Cage Database

Created: 25 February 2015
Last edited: 27 February 2015

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Valentina Santolini

Kim Jelfs Group

MC1

2) CCDC NAME: EKUKUR

CCDC NUMBER: 789520

SA_{BET} = 1375 m_2/g

CCDC structure: Red crystals from DMSO, cracking instantly [**β**]

Surface area: as-synthesised microcystalline powder from THF [**α**]

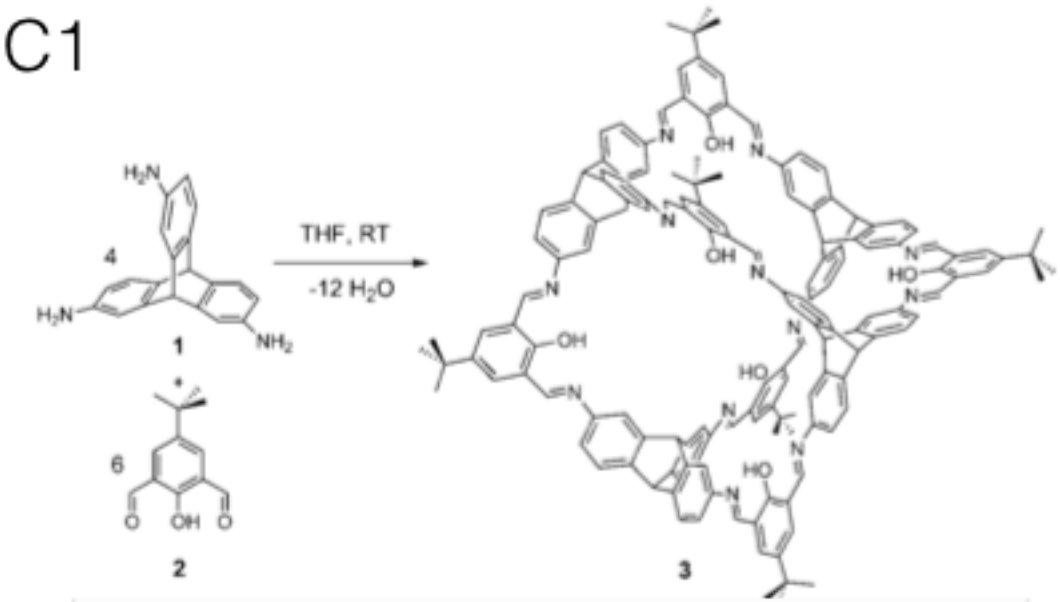
Explanation: **α** is more thermodynamically stable polymorph, whereas **β** is a kinetically formed polymorph

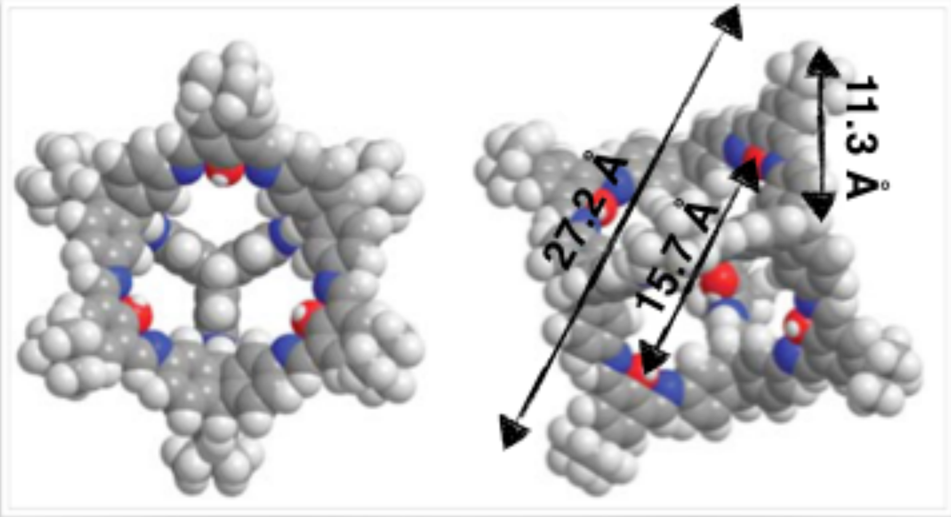
3) **α** was recrystallised from hot DMSO, so is it just better crystal of **β**?

SA_{BET} = 2071 m_2/g (Crystalline **β**)

SA_{BET} = 1377 m_2/g (Crystalline **α**)

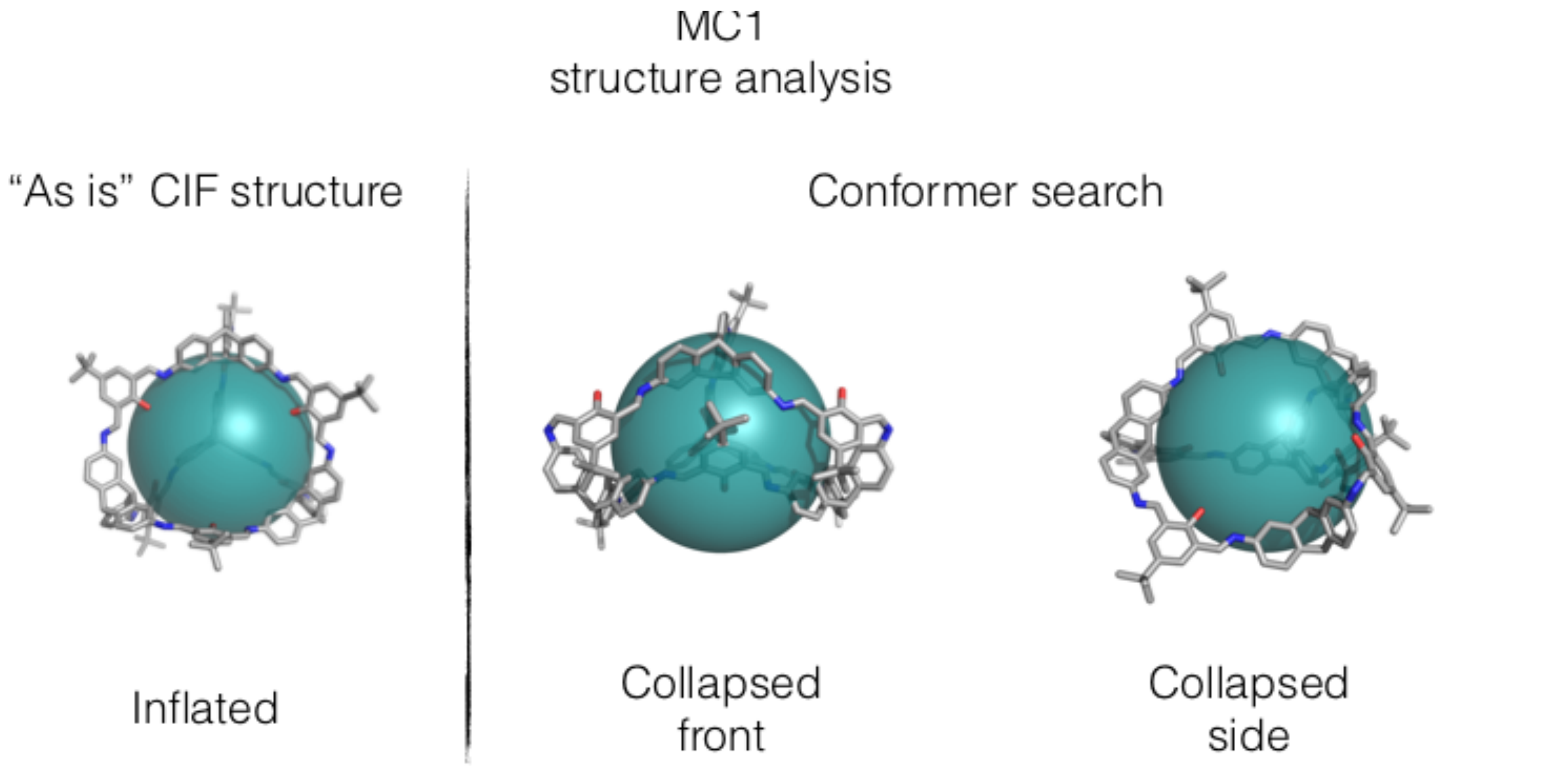
SA_{BET} = 951 m_2/g (Not defined - probably amorphous)





(1) Mastalerz, M. Chem. Commun. 2008, 4756.
(2) Mastalerz, M.; Schneider, M. W.; Oppel, I. M.; Presly, O. Angew. Chem. Int. Ed. Engl. 2011, 50, 1046.
(3) Schneider, M. W.; Oppel, I. M.; Ott, H.; Lechner, L. G.; Hauswald, H.-J. S.; Stoll, R.; Mastalerz, M. Chemistry 2012, 18, 836.

Mastalerz Cages



Mastalerz Cages

MC1

structure analysis

Extrinsic porosity:
green sphere diameter = 17.0 Å

Intrinsic porosity:
yellow sphere diameter = 9.8 Å

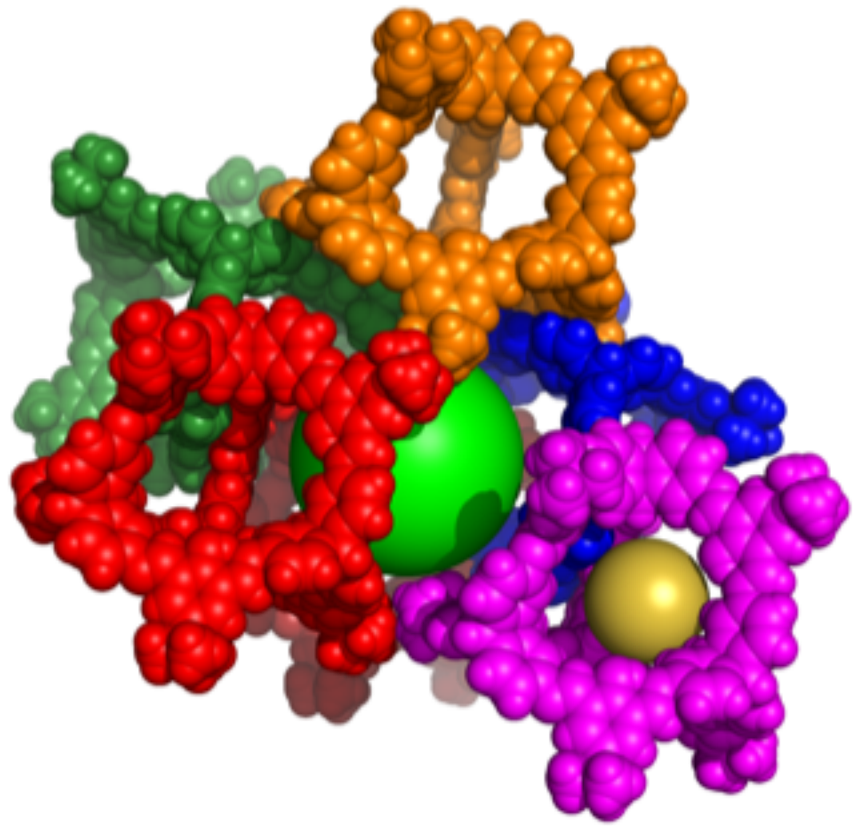
- some cage windows are fully facing extrinsic pore, some are obstructed by neighbours cages tBu groups, decreasing window diameter.

- some tBu groups of neighbouring cages are also invading intrinsic pores reducing their volume.

- cage packing is very inefficient

ZEO++ RES file:

Pore Limiting Diameter: 5.7 Å
Largest Included Sphere: 15.9 Å



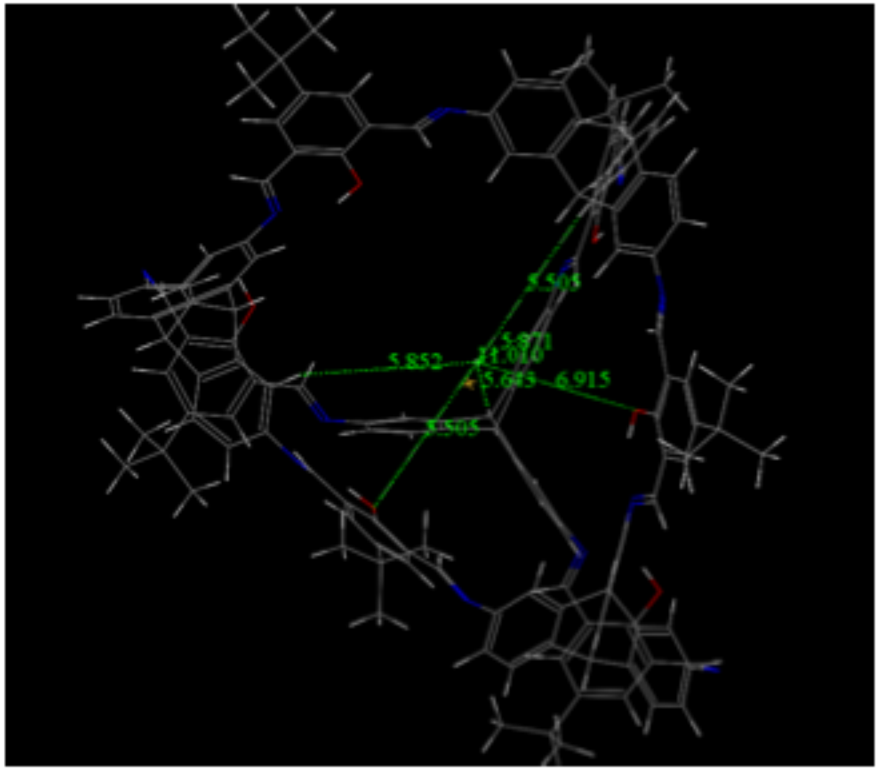
Mastalerz Cages

MC1
structure analysis

MC1 inflated d = 11.19 Å
(between two closest hydrogen atoms, diameter passing through COM)

MC1 collapsed d = 9.7 Å
(between two closest atoms: hydrogen and oxygen, diameter is not passing through COM, as cage is collapsed on one side only.

MC1 inflated V_{pore} = 524.5 Å^3
MC1 collapsed V_{pore} = 394.1 Å^3



Mastalerz Cages

MC1
parameters comparison

	Reported	ZEO++ r=1.55Å	ZEO++ r=1.82Å
β[1]	2071 m^2/g	4263 m^2/g	4049 m^2/g
α[1]	1377 m^2/g		
n.d.[1]	951 m^2/g		

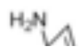
(1) Schneider, M. W.; Oppel, I. M.; Ott, H.; Lechner, L. G.; Hauswald, H.-J. S.; Stoll, R.; Mastalerz, M. Chemistry 2012, 18, 836.

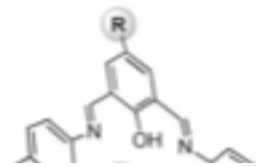
Mastalerz Cages

MC2

1) CCDC NAME: TATVER

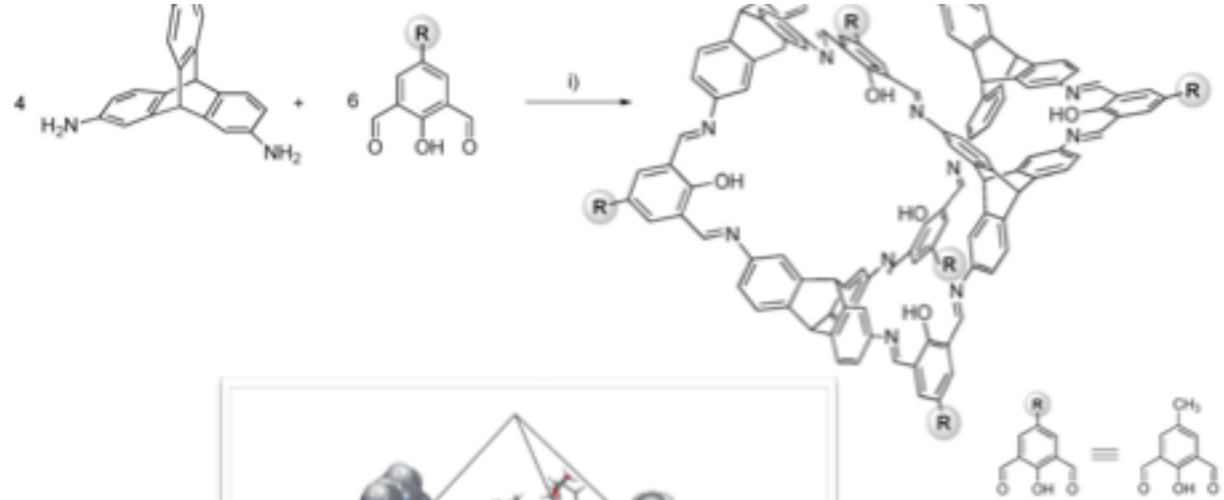
CCDC NUMBER: 847748

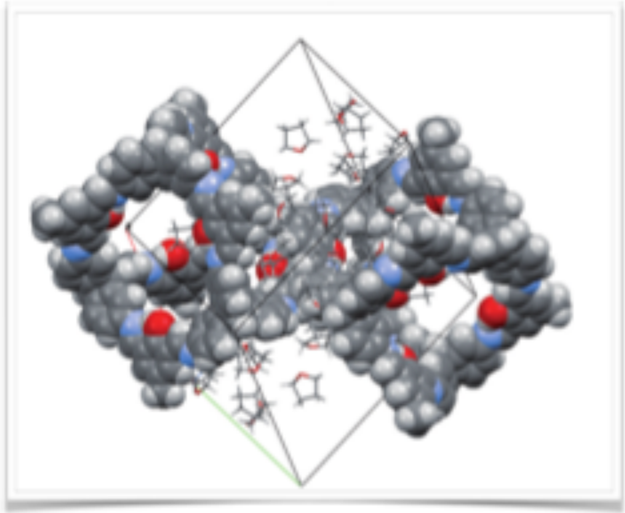




SA_{BET} = 1291 m^2/g

They report SA for two amorphous MC2 and for crystalline (mentioned above)





(1) Schneider, M. W.; Oppel, I. M.; Ott, H.; Lechner, L. G.; Hauswald, H.-J. S.; Stoll, R.; Mastalerz, M. Chemistry 2012, 18, 836.

Mastalerz Cages

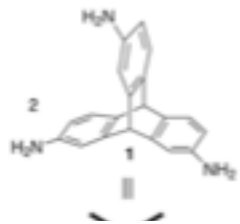
*All figures and values from ref. 1

MC3

[2+3]

1) CCDC NAME: SATJAA

CCDC NUMBER: 860485



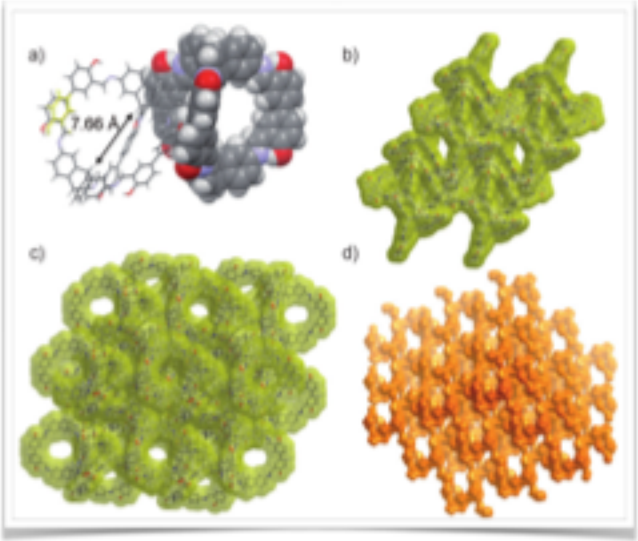
MC4

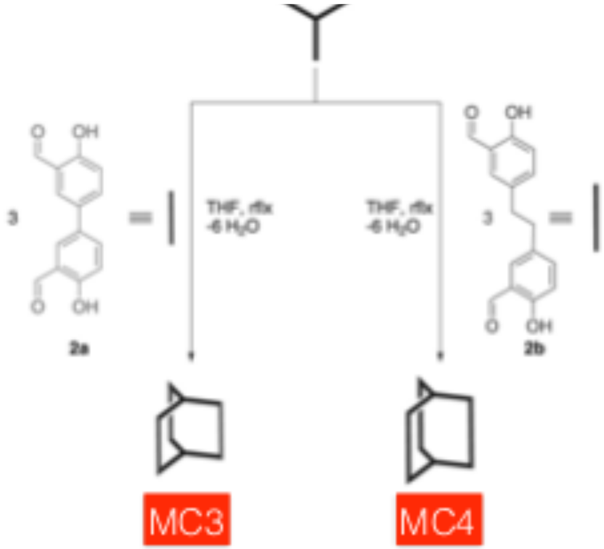
[2+3]

1) CCDC NAME: SATJEE

CCDC NUMBER: 860486

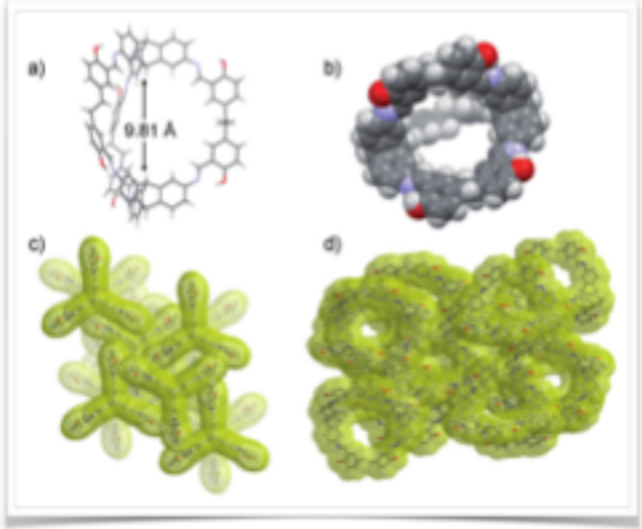
SA_{BET} = 744 m²/g





SA_{BET} = 30 m²/g*

*Phase transition upon guess uptake/removal as a result of more flexible linker[1]



(1) Schneider, M. W.; Oppel, I. M.; Mastalerz, M. Chemistry 2012, 18, 4156.
(2) Brutschy, M.; Schneider, M. W.; Mastalerz, M.; Waldvogel, S. R. Adv. Mater. 2012, 24, 6049.
(3) Mastalerz, M. Synlett 2013, 24, 781.

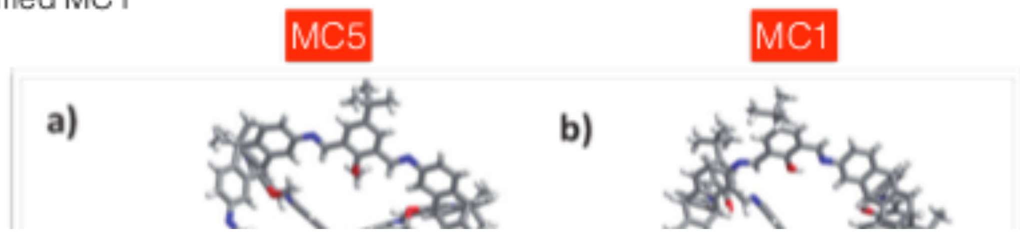
Mastalerz Cages

MC5

post-modified MC1

1) CCDC NAME: FEQXAC

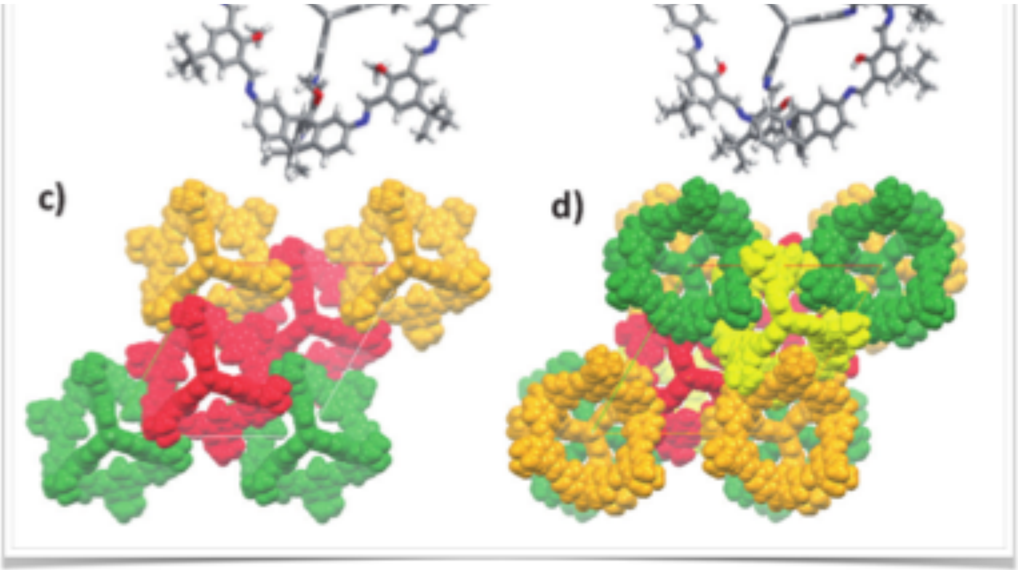
   CCDC NUMBER: 904717



SA_{BET} = 824 m^2/g (amorphous)

SA_{BET} = 741 m^2/g (crystalline activated at 200°C)

SA_{BET} = 1700 m^2/g (crystalline room-temperature)



(1) Schneider, M. W.; Oppel, I. M.; Griffin, A.; Mastalerz, M. Angew. Chem. Int. Ed. Engl. 2013, 52, 3611.

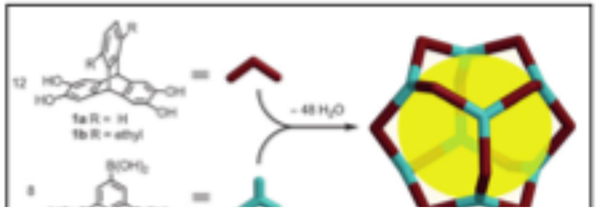
Mastalerz Cages

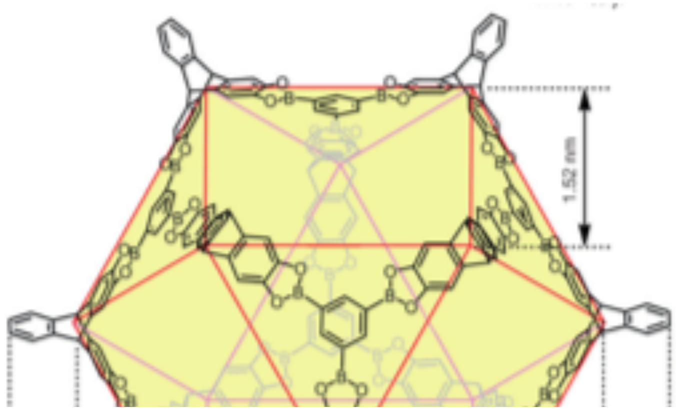
MC6

boronate-type cage

1) CCDC NAME: ZIRCIO

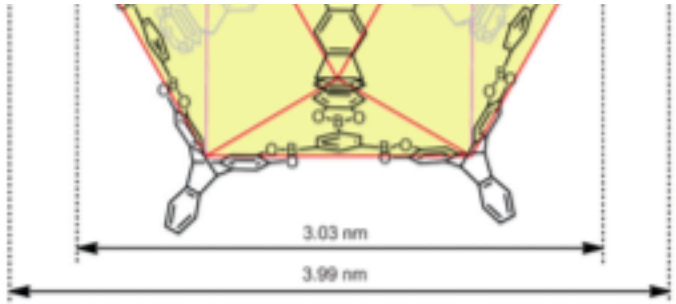
CCDC NUMBER: 948612

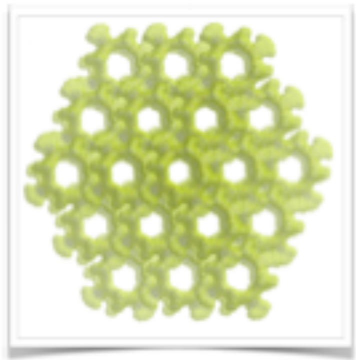


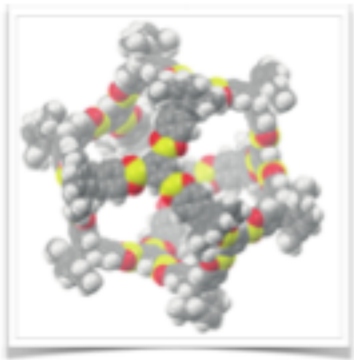


SA$_{BET}$ = 3758 m^2/g

*For 3a substrates are insoluble
Only 3b was reported (MC6)







(1) Zhang, G.; Presly, O.; White, F.; Oppel, I. M.; Mastalerz, M. Angew. Chemie Int. Ed. 2014, 53, 1516.

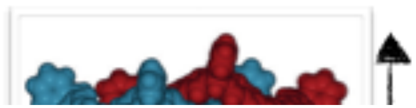
Mastalerz Cages

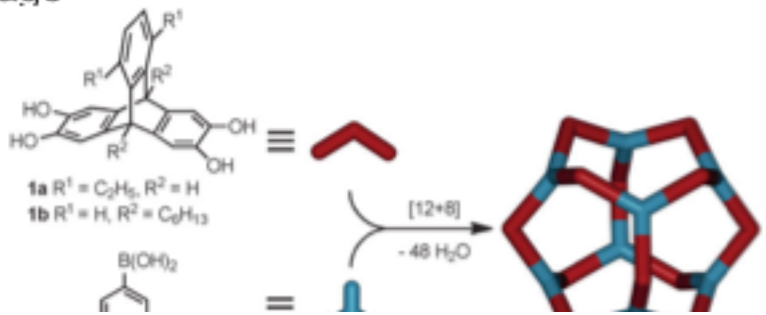
MC7

boronate-type interlocked catenane cage

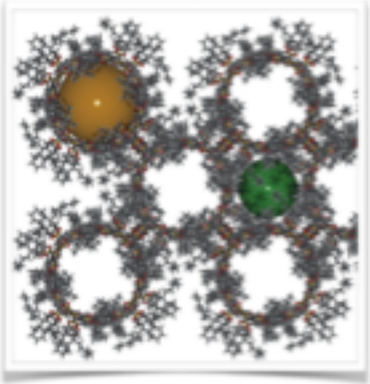
1) CCDC NAME: HIWHOM

CCDC NUMBER: 980837

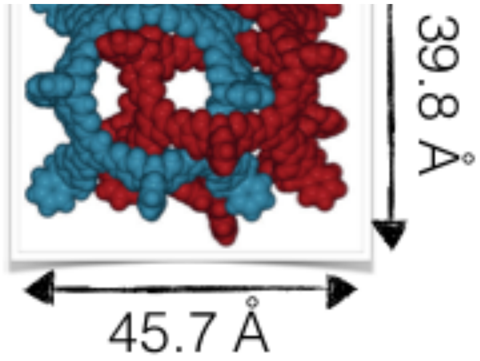


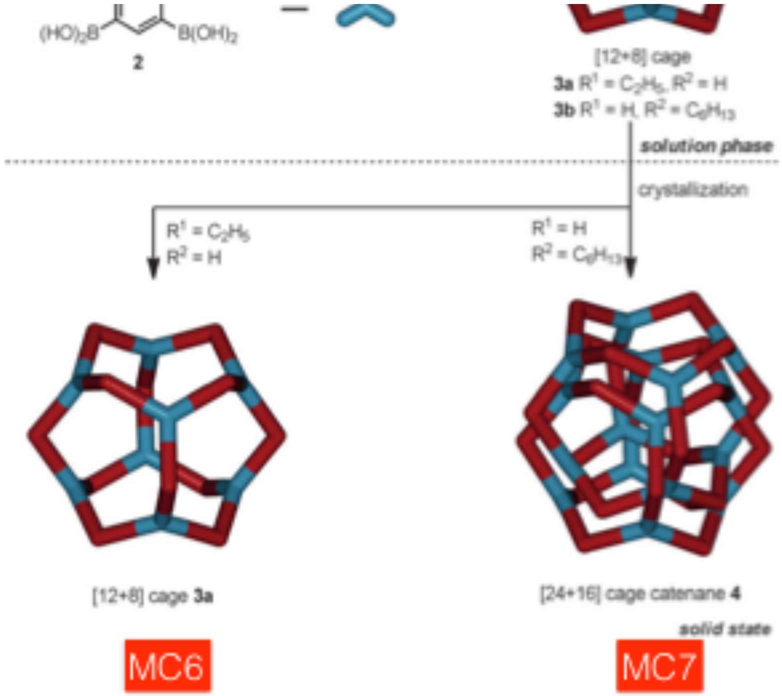


SA_{BET} = 1540 m^2/g



Internal pore (orange)
d = 20
External pore (green)
d = 14





(1) Zhang, G.; Presly, O.; White, F.; Oppel, I. M.; Mastalerz, M. Angew. Chem. Int. Ed. Engl. 2014, 53, 5126.

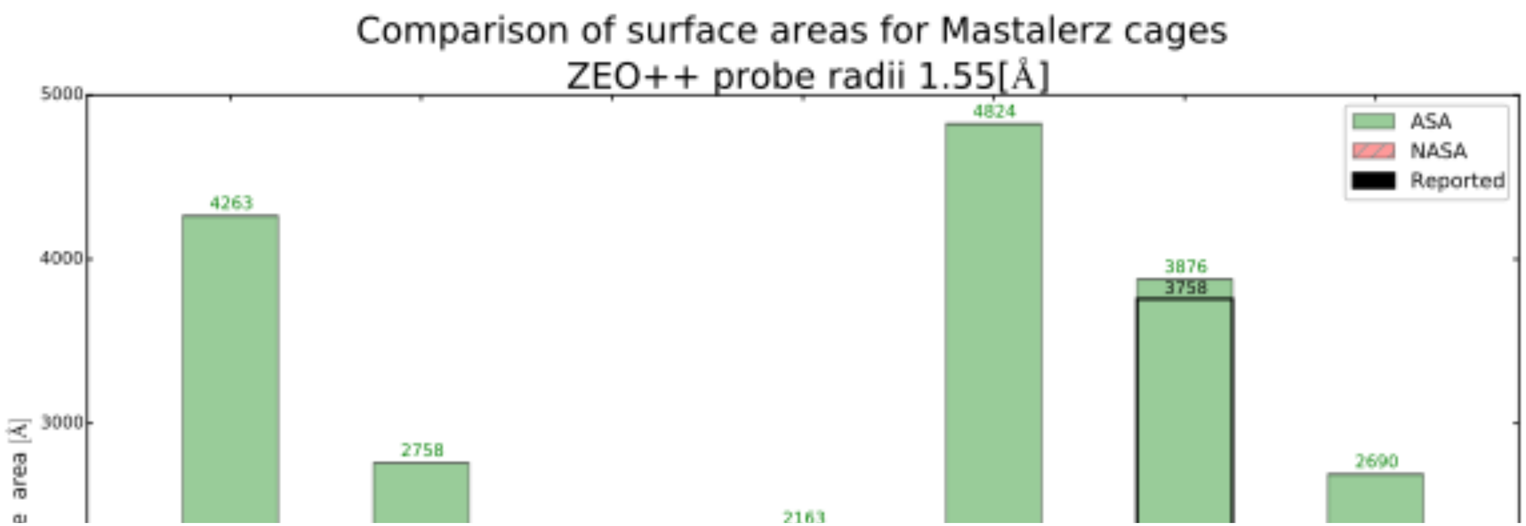
Mastalerz Cages

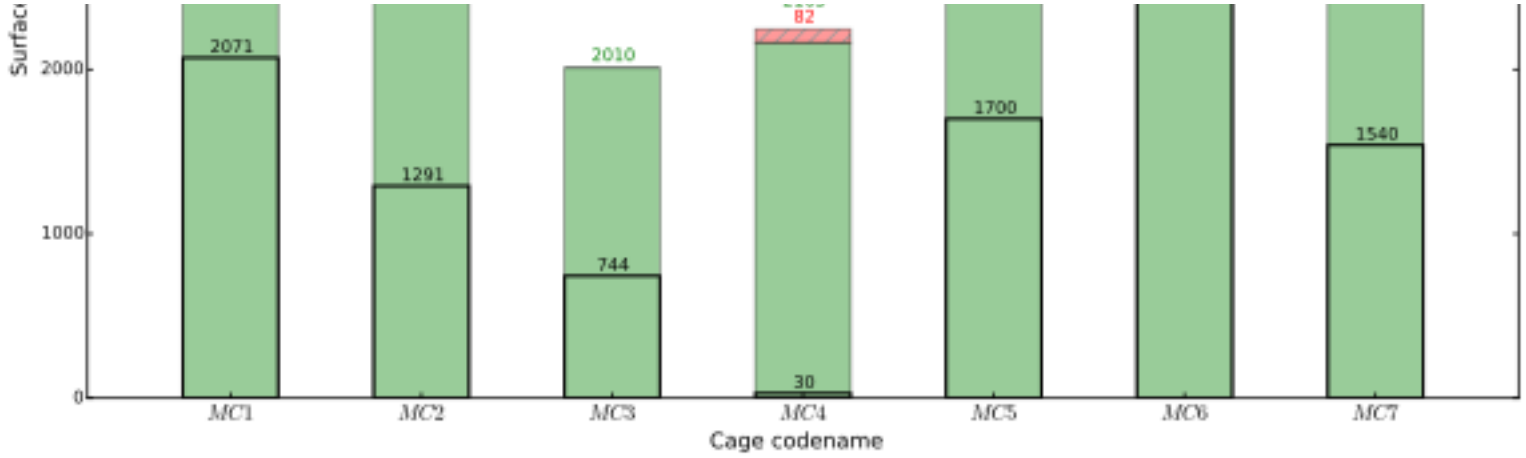
Comparison of Surface Areas

m^2/g	Reported (best to my knowledge)	ZEO++ (r=1.55Å)	ZEO++ (r=1.82Å)
MC1	2071 (cryst.)	4263 (0)	4049 (0)
MC2	1291 (cryst.)	2758 (0)	2408 (0)

MC3	744	2010 (0)	1663 (0)
MC4	30	2163 (82)	1531 (39)
MC5	1700 (cryst.)	4824 (0)	4499 (0)
MC6	3758	3876 (0)	3704 (0)
MC7	1540	2690 (0)	2422 (0)

Mastalerz Cages



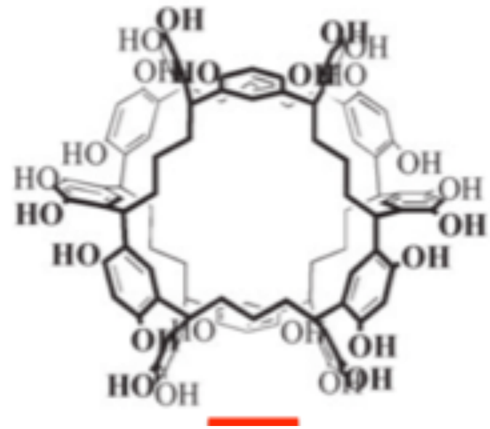


Noria Cages

NC1

CCDC Name: GUMCIB
CCDC Number: 717929

Ref. 1

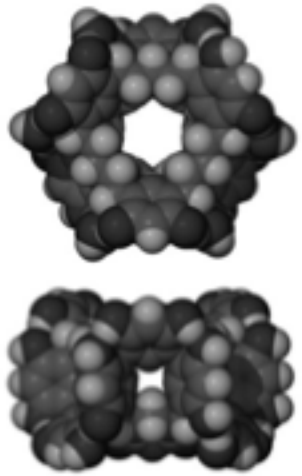


2) Amorphous NC1

SA_{BET} (N2) = 40 m^2/g
SA_{BET}(CO2)= 250-280 m^2/g

$S_{ABET}(CO_2) = 230\text{-}280\ m^2/g$

noria



Ref. 2

'Failed to isolate crystalline guest free powders'

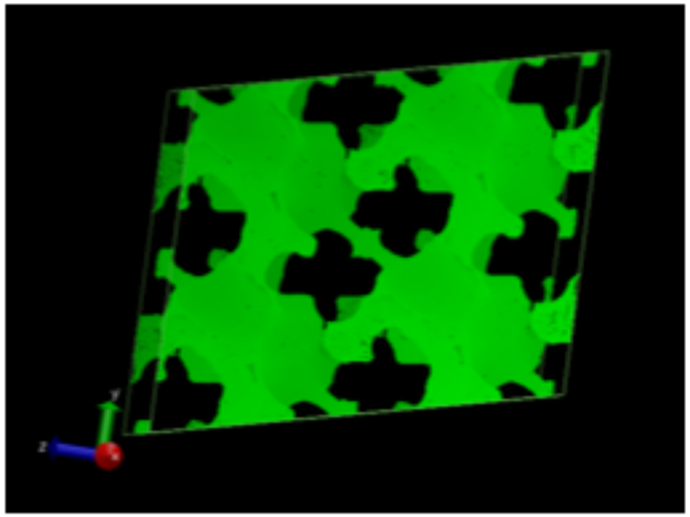
First reported:

1. Kudo, H.; Hayashi, R.; Mitani, K.; Yokozawa, T.; Kasuga, N. C.; Nishikubo, T. Angew. Chemie Int. Ed. 2006, 45, 7948.

Crystal structure and best description:

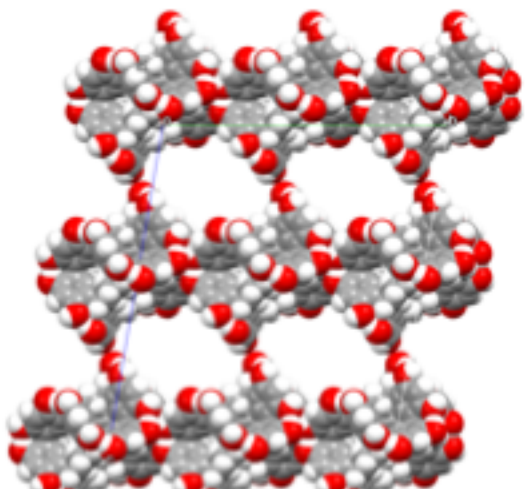
2. Tian, J.; Thallapally, P. K.; Dalgarno, S. J.; McGrail, P. B.; Atwood, J. L. Angew. Chemie Int. Ed. 2009, 48, 5492.

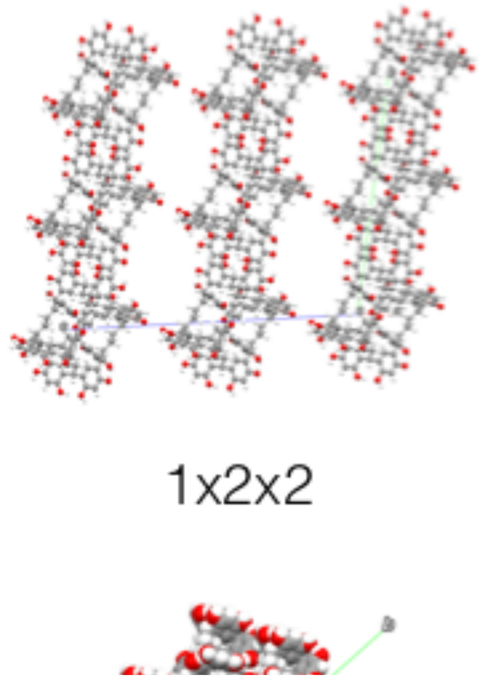
Noria Cages



NC1

crystal packing

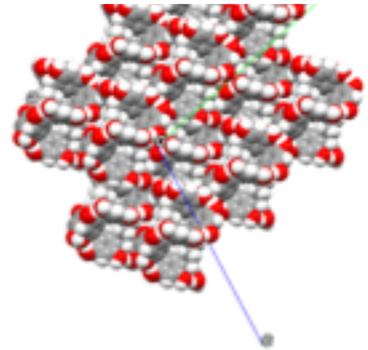




1x2x2

1.55Å 30K

view along a* plane



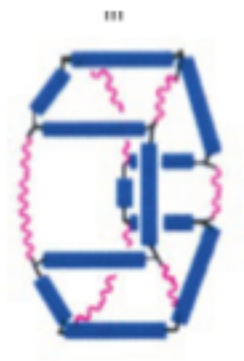
2x2x1

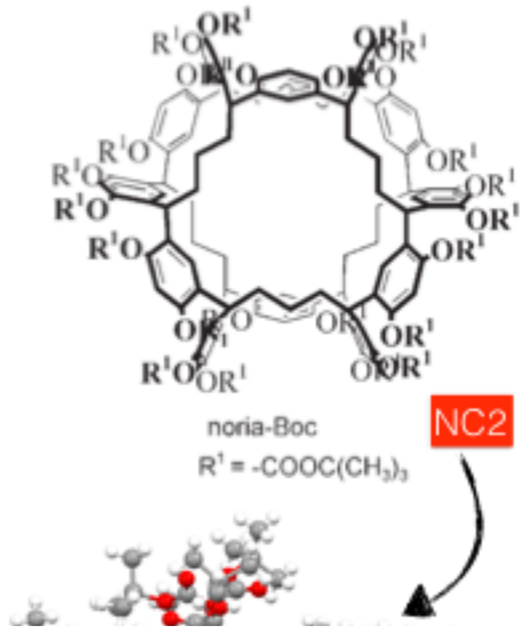
Noria Cages

NC2

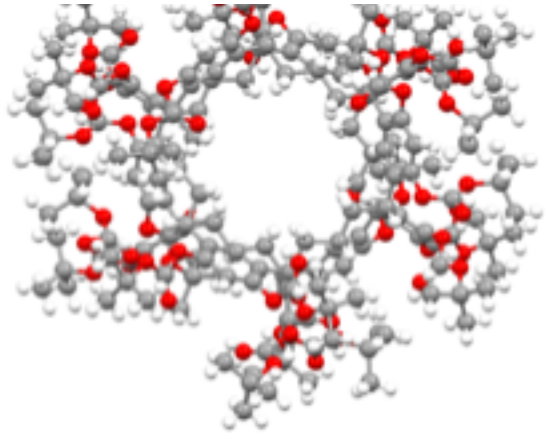
1.NC2 - noria with *tert*-butylcarbonate protective group (for better solubility)

- noria-COOEt (NC3) selective towards Rb^{+} cations extraction from solution (over Na^{+},K^{+},Cs^{+})





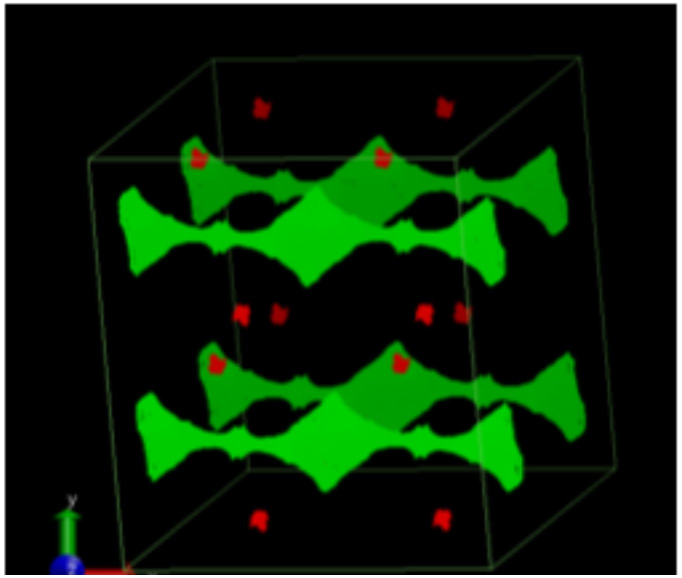
waterwheel

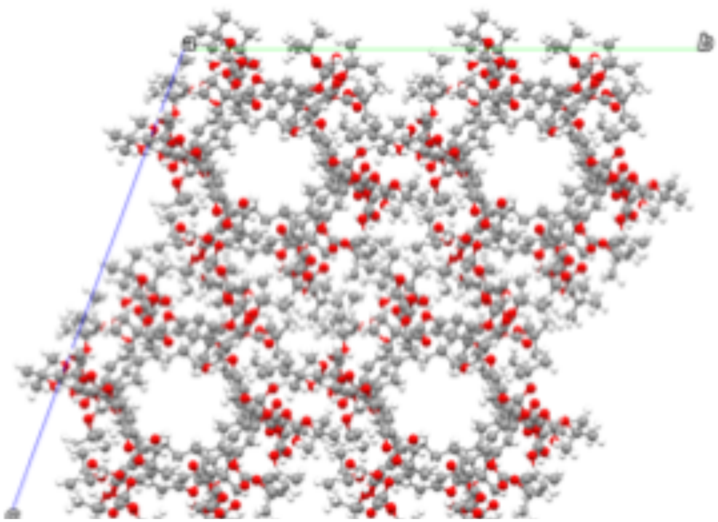


(1) Kudo, H.; Hayashi, R.; Mitani, K.; Yokozawa, T.; Kasuga, N. C.; Nishikubo, T. Angew. Chemie Int. Ed. 2006, 45, 7948.

Noria Cages

NC2





1.55 30K

2x2x2 - view along a plane

Noria Cages

Comparison of Surface Areas

m^2/g	Reported (best to my knowledge)	ZEO++ (r=1.55Å)	ZEO++ (r=1.82Å)
NC1	40 (N_2) 280 (CO_2)	3160	2568

NC2	n/a	311	226

Noria Cages

Properties and applications
(there are several noria derivatives)

Noria used as a template in template polymerisation
Saito Y., Saito R., Kudo H., Nishikubo T., *Macromol.* 2008, 41, 3755-3757

Extreme ultraviolet resist materials
for example: Kudo H., Suyama Y., Oizumi H., Itani T., Nishikubo T., J. Mater. Chem., 2010, 20 4445-4450

Proton carriers in Nafion-perfluorinated ionomer membranes
Nazir N. A., Kudo H., Nishikubo T., Kyu T., J. Mater. Sci., 2012, 47, 7269-7279

For protein stabilisation and activation
Jebors S., Tauran Y., Aghajari N., Boudebbouze S., Maguin E., Haser R., Coleman A. W., Rhimi M., Chem. Commun., 2011, 47, 12307-12309

Environmentally friendly pattering of noria with supercritical carbon dioxide
Tanaka M., Rastogi A., Kudo H., Watanabe., Nishikubo T., Ober C. K., J. Mater. Chem, 2009, 19 4622-4626

Photo-cross-linking reaction of noria derivatives containing photo reactive groups
Kudo H., Niina N., Hayashi R., Kojima K., Nishikubo., Macromol., 2010, 43, 4822-4826

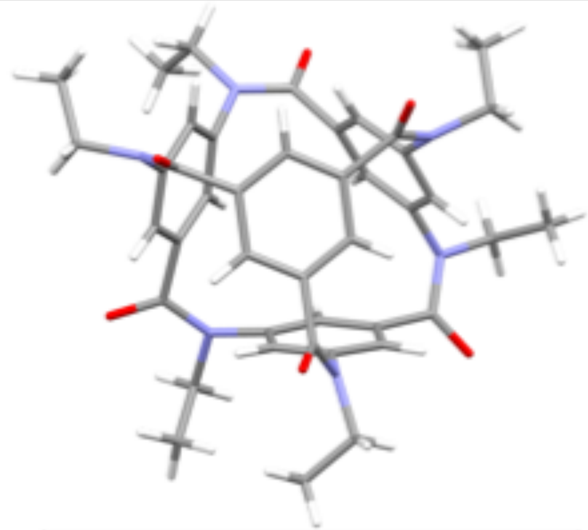
DFT electronic structure calculations of noria
Peerannawar S. R., Shridhar G. P., Comp. Theor. Chem., 2013, 1015, 44-51

Warmuth Cages

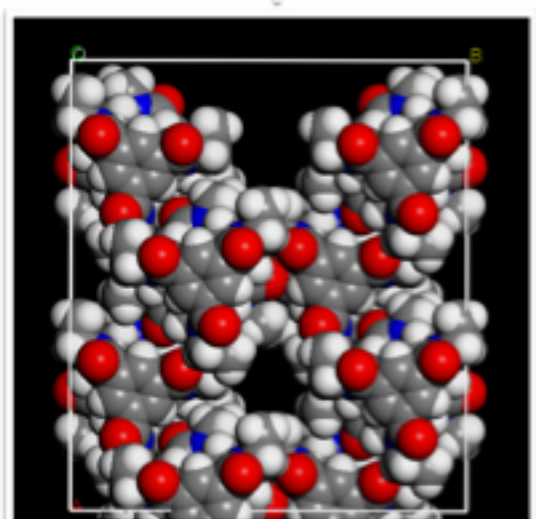
No crystal structures

Azumaya 'Tiny' Cages

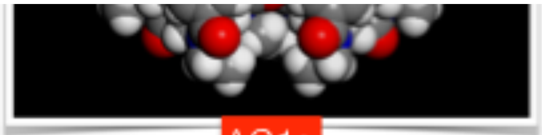
AC1



1. Amide-type chiral cage
2. Intrinsic void is present, but too small windows even for H_2
3. Racemic crystal creates extrinsically porous 1D channels, enantiopure crystals does not (AC1b).



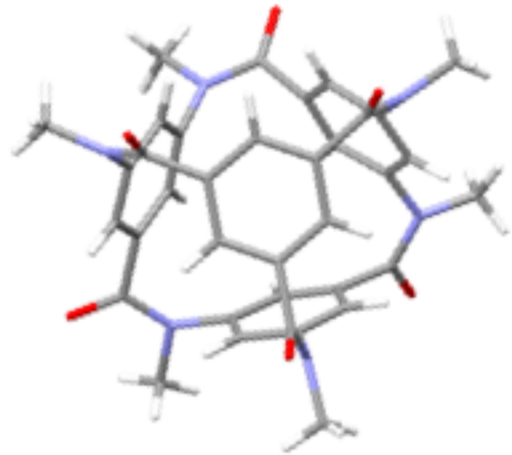
(1) Masu, H.; Katagiri, K.; Kato, T.; Kagechika, H.; Tominaga, M. J. Org. Chem. 2008, 5143.



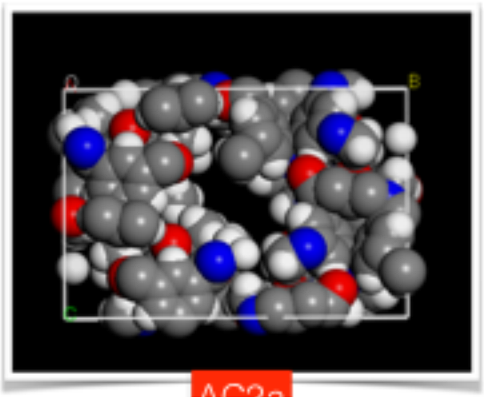
AC1a

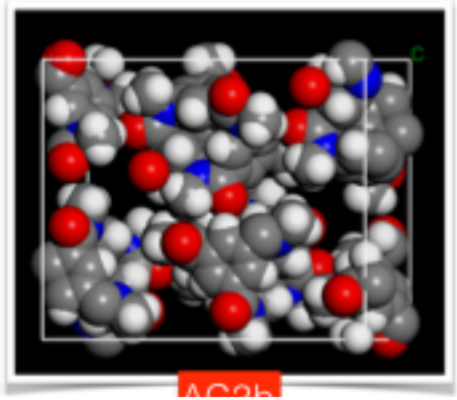
Azumaya ‘Tiny’ Cages

AC2



1. Amide-type chiral cage (same as AC1, only terminal groups are methyls instead of ethyls)
2. Intrinsic void is present, but too small windows even for H_2
3. Two polymorphs, similarly to AC1-racemate, they create 1D extrinsic channels, that are occupied with solvent molecules

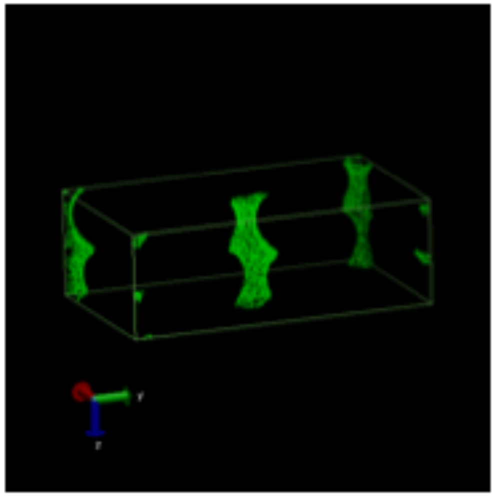




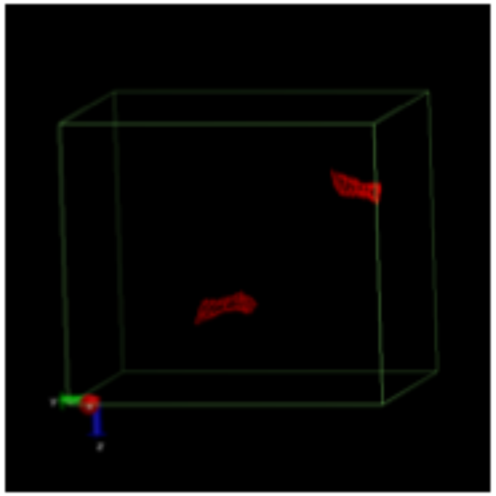
(1) Masu, H.; Sagara, Y.; Imabeppu, F.; Takayanagi, H.; Katagiri, K.; Kawahata, M.; Tominaga, M.; Kagechika, H.; Yamaguchi, K.; Azumaya, I. CrystEngComm 2011, 13, 406.

Azumaya 'Tiny' Cages

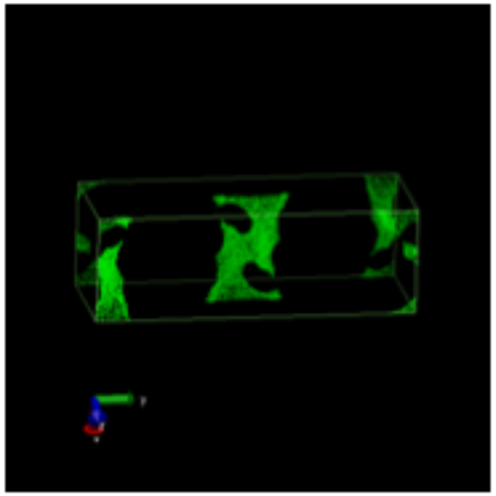
Surface areas visualisation (VMD 1.55Å 10000)



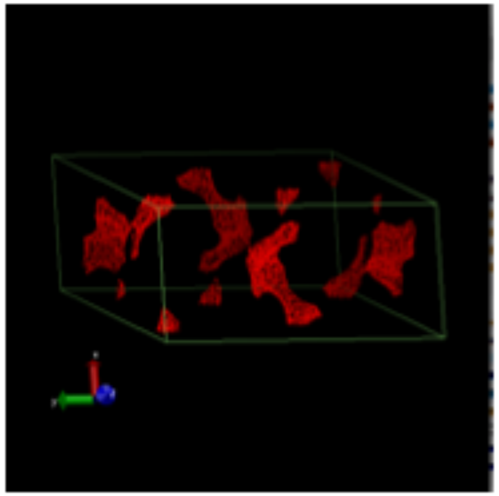
AC1a



AC1b



AC2a



AC2b

Azumaya 'Tiny' Cages

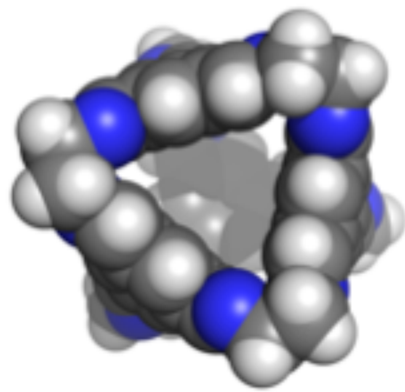
Surface areas

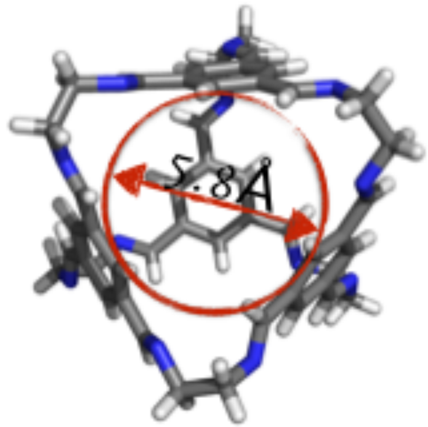
m^2/g	Reported (best to my knowledge)	ZEO++ (r=1.55Å)	ZEO++ (r=1.82Å)
AC1a	n/a	326 (0)	217(0)
AC1b	n/a	0 (51)	0 (6)
AC2a	n/a	562 (0)	0 (172)
AC2b	n/a	0 (567)	0 (176)

Cooper Cages

CC1

1) Two polymorphs
   CCDC Name: PUDWUH [**α**] ELALAF [**β**]
   CCDC Number: 720848 [**α**]
   SA_{BET}= 24 m^2/g [**α**]
   SA_{BET}= 550 m^2/g [**β**]
   α is formally non-porous, upon desolvation group symmetry changes, but remains non-porous and crystal is of poor quality
   β is obtained by recrystallisation of **α** from o-xylene and is porous

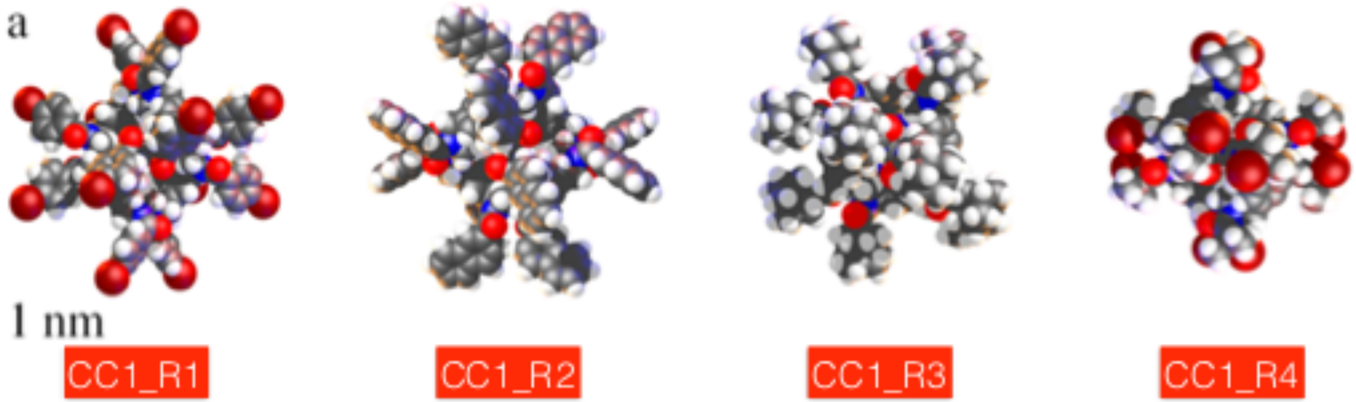




(1) Tozawa, T.; Jones, J. T. A.; Swamy, S. I.; Jiang, S.; Adams, D. J.; Shakespeare, S.; Clowes, R.; Bradshaw, D.; Hasell, T.; Chong, S. Y.; Tang, C.; Thompson, S.; Parker, J.; Trewin, A.; Bacsa, J.; Slawin, A. M. Z.; Steiner, A.; Cooper, A. I. Nat. Mater. 2009, 8, 973.

Cooper Cages Nanoporous 'dendrimers'

CC1 derivatives



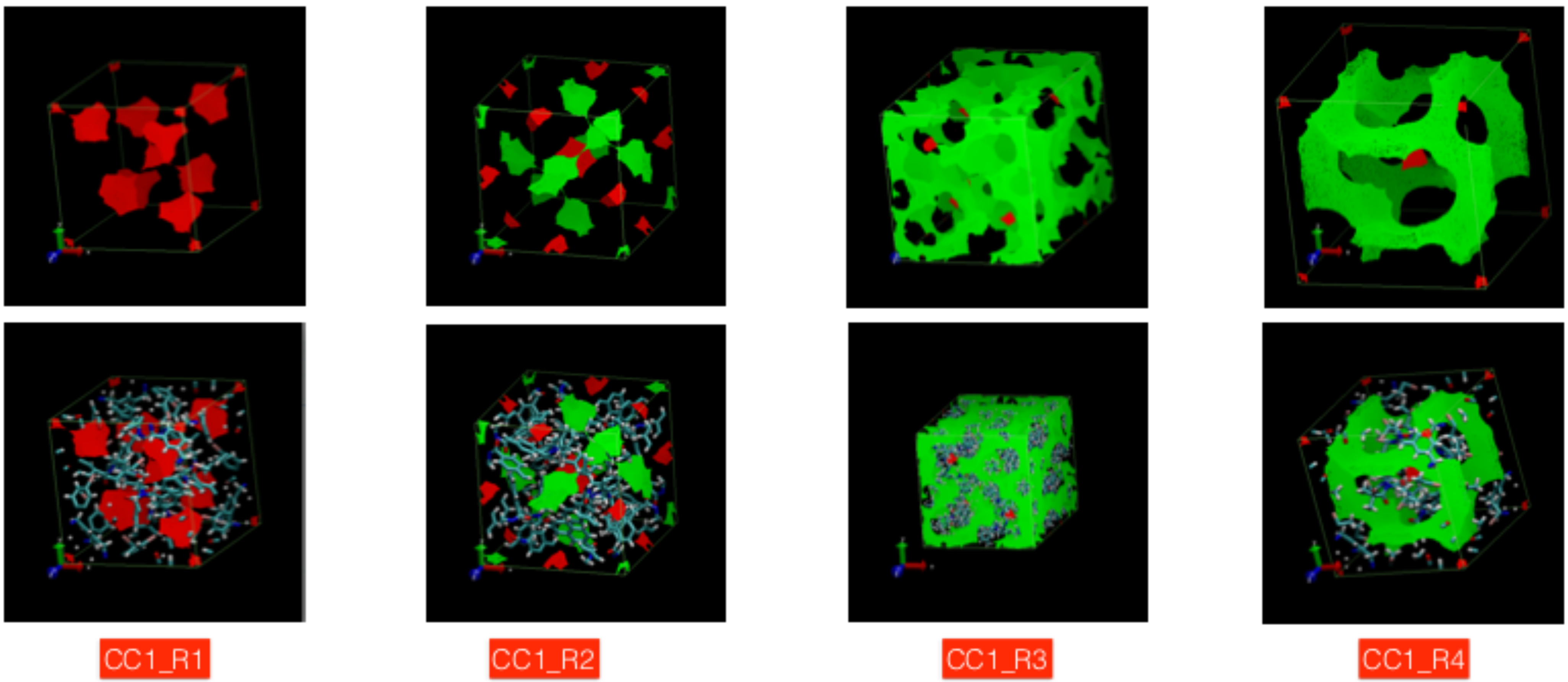
1. First cage 1 was reduced and than several dodecaamides were synthesised
2. Although, crystal structures are available, upon desolvation all of them become amorphous and completely not porous for N_2 or H_2

R1 = 4-bromobenzoyl
R2 = napthoyl
R3 = 1-adamantanecarbonyl
R4 = 2-bromoisobutyryl

(1) Culshaw, J. L.; Cheng, G.; Schmidtmann, M.; Hasell, T.; Liu, M.; Adams, D. J.; Cooper, A. I. J. Am. Chem. Soc. 2013, 135, 10007.

Cooper Cages

CC1 derivatives



Cooper Cages

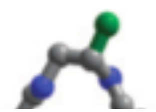
CC1 derivatives surface areas

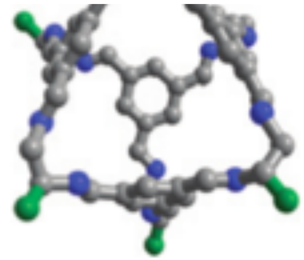
CC1 derivatives surface areas

m^2/g	Reported (best to my knowledge)	ZEO++ (r=1.55Å)	ZEO++ (r=1.82Å)
CC1_R1	n/a	0 (684)	0 (437)
CC1_R2	n/a	598 (217)	0 (505)
CC1_R3	n/a	2537 (44)	1963 (17)
CC1_R4	n/a	1798 (41)	1498 (18)

Cooper Cages

CC2

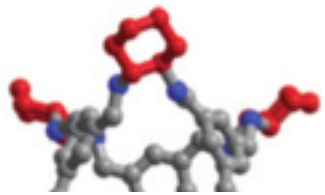


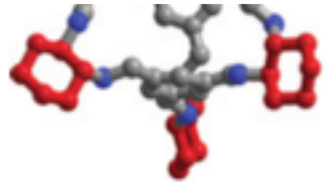


(1) Tozawa, T.; Jones, J. T. A.; Swamy, S. I.; Jiang, S.; Adams, D. J.; Shakespeare, S.; Clowes, R.; Bradshaw, D.; Hasell, T.; Chong, S. Y.; Tang, C.; Thompson, S.; Parker, J.; Trewin, A.; Bacsa, J.; Slawin, A. M. Z.; Steiner, A.; Cooper, A. I. Nat. Mater. 2009, 8, 973.

Cooper Cages

CC3

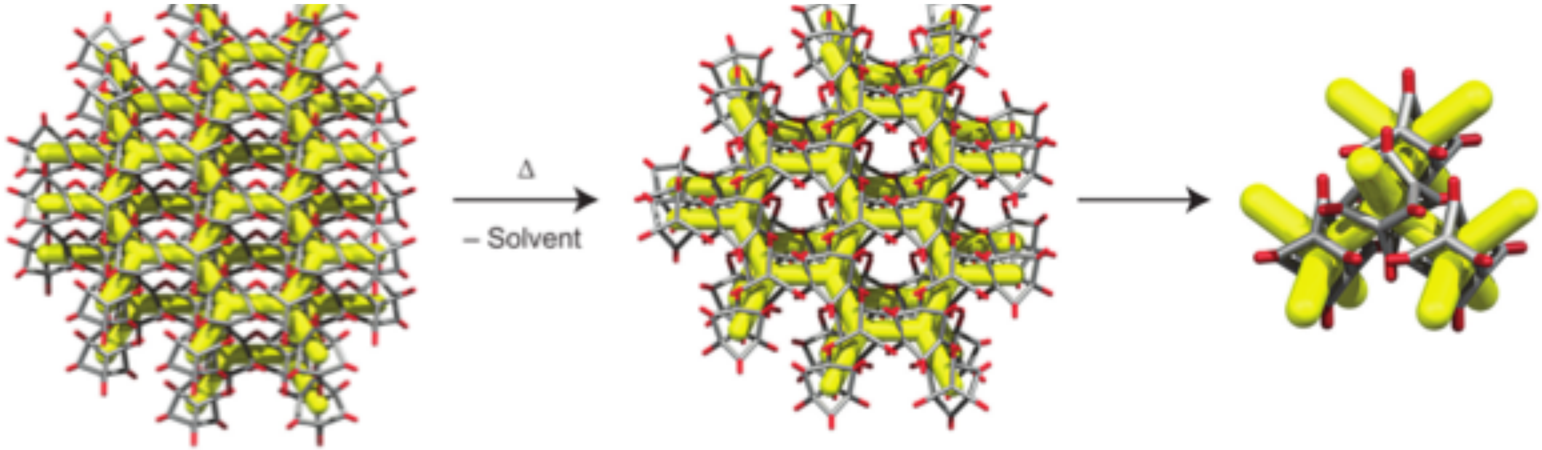




(1) Tozawa, T.; Jones, J. T. A.; Swamy, S. I.; Jiang, S.; Adams, D. J.; Shakespeare, S.; Clowes, R.; Bradshaw, D.; Hasell, T.; Chong, S. Y.; Tang, C.; Thompson, S.; Parker, J.; Trewin, A.; Bacsa, J.; Slawin, A. M. Z.; Steiner, A.; Cooper, A. I. Nat. Mater. 2009, 8, 973.

Cooper Cages

CC3



Phase I Phase II CC3*α*

(1) Little, M. A.; Briggs, M. E.; Jones, J. T. A.; Schmidtmann, M.; Hasell, T.; Chong, S. Y.; Jelfs, K. E.; Chen, L.; Cooper, A. I. Nat. Chem. 2015, 7, 153.

CC4

Cooper Cages

CC5

Cooper Cages

CC6

Cooper Cages

CC7

Cooper Cages

CC8

Cooper Cages

CC9

Cooper Cages

CC10

Cooper co-crystals

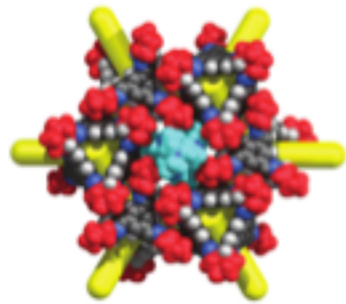
CC1*S*-CC3*R*

Cooper co-crystals

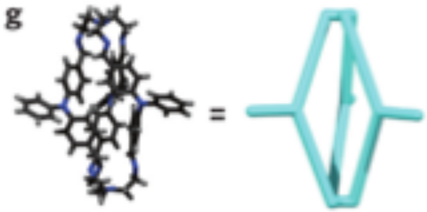
CC3*R*-CC5

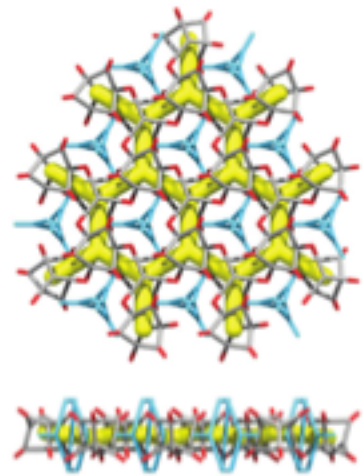
1) One co-crystal is presented here CC3R-CC5 several structures are submitted to CCDC:

CCDC NAME	CCDC NUMBER	Description
MOTWUP	979932	400K, desolvated
MOTWUP01	979933	450K, desolvated
MOTWUP02	979934	100K, desolvated
MOTWUP03	979935	RT, normal p, desolvated

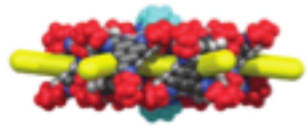


g

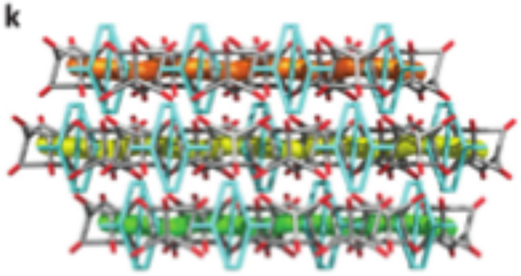




MOTWUP04	979936	RT, low p, desolvated
MOTWUP05	979931	copy of MOTWUP02?
MOVBUW	979942	CC3α Phase 1
PUDXES04	979941	CC3α Phase 2
Several additional structures for this paper, but less relevant		



k



(1) Little, M. A.; Briggs, M. E.; Jones, J. T. A.; Schmidtmann, M.; Hasell, T.; Chong, S. Y.; Jelfs, K. E.; Chen, L.; Cooper, A. I. Nat. Chem. 2015, 7, 153.

Cooper co-crystals

Table S5. Predicted surface areas and pore volumes for **phase 1**, **phase 2**, and **$(CC3\text{-}R)_2\cdot[3+2]_{rs}$** derived from their single crystal structure.

Single Crystal Structure	Predicted surface area for N_2 (probe radius 1.82 Å) [$m^2\,g^{-1}$]	Predicted pore volumes for N_2 (pore radius 1.82 Å) ($cm^3\,g^{-1}$)
Phase 1[a]	1277[c]	0.0963057
Phase 2	923	0.0625906
$(CC3\text{-}R)_2\cdot[3+2]_{rs}$[b]	2144	0.155531

[a] Calculated after artificial removal of lattice solvent. [b] Calculated after artificial removal of **[3+2]$_{rs}$** (CCDC # 979936) . [c] For the static structure 1042 $m^2\,g^{-1}$ of this volume is non-accessible.

	Reported	ZEO++ r=1.55	ZEO++ r=1.82
CC3-5a	242*	0 (552)	0 (357)
CC3-5a_del	2144**	2832 (0)	0 (2145)
CC3-5b	-	0 (585)	0 (372)
CC3-5b_del	-	3008 (0)	0 (2275)
CC3-5c	-	0 (511)	0 (330)
CC3-5c_del	-	2650 (0)	0 (1983)
CC3-5d	-	0 (557)	0 (356)
CC3-5d_del	-	2866 (0)	0 (2168)

CC3-5e	-	0 (592)	0 (384)
CC3-5e_del	-	3012 (0)	0 (2287)
CC3α Phase I	1277**	2016 (0)	243 (1049)
CC3α Phase II	923**	1381 (4)	0 (924)

* Calculated for CO2 at 273K as CC3R-CC5 is not penetrable for N2!!!
** See table on the left side

(1) Little, M. A.; Briggs, M. E.; Jones, J. T. A.; Schmidtmann, M.; Hasell, T.; Chong, S. Y.; Jelfs, K. E.; Chen, L.; Cooper, A. I. Nat. Chem. 2015, 7, 153.

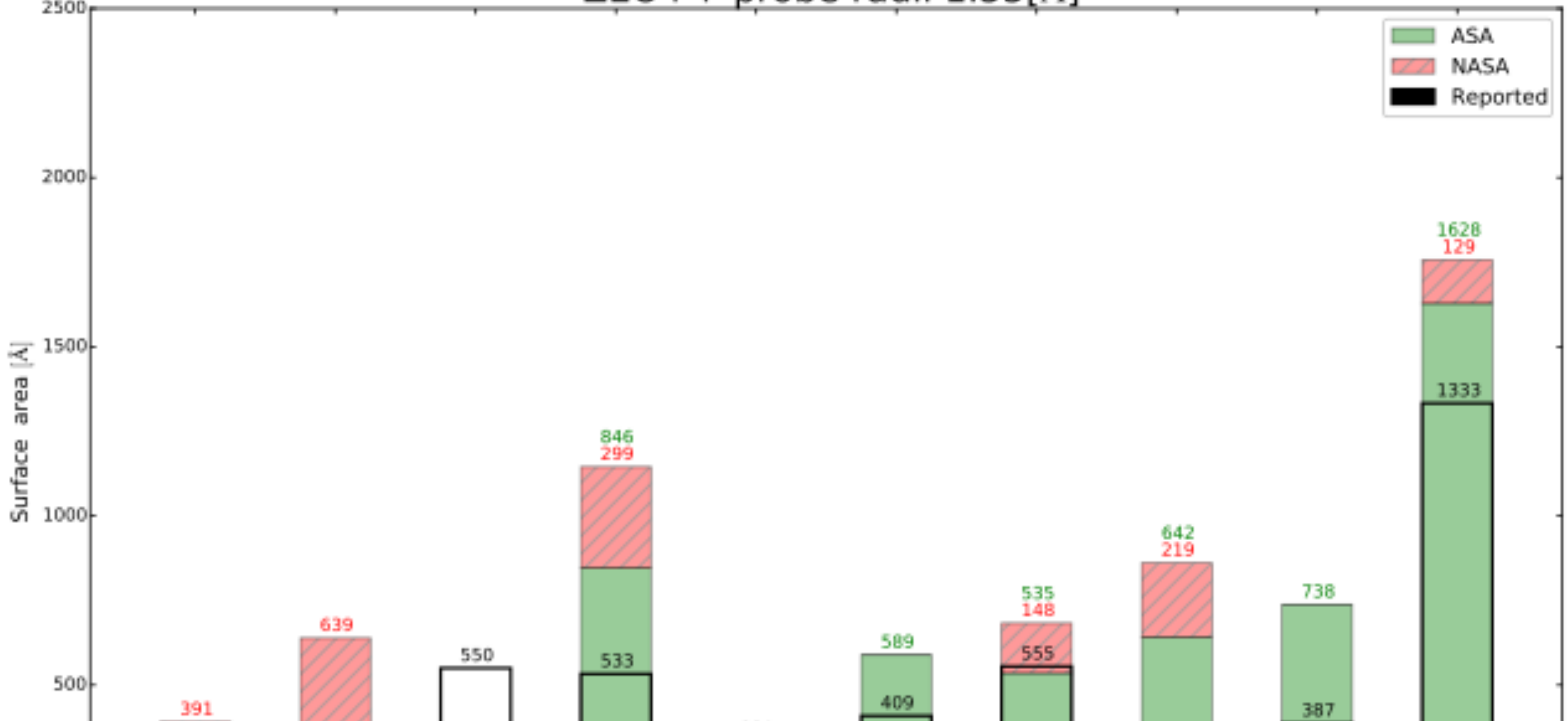
Cooper Cages

Comparison of Surface Areas

	Reported	ZEO++ r=1.55Å (nitrogen end-on)	ZEO++ r=1.82Å (nitrogen kinetic)
CC1α	24	0 (391)	0 (173)
CC1β		0 (639)	0 (234)
CC1γ	550		
CC2α		846 (299)	630 (163)
CC3α	408	589 (0)	292 (0)
CC3β		535 (148)	0 (204)
CC4α		643 (219)	0 (372)
CC4β		738 (0)	449 (0)
CC5		1628 (129)	1434 (62)
CC6		180 (78)	0 (53)
CC7		5475 (0)	4914 (0)
CC8		5611 (0)	5050 (0)
CC9		0 (475)	0 (200)
CC10		0 (184)	0 (45)
CC11		350 (163)	0 (279)

CC11	350 (163)	0 (279)
CC12	0 (243)	0 (88)
CC1-CC3α	794 (533)	483 (332)
CC1-CC3β	839 (595)	527 (435)
CC1-CC3γ	788 (521)	468 (334)

Comparison of surface areas for Mastalerz cages
ZEO++ probe radii 1.55[Å]



References for the reported surface areas:

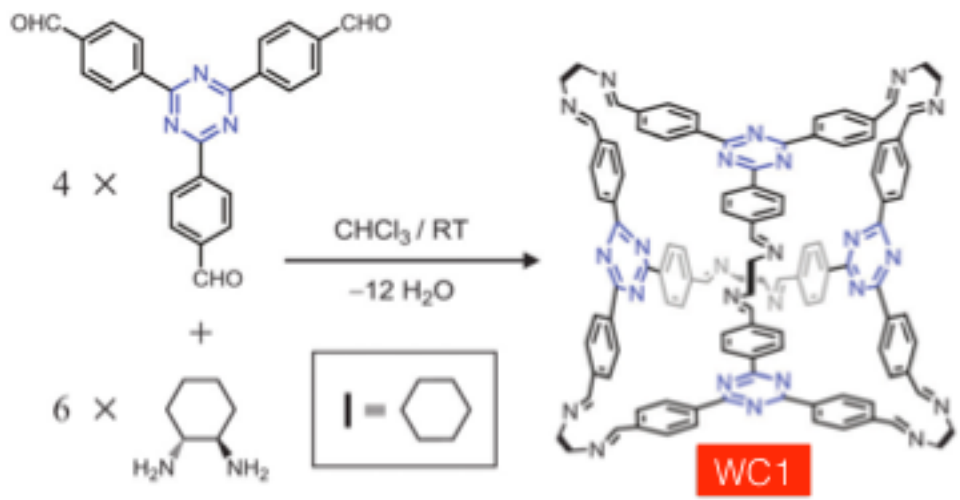
Wang Cages

WC1

1) CCDC Name: TOVWUY
   CCDC Number: 1022375

SABET = 1181 m^2/g (amorphous)

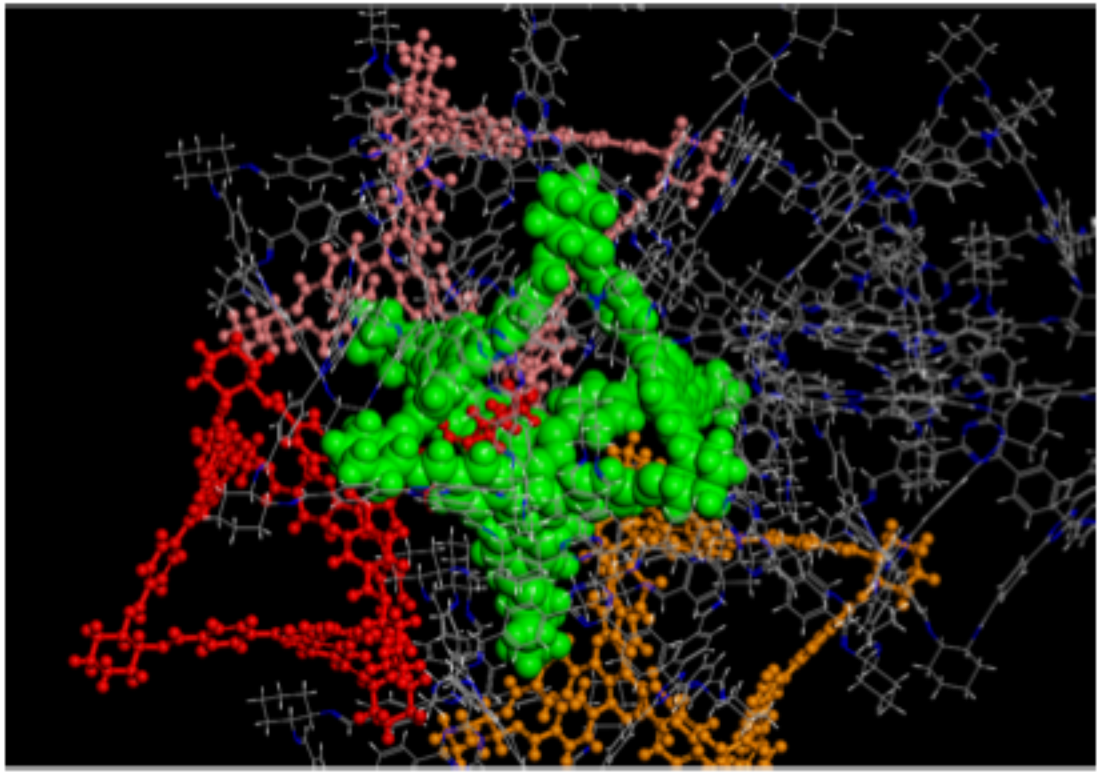
Reported selectivity of CO_2 over N_2



(1) Ding, H.; Yang, Y.; Li, B.; Pan, F.; Zhu, G.; Zeller, M.; Yuan, D.; Wang, C. Chem. Commun. 2015, 51, 1976.

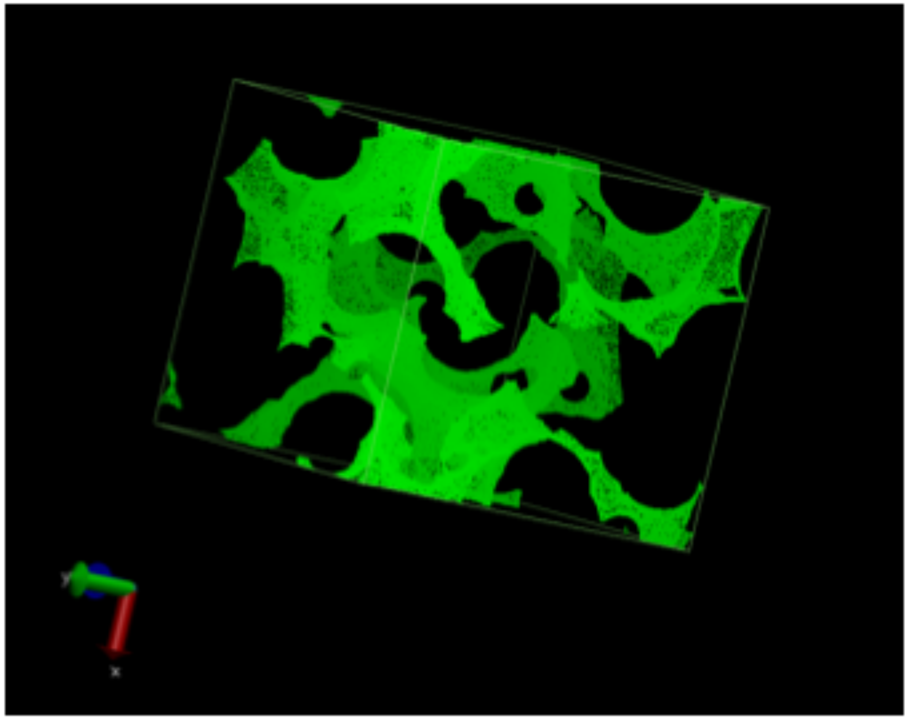
Wang Cages

WC1
crystal packing

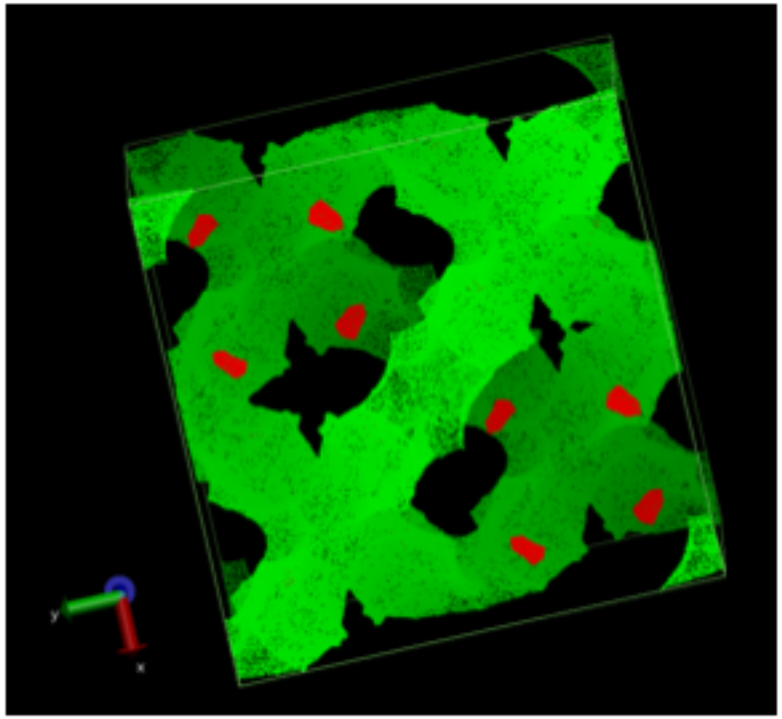


Wang Cages

WC1
comparison of porous networks of WC1 and CC5



VS

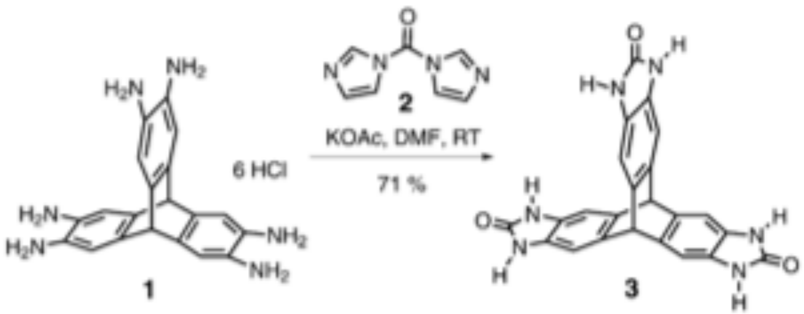


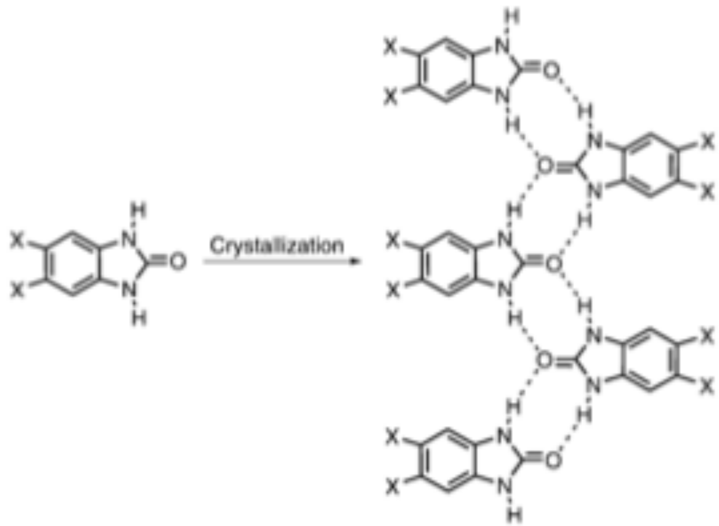
WC1

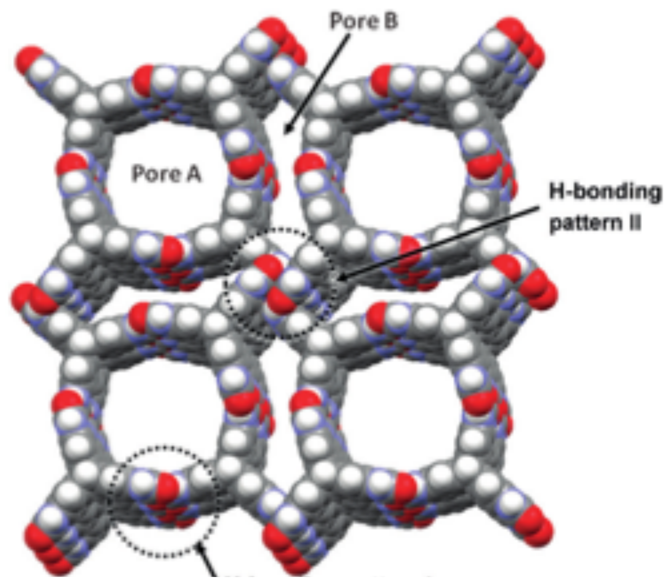
CC5

Mastalerz extrinsically porous ‘cage’

MEX 1







SA_{BET} = 2796 m^2/g

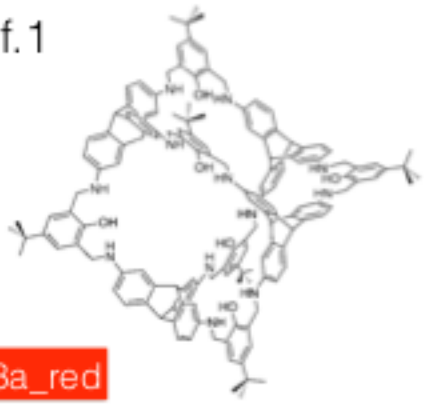
CCDC NAME: DEBXIT
CCDC NUMBER: 866091

(1) Mastalerz, M.; Oppel, I. M. Angew. Chem. Int. Ed. Engl. 2012, 51, 5252.

Mastalerz Cages

No crystal structures yet

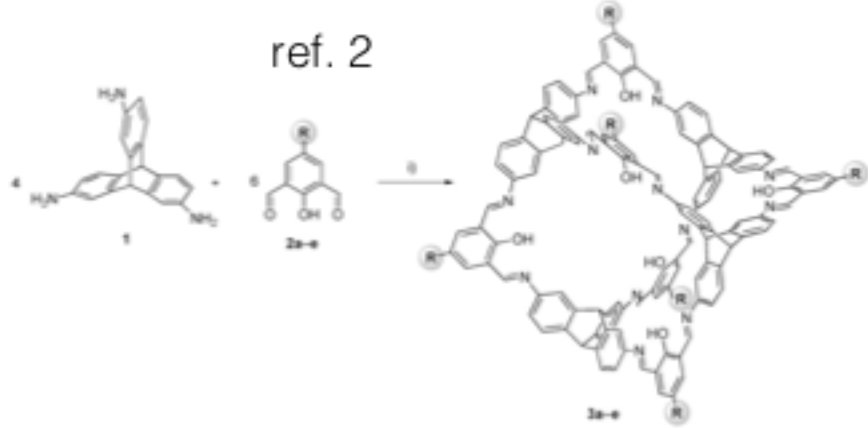
ref.1

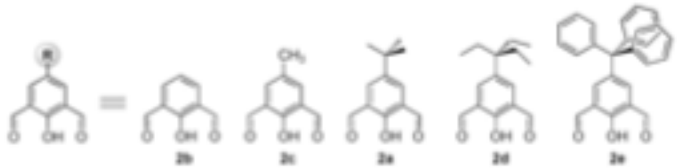


3a_red

$SA_{BET} < 1\ m^2/g$

ref. 2





3b 3c 3a 3d 3e

3a <— MC1
3a_red <— reduced MC1
3b <— unseperatable
3c <— MC2
3d <— cage
3e <— cage

Table 2. Summary of nitrogen gas-sorption experiments.

Entry	Cpd.	Polymorph	SA_{BET} [m^2g^{-1}]	$SA_{Langmuir}$ [m^2g^{-1}]	V_{micro}[a] [cm^3g^{-1}]	V_{pore}[b] [cm^3g^{-1}]	Micropore area[a] [%]
1[c]	3a[a]	cryst (α)	1377	1566	0.42	0.60	80
2	3a[b]	n.d.[d]	951	1084	0.29	0.48	79
3	3a[c][d]	cryst (β)	2071	2327	0.77	0.86	91
4	3c[a]	mainly amorph	729	821	0.23	0.37	73
5	3c[b]	mainly amorph	700	810	0.23	0.34	76
6	3c[c]	cryst	1291	1404	0.48	0.51	93
7	3d[b]	amorph	727	817	0.19	0.36	66
8	3d[c]	cryst	309	365	0.07	0.21	47
9	3e[b]	amorph	690	789	0.19	0.34	67
10	3e[c]	cryst	22	25	0.00	0.01	0

[a] Calculated with the t-plot method. [b] Calculated by NL-DFT methods. [c] Values taken from ref. [25]. [d] Not determined.

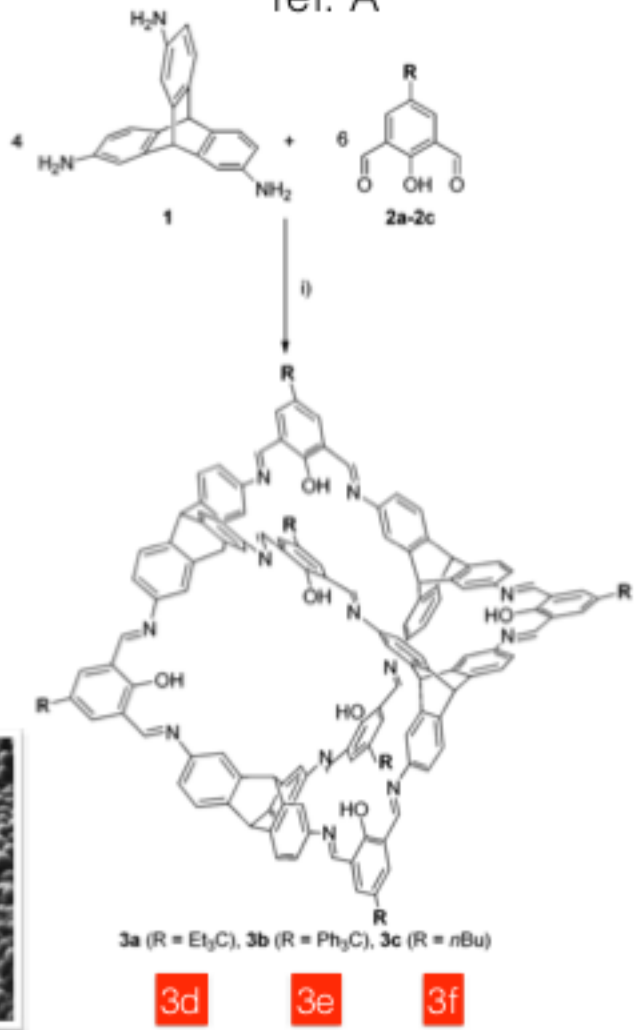
ref. 2

(1) Mastalerz, M.; Schneider, M. W.; Oppel, I. M.; Presly, O. Angew. Chem. Int. Ed. Engl. 2011, 50, 1046.
(2) Schneider, M. W.; Oppel, I. M.; Ott, H.; Lechner, L. G.; Hauswald, H.-J. S.; Stoll, R.; Mastalerz, M. Chemistry 2012, 18, 836.

Mastalerz Cages

No crystal structures yet (II)

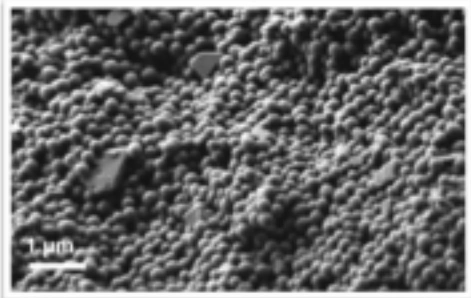
ref. A



Once again 3d and 3e with new one 3f (R=*n*Bu).
This time new form 'nanospheres'

SA_{BET} (m^2/g)	amorphous	crystalline	nanospheres
3d	727[b]	309[b]	38[a]
3e	690[b]	22[b]	36[a]
3f	-	174[a]	148[a]

"If we compare bulk amorphous, nanospheric amorphous and bulk crystalline materials of those compounds, it seems for now that the nanospheric materials properties are closer to the bulk crystalline ones."



ref. A

A. Schneider, M. W.; Lechner, L. G.; Mastalerz, M. J. Mater. Chem. 2012, 22, 7113.
B. Schneider, M. W.; Oppel, I. M.; Ott, H.; Lechner, L. G.; Hauswald, H.-J. S.; Stoll, R.; Mastalerz, M. Chemistry 2012, 18, 836.

Mastalerz Cages

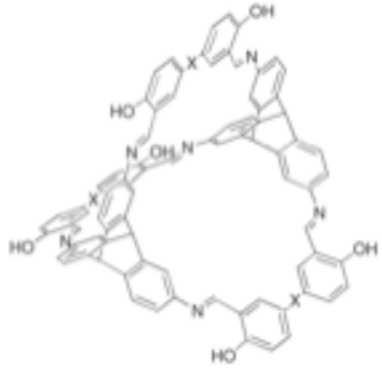
No crystal structures yet (III)

[22] We re-investigated the reduced cage compound 3 by nitrogen-sorption at 77 K. The adsorption and desorption isotherms show a pronounced hysteresis, which can be explained by the higher degree of flexibility resulting in a breathing-type effect. With 252 m^2g^{-1} the measured BET surface area is significantly higher than originally reported (ref. [12c]), probably because we used another protocol for precipitating the amorphous material. See also Supporting Information.

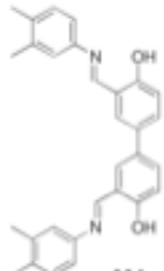
ref. 1

3a_red² (amorphous)	<1 m²/g
3a_red¹ (amorphous)	252 m²/g

ref. 1

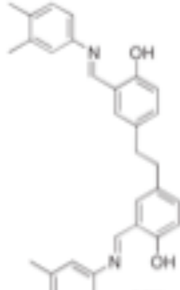


4 (X = ' ')
5 (X = 1,4-C_6H_4-)
6 (X = 1,4-biphenylene)
7 (X = -C_2H_4-)



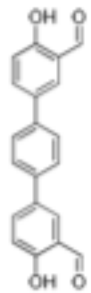
M4

4 = MC3

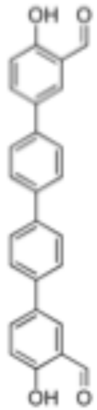


M7

7 = MC4



5



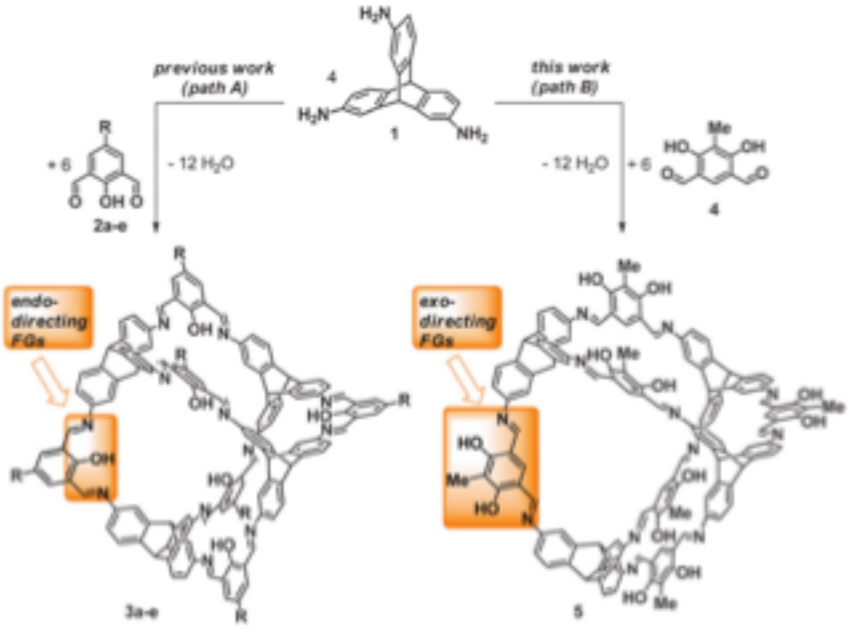
6

(1) Brutschy, M.; Schneider, M. W.; Mastalerz, M.; Waldvogel, S. R. Adv. Mater. 2012, 24, 6049.
(2) Mastalerz, M.; Schneider, M. W.; Oppel, I. M.; Presly, O. Angew. Chem. Int. Ed. Engl. 2011, 50, 1046.

Mastalerz Cages

No crystal structures yet (IV)

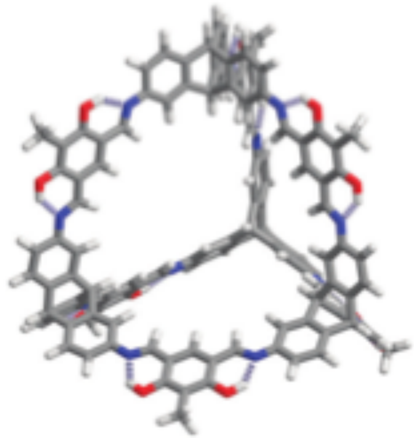
ref.1



3x

8

8. SA_{BET} = 919 m2/g (amorphous)[1]



ref.1

(1) Schneider, M. W.; Hauswald, H.-J. S.; Stoll, R.; Mastalerz, M. Chem. Commun. (Camb). 2012, 48, 9861.

Mastalerz Cages

No crystal structures yet (V)

9a. —> MC5

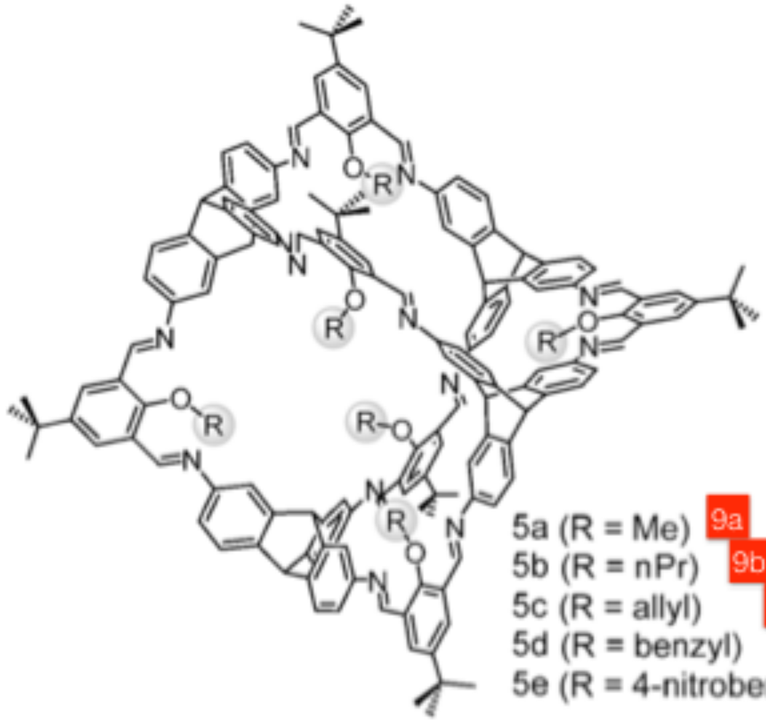
9b.cage

9c.cage

9d.cage

9e.? (they report that was isolated)

Compound	SA_{BET} [m^2/g]
9a (amorphous)	824
9a (cryst. 200°C)	741
9a (cryst. rt)	1700
9b	491
9c	333
9d	119
9e	n.d.

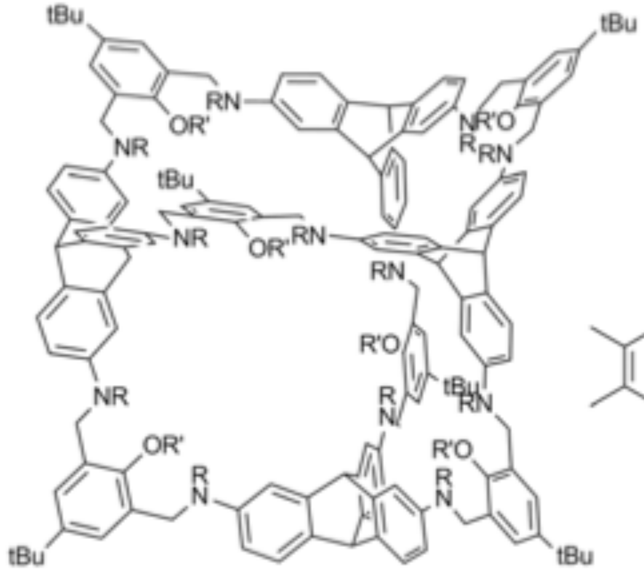


5a (R = Me) 9a
5b (R = nPr) 9b
5c (R = allyl) 9c
5d (R = benzyl) 9d
5e (R = 4-nitrobenzyl) 9e

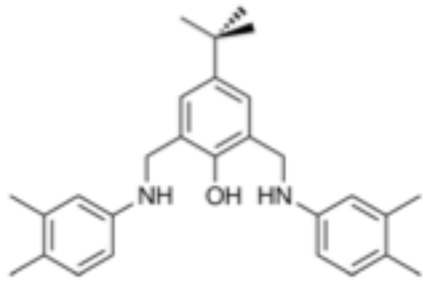
(1) Schneider, M. W.; Oppel, I. M.; Griffin, A.; Mastalerz, M. Angew. Chem. Int. Ed. Engl. 2013, 52, 3611.

Mastalerz Cages

No crystal structures yet (VI)



2 (R = H; R' = H) 3a_red
3 (R = Me; R' = H) 10a
4 (R = H; R' = Me) 10b
5 (R = Me; R' = Me) 10c



M2

ref. 1

(1) Brutschy, M.; Schneider, M. W.; Mastalerz, M.; Waldvogel, S. R. Chem. Commun. 2013, 49, 8398.

Mastalerz Cages

No crystal structures yet (VII)

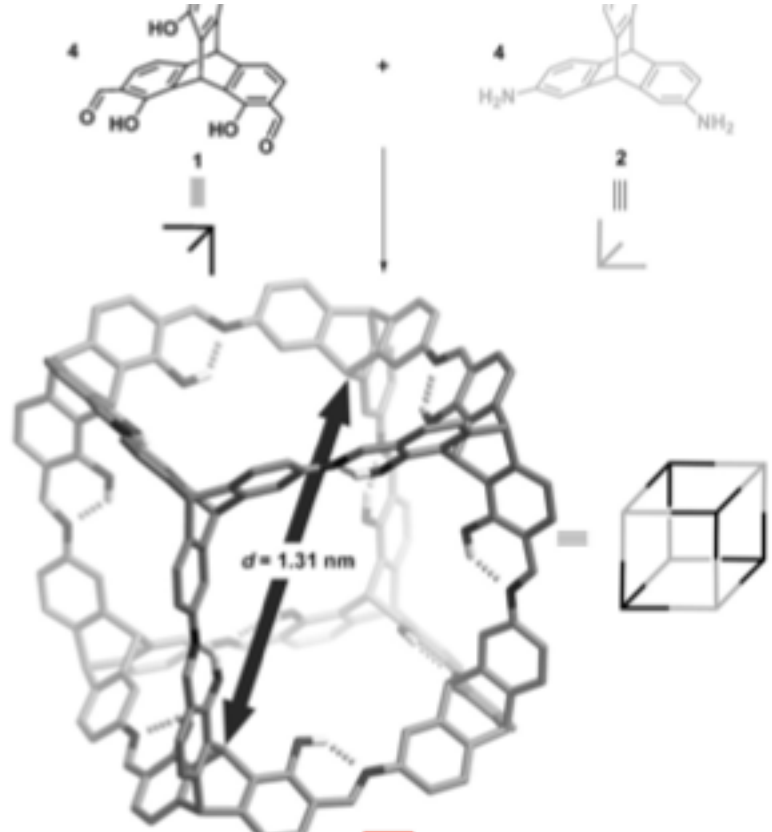
11 [4+4] cage imine-bond type

11: [4+4] cage imine-bond type

Confirmed by MS - no crystal structure so far, they don't mention it in SI

SA_{BET} = 1014 m^2/g (amorphous)

Window diameter: 10.1 - 11.4 Å
Inner diameter: 13.1 Å



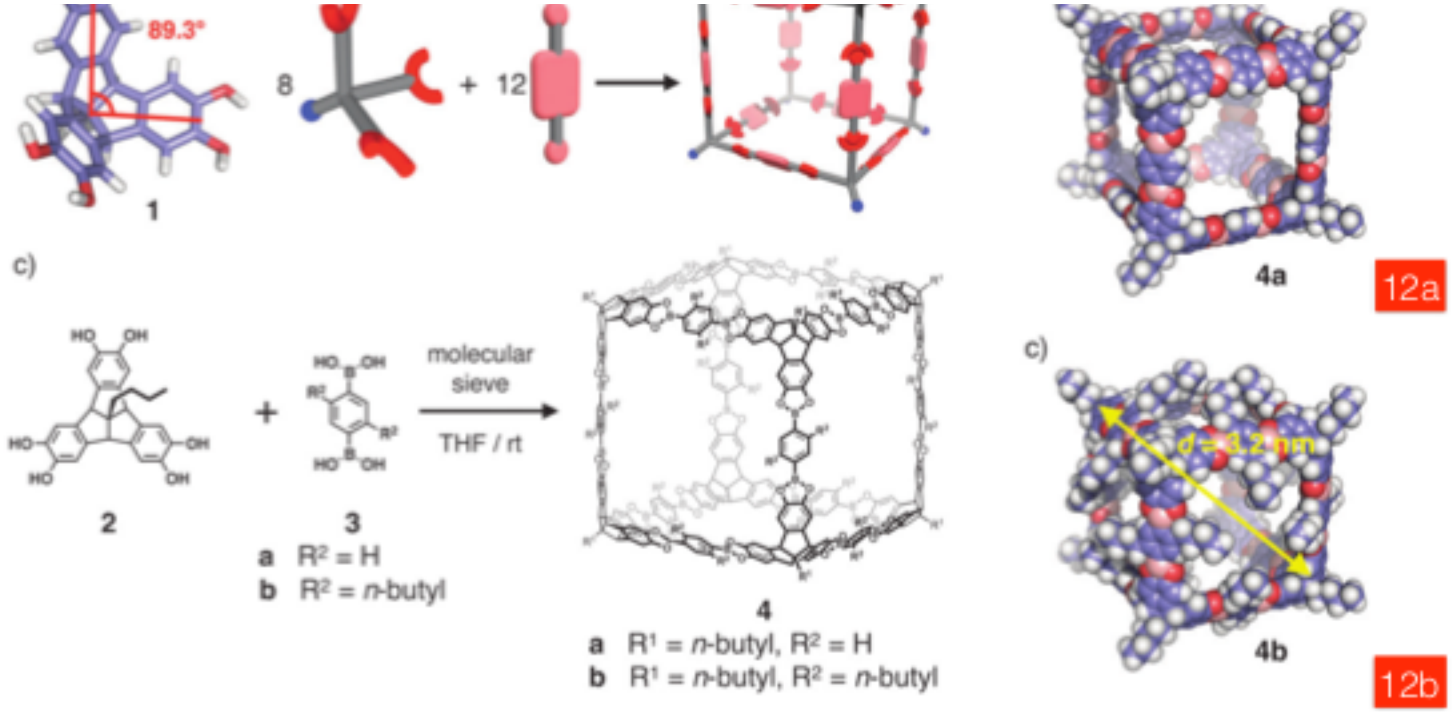
11

(1) Elbert, S. M.; Rominger, F.; Mastalerz, M. Chem. - A Eur. J. 2014, 50, 16707.

Other cages with no crystal structures available I

Boronate type cage

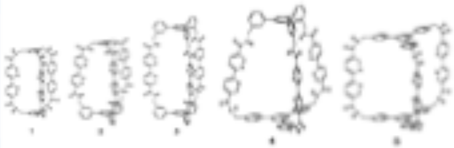
Boronate-type cage



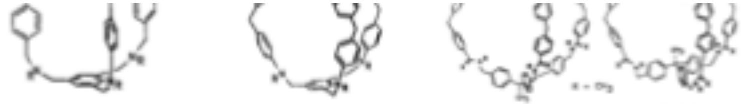
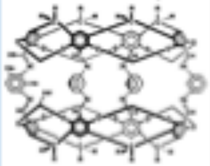
(1) Klotzbach, S.; Scherpf, T.; Beuerle, F. Chem. Commun. (Camb). 2014, 50, 12454.

Historical approach

Year	Description/Publication

1977		**Hydrocarbon [2+3] cage (by 6-fold Witting reaction)** H.-E. Ho:gberg, B. Thulin and O. Wennerstro ¨m, Tetrahedron Lett., 1977, 11, 931
1984		**Amid type [2+3] cage with functional groups (used in complexation of Fe^{3+})** W. Kiggen and F. Vogtle, Angew. Chem., Int. Ed. Engl., 1984, 23, 714
1985		**Two carcerand units connected kinetically with tioether bridges** D. J. Cram, S. Karbach, Y. H. Kim, L. Baczynskyj and G. W. Kalleymeyn, J. Am. Chem. Soc., 1985, 107, 2575
1989		**Amide type [2+3] cages** F. Ebmeyer and F. Vogtle, Angew. Chem., Int. Ed. Engl., 1989, 28, 79

Year		Description/Publication
		**Amid type [2+3] cages**

1990		A. Wallon, J. Peter-Katalinica, U. Werner, W. M. Muller and F. Vogtle, Chem. Ber., 1990, 123, 375 B. F. Ebmeyer and F. Vogtle, Chem. Ber., 1989, 122, 1725
1991		**Shape persistent imine type cage - two carcerands [2+4]** **First time when reversible mine bond was used to synthesise a cage in high yields** M. L. C. Quan and D. J. Cram, J. Am. Chem. Soc., 1991, 113, 2754

Year	Description/Publication