DESIGN AND CONSTRUCTION OF TARGETED EXTENDED STRUCTURES USING PRE-ORGANIZED BUILDING BLOCKS

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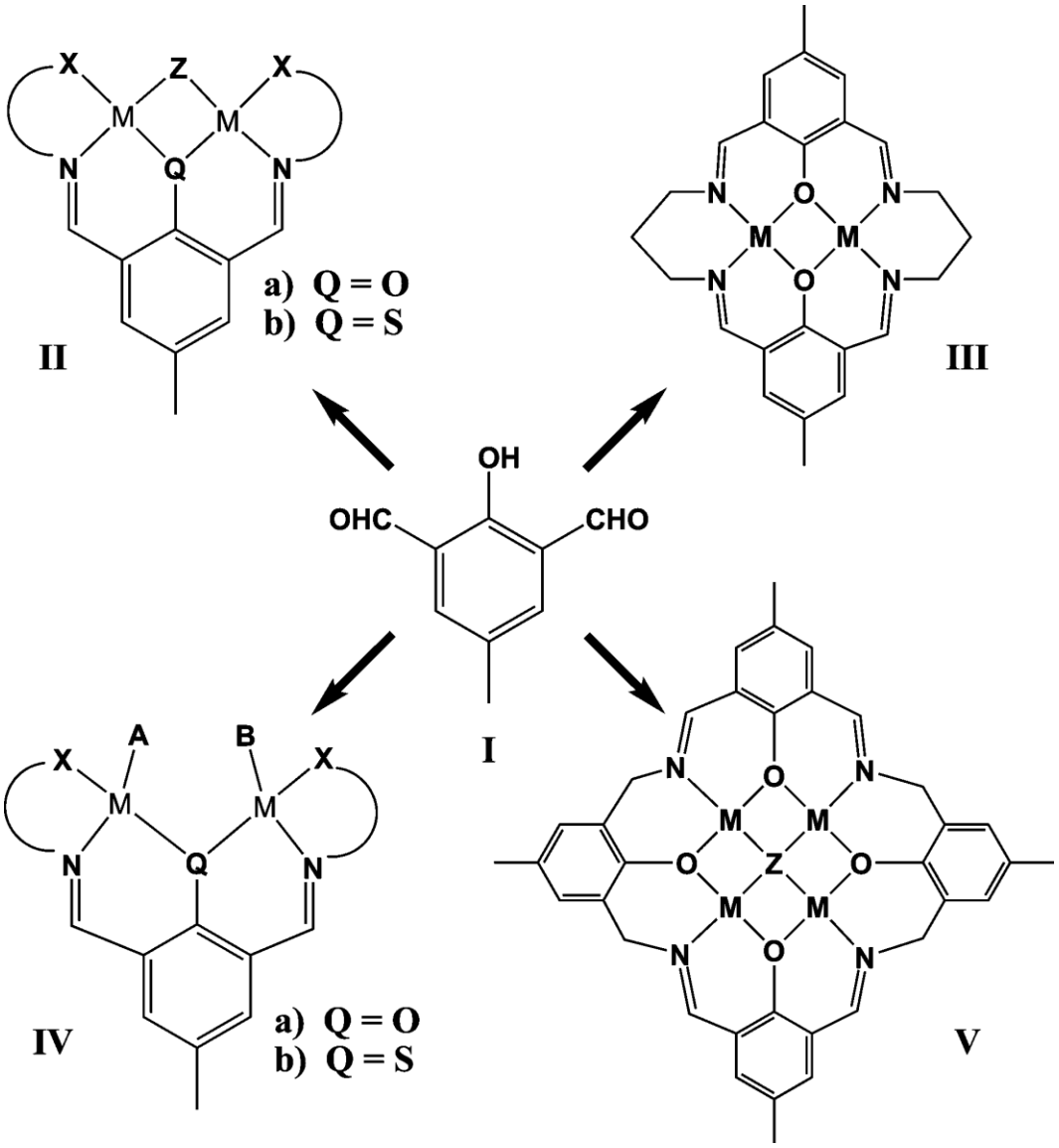
PRE-ORGANIZATION

The design of chemical functionality and geometry in reactant species that predisposes them, when they are brought together, to form bonds in a specific, intended manner, leading to the spontaneous self-assembly of a targeted structure.



Pre-organized discrete systems. (mid-1960's- 80's).

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“If we were to substitute molecules for balls and chemical bonds for rods/sticks, might it be possible that **appropriately pre-organized building blocks** would undergo spontaneous self assembly to yield extended networks of targeted structure?”

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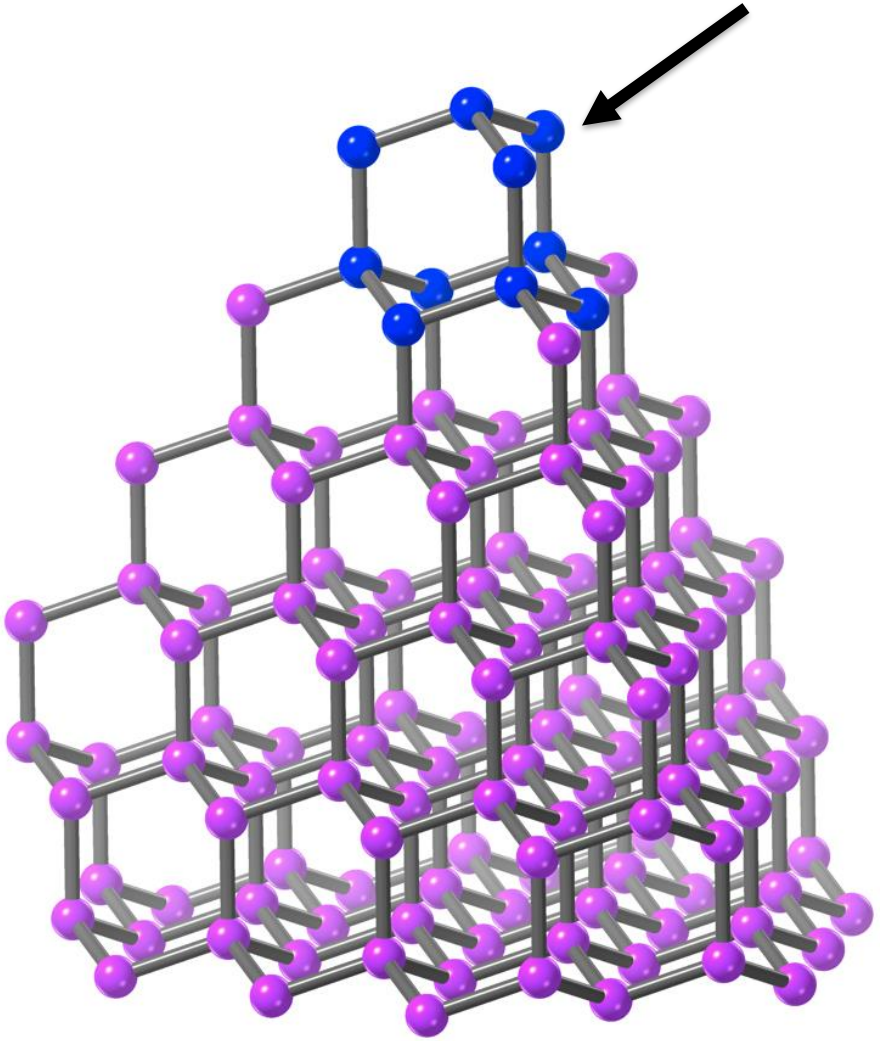
“If we were to substitute molecules for balls and chemical bonds for rods/sticks, might it be possible that appropriately pre-organized building blocks would undergo spontaneous self assembly to yield extended networks of targeted structure?”

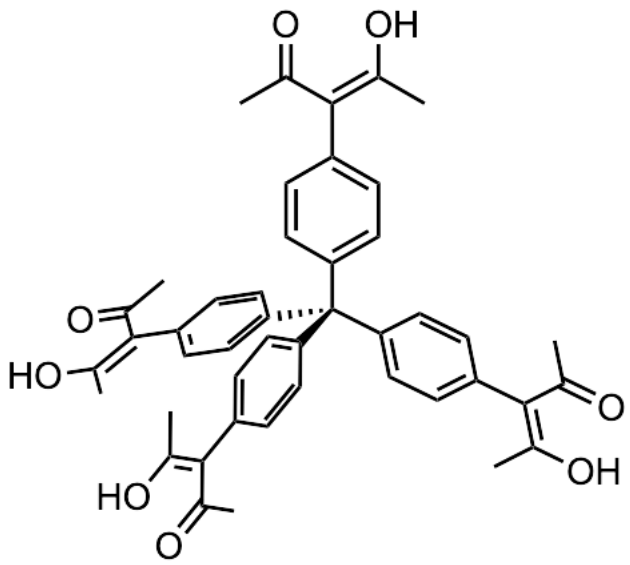
Coordination chemistry – ligand-to-metal bond formation – appeared ideally suited to this sort of exploration.

Diamond

Chosen as the simplest target for initial attempts at framework construction. MID-80's

A characteristic feature of the diamond structure is the adamantane unit.

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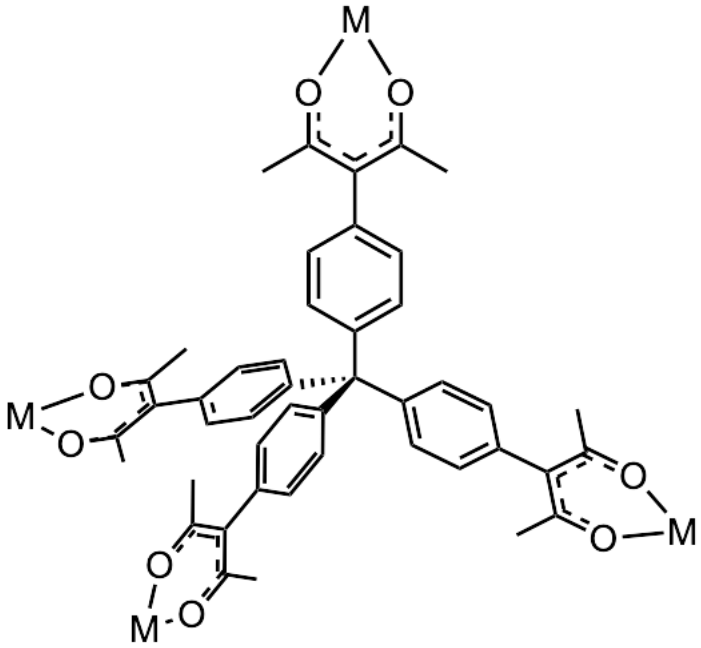
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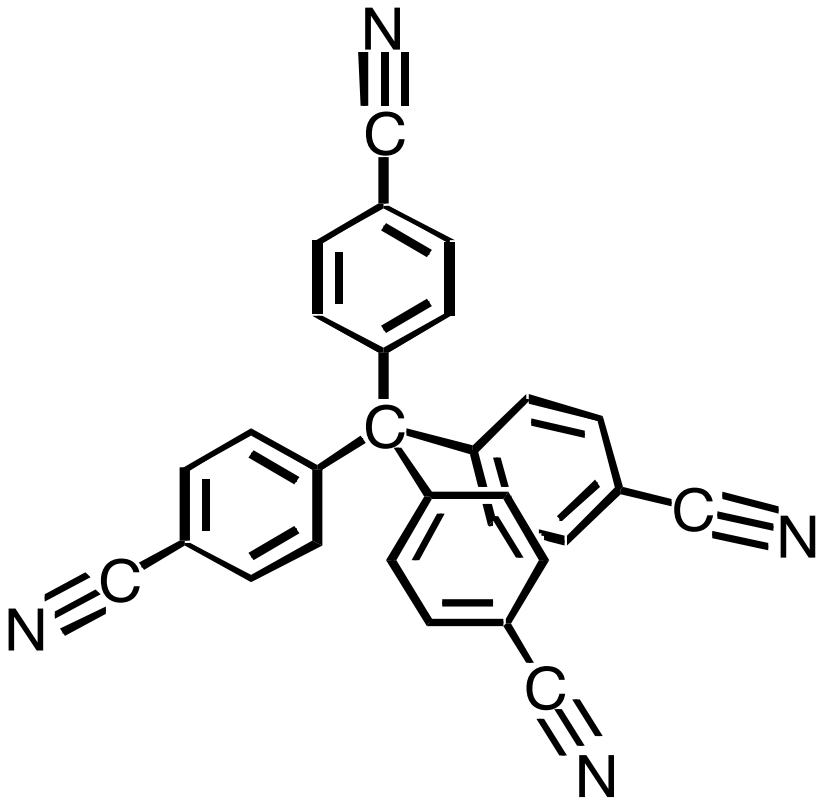
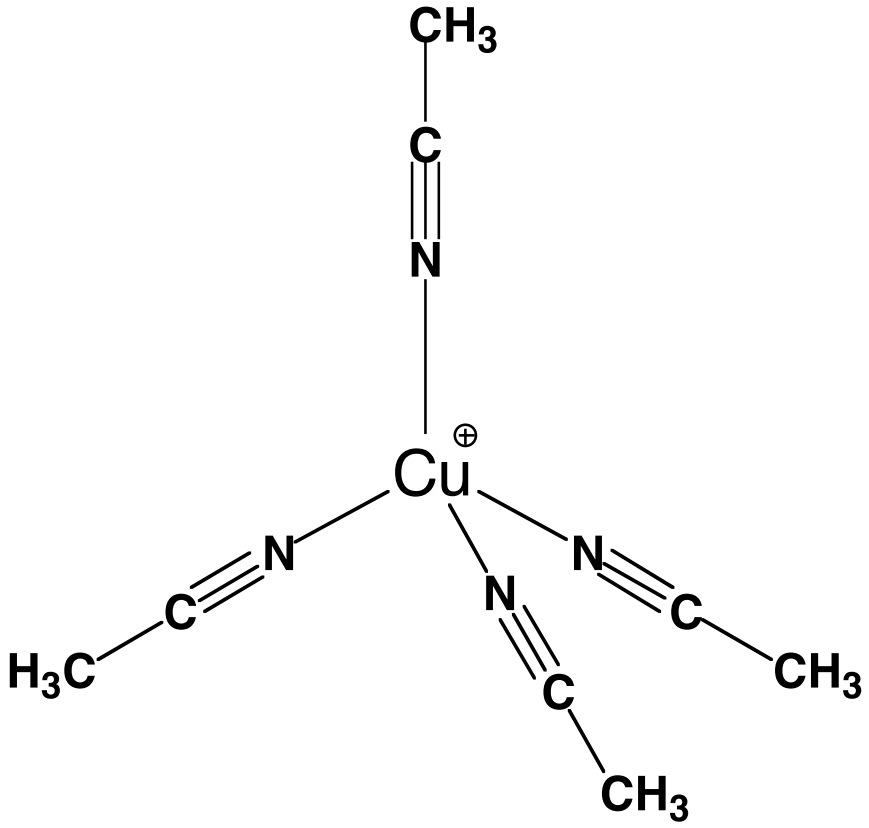
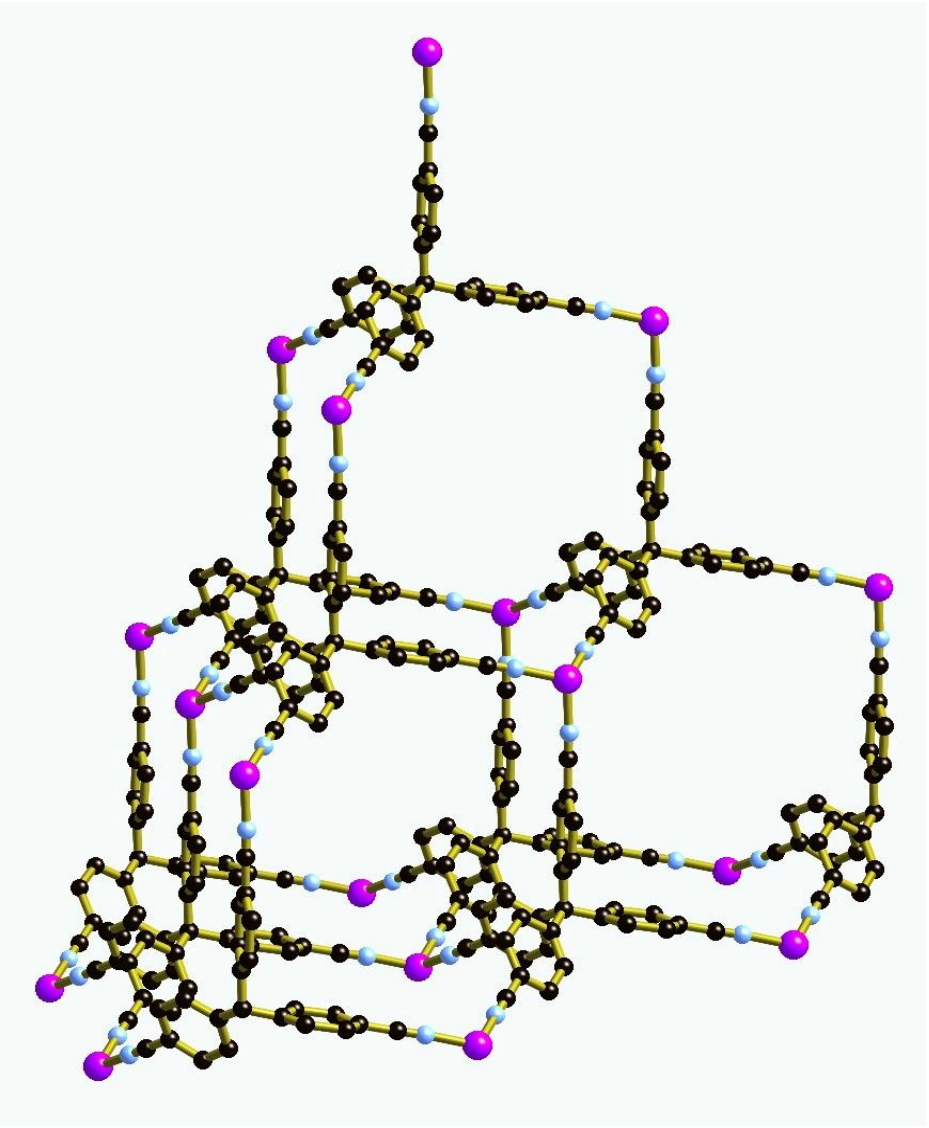




$C(para\text{-}C_6H_4\text{-}CN)_4 + [Cu(CH_3CN)_4][BF_4]$



Anion exchange with retention of single crystal character.

$CH_3CN/C_6H_5NO_2$

$Cu[C(C_6H_4CN)_4]BF_4.xC_6H_5NO_2$

B. F. Hoskins and R. Robson,
J. Am.Chem. Soc.,
Preliminary note: **111**, 5962, **1989**.
Full paper: **112**, 1546, **1990**.

At that time this was a most unusual material –

-- because although it was undoubtedly crystalline, more than half the volume was occupied by fluid.

In the **1990 JACS** paper we also proposed *a much more general, wider ranging approach* to the future construction of what we anticipated might be a very extensive new class of coordination polymer networks that might provide useful tailor-made materials of the future.

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The following general suggestions were made in that paper that seemed likely to be of relevance in the (anticipated) future development of the coordination polymer field:

1990 Suggestions for the future development of the coordination polymer field

Suggestion 1

An almost limitless range of connecting ligands can be readily imagined, with all sorts of connectivities, geometries and chemical functionalities.

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It was clear that

IF crystalline coordination polymers in general could be obtained, as easily as I had obtained $Cu[C(C_6H_4.CN)_4]BF_4$

they could afford an enormous range of materials with a great diversity of architectures and properties.

1990 Suggestions for the future development of the coordination polymer field

Suggestion 2

The polymers envisaged might provide

quote

“materials combining good or even high thermal, chemical and mechanical stability with unusually low density.”

Ie. lots of internal space

1990 Suggestions for the future development of the coordination polymer field

Suggestion 3

It might be possible to introduce catalytically active sites into the individual building blocks, either before or after framework construction.

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Suggestion 4

It might be crucial in the growth of truly crystalline arrangements that the bond forming step whereby that growth occurs be appropriately reversible –

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It might be crucial in the growth of truly crystalline arrangements that the bond forming step whereby that growth occurs be appropriately reversible –

- so that, if a “wrong step” were taken the system would be able to “backtrack” to eliminate the error and then the orderly build-up could continue.

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R. Robson, Comprehensive Supramolecular Chemistry, ed J.-M. Lehn, Pergamon, 1996, vol 6, 734.

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- In which the importance of reversibility in the formation of truly crystalline coordination polymers was discussed -
= followed by the passage:-

"Nevertheless, there is no obvious reason why the link-up chemistry could not be extended to certain C-O, C-N and C-C bond-forming steps to engineer truly crystalline 3D organic polymers."

1990 Suggestions for the future development of the coordination polymer field

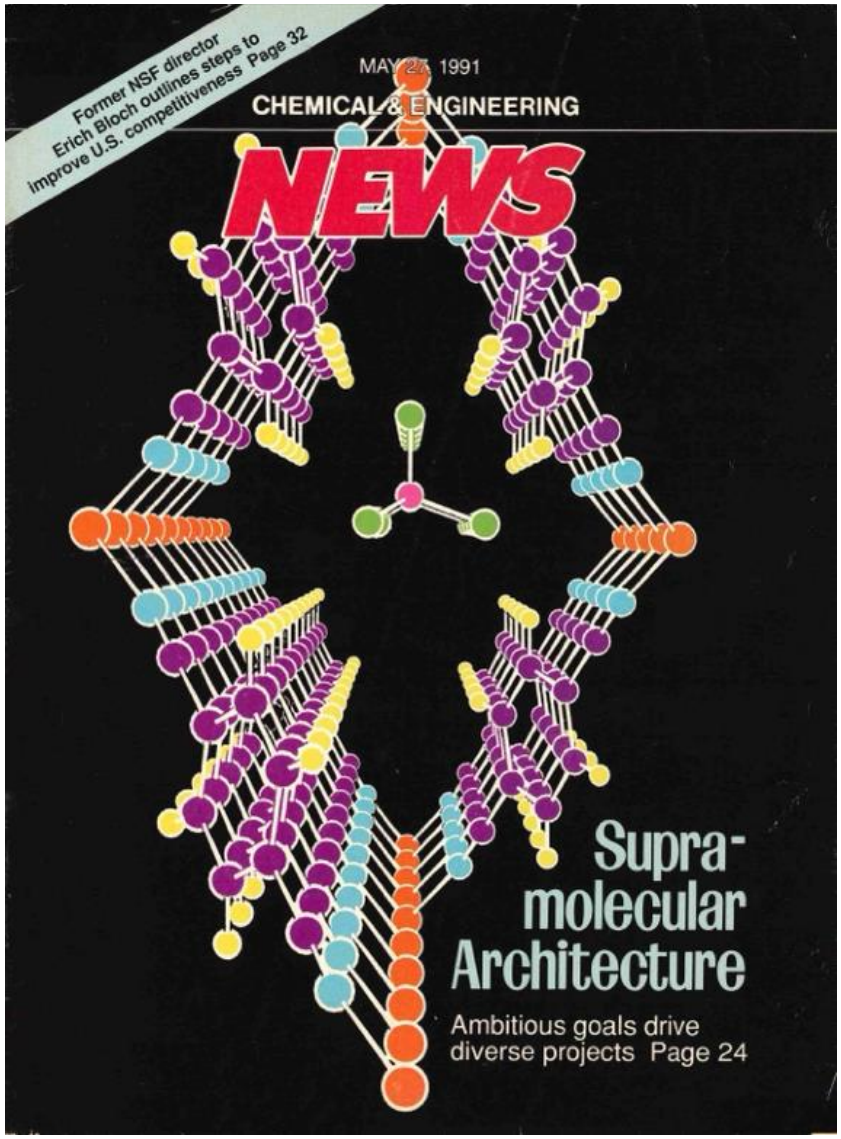
Suggestion 5

Pre-organized bridging ligands bearing chelating sites for metal binding might afford significantly more robust framework structures.

201st National Meeting of the American Chemical Society , Atlanta, April,, 1991.

ACS Symposium Series, 499,
Ed., Thomas Bein, SupramolecularArchitecture,
page 256.

Our general approach to network construction using pre-organized building blocks was first presented at the 1991 Atlanta meeting.



CHEMICAL & ENGINEERING NEWS
Volume 69, Number 21
CENEAR 69 (21) 1–48
ISSN 0009-2347
MAY 27, 1991

News of the Week

- Speculation grows over possible takeover of ICI by U.K. conglomerate Hanson plc. Page 4
- Soviet thermionic space power system trapped in U.S. finally will be allowed to go home after falling into legal limbo. Page 5
- Health effects of Chernobyl nuclear reactor accident were less serious than projected, concludes an international study. Page 5
- UN panel charged with eliminating Iraq's nuclear and chemical weapons capability issues its first action plan. Page 6
- Two California utilities have pledged to cut their carbon dioxide emissions 20% by the year 2010. Page 6
- Statutory exemption permitting mandatory retirement of tenured faculty at U.S. universities should be allowed to expire, says National Research Council study. Page 6

Cover: Perspective view down one of the rhombic channels of $Cu(1,4\text{-dicyanobenzene})_2(BF_4)_x$, a diamondlike structure that contains five independent, interpenetrating frameworks. Each edge of the channel consists of a Cu-NC_6H_4-CN-Cu unit. Inside the channel are BF_4^- ions. Drawing courtesy of Richard Robson, University of Melbourne, Australia.

Business

European Chemical Industry Council (CEFIC) will adopt new structure incorporating both associations and companies to work better within a stronger Europe. Page 13

Petrochemicals business likely will become more volatile because of forecasting difficulties, other factors. Page 16

Government

Defense Department releases plan for critical defense technologies it considers vital for maintaining the qualitative superiority of U.S. weapons systems. Page 19

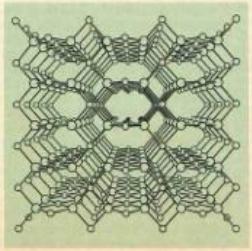
EPA regulation of pesticides leaching into groundwater draws criticism in recent report from the General Accounting Office. Page 21

Science/Technology

Instruments phased in at Cold Neutron Research Facility offer improved U.S.-based research capability in materials science. Page 31

Viewpoint

Erich Bloch, former NSF director, talks about U.S. competitiveness and ways to improve it as the country faces increasing international economic competition. Page 32



Cover Story

Assembling complex multimolecules poses challenges for chemists but promises boon to many areas, including microelectronics, optics, catalysis. Page 24

Chemical and Engineering News, May, 1991.

OUR APPROACH TO CONSTRUCTING TARGETED COORDINATION NETWORKS USING PREORGANIZED BUILDING BLOCKS (Atlanta 1991)

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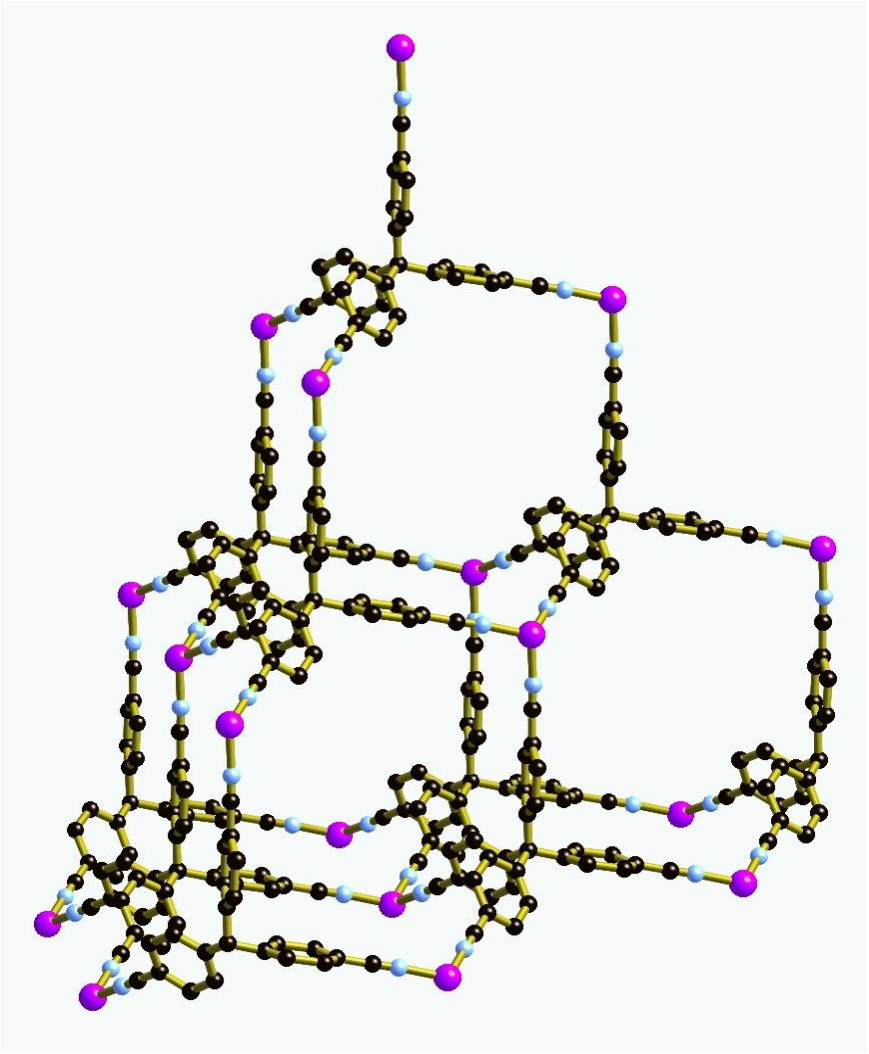
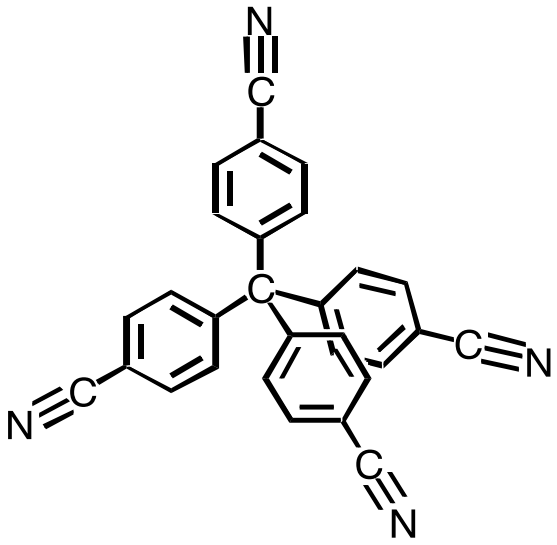
2). Devise and construct pre-organized building blocks with a chemical functionality, a geometry and a connectivity appropriate to the chosen target.
3). Devise reaction conditions which allow the building blocks spontaneously to combine to generate the target network in the form of ordered crystalline material. (chemical intuition is important at this step).

A quick word about step 3, ie. obtaining single crystals.
Chemical intuition is important.



$[Cu(CH_3CN)_4][BF_4]$
CH_3CN solution
(volatile)



Generally pretty insoluble in organic solvents but nicely soluble in nitrobenzene (high b.pt,)

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DIAMOND	**TETRAHEDRAL**
alpha-Po	**OCTAHEDRAL**
(10-3)-*a*	**TRIGONAL**
RUTILE	**TRIGONAL + OCTAHEDRAL**
PtS	**TETRAHEDRAL +SQUARE PLANAR**
BORACITE	**TETRAHEDRAL + TRIGONAL**
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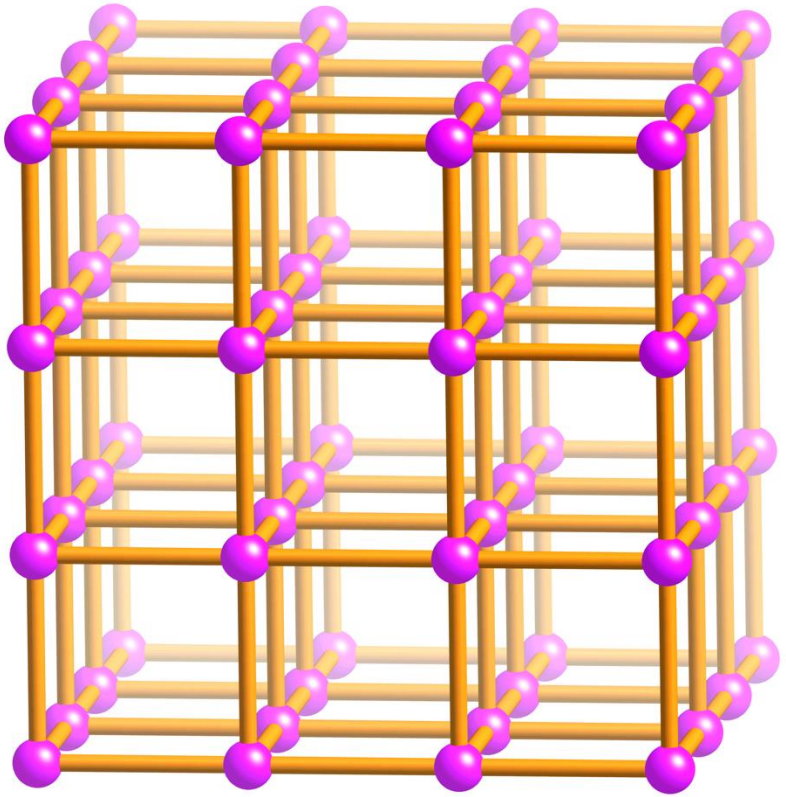
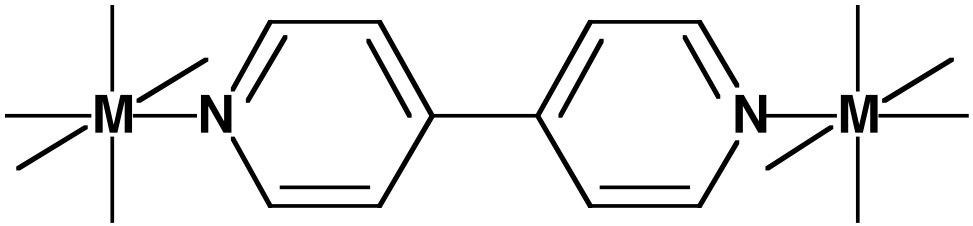
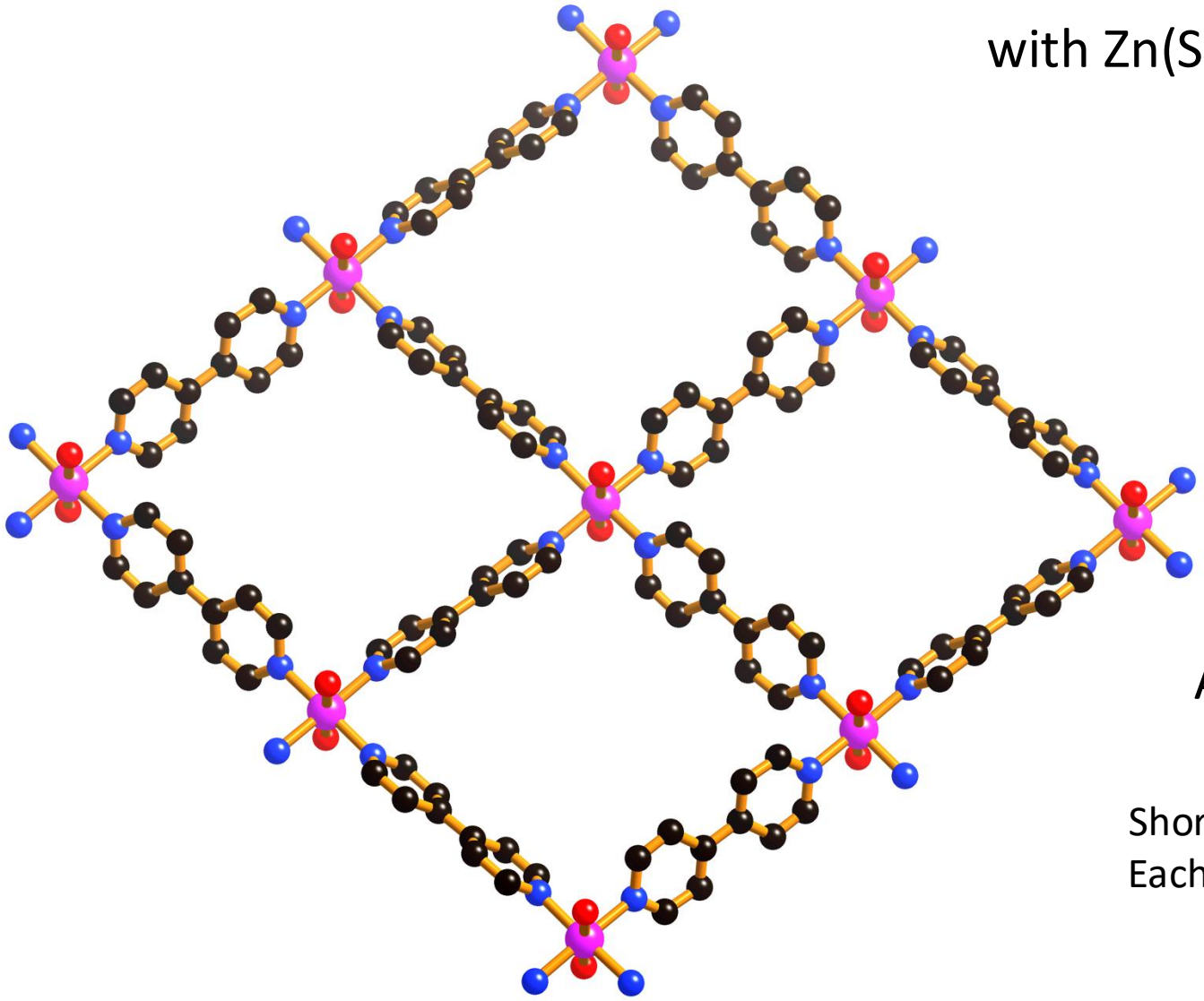
The alpha-polonium net



QUESTION (late 80's) – will 4,4'-bipyridine combine with octahedral metal centres to give an α-Po net?



Product from reaction of 4,4'-bipy with $Zn(SiF_6)_2$ in H_2O.



Trans $(H_2O)_2$ on each Zn

A (4,4) sheet

Ie.
Shortest circuits 4 nodes
Each node 4-connecting.

R. W. Gable, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.,* 1677, **1990.**

Our 1990 report of $Zn(4,4'\text{-bipy})_2](SiF_6)$ was followed by large numbers of papers from other workers dealing with coordination polymers of 4,4'-bipyridine and related ligands.

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One of these reported a Cu/bipy coordination polymer,
$(Cu(4,4'\text{-bipyr})_{1.5}NO_3.1.5H_2O)$,
which was, to the best of my knowledge,
the first coordination polymer to be referred to as a MOF.

"*Hydrothermal Synthesis of a* ***Metal-Organic Framework*** *Containing Large Rectangular Channels*"
O. M. Yaghi and H. Li. *J. Am. Chem. Soc*., **1995**, 117, 10401.

OUR APPROACH TO CONSTRUCTING TARGETED COORDINATION NETWORKS USING PREORGANIZED BUILDING BLOCKS (Atlanta 1991)

1). Choose a target network.
2). Devise and construct pre-organized building blocks with a chemical functionality, a geometry and a connectivity appropriate to the chosen target.
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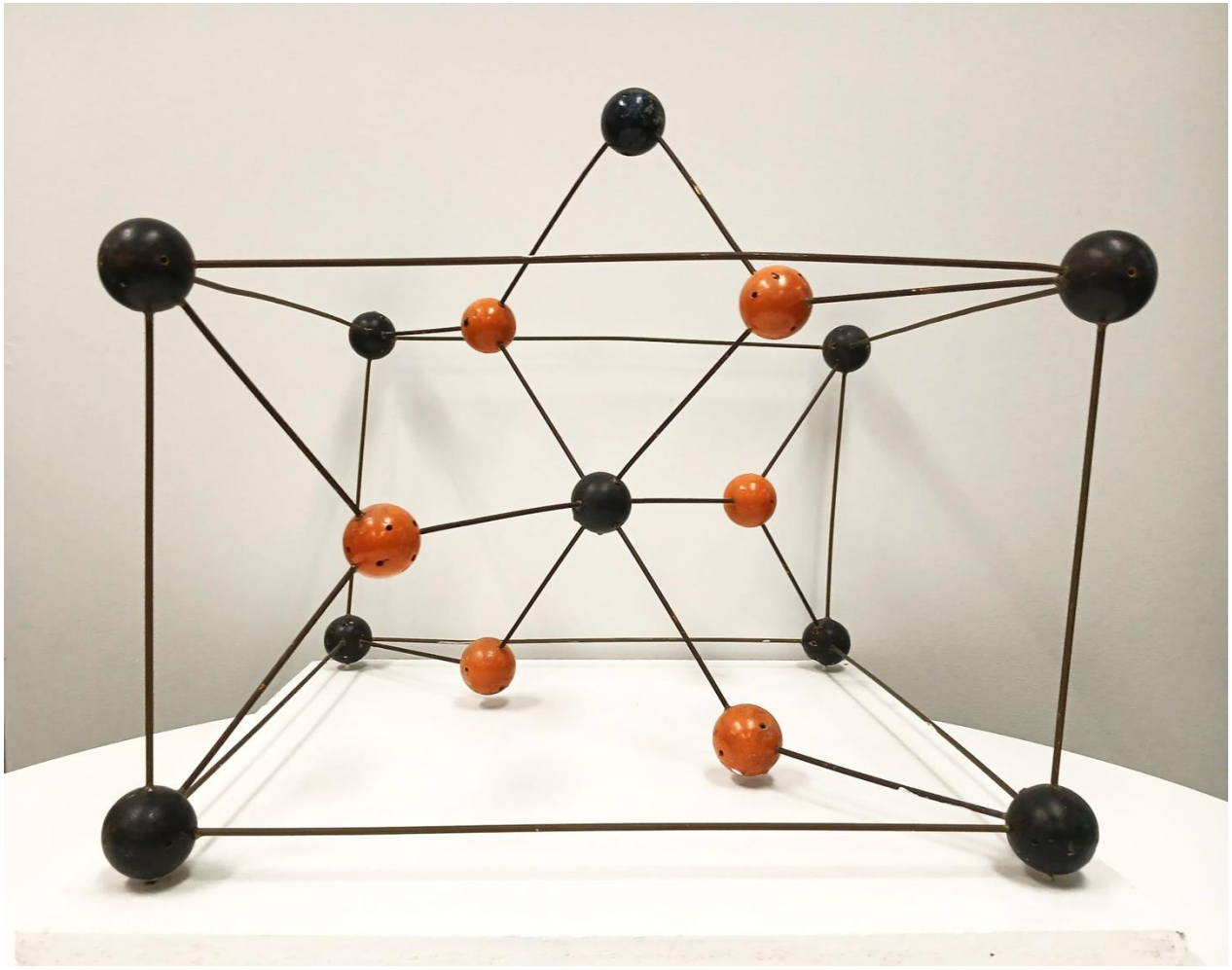
"Pt_3O_4"	TRIGONAL + SQUARE PLANAR

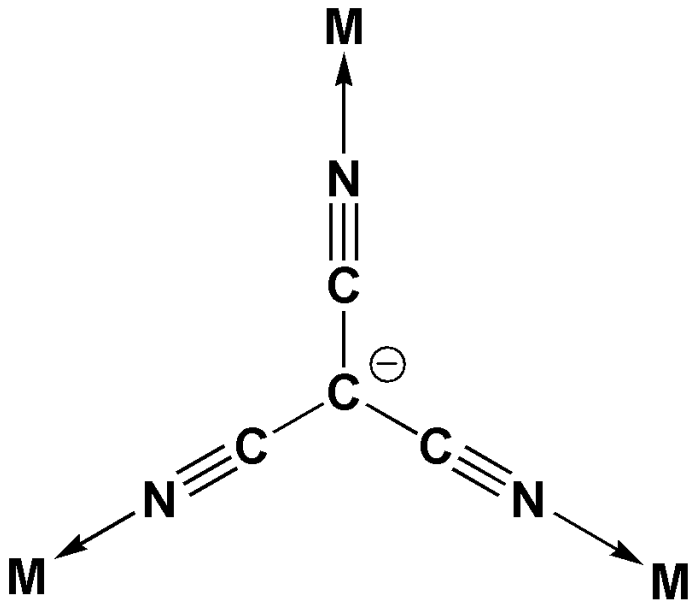
Ball and stick model of the Rutile structure



What we required in those very early days of exploration were building blocks that were

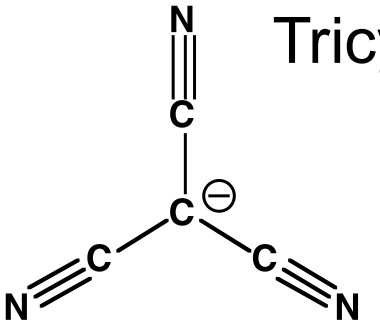
1) Simple,
2) Readily available and
3) Stable.

THE RUTILE CONNECTIVITY AS A TARGET



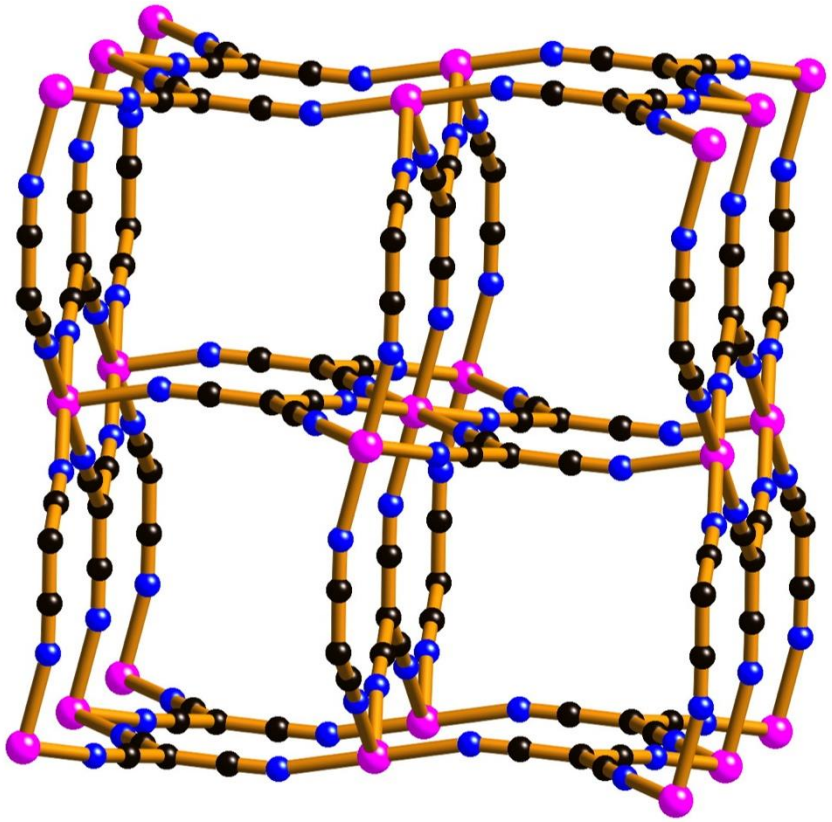
The simplest pre-organized building block we could think of intended to bind 3 metal centres at the corners of an equilateral triangle was the tricyanomethanide ion.

Various metal cations with a preference for octahedral coordination geometry were obvious choices for the role of octahedral node.



Tricyanomethanide, tcm^-

Stuart Batten's B.Sc.(Hons) research project, 1990.



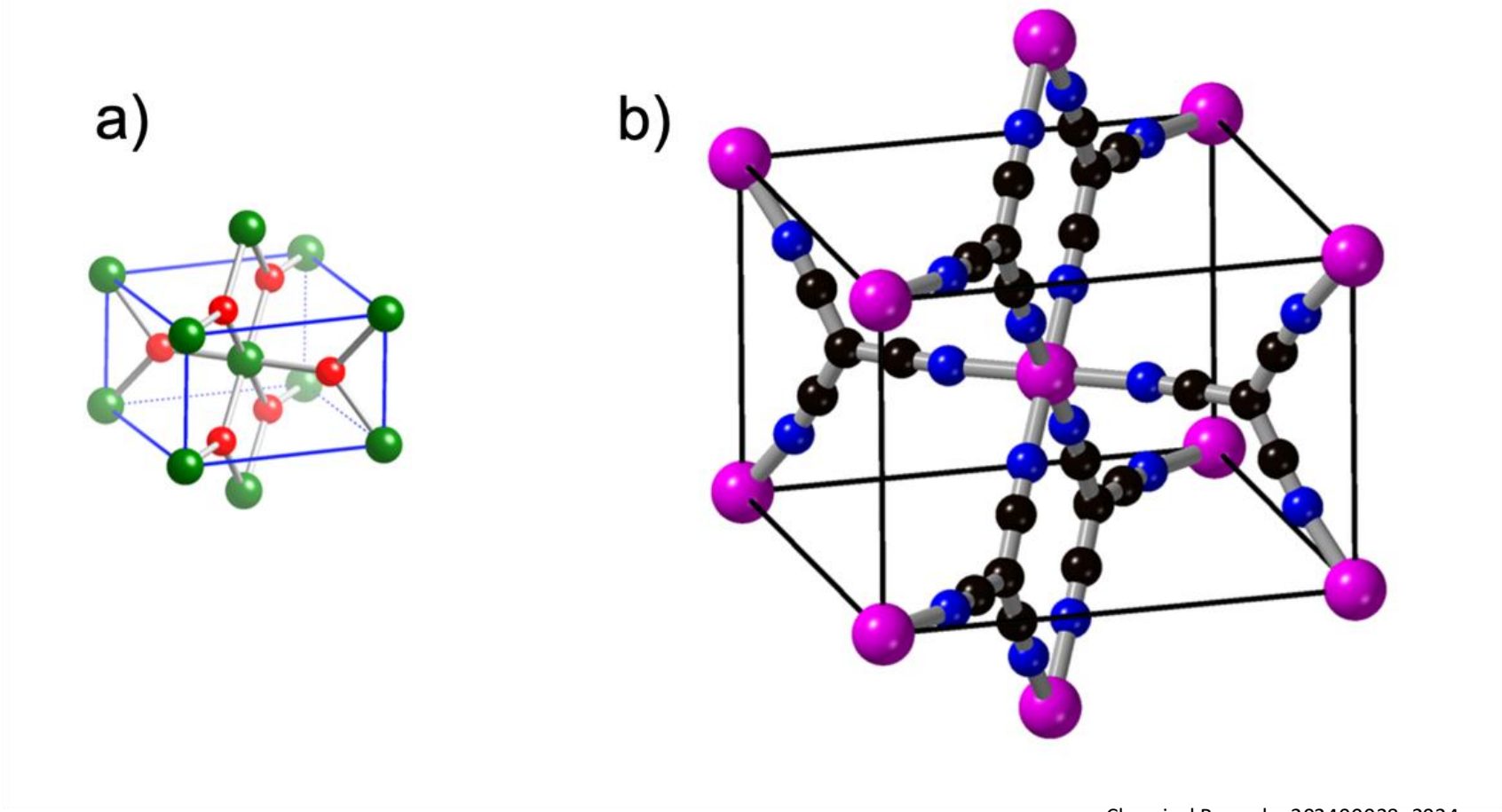
Isomorphous crystals of composition

$M(tcm)_2$

were obtained for

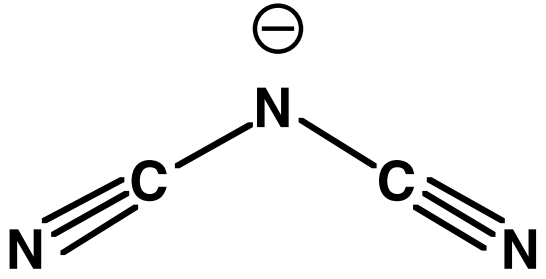
M^{II} = Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Hg.

BATTEN, HOSKINS, ROBSON, *J. Chem. Soc., Chem. Commun.*, 445-447, **1991**.



Chemical Record, e202400038, 2024

Representations to scale of a) rutile, TiO_2 and b) the $Zn(tcm)_2$ coordination network.



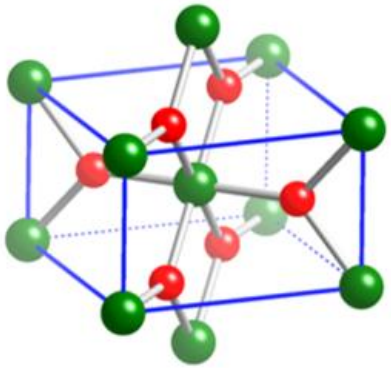
Dicyanoamide anion, dca-

Intended to bind 3 metal centres, one at each N.

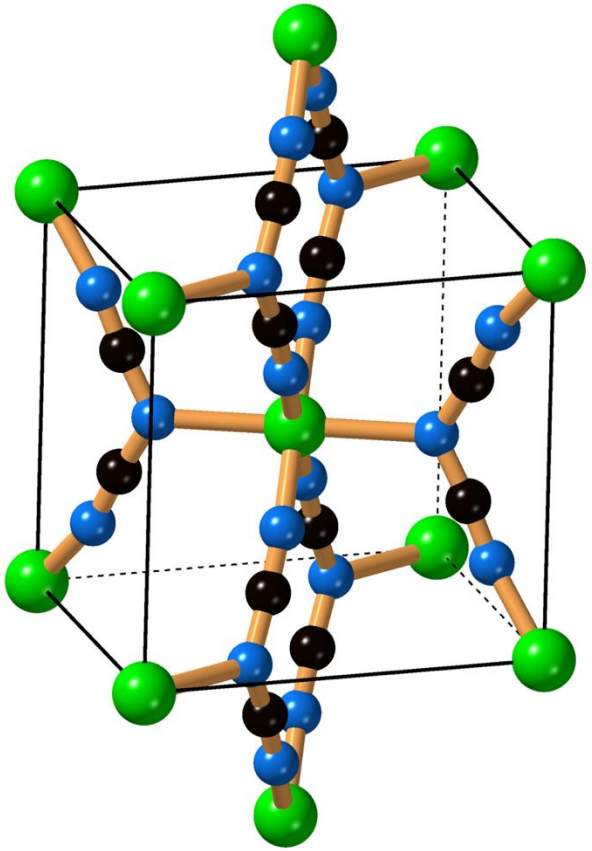
$M(dca)_2$

M = Co, Ni,Cu.

S. R. Batten, P. Jensen, B. F. Moubaraki, K. S. Murray, R. Robson, *Chem. Commun.*, 1998, 439.



Rutile, TiO_2



$Cu(dca)_2$

$Co(dca)_2$ and $Ni(dca)_2$ behave as **FERROMAGNETS** at low temperature (T_c, 9 and 20K respectively).

ie. **Cooperative electronic interactions throughout the entire network.**

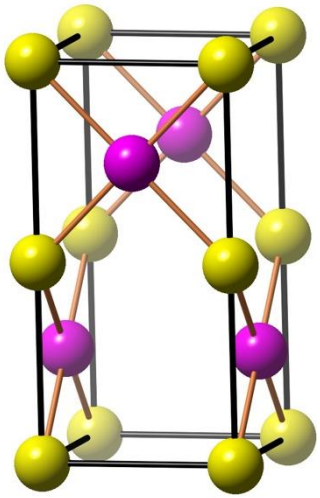
OUR APPROACH TO CONSTRUCTING TARGETTED COORDINATION NETWORKS USING PREORGANIZED BUILDING BLOCKS (1991)

1). Choose a target net.
2). Devise and construct predisposed building blocks with a chemical functionality, a geometry and a connectivity appropriate to the chosen target net.
3). Devise reaction conditions which allow the building blocks spontaneously to combine to generate the target network in the form of ordered crystalline material.

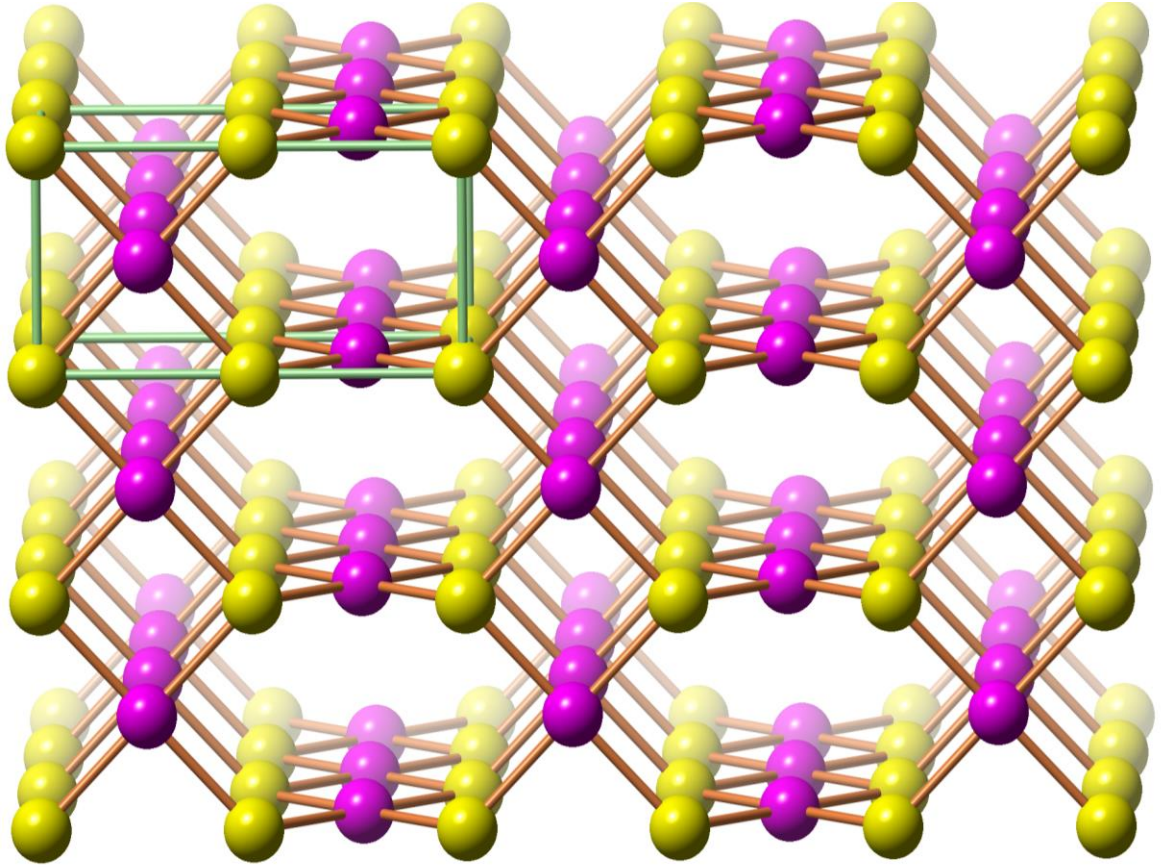
TARGET NETS	BUILDING BLOCK GEOMETRY REQUIRED
DIAMOND	TETRAHEDRAL
alpha-Po	OCTAHEDRAL
(10-3)-a)	TRIGONAL
RUTILE	TRIGONAL + OCTAHEDRAL
PtS	TETRAHEDRAL +SQUARE PLANAR
BORACITE	TETRAHEDRAL + TRIGONAL
"Pt_3O_4"	TRIGONAL + SQUARE PLANAR

The PtS net as a target.

PtS topology - equal numbers of tetrahedral and square planar nodes, each connected to four of the other type.



PtS
unit cell.



Chemical Record, e202400038, 2024

The PtS net

Initially I sought the simplest components I could think of to test whether appropriately pre-organized square planar and tetrahedral units might combine to generate spontaneously a network with the PtS connectivity.

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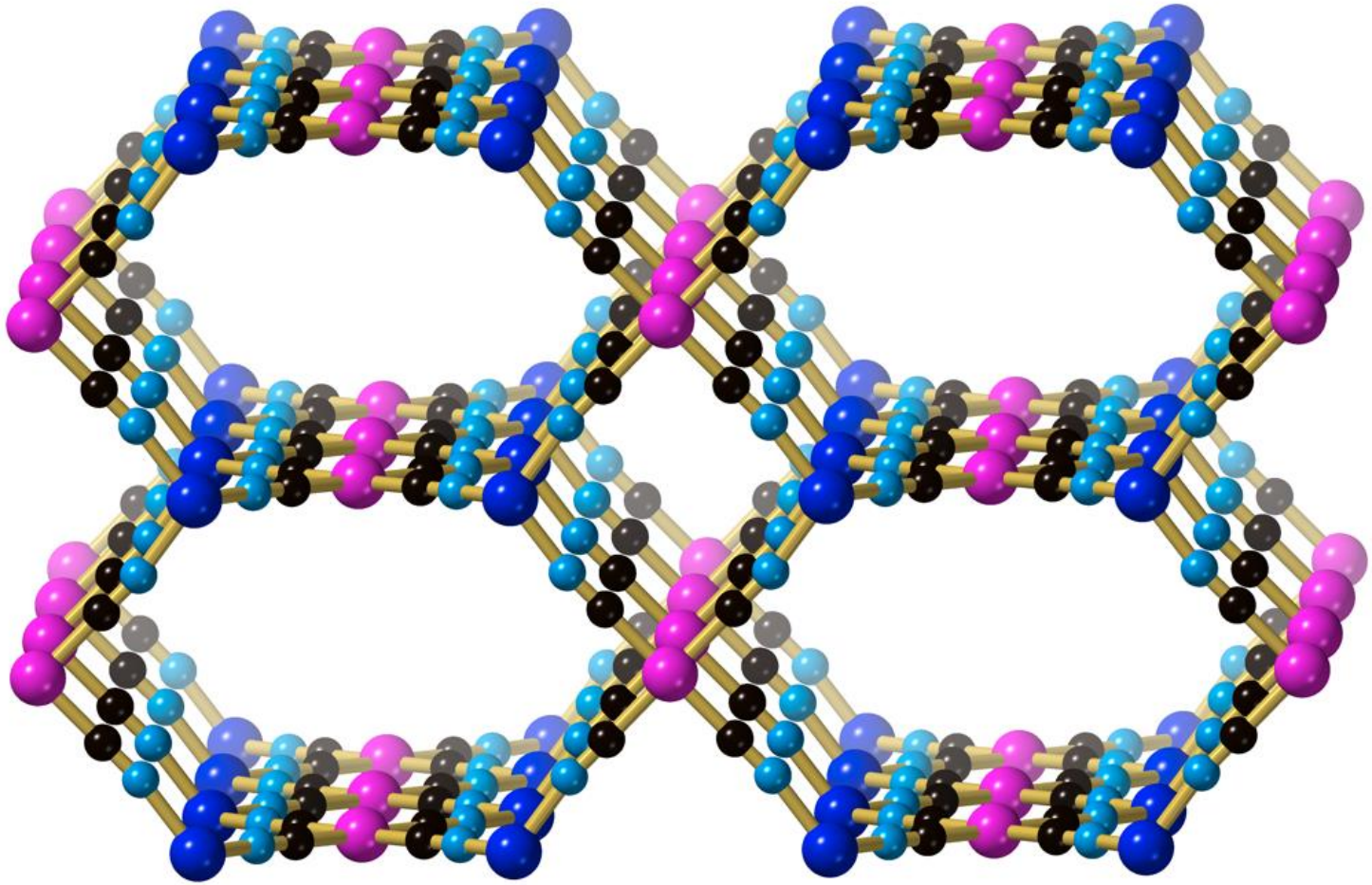
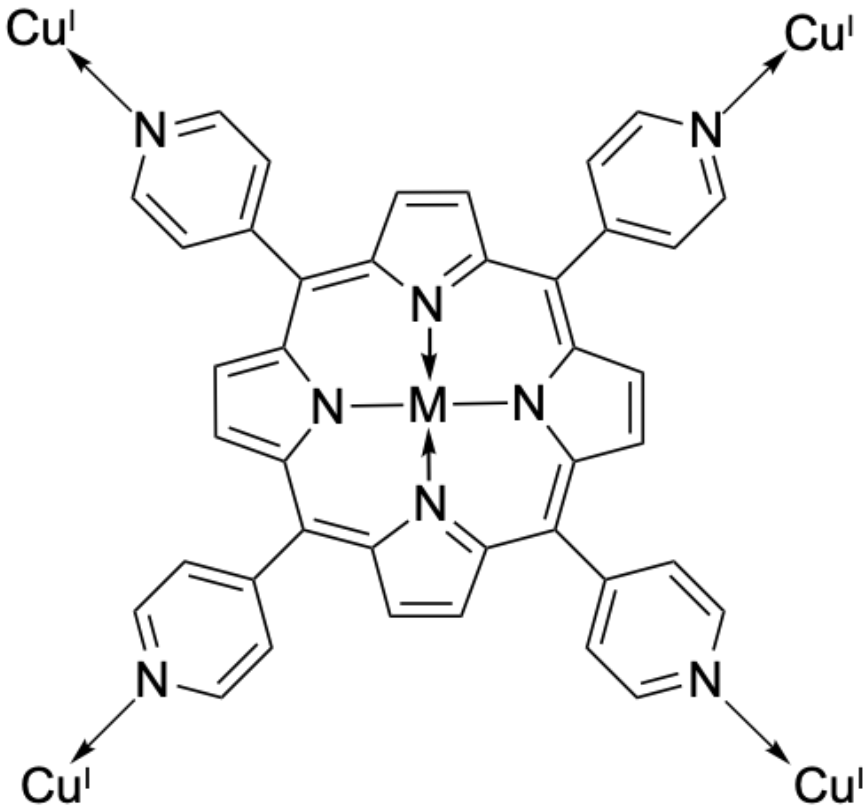
I chose $Pt(CN)_4^{2-}$ as the intended square planar node and Cu^{I} as the intended tetrahedral node.

$Cu^{I}(CH_3CN)_4BF_4 + K_2Pt(CN)_4 + NMe_4BF_4 \longrightarrow NMe_4\{CuPt(CN)_4\}$ crystals



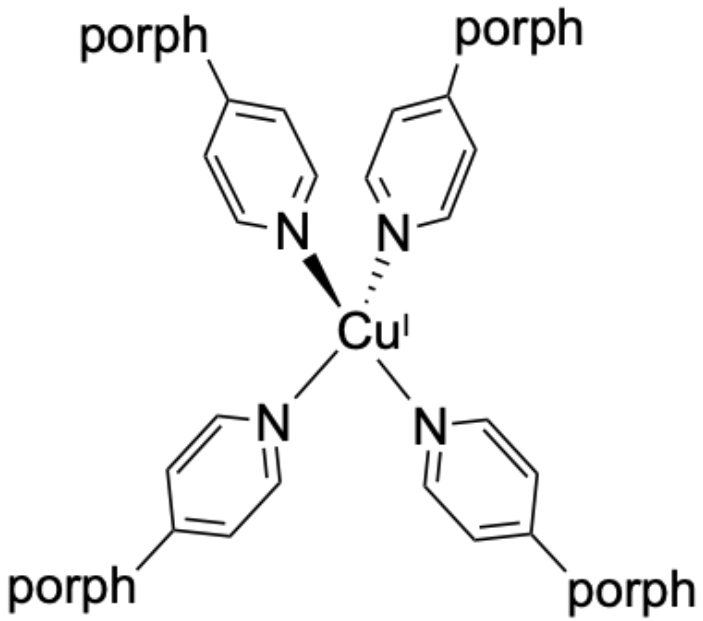
The $Cu^{I}[Pt(CN)_4]^{-}$ network did have the intended PtS-like topology

R. W. Gable, B. F. Hoskins and R. Robson, Chem. Comm., **1990**, p. 762.



M^{II}-tetrapyridylporphyrin,
ie. M^{II}tpp, M = Pd or Cu

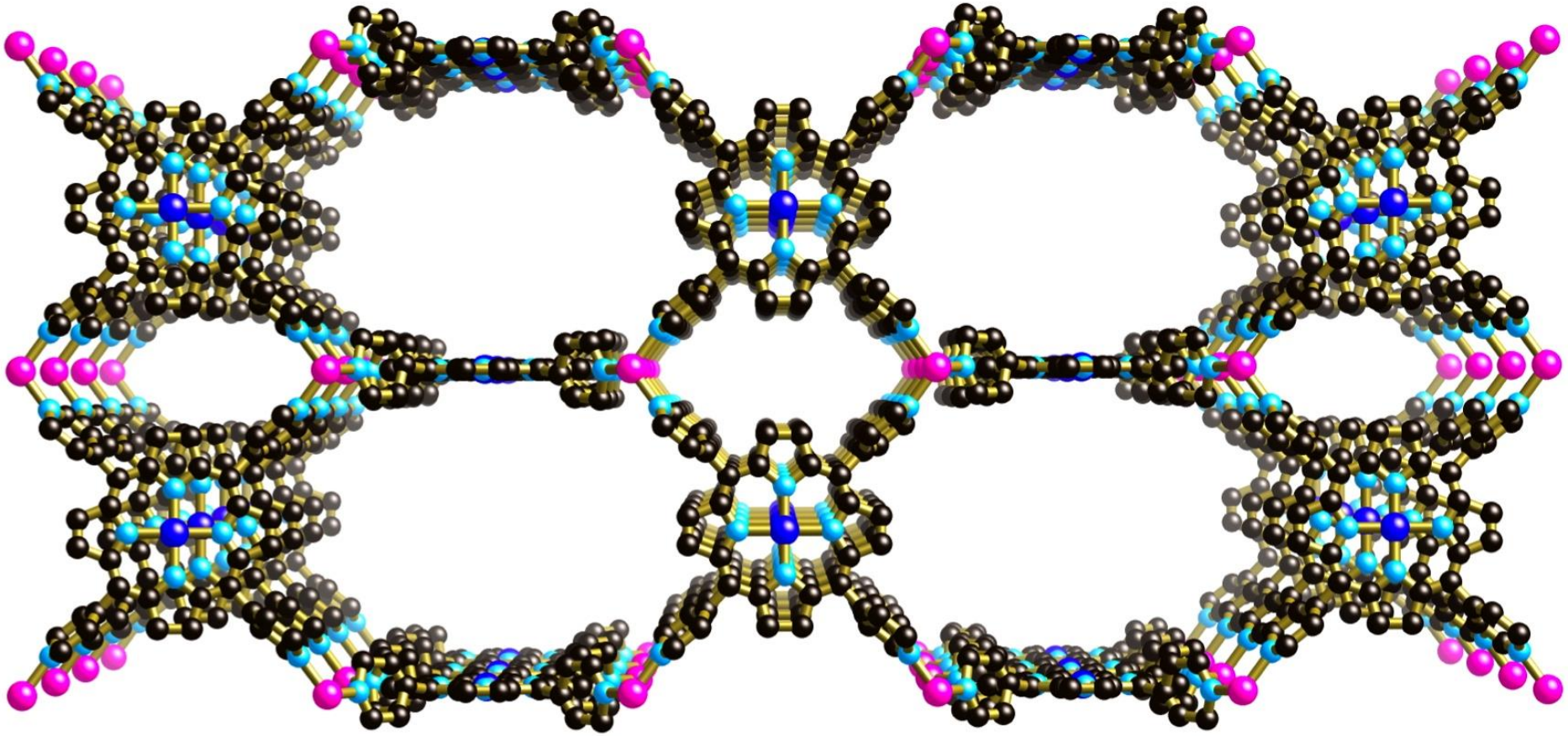
- intended to serve as the planar 4-connecting node in a PtS-like network



Cu^{I}
- intended to serve as the tetrahedral node in a PtS-like network

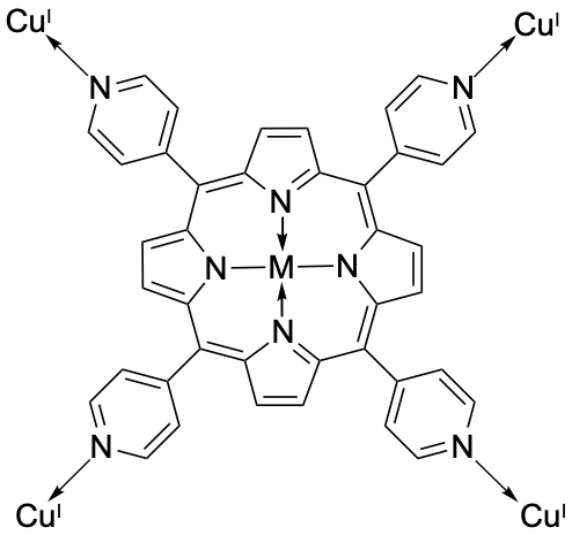
PhD student, **DIANNE MICHAEL**, using Cu^{II}-tetrapyridylporphyrin as the square planar building block together with Cu^{I} (or Ag^{I}) as the tetrahedral component, was able to obtain crystalline coordination polymers and to show that they really did have the intended PtS-like topology.

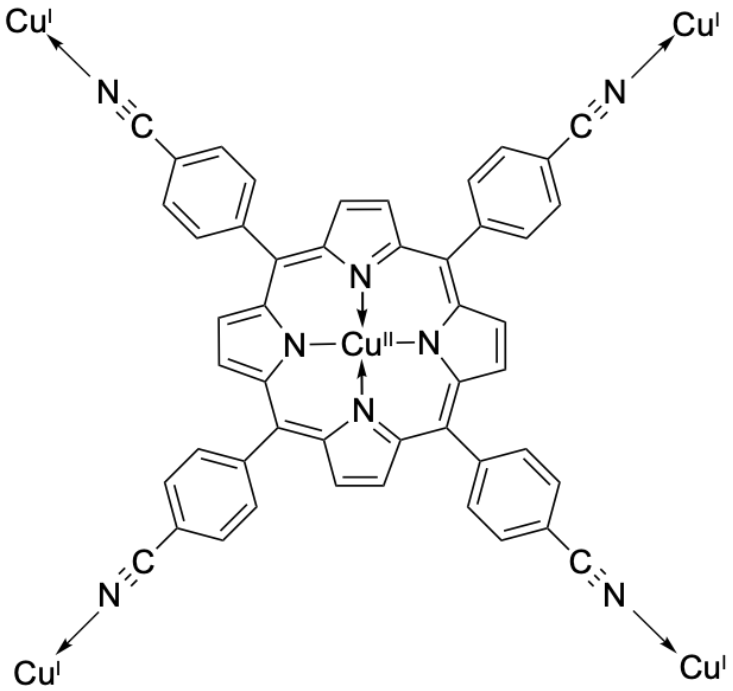
$Cu^{II}tpp + Cu^{I}(CH_3CN)_4BF_4 \longrightarrow \{[Cu^{II}tpp]Cu^{I}\}BF_4.nC_6H_5NO_2$

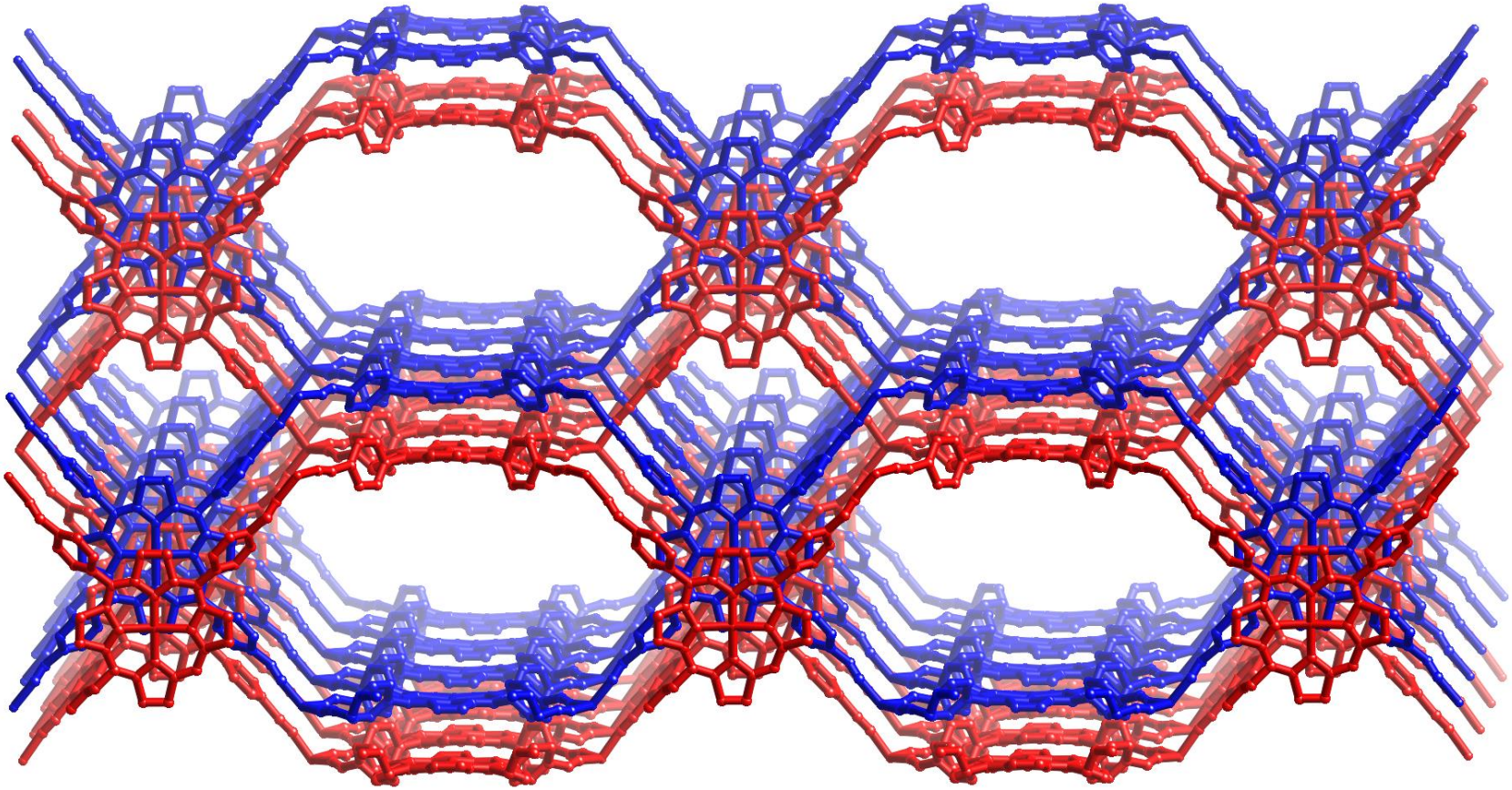


Chemical Record, e202400038, 2024

B. F. Abrahams, B. F. Hoskins, **DIANNE MICHAEL,** and R. Robson, *Nature*, **369**, 727, **1994**


Cu^{I}
N
N
Cu^{I}
N
N
M
N
N
N
N
Cu^{I}
Cu^{I}


Cu^{I}
N
C
N
Cu^{I}
C
N
N
N
Cu^{II}
N
N
C
N
C
N
Cu^{I}
Cu^{I}

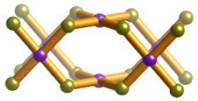


Two interpenetrating $Cu^{I}\{Cu^{II}$[tetra-(4-cyanophenyl)porphyrin]$\}^{+}$ networks with the PtS topology.

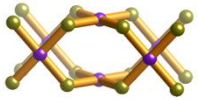
Spacious channels are left within the paired-up networks which

<u>together</u> *occupy* ***<u>only ~30%</u>*** of the volume of the crystal.

Nature, 1994, **369**, 727.



The PtS prototype



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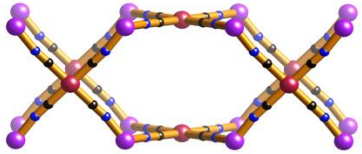
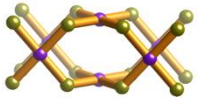


The $\{\{Cu^{I}[Pt(CN)_4]\}^-$ network. **1990**.



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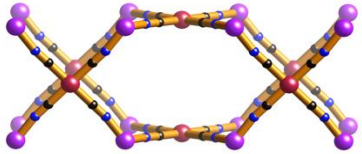

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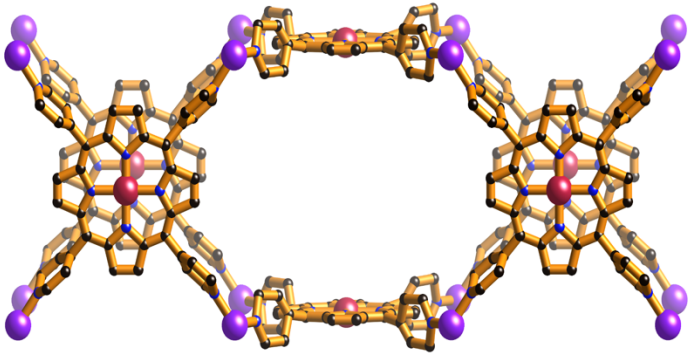
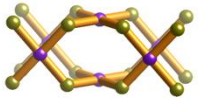


The $\{Cu^{I}[Cu^{II}$(tetra-4-pyridylporphyrin)$]\}^+$ network.



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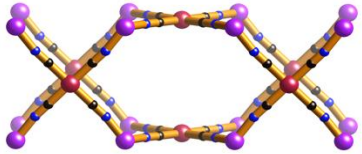

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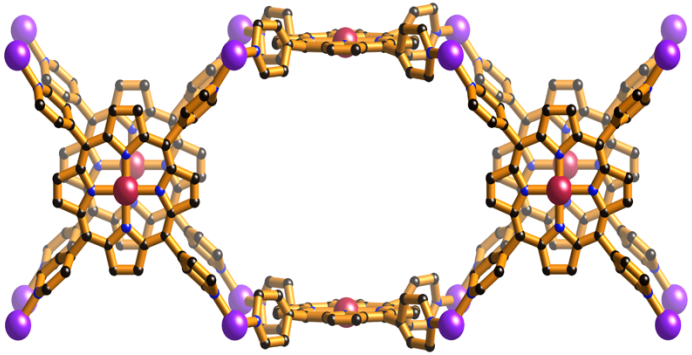

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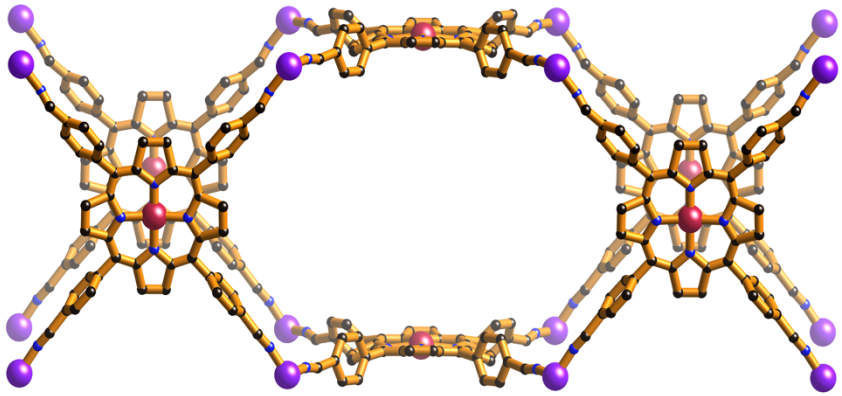
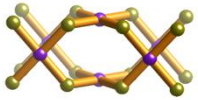


The $\{Cu^{I}[Cu^{II}$(tetra-4-cyanophenylporphyrin)]$\}^+$ network. **1994**.



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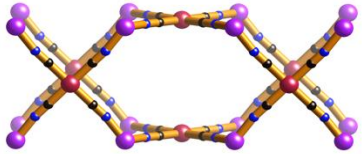

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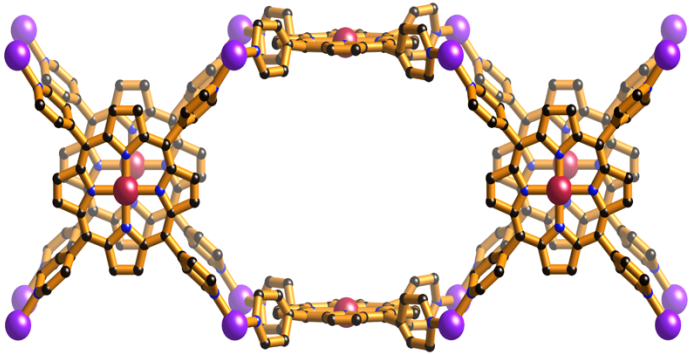

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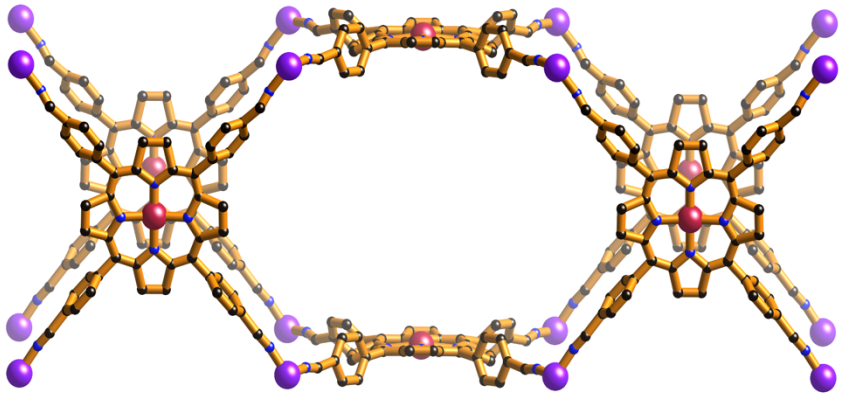

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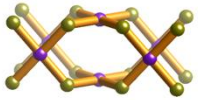
The expansionary "process" seen here was subsequently given the name

ISORETICULAR EXPANSION



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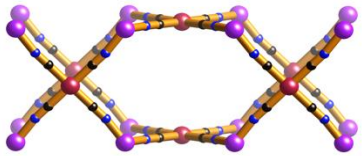

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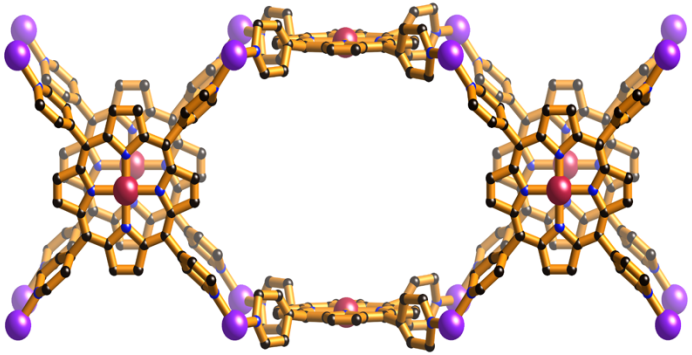

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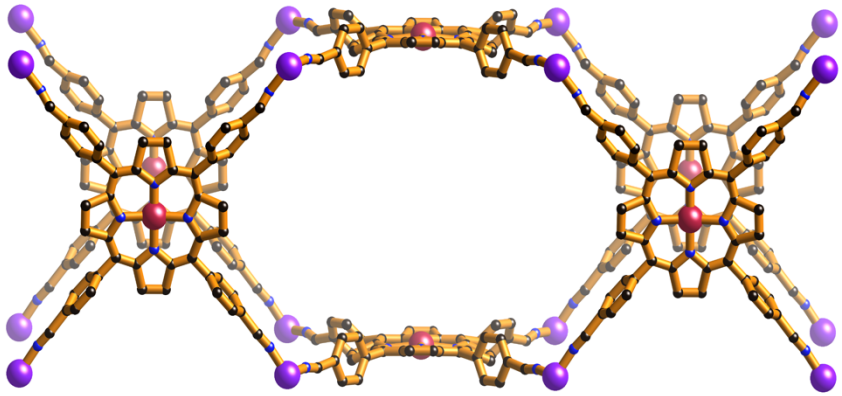

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ISORETICULAR EXPANSION

AND

Network construction was renamed

RETICULAR SYNTHESIS

The simplest, most symmetrical 3D network consisting of **4-connecting, tetrahedral** building blocks is that seen in diamond.

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The 3-connected analogue,
ie. the simplest, most symmetrical 3D network consisting of **3-connecting, trigonal** building blocks is that seen in the little known (*at least in the 1990's*) (10,3)-*a* net.

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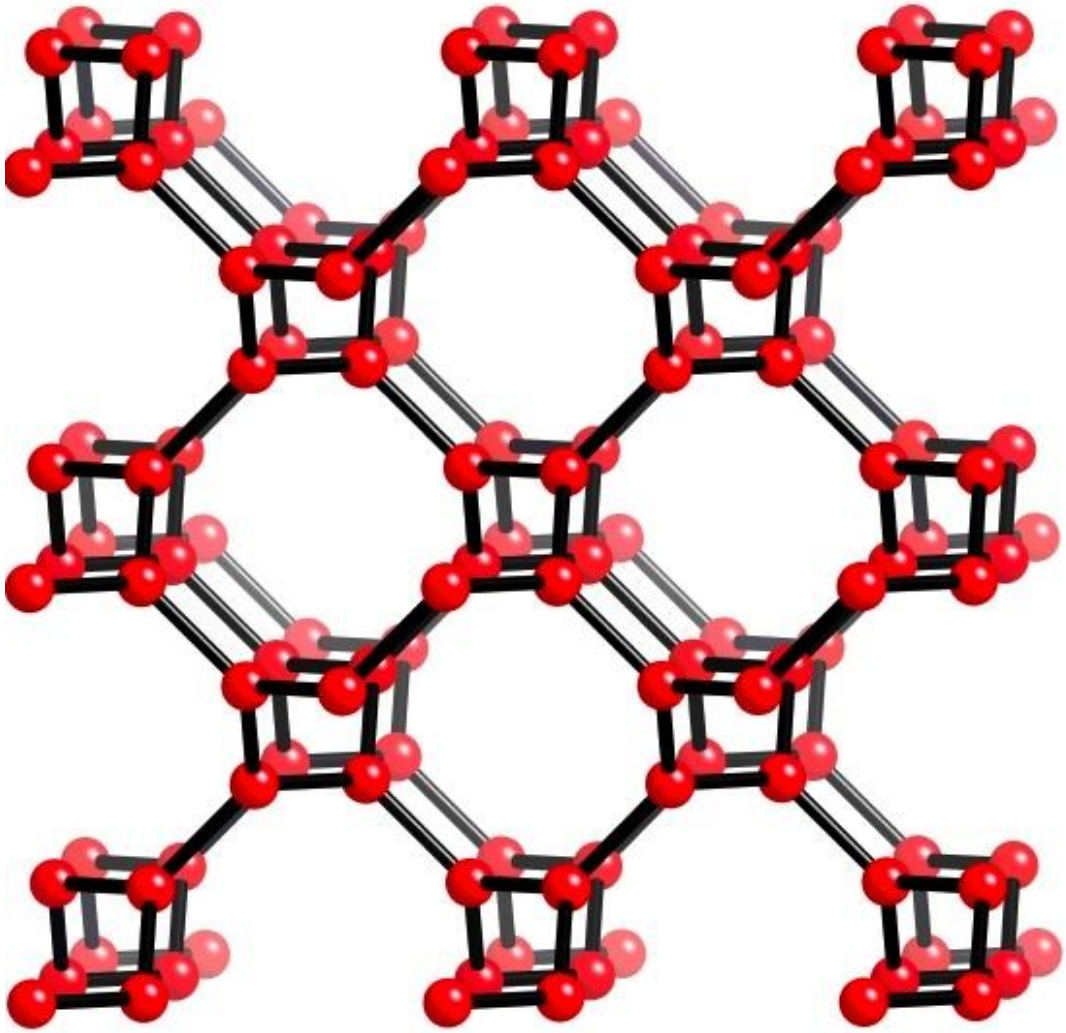
ie. the simplest, most symmetrical 3D network consisting of **3-connecting, trigonal** building blocks is that seen in the little known (*at least in the 1990's*) (10,3)-*a* net.

As a target for construction the (10, 3)-*a* topology was mouthwateringly attractive.

THE (10,3)-*a* NET - cubic and chiral

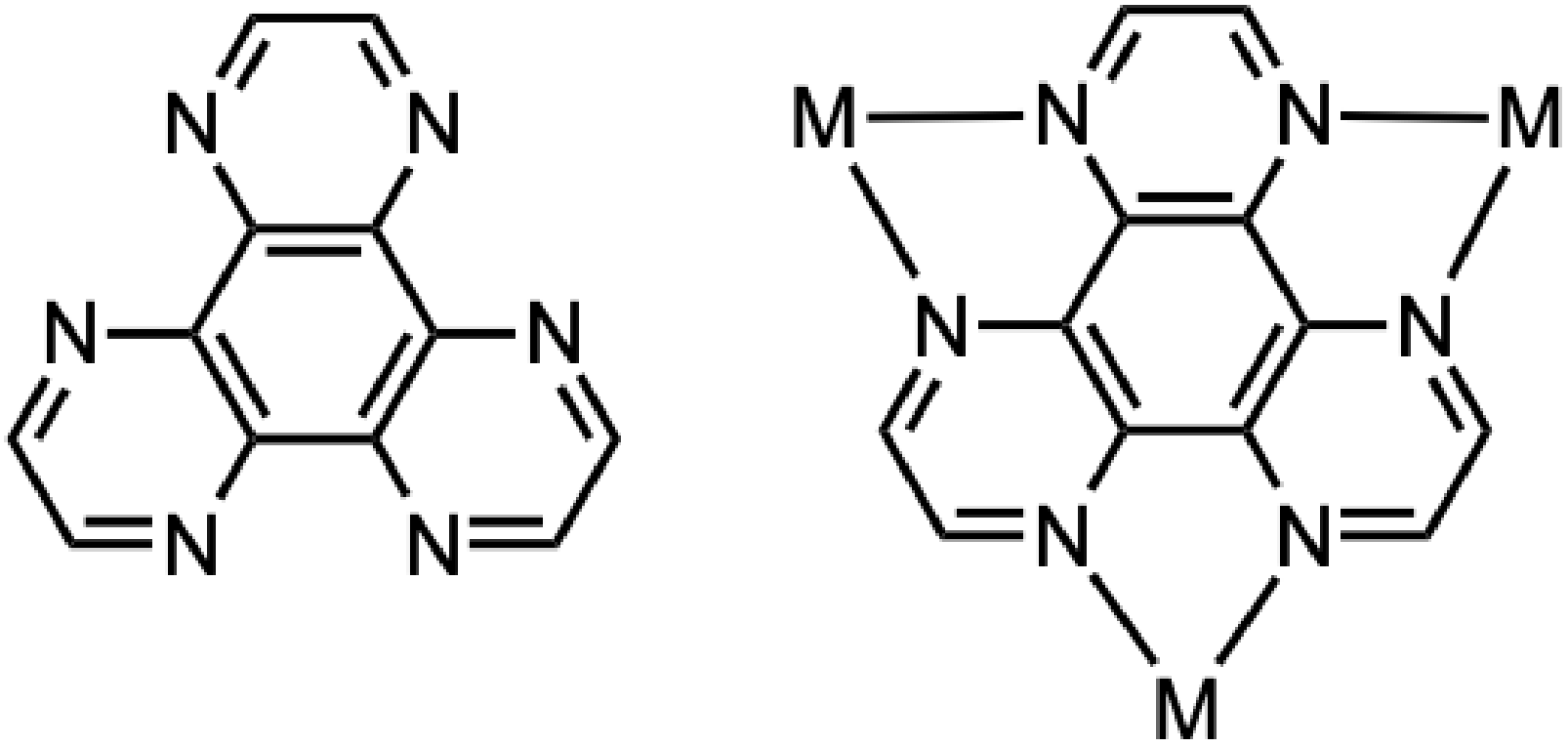


The (10,3) description indicates that the shortest circuits are 10-gons, the nodes are 3-connecting, and the *a* indicates this is the most symmetrical of several possible (10,3) nets.

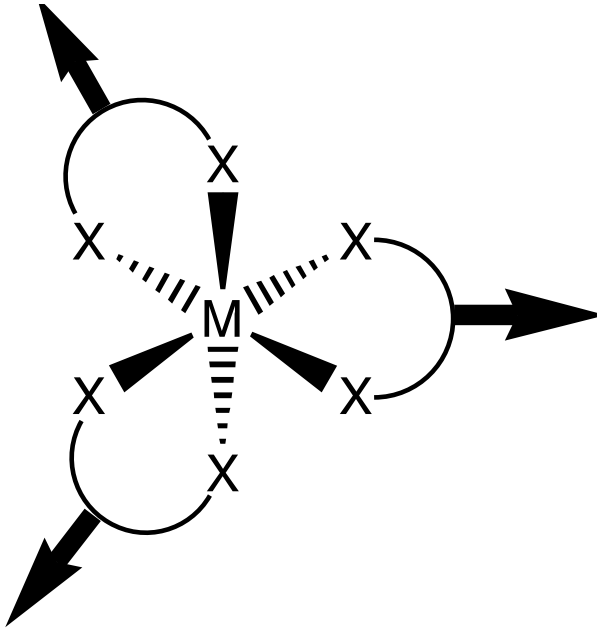
OUR APPROACH TO CONSTRUCTING TARGETED COORDINATION NETWORKS USING PREORGANIZED BUILDING BLOCKS (Atlanta 1991)

1). Choose a target network.
2). Devise and construct pre-organized building blocks with a chemical functionality, a geometry and a connectivity appropriate to the chosen target.
3). Devise reaction conditions which allow the building blocks spontaneously to combine to generate the target network in the form of ordered crystalline material.

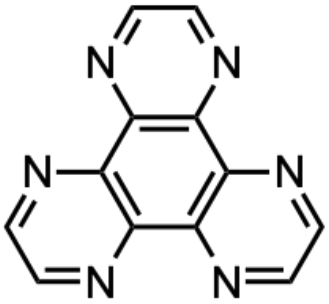
TARGET NETS	BUILDING BLOCK GEOMETRY REQUIRED
DIAMOND	TETRAHEDRAL
alpha-Po	OCTAHEDRAL
(10-3)-*a*	TRIGONAL
RUTILE	TRIGONAL + OCTAHEDRAL
PtS	TETRAHEDRAL +SQUARE PLANAR
BORACITE	TETRAHEDRAL + TRIGONAL
"Pt_3O_4"	TRIGONAL + SQUARE PLANAR



The ligand hexaazatriphenylene (abbreviated hat) is **pre-organized** to chelate three metal ions at the corners of an equilateral triangle.



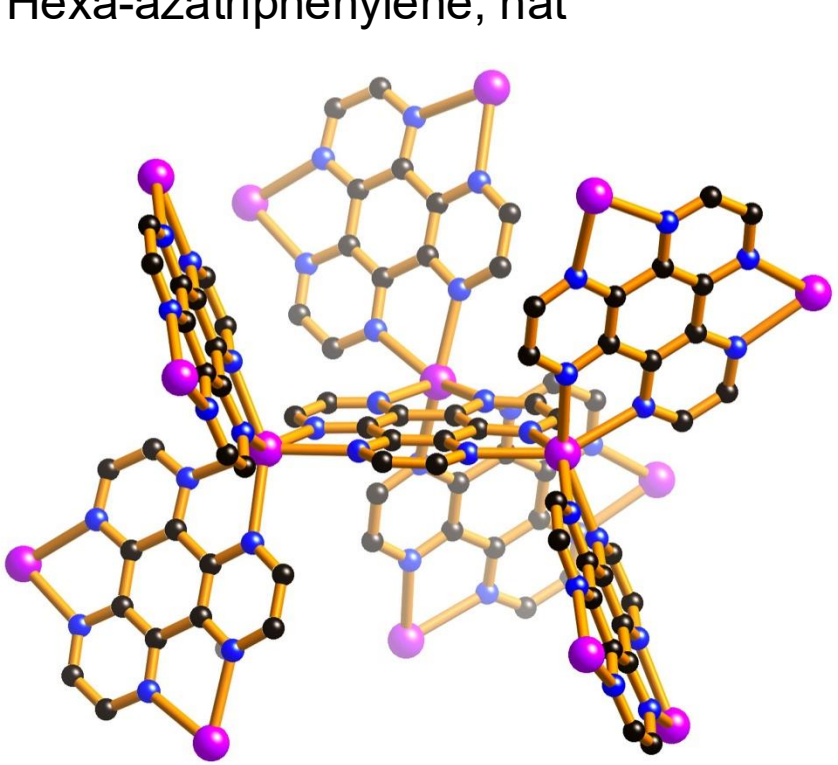
We recognized that when octahedral metal centres are coordinated by three bridging ligands with BIDENTATE metal binding sites, the metal centres **themselves** become **pre-organized** 3-connecting, trigonal nodes.

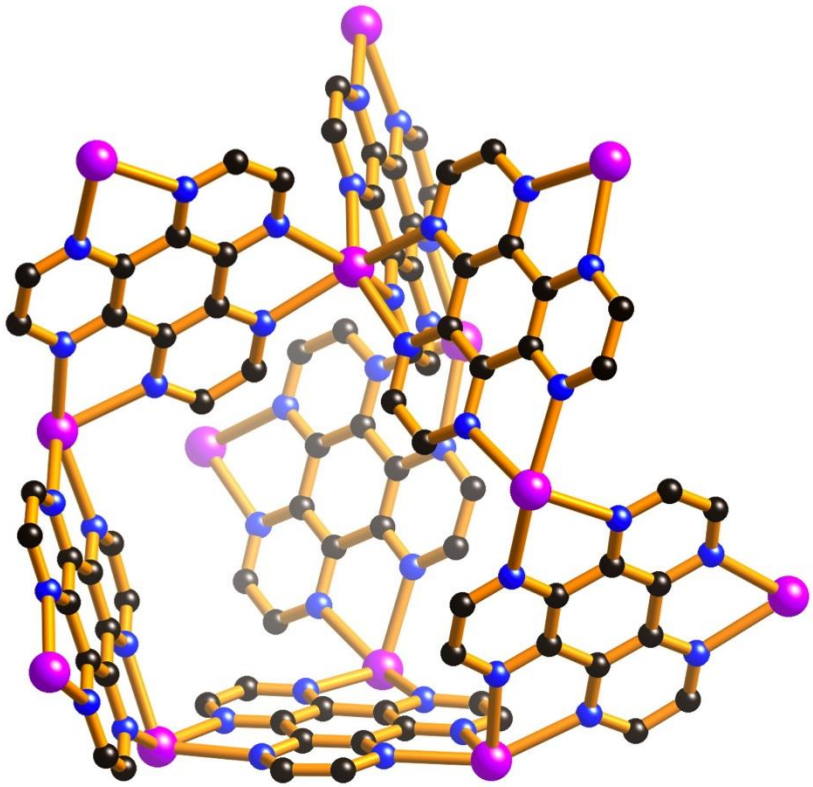


Hexa-azatriphenylene, hat

Ag^+ + hat gives a $[(Ag.hat)^+]_n$ network with (10,3)-*a* topology.

Both Ag and hat act as trigonal 3-connecting nodes.





Chemical Record, e202400038, 2024

B. F. Abrahams, PATRICIA JACKSON and R. Robson, *Ang. Chem.*,1998, 37, 2656.

By the late 90’s the pre-organized building block approach was well founded.

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What our work had shown was that it would be possible to make large (practically unlimited) numbers of coordination polymers with designed structures/topologies.

Around the start of this century there was an avalanche of reports concerned with coordination polymers
(some referred to as MOFs).

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(some referred to as MOFs).

- an outpouring that has continued unabated.

Acknowledgements

Family

Dr. Bernard Hoskins.
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Prof. Stuart Batten
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Dr. Elizabeth Sutherland

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