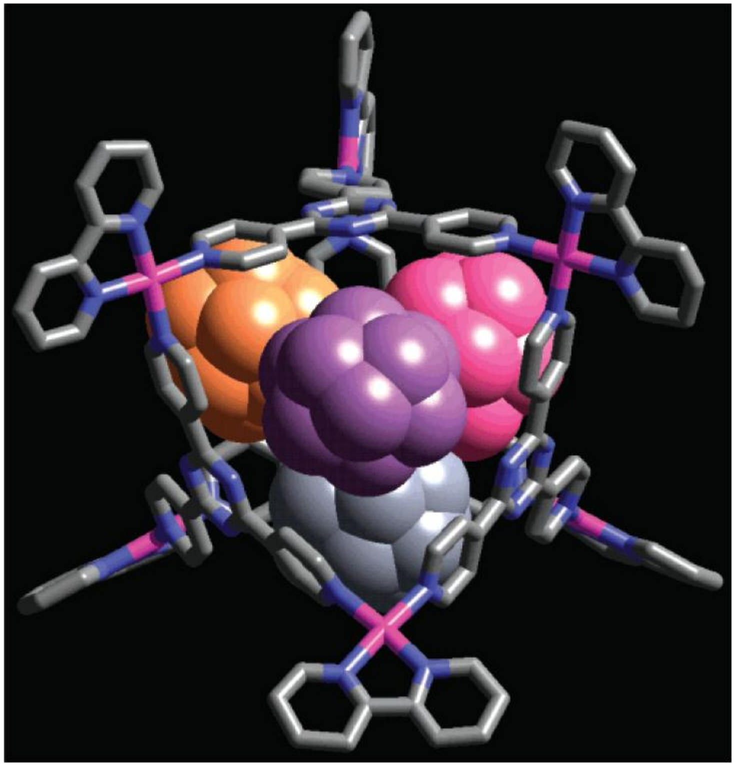
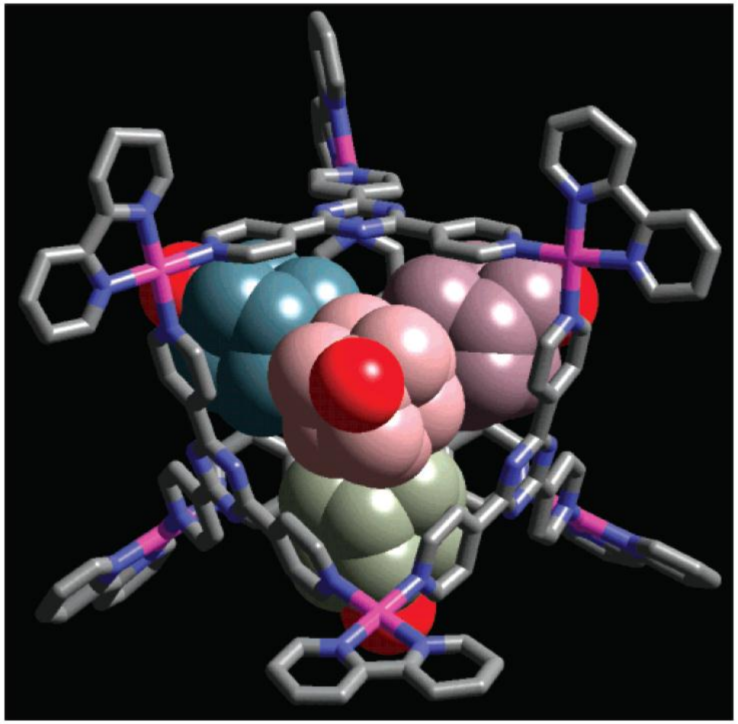
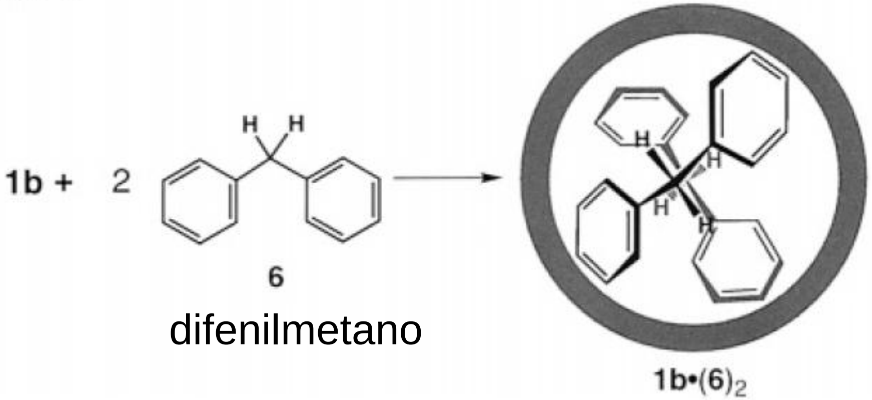


Figure 1. ^{1}H NMR observations of the enclathration of guest molecules in **1b**. (a) $\mathbf{1b}\cdot(\mathbf{4})_4$. (b) $\mathbf{1b}\cdot(\mathbf{5})_4$. (c) Empty **1b** (∗: impurities).





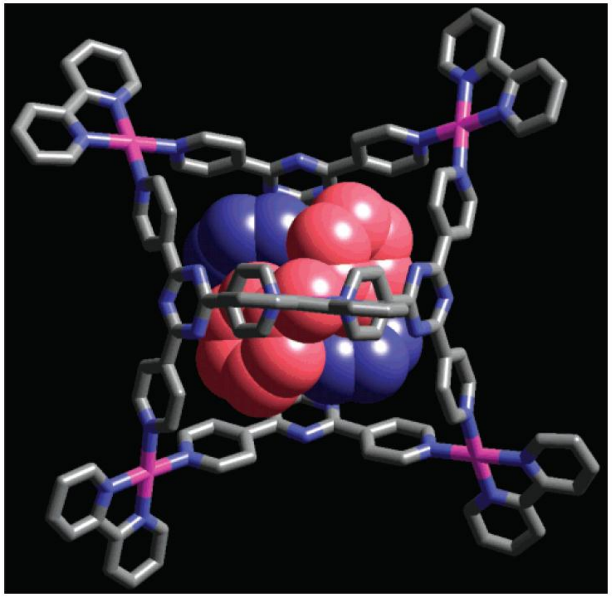
Scheme 2



6

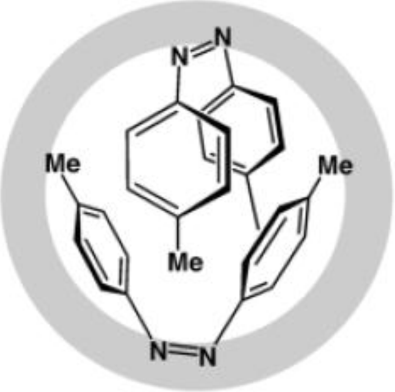
difenilmetano

1b•(6)$_2$

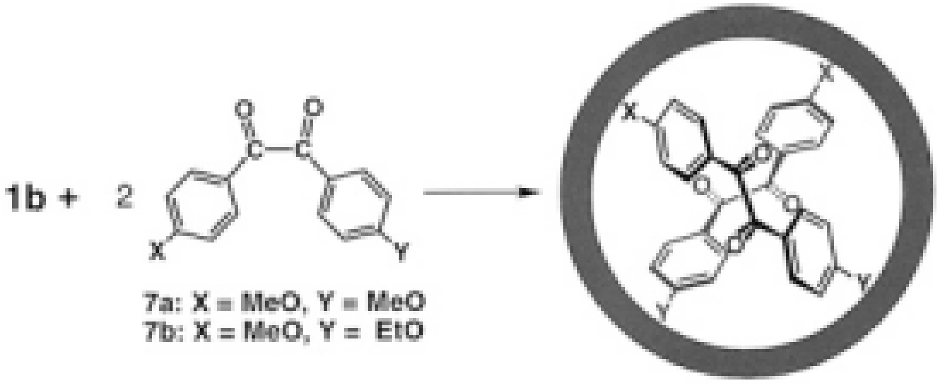


cis-azobenzene

cis-stilbene



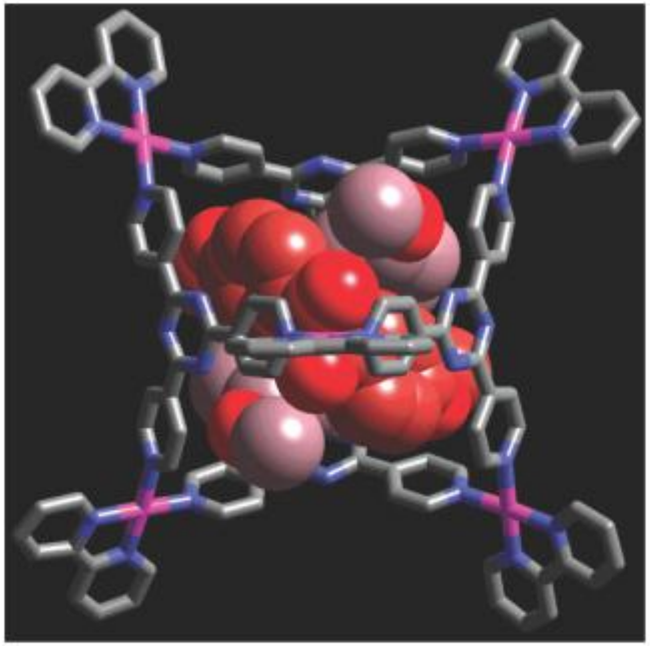
Scheme 3

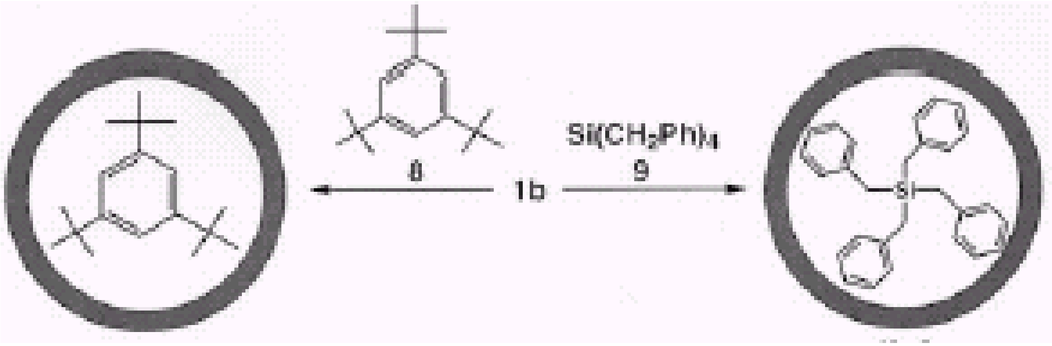


7a: X = MeO, Y = MeO
7b: X = MeO, Y = EtO

1b•(7)$_2$

4,4’-dimetossi-dibenzoile





tri-*tert*-butilbenzene **tetrabenzilsilano**

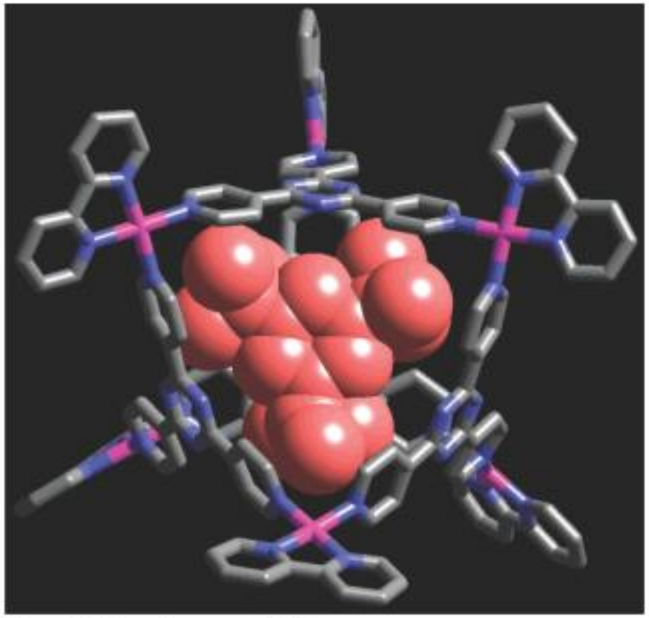
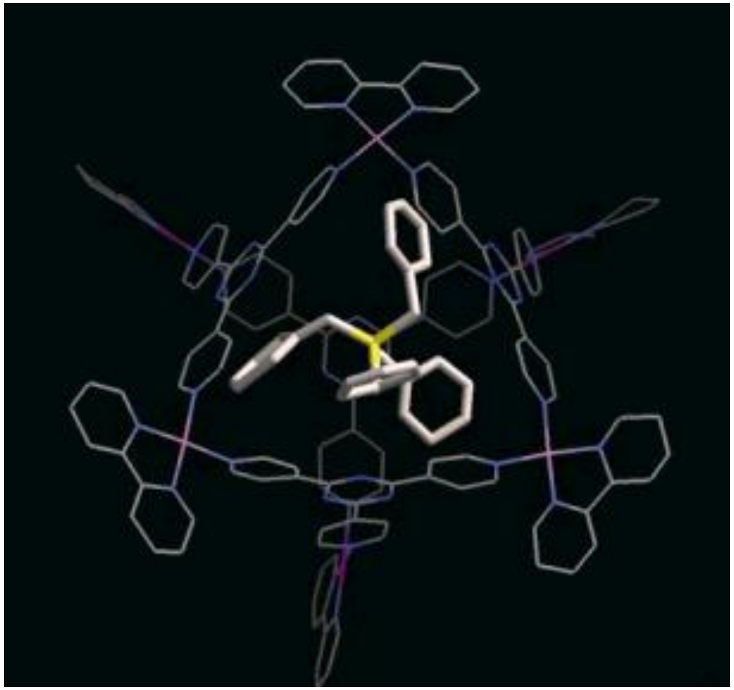
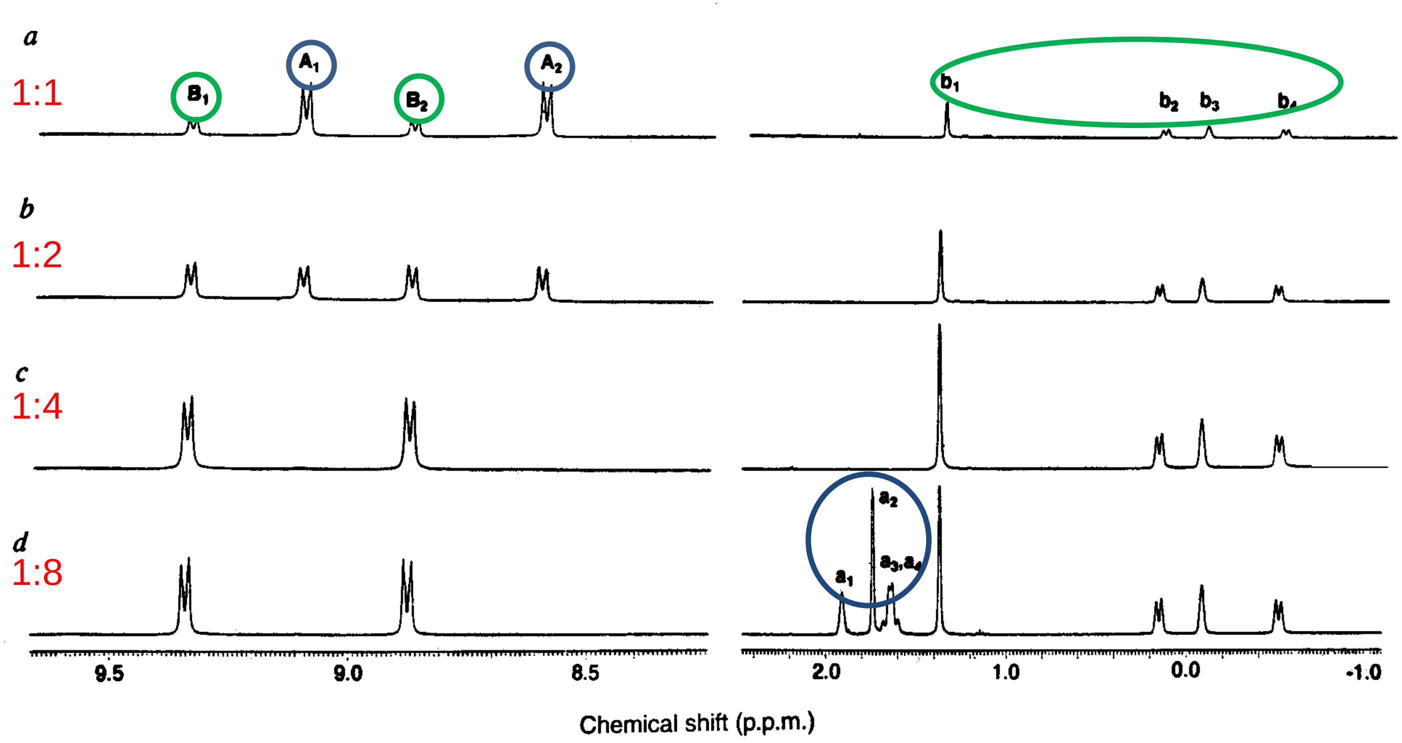


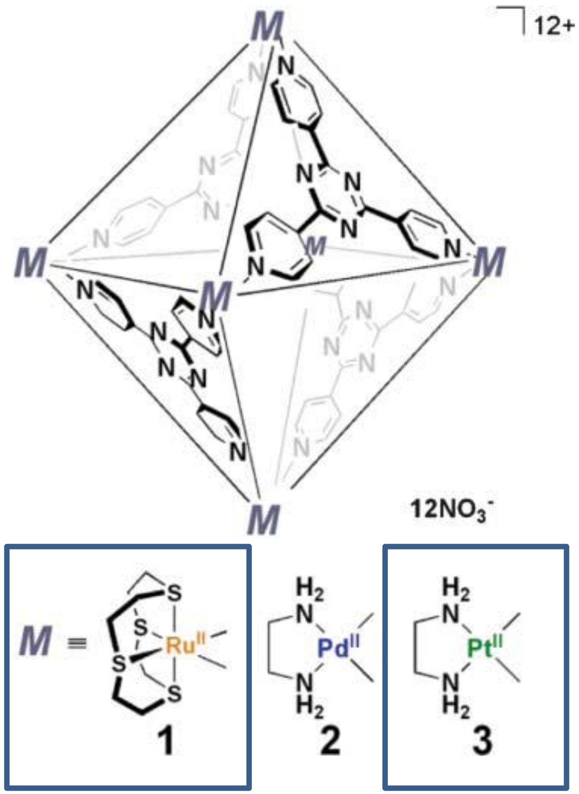
Figure 8. Crystal structure of **1b·8**.

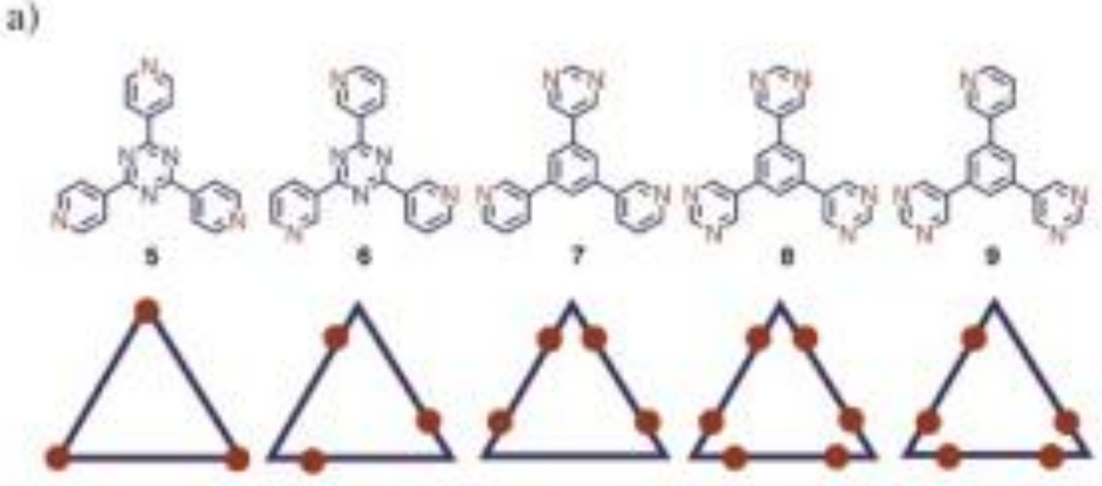


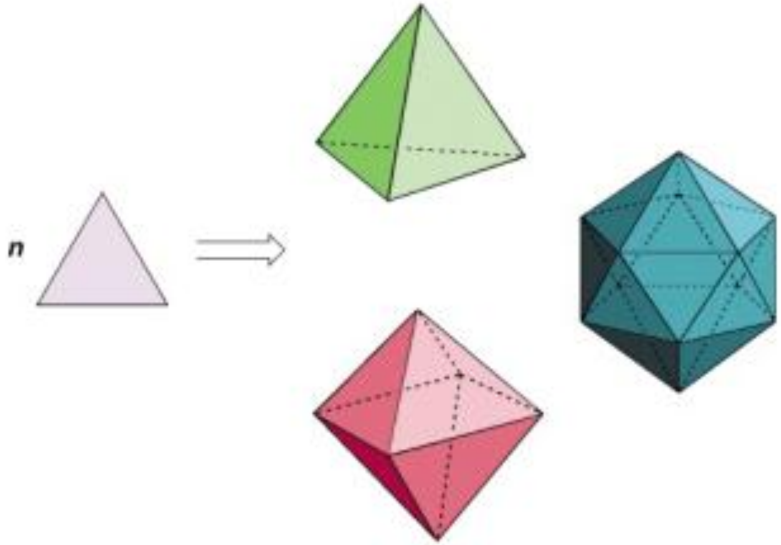


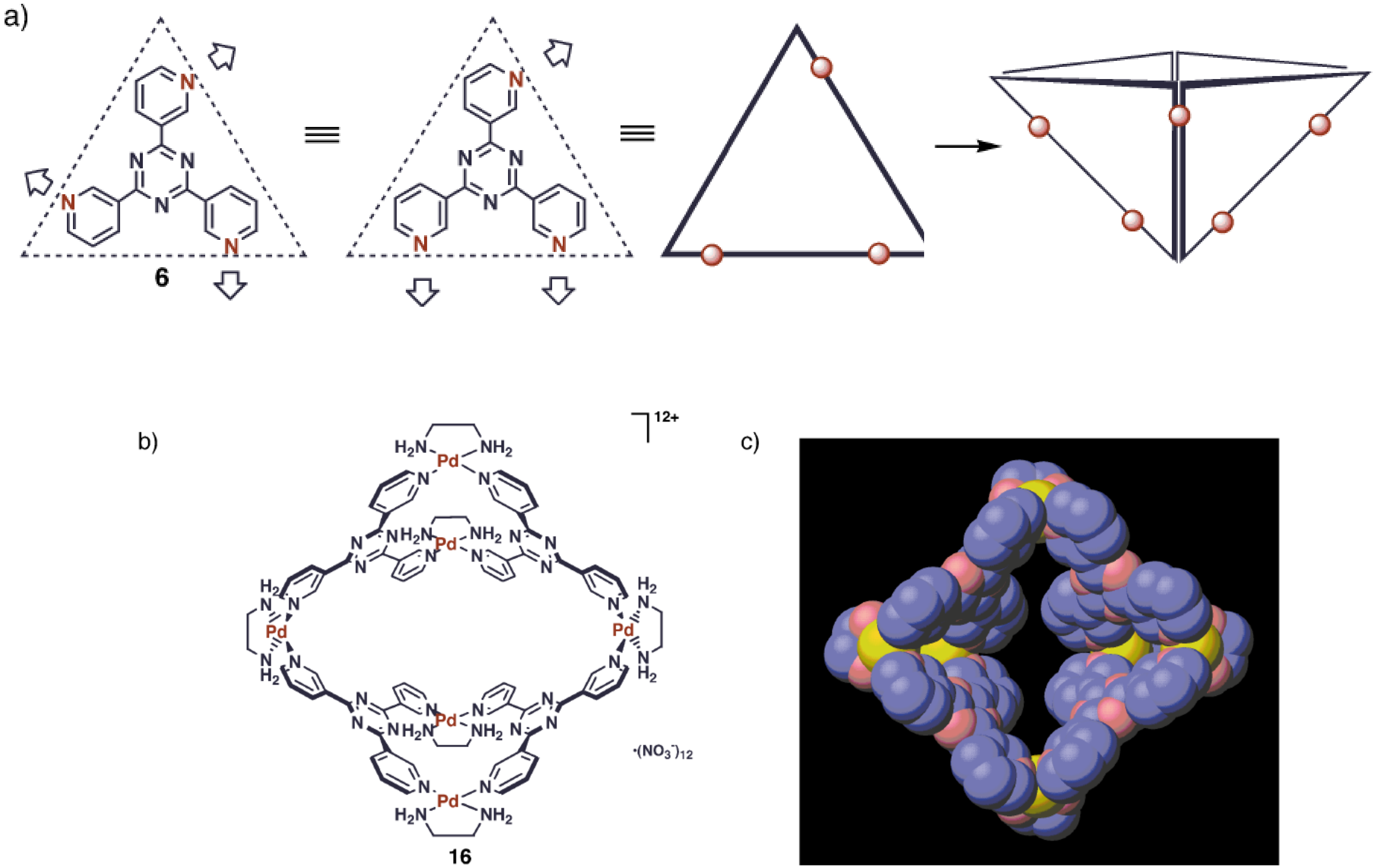
M_6L_4/adamantancarbossilato$_4$

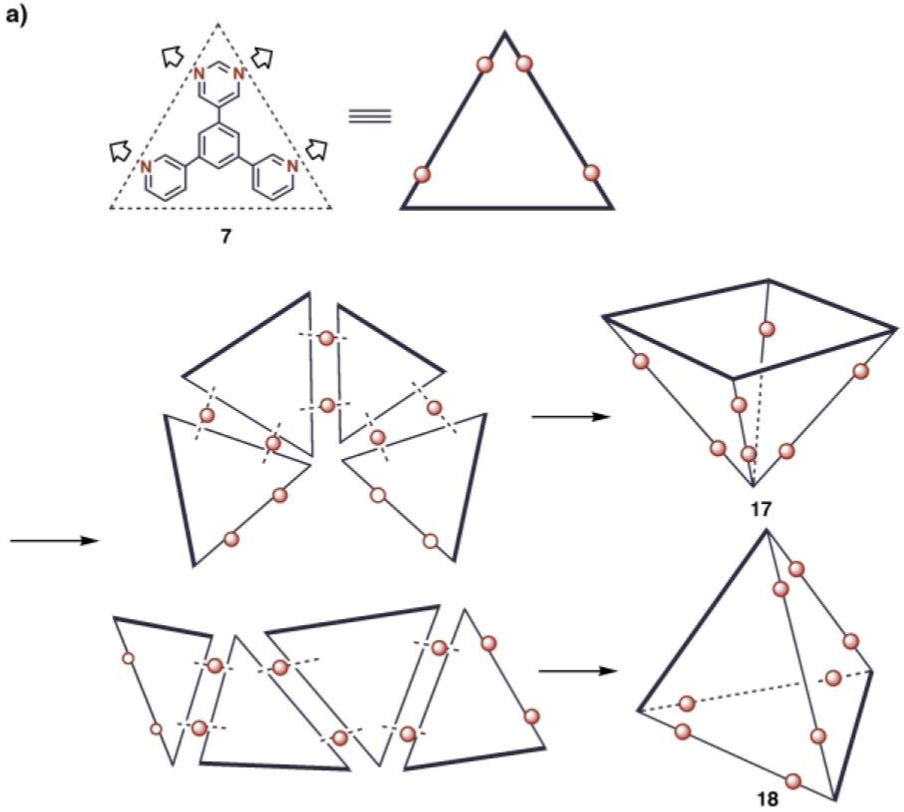
Effetto allosterico!

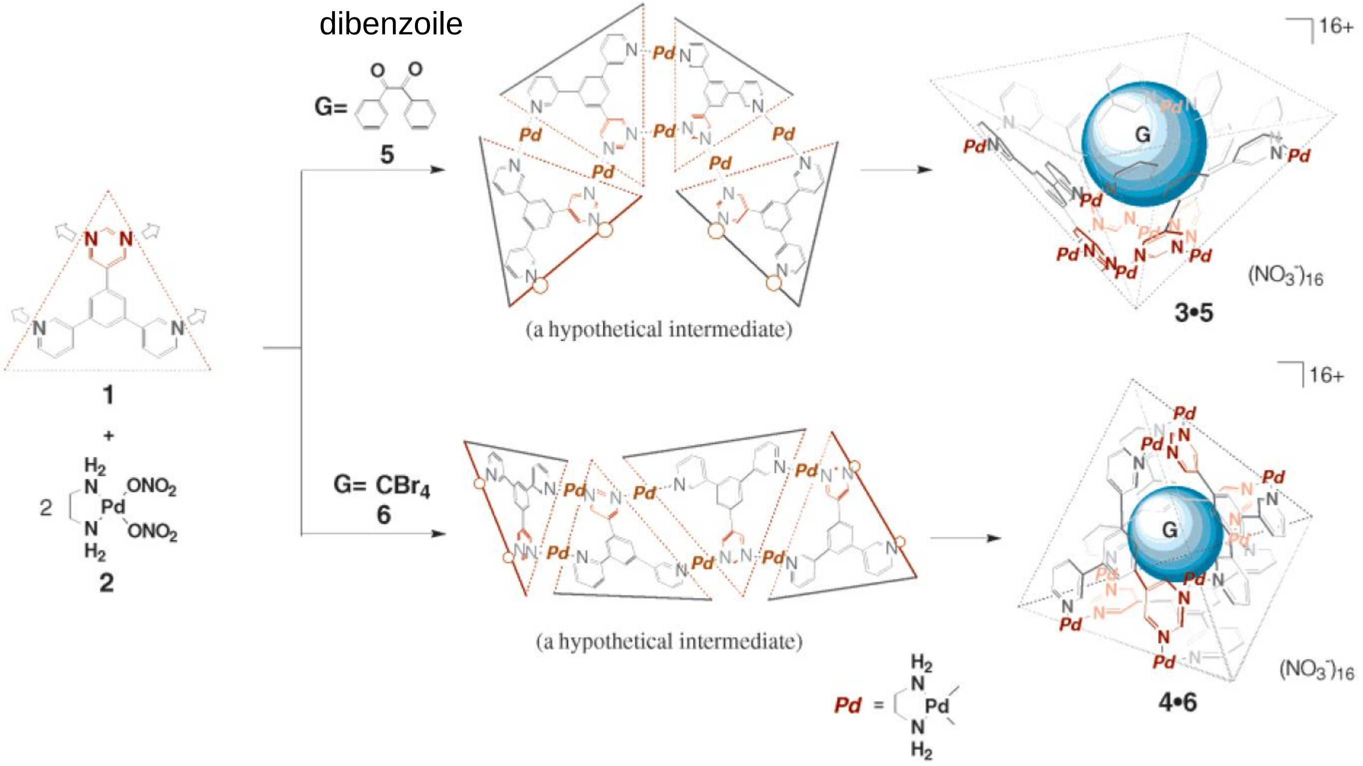
12+
M
N
12NO₃⁻
M =
S
Ruᴵᴵ
H₂
Pdᴵᴵ
Ptᴵᴵ
1
2
3

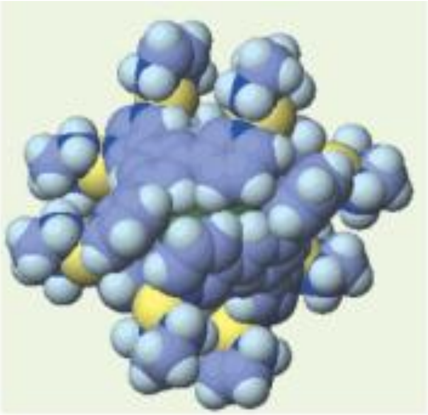

a)
N
5
6
7
8
9

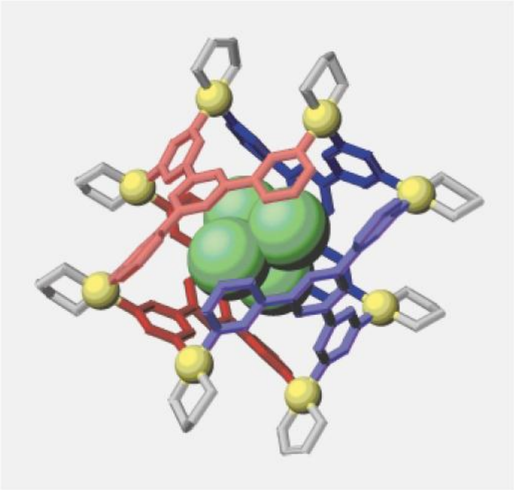

n

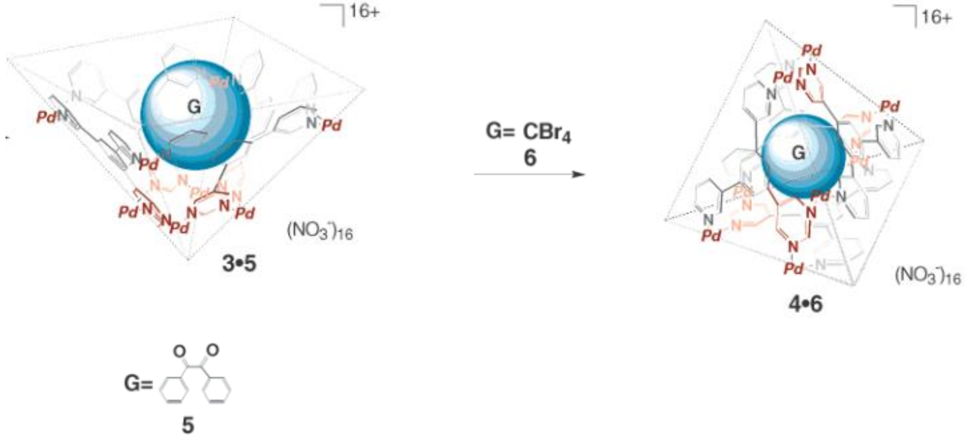

a)
N
N
N
N
N
N
6
≡
≡
b)
12+
H₂N
Pd
NH₂
N
N
Pd
•(NO₃⁻)₁₂
16
c)


a)
N
N
N
N
7
17
18


dibenzoile
G=
5
1
+
2
G= CBr4
6
(a hypothetical intermediate)
(a hypothetical intermediate)
16+
(NO3-)16
3•5
16+
(NO3-)16
4•6
Pd =







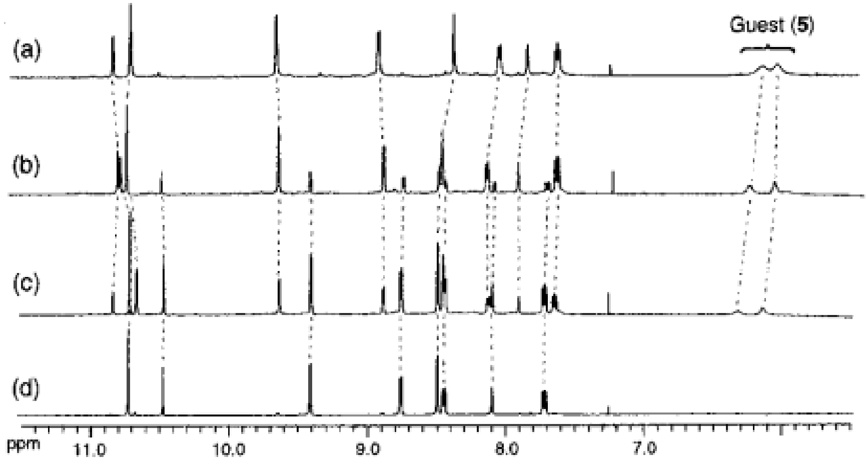
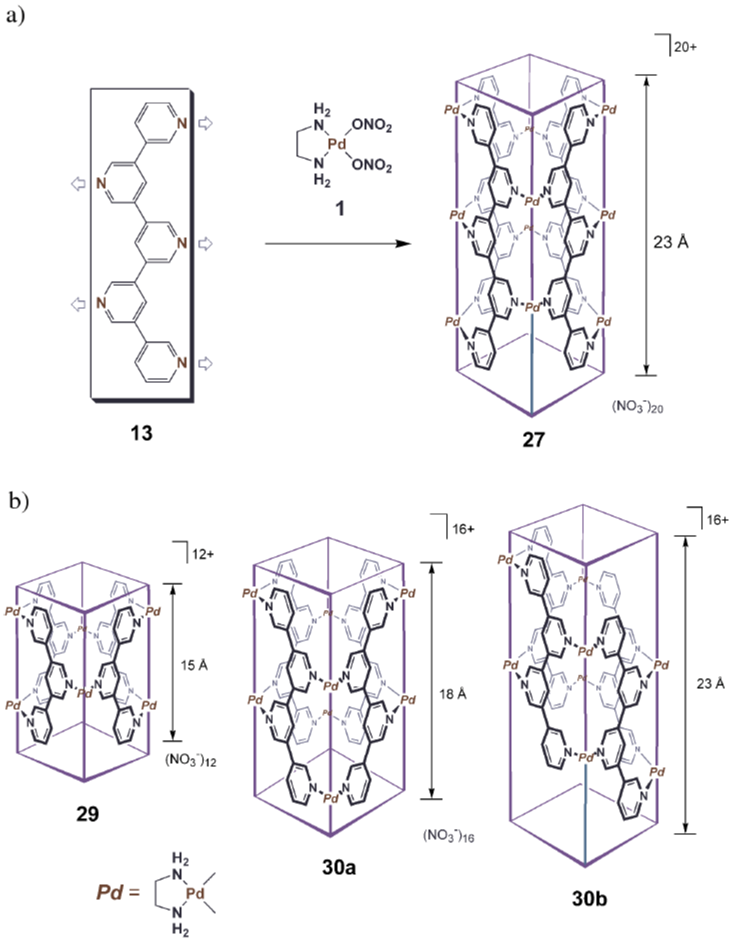
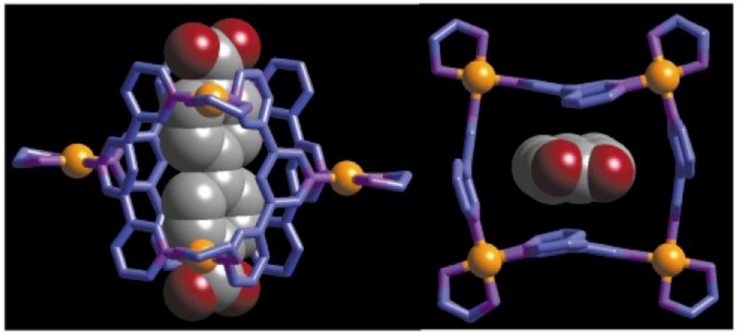
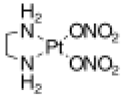


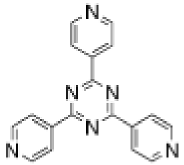
Figure 2. The ^1H NMR monitoring of reorganization process from **3·5** to **4·6** via guest exchange. (a) **3·5** complex in D_2O; (b−d) After the addition of excess amount of **6** at 25 °C ((b) 3 h, (c) 8 h, (d) 24 h). Note that free **5** is immiscible in water and, after guest exchange, becomes invisible in the spectrum.


a)
N
13
H_2
N
Pd
ONO_2
ONO_2
N
H_2
1
20+
Pd
N
23 Å
$(NO_3^-)_{20}$
27
b)
12+
15 Å
$(NO_3^-)_{12}$
29
16+
18 Å
$(NO_3^-)_{16}$
30a
16+
23 Å
30b
Pd =
H_2
N
Pd
N
H_2





1



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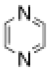

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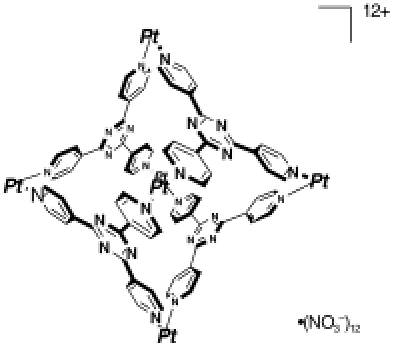

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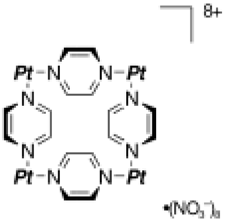

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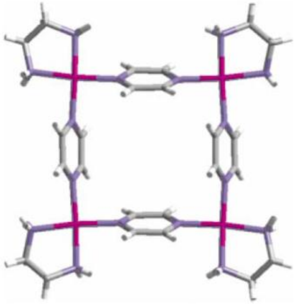
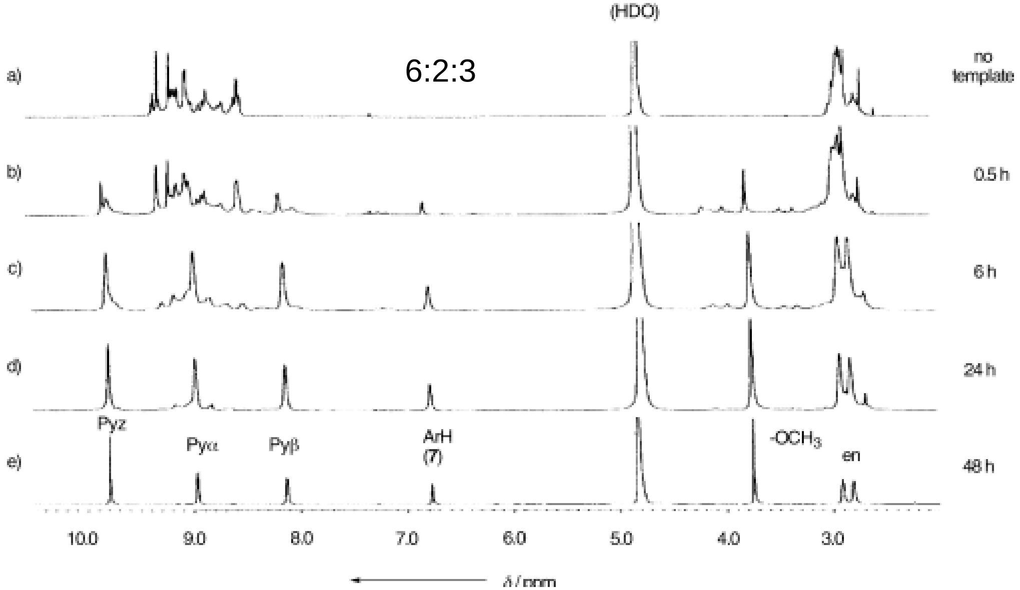
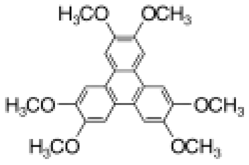
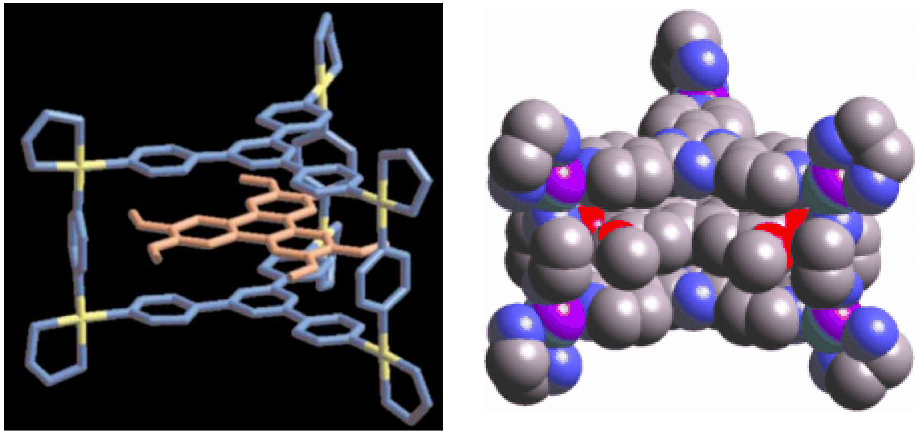






7

Figure 1. ^{1}H NMR spectra showing the guest-templated assembly of **7**$\subset$**4** complex (500 MHz, D_2O, 25 °C). a) A mixture of **1**, **2**, and **3**. Template **7** was added to this solution and the mixture was heated at 100 °C for b) 0.5 h, c) 6 h, d) 24 h, and e) 48 h. Pyz = pyrazine.



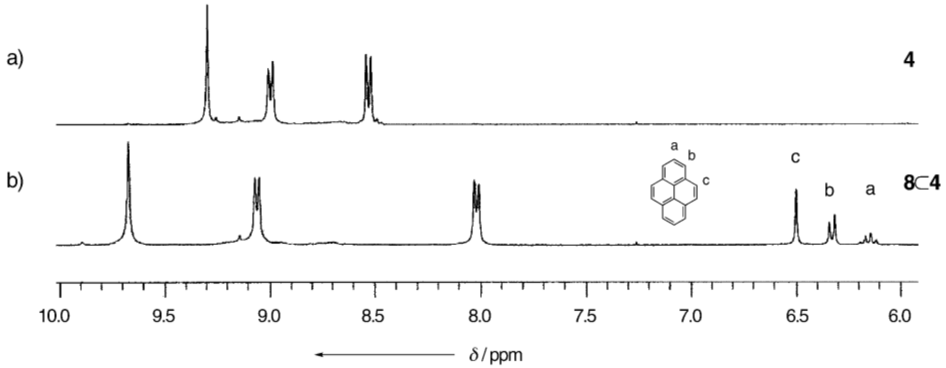
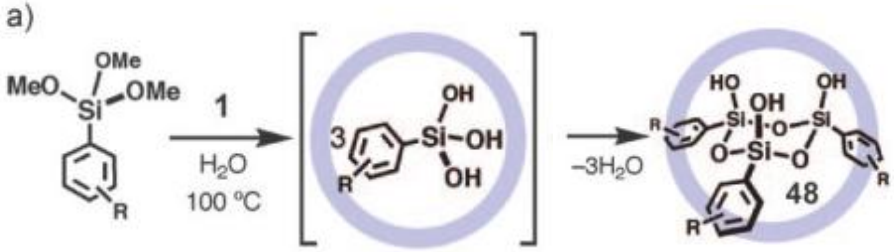
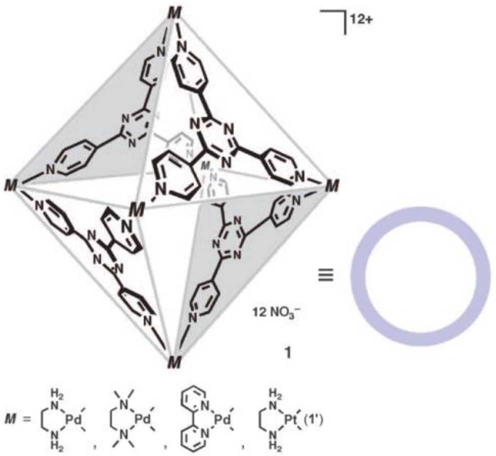
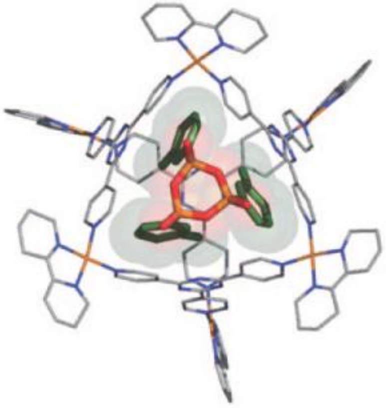


Figure 4. ^{1}H NMR spectra (300 MHz, D_2O, 25 °C) of aromatic regions of a) free **4** after extraction of template and b) **8**⊂**4** after the subsequent reinclusion of **8**.

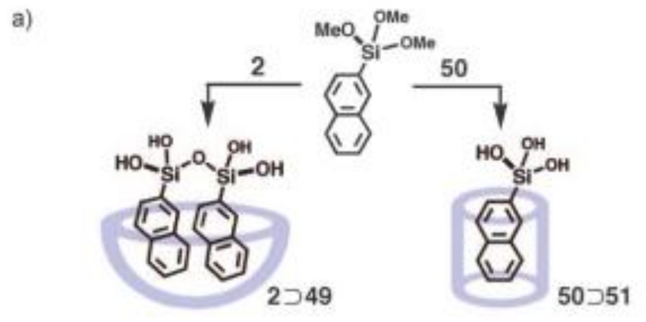
Stabilizzazione di intermedi reattivi: alcossi-silani ciclici
Ship in a Bottle

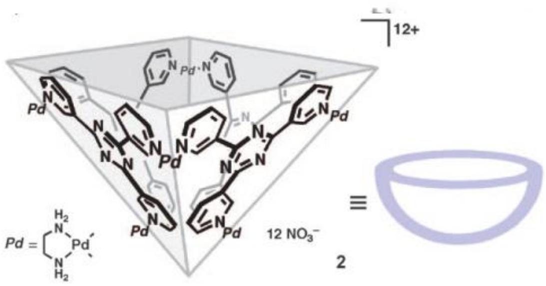


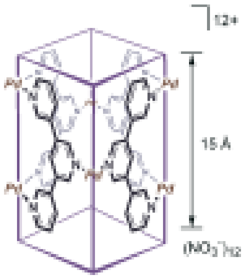




Stabilizzazione di intermedi reattivi: Oligomerizzazione di tri alcossi-silani







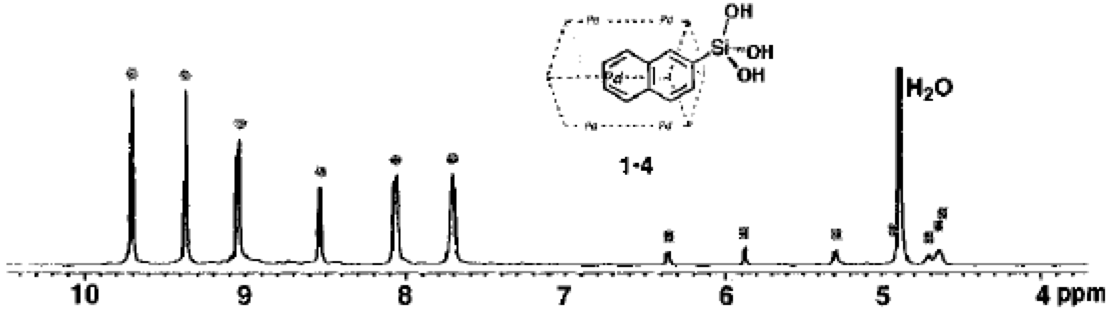
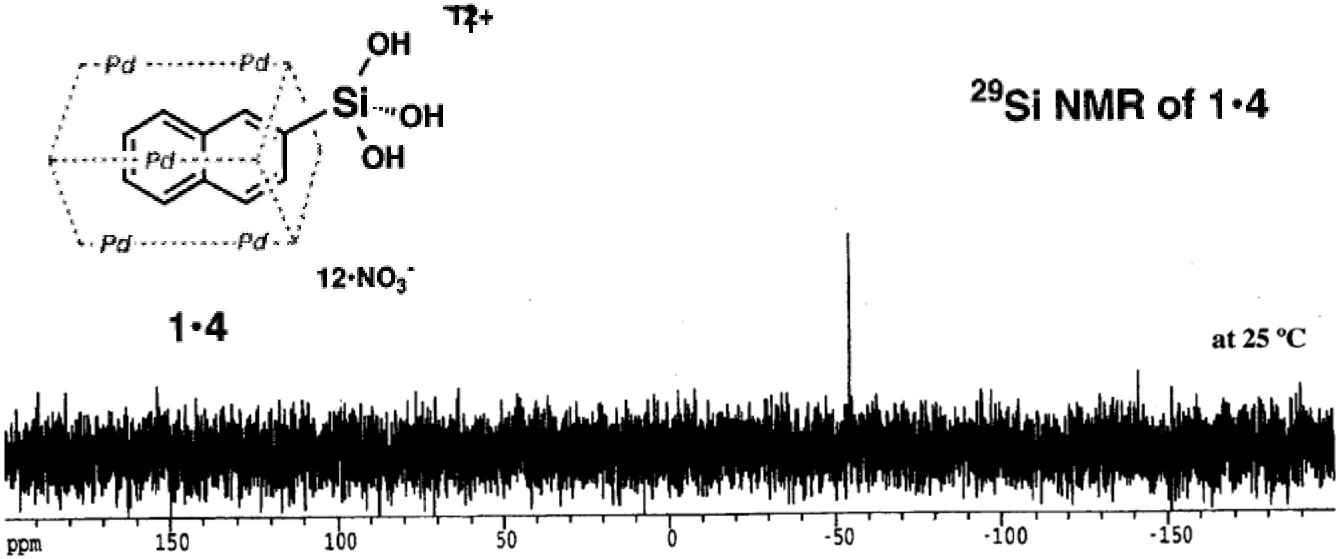


Figure 1. ^{1}H NMR spectrum (500 MHz, D_2O, TMS as an external standard) of **1·4** at 27 °C. Circles and squares indicate host and guest signals, respectively.



^{29}Si NMR of 1•4

1•4

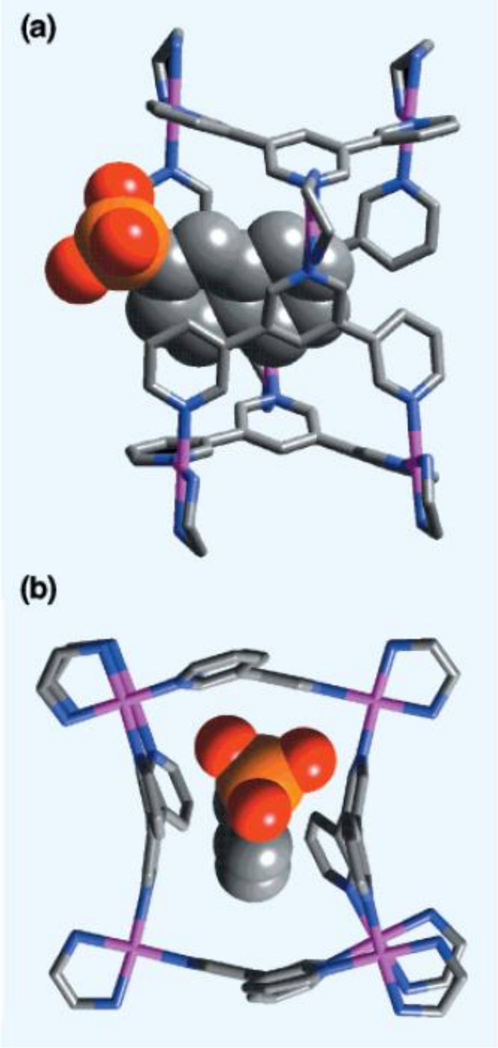
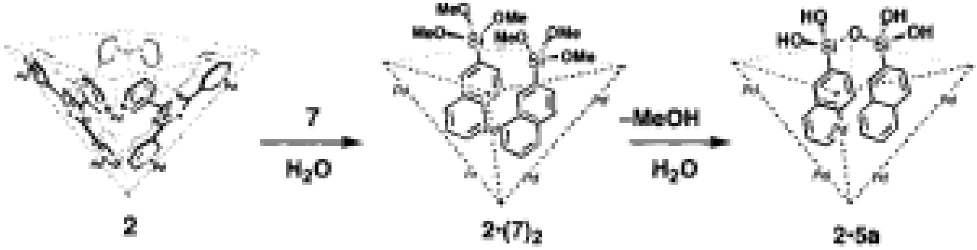
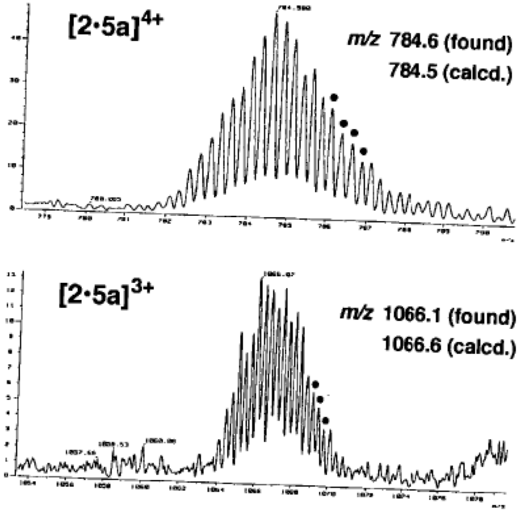
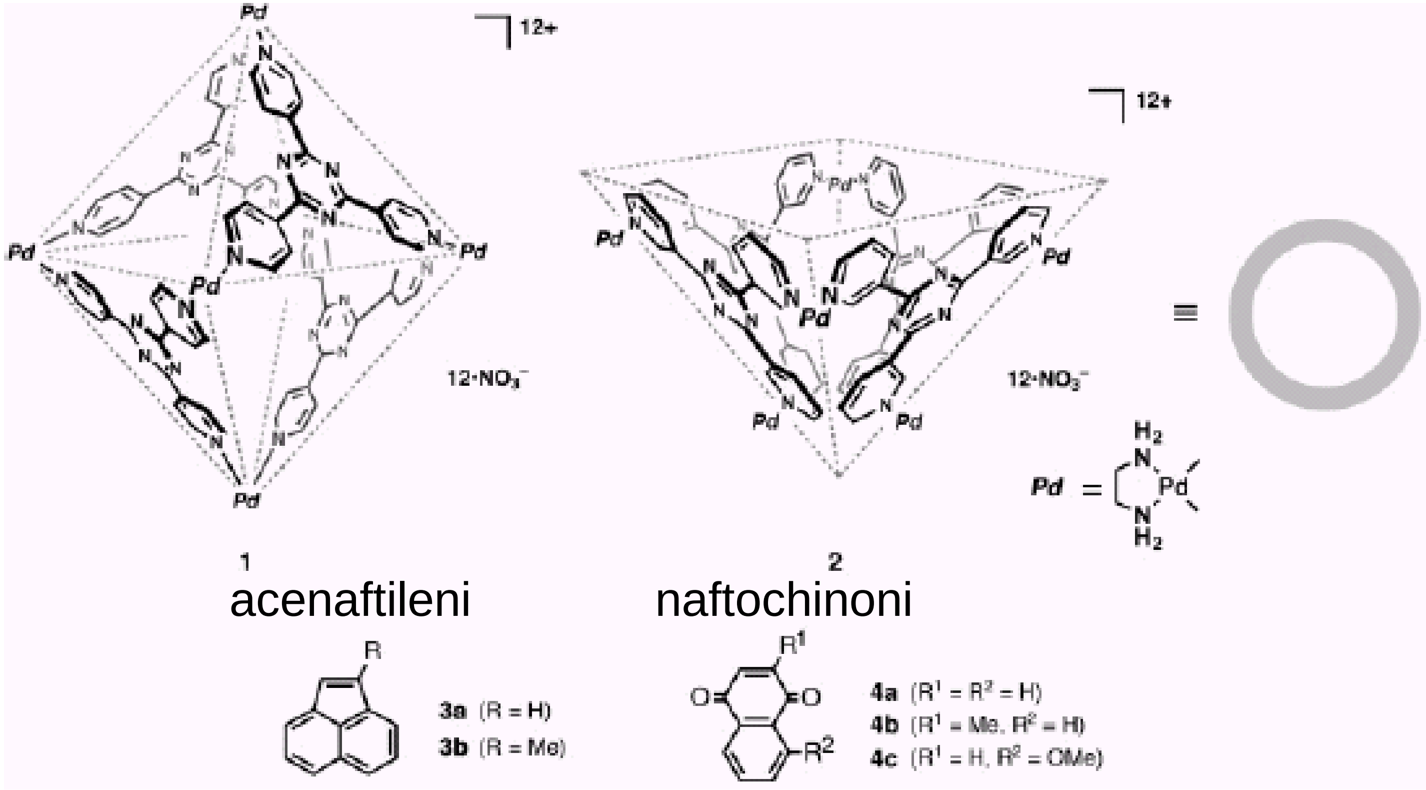


Figure 2. The crystal structure of **1·4**: (a) side view and (b) top view.


MeO
MeO
OMe
MeO
OMe
OMe
Si
Si
HO
HO
OH
OH
O
Si
Si
Pd
7
H$_2$O
−MeOH
H$_2$O
2
2•(7)$_2$
2•5a


[2•5a]$^{4+}$
784.590
m/z 784.6 (found)
784.5 (calcd.)
[2•5a]$^{3+}$
1066.07
m/z 1066.1 (found)
1066.6 (calcd.)

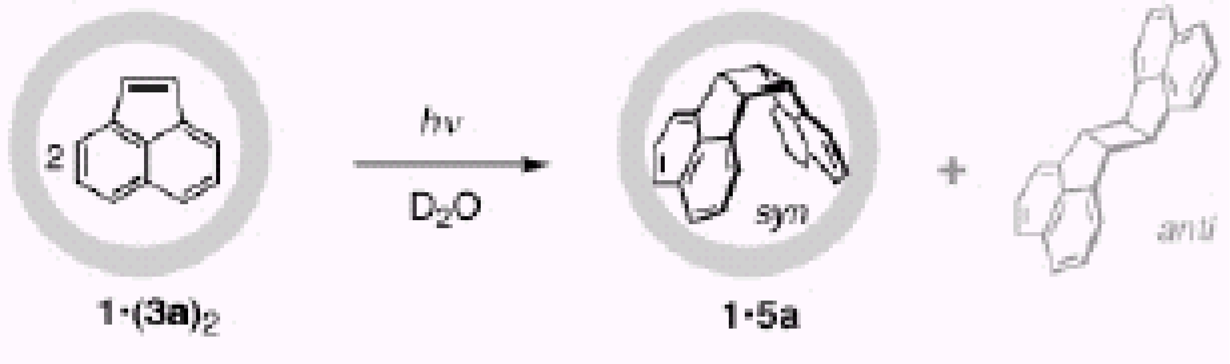
Fotodimerizzazioni 2+2



acenaftileni

naftochinoni

acenaftilene



controllo stereochimica, [ ] 2mM resa > 98%

benzene: [ ] 150mM, 3h, resa 40%, no stereoselettività

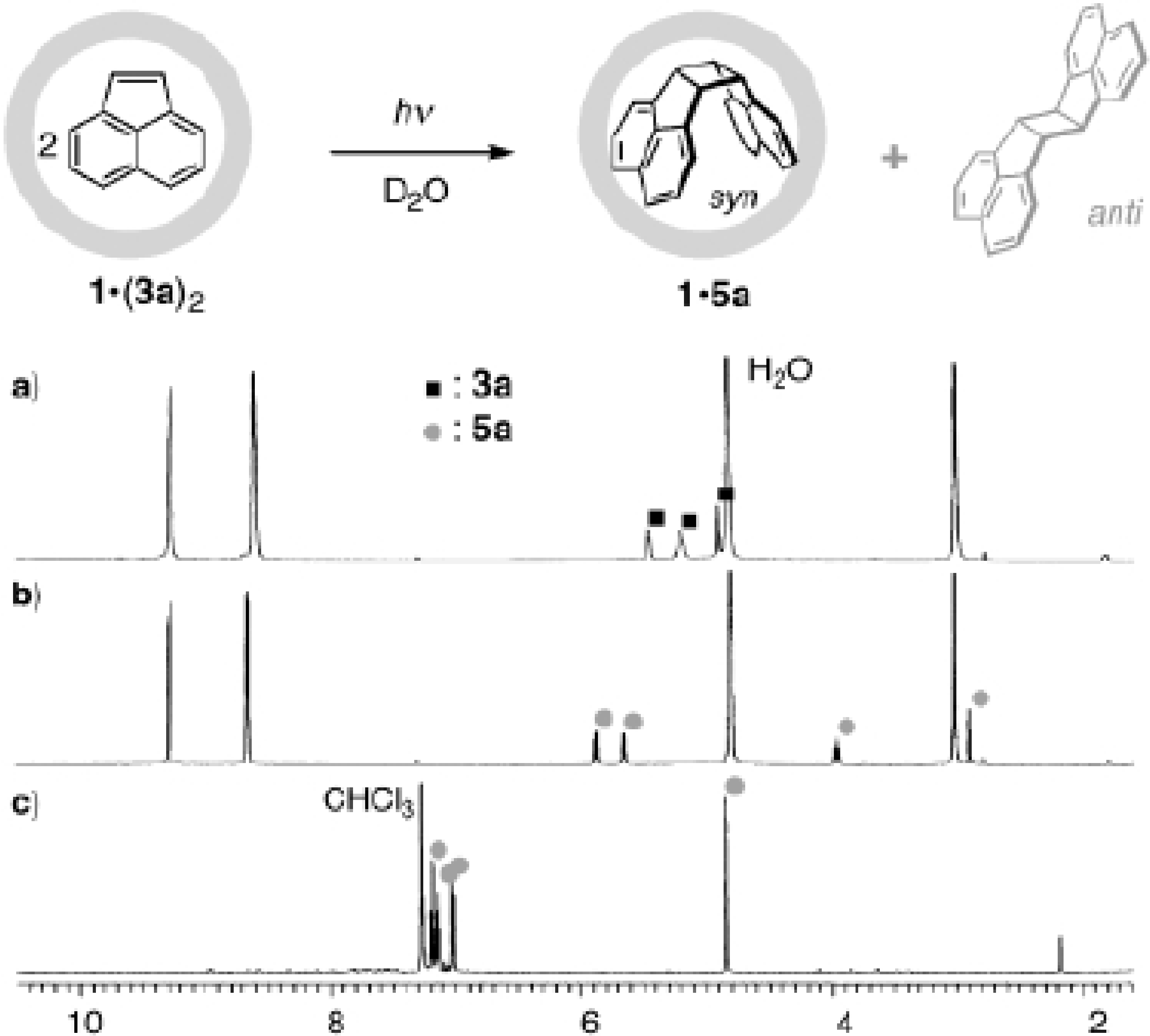
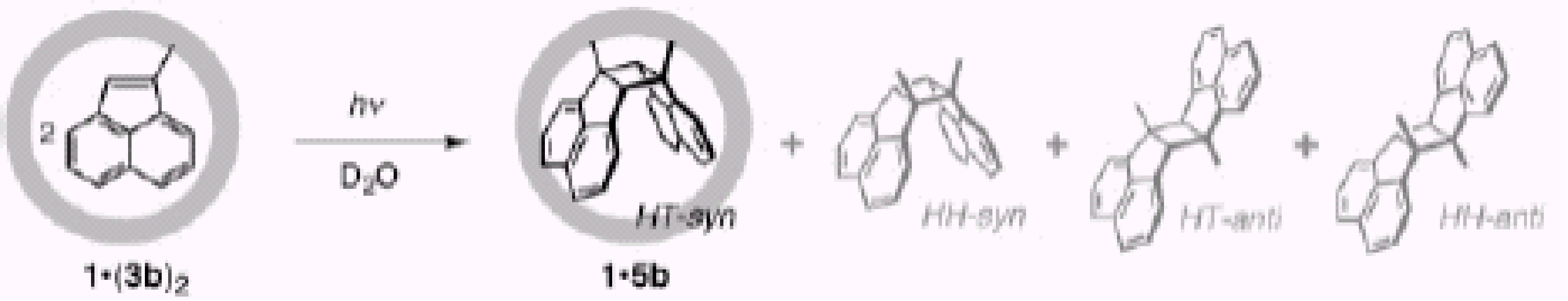


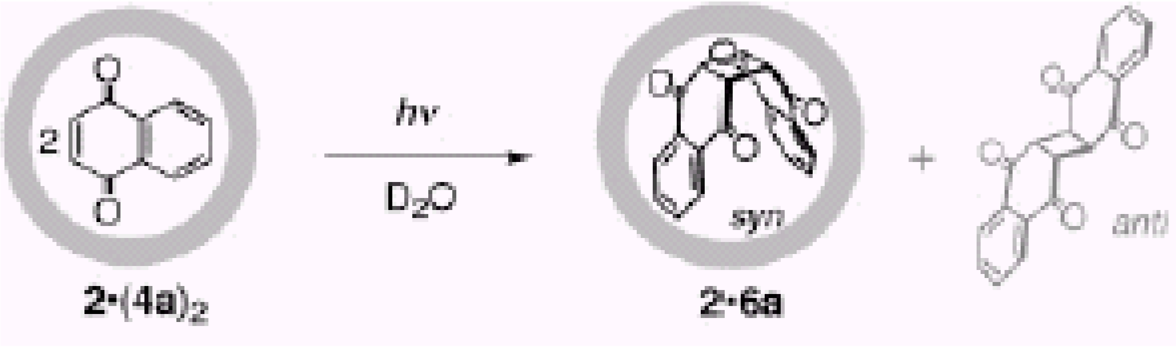
Figure 1. ^{1}H NMR spectroscopic analysis (500 MHz, D_2O, 27 °C) of the photodimerization of **3a** within cage **1:** a) before irradiation (**1**·(**3a**)$_2$) in D_2O; b) after irradiation (400 W) for 0.5 h; c) after extraction with $CDCl_3$.

1-metil-acenaftilene



Controllo regiochimica, [ ] 2mM resa > 98%

naftochinone



controllo stereochimica, [ ] 2mM resa > 98%

benzene: [ ] > >, t > >, resa 25%, 21% *anti*

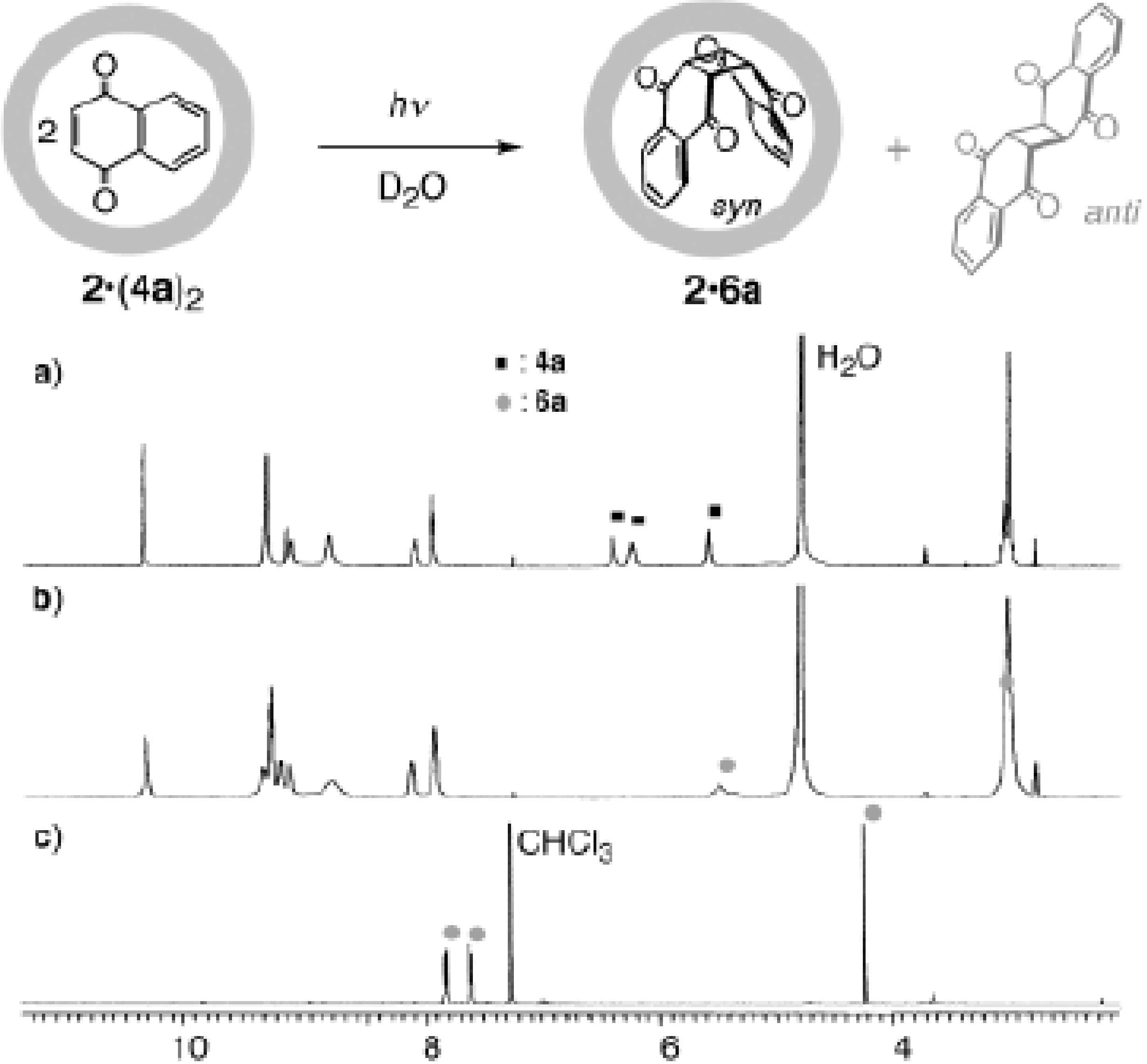


Figure 2. ^{1}H NMR spectroscopic analysis (500 MHz, D_2O, 27 °C) of the photodimerization of **4a** within bowl **2**: a) before reaction (**2**·(**4a**)$_2$) in D_2O; b) after irradiation (400 W) for 3 h; c) after extraction with $CDCl_3$.

Diels-Alder in Aqueous Molecular Hosts: Unusual Regioselectivity and Efficient Catalysis

Michito Yoshizawa, Masazumi Tamura, Makoto Fujita*

SCIENCE VOL 312 14 APRIL 2006 251

ERRATUM

Post date 9 June 2006

Reports: "Diels-Alder in aqueous molecular hosts: unusual regioselectivity and efficient catalysis" by M. Yoshizawa *et al.* (14 Apr. 2006, p. 251). Due to a nomenclature error, all references to "phthalimides" in the text and Supporting Online Material should instead refer to "maleimides." The chemical structures in the schemes and figures are all correct as drawn.

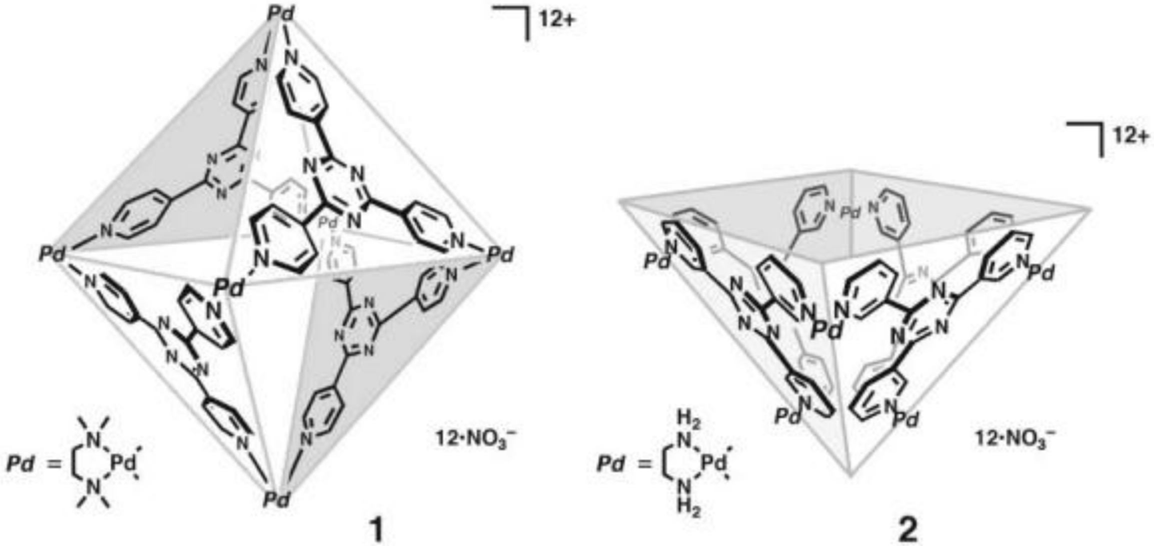
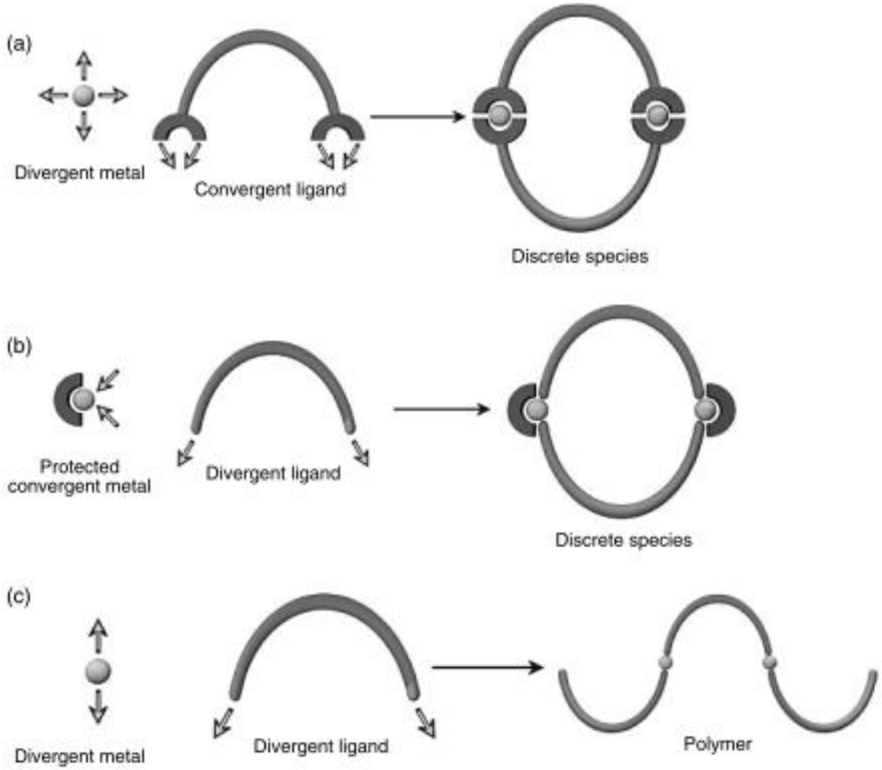
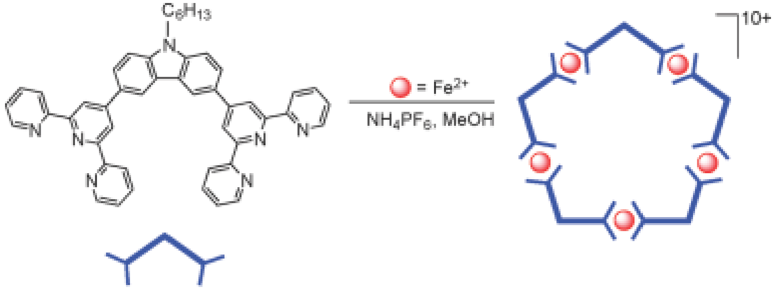
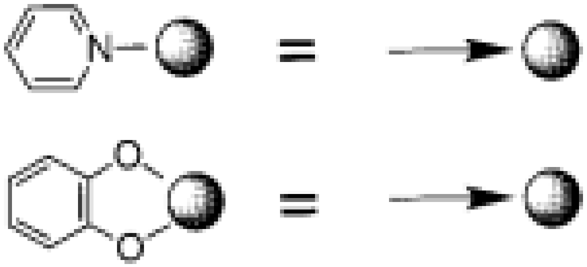
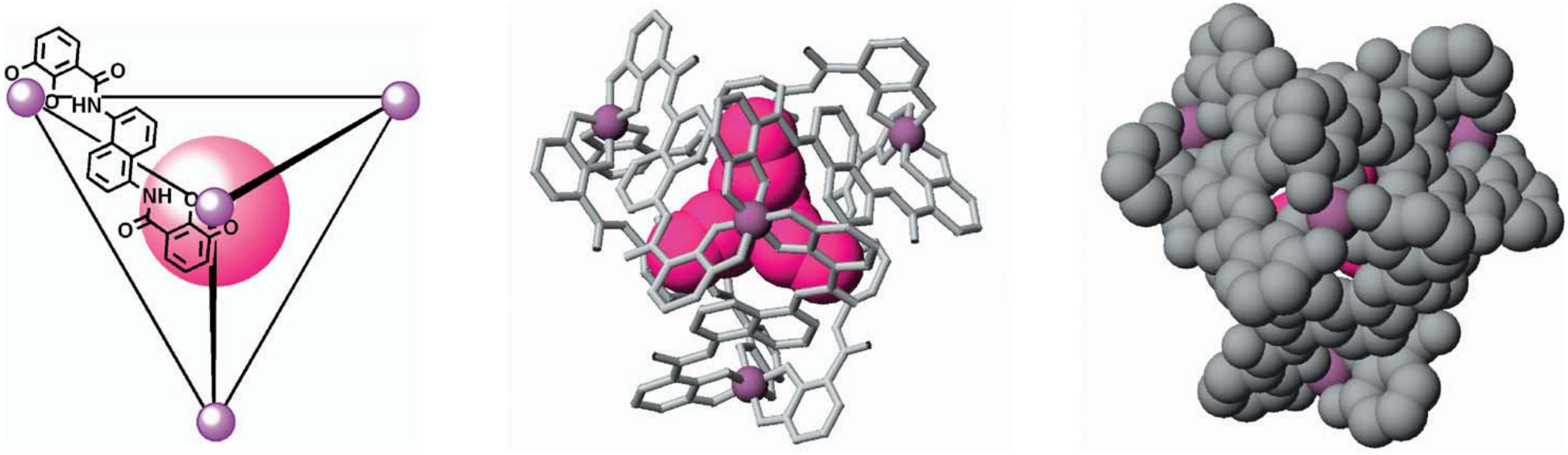


Fig. 1. Self-assembled coordination cages (**1** and **2**), which are prepared by simple mixing of an exo-tridentate organic ligand and an end-capped Pd(II) ion in a 4:6 ratio in water.

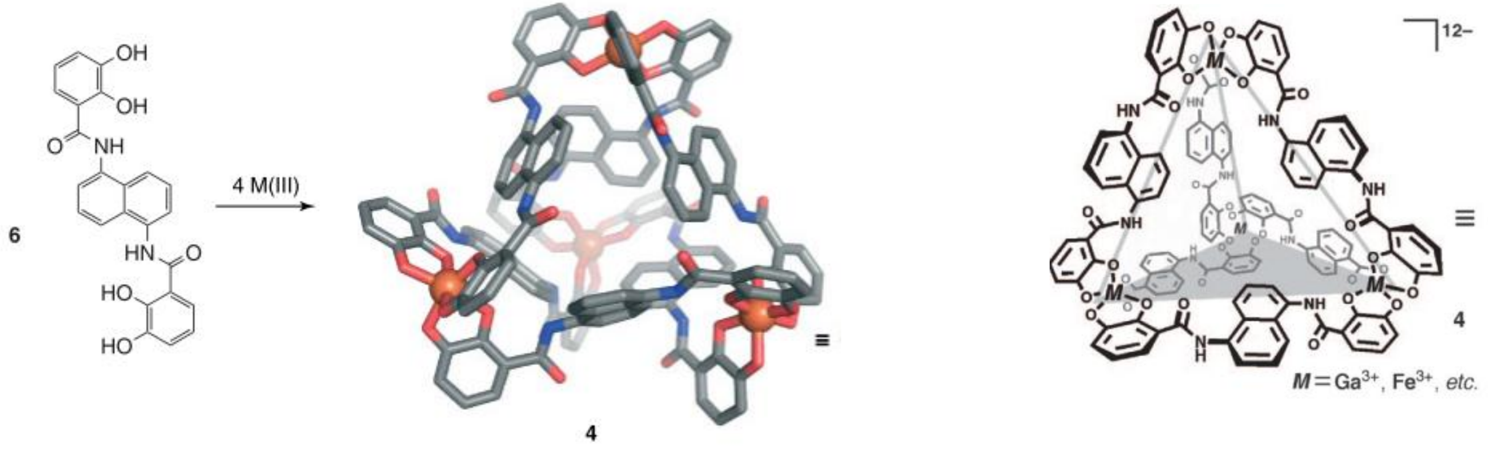

(a)
Divergent metal
Convergent ligand
Discrete species
(b)
Protected convergent metal
Divergent ligand
Discrete species
(c)
Divergent metal
Divergent ligand
Polymer


C_6H_{13}
N
N
N
N
N
N
N
= Fe^{2+}
NH_4PF_6, MeOH
10+


N
O
O
=
=



M_4L_6, (Ga^{3+}, Fe^{3+}; biscatecol-amidi) 12^-, ΔΔΔΔ, ΛΛΛΛ, 300-350 Å
Stabilizzazione di cationi organici



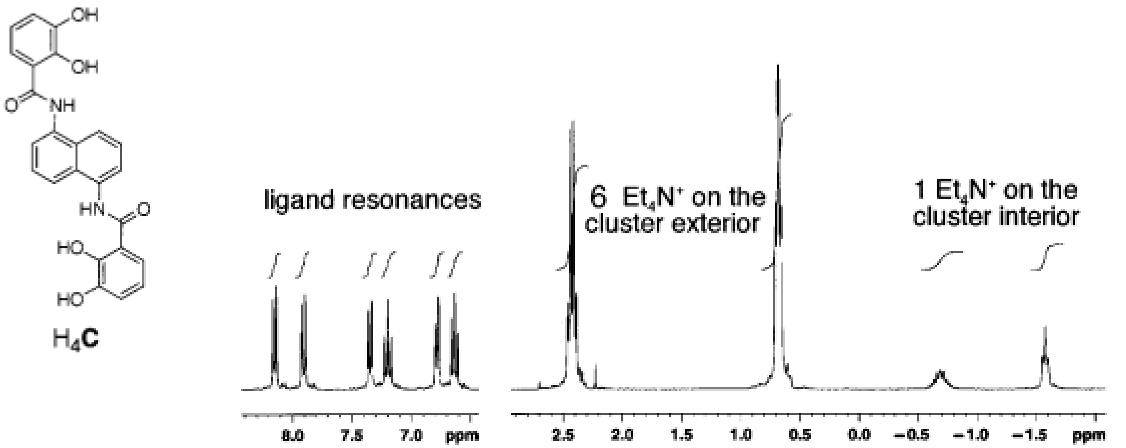


Figure 14. ^{1}H NMR (D_2O) depicting the two sets of Et_4N^+ resonances characteristic of the exterior and encapsulated cations.

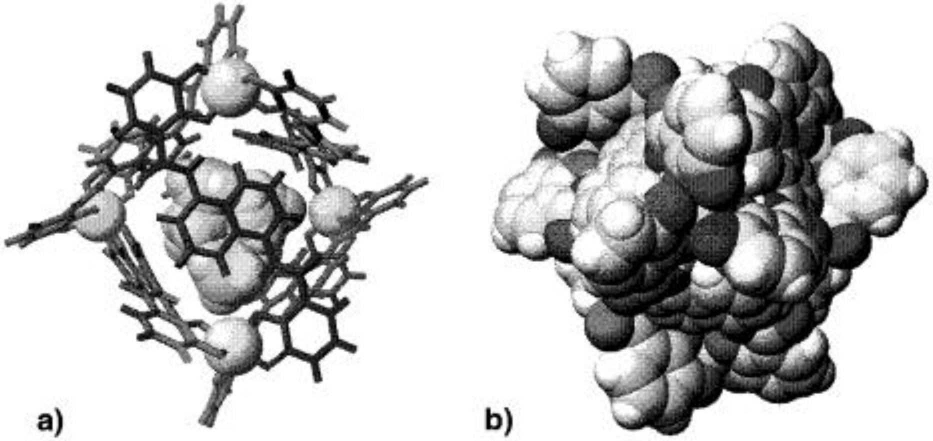
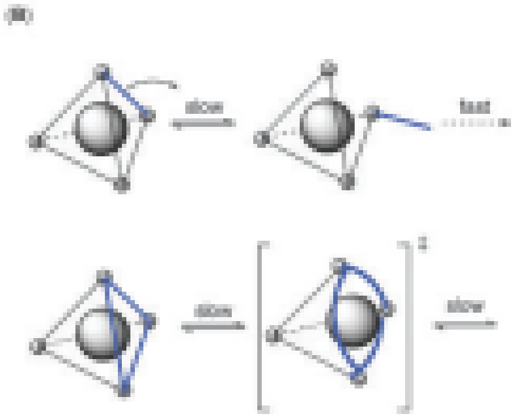
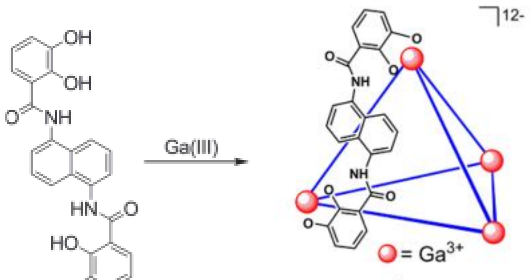


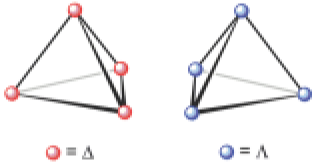
Figure 15. Based on the X-ray structure coordinates, $Et_4N^+ \subset [Fe_4C_6]^{12-}$ in both (a) wire-frame and (b) space-filling representations.


(a)
slow
fast
slow
‡
slow



1

racemic mixture of ΔΔΔΔ and ΛΛΛΛ



(racemic mixture)

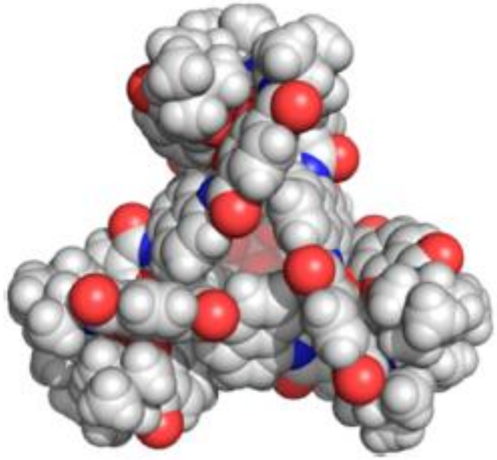
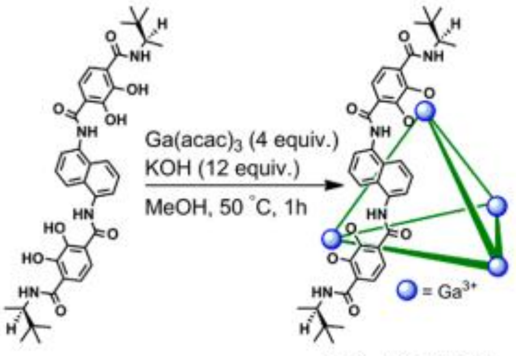


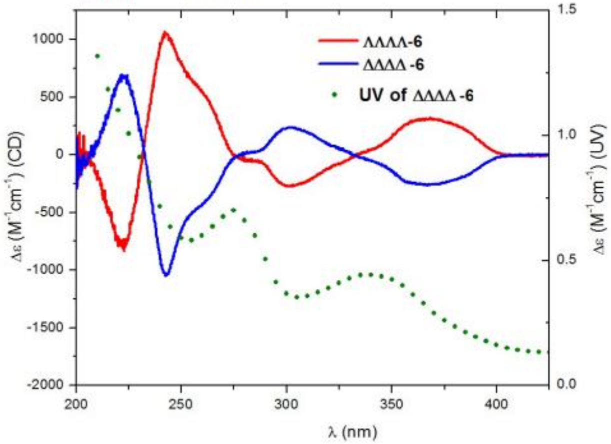
Figure 2. X-ray structure of ΔΔΔΔ-6.



***(R)*-5** (6 equiv.)

6, $K_{12}[Ga_4(R)\text{-}5_6]$
78% isolated yield

CD and UV-Vis Absoprtion Spectra of ΛΛΛΛ-6 and ΔΔΔΔ-6



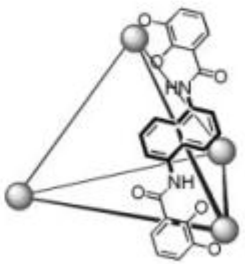
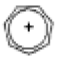


Figure 1. Schematic drawing of the $[Ga_4L_6]^{12-}$ tetrahedron showing the structure of the ligand L; lines represent additional ligand molecules, one is shown, and spheres represent gallium ions



4

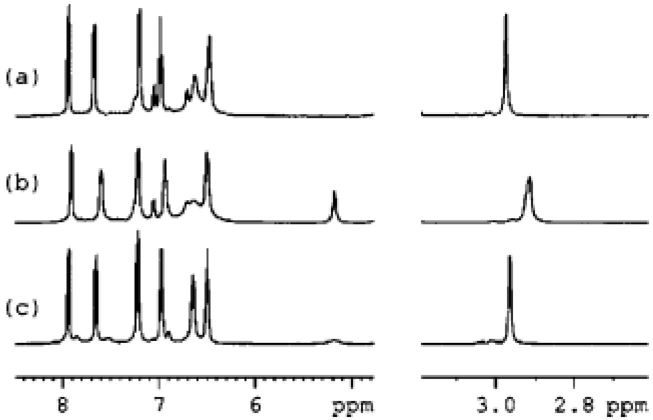
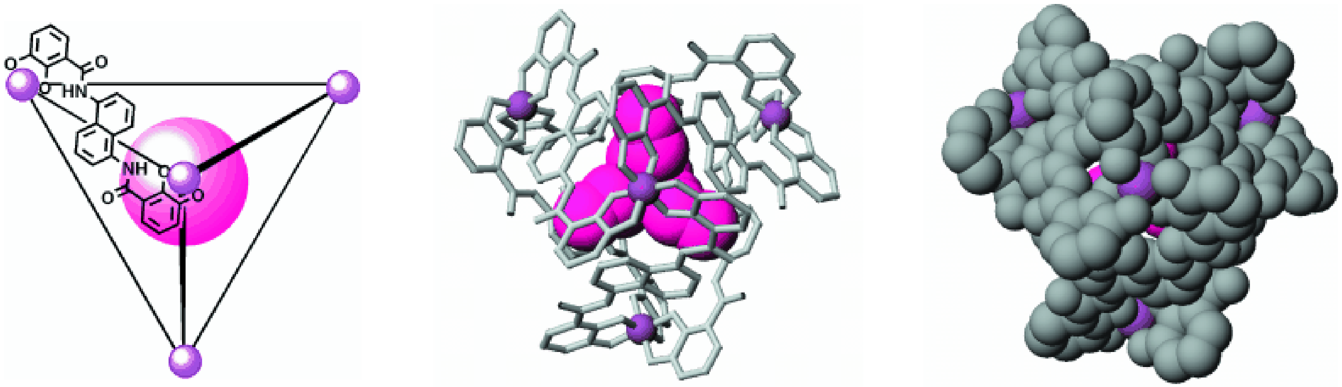


Figure 4. ^1H NMR spectra in D_2O of (a) the $[Ga_4L_6]^{12-}$ assembly + 1 equiv. **4**; (b) + 2 equiv. **4**; (c) sample in spectrum b after 20 h

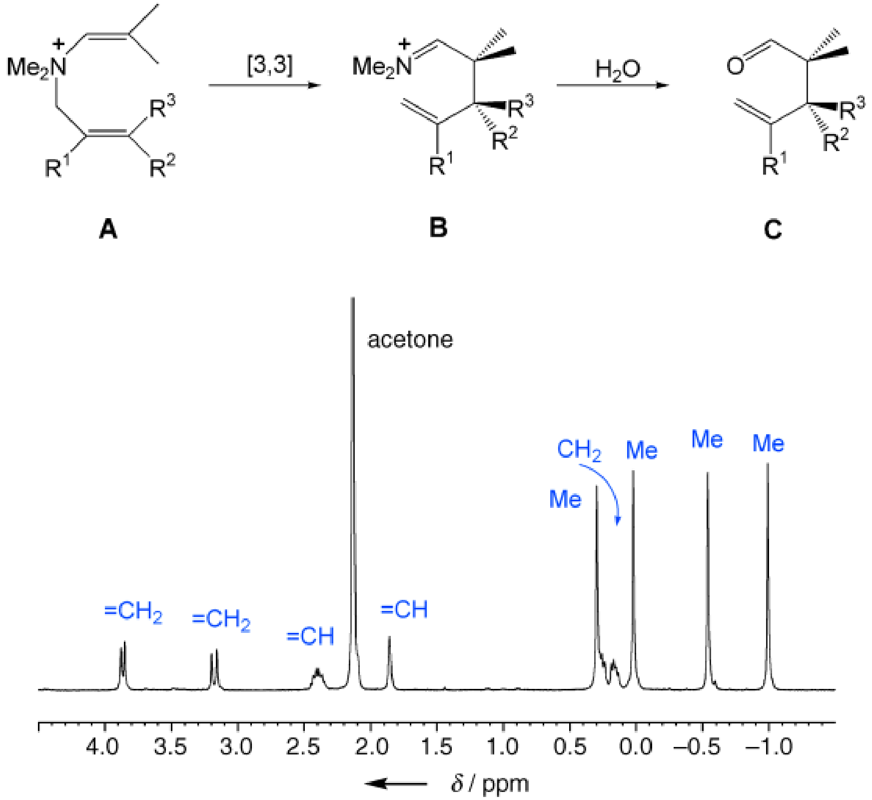
Supramolecular Catalysis of a Unimolecular Transformation: Aza-Cope Rearrangement within a Self-Assembled Host



Left: A schematic view of the [G⊂M_4L_6] (G=guest) supramolecular tetrahedral assembly, looking down the C_3-axis. For clarity only one ligand is drawn, the other ligands are represented as sticks. Middle: CAChe model of $[NPr_4 \subset Fe_4L_6]^{11-}$, the guest molecule is shown in a space-filling view, the hydrogen atoms are omitted for clarity. Right: The same CAChe model as in the middle, now with host and guest in space filling view. This representation shows that the guest molecule is not exposed to the assembly exterior, but rather is tightly surrounded by the host.

Supramolecular Catalysis of a Unimolecular Transformation: Aza-Cope Rearrangement within a Self-Assembled Host, Volume: 43, Issue: 48, Pages: 6748-6751, First published: 08 December 2004, DOI: (10.1002/anie.200461776)

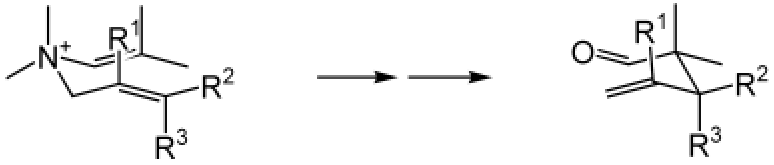
Supramolecular Catalysis of a Unimolecular Transformation: Aza-Cope Rearrangement within a Self-Assembled Host



Top: A general reaction scheme of the 3-aza-Cope rearrangement. Starting from the enammonium cation **A**, [3,3] sigmatropic rearrangement leads to iminium cation **B**, which then hydrolyzes to the aldehyde, **C**. Bottom: ^{1}H NMR spectrum of [**1**$\subset$Ga$_4$L$_6$]$^{11-}$ (**1**: R^1, R^2, R^3=H). The observed upfield shift of guest resonance signals illustrates the close contact between host and guest.

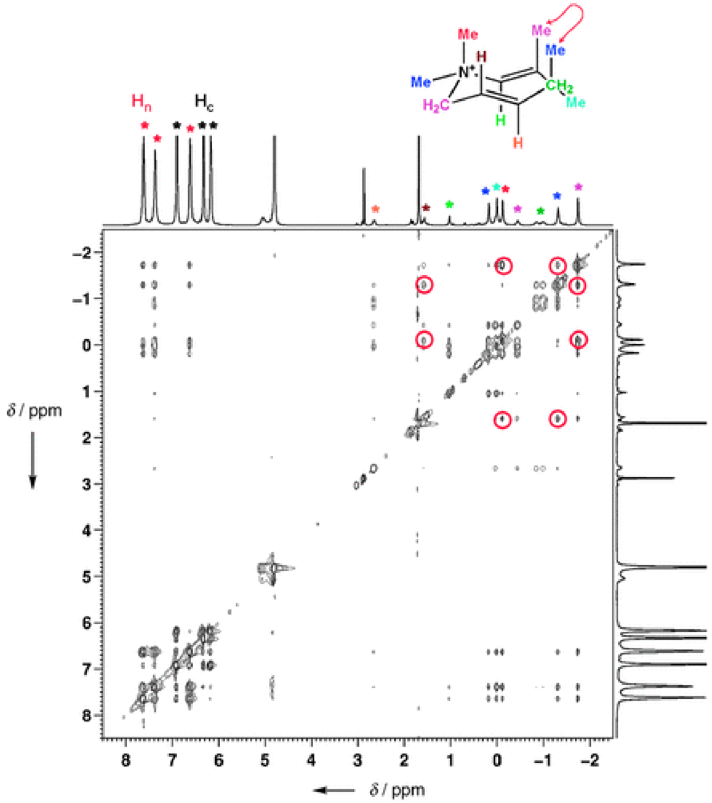
Supramolecular Catalysis of a Unimolecular Transformation: Aza-Cope Rearrangement within a Self-Assembled Host, Volume: 43, Issue: 48, Pages: 6748-6751, First published: 08 December 2004, DOI: (10.1002/anie.200461776)

Table 1. Rate constants for free (k_{free}) and encapsulated (k_{encaps}) rearrangements (measured at 50 °C) and their acceleration factors.



Substrate	R^1	R^2	R^3	k_{free} [$\times 10^{-5}$ s^{-1}]	k_{encaps} [$\times 10^{-5}$ s^{-1}]	Acceleration
1	H	H	H	3.49	16.3	5
2	Me	H	H	7.61	198	26
3	H	Et	H	3.17	446	141
4	H	H	Et	1.50	135	90
5	H	*n*Pr	H	4.04	604	150
6	H	H	*n*Pr	1.69	74.2	44
7	H	*i*Pr	H	0.37	316	854

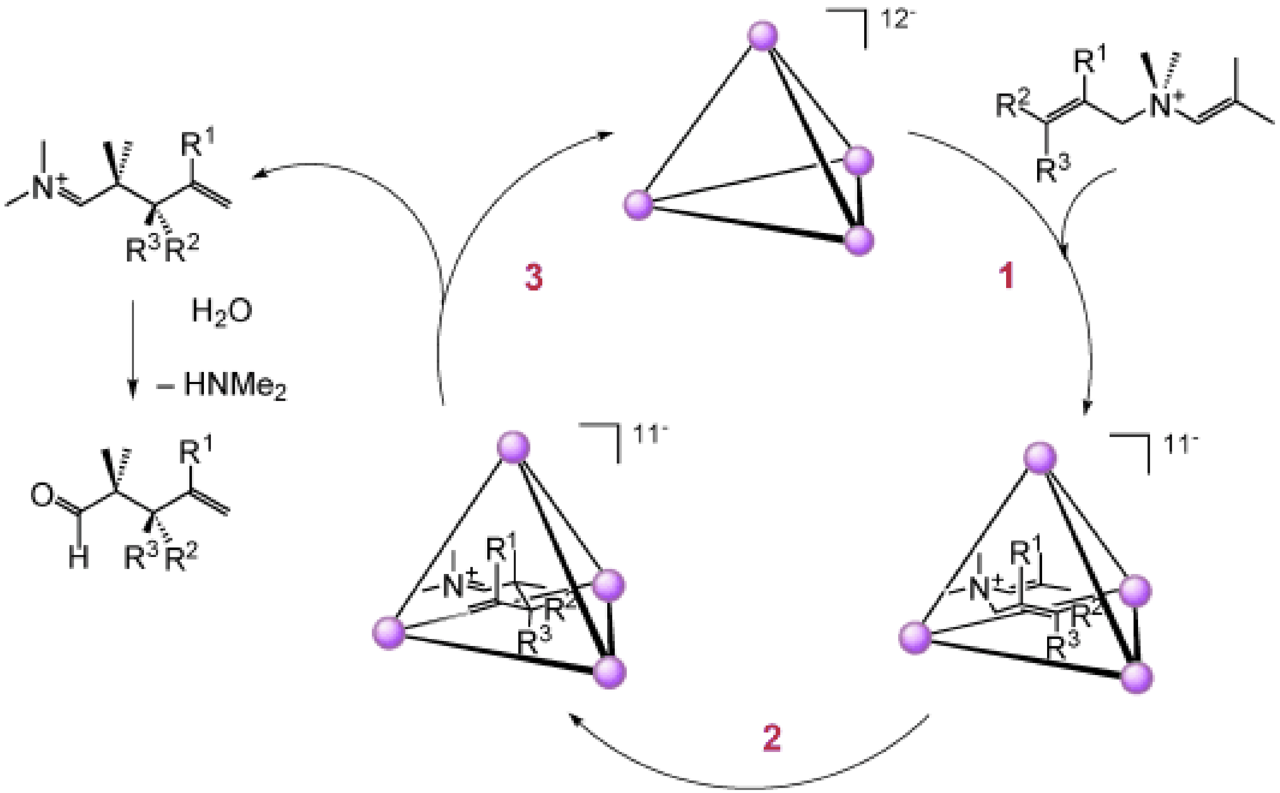
Supramolecular Catalysis of a Unimolecular Transformation: Aza-Cope Rearrangement within a Self-Assembled Host, Volume: 43, Issue: 48, Pages: 6748-6751, First published: 08 December 2004, DOI: (10.1002/anie.200461776)



The 2D NOESY spectrum of $[\mathbf{3}\subset Ga_4L_6]^{11-}$ in a D_2O/MeOD mixture (70:30) recorded at −10 °C, mixing time 100 ms. Indicated in red are selected NOEs. The correlation between Me and Me at the two distal ends of the molecule demonstrates the cavity's enforcement of a compressed and folded guest conformation. H_n=naphthyl protons, H_c=catechol protons.

Supramolecular Catalysis of a Unimolecular Transformation: Aza-Cope Rearrangement within a Self-Assembled Host, Volume: 43, Issue: 48, Pages: 6748-6751, First published: 08 December 2004, DOI: (10.1002/anie.200461776)

Supramolecular Catalysis of a Unimolecular Transformation: Aza-Cope Rearrangement within a Self-Assembled Host



Proposed catalytic cycle for the cationic 3-aza-Cope rearrangement, see text for details.

Supramolecular Catalysis of a Unimolecular Transformation: Aza-Cope Rearrangement within a Self-Assembled Host, Volume: 43, Issue: 48, Pages: 6748-6751, First published: 08 December 2004, DOI: (10.1002/anie.200461776)

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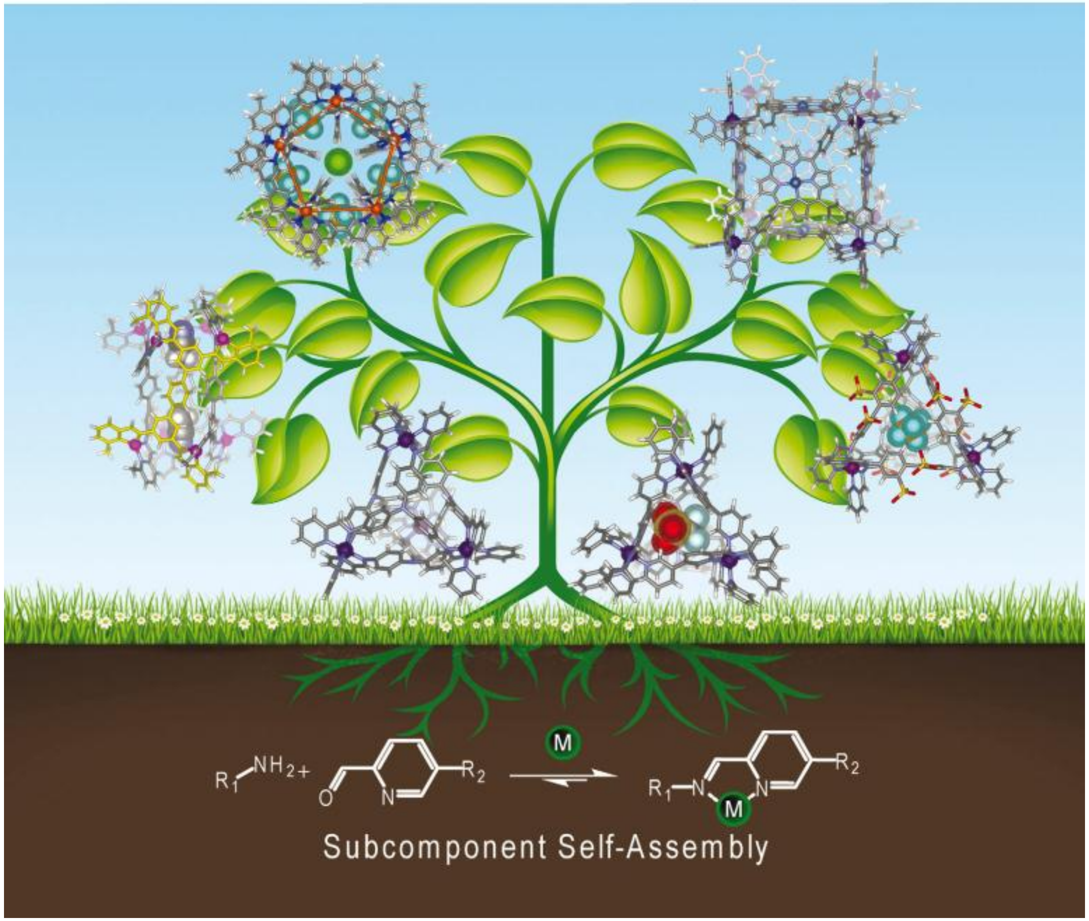
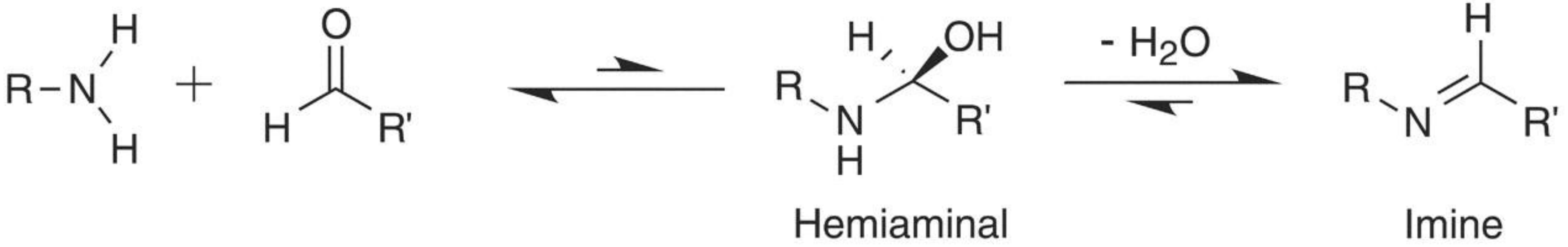
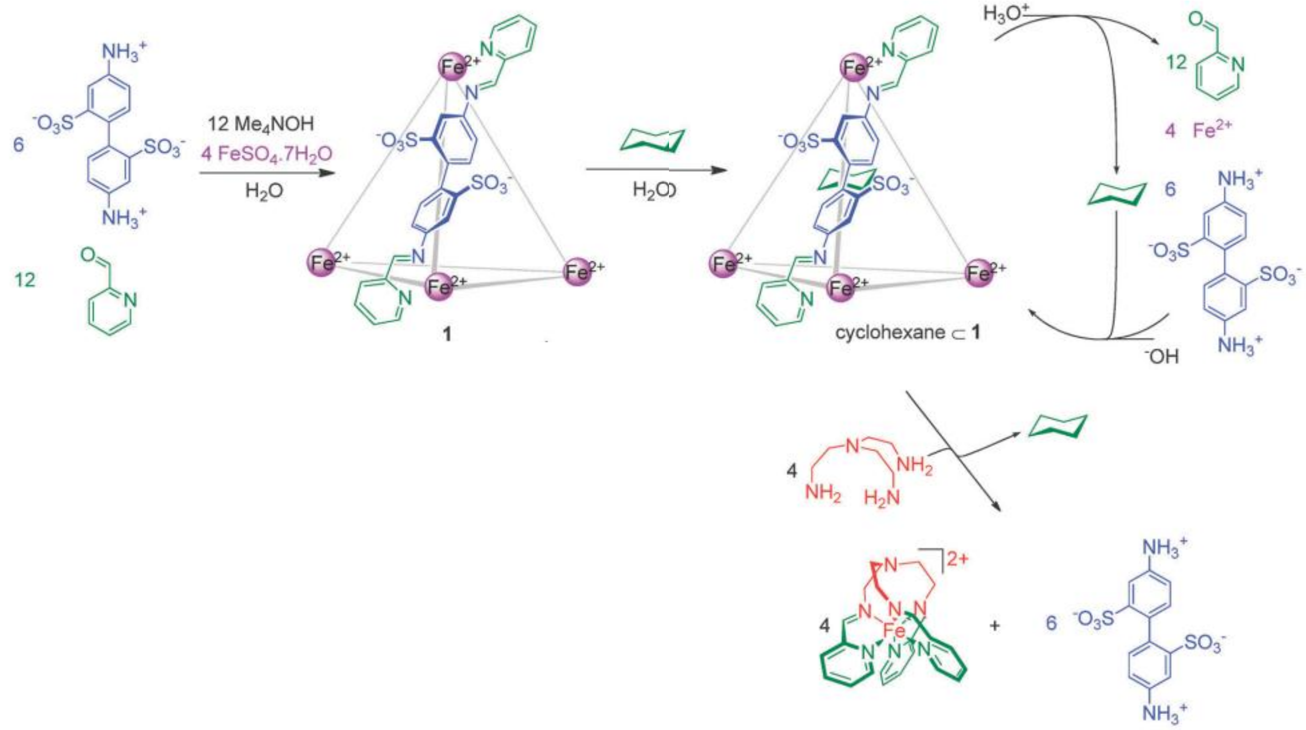


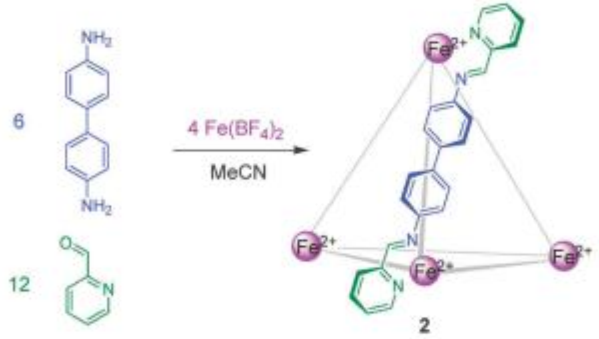

R
N
H
H
O
H
R'
H
OH
R
N
H
R'
- H_2O
H
R
N
R'
Hemiaminal
Imine

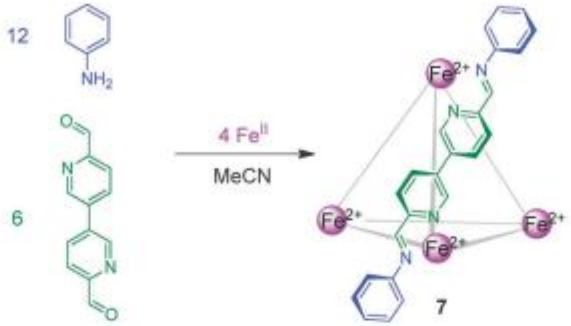

6
NH_3^+
^-O_3S
SO_3^-
NH_3^+
12
O
N
12 Me_4NOH
4 $FeSO_4 \cdot 7H_2O$
H_2O
Fe^{2+}
N
^-O_3S
SO_3^-
N
Fe^{2+}
N
Fe^{2+}
Fe^{2+}
N

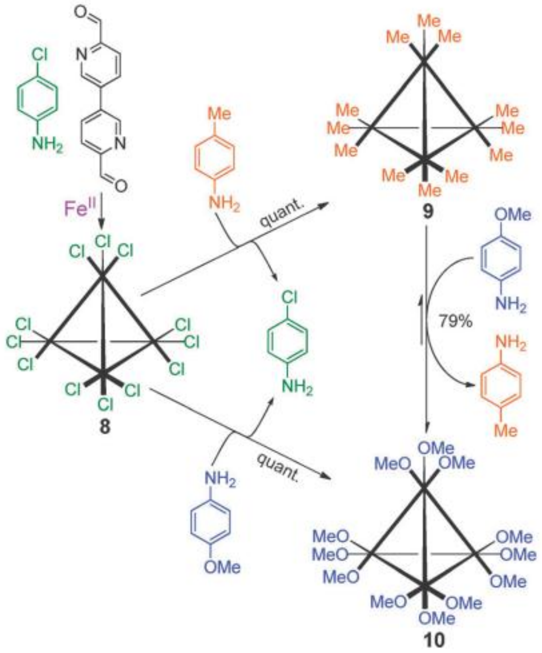
1

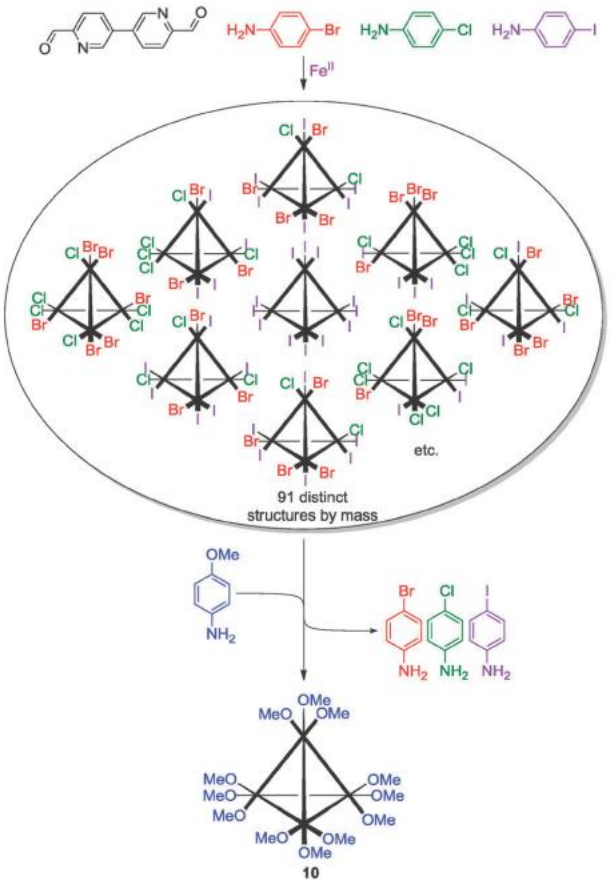


6
NH_3^+
^-O_3S
SO_3^-
12
12 Me_4NOH
4 $FeSO_4.7H_2O$
H_2O
Fe^{2+}
N
1
H_2O
cyclohexane ⊂ **1**
H_3O^+
12
4 Fe^{2+}
^-OH
4
NH_2
H_2N
2+
Fe
+


6
NH₂
NH₂
12
O
N
4 Fe(BF₄)₂
MeCN
Fe2+
Fe2+
Fe2+
Fe2+
N
N
N
N
2


12
NH₂
6
O
N
N
O
4 Fe^II
MeCN
Fe2+
Fe2+
Fe2+
Fe2+
N
N
N
N
7


Fe^II
quant.
quant.
79%
8
9
10


Fe^II
91 distinct
structures by mass
etc.
10

White Phosphorus Is Air-Stable Within a Self-Assembled Tetrahedral Capsule

Prasenjit Mal,[1] Boris Breiner,[1] Kari Rissanen,[2] Jonathan R. Nitschke[1]*

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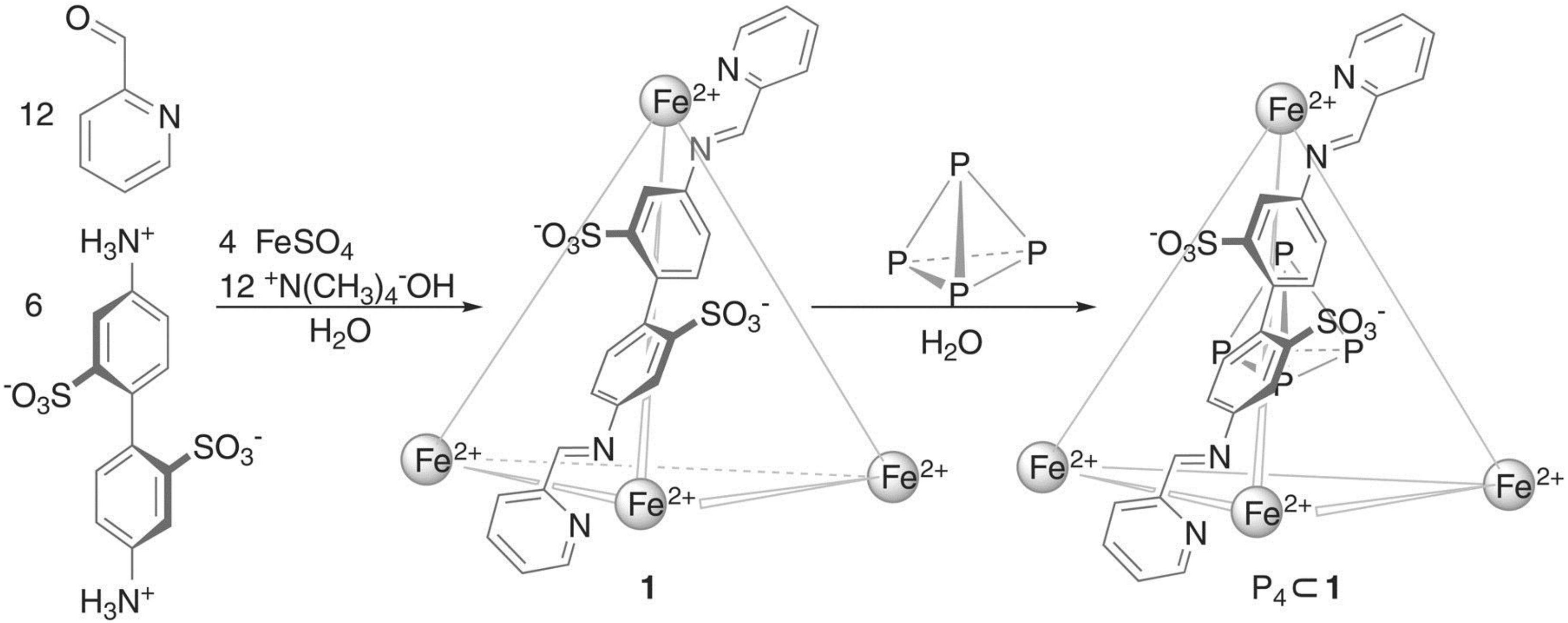


Fig. 1 Synthesis of tetrahedral cage 1 and subsequent incorporation of P4.

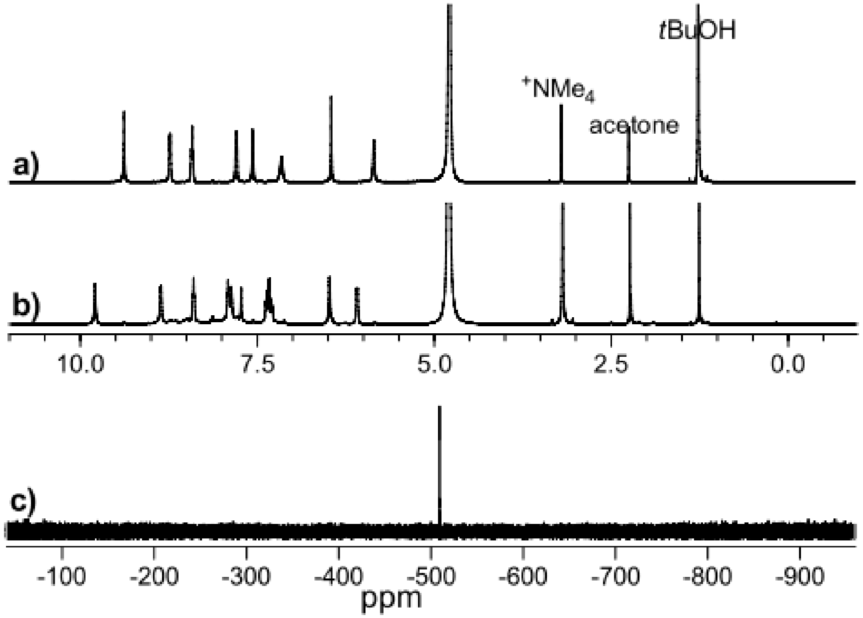


Figure S1. ^{1}H NMR spectra in D_2O of cage **1** (top), of $P_4\subset$**1** (middle), and ^{31}P NMR spectrum of $P_4\subset$**1** (bottom).

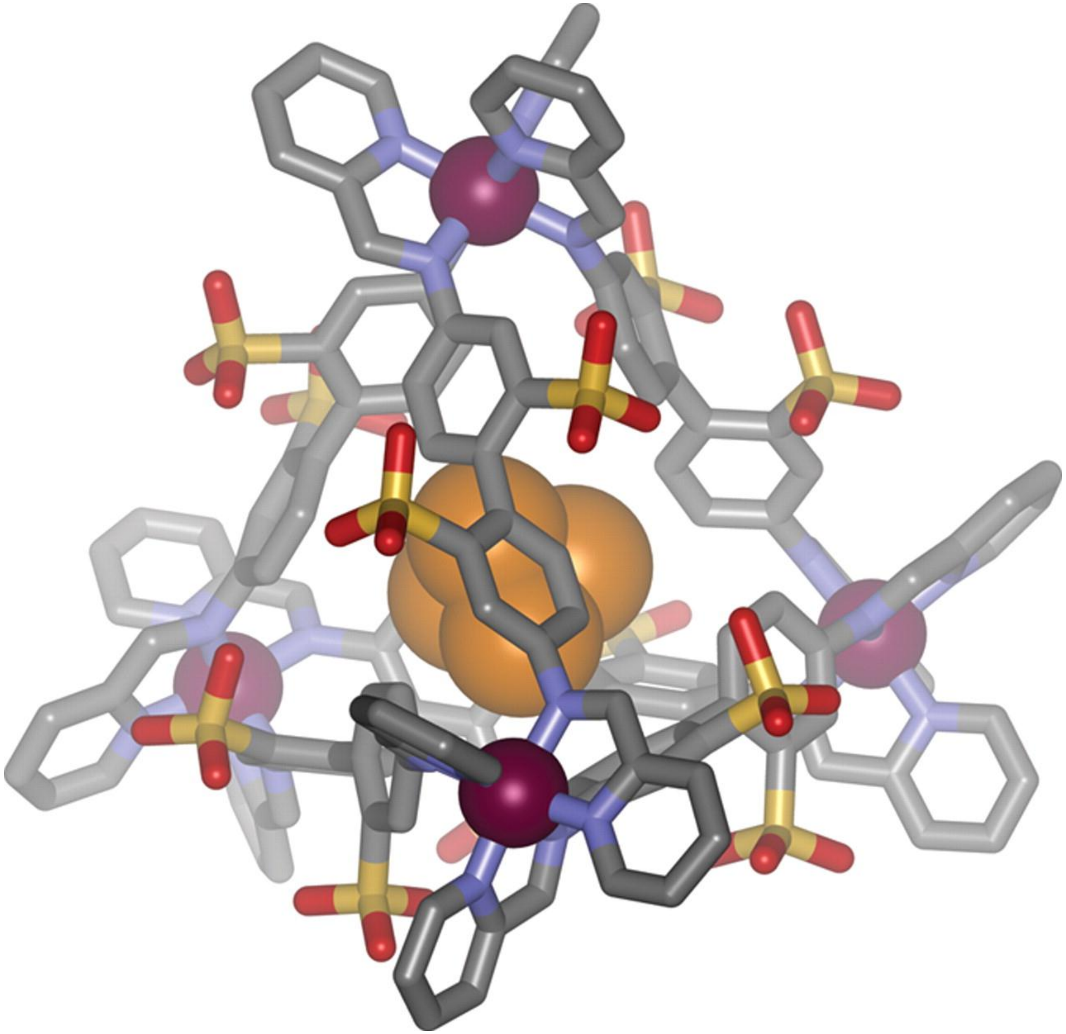


Fig. 2 Crystal structure of P4⊂1.

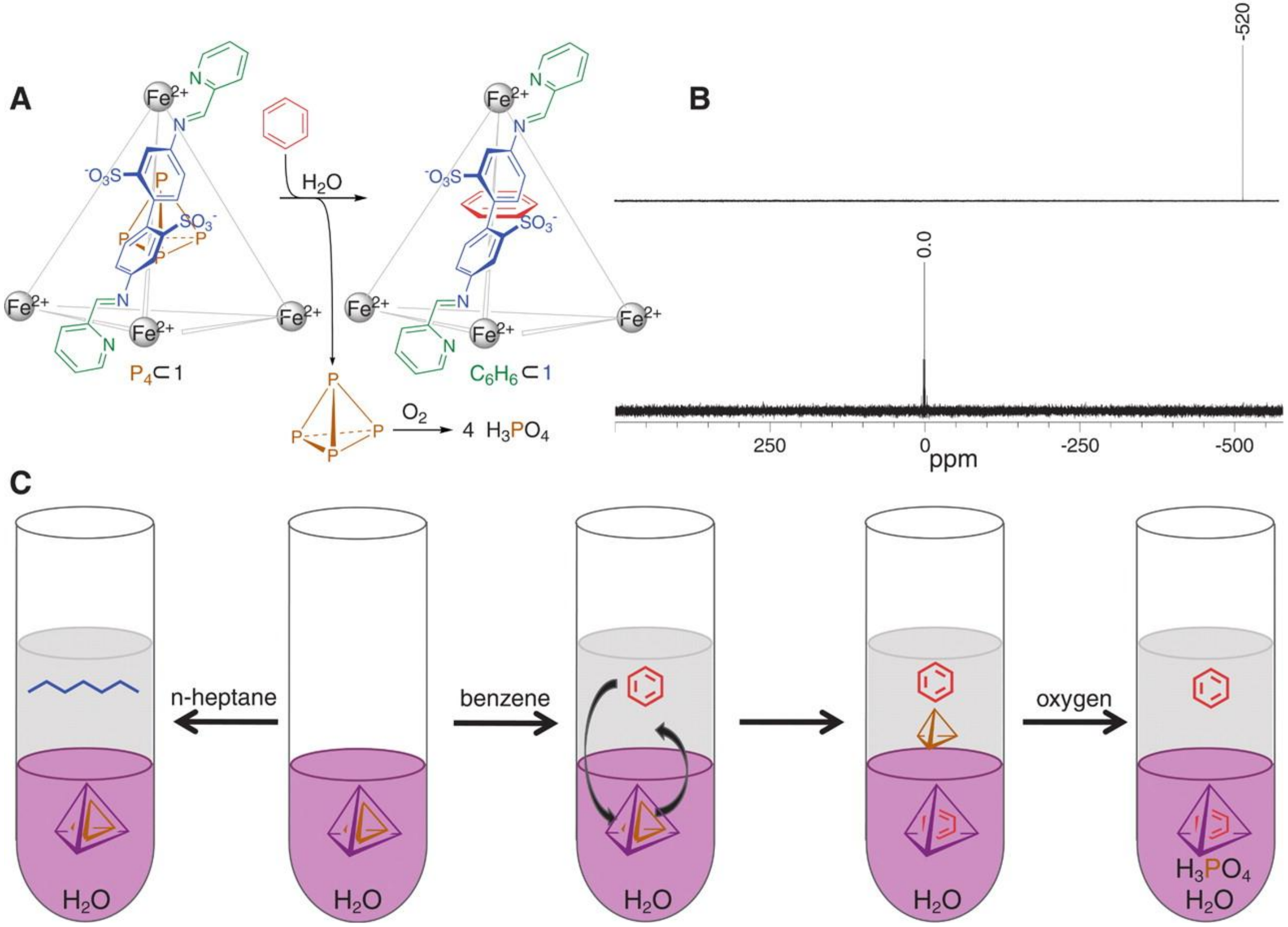
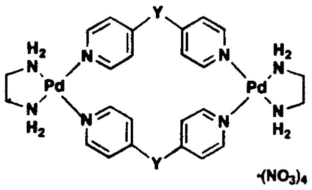
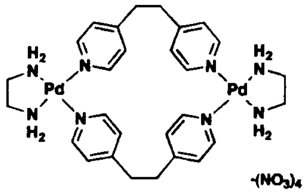
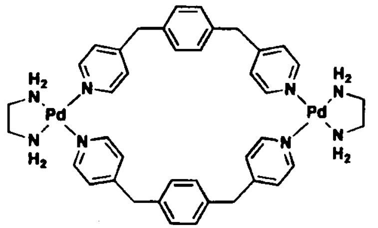


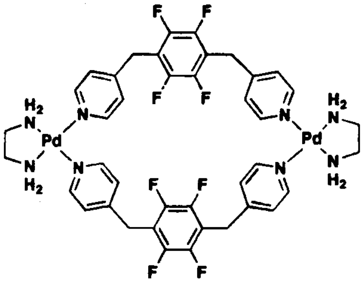
Fig. 3 Extraction of P4 from 1 by n-heptane is not possible, whereas replacing P4 with another suitable guest (benzene or cyclohexane) results in the facile removal of P4 into the organic solvent.

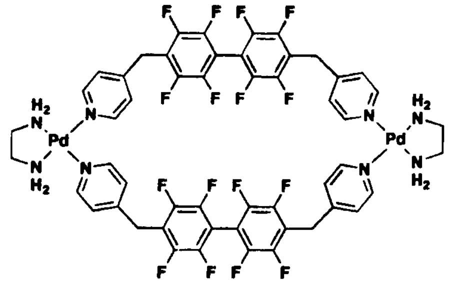


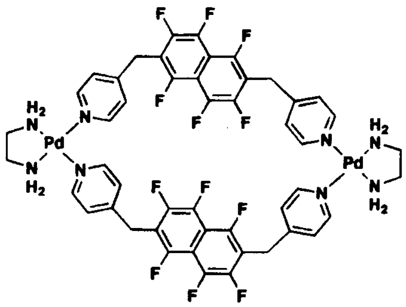
$Y = CH_2$
$Y = C(OH)_2$

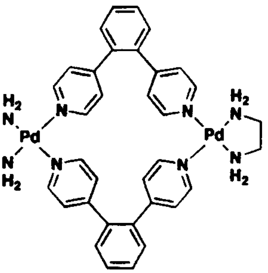


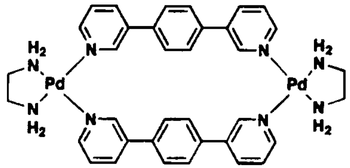


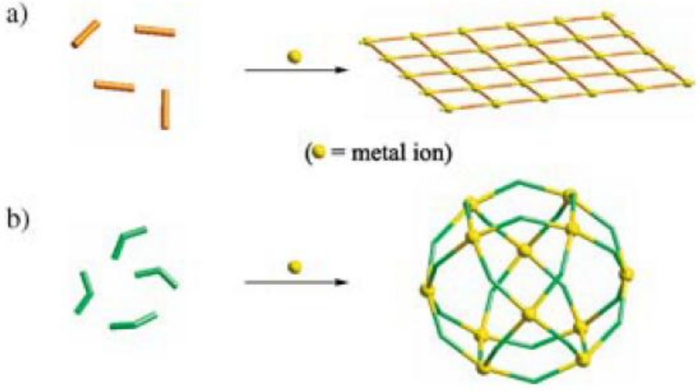


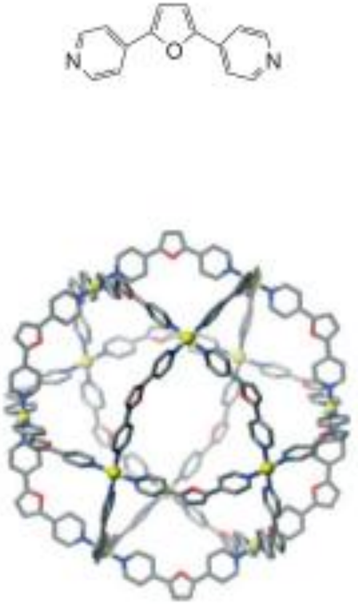












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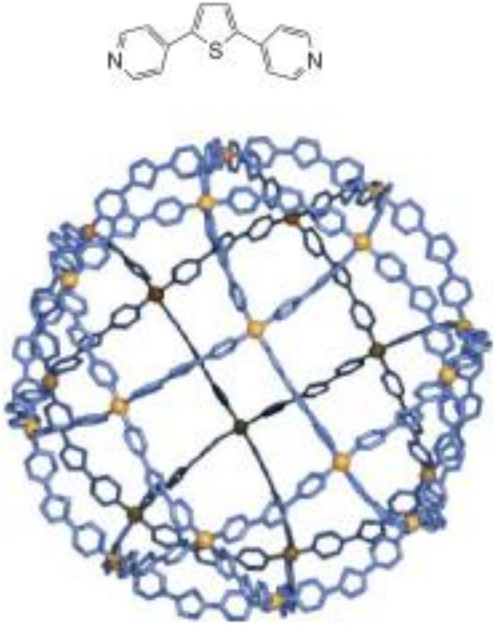

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