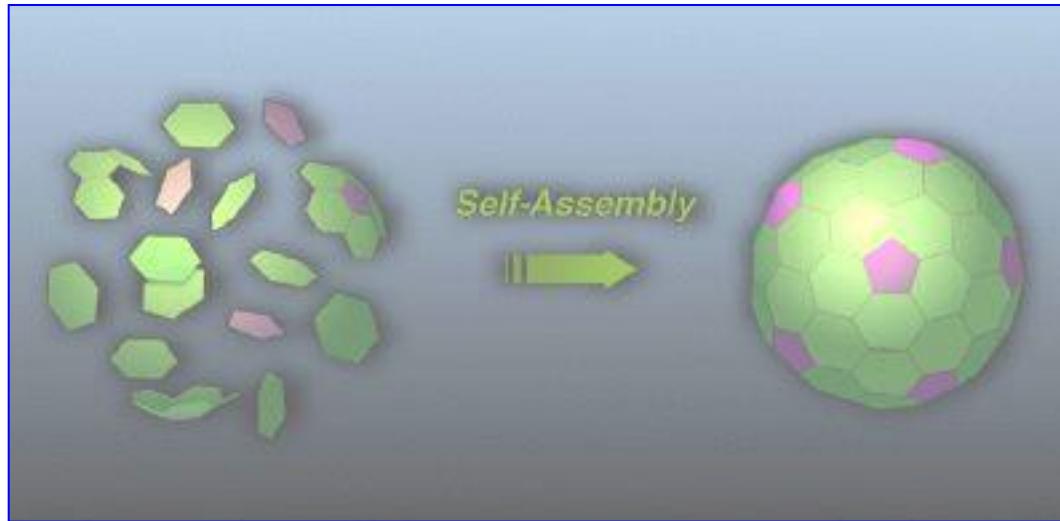
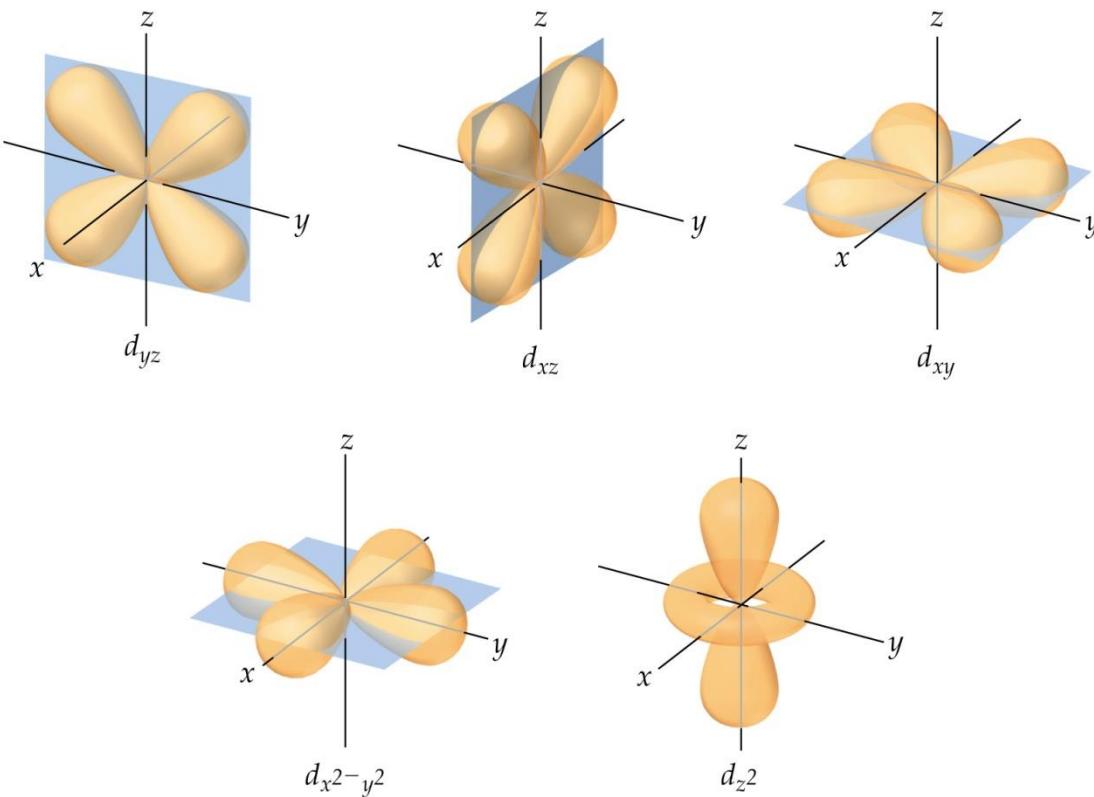


Self-Assembly

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

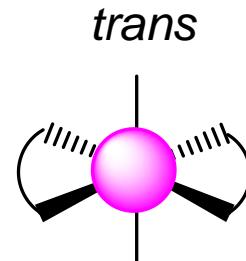
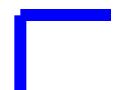
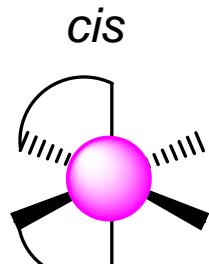
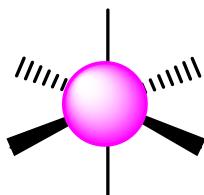
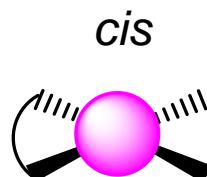
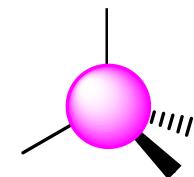
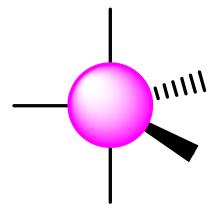
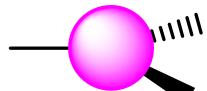


Metal as **connector** :

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

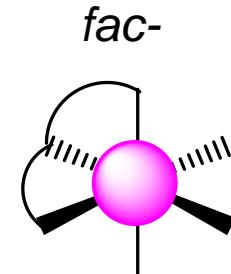
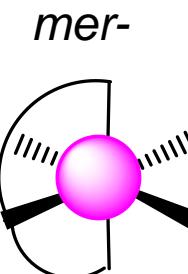
Metal as **functional group** :

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

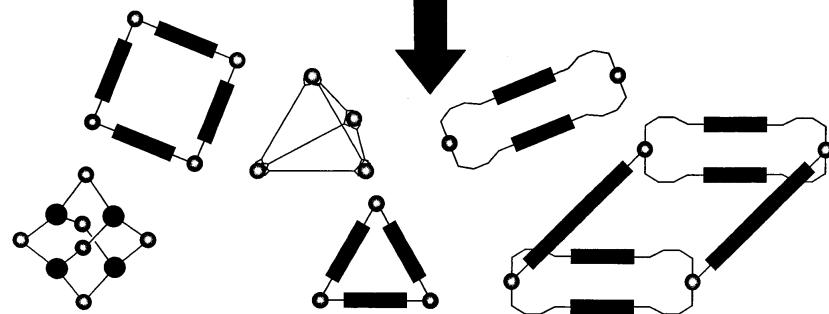
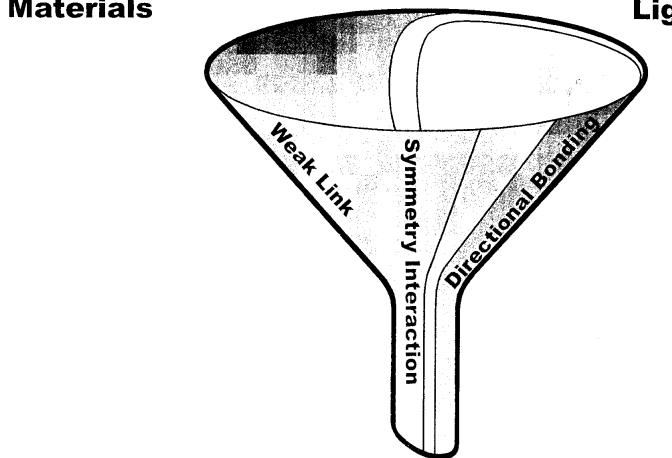
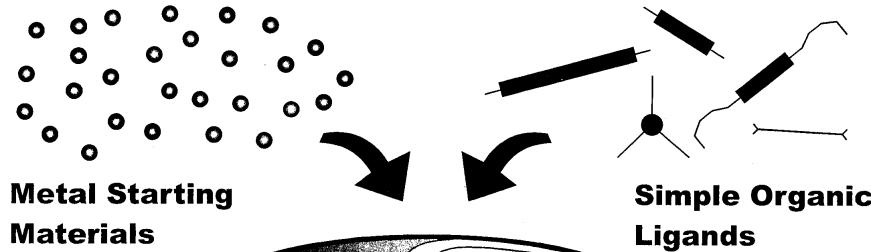


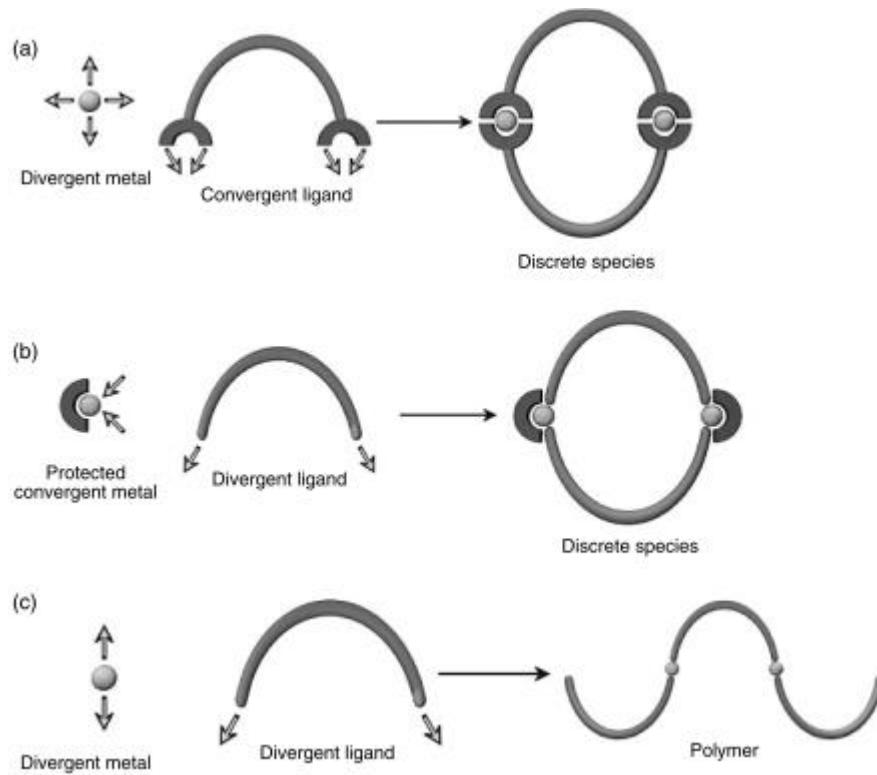
Classical metals used:

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



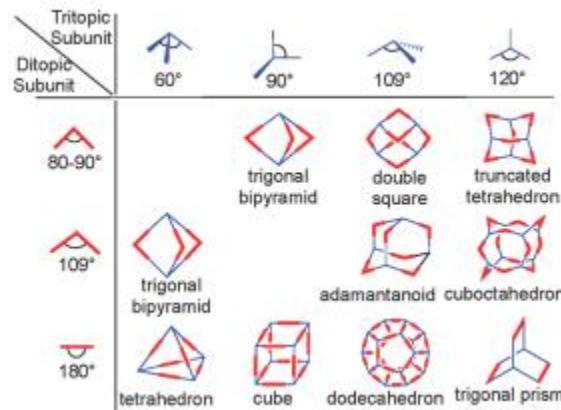
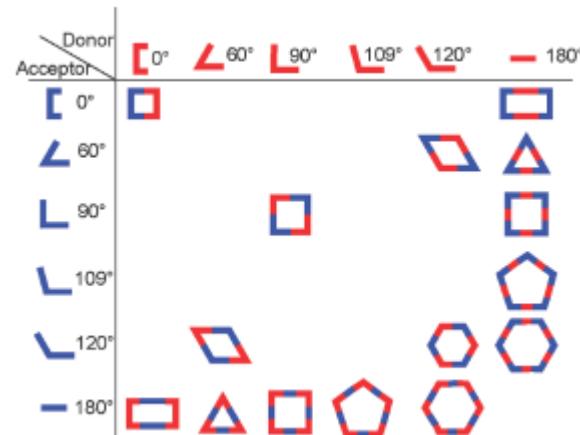
Supramolecular Coordination Chemistry





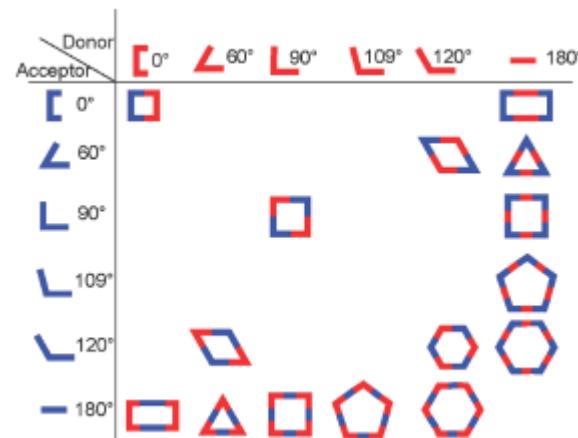
Directional Bonding Approach

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

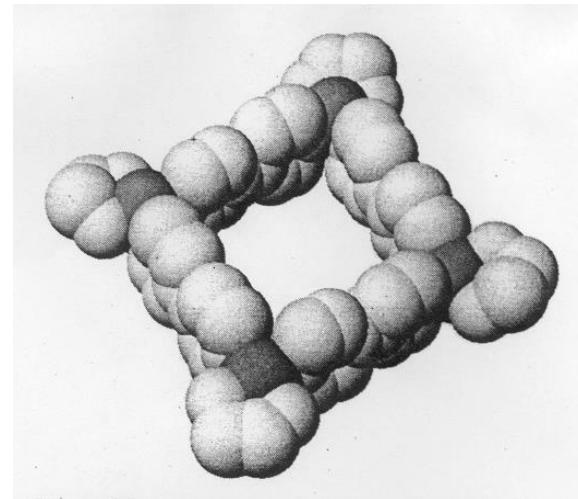
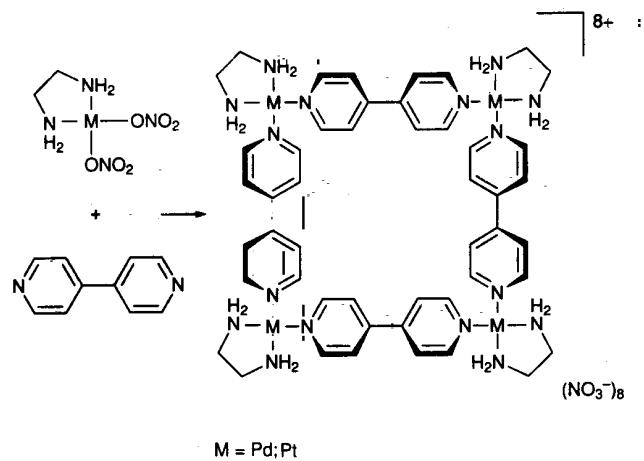


Directional Bonding Approach

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



Specie poligonali 2D



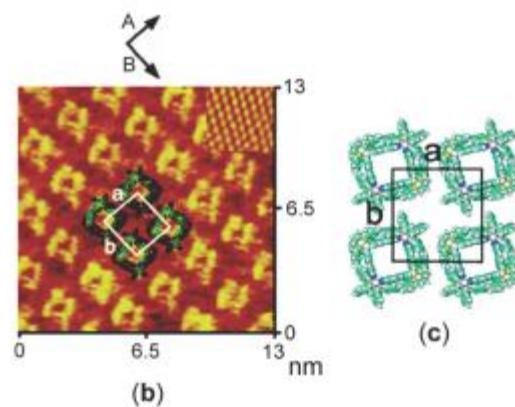
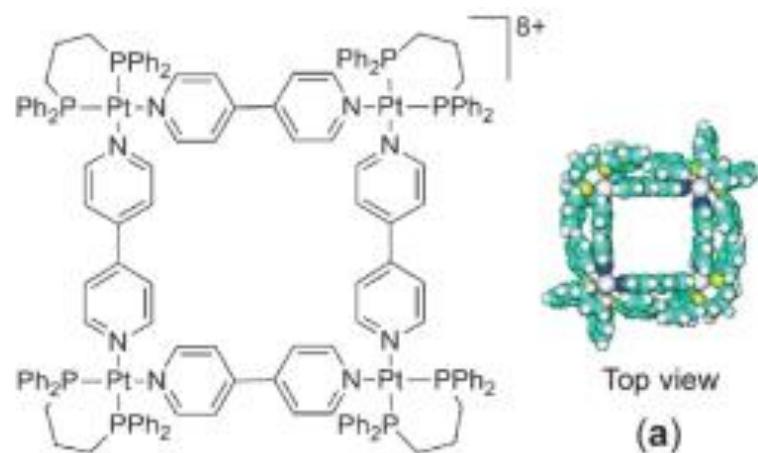
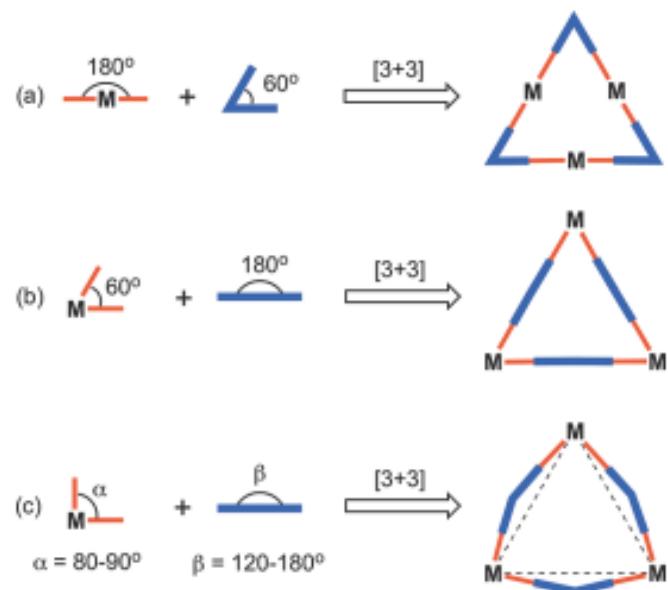
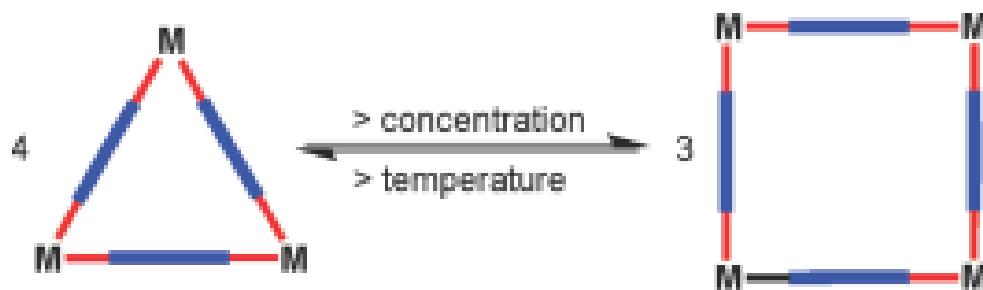


Figure 41. (a) Space-filling model of molecular square $[\text{Pt}(\text{dppp})(4,4'\text{-bipyridine})]_4(\text{PF}_6)_8$, (b) high-resolution STM images of the adlayer of square on Au(111), and (c) structural model of the adlayer.

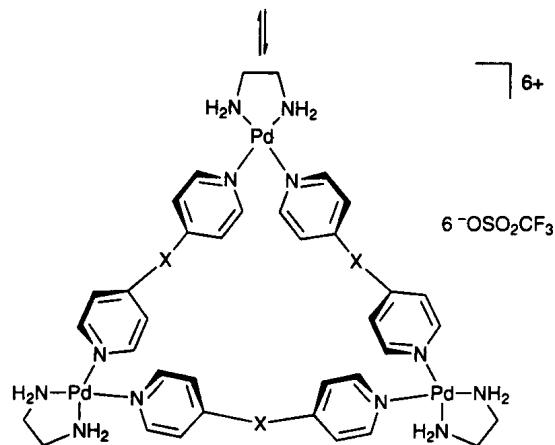
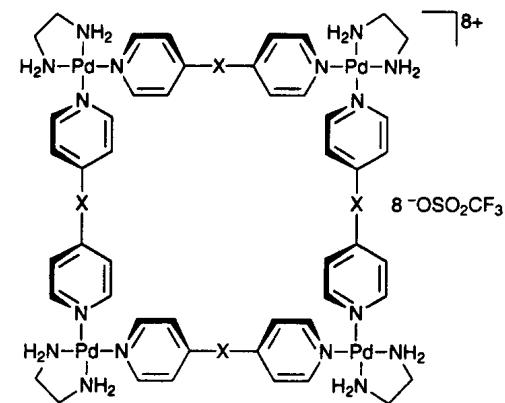
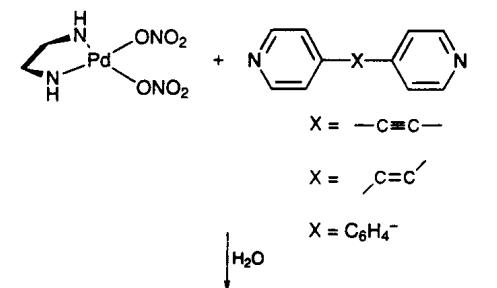
Triangoli Molecolari

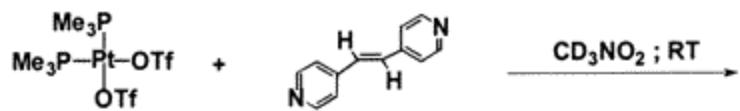




Square = Triangle endothermic $\Delta H < 0$
 $\Delta S < \Delta S < 0$

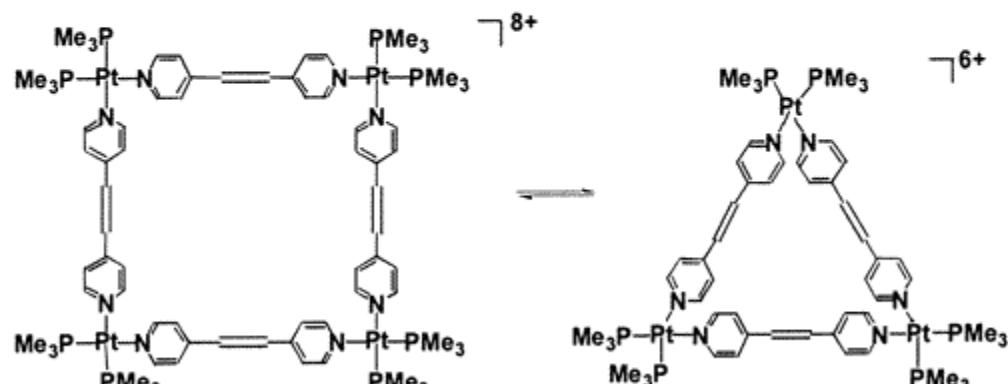
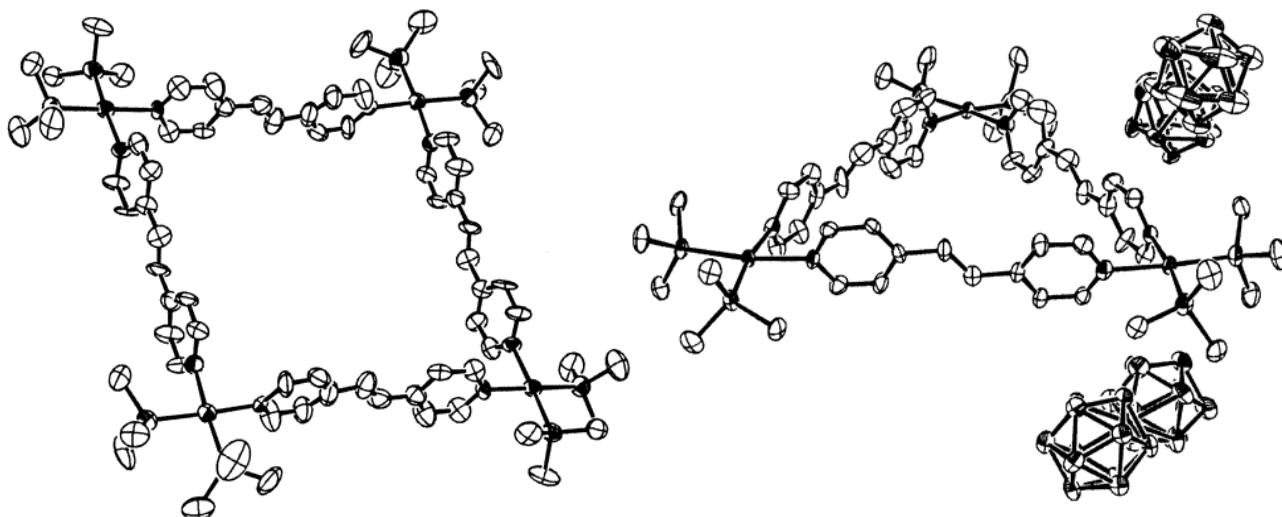
Solvent
Concentration
Temperature

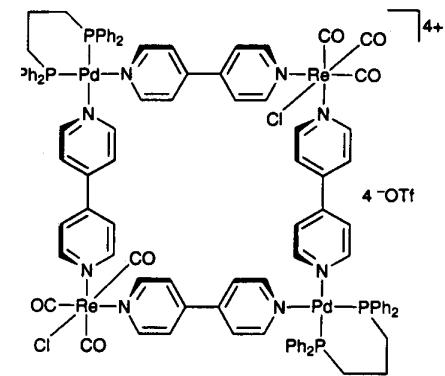
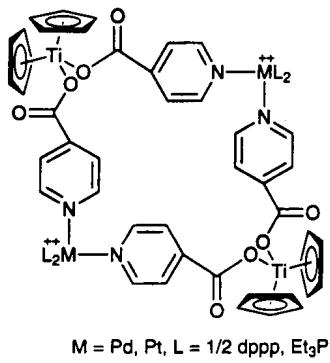
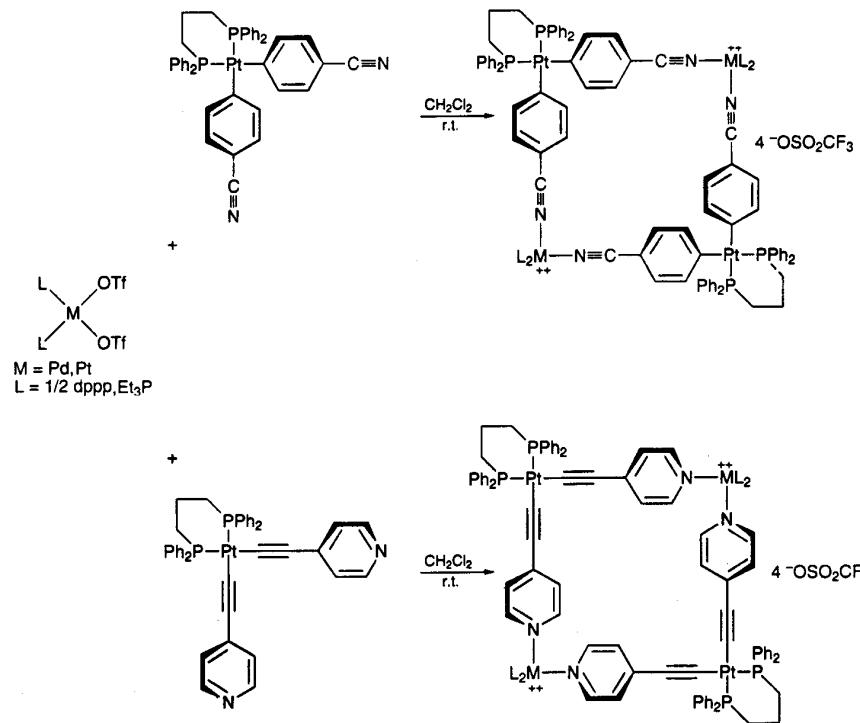


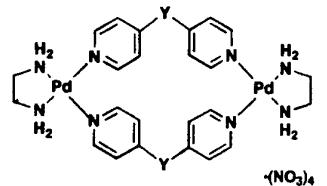


1

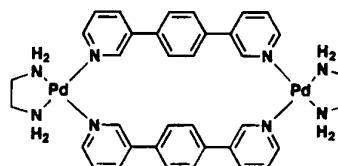
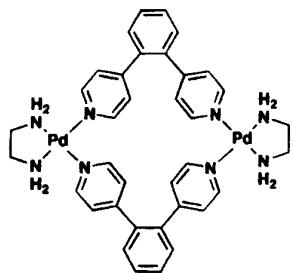
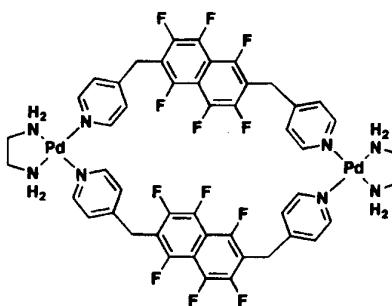
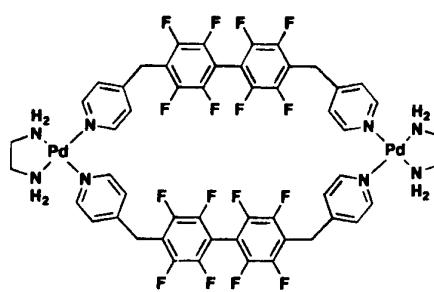
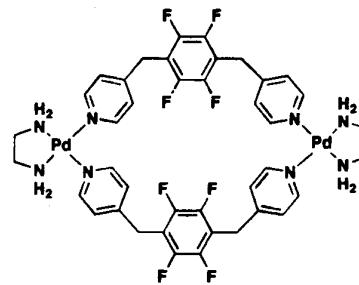
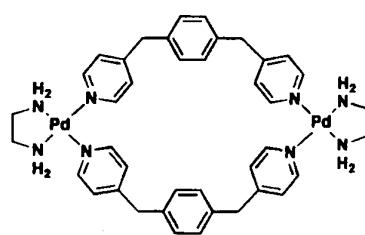
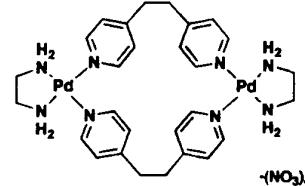
2

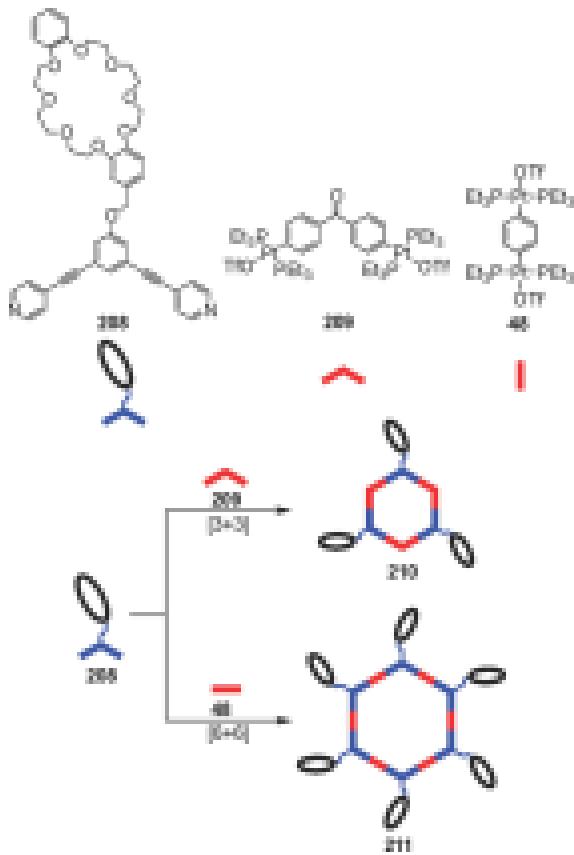
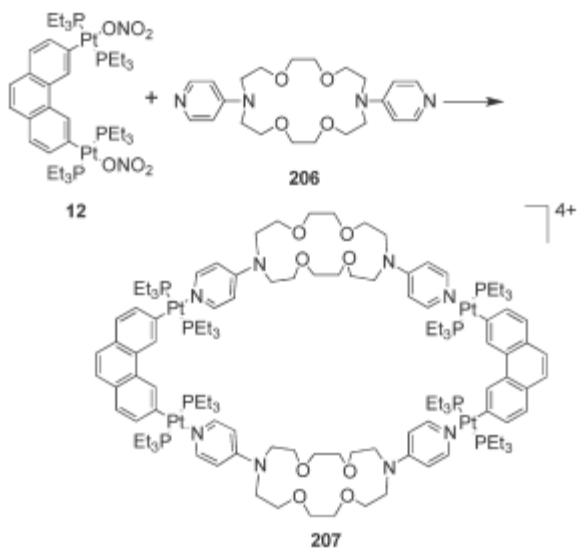
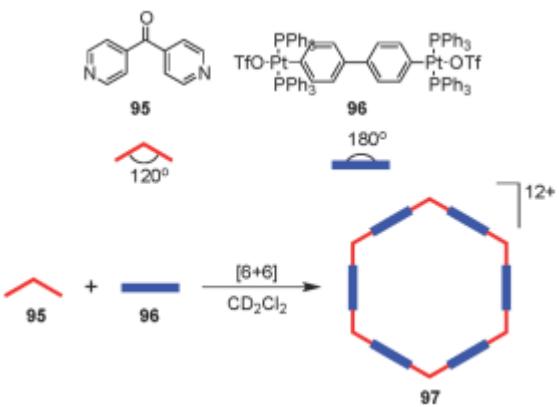
 $8 \text{ CF}_3\text{SO}_3^-$ $6 \text{ CF}_3\text{SO}_3^-$ 





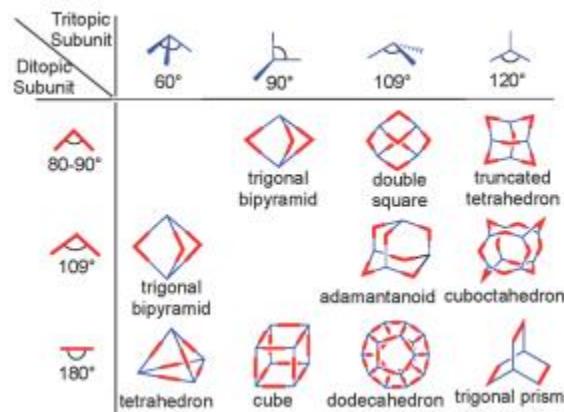
$\text{Y} = \text{CH}_2$
 $\text{Y} = \text{C}(\text{OH})_2$



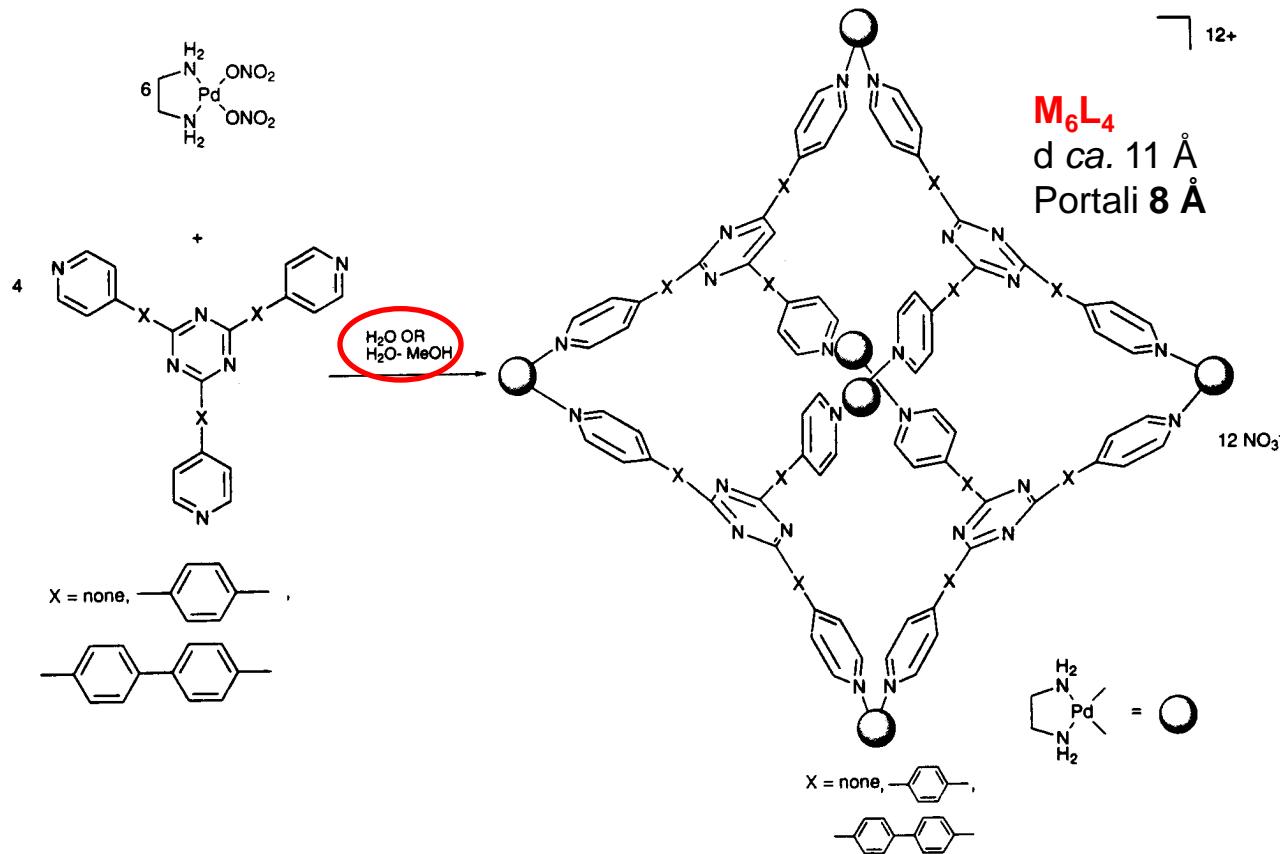


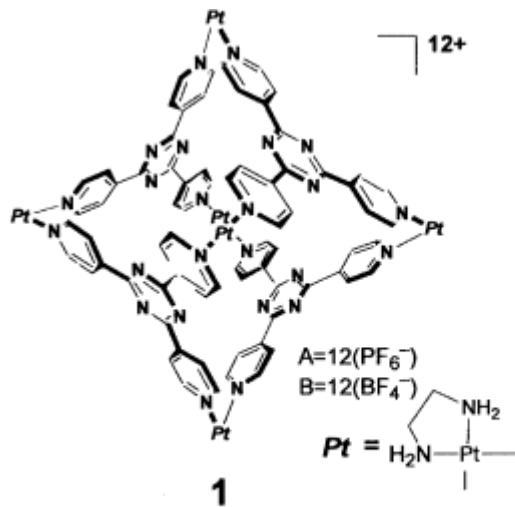
Directional Bonding Approach

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



Gabbie Molecolari





a: $(\text{C}_{84}\text{H}_{96}\text{N}_{36}\text{Pt}_6)^{12+} \cdot 12(\text{PF}_6^-)$
FW. 4519.98

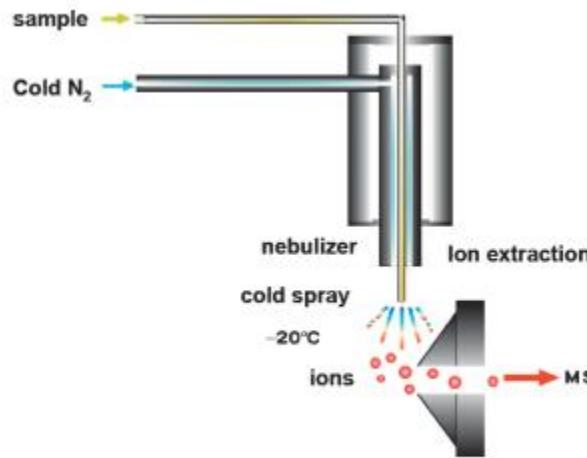


Fig. 1. Schematic illustration of the cold spray.

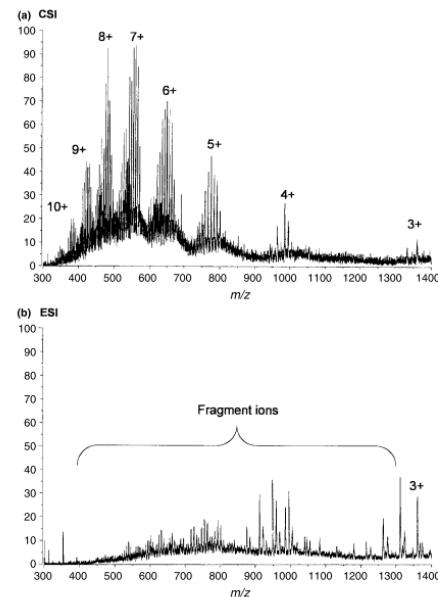
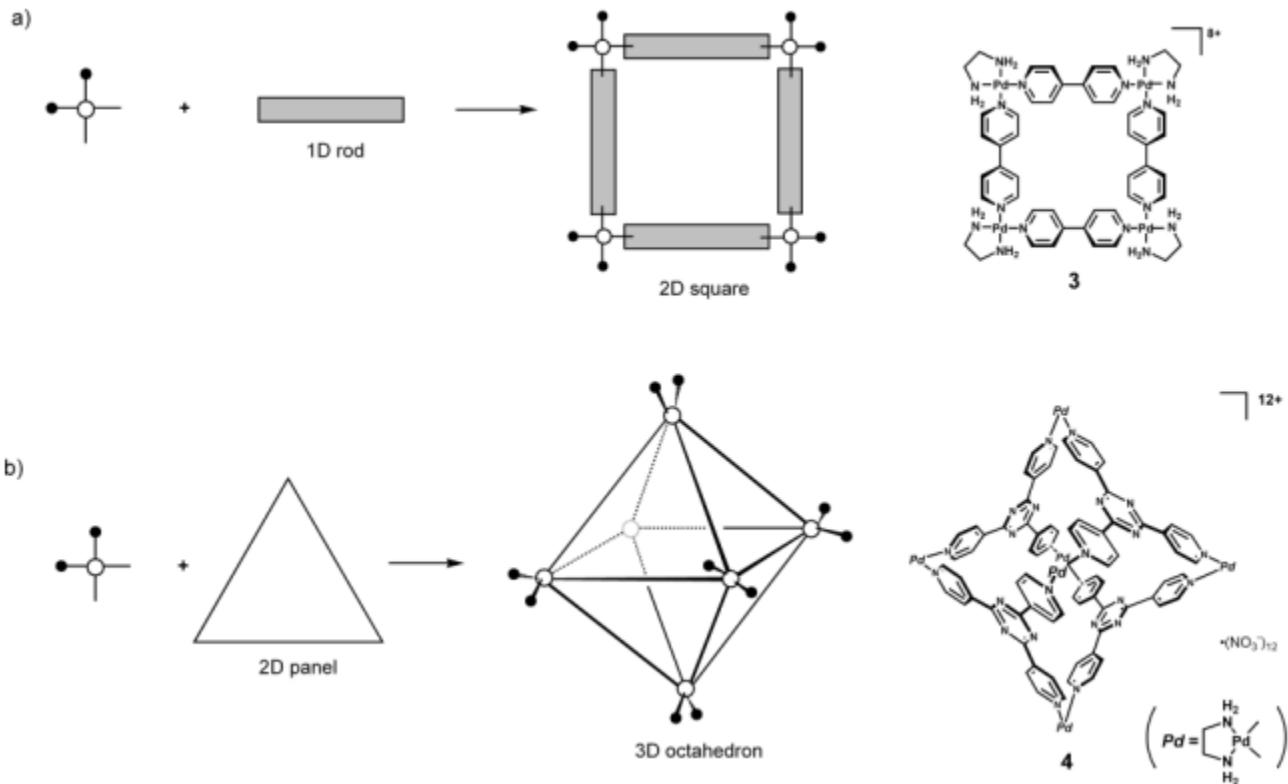
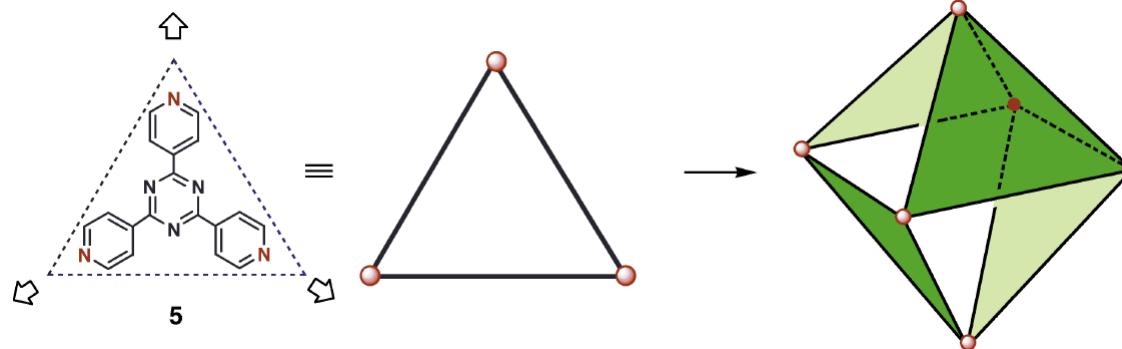
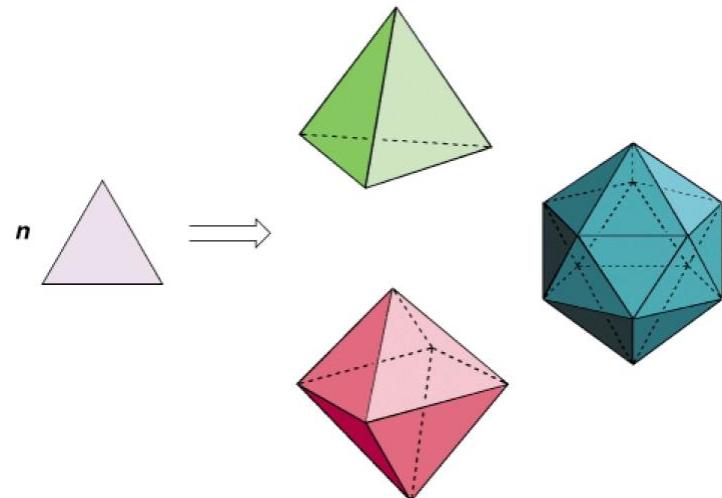
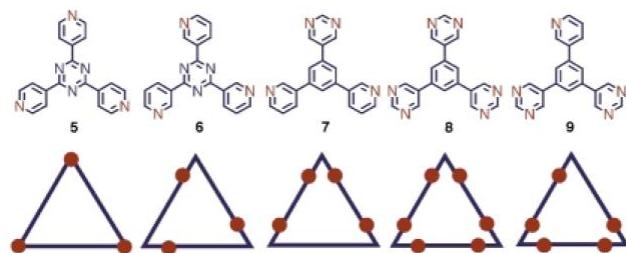


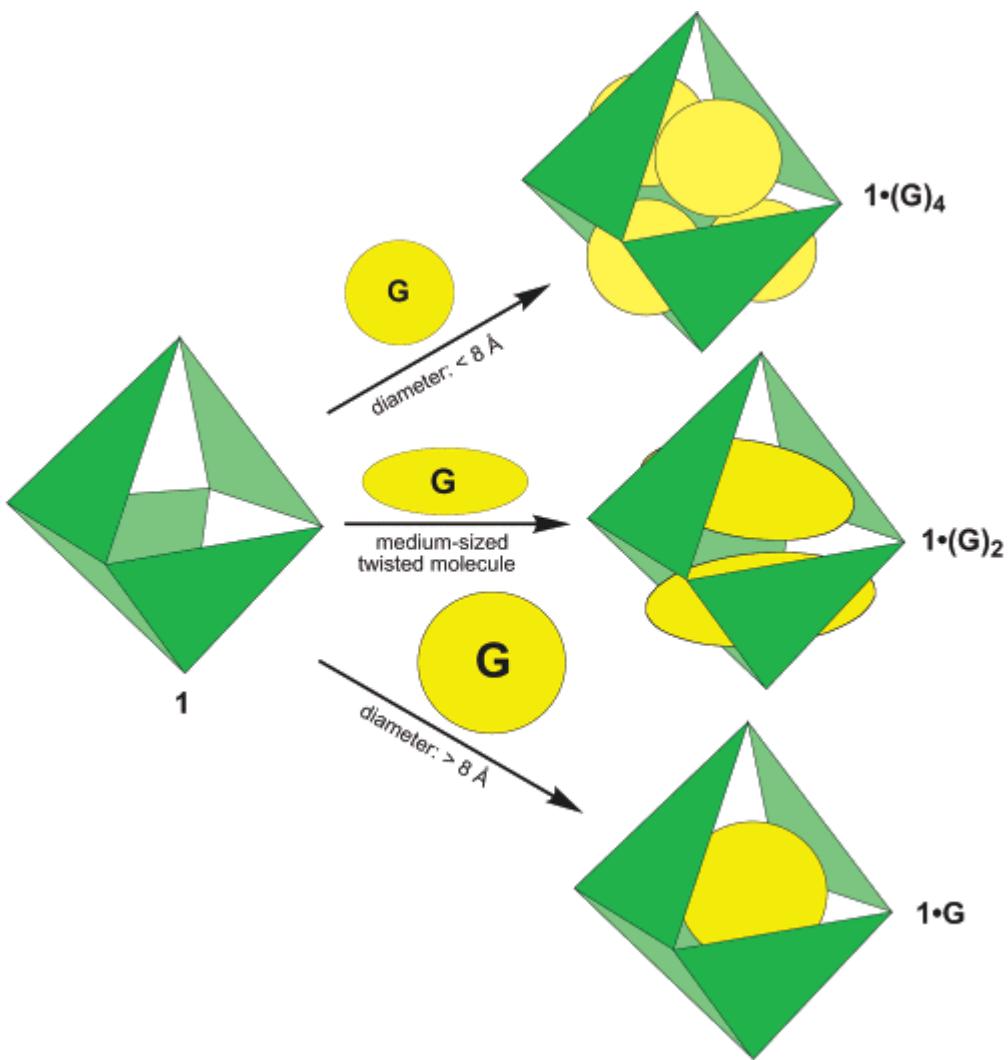
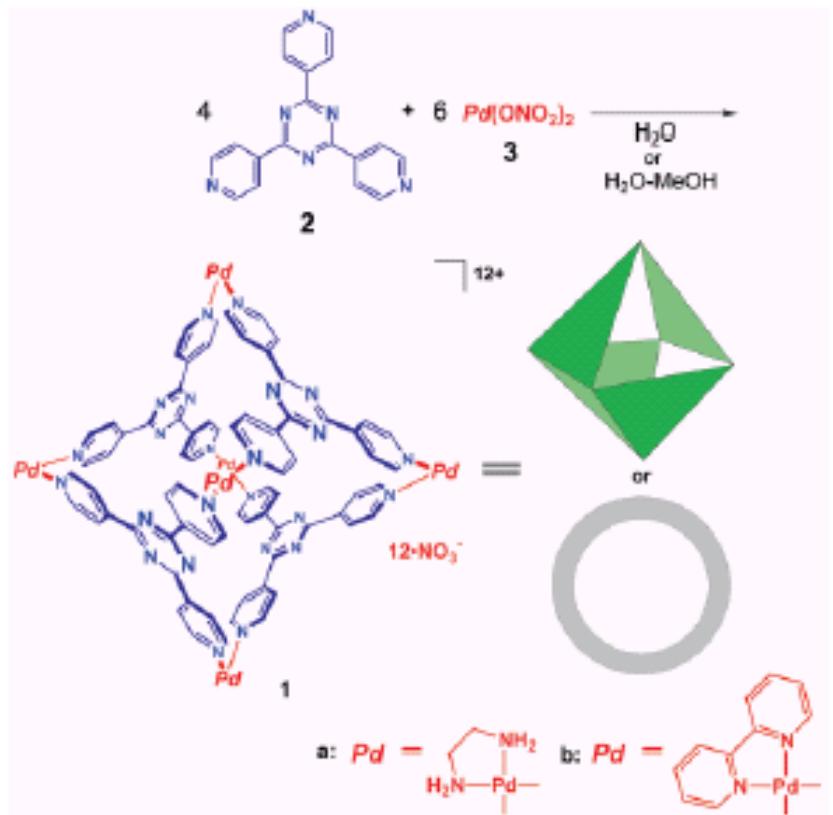
Figure 3. Comparison of (a) CSI and (b) ESI mass spectra of **1a**. Reprinted from Ref. 2 with permission from Elsevier.



Molecular Paneling

a)





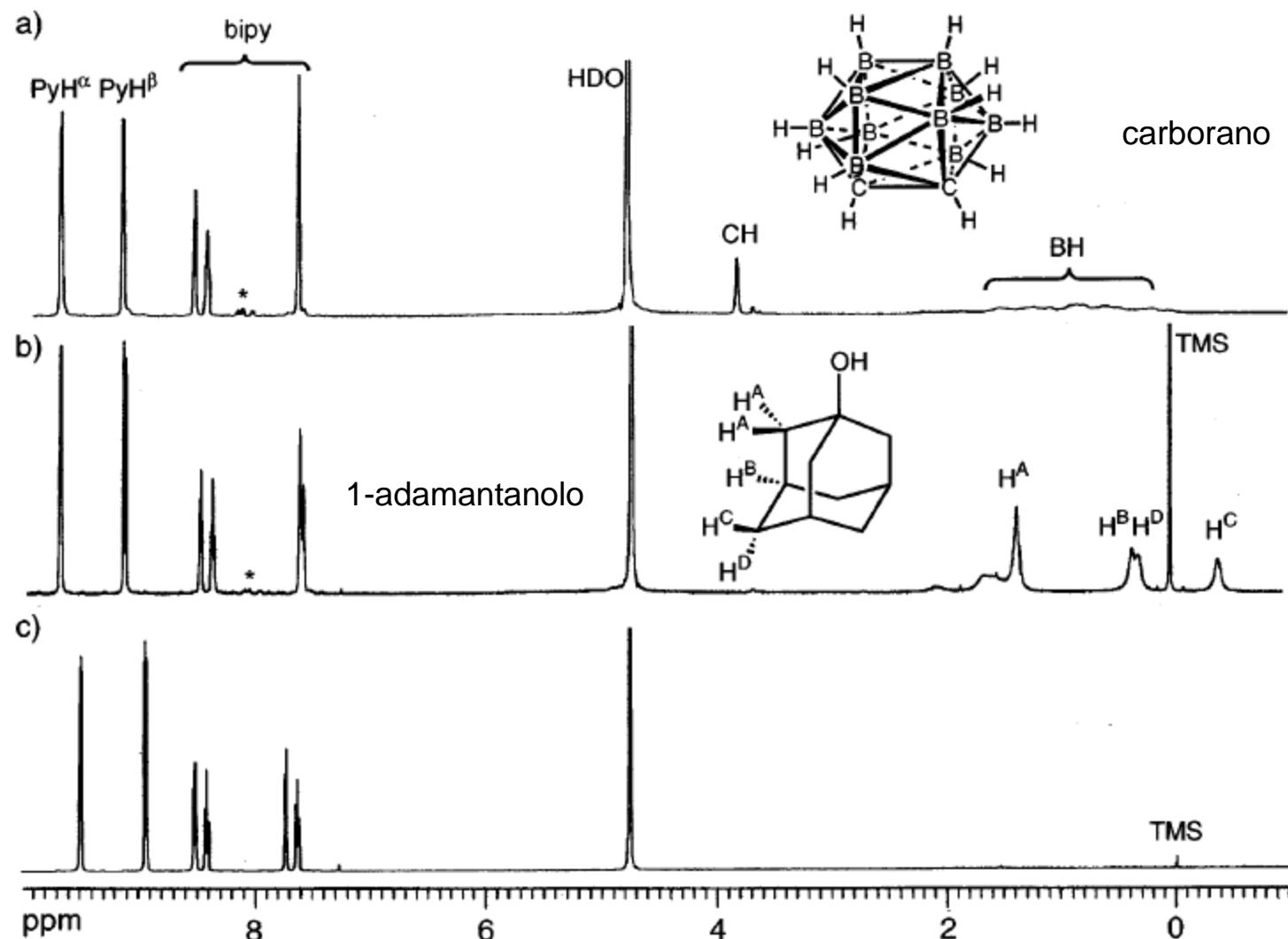
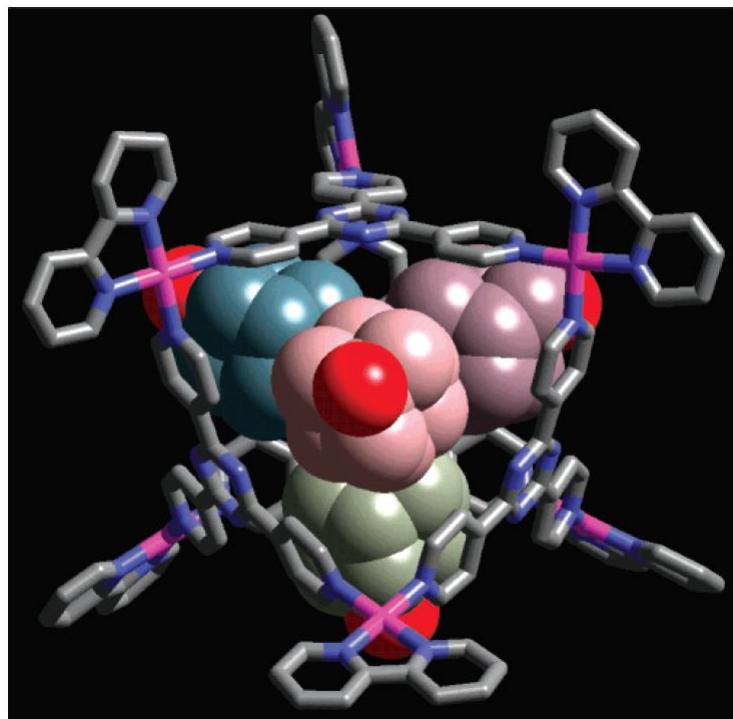
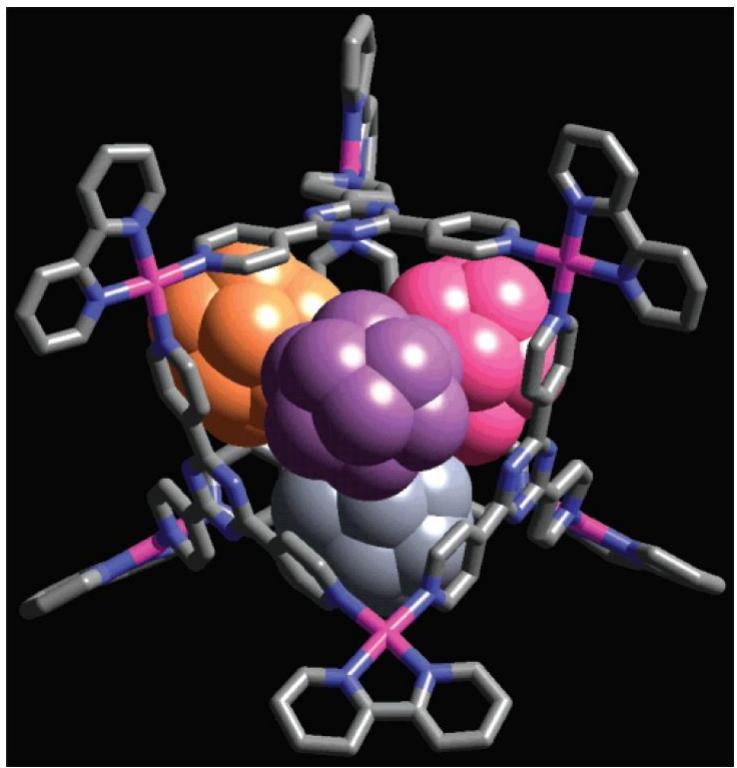
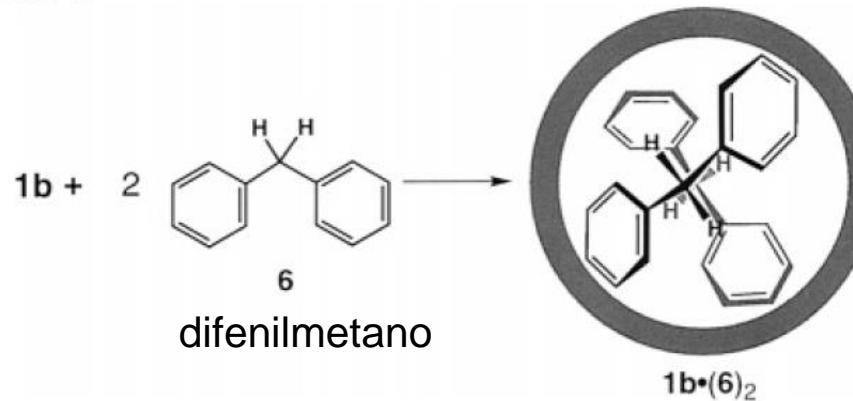


Figure 1. ^1H NMR observations of the enclathration of guest molecules in 1b. (a) 1b-(4)4. (b) 1b-(5)4. (c) Empty 1b (*: impurities).

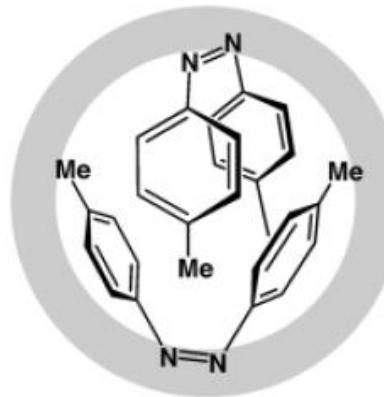


Scheme 2

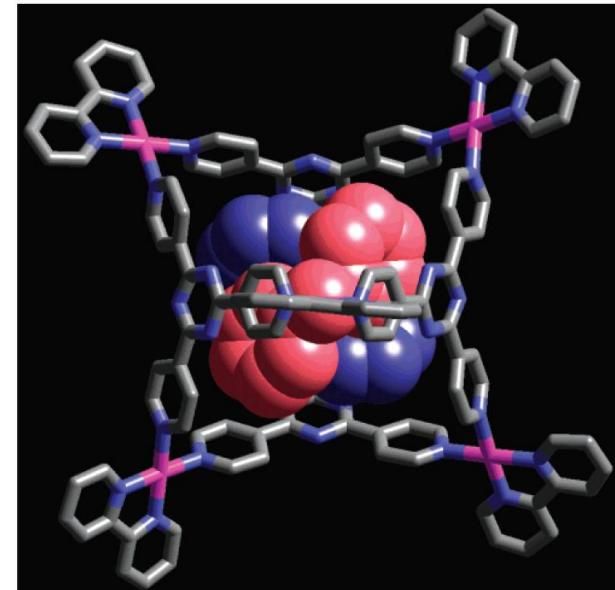


6
difenilmetano

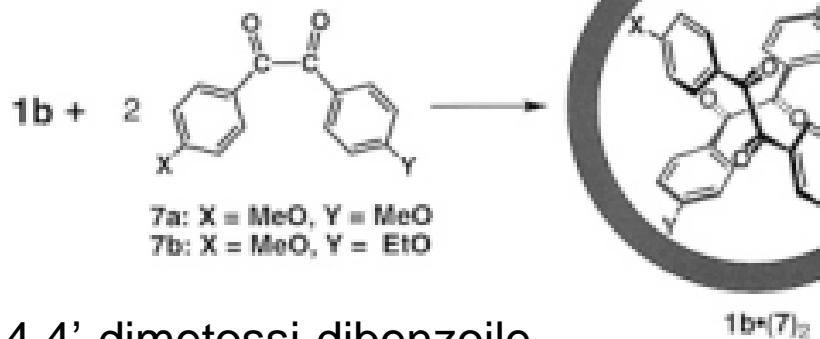
cis-azobenzene



cis-stilbene



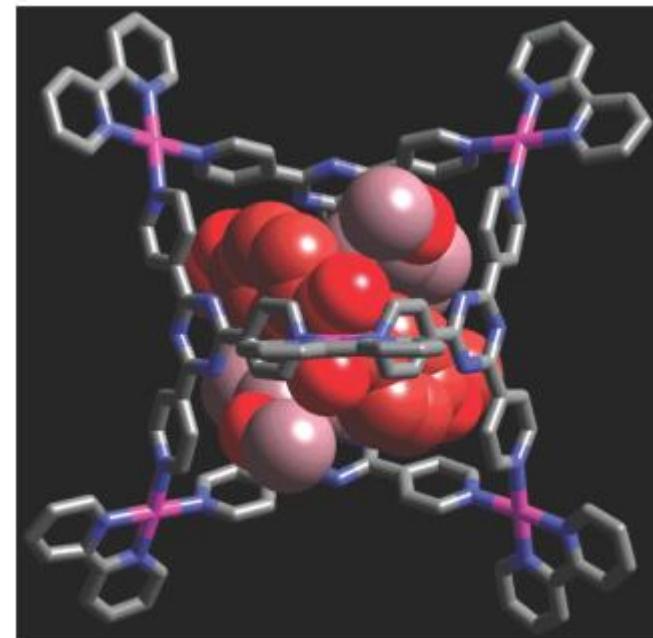
Scheme 3

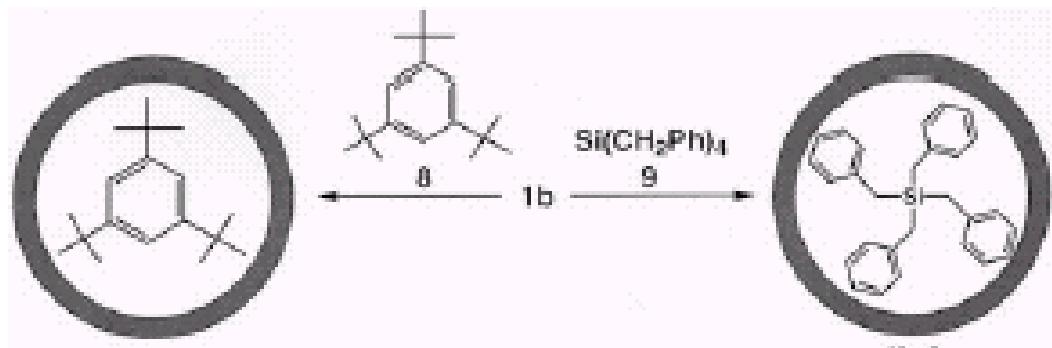


7a: X = MeO, Y = MeO

7b: X = MeO, Y = EtO

4,4'-dimetossi-dibenzoile





tri-*tert*-butylbenzene

tetrabenzilsilano

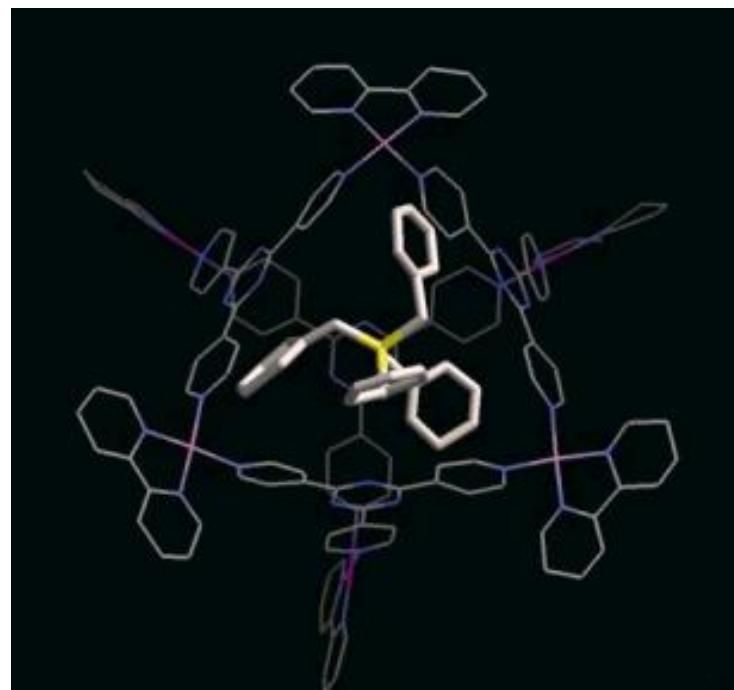
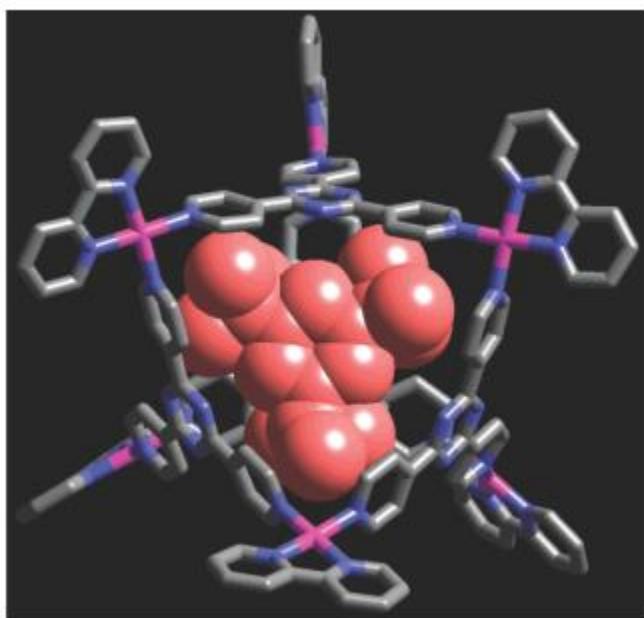
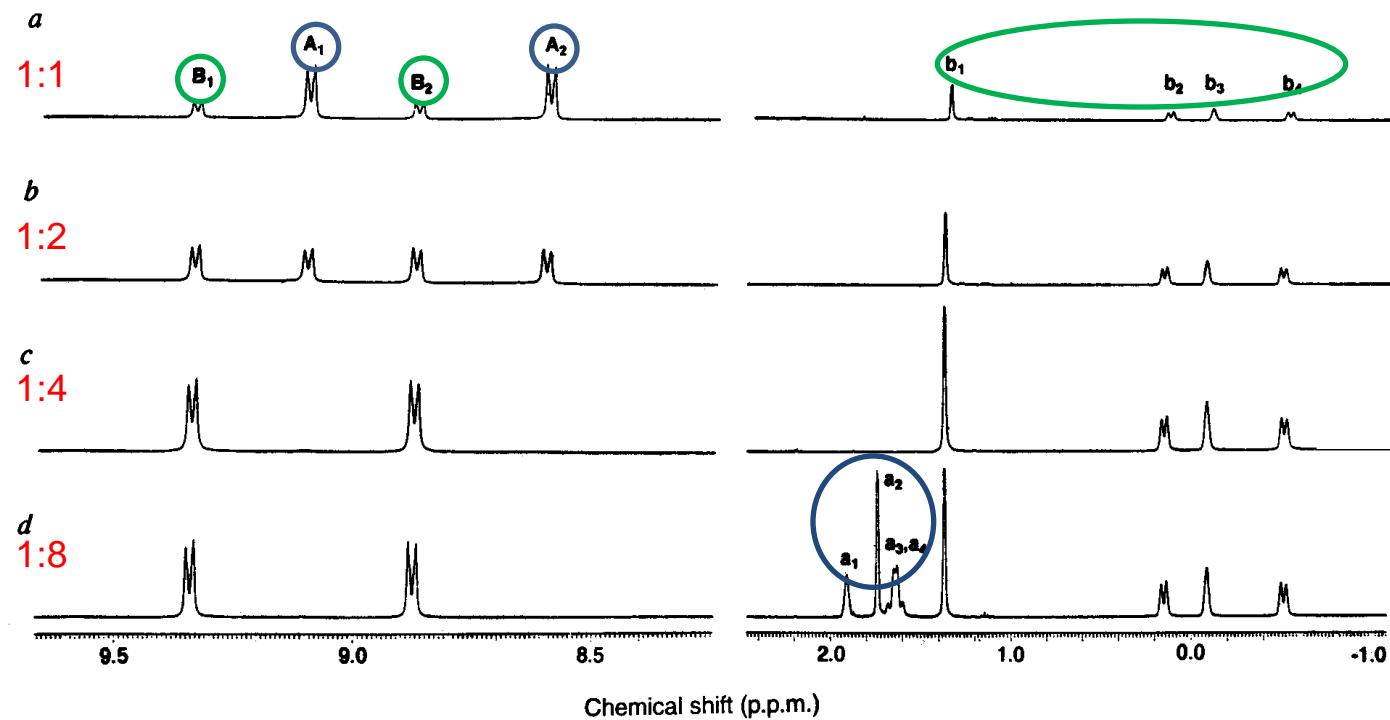
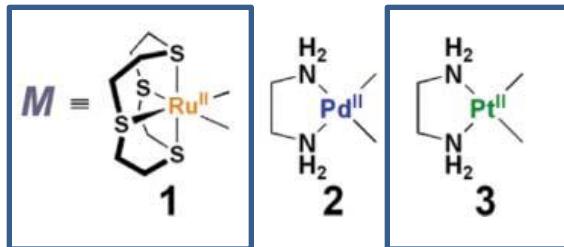
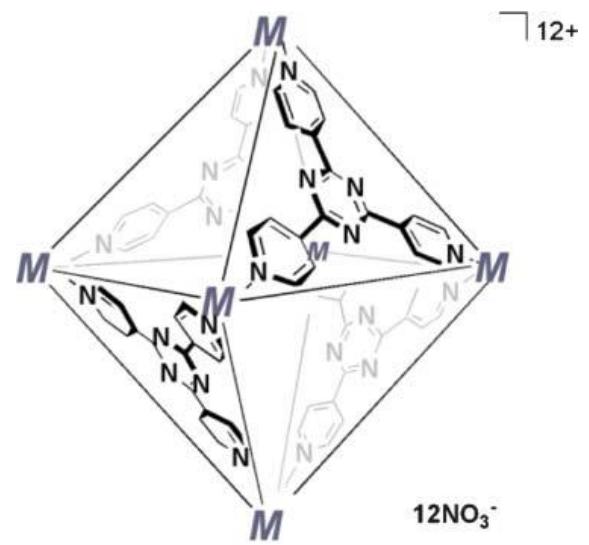


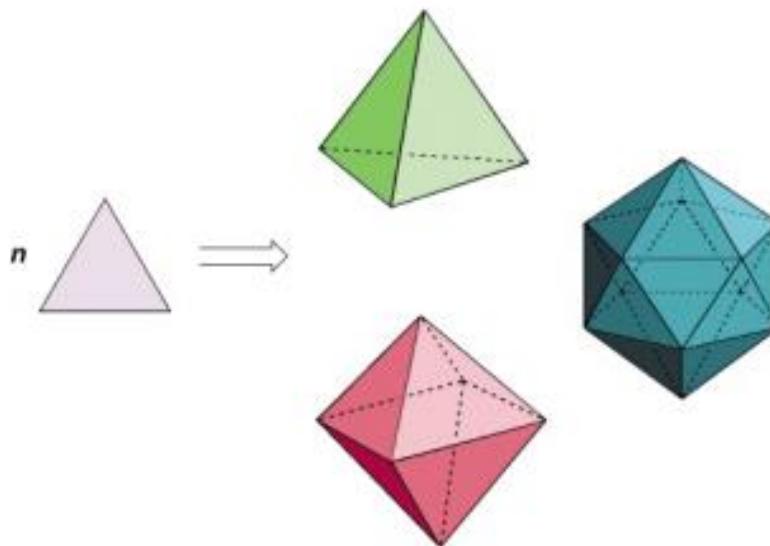
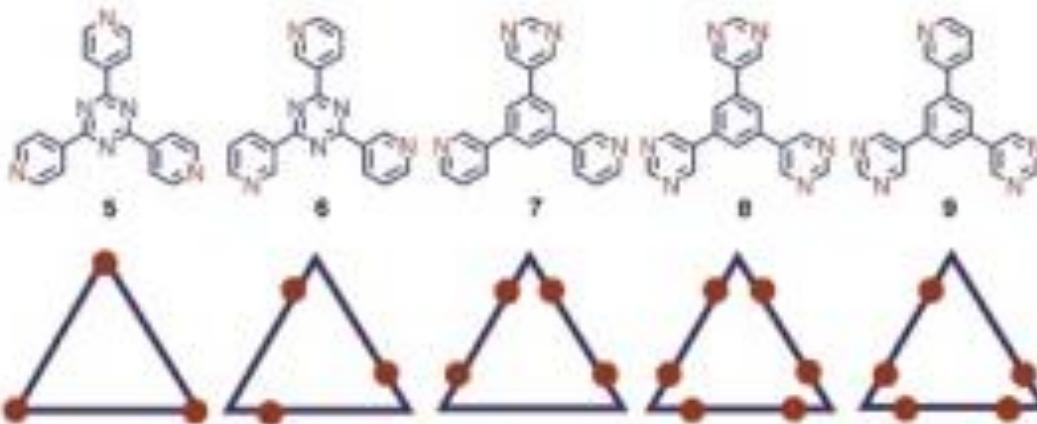
Figure 8. Crystal structure of 1b·8.

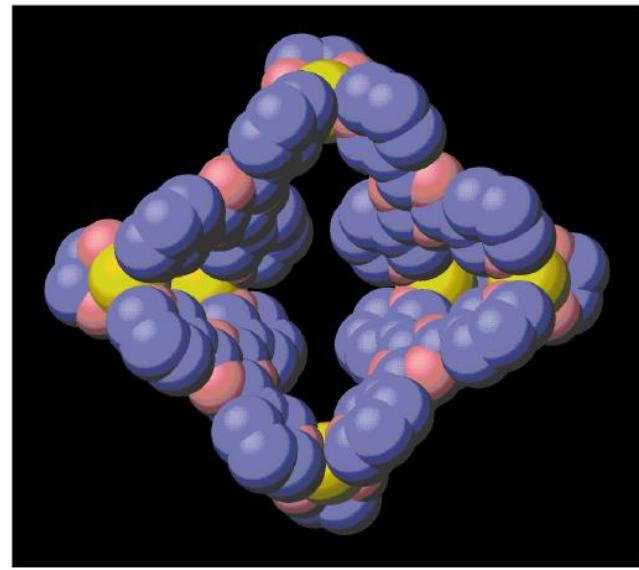
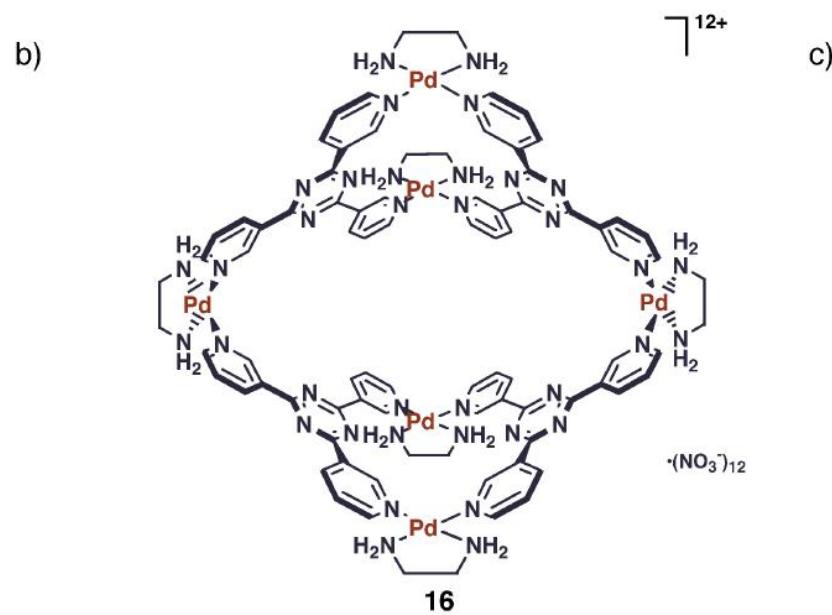
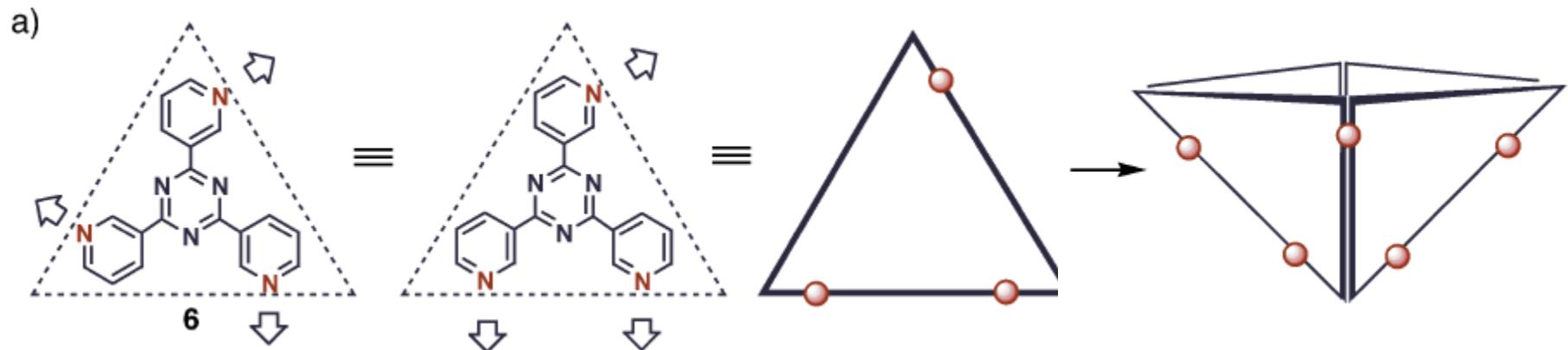


$M_6L_4/\text{adamantancarbossilato}_4$
Effetto allosterico!

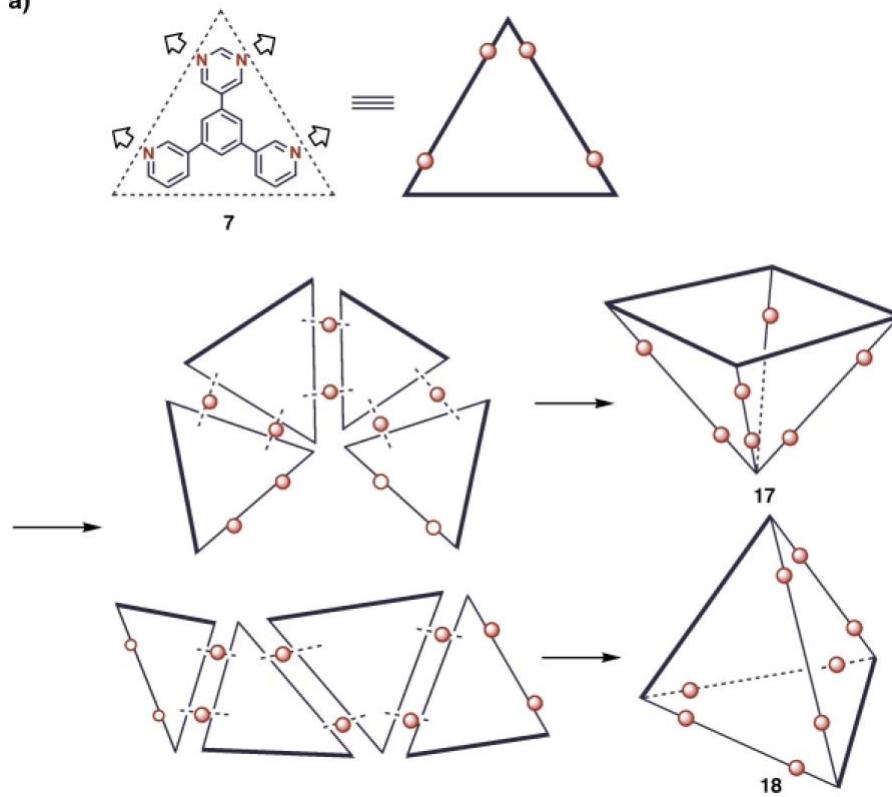


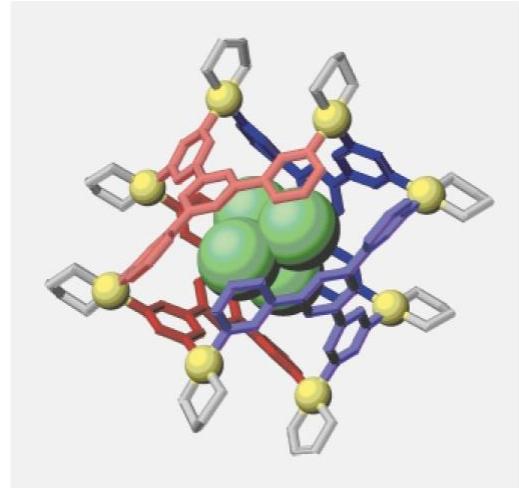
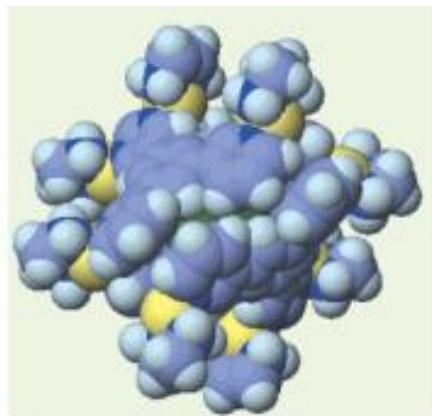
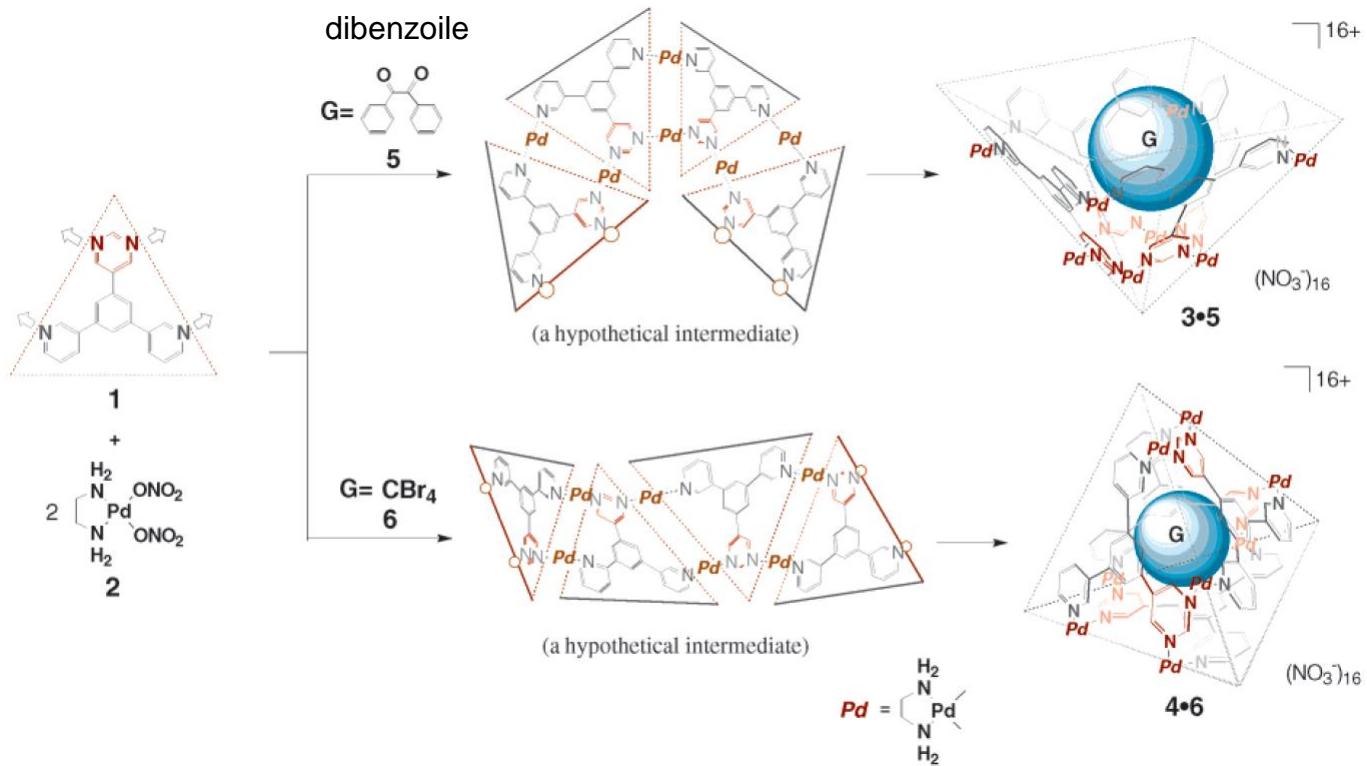
a)





a)





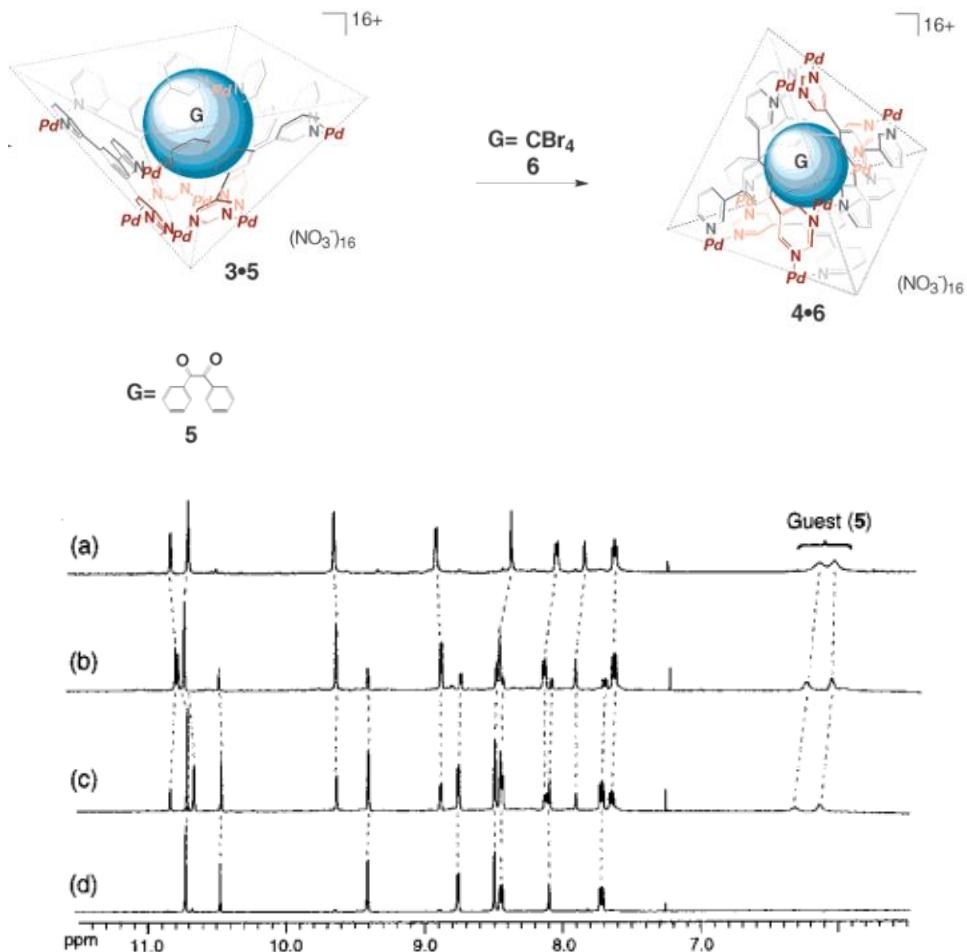
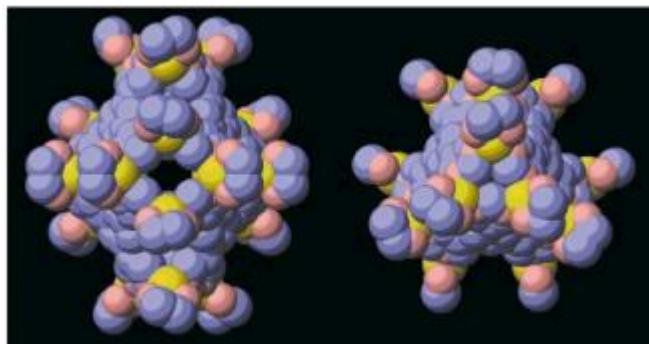
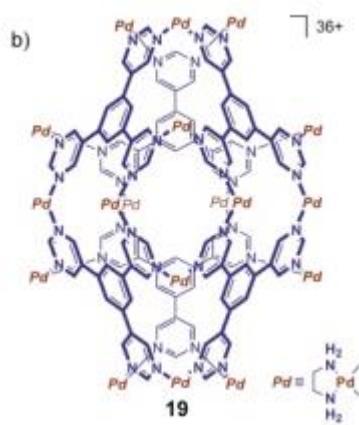


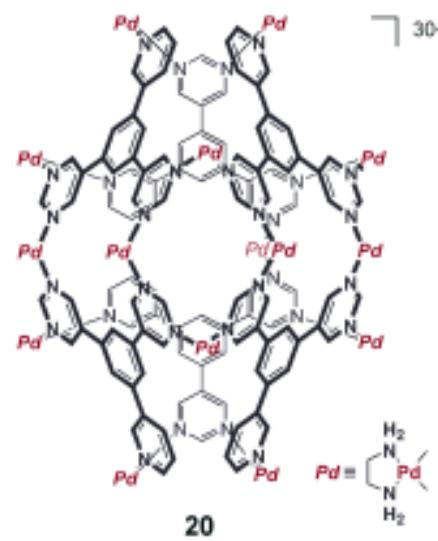
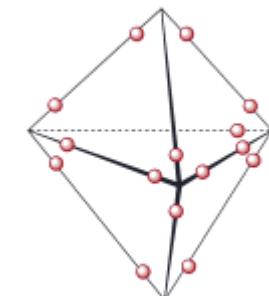
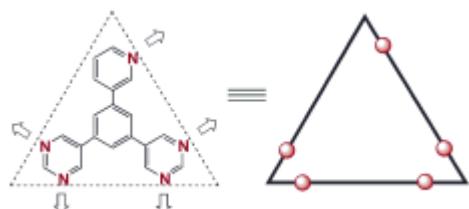
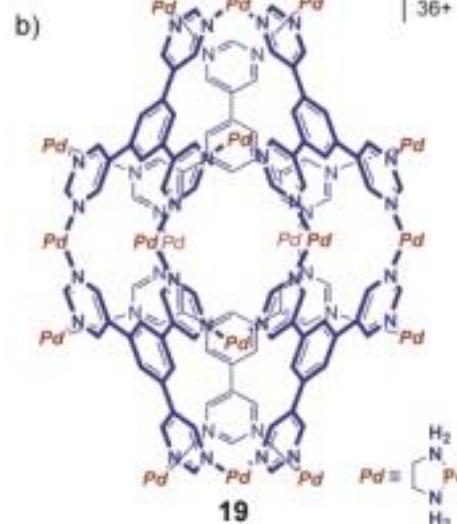
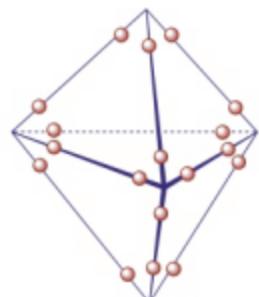
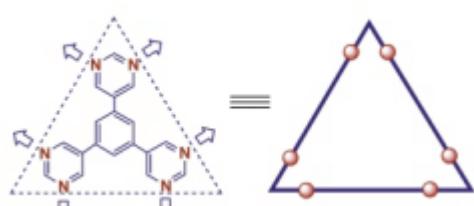
Figure 2. The ¹H NMR monitoring of reorganization process from **3·5** to **4·6** via guest exchange. (a) **3·5** complex in D₂O; (b-d) After the addition of excess amount of **6** at 25 °C ((b) 3 h, (c) 8 h, (d) 24 h). Note that free **5** is immiscible in water and, after guest exchange, becomes invisible in the spectrum.

A nanometre-sized hexahedral coordination capsule assembled from 24 components

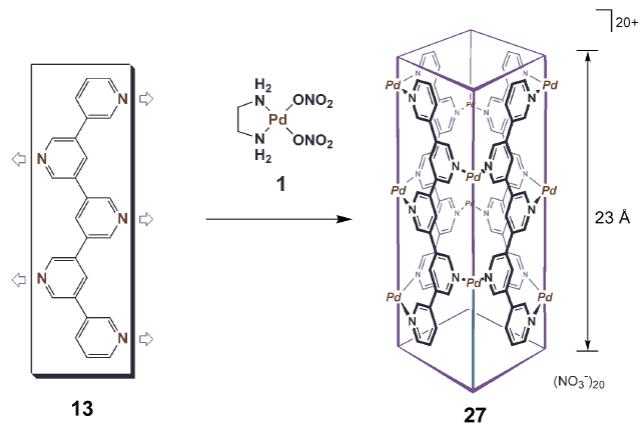
NATURE | VOL 398 | 29 APRIL 1999 | www.nature.com

Nobuhiro Takeda*, Kazuhiko Umemoto†,
Kentaro Yamaguchi‡ & Makoto Fujita*

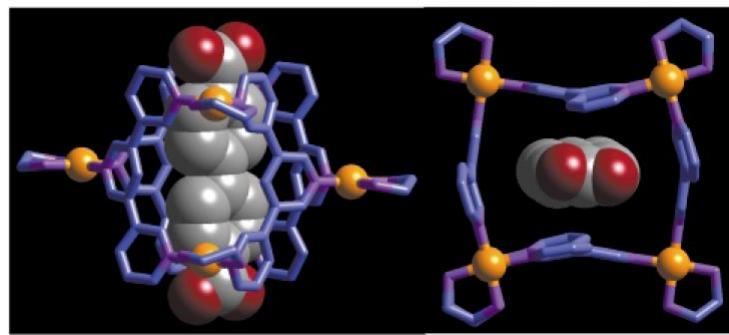
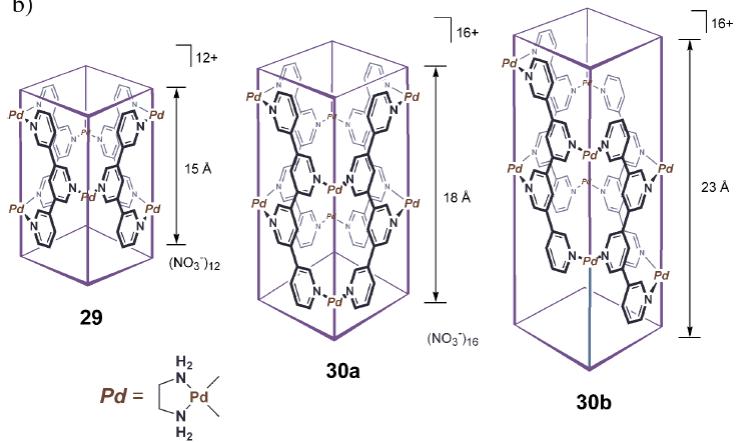


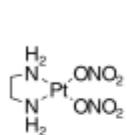


a)

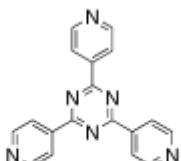


b)





1



2



3

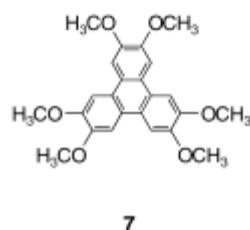
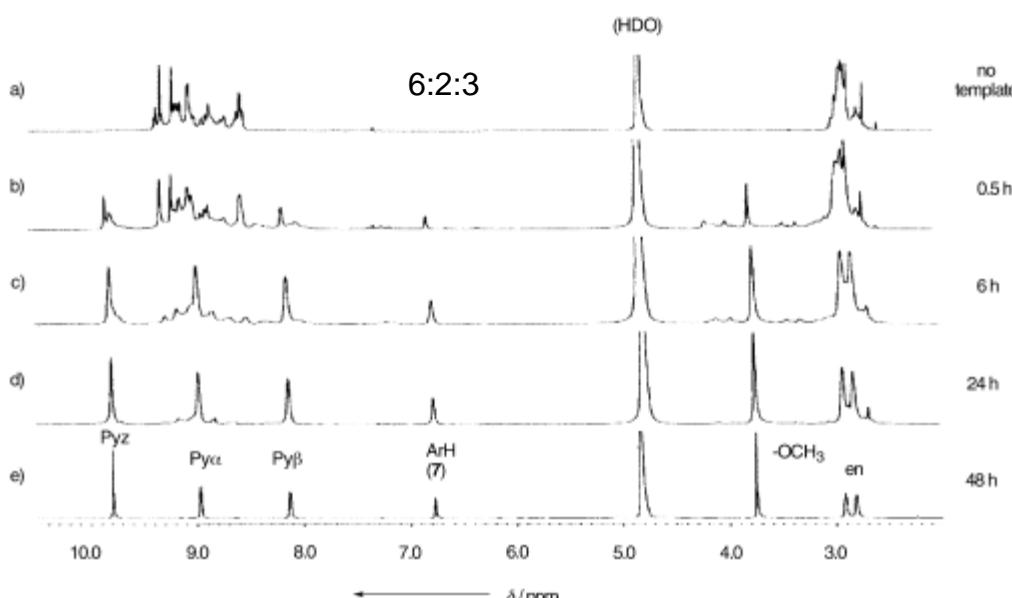
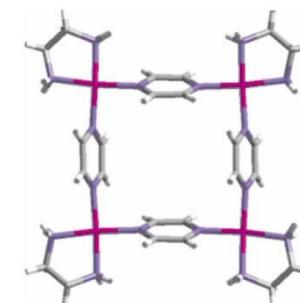
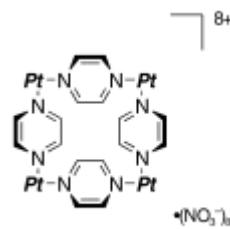
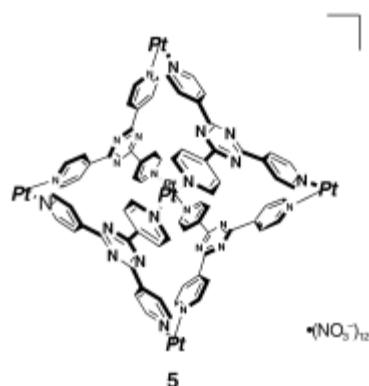
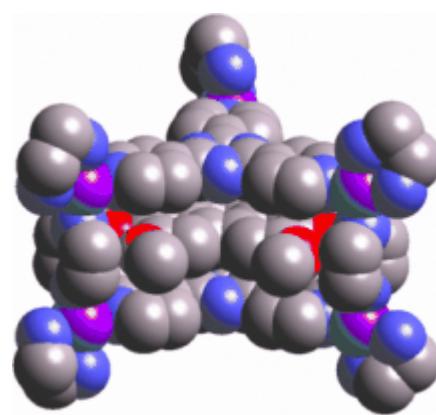
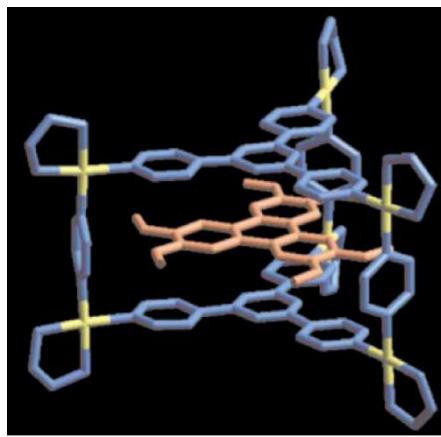
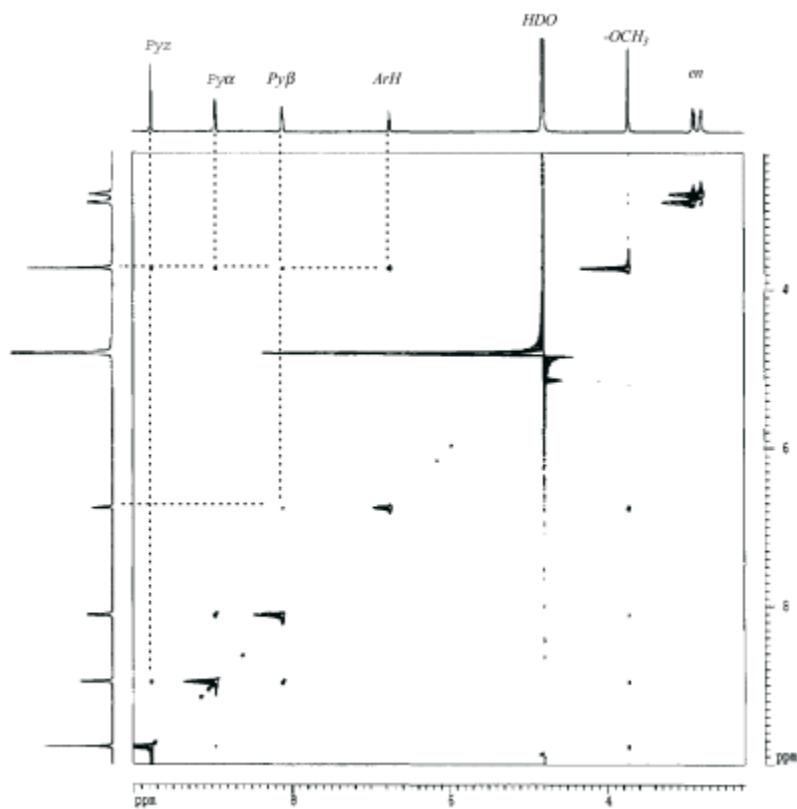


Figure 1. ^1H NMR spectra showing the guest-templated assembly of **7**–**4** complex (500 MHz, D_2O , 25 °C). a) A mixture of **1**, **2**, and **3**. Template **7** was added to this solution and the mixture was heated at 100 °C for b) 0.5 h, c) 6 h, d) 24 h, and e) 48 h. Pyz = pyrazine.





NOESY of 7c4

```

DOSY Data Parameters
S000 41.0000
E000 5
R000 1

T1 - Repetition Time(s)
2011221
1006115
5030208 4000.000 sec-1
2020000 1000.000 sec-1
1010000 500.000 sec-1
505000 250.000 sec-1
252500 125.000 sec-1
126250 62.500 sec-1
63125 31.250 sec-1
31625 15.625 sec-1
158125 7.8125 sec-1
790625 3.90625 sec-1
3953125 1.953125 sec-1
19765625 0.9765625 sec-1
98828125 0.494140625 sec-1
494140625 0.2470703125 sec-1
2470703125 0.1235351625 sec-1
1235351625 0.06176758125 sec-1
6176758125 0.030883790625 sec-1
30883790625 0.0154418953125 sec-1
154418953125 0.007720947751953125 sec-1
7720947751953125 0.003860473875976562 sec-1
3860473875976562 0.001930236937988281 sec-1
1930236937988281 0.0009651184689941406 sec-1
930236937988281 0.0004825592344970703 sec-1
4825592344970703 0.0002412796172485352 sec-1
2412796172485352 0.0001206398086242676 sec-1
1206398086242676 60.31968875 sec-1
6031968875 30.159844375 sec-1
30159844375 15.0799221875 sec-1
150799221875 7.53996109375 sec-1
753996109375 3.769980546875 sec-1
3769980546875 1.8849902734375 sec-1
18849902734375 0.94249513671875 sec-1
0.94249513671875 0.471247568359375 sec-1
0.471247568359375 0.2356237841801875 sec-1
0.2356237841801875 0.1178118920900937 sec-1
0.1178118920900937 0.05890594604504688 sec-1
0.05890594604504688 0.02945297302252344 sec-1
0.02945297302252344 0.01472648651126172 sec-1
0.01472648651126172 0.00736324325563086 sec-1
0.00736324325563086 0.00368162162781543 sec-1
0.00368162162781543 0.00184081081390771 sec-1
0.00184081081390771 0.000920405406953855 sec-1
0.000920405406953855 0.0004602027034769275 sec-1
0.0004602027034769275 0.0002301013517384637 sec-1
0.0002301013517384637 0.0001150506758692318 sec-1
0.0001150506758692318 5.75253379346159e-05 sec-1
5.75253379346159e-05 2.876266896730795e-05 sec-1
2.876266896730795e-05 1.438133448365397e-05 sec-1
1.438133448365397e-05 7.190667241832687e-06 sec-1
7.190667241832687e-06 3.595333620916344e-06 sec-1
3.595333620916344e-06 1.797666810458172e-06 sec-1
1.797666810458172e-06 8.98833405229086e-07 sec-1
8.98833405229086e-07 4.49416702614543e-07 sec-1
4.49416702614543e-07 2.247083513072717e-07 sec-1
2.247083513072717e-07 1.123541756536358e-07 sec-1
1.123541756536358e-07 5.61770878268179e-08 sec-1
5.61770878268179e-08 2.808854391340895e-08 sec-1
2.808854391340895e-08 1.404427195670447e-08 sec-1
1.404427195670447e-08 7.022135978352235e-09 sec-1
7.022135978352235e-09 3.511067989176118e-09 sec-1
3.511067989176118e-09 1.755533994588059e-09 sec-1
1.755533994588059e-09 8.777669972940295e-10 sec-1
8.777669972940295e-10 4.388834986470148e-10 sec-1
4.388834986470148e-10 2.194417493235074e-10 sec-1
2.194417493235074e-10 1.097208746617537e-10 sec-1
1.097208746617537e-10 5.486043733087687e-11 sec-1
5.486043733087687e-11 2.743021866543844e-11 sec-1
2.743021866543844e-11 1.371510933271922e-11 sec-1
1.371510933271922e-11 6.857554666359611e-12 sec-1
6.857554666359611e-12 3.428777333179806e-12 sec-1
3.428777333179806e-12 1.714388666589903e-12 sec-1
1.714388666589903e-12 8.571943332949516e-13 sec-1
8.571943332949516e-13 4.285971666474758e-13 sec-1
4.285971666474758e-13 2.142985833237379e-13 sec-1
2.142985833237379e-13 1.071492916618689e-13 sec-1
1.071492916618689e-13 5.357464583059345e-14 sec-1
5.357464583059345e-14 2.678732291529673e-14 sec-1
2.678732291529673e-14 1.339366145764837e-14 sec-1
1.339366145764837e-14 6.696830728824187e-15 sec-1
6.696830728824187e-15 3.348415364412094e-15 sec-1
3.348415364412094e-15 1.674207682206047e-15 sec-1
1.674207682206047e-15 8.371038411030237e-16 sec-1
8.371038411030237e-16 4.185519205515119e-16 sec-1
4.185519205515119e-16 2.092759602757559e-16 sec-1
2.092759602757559e-16 1.046379801378779e-16 sec-1
1.046379801378779e-16 5.231899006893895e-17 sec-1
5.231899006893895e-17 2.615949503446948e-17 sec-1
2.615949503446948e-17 1.307974751723474e-17 sec-1
1.307974751723474e-17 6.53987375861737e-18 sec-1
6.53987375861737e-18 3.269936879308687e-18 sec-1
3.269936879308687e-18 1.634968439654344e-18 sec-1
1.634968439654344e-18 8.17484219827212e-19 sec-1
8.17484219827212e-19 4.08742109913606e-19 sec-1
4.08742109913606e-19 2.04371054956803e-19 sec-1
2.04371054956803e-19 1.021855274784016e-19 sec-1
1.021855274784016e-19 5.10927637392008e-20 sec-1
5.10927637392008e-20 2.55463818696004e-20 sec-1
2.55463818696004e-20 1.27731909348002e-20 sec-1
1.27731909348002e-20 6.3865954674001e-21 sec-1
6.3865954674001e-21 3.19329773370005e-21 sec-1
3.19329773370005e-21 1.596648866850025e-21 sec-1
1.596648866850025e-21 7.983244334250125e-22 sec-1
7.983244334250125e-22 3.991622167125062e-22 sec-1
3.991622167125062e-22 1.995811083562531e-22 sec-1
1.995811083562531e-22 9.979055417812655e-23 sec-1
9.979055417812655e-23 4.989527708906327e-23 sec-1
4.989527708906327e-23 2.494763854453164e-23 sec-1
2.494763854453164e-23 1.247381927226582e-23 sec-1
1.247381927226582e-23 6.23690963613291e-24 sec-1
6.23690963613291e-24 3.118454818066455e-24 sec-1
3.118454818066455e-24 1.559227409033227e-24 sec-1
1.559227409033227e-24 7.796137045166137e-25 sec-1
7.796137045166137e-25 3.898068522583068e-25 sec-1
3.898068522583068e-25 1.949034261291534e-25 sec-1
1.949034261291534e-25 9.74517130645767e-26 sec-1
9.74517130645767e-26 4.872585653228835e-26 sec-1
4.872585653228835e-26 2.436292826614417e-26 sec-1
2.436292826614417e-26 1.218146413307208e-26 sec-1
1.218146413307208e-26 6.09073206653604e-27 sec-1
6.09073206653604e-27 3.04536603326802e-27 sec-1
3.04536603326802e-27 1.52268301663401e-27 sec-1
1.52268301663401e-27 7.61341508317005e-28 sec-1
7.61341508317005e-28 3.806707541585025e-28 sec-1
3.806707541585025e-28 1.903353770792512e-28 sec-1
1.903353770792512e-28 9.51676885396256e-29 sec-1
9.51676885396256e-29 4.75838442748128e-29 sec-1
4.75838442748128e-29 2.37919221374064e-29 sec-1
2.37919221374064e-29 1.18959610687032e-29 sec-1
1.18959610687032e-29 5.9479805343516e-30 sec-1
5.9479805343516e-30 2.9739902671758e-30 sec-1
2.9739902671758e-30 1.4869951335879e-30 sec-1
1.4869951335879e-30 7.4349756679395e-31 sec-1
7.4349756679395e-31 3.71748783396975e-31 sec-1
3.71748783396975e-31 1.858743917984875e-31 sec-1
1.858743917984875e-31 9.29371958992437e-32 sec-1
9.29371958992437e-32 4.646859794962185e-32 sec-1
4.646859794962185e-32 2.323429897481092e-32 sec-1
2.323429897481092e-32 1.161714948740546e-32 sec-1
1.161714948740546e-32 5.80857474370273e-33 sec-1
5.80857474370273e-33 2.904287371851365e-33 sec-1
2.904287371851365e-33 1.452143685925682e-33 sec-1
1.452143685925682e-33 7.26071842962841e-34 sec-1
7.26071842962841e-34 3.630359214814205e-34 sec-1
3.630359214814205e-34 1.815179607407102e-34 sec-1
1.815179607407102e-34 9.07589803703551e-35 sec-1
9.07589803703551e-35 4.537949018517755e-35 sec-1
4.537949018517755e-35 2.268974509258877e-35 sec-1
2.268974509258877e-35 1.134487254629438e-35 sec-1
1.134487254629438e-35 5.67243627314719e-36 sec-1
5.67243627314719e-36 2.836218136573595e-36 sec-1
2.836218136573595e-36 1.418109068286797e-36 sec-1
1.418109068286797e-36 7.09054534143398e-37 sec-1
7.09054534143398e-37 3.54527267071699e-37 sec-1
3.54527267071699e-37 1.772636335358495e-37 sec-1
1.772636335358495e-37 8.86318167679247e-38 sec-1
8.86318167679247e-38 4.431590838396235e-38 sec-1
4.431590838396235e-38 2.215795419198118e-38 sec-1
2.215795419198118e-38 1.107897709599059e-38 sec-1
1.107897709599059e-38 5.539488547995295e-39 sec-1
5.539488547995295e-39 2.769744273997647e-39 sec-1
2.769744273997647e-39 1.384872136998824e-39 sec-1
1.384872136998824e-39 6.92436068499412e-40 sec-1
6.92436068499412e-40 3.46218034249706e-40 sec-1
3.46218034249706e-40 1.73109017124853e-40 sec-1
1.73109017124853e-40 8.65545085624265e-41 sec-1
8.65545085624265e-41 4.327725428121325e-41 sec-1
4.327725428121325e-41 2.163862714060662e-41 sec-1
2.163862714060662e-41 1.081931357030331e-41 sec-1
1.081931357030331e-41 5.409656785150156e-42 sec-1
5.409656785150156e-42 2.704828392575078e-42 sec-1
2.704828392575078e-42 1.352414196287539e-42 sec-1
1.352414196287539e-42 6.762070981437695e-43 sec-1
6.762070981437695e-43 3.381035490718847e-43 sec-1
3.381035490718847e-43 1.700517745359424e-43 sec-1
1.700517745359424e-43 8.49758872679712e-44 sec-1
8.49758872679712e-44 4.24879436339856e-44 sec-1
4.24879436339856e-44 2.12439718169928e-44 sec-1
2.12439718169928e-44 1.06219859084964e-44 sec-1
1.06219859084964e-44 5.3109929542492e-45 sec-1
5.3109929542492e-45 2.6554964771246e-45 sec-1
2.6554964771246e-45 1.3277482385623e-45 sec-1
1.3277482385623e-45 6.6387411928116e-46 sec-1
6.6387411928116e-46 3.3193705964058e-46 sec-1
3.3193705964058e-46 1.6596852982029e-46 sec-1
1.6596852982029e-46 8.2984264910145e-47 sec-1
8.2984264910145e-47 4.14921324550725e-47 sec-1
4.14921324550725e-47 2.07460662275363e-47 sec-1
2.07460662275363e-47 1.03730331137681e-47 sec-1
1.03730331137681e-47 5.18651655688405e-48 sec-1
5.18651655688405e-48 2.593258278442025e-48 sec-1
2.593258278442025e-48 1.306629139221013e-48 sec-1
1.306629139221013e-48 6.533145696105065e-49 sec-1
6.533145696105065e-49 3.266572848052532e-49 sec-1
3.266572848052532e-49 1.633286424026266e-49 sec-1
1.633286424026266e-49 8.16643212013133e-50 sec-1
8.16643212013133e-50 4.083216060065665e-50 sec-1
4.083216060065665e-50 2.041608030032832e-50 sec-1
2.041608030032832e-50 1.020804015016416e-50 sec-1
1.020804015016416e-50 5.10402007500808e-51 sec-1
5.10402007500808e-51 2.55201003750404e-51 sec-1
2.55201003750404e-51 1.27600501875202e-51 sec-1
1.27600501875202e-51 6.3800250093801e-52 sec-1
6.3800250093801e-52 3.19001250469005e-52 sec-1
3.19001250469005e-52 1.595006252345025e-52 sec-1
1.595006252345025e-52 7.975031261725125e-53 sec-1
7.975031261725125e-53 3.897515630862562e-53 sec-1
3.897515630862562e-53 1.948757815431281e-53 sec-1
1.948757815431281e-53 9.743789077156405e-54 sec-1
9.743789077156405e-54 4.871894538578203e-54 sec-1
4.871894538578203e-54 2.435947269289101e-54 sec-1
2.435947269289101e-54 1.218473634644551e-54 sec-1
1.218473634644551e-54 6.092368173222755e-55 sec-1
6.092368173222755e-55 3.046184086611377e-55 sec-1
3.046184086611377e-55 1.523092043305688e-55 sec-1
1.523092043305688e-55 7.61546021652844e-56 sec-1
7.61546021652844e-56 3.80773010826422e-56 sec-1
3.80773010826422e-56 1.90386505413211e-56 sec-1
1.90386505413211e-56 9.51932527066055e-57 sec-1
9.51932527066055e-57 4.759662635330275e-57 sec-1
4.759662635330275e-57 2.379831317665138e-57 sec-1
2.379831317665138e-57 1.189915658832569e-57 sec-1
1.189915658832569e-57 5.949578294162845e-58 sec-1
5.949578294162845e-58 2.974789147081422e-58 sec-1
2.974789147081422e-58 1.487394573540711e-58 sec-1
1.487394573540711e-58 7.437972867703555e-59 sec-1
7.437972867703555e-59 3.718986433851777e-59 sec-1
3.718986433851777e-59 1.859493216925888e-59 sec-1
1.859493216925888e-59 9.29746608462944e-60 sec-1
9.29746608462944e-60 4.64748304231472e-60 sec-1
4.64748304231472e-60 2.32374152115736e-60 sec-1
2.32374152115736e-60 1.16187076057868e-60 sec-1
1.16187076057868e-60 5.80935380289034e-61 sec-1
5.80935380289034e-61 2.90467690144517e-61 sec-1
2.90467690144517e-61 1.45233845072258e-61 sec-1
1.45233845072258e-61 7.2626922536129e-62 sec-1
7.2626922536129e-62 3.63134612680645e-62 sec-1
3.63134612680645e-62 1.81567306340323e-62 sec-1
1.81567306340323e-62 9.07836531701617e-63 sec-1
9.07836531701617e-63 4.53718265850809e-63 sec-1
4.53718265850809e-63 2.26890132925404e-63 sec-1
2.26890132925404e-63 1.13445066462702e-63 sec-1
1.13445066462702e-63 5.67225332313501e-64 sec-1
5.67225332313501e-64 2.83612666156751e-64 sec-1
2.83612666156751e-64 1.41806333078375e-64 sec-1
1.41806333078375e-64 7.09031665391875e-65 sec-1
7.09031665391875e-65 3.54515832695938e-65 sec-1
3.54515832695938e-65 1.77257916347969e-65 sec-1
1.77257916347969e-65 8.8629958172984e-66 sec-1
8.8629958172984e-66 4.4315391986492e-66 sec-1
4.4315391986492e-66 2.2152795993246e-66 sec-1
2.2152795993246e-66 1.1071397996623e-66 sec-1
1.1071397996623e-66 5.5396989983316e-67 sec-1
5.5396989983316e-67 2.7698494991658e-67 sec-1
2.7698494991658e-67 1.3844747495829e-67 sec-1
1.3844747495829e-67 6.9233737479145e-68 sec-1
6.9233737479145e-68 3.4617868739572e-68 sec-1
3.4617868739572e-68 1.7317934369786e-68 sec-1
1.7317934369786e-68 8.658967184893e-69 sec-1
8.658967184893e-69 4.2494935924468e-69 sec-1
4.2494935924468e-69 2.1244967962234e-69 sec-1
2.1244967962234e-69 1.0622483981117e-69 sec-1
1.0622483981117e-69 5.3112419995558e-70 sec-1
5.3112419995558e-70 2.6556209997778e-70 sec-1
2.6556209997778e-70 1.3278104998889e-70 sec-1
1.3278104998889e-70 6.6390524999445e-71 sec-1
6.6390524999445e-71 3.3195262499722e-71 sec-1
3.3195262499722e-71 1.6597631249861e-71 sec-1
1.6597631249861e-71 8.2990265624805e-72 sec-1
8.2990265624805e-72 4.1498132812402e-72 sec-1
4.1498132812402e-72 2.0749066406201e-72 sec-1
2.0749066406201e-72 1.0374533203100e-72 sec-1
1.0374533203100e-72 5.1872666015500e-73 sec-1
5.1872666015500e-73 2.5536333007750e-73 sec-1
2.5536333007750e-73 1.27681665
```

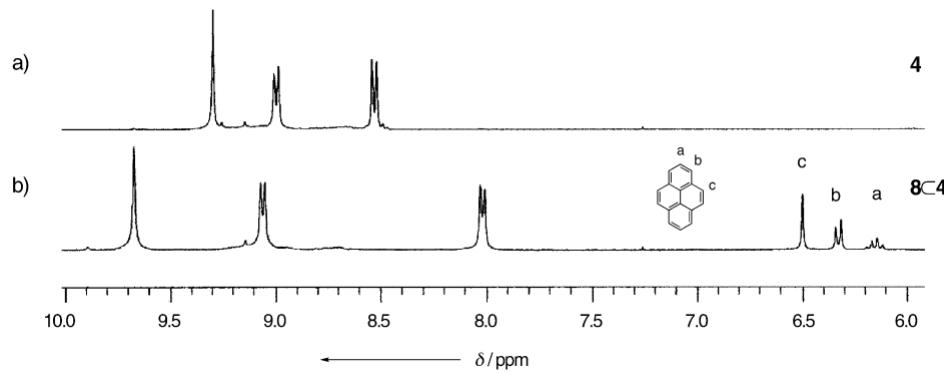
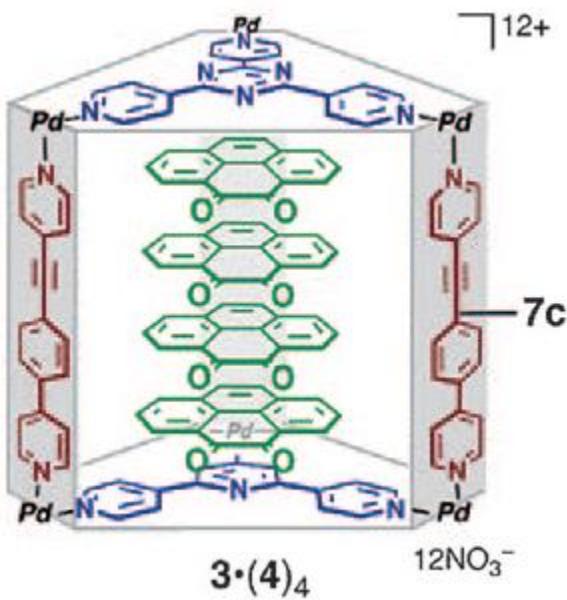
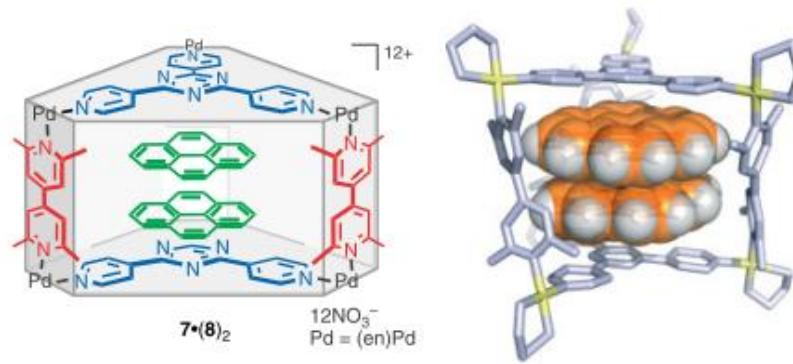
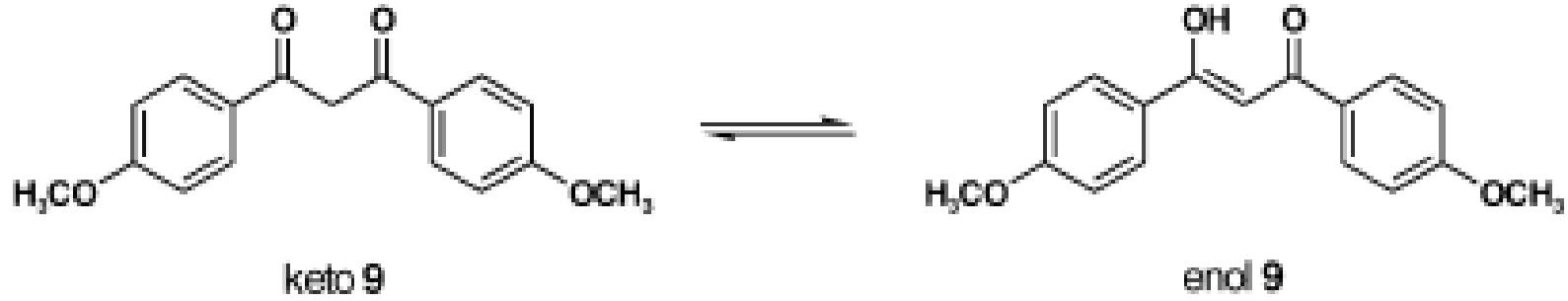
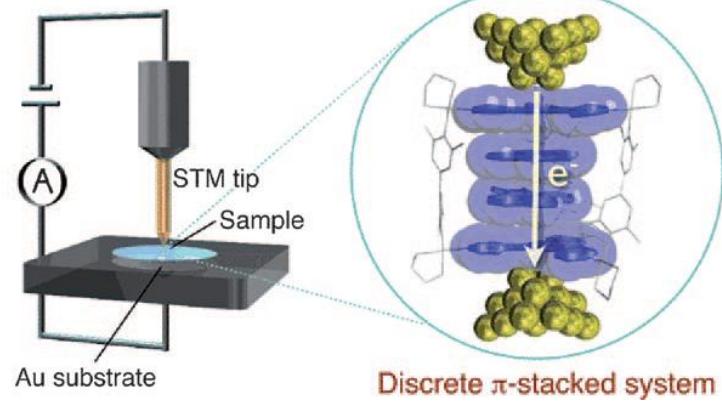
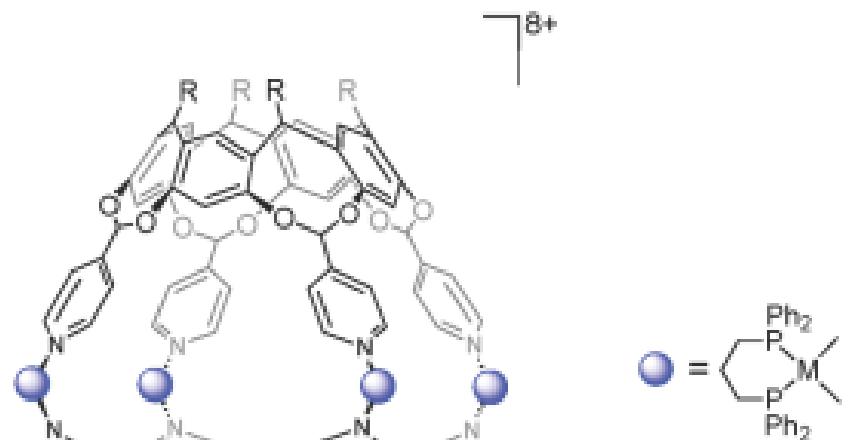
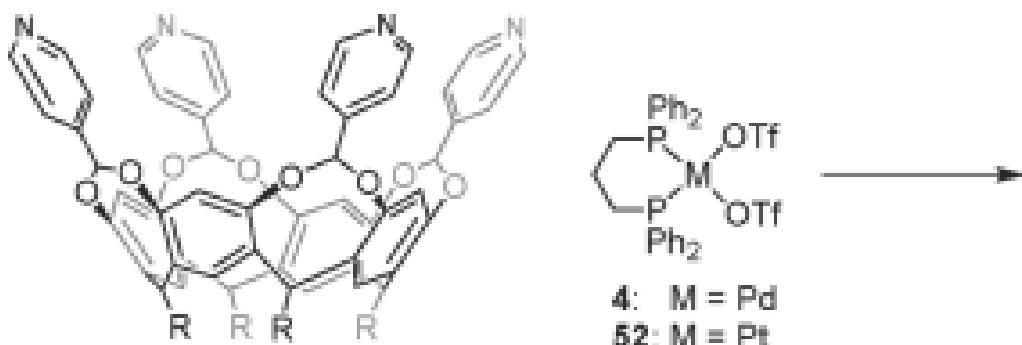


Figure 4. ¹H NMR spectra (300 MHz, D₂O, 25 °C) of aromatic regions of a) free **4** after extraction of template and b) **8** \subset **4** after the subsequent reincorporation of **8**.



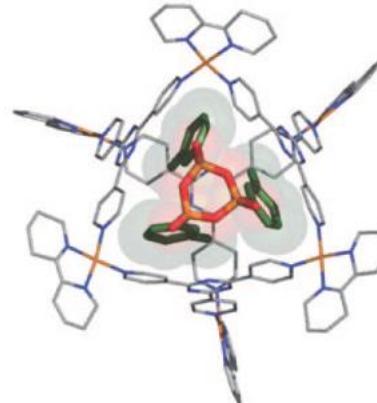
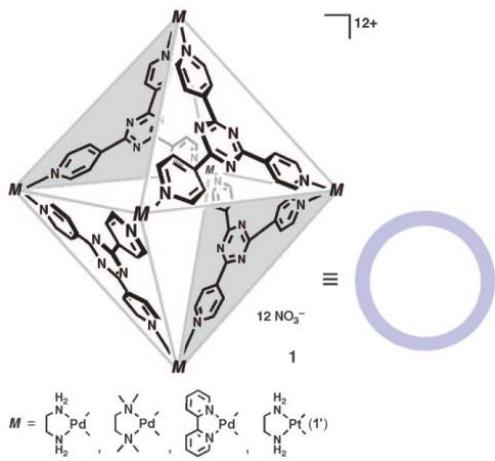
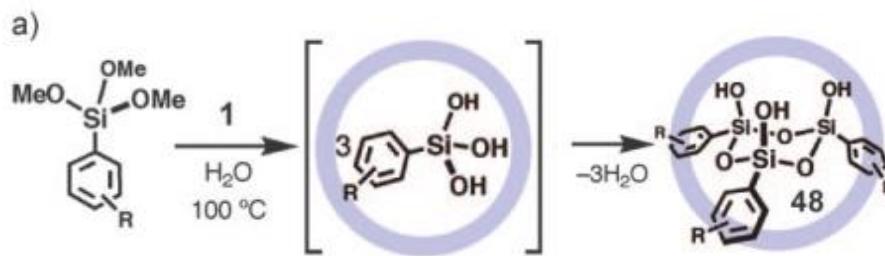
b)





472: M = Pd
473: M = Pt

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



Stabilizzazione di intermedi reattivi: Oligomerizzazione di tri alcossi-silani

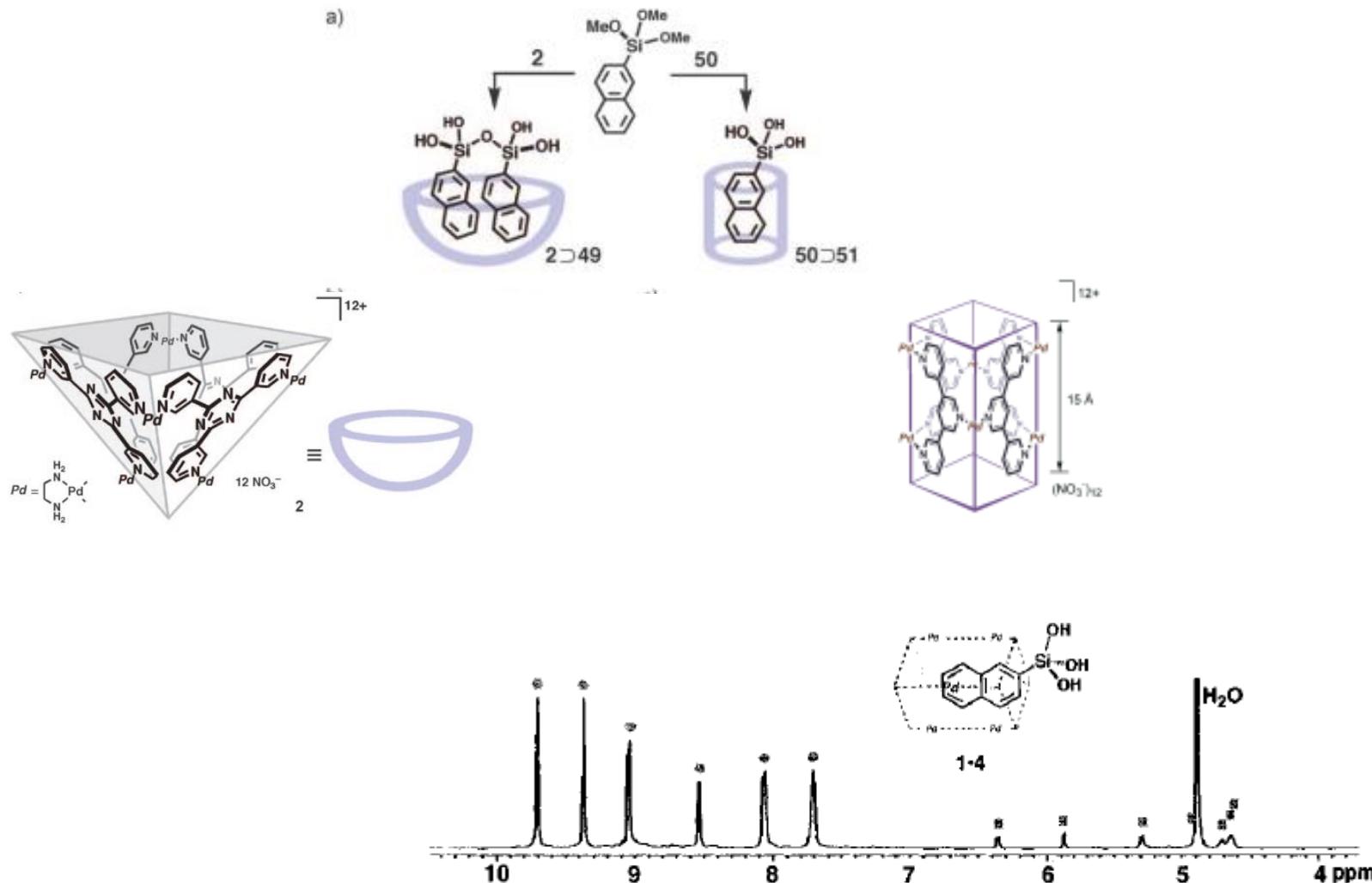
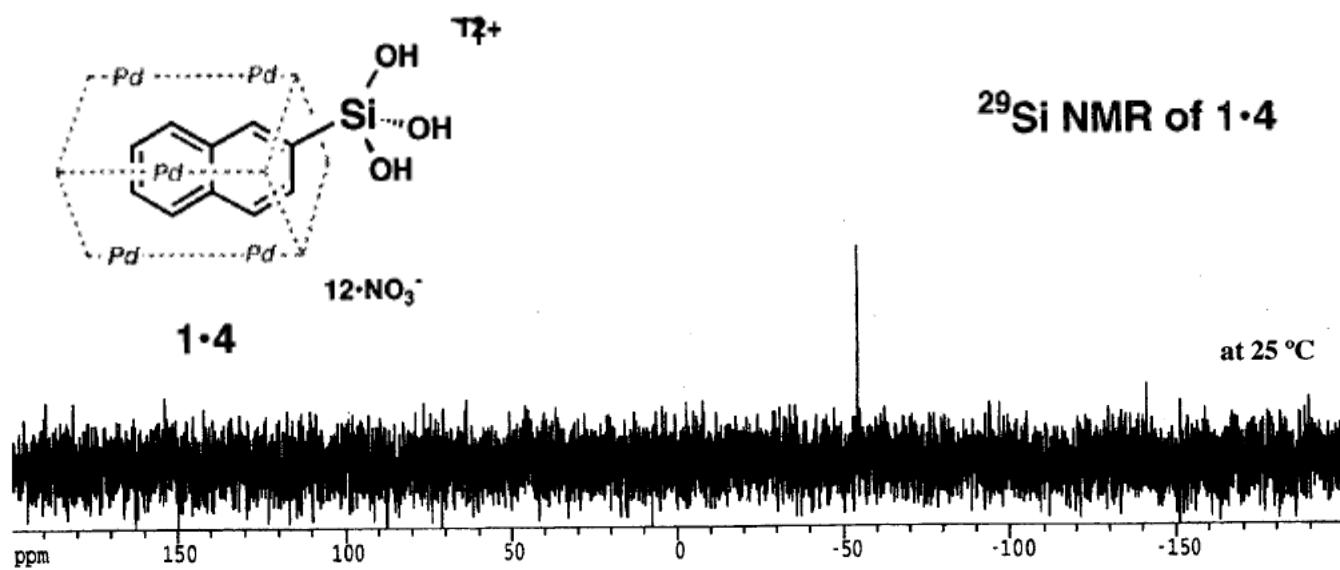


Figure 1. ¹H NMR spectrum (500 MHz, D₂O, TMS as an external standard) of **1·4** at 27 °C. Circles and squares indicate host and guest signals, respectively.



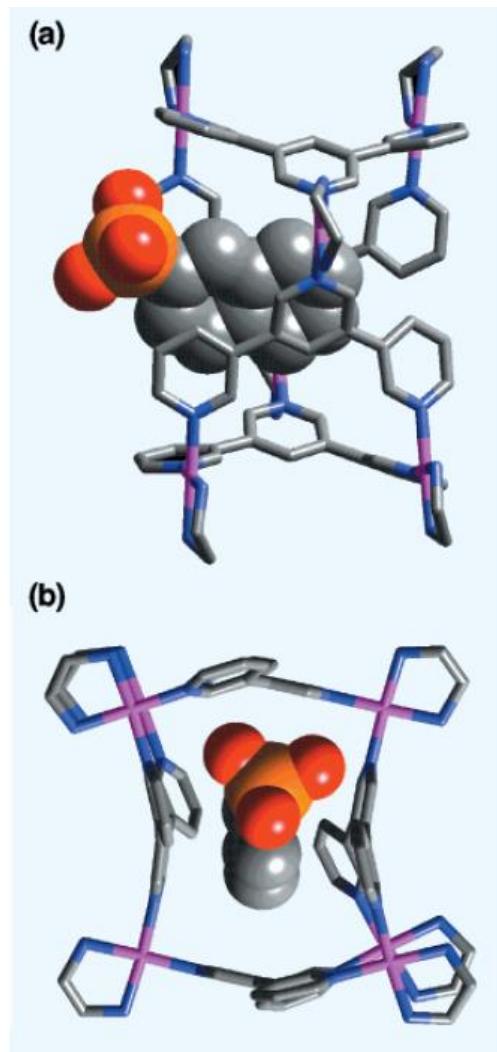


Figure 2. The crystal structure of **1·4**: (a) side view and (b) top view.

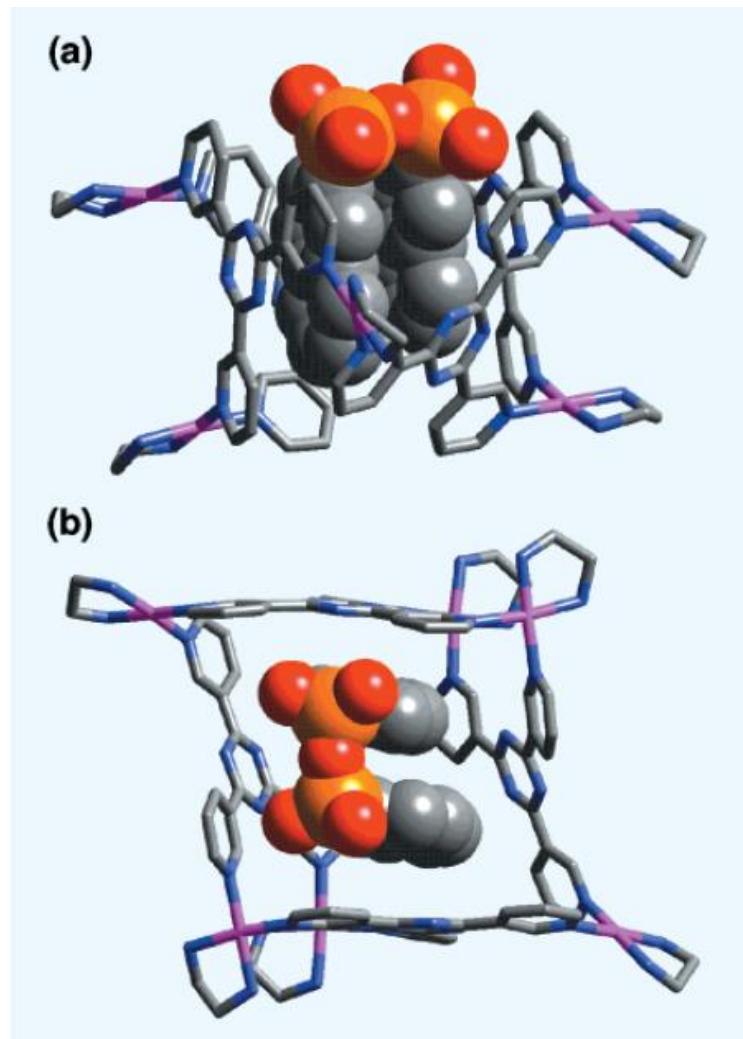
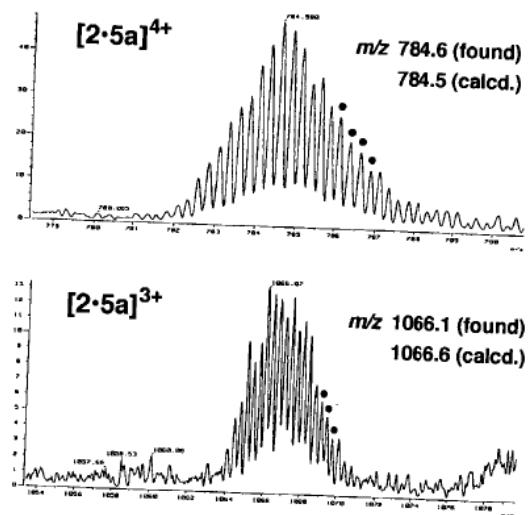
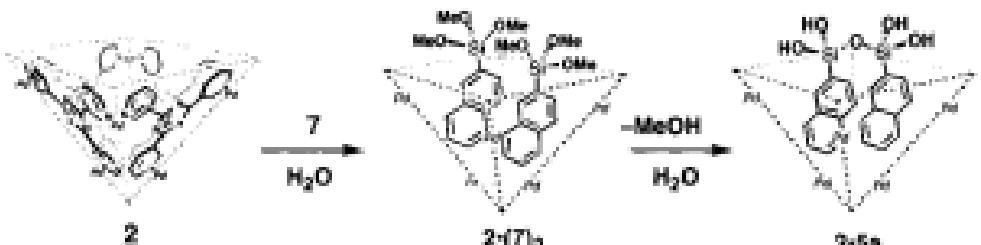


Figure 4. The crystal structure of **2·5a**: (a) side view and (b) top view.

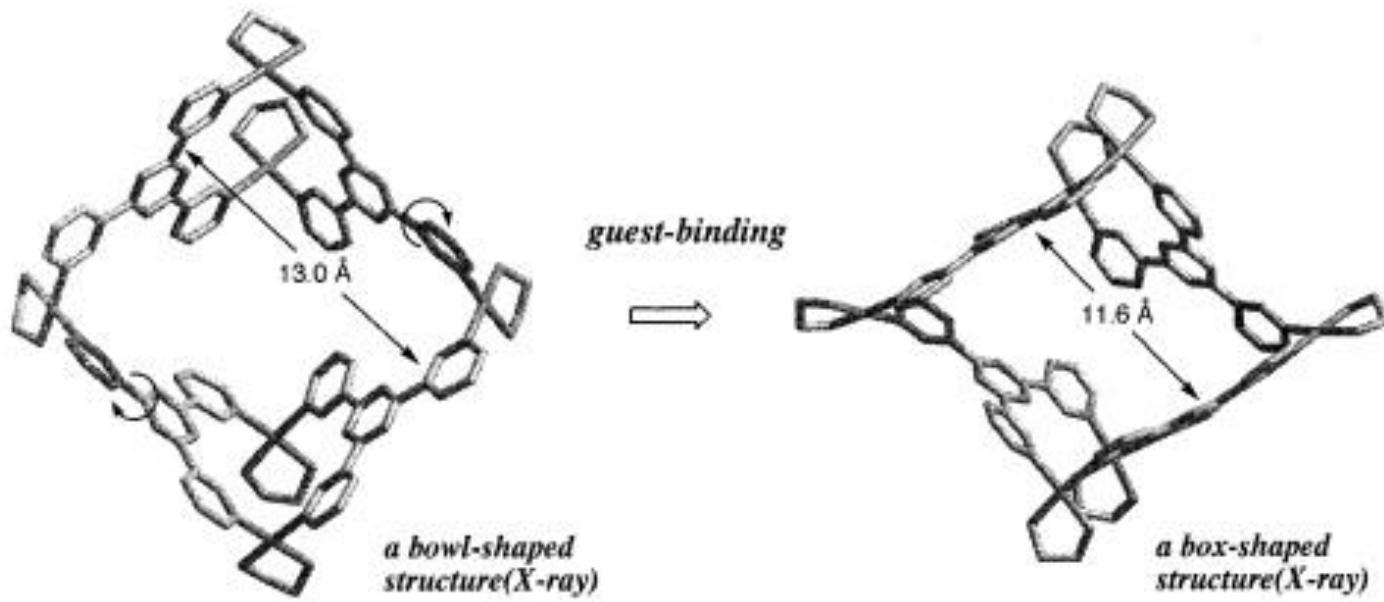
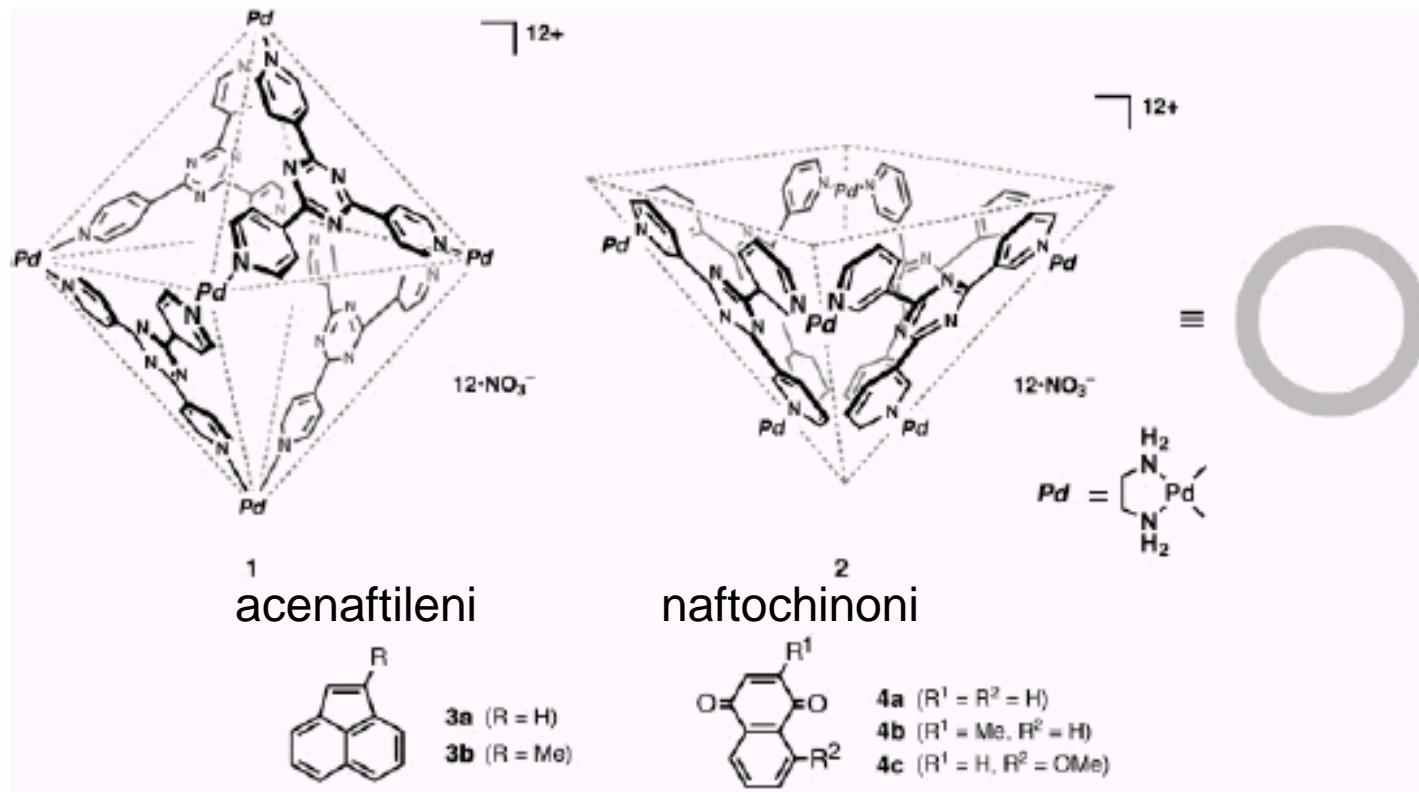
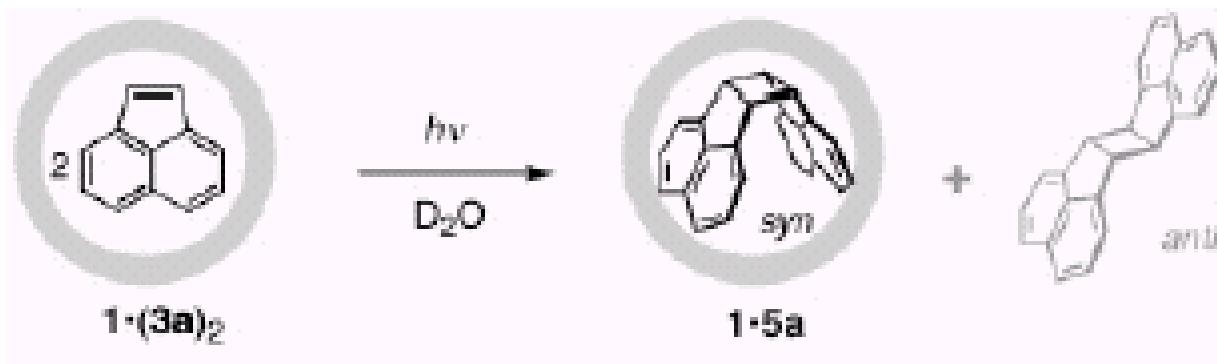


Figure 5. Bowl-to-box conformational change of **2·5a** is triggered by the guest binding. For clarity, guest molecules are omitted.

Fotodimerizzazioni 2+2



acenaftilene



controllo stereochimica, [] 2mM resa > 98%

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

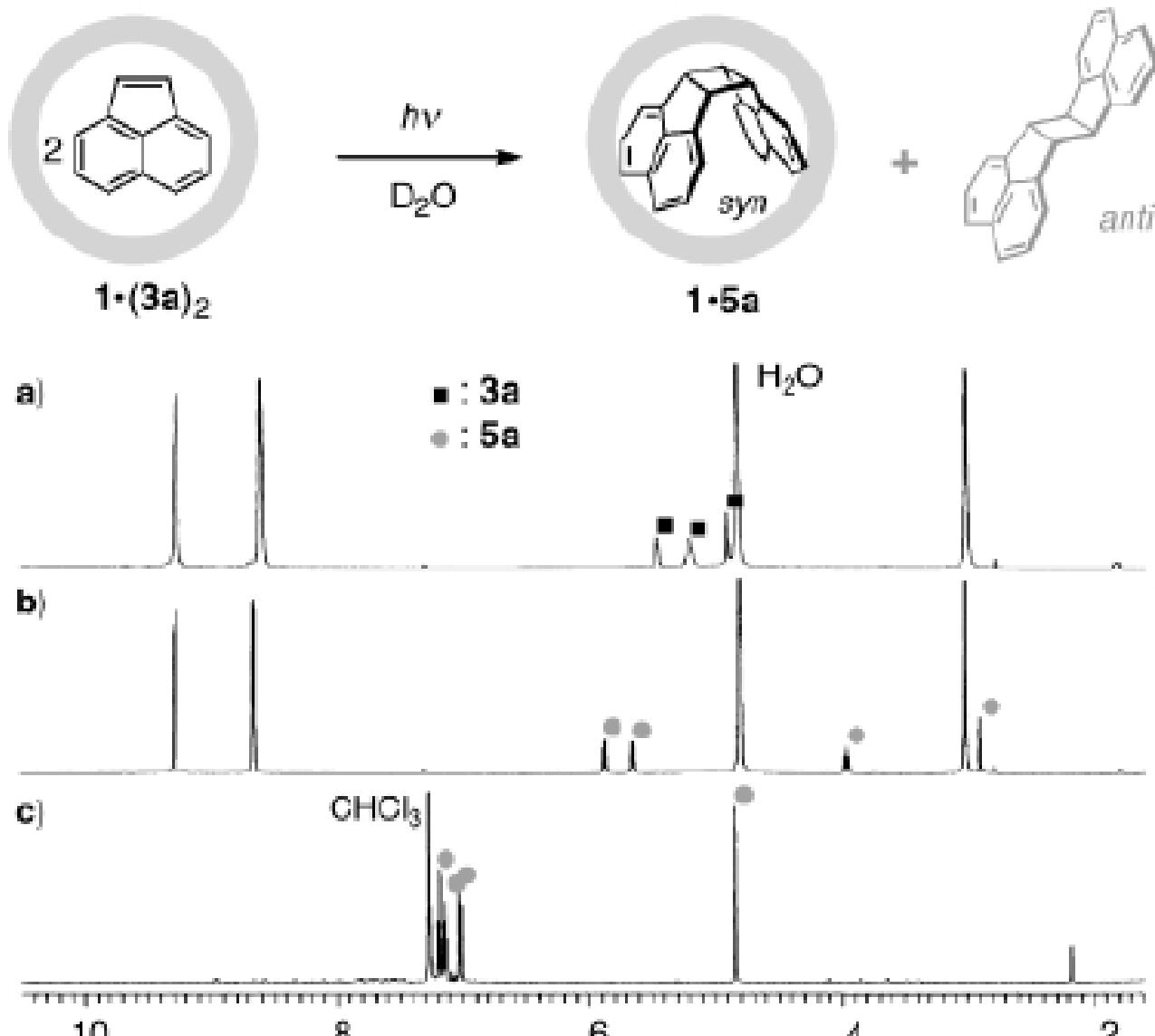
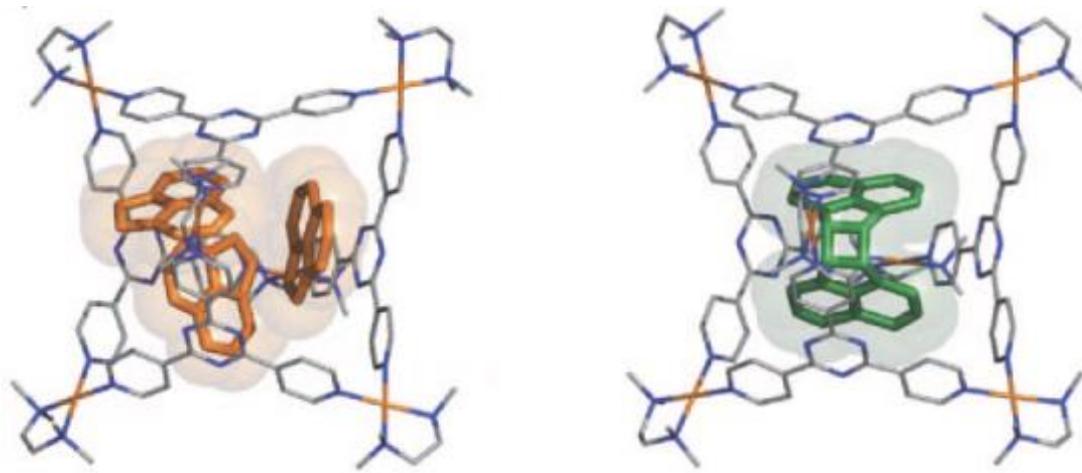
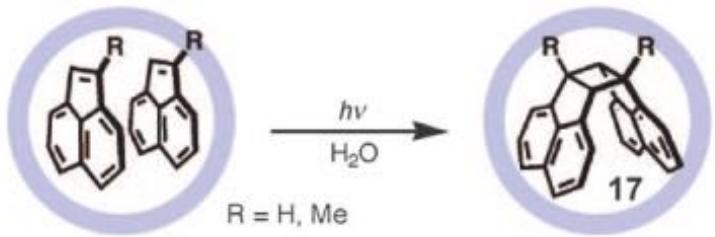
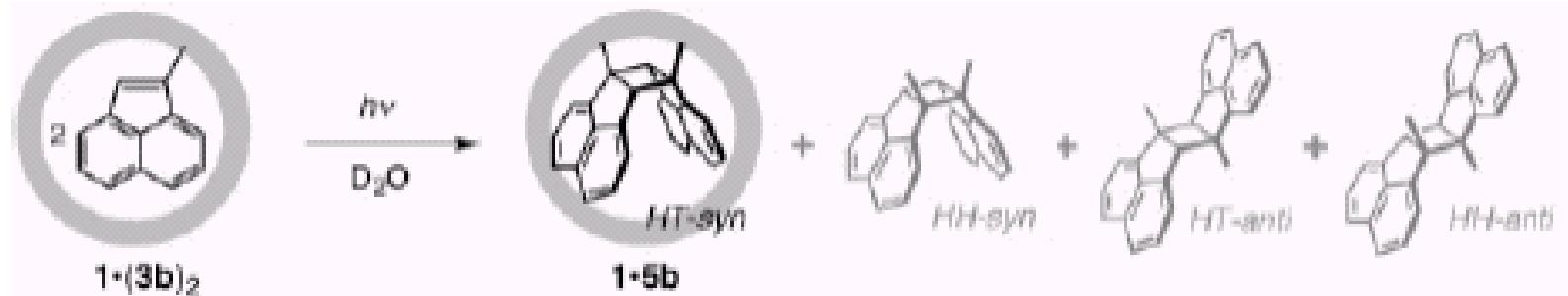


Figure 1. ¹H NMR spectroscopic analysis (500 MHz, D_2O , 27 °C) of the photodimerization of **3a** within cage **1**: a) before irradiation (**1·(3a)₂**) in D_2O ; b) after irradiation (400 W) for 0.5 h; c) after extraction with CDCl_3 .

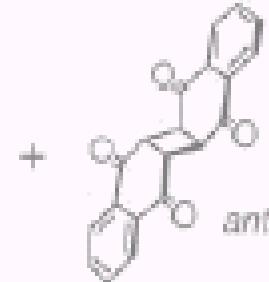
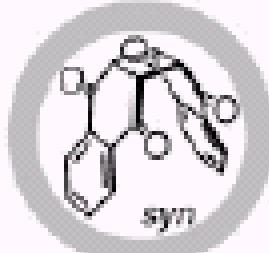
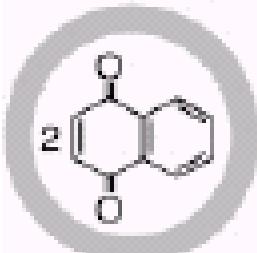


1-metil-acenaftilene



Controllo regiochimica, [] 2mM resa > 98%

naftochinone



controllo stereochimica, [] 2mM resa > 98%

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

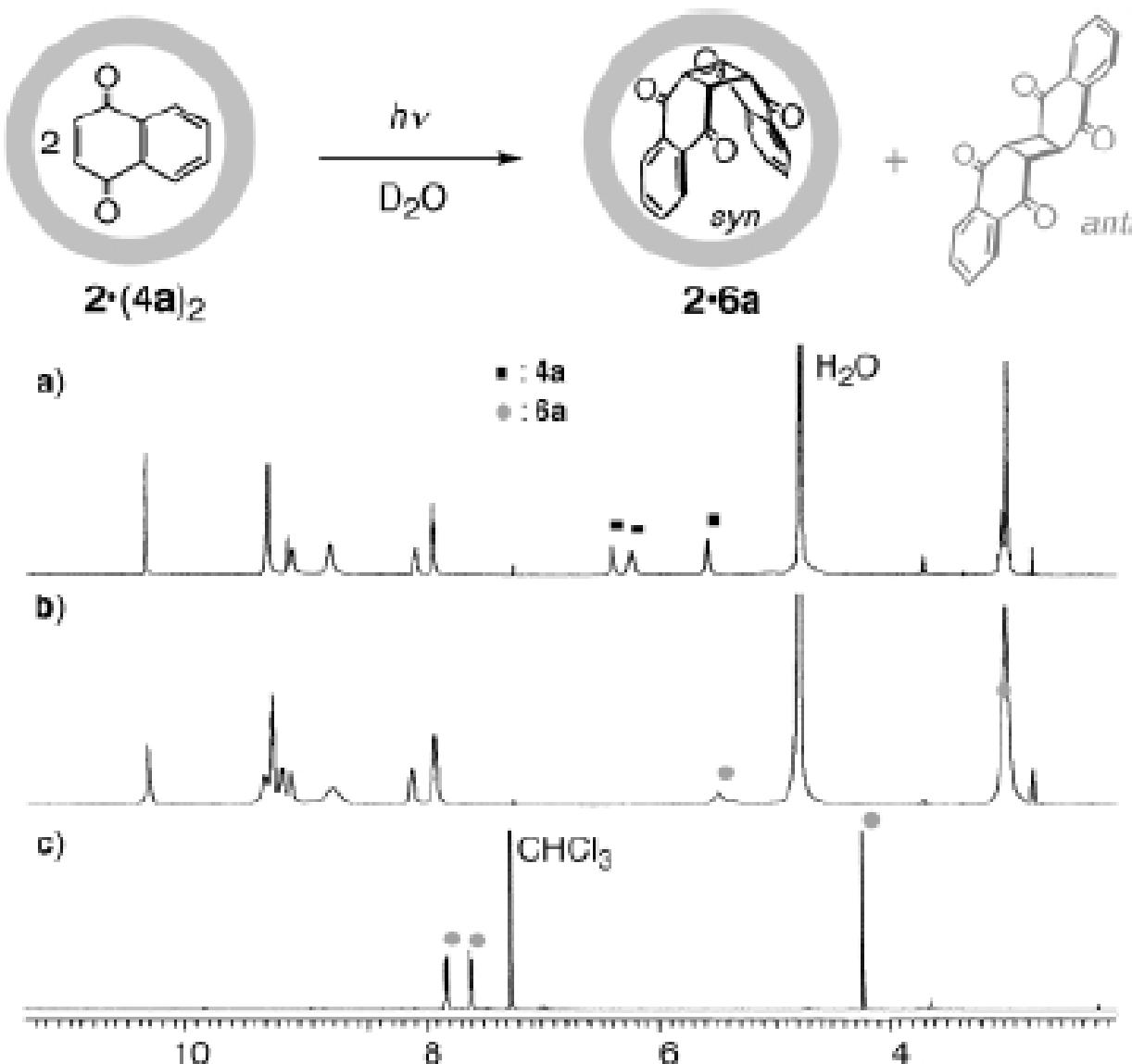
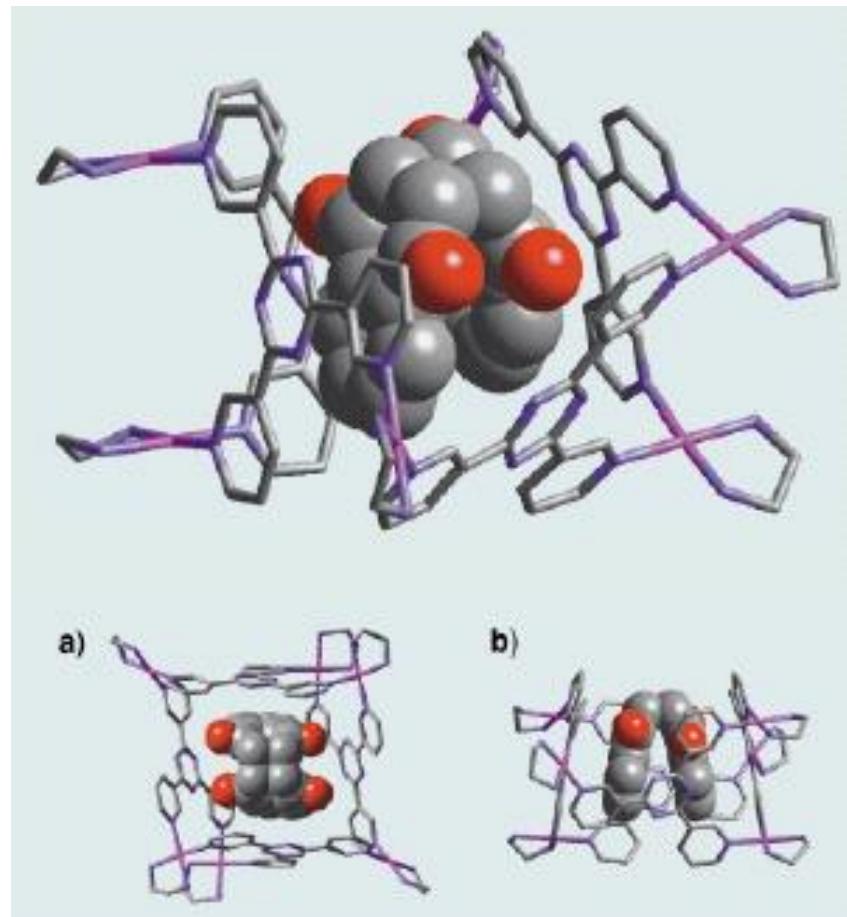
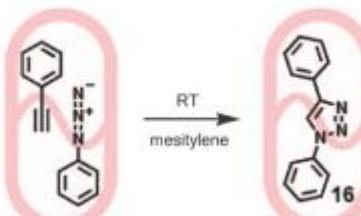
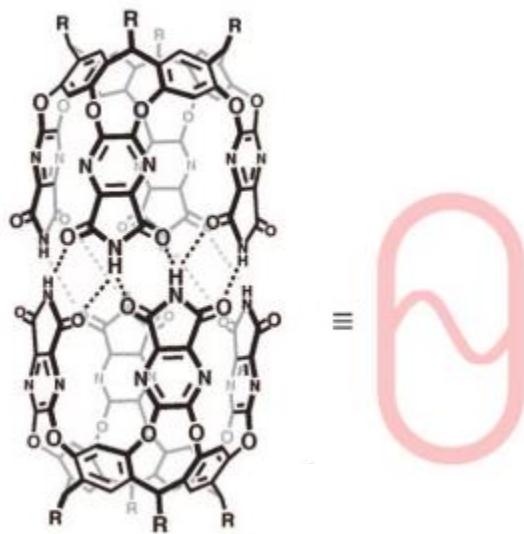
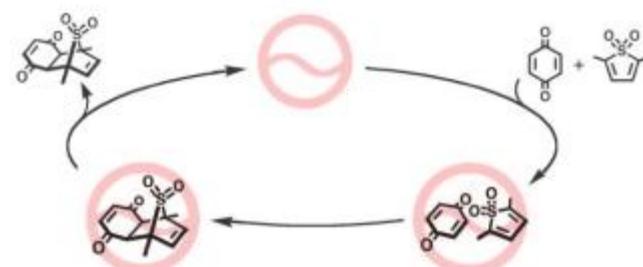
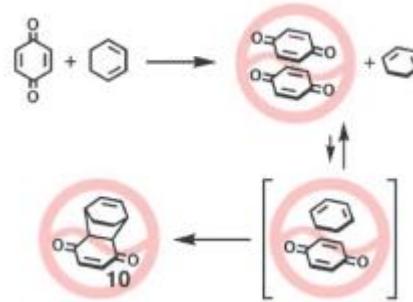
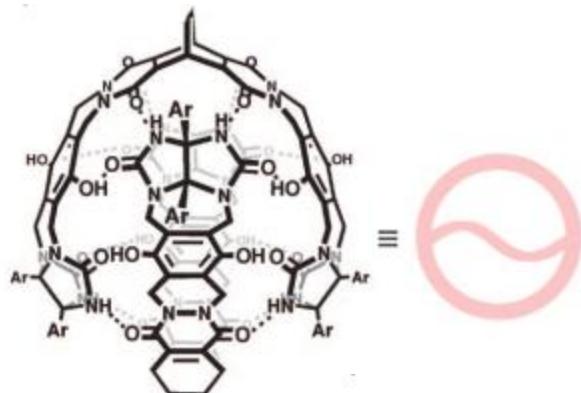
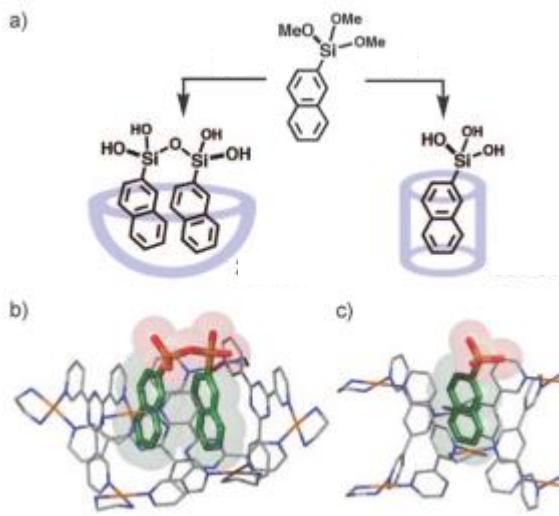
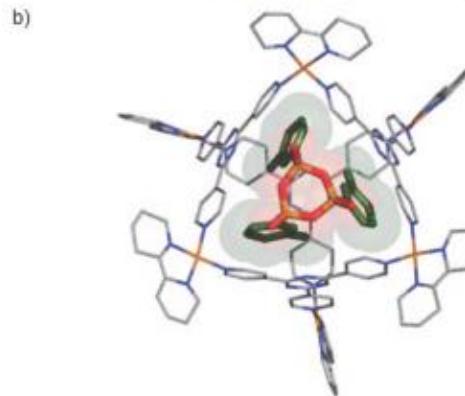
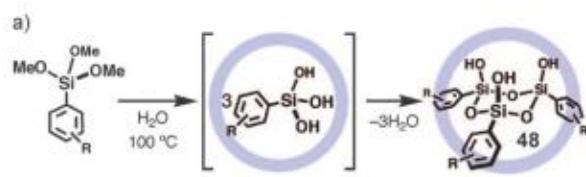
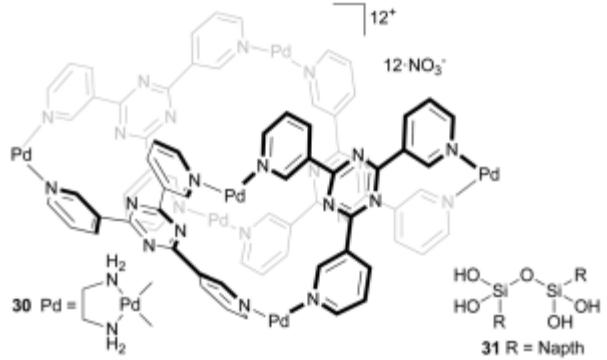
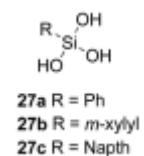
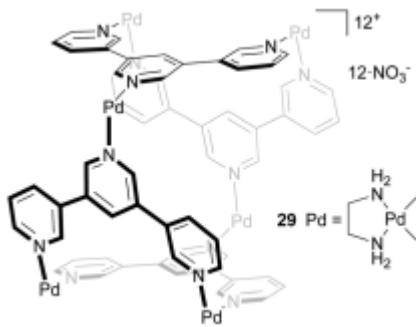
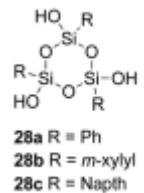
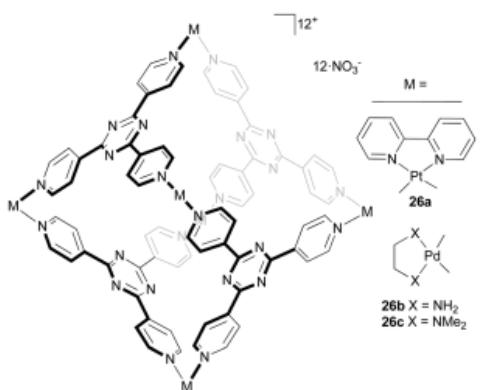
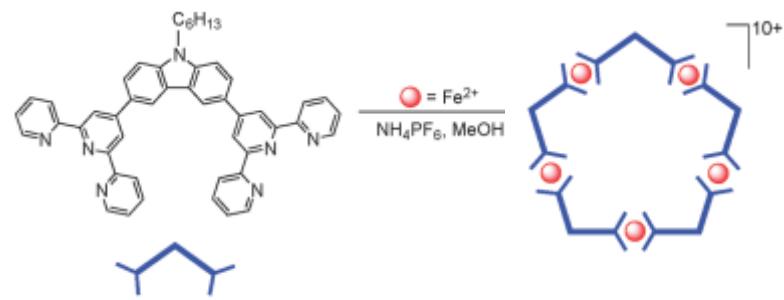
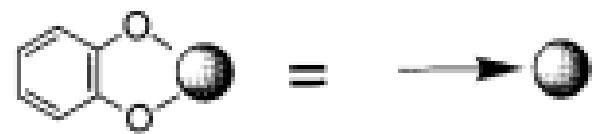


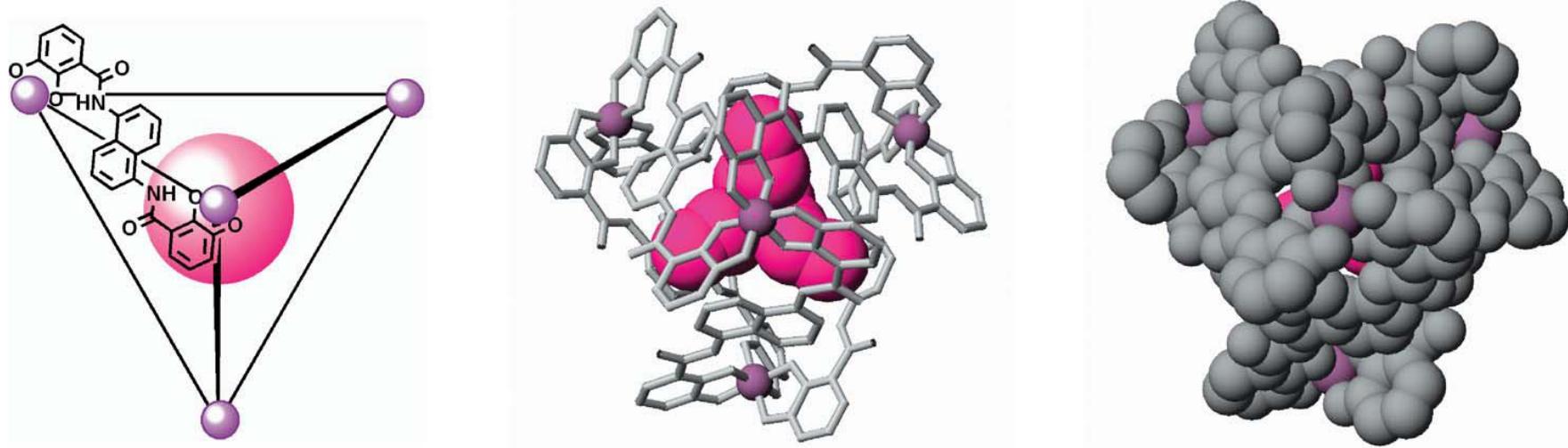
Figure 2. ^1H NMR spectroscopic analysis (500 MHz, D_2O , 27 °C) of the photodimerization of **4a** within bowl **2**: a) before reaction (**2·(4a)₂**) in D_2O ; b) after irradiation (400 W) for 3 h; c) after extraction with CDCl_3 .



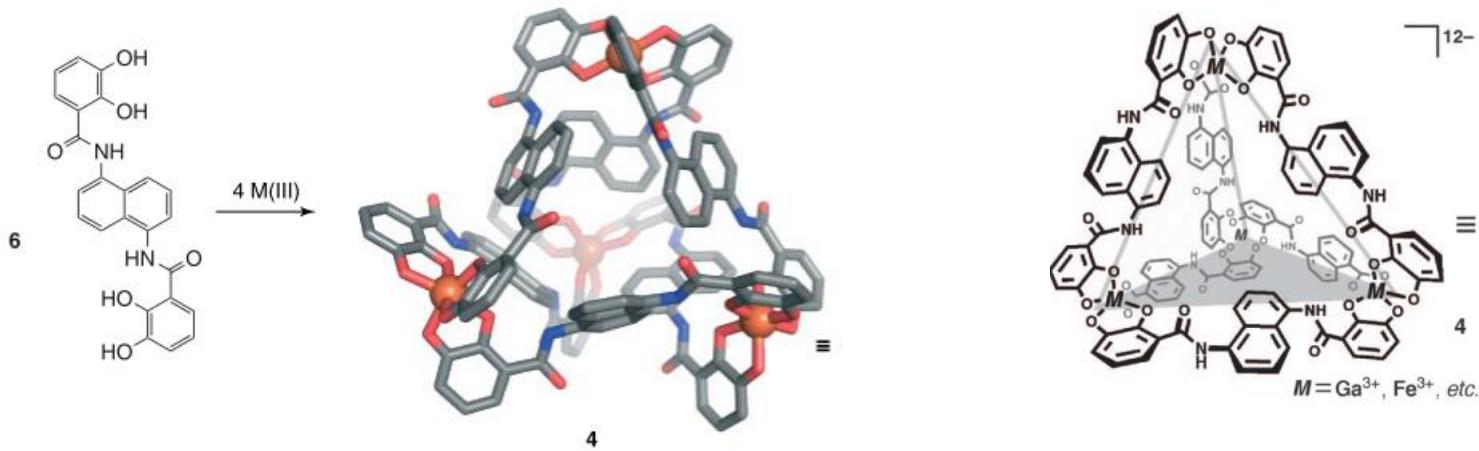




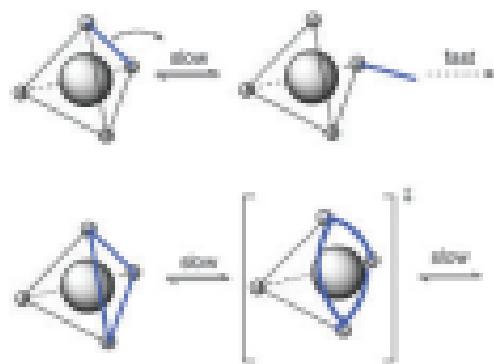




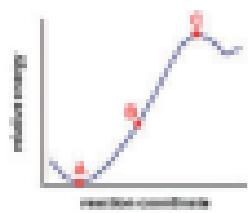
M_4L_6 , (Ga^{3+} , Fe^{3+} ; biscatecol-amidi) 12^- , $\Delta\Delta\Delta\Delta$, $\Lambda\Lambda\Lambda\Lambda$, $300-350 \text{ \AA}$
Stabilizzazione di cationi organici

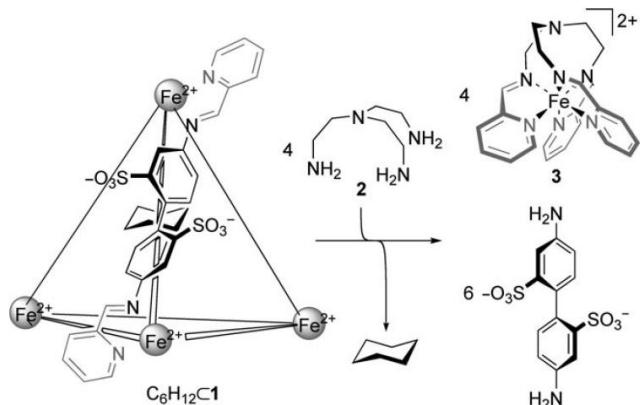


(B)

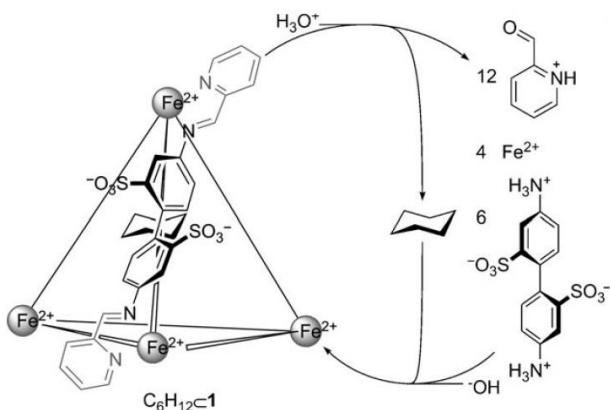


(C)





Scheme 3. Liberation of the cyclohexane guest within **1** by the addition of chelating amine **2**.



Scheme 4. “Unlocking” of cage **1** through the addition of acid and subsequent base-driven “relocking” of cyclohexane within **1**.

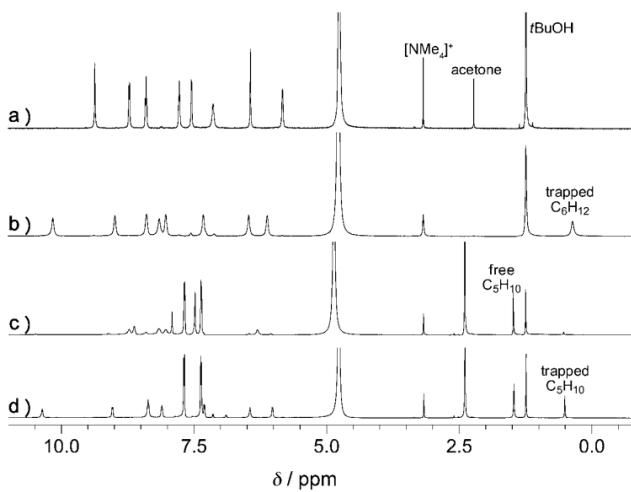


Figure 2. ^1H NMR spectra of a) cage **1**, b) $\text{C}_6\text{H}_{12}\subset\mathbf{1}$, c) $\text{C}_6\text{H}_{12}\subset\mathbf{1}$ after reaction with toslic acid (10 equiv) and in presence of excess cyclopentane, d) generation of complex $\text{C}_5\text{H}_{10}\subset\mathbf{1}$ after the addition of sodium bicarbonate (15 equiv).

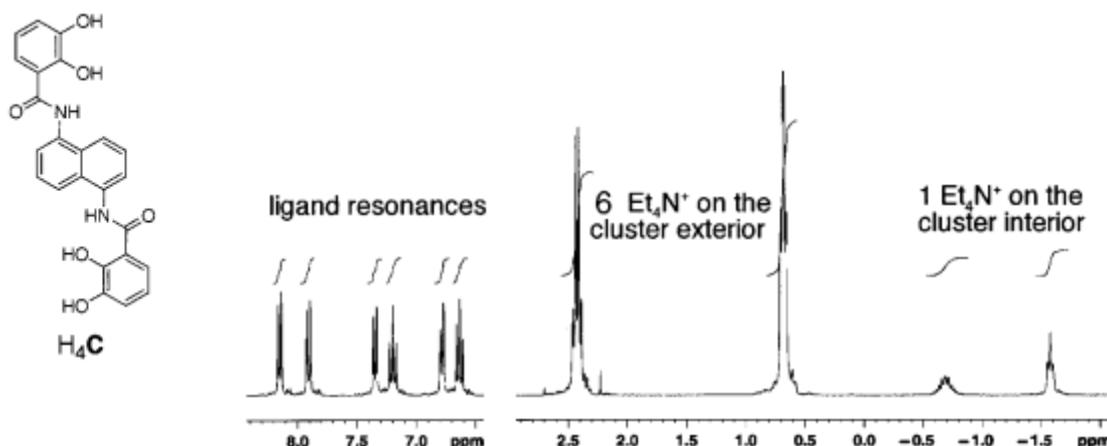


Figure 14. ^1H NMR (D_2O) of $\text{K}_5(\text{Et}_4\text{N})_7[\text{Ga}_4\text{C}_6]$ depicting the two sets of Et_4N^+ resonances characteristic of the exterior and encapsulated cations.

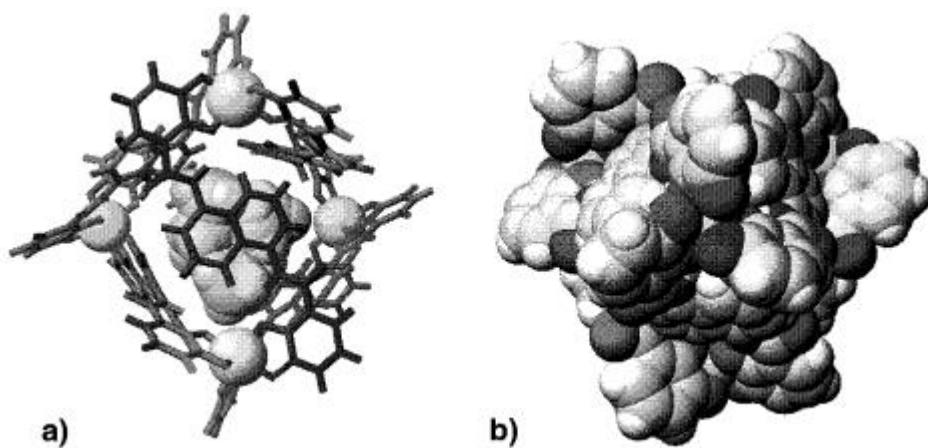
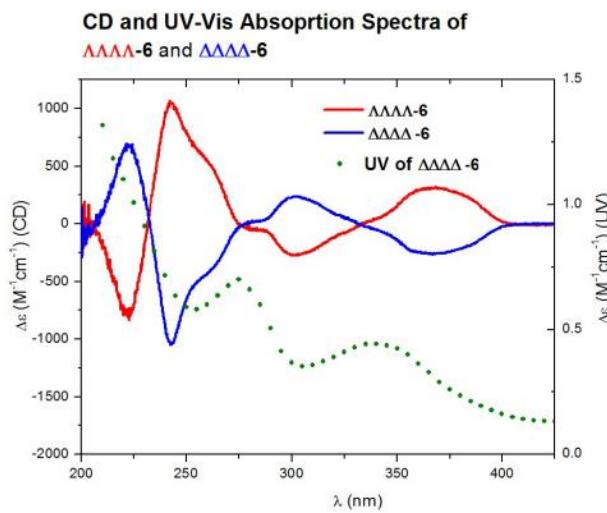
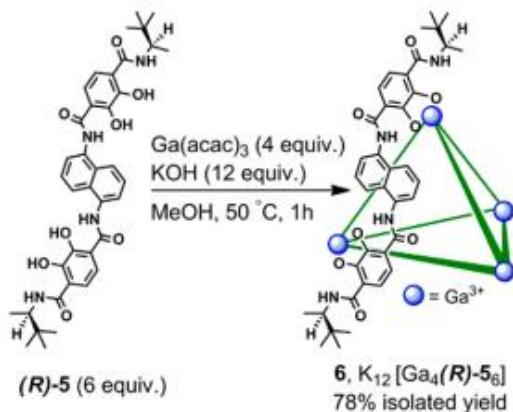
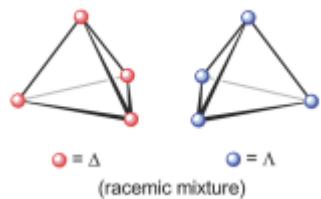
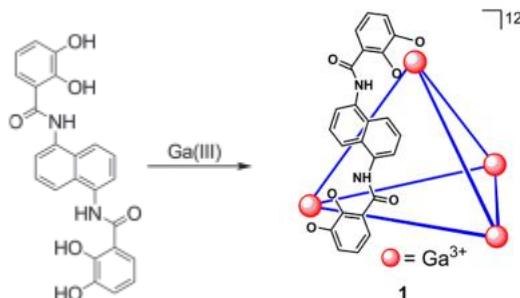
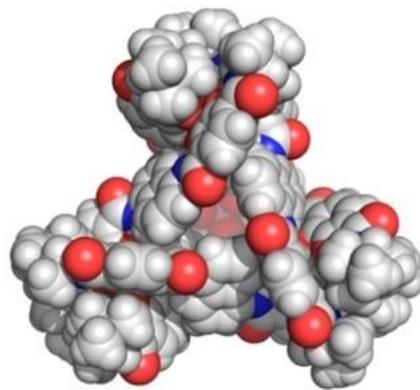
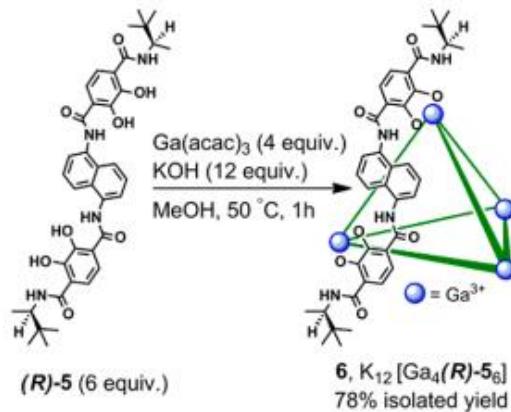
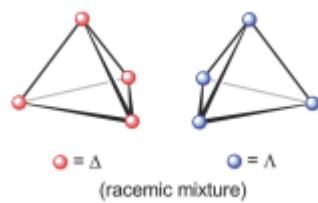
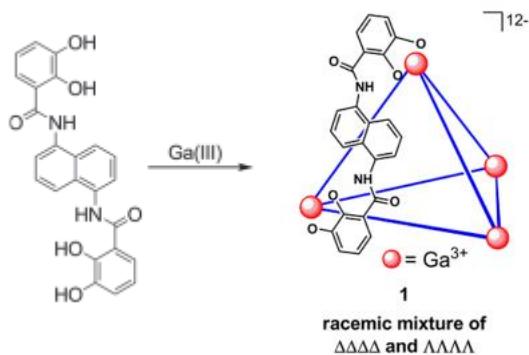


Figure 15. Based on the X-ray structure coordinates, $\text{Et}_4\text{N}^+ \subset [\text{Fe}_4\text{C}_6]^{12-}$ in both (a) wire-frame and (b) space-filling representations.





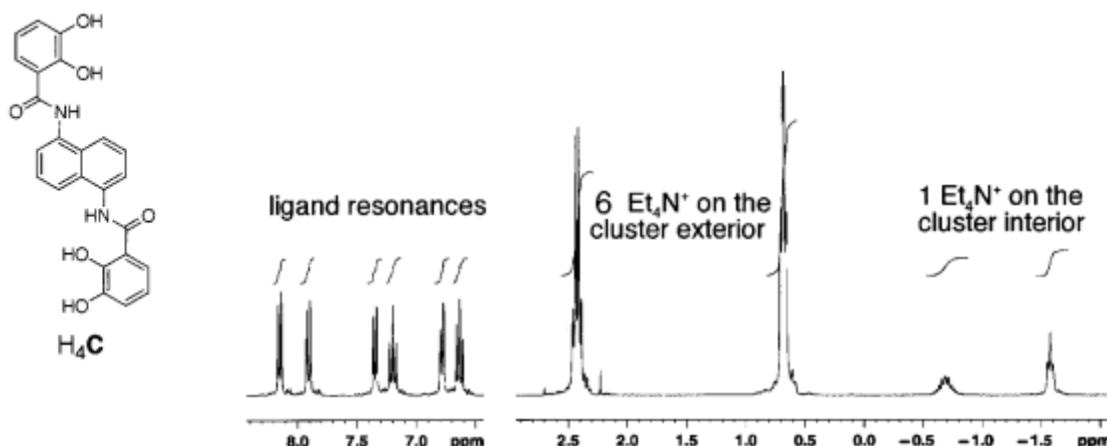


Figure 14. ^1H NMR (D_2O) of $\text{K}_5(\text{Et}_4\text{N})_7[\text{Ga}_4\text{C}_6]$ depicting the two sets of Et_4N^+ resonances characteristic of the exterior and encapsulated cations.

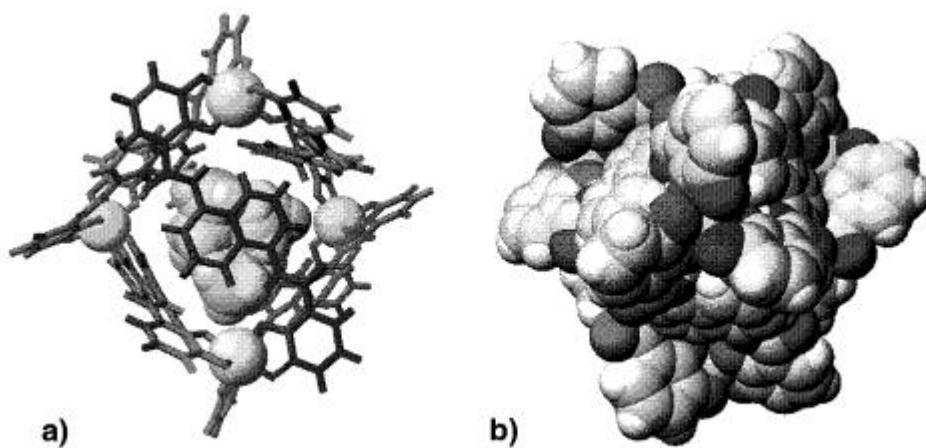
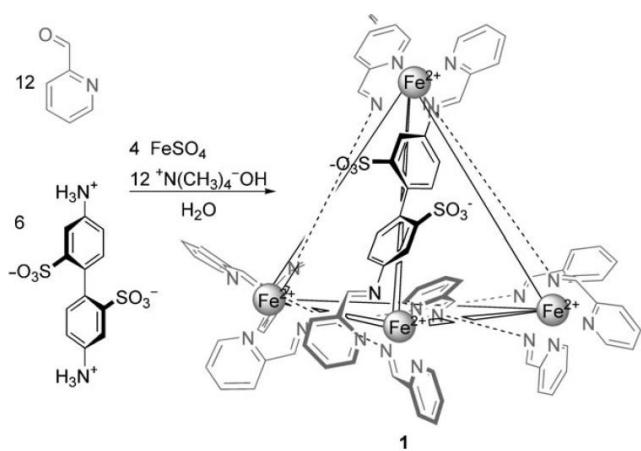


Figure 15. Based on the X-ray structure coordinates, $\text{Et}_4\text{N}^+ \subset [\text{Fe}_4\text{C}_6]^{12-}$ in both (a) wire-frame and (b) space-filling representations.

An Unlockable–Relockable Iron Cage by Subcomponent Self-Assembly**

Prasenjit Mal, David Schultz, Kodiah Beyeh, Kari Rissanen,* and Jonathan R. Nitschke*



Scheme 1. Preparation of tetrahedral cage **1** salt by aqueous subcomponent self-assembly;^[14] the structure of only one edge is fully shown for clarity.

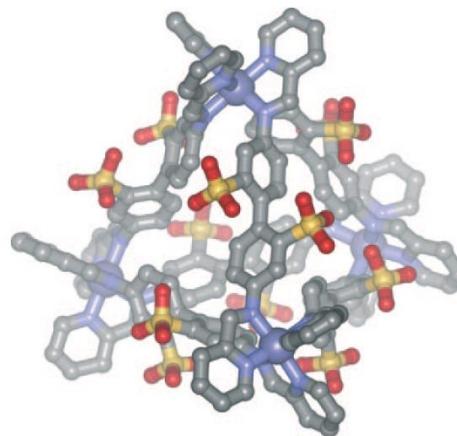
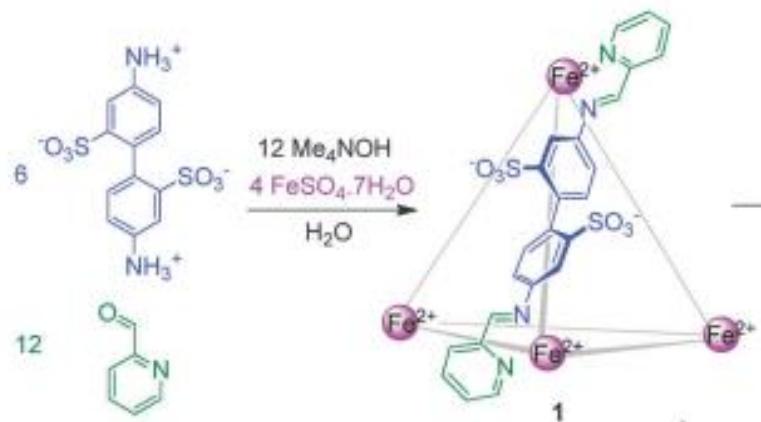
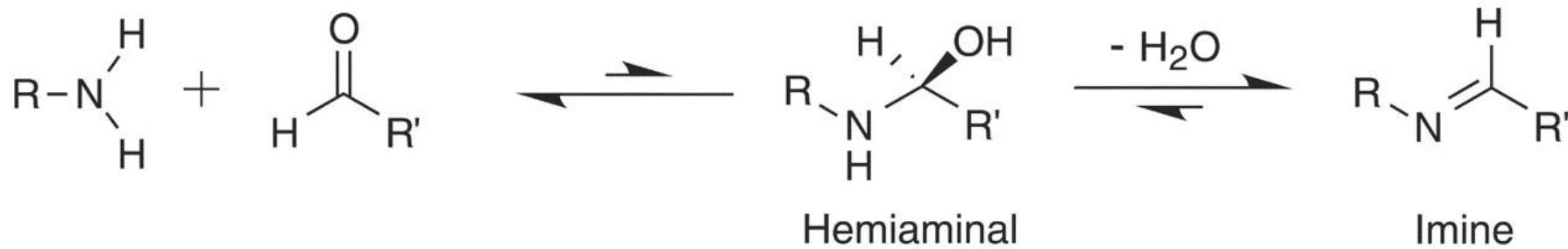
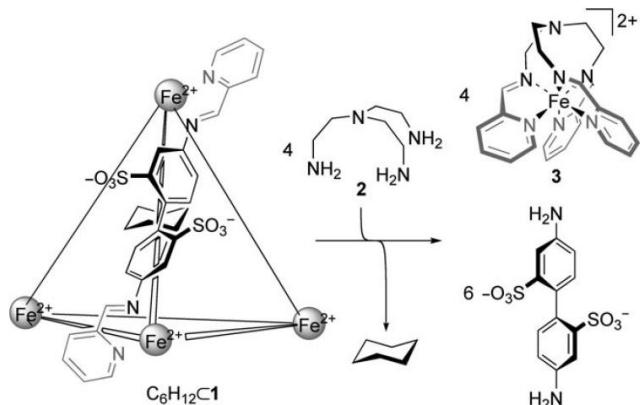
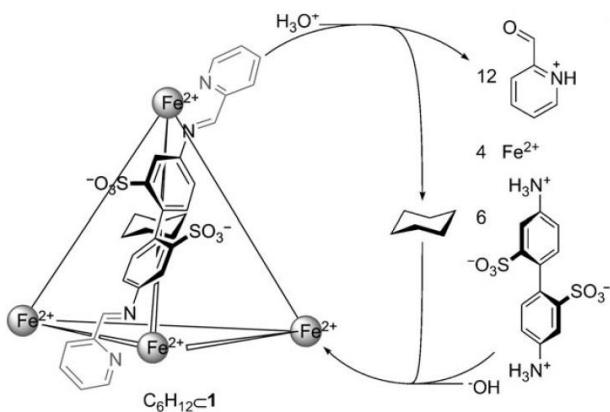


Figure 1. View of the crystal structure of **1**; cations, hydrogen atoms, and solvent of crystallization are not shown for clarity. Fe violet-gray, N blue, S yellow, O red, C gray.





Scheme 3. Liberation of the cyclohexane guest within **1** by the addition of chelating amine **2**.



Scheme 4. “Unlocking” of cage **1** through the addition of acid and subsequent base-driven “relocking” of cyclohexane within **1**.

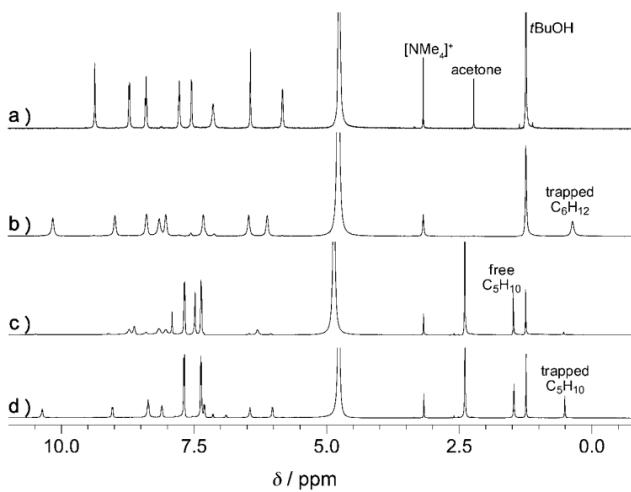
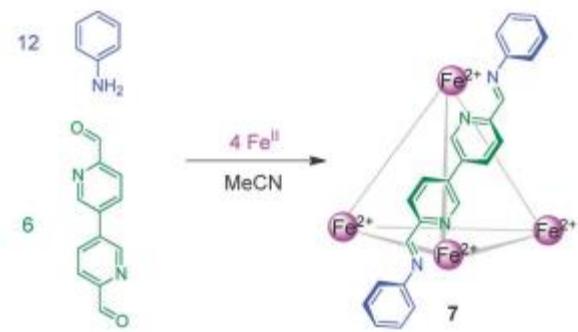
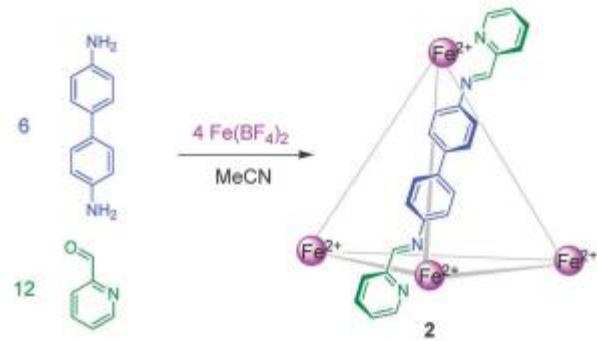
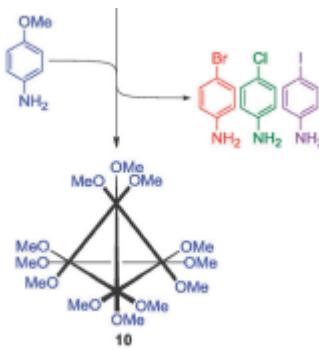
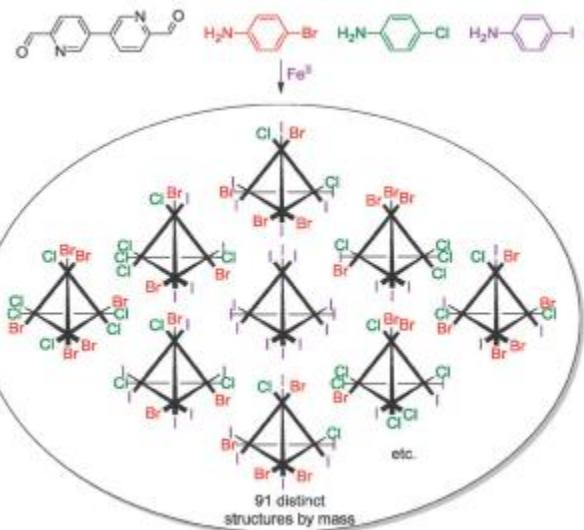
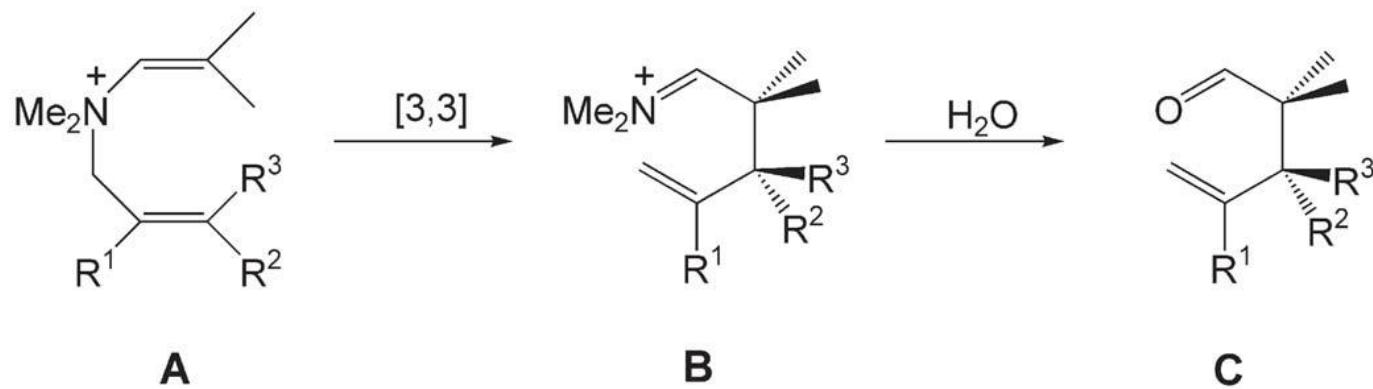


Figure 2. ^1H NMR spectra of a) cage **1**, b) $\text{C}_6\text{H}_{12}\text{-} \mathbf{1}$, c) $\text{C}_6\text{H}_{12}\text{-} \mathbf{1}$ after reaction with toslic acid (10 equiv) and in presence of excess cyclopentane, d) generation of complex $\text{C}_5\text{H}_{10}\text{-} \mathbf{1}$ after the addition of sodium bicarbonate (15 equiv).

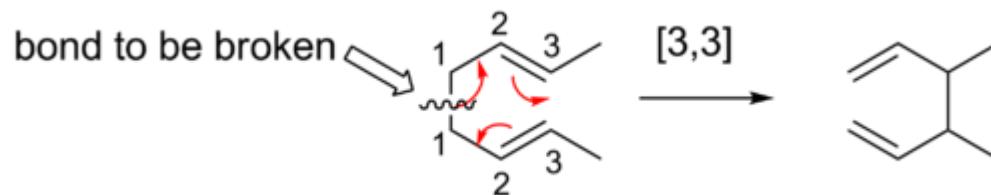




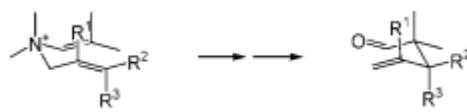
Catalisi Supramolecolare



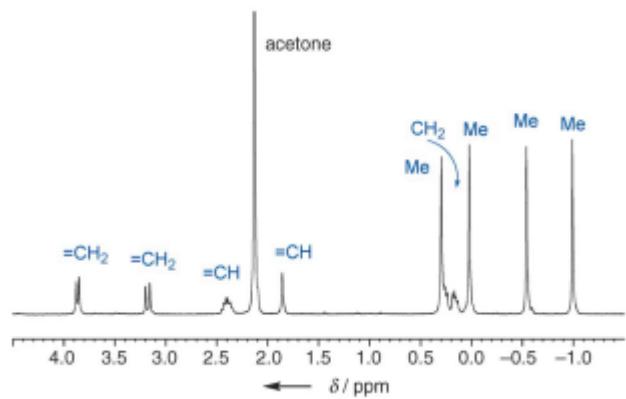
Riarrangiamento 3-aza-Cope ione ammonio



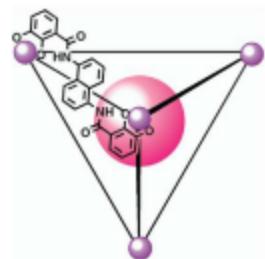
Substrate	R ¹	R ²	R ³	Acceleration
1	H	H	H	5
2	Me	H	H	26
3	H	Et	H	141
4	H	H	Et	90
5	H	<i>n</i> Pr	H	150
6	H	H	<i>n</i> Pr	44
7	H	<i>i</i> Pr	H	854

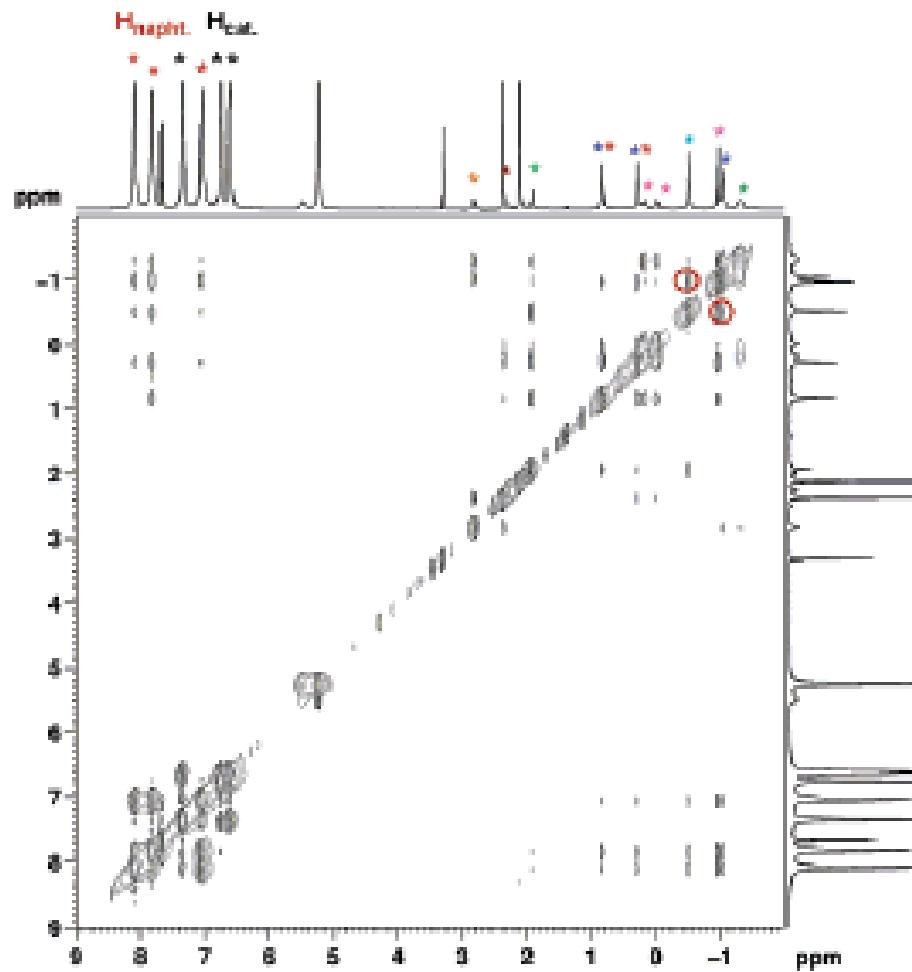
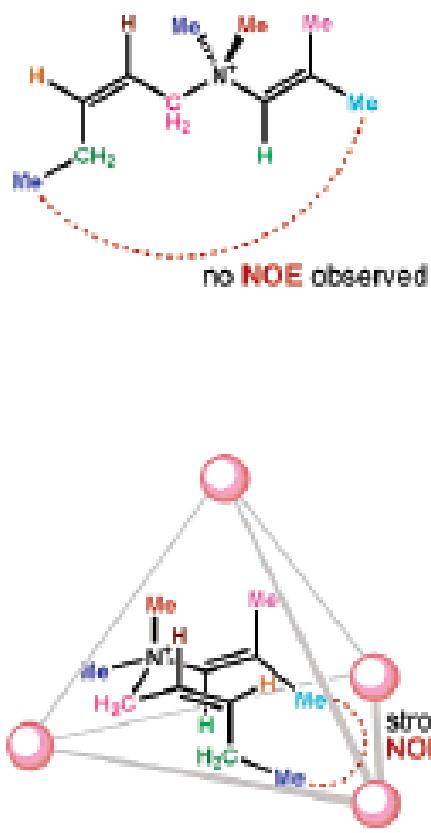


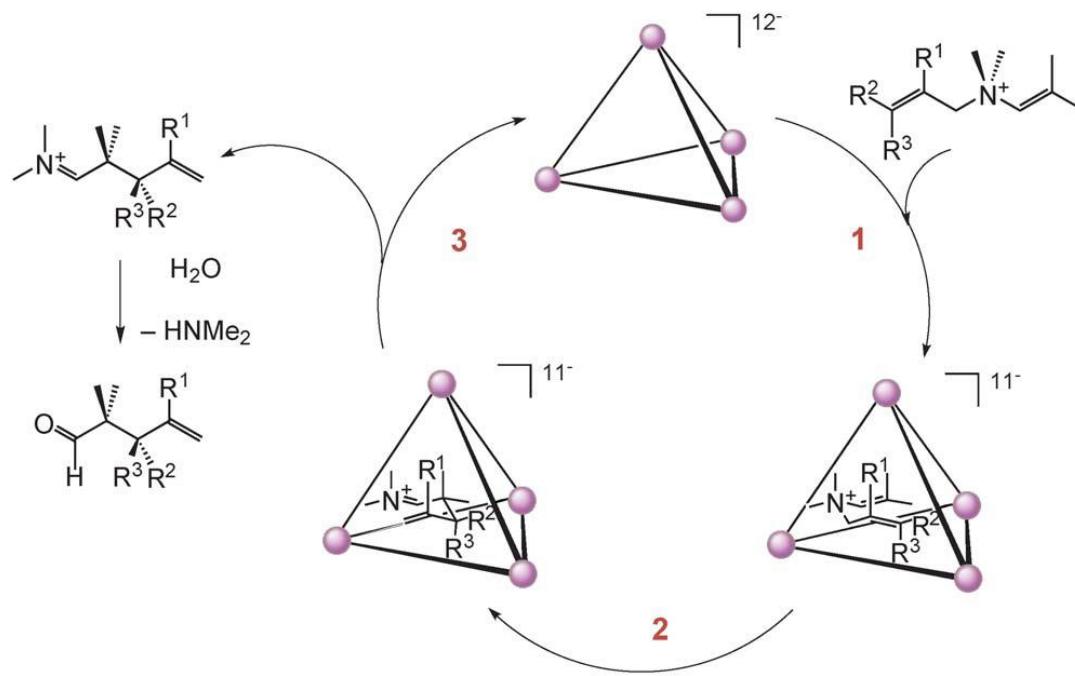
Substrate	R ¹	R ²	R ³
1	H	H	H
2	Me	H	H
3	H	Et	H
4	H	H	Et
5	H	nPr	H
6	H	H	nPr
7	H	iPr	H



¹H NMR spectrum of $[1 \subset Ga_4L_6]^{11-}$ (**1**: R¹, R², R³=H). The observed upfield shift of guest resonance signals illustrates the close contact between host and guest.







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

Michito Yoshizawa, Masazumi Tamura, Makoto Fujita*

SCIENCE VOL 312 14 APRIL 2006

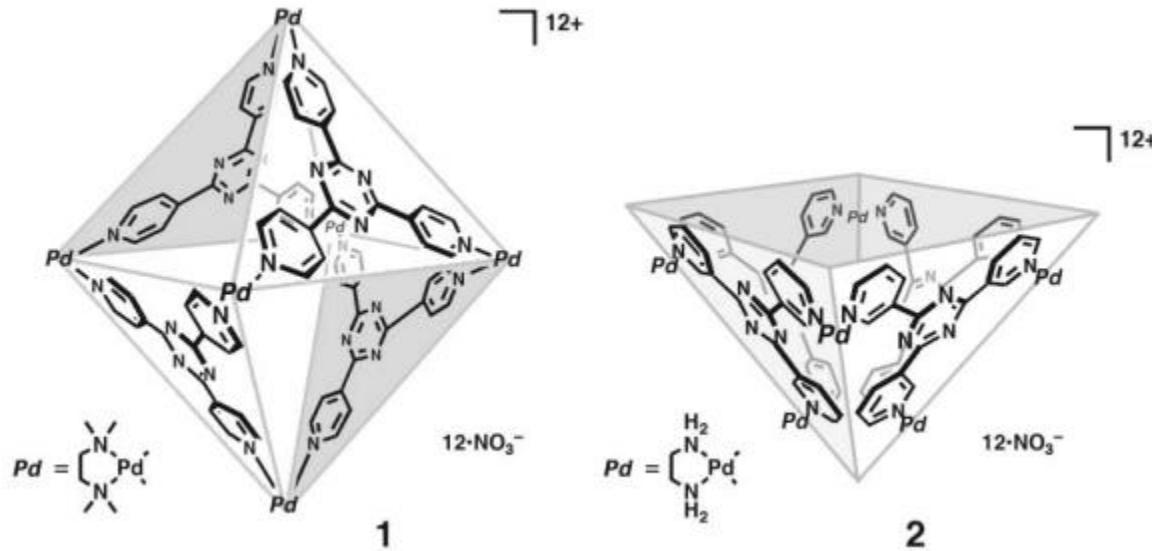
251

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.



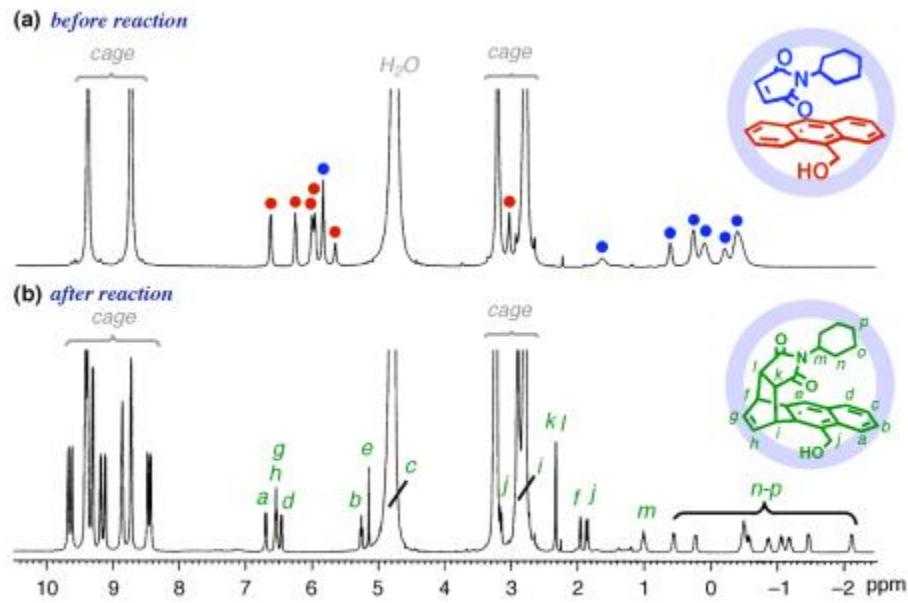
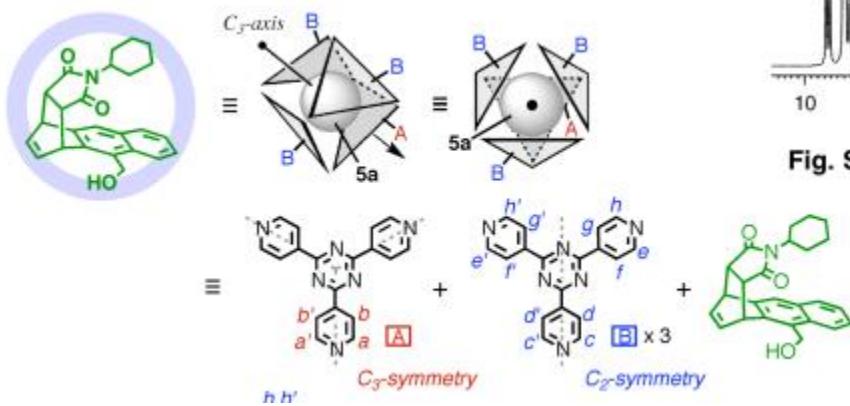
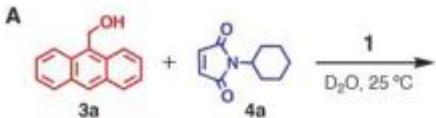
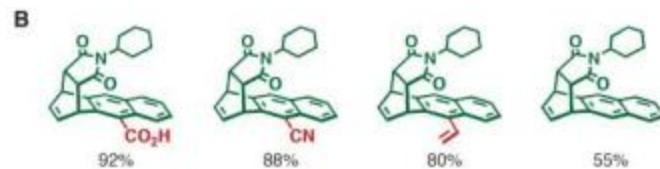


Fig. S1. ^1H -NMR spectra (500 MHz, D_2O , r.t.) of (a) $1\Box(3\text{a}\bullet 4\text{a})$ and (b) $1\Box 5$.



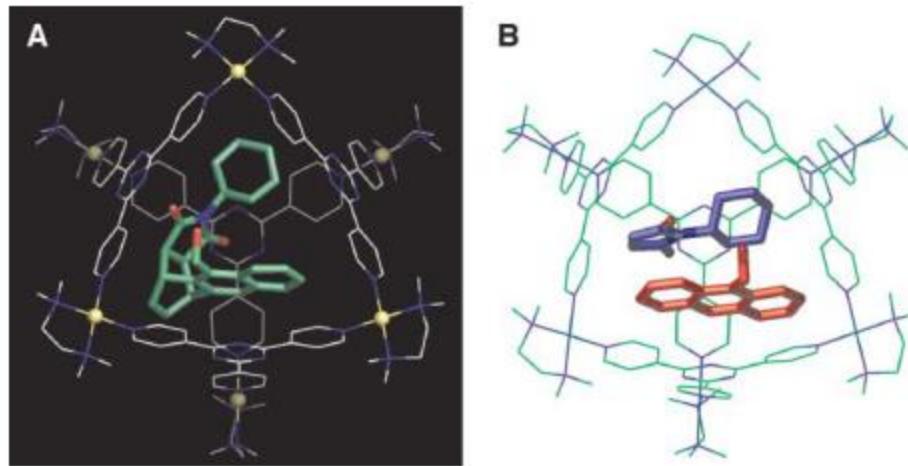


Fig. 3. (A) Crystal structure of **1** ⊙ **5** and (B) optimized structure of **1** ⊙ (**3a**•**4a**) by a force-field calculation.

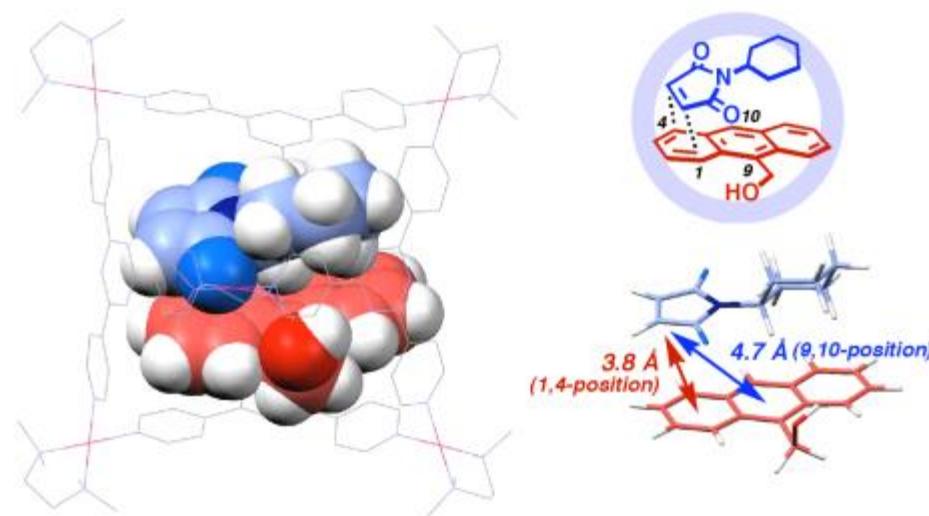


Fig. S17. Optimized structure of **1** ⊙ (**3a**•**4a**) by a force-field calculation and the distance between the C=C bond of **4a** and the 1,4-position or 9,10-position of **3a**.

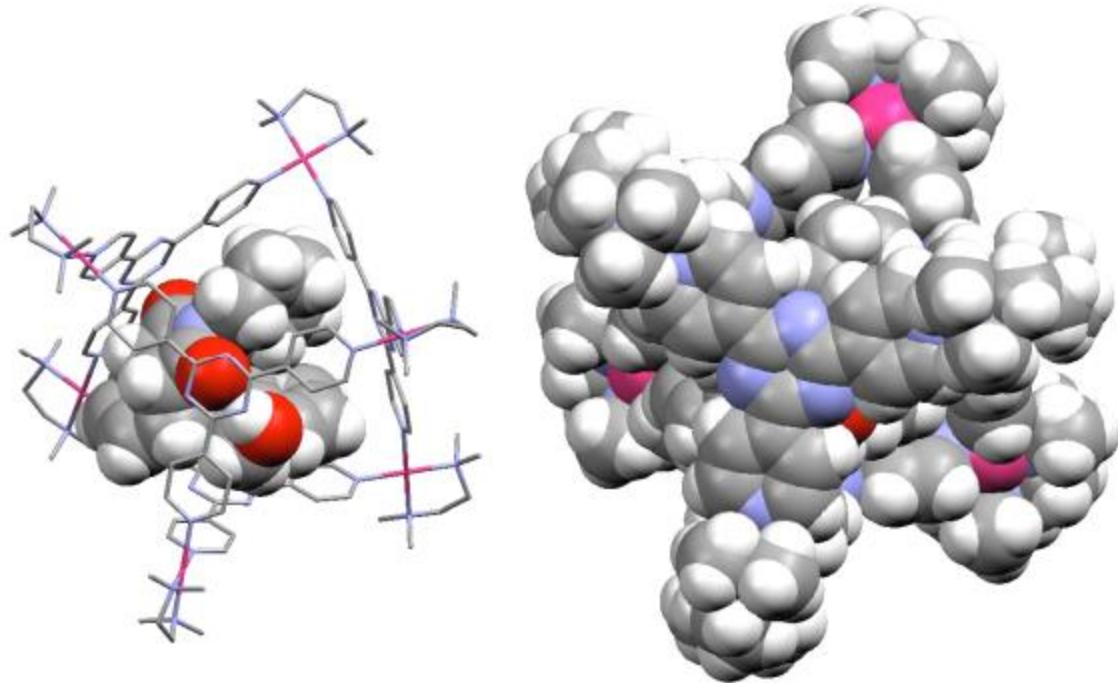


Fig. S16. Cylinder and/or Space-filling drawing of **1D5**.

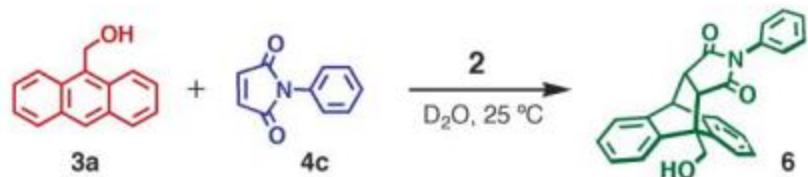


Fig. 4. Catalytic Diels-Alder reaction of 9-hydroxymethylnanthracene (**3a**) and *N*-phenylphthalimide (**4c**) in the aqueous solution of bowl **2**, leading to 9,10-adduct **6**.

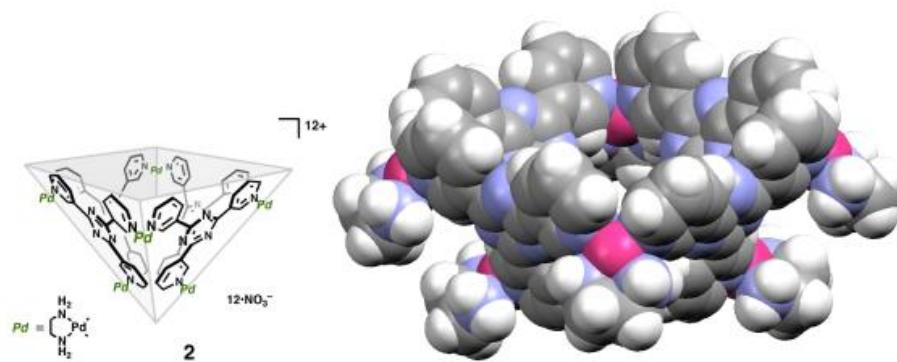


Fig. S18. Chemical structure of **2** and the Space-filling drawing.

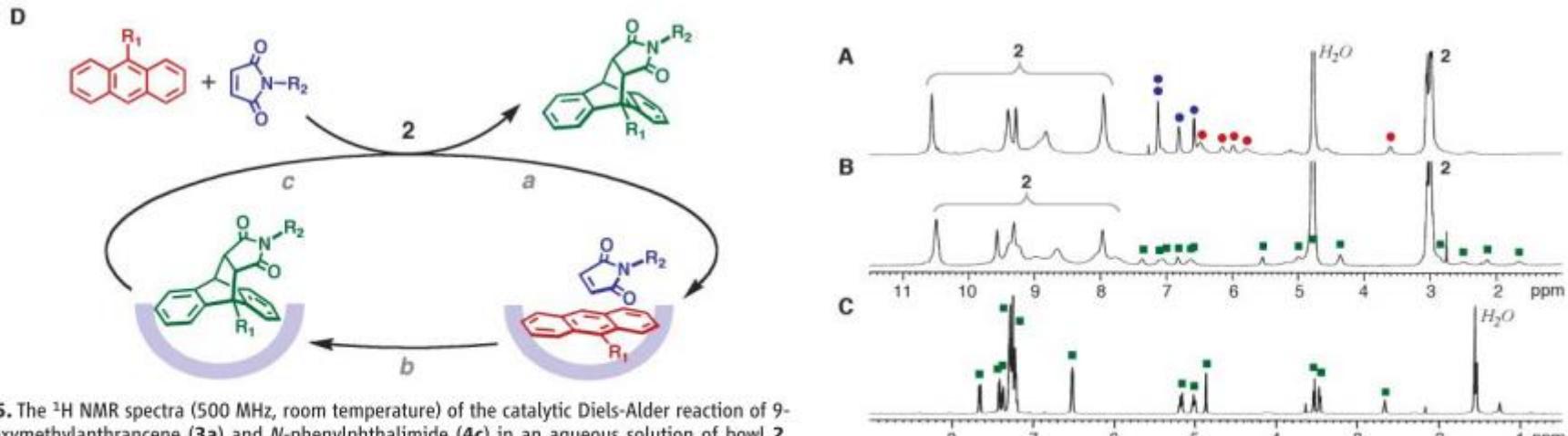
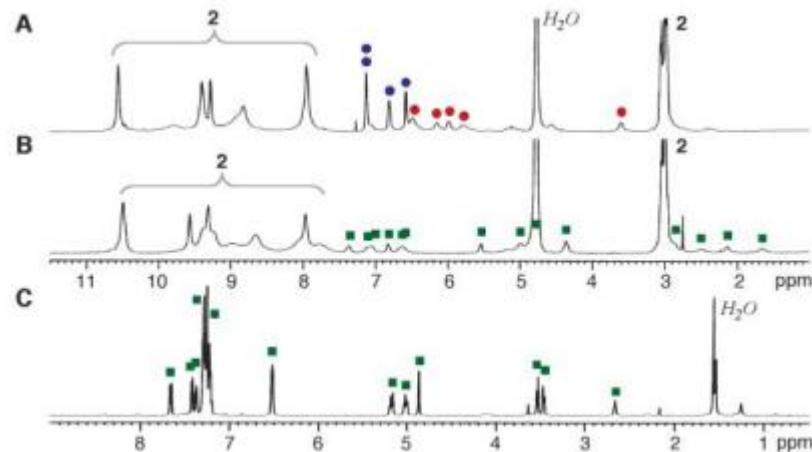
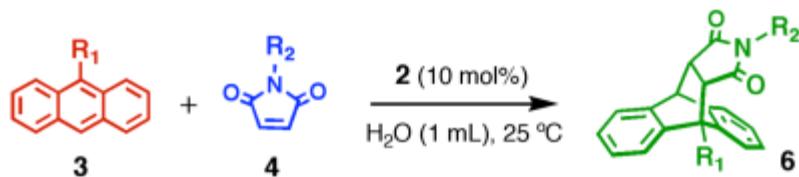


Fig. 5. The ^1H NMR spectra (500 MHz, room temperature) of the catalytic Diels-Alder reaction of 9-hydroxymethylanthracene (**3a**) and *N*-phenylphthalimide (**4c**) in an aqueous solution of bowl **2**. (A) Before and (B) after the reaction at room temperature for 5 hours (red circles, **3a**; blue circles, **4c**; and green squares, **6**). (C) Diels-Alder product **6** after extraction with CDCl_3 . (D) Schematic representation of the catalytic Diels-Alder reaction of anthracenes and phthalimide in the presence of bowl **2**. Autoinclusion of substrates into **2** (step a) and autoexclusion of the product from **2** (step c) underlie the efficient catalytic Diels-Alder reaction.





Entry	Substrate		Time	Yield(%) of 6		
	3 (R₁)	4 (R₂)		with 2	without 2	in CHCl ₃ [†]
1	-CH ₂ OH	propyl	5 h	>99	8	0
2	-CH ₂ OH	cyclohexyl	15 h	98	0	6
3	-CH ₂ OH	phenyl	5 h	>99 ^{a,†}	3	9
4	-CH ₂ OH	phenyl	15 h	6	7	21
5	-CH ₂ OH	benzyl	5 h	>99	trace	0
6	-CH ₂ OH	xylyl	15 h	94	0	17
7	-CH ₃	cyclohexyl	7 h	>99	0	5
8	-CH ₃	phenyl	3 h	>99	5	17
9	-CH=CH ₂	phenyl	1 d	88	0	trace
10	-CH=CH ₂	benzyl	1 d	97	5	4
11	-CO ₂ H	benzyl	1 d	12	0	0
12	-CH ₂ OH	phenyl	1 d	>99 [‡]	—	—

^a(en)Pd(NO₃)₂: 10 mol%

[†]without **2**

[‡]**2** : 1 mol%, hexane (1 mL)

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

Prasenjit Mal,¹ Boris Breiner,¹ Kari Rissanen,² Jonathan R. Nitschke^{1*} SCIENCE VOL 324 26 JUNE 2009

1697

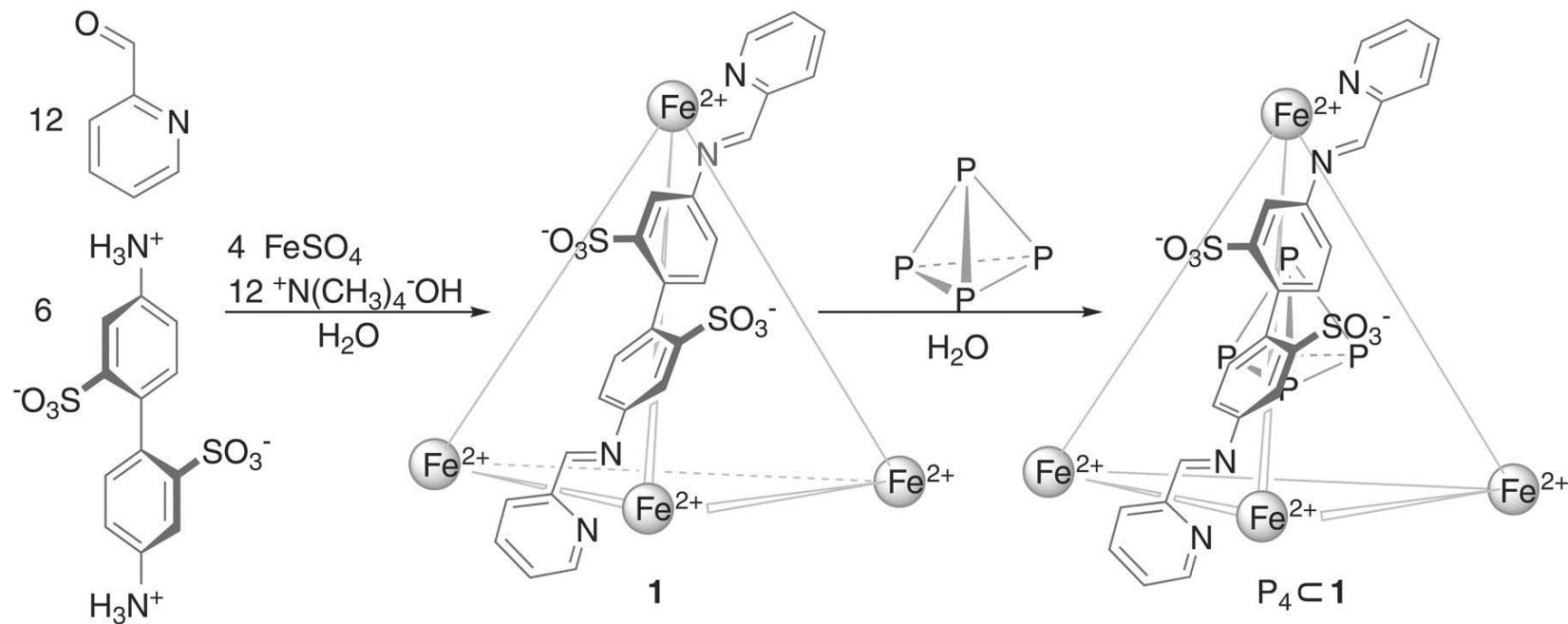


Fig. 1 Synthesis of tetrahedral cage **1** and subsequent incorporation of P₄.

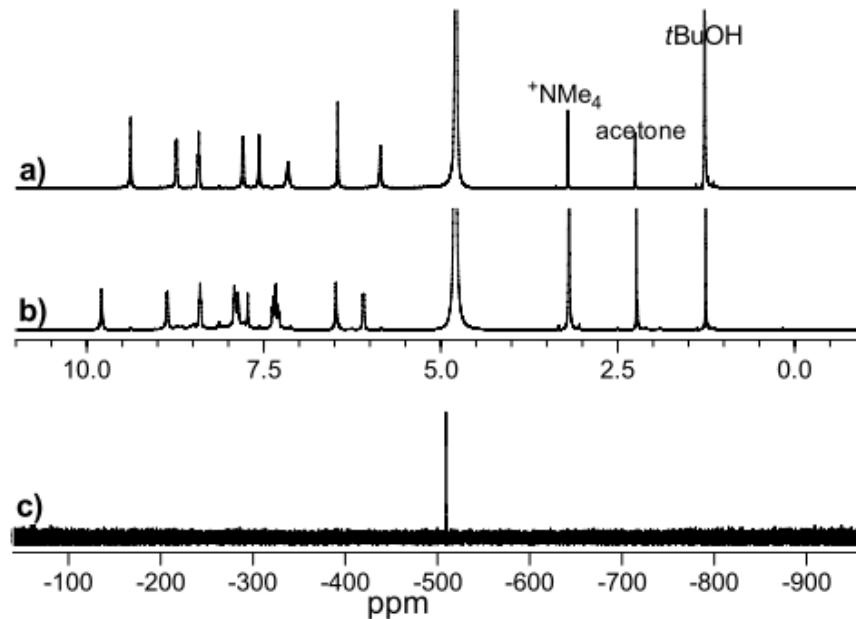


Figure S1. ¹H NMR spectra in D₂O of cage **1** (top), of P₄⊂**1** (middle), and ³¹P NMR spectrum of P₄⊂**1** (bottom).

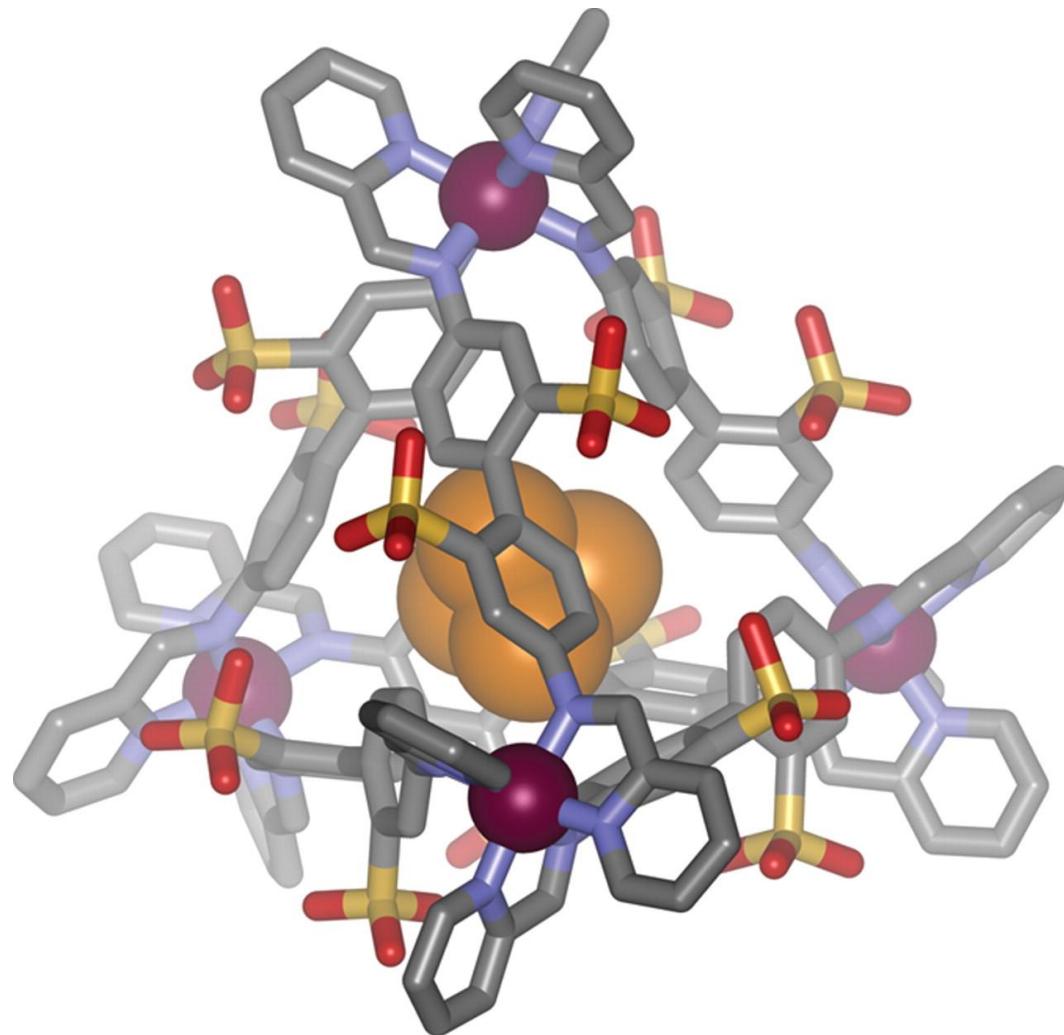


Fig. 2 Crystal structure of P4c1.

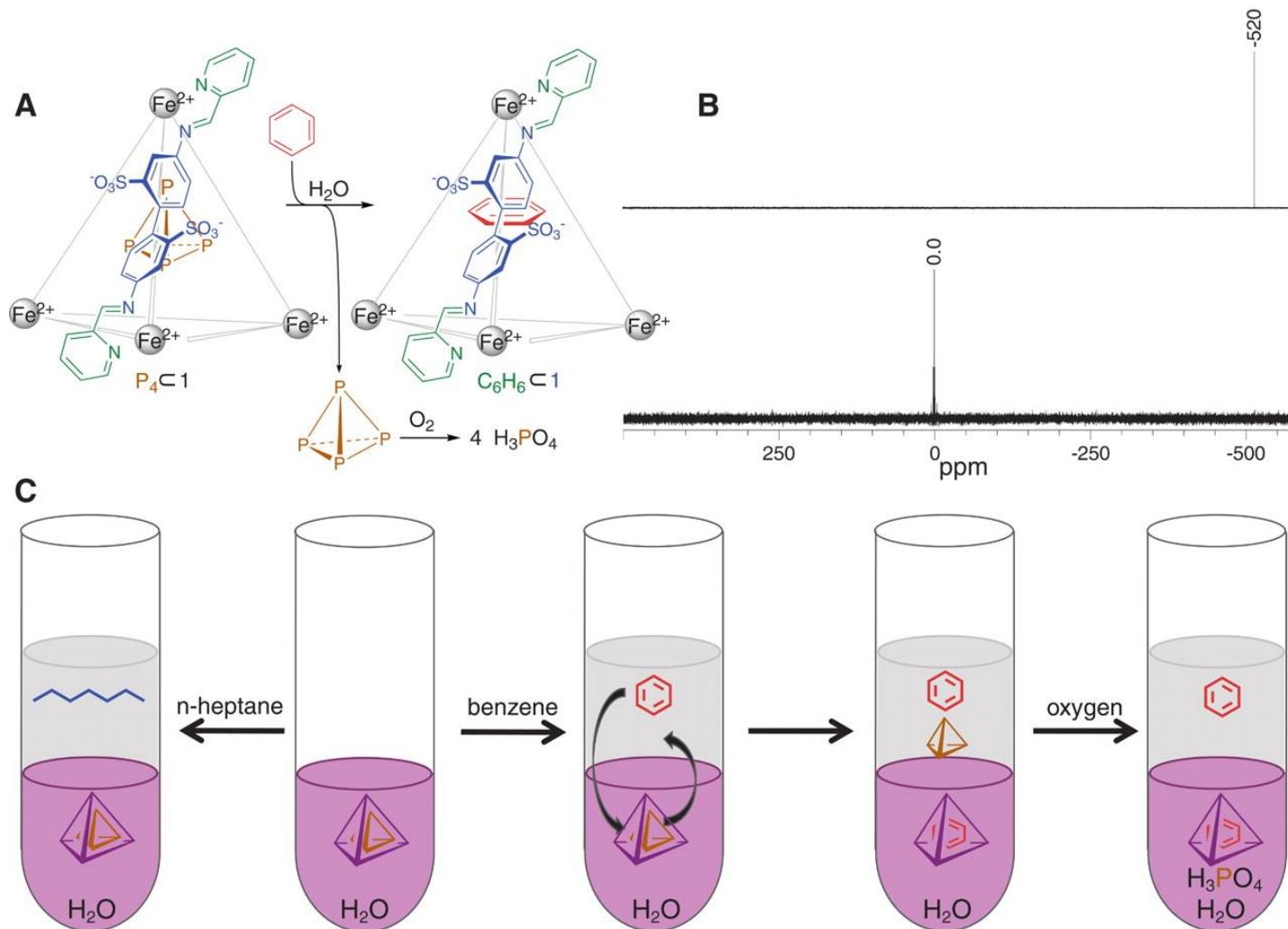
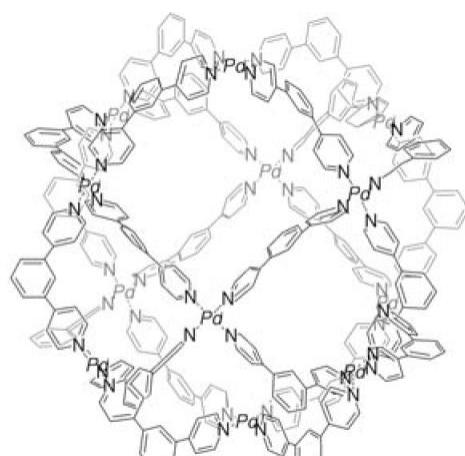
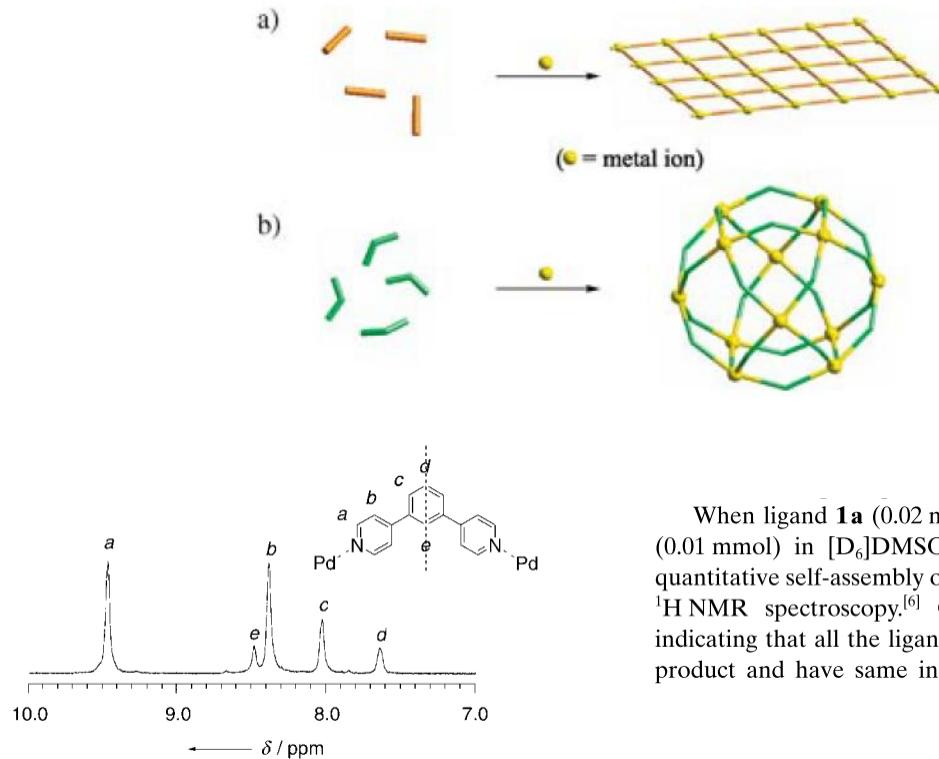
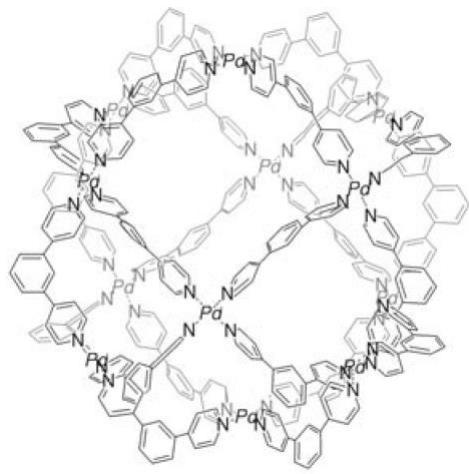


Fig. 3 Extraction of P4 from 1 by n-heptane is not possible, whereas replacing P4 with another suitable guest (benzene or cyclohexane) results in the facile removal of P4 into the organic solvent.

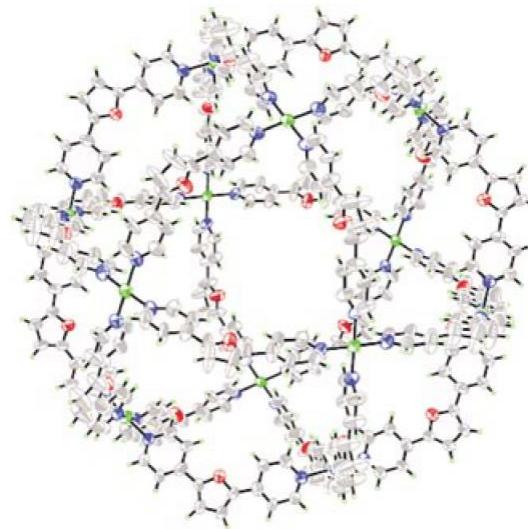


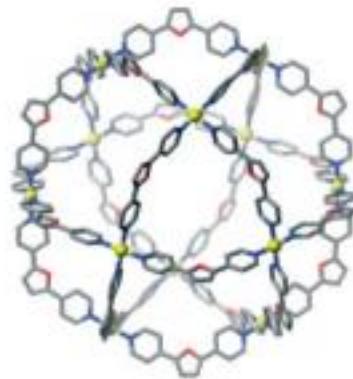
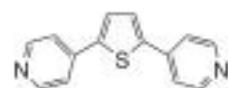
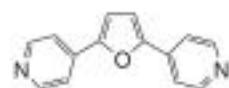
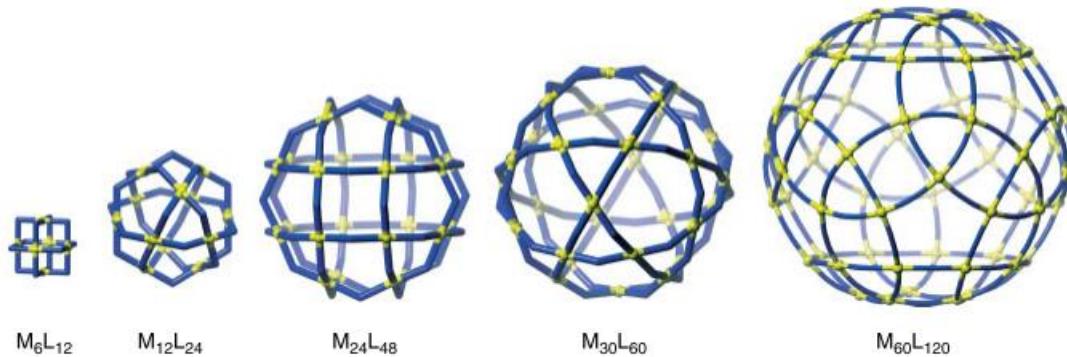
When ligand **1a** (0.02 mmol) was treated with $\text{Pd}(\text{NO}_3)_2$ (0.01 mmol) in $[\text{D}_6]\text{DMSO}$ (1.0 mL) at 70°C for 4 h, the quantitative self-assembly of a single product was detected by ^1H NMR spectroscopy.^[6] Only five signals are observed indicating that all the ligands are located equivalently in the product and have same inherent symmetry (Figure 2). The

complexation. Diffusion-ordered NMR spectroscopy (DOSY) showed a single band at the diffusion coefficient of $1.1 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, from which the diameter of the product was roughly estimated to be 3.6 nm.^[7] After anion exchange from $[\text{NO}_3]^-$ to $[\text{PF}_6]^-$ ions, cold-spray ionization mass spectrometry (CSI-MS)^[8] clearly indicated an $\text{M}_{12}\text{L}_{24}$ composition with the molecular weight of 10330 Da by a series of $[\text{M}-(\text{PF}_6^-)_n]^{n+}$ ($n=6-13$) peaks (Figure 3).^[9] Fragmentation in the MS measurement was hardly observed except the dissociation of counteranions, which demonstrates the remarkable stability of the product in solution. Elemental analysis was also consistent with the $\text{M}_{12}\text{L}_{24}$ composition.

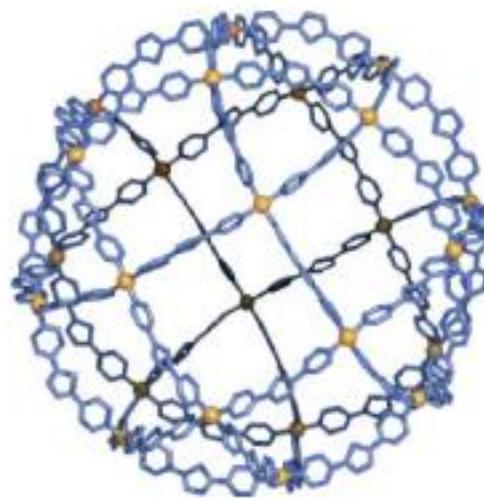


$[M_{12}L_{24}]^{12+}$





15



16