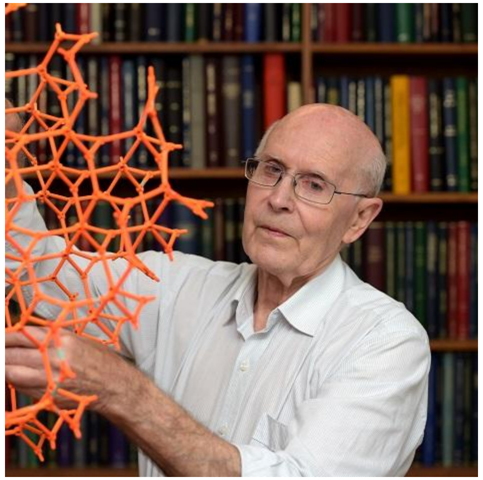
COVALENT ORGANIC FRAMEWORKS

Nobel prize in Chemistry 2025

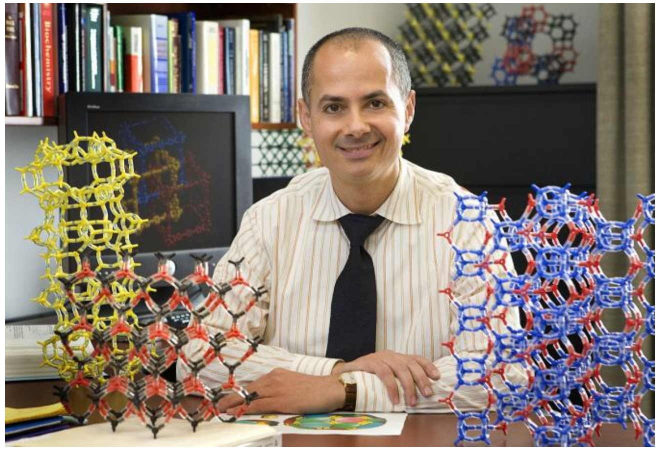
Susumu Kitagawa

For pioneering the concept and creation of MOFs



Richard Robson

For his foundational work in designing porous coordination polymers



Omar M. Yaghi

For his immense contributions in synthesizing diverse MOFs, including those for water harvesting

“for the development of metal–organic frameworks”

Covalent organic frameworks (COFs) are crystalline porous polymers formed by a bottom-up approach from molecular building units having a predesigned geometry that are connected through covalent bonds. They offer positional control over their building blocks in two and three dimensions. This control enables the synthesis of rigid porous structures with a high regularity and the ability to fine-tune the chemical and physical properties of the network.

Structures
Synthesis
Applications

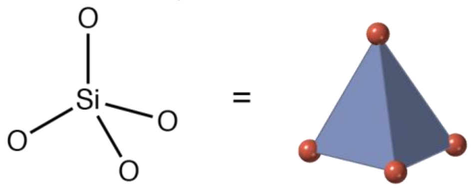
letteratura

Science **2005**, *310*, 1166−1170
Chem. Rev. **2020**, *120*, 8814−8933
Adv. Funct. Mater. **2018**, *28*, 1705553
J. Am. Chem. Soc. **2019**, *141*, 1807−1822
Chem. Soc. Rev., **2020**, *49*, 6248

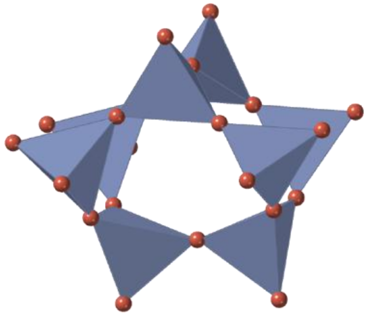
zeolites

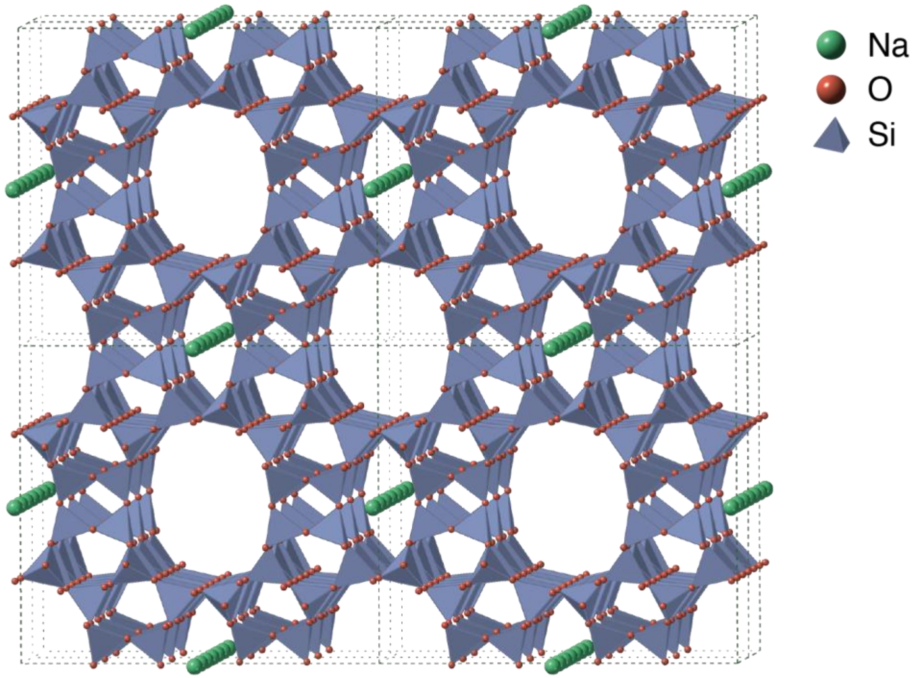
prendono il nome dal greco ζέω (zéō), bollire, e λίθος (líthos), pietra, da cui *pietra che bolle*, dato che, scaldate, rilasciano l'acqua occlusa nei pori. Le zeoliti costituiscono una classe di tectoalluminosilicati cristallini scoperti nel 1756 da Axel Fredrik Cronstedt; ad oggi se ne conoscono circa 200, di cui 40 naturali e il resto da sintesi ottimizzate dai chimici in laboratorio.

SiO_4 tetrahedron



secondary building unit (cage)





Mordenite (MOR framework)

Metal Organic Frameworks

Selective binding and removal of guests in a microporous metal–organic framework

O. M. Yaghi, Guangming Li & Hailian Li

Department of Chemistry and Biochemistry,
Goldwater Center for Science and Engineering,
Arizona State University, Tempe, Arizona 85287-1604 USA

Nature 1995, 378, 703

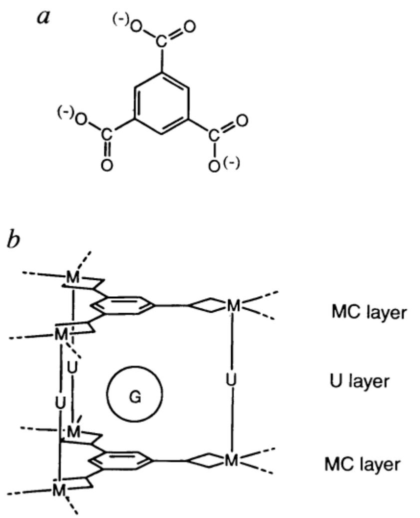


FIG. 1 *a*, Structural formula 1,3,5-benzenetricarboxylate (BTC), and *b*, its coordination to a metal ion to form alternating metal-carboxylate and spacer unit layers to form voids where guest inclusions are accommodated.

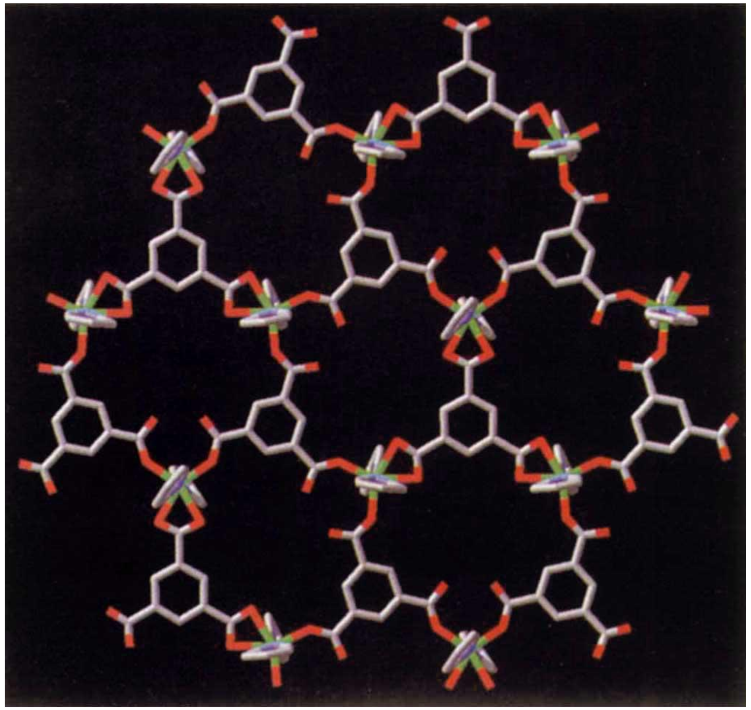


FIG. 2 A single layer of the extended porous network of $CoC_6H_3(COOH_{1/3})_3(NC_5H_5)_2 \cdot 2/3\ NC_5H_5$. The metal-carboxylate layer is shown approximately along the *x–y* plane: green, Co; red, O; blue, N; grey, C. Only one of the two preferred orientations about the Co–N bond is shown for the statistically disordered coordinated pyridine molecules. The hydrogen atoms on the pyridines and BTC units are omitted for clarity.

metal organic frameworks (MOF)

Dal 1999, l'affascinante MOF-5 costituisce il capostipite di una nuova classe di materiali ultra- porosi (con aree superficiali che vanno da 1000 a 10.000 m^2g^{-1}), da allora chiamati metal-organic frameworks (MOF): solidi cristallini composti da ioni metallici o cluster di ioni metallici (i "nodi" o "secondary building units, SBU"), collegati tra loro da molecole organiche, (i "linkers")

Omar Yaghi et al. *Nature*, **1999**, ***402***, 276

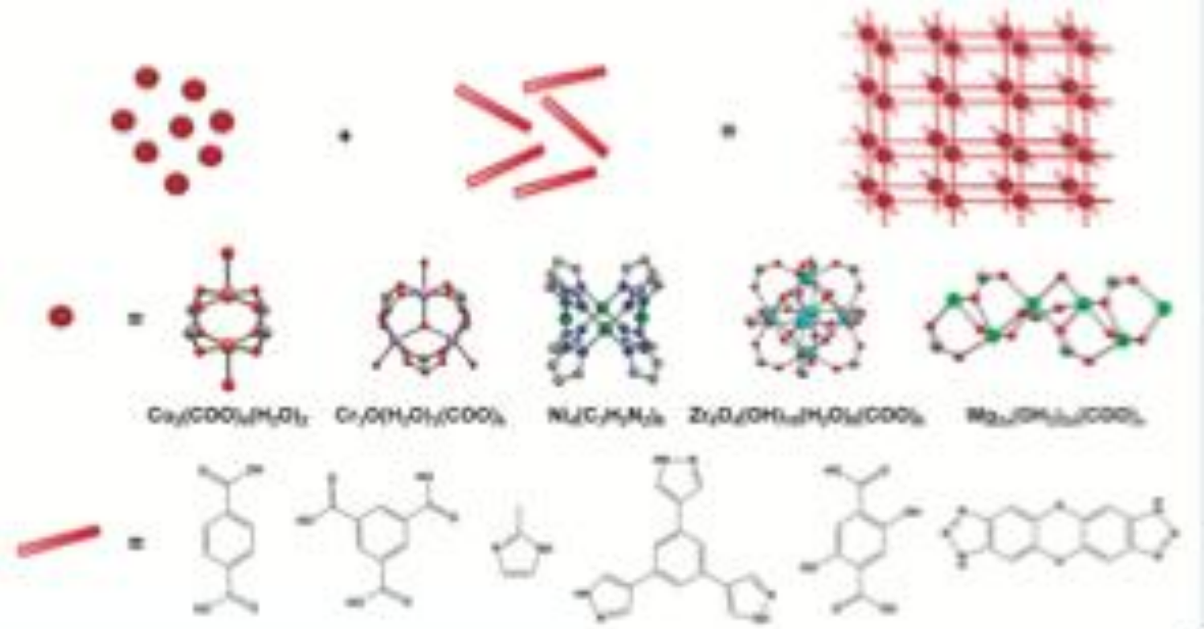


Fig. 2 - Descrizione schematica del concetto di "reticular chemistry"

metal organic frameworks (MOF)

Omar Yaghi et al. *Nature*, **1999**, ***402***, 276

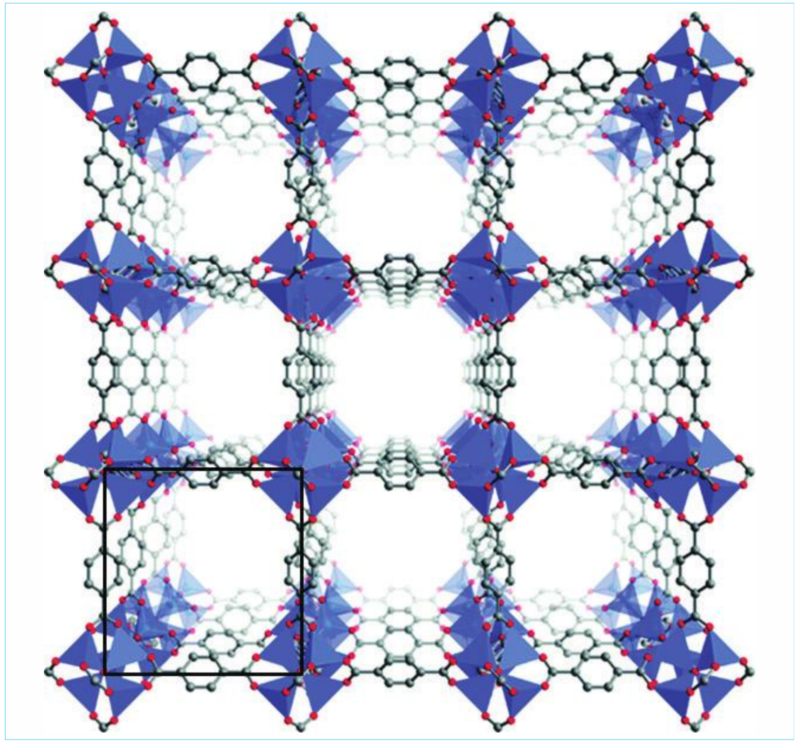


Fig. 1 - L'architettura cubica cristallina del MOF-5, $Zn_4O(bdc)_3$ - gruppo spaziale *Fm*-3*m*, a=25,6690(3) Å, V=16913,2(3) Å^3 - costituita da clusters tetraedrici di formula Zn_4O connessi tra loro da leganti organici lineari (tereftalato, bdc^{2-}). Otto clusters costituiscono una cella unitaria che racchiude una grande cavità vuota di diametro di 18,5 Å. La densità del materiale è eccezionalmente bassa, 0,59 g cm^{-3}. Codice colore: Zn, azzurro; O, rosso; C, grigio. Gli H non sono mostrati per semplicità grafica

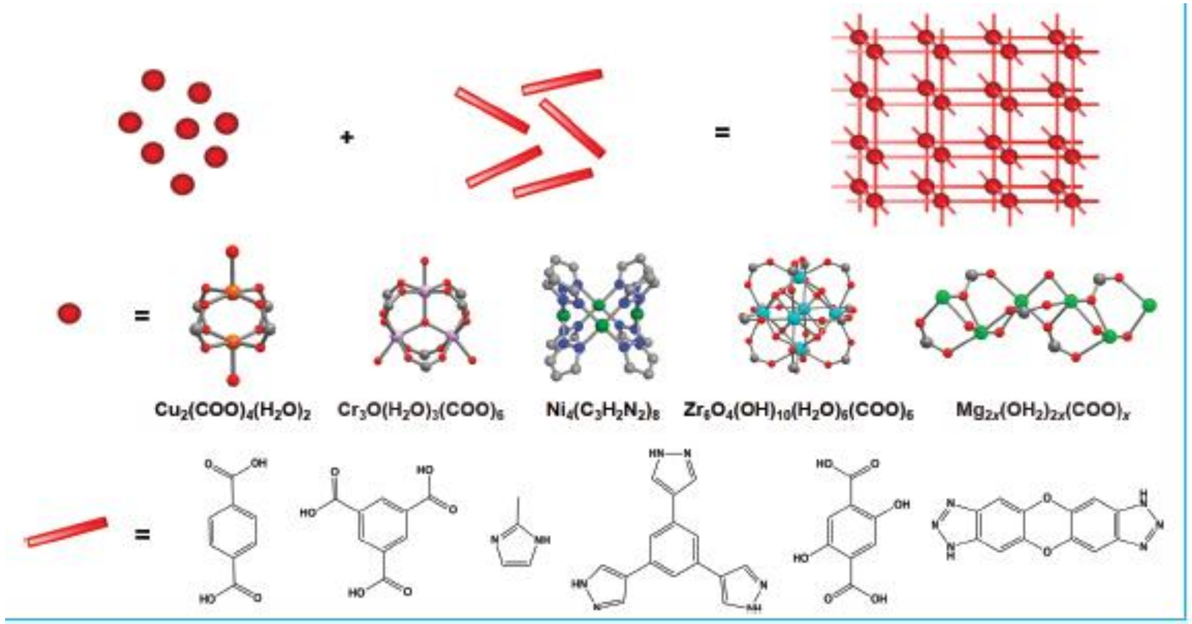


Fig. 2 - Descrizione schematica del concetto di "reticular chemistry"

bdc^{2-} è l'anione dell'acido tereftalico

Dynamic Covalent Chemistry

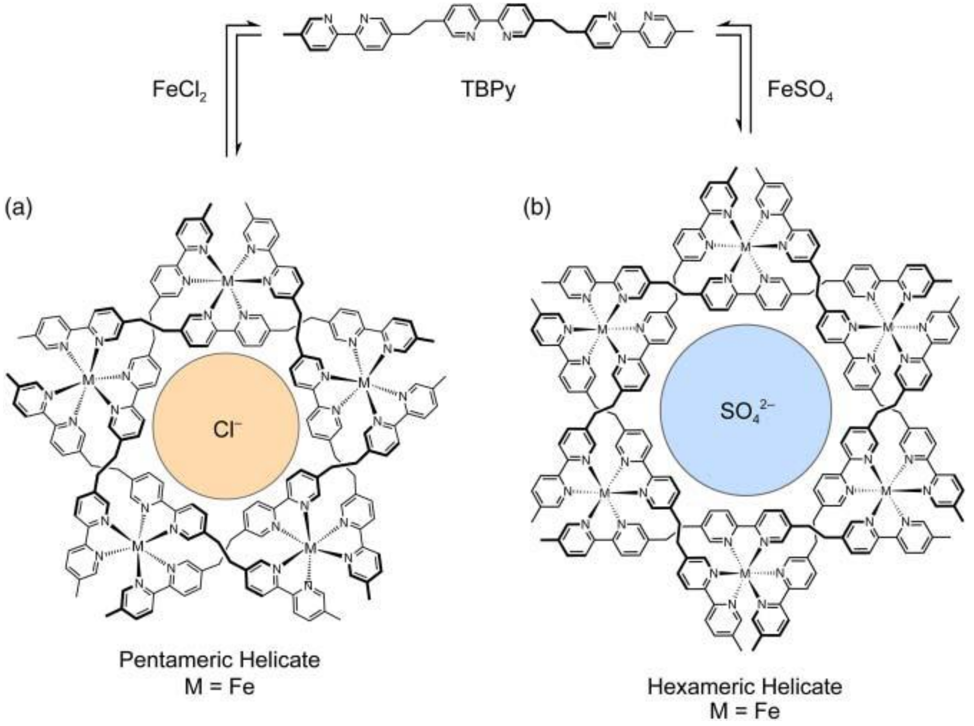


Figure 7.5 Synthesis of pentameric and hexameric circular helicates assisted by metal templation. Reacting linear TBPy with $FeCl_2$ yields the ninefold negatively charged pentameric circular helicate. The central pocket in the assembly is of the right size to accommodate a chloride ion, which templates the formation of the structure. In contrast, reaction of the linker with $Fe(SO_4)$ results in the formation of the 12-fold negatively charged hexameric circular helicate. Here, the sulfate ion resides in the central pocket. The only difference in the reaction conditions between the two systems is the counter anion, which controls the formation of one structure over the other. This fact highlights the dynamic nature of the assembly process.

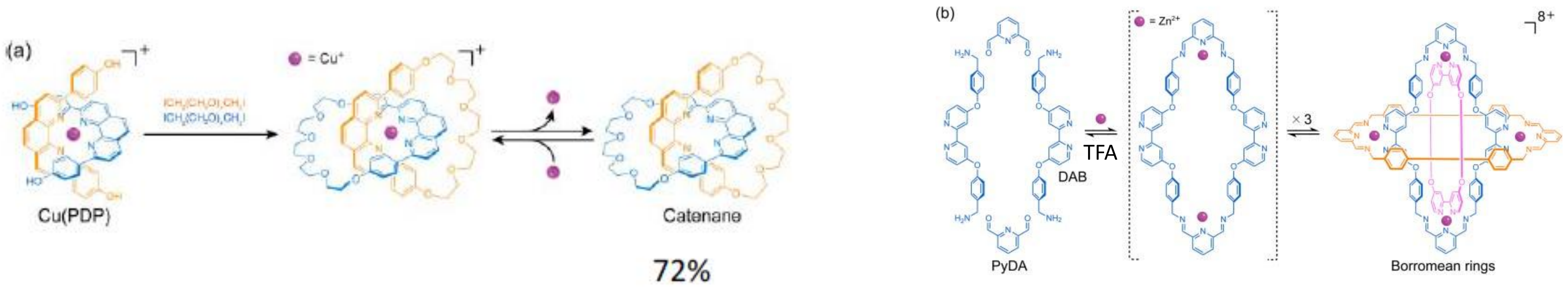
the assembly process through non-covalent interactions is microscopically reversible and can be carried out under **thermodynamic control**. This is very powerful as it allows to generate the resulting products with 100% yield and without the need for purification.

Dynamic Covalent Chemistry

It is therefore desirable to carry out covalent organic reactions under conditions allowing for **microscopic reversibility and thus for error correction**. The reversibility of several organic transformations had been reported but the notion of strategically carrying out organic chemistry under thermodynamic control was not conceptualized until 1999.

The development of what was termed “dynamic covalent chemistry” was in large carried by the field of mechanically interlocking molecules.

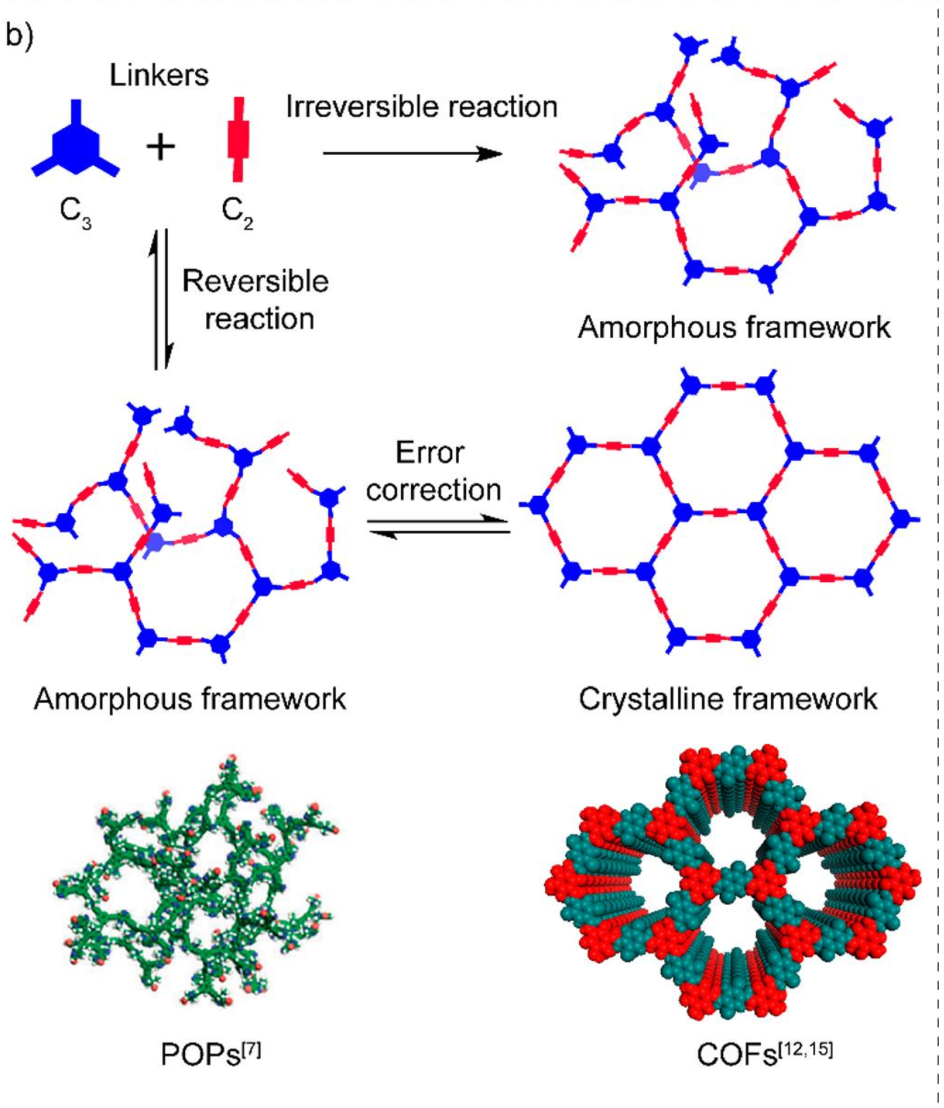
The simplest example of such species are catenanes (from Latin “catena” for “chain”) where two or more molecular rings are interlocking, thus being held together by mechanical rather than chemical bonding.



Stoddart 2004

Synthetic approach toward (a) a molecular catenane and (b) molecular Borromean rings. (a) Reaction of the CBP complex, serving as a point of registry, with DIT, followed by demetalation of the structure with potassium cyanide results in the formation of a molecular catenane. (b) Reversible imine bond formation between DFP and DAB in the presence of trifluoro acetic acid as a catalyst ensures the formation of the macrocycles with 100% yield where the Zn^{2+} ions serve as templates to bring the individual rings together in the exact manner necessary for the Borromean ring topology.

many different dynamic covalent reactions such as **imine bond formation**, **disulfide bond formation**, and alkene **metathesis** have been employed



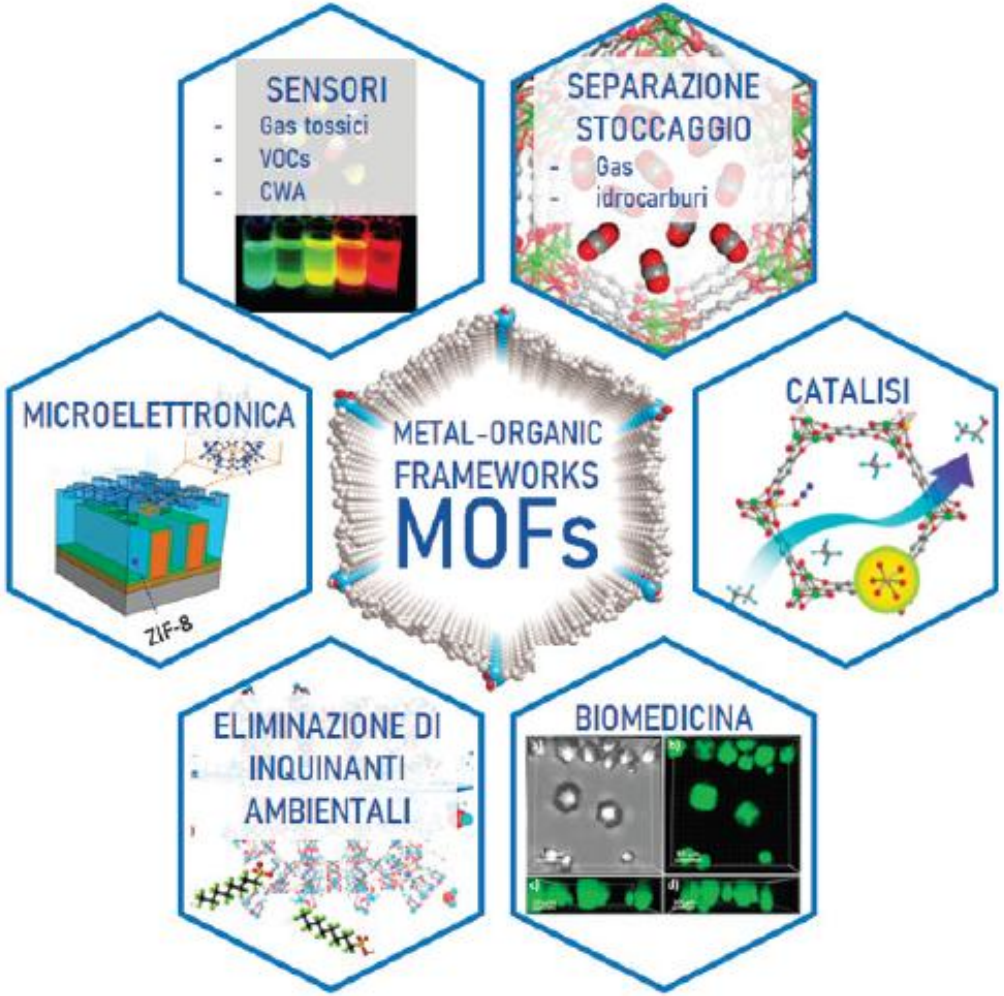


Fig. 3 - Applicazioni dei metal-organic frameworks

Porous, Crystalline, Covalent Organic Frameworks

Adrien P. Coˆte´,[1]* Annabelle I. Benin,[1] Nathan W. Ockwig,[1]
Michael O'Keeffe,[2] Adam J. Matzger,[1] Omar M. Yaghi[1]*

Covalent organic frameworks (COFs) have been designed and successfully synthesized by condensation reactions of phenyl diboronic acid $\{C_6H_4[B(OH)_2]_2\}$ and hexahydroxytriphenylene $[C_{18}H_6(OH)_6]$. Powder x-ray diffraction studies of the highly crystalline products $(C_3H_2BO)_6$&$(C_9H_{12})_1$(COF-1) and $C_9H_4BO_2$ (COF-5) revealed expanded porous graphitic layers that are either staggered (COF-1, P6$_3$/mmc) or eclipsed (COF-5, P6/mmm). Their crystal structures are entirely held by strong bonds between B, C, and O atoms to form rigid porous architectures with pore sizes ranging from 7 to 27 angstroms. COF-1 and COF-5 exhibit high thermal stability (to temperatures up to 500- to 600-C), permanent porosity, and high surface areas (711 and 1590 square meters per gram, respectively).

Science, **2005**, *310*, 1166.

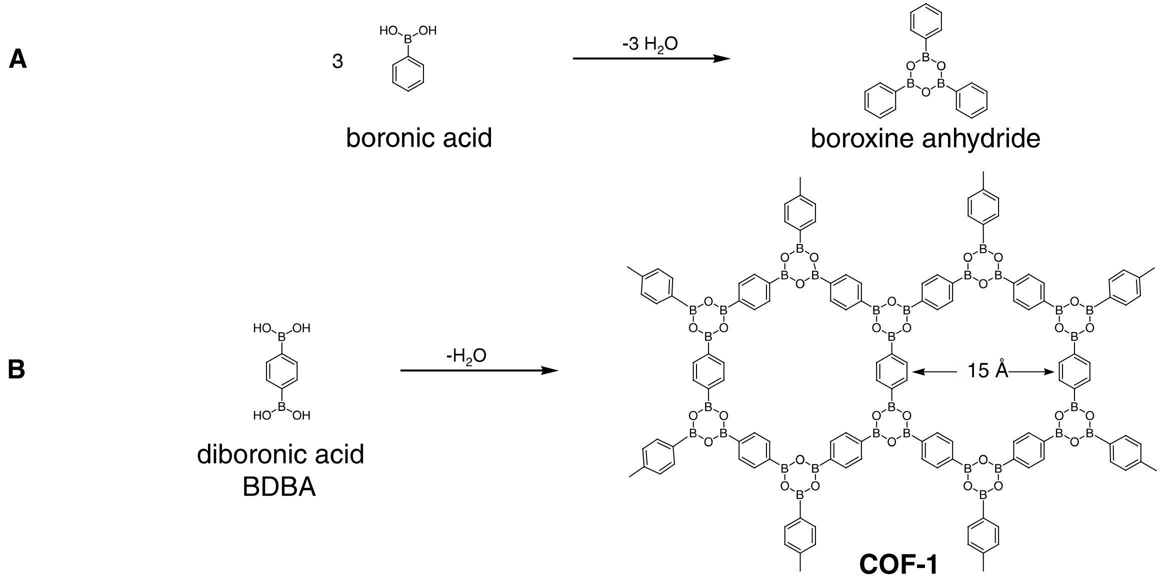
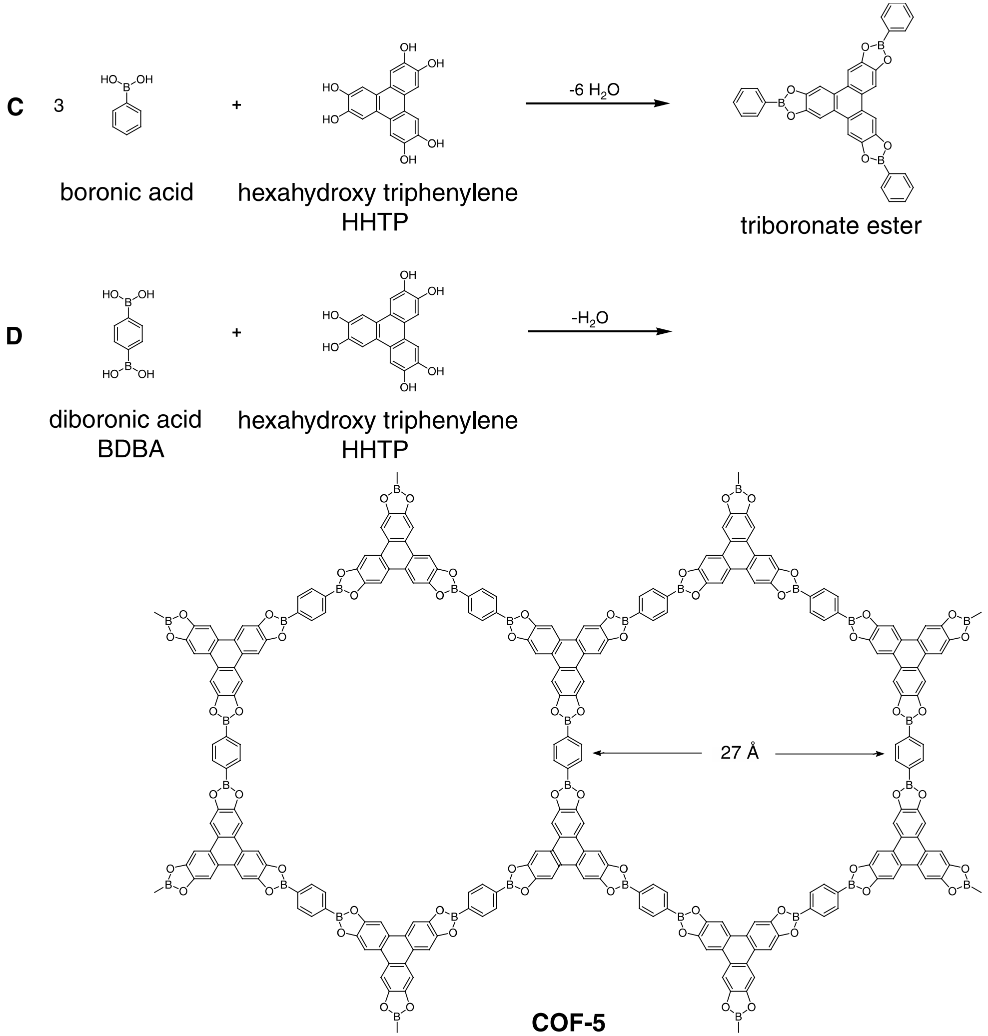


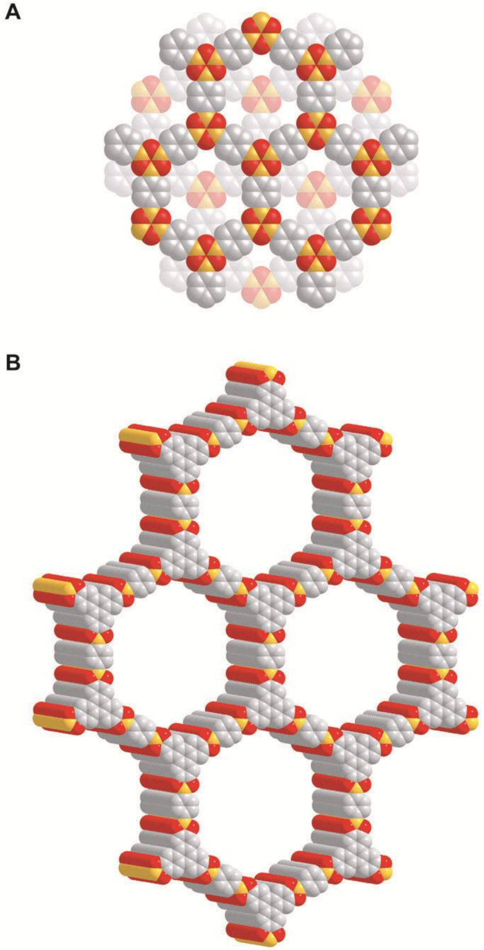
Fig. 1. (**A** to **D**) Condensation reactions of boronic acids used to produce discrete molecules and extended COFs.

COF-1 was synthesized by the heating of BDBA at 120 °C for 72 hours under a 1:1 mesitylene-dioxane solution in a sealed Pyrex tube. Isolated as white powder in 71 % yield.



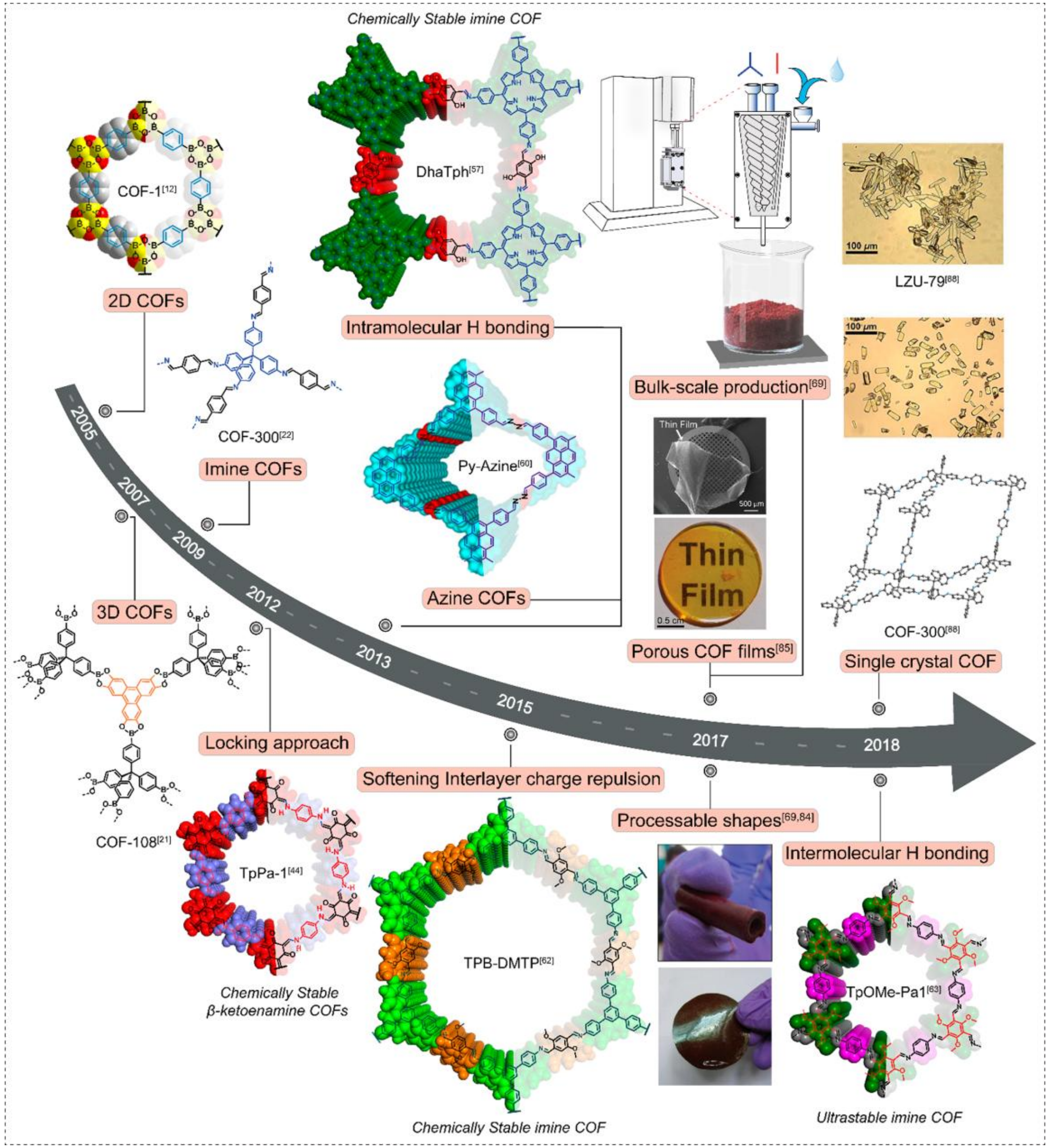
COF-5 was synthesized in 73% yield from a 3:2 stoichiometric ratio of BDBA to HHTP. COF-5 was obtained as a gray-purple solid

PXRD
SEM
FTIR
^{11}B ssNMR



Structural representations of (A) COF-1 and (B) COF-5 based on powder diffraction and modeling projected along their c axes (H atoms are omitted). Carbon, boron, and oxygen are represented as gray, orange, and red spheres, respectively.

➡ COF-1 and COF-5 exhibit high thermal stability (to temperatures up to 500 to 600 °C), permanent porosity, and high surface areas (711 and 1590 square meters per gram, respectively).



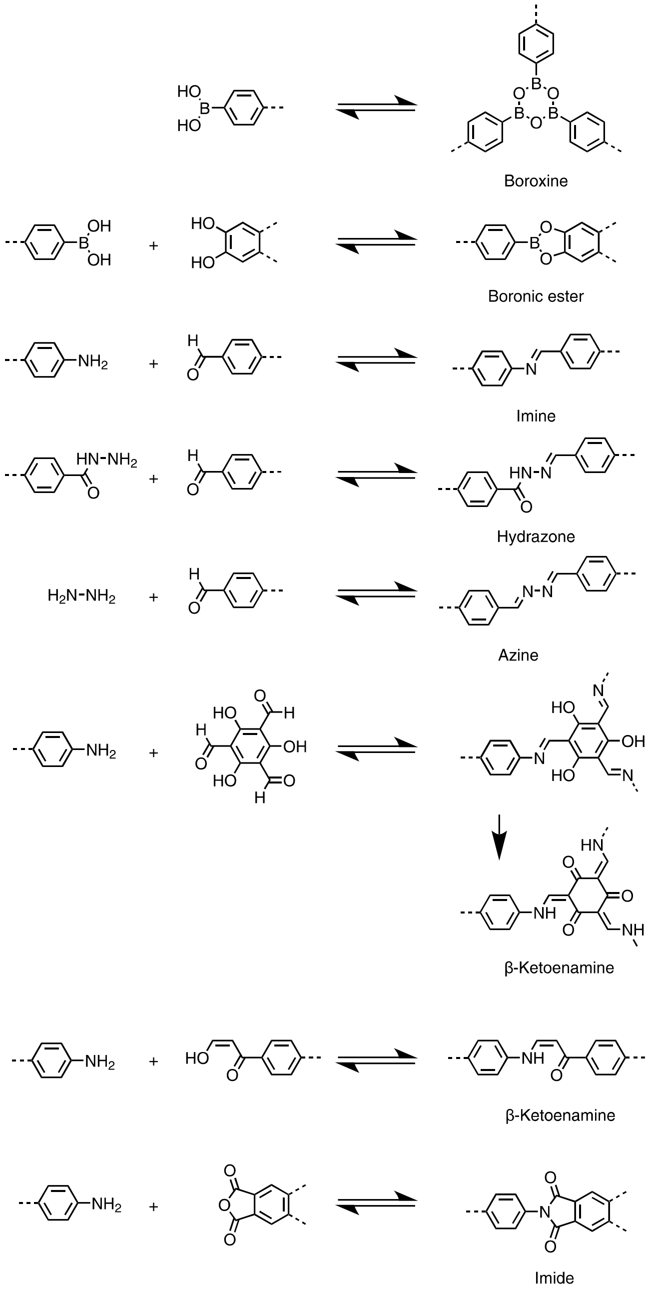
applications

molecular and gas storage
sensing
catalysis
optoelectronics
electrochemical energy storage

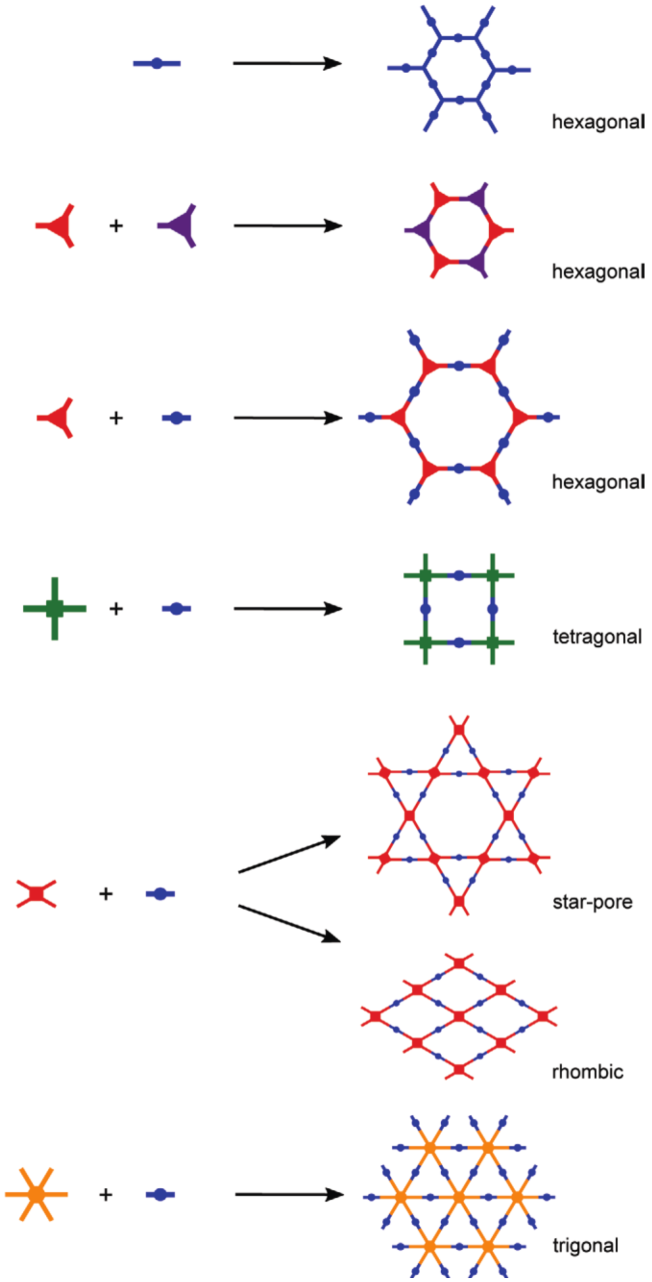
Evolution of the covalent organic framework chemistry. Important advances starting from unstable powder COFs to ultrastable processable forms.

condensation reactions for the formation of COFs

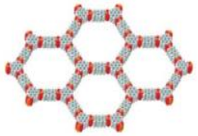
increased stability

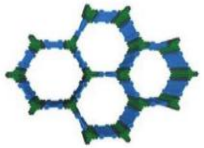


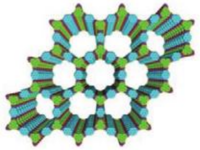
Common linker geometries and the resulting structural patterns realized in 2D COFs

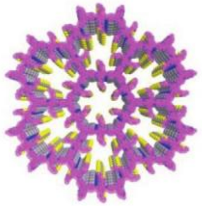


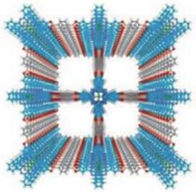
representative COF networks (2D and 3D COFs)

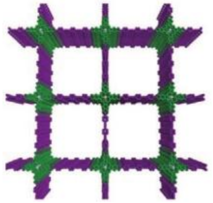

COF-10[a]

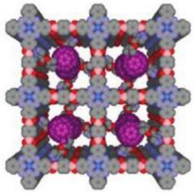

HHTP-DPB COF[b]

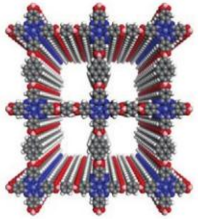

TP-COF[c]

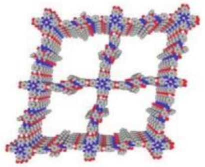

COF-S-SH[d]

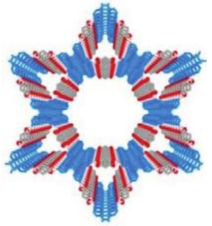

NiPc COF[e]

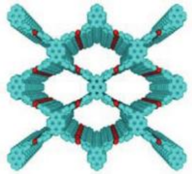

ZnPc-PPE COF[f]


[C_{60}]-ZnPc-COF[g]


MC-COF-NiPc-E_1E_7[h]

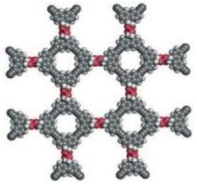

CuPc-FPBA-DETHz[i]

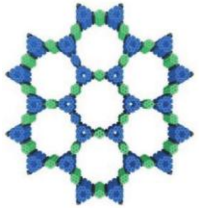

TPE-Ph COF[j]

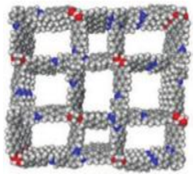

Py-Azine COF[k]

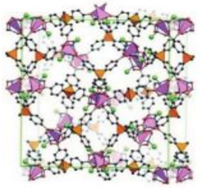

TTF-Py-COF[l]

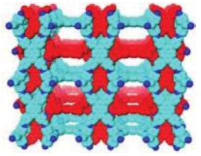

HBC-COF[m]


ICOF-2[n]


Star-COF-2[o]


CCOF-2[p]


COF-202[q]


3D-Py-COF[r]


COF-102[s]

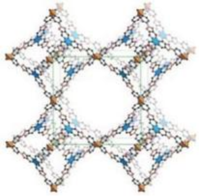

COF-108[t]

Table 2. Building blocks of boroxine-linked COFs. t.b.n: structure to be named.

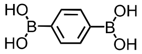
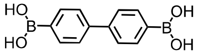
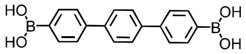
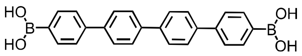
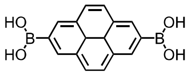
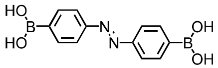
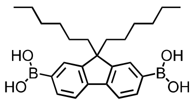
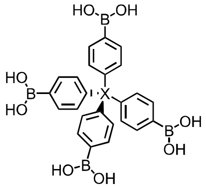
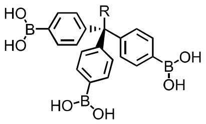
 BDBA/BDA/PBBA/BPBA COF-1[14,35–53] SCOF-1[54] SCOF-2[55]	 BPDA/BPBA SCOF-2[38,52] SCOF-1[55]	 t.b.n.[38]
 t.b.n.[38]	 PDBA PPy-COF[38,56] Pyrene-COF[57]	 ABBA/ABDA surface COF ABBA[58]
 DFBA SCOF-3[55]	 X = C: TBPM, X = Si: TBPS X = C COF-102[34,53,59–61] X = Si COF-103[34]	 R = Tolyl COF-102-tolyl[61] R = allyl COF-102-allyl[33,62] R = $-(CH_2)_{11}-CH_3$ COF-102-C_{12}[33] (all mixed with the tetraboronic acid TBPM)

Table 3. Linker molecule combinations of boronic acids with linear catechols.

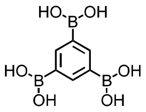
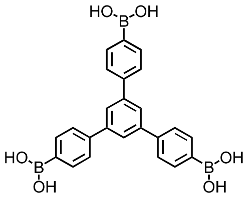
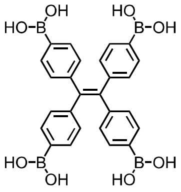
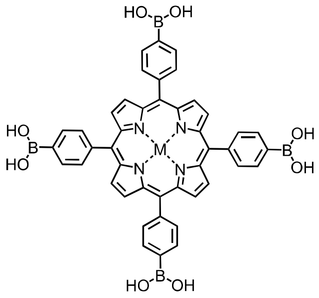
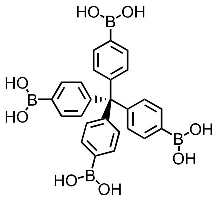
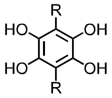
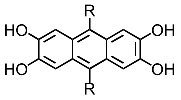
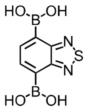
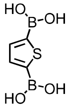
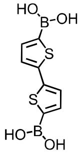
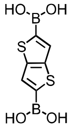
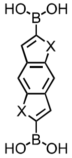
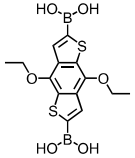
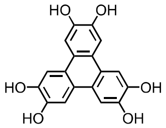
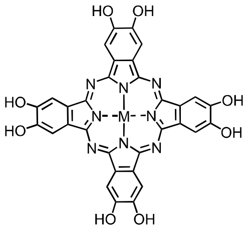
	 BTBA/TBA	 BTPB/BTPA	 TPEBA	 MP/TDHB-MP/TBPP	 TBPM
 R = H: THB	R = H COF-18Å[63–65] R = CH_3 COF-16Å[64,65] R = CH_2CH_3 COF-14Å[64,65] R = $CH_2CH_2CH_3$ COF-11Å[64,65]		R = H TPE-Ph COF[24]	R = H, M = H_2 H_2-COF[68] R = H, M = Zn ZnP-COF[68,69] R = H, M = Cu CuP-COF[68]	R = H MCOF-1[70]
 R = H: THAn R = CH_3: THDMA	R = H Ph-An-COF[67]	R = CH_3 BTP-COF[66]		M = H_2, R = H COF-66[71]	

Table 4. COFs with boronic ester linkage with heteroatoms in the backbone of the boronic acid. a.p.c.: the catechol linker was applied in the synthesis as acetonide protected catechol; BDBA: benzene-1,4-diboronic acid; BDT-OEt: (4,8-diethoxybenzo[1,2-b:4,5-b′]dithiophene-2,6-diyl)diboronic acid.

	 BTDADA	 H_4TDB	 H_4BTDB	 H_4TTDB/TTBA/ TTDA	 X = S: BDT/BDTBA/ H_2BDS/BDTDA X = Se: H_2BDSe X = Te: H_2BDTe	 BDT-OEt
 HHTP/TP	2D D-A COF[107]	T-COF-1[103] T-COF 2 (with additional boroxine formation)[103]	T-COF 3[103]	TT-COF[102,108] T-COF 4[103]	X = S BDT-COF[57,104,105,109] 1-S[106] X = Se 1-Se[106] X = Te 1-Te[106]	BDT-OEt COF (also mixed with BDT)[105]
 Pc/MPc/[OH]$_8$MPc/ MPc[OH]$_8$	M = Ni 2D-NiPc-BTDA COF[110]					

Reticular Chemistry

In order to afford an **extended crystalline solid**, **the formation of linkages should be reversible** and the reaction rates must be on a time scale that allows for **self-correction of defects**.
Thus, it is important to find the conditions under which reversible bond formation is possible without resorting to extreme temperatures or pressures.

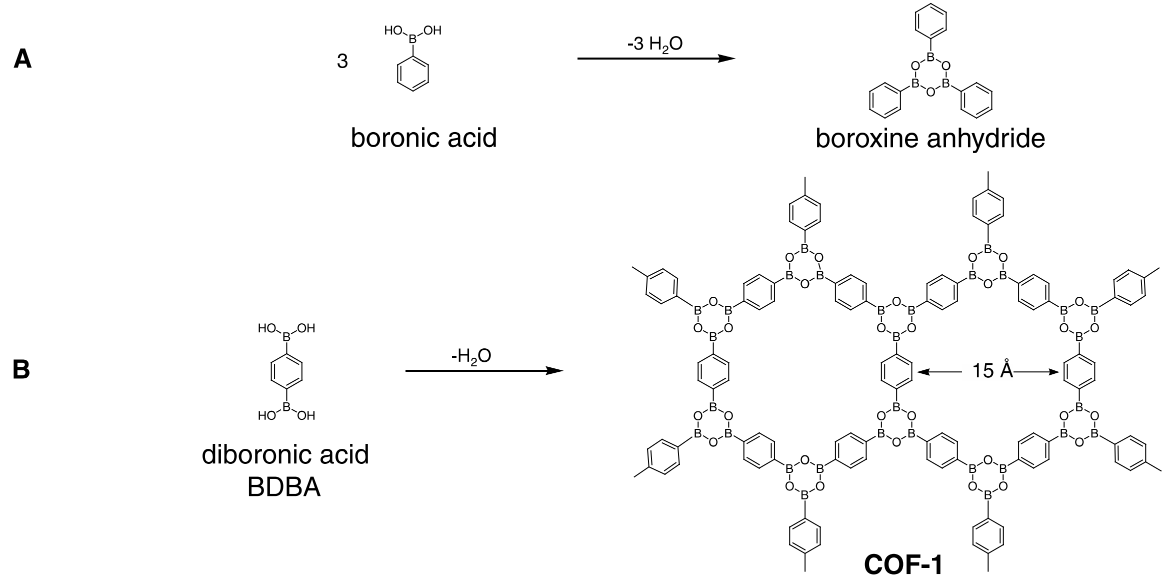


Fig. 1. (A to D) Condensation reactions of boronic acids used to produce discrete molecules and extended COFs.

1 : 1 v/v dioxane/mesitylene
To ensure the reversibility of framework formation, the reaction is carried out in a sealed Pyrex tube preventing the evaporation of water liberated in the condensation.