

Review

Triptycene Based 3D Covalent Organic Frameworks (COFs)—An Emerging Class of 3D Structures

Monika Borkowska¹ and Radosław Mrówczyński^{1,2,*} 

¹ Faculty of Chemistry, Adam Mickiewicz University in Poznań, Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland

² Centre for Advanced Technologies, Adam Mickiewicz University in Poznań, Uniwersytetu Poznańskiego 10, 61-614 Poznań, Poland

* Correspondence: radoslaw.mrowczynski@amu.edu.pl

Abstract: Covalent Organic Frameworks (COFs) are a newly emerged class of porous materials consisting of organic building blocks linked by strong covalent bonds. The physical and chemical properties of COFs, i.e., modularity, porosity, well-developed specific surface area, crystallinity, and chemical-thermal stability, make them a good application material, especially in the aspects of adsorption and gas separation. The organic compositions of their building blocks also render them with biocompatible properties; therefore, they also have potential in biomedical applications. Depending on the symmetry of the building blocks, COF materials form two-dimensional (2D COF) or three-dimensional (3D COF) crystal structures. 3D COF structures have a higher specific surface area, they are much lighter due to their low density, and they have a larger volume than 2D COF crystals, but, unlike the latter, 3D COF crystals are less frequently obtained and studied. Selecting and obtaining suitable building blocks to form a stable 3D COF crystal structure is challenging and therefore of interest to the chemical community. Triptycene, due to its 3D structure, is a versatile building block for the synthesis of 3D COFs. Polymeric materials containing triptycene fragments show good thermal stability parameters and have a very well-developed surface area. They often tend to be characterized by more than one type of porosity and exhibit impressive gas adsorption properties. The introduction of a triptycene backbone into the structure of 3D COFs is a relatively new procedure, the results of which only began to be published in 2020. Triptycene-based 3D COFs show interesting physicochemical properties, i.e., high physical stability and high specific surface area. In addition, they have variable porosities with different pore diameters, capable of adsorbing both gases and large biological molecules. These promising parameters, guaranteed by the addition of a triptycene backbone to the 3D structure of COFs, may create new opportunities for the application of such materials in many industrial and biomedical areas. This review aims to draw attention to the symmetry of the building blocks used for COF synthesis. In particular, we discussed triptycene as a building block for the synthesis of 3D COFs and we present the latest results in this area.

Keywords: 3D structures; COF; symmetrical structures; topology



Citation: Borkowska, M.; Mrówczyński, R. Triptycene Based 3D Covalent Organic Frameworks (COFs)—An Emerging Class of 3D Structures. *Symmetry* **2023**, *15*, 1803. <https://doi.org/10.3390/sym15091803>

Academic Editors: Maria Koyioni and László Hegedűs

Received: 14 July 2023

Revised: 12 September 2023

Accepted: 18 September 2023

Published: 21 September 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Covalent Organic Frameworks (COFs) are a new class of porous materials built from building blocks composed of light elements, i.e., C, H, N, and B. The name of this class of materials (Covalent Organic Frameworks) refers directly to the covalent bonds that link the building blocks of these structures together. Covalent bonds in COF synthesis are based on the Dynamic Covalent Chemistry (DCC) regulations. This means that the formation of the crystalline covalent structure of COFs occurs under thermodynamic control and depends only on the relative stabilities of the final products. The forming bonds are subjected to “error checking” and “self-healing processes”; they are being created and broken in reversible reactions between the building blocks until sufficiently strong

and thermodynamically stable bonds and crystal architectures are obtained under given conditions [1–3]. Examples of the covalent bonds most commonly used to synthesize COFs are shown in Table 1. The strong covalent bonds in Covalent Organic Frameworks provide them with high chemical stability; most COFs are insoluble in common organic solvents and are resistant to strong acids and bases [1,2,4].

Table 1. COF linkage types.

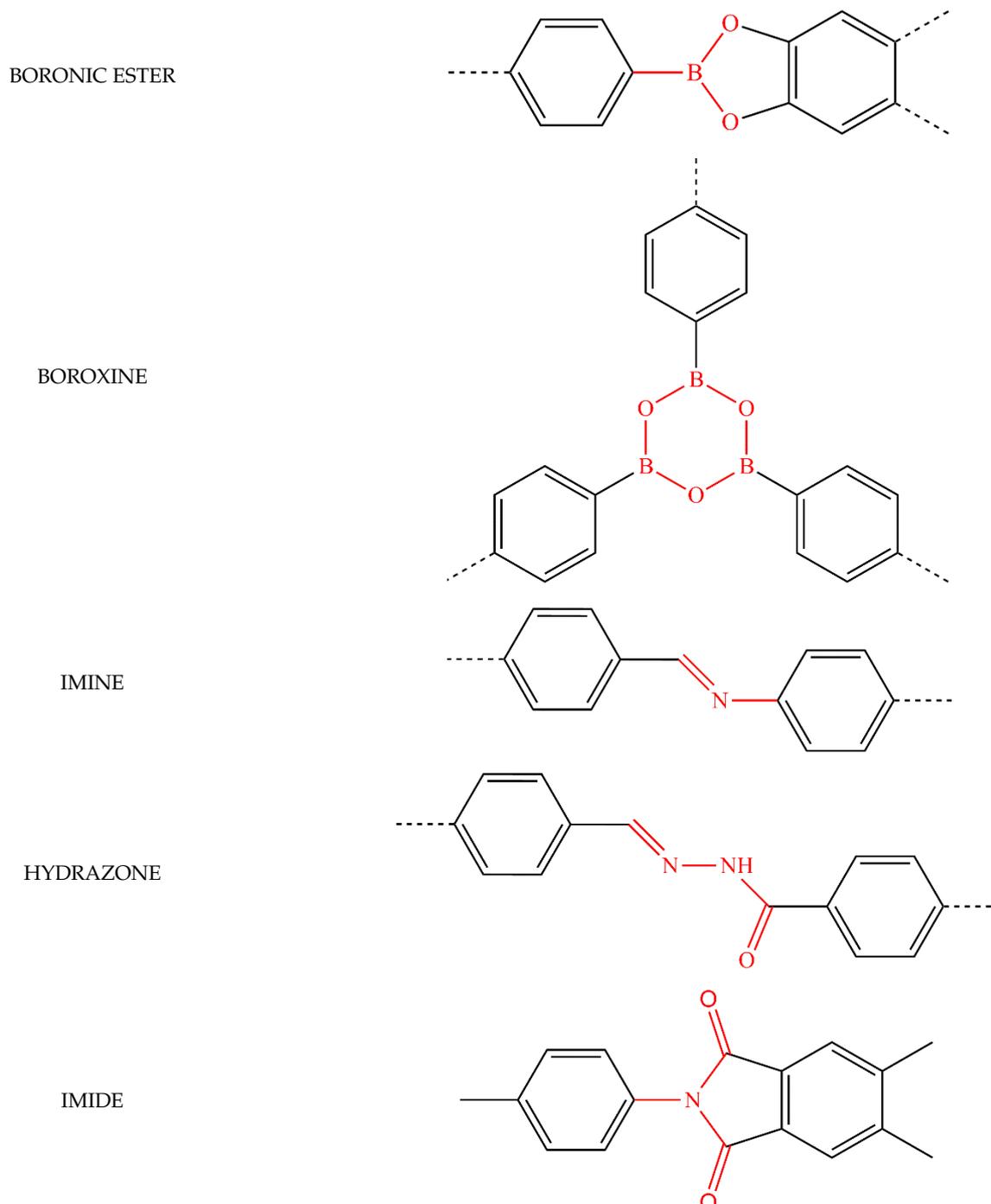
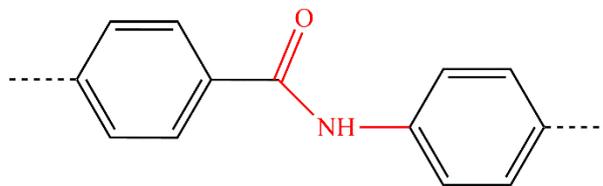
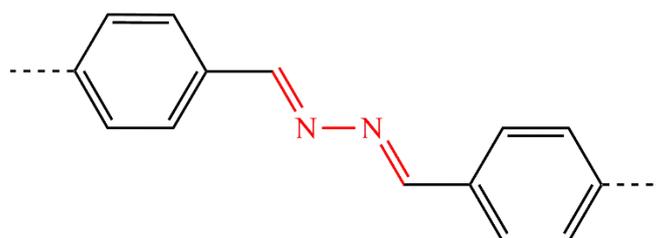
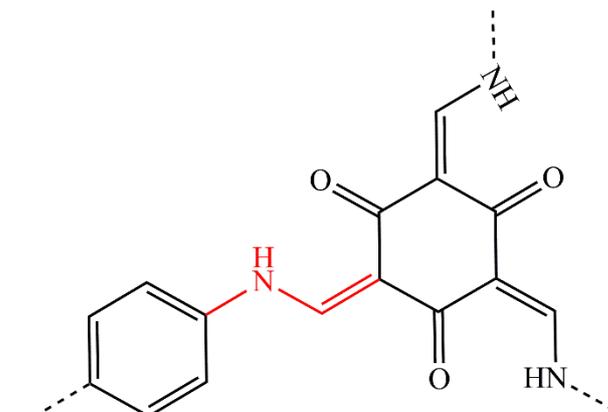
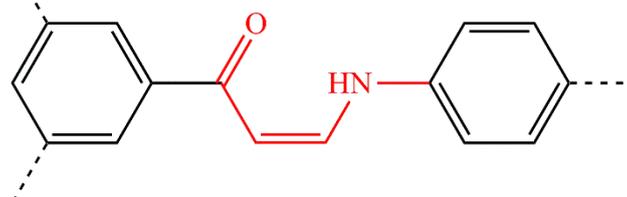


Table 1. Cont.

AMIDE



AZINE

 β -KETOENAMINE β -KETOENAMINE

BORAZINE

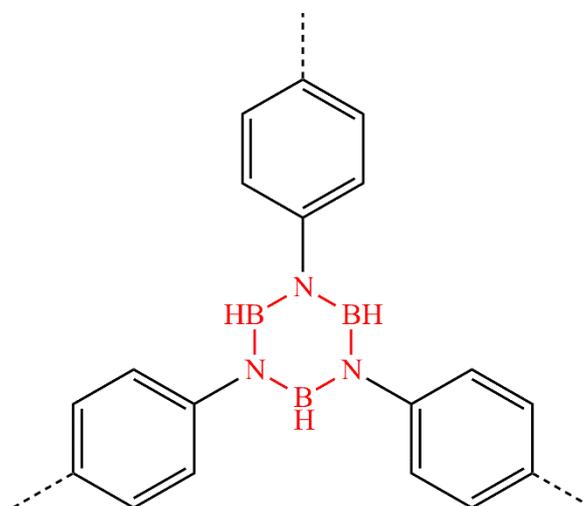
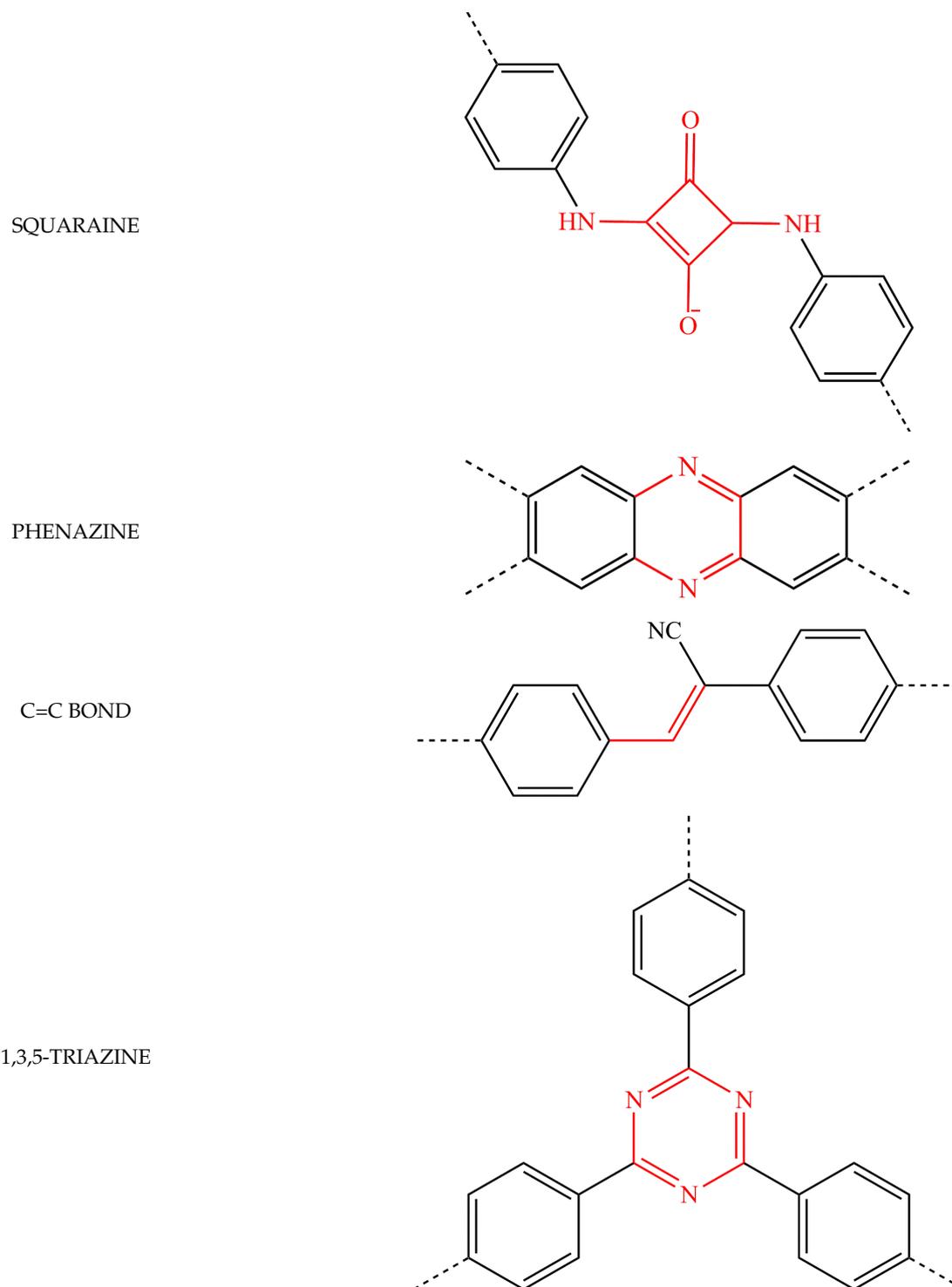


Table 1. Cont.



The construction and design of COF materials is based on the principles of reticular chemistry. The selected building blocks for COF synthesis should be geometrically and spatially compatible with each other to obtain a thermodynamically-stable crystal structure with an optimal shape and spatial dimensions [5]. Examples of two-dimensional (2D) and three-dimensional (3D) networks formed by COFs, as well as their symmetry, are shown in Figure 1. However, thanks to computational chemistry, the appropriate building blocks

for COF synthesis can be easily and more feasibly identified. Many recently discovered COF structures, especially 3D COFs, have been simulated and successfully synthesized with computational predictions, which include thermodynamical stability and even potential application destinations [6,7]. To design and predict new COF structures and their possible capacity for methane storage, Martin et al. [6] and Mercado et al. [8] used grand-canonical Monte Carlo simulations. Other options for designing COF structures include the materials–genomics–method–based QReaxAA (Quasi-Reactive Assembly Algorithms) for structure generation, which mimics the natural growth processes of COFs [9]. In order to categorize and catalogue already synthesized COFs, both 2D and 3D, as well as those simulated and ready to be synthesized, certain approaches have been made to make a proper database for these structures. Moreover, the currently developed libraries and the aforementioned database, which is still being developed, not only collect constructive information about the architecture of COFs, but also focus on their direct application. For example, Ongari et al. prepared a library consisting of CURATED COFs (CURATED = Clean, Uniform, and Refined with Automatic Tracking from Experimental Database) for characterizing and investigating their CO₂ adsorption properties [10]. The CoRe COF database, developed by M. Tong et al., was established based on the structure–property relationships of COFs and noble gases in order to investigate the COFs' abilities in their separation [11]. One of the most updated and newly published COF databases is ReDD-COFFEE (Ready-to-use and Diverse Database of Covalent Organic Frameworks with Force field based Energy Evaluation) [12]. This database has collected an enormous number of structures (268,687 COFs) with a high diversity in terms of geometric CH₄ storage properties.

Reticular synthesis makes it possible to obtain COFs in a modular manner, thus their final crystal construction is strictly dependent on the structure of the selected building blocks. This also means that the properties of their specific surface area and pore size can be directly influenced [1,13]. COFs are characterized by a very well-developed specific surface area and porosity, comparable to other classes of porous materials, such as MOFs and zeolites. Nonetheless, with the increasing incidence of cancer and the often-presented side effects of currently used cancer prophylaxes, together with the growing need for innovative therapy, COFs have also begun to emerge with applications in this area. COF building blocks are based on organic compounds with the rare use of heavy metals, allowing them to provide both biocompatible and non-toxic matrix material as a drug delivery vehicle [4]. In addition, the building blocks used to synthesize COFs are readily modifiable and functionalized, both before and after material synthesis, making the material itself adaptable to a wide range of applications. In addition, a significant part of the building blocks are cyclic aromatic compounds, which, due to their flat structure and the presence of p-electron conjugated systems, enrich the crystal structure with inductive interactions [2]. The unique properties of COFs make them mainly applicable in gas storage and selective separation [14,15], dye adsorption [16,17], and also as catalysts [18–20]. Such properties create potential applications of COFs for biomarkers, biosensors and photosensors [21–23].

3D COFs—Synthesis and Properties

COF-type materials, depending on the chosen building blocks, form crystal lattices in two ways: two-dimensional (2D), yielding 2D COFs, and three-dimensional (3D), yielding 3D COFs. A two-dimensional spatial network requires the use of planar building blocks, rich in conjugated p-electron systems. In a single 2D layer, the building blocks connect to each other through covalent bonds. The p-p electron interactions, produced by the conjugated p-electron systems of the building blocks, connect successive overlapping 2D layers, forming a 2D COF crystalline spatial network stabilized by two types of interactions. Through interlayer interactions, 1D modular channels are produced between the layers [24,25]. In order to synthesize three-dimensional crystal materials (3D COFs), one of two options for building block combination must be achieved. The first requires at least one non-planar building block (tetrahedral or triangular-pyramid shaped).

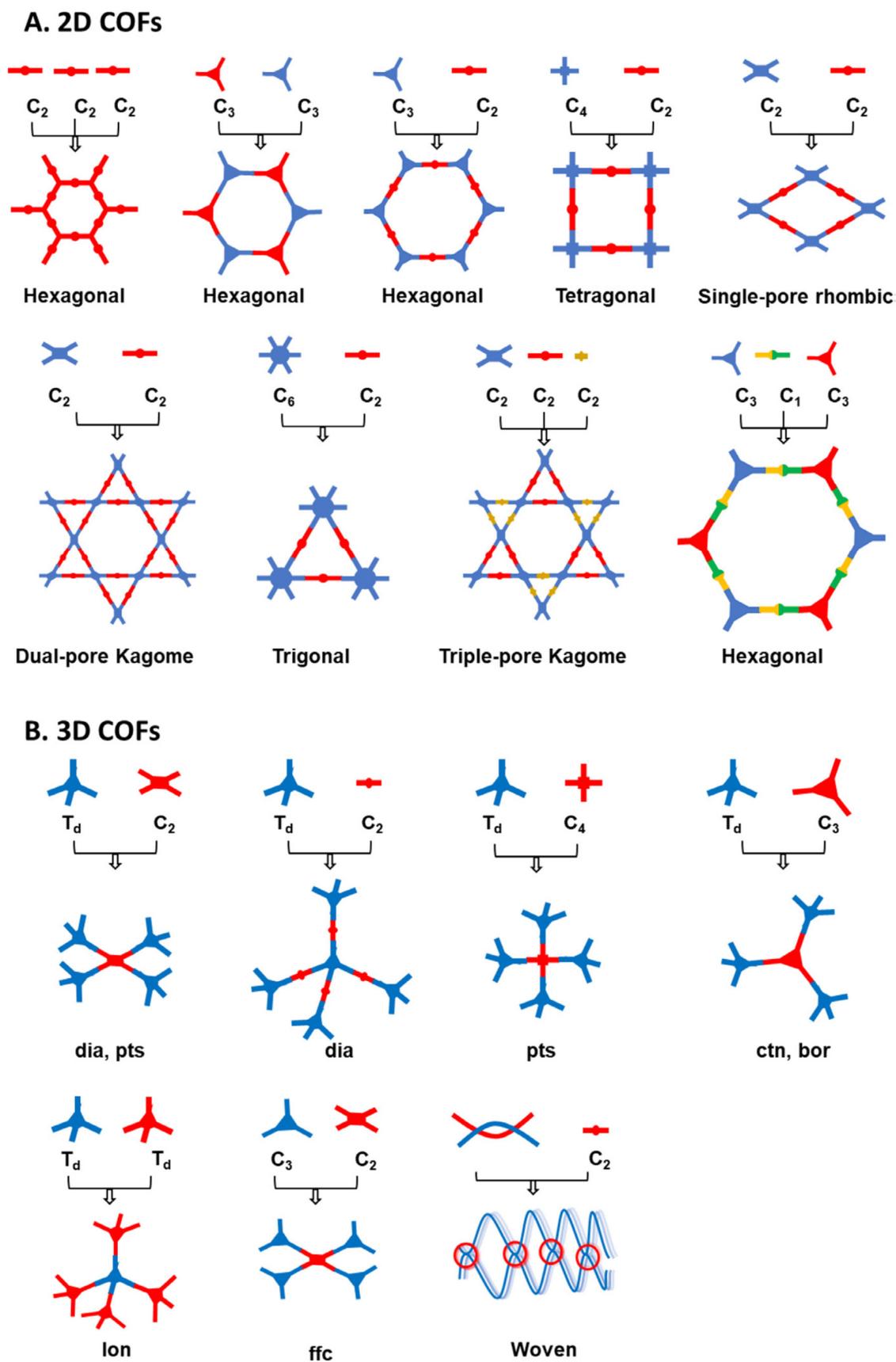


Figure 1. Topology diagram representing a general basis for design and construction of (A) 2D COFs and (B) 3D COFs [2].

The second option is similar to the synthesis of 3D MOF materials; the chosen combination of planar building blocks, e.g., 4-c and 3-c, must generate two types of vertices and one type of edge, resulting in three 3D structures [26–28]. However, 3D COF synthesis from planar building blocks is highly dependent on forming linkages of conformational flexibility, because under different conditions, 3D COF material or 2D COFs can be obtained from the same building blocks [26].

The interconnections that stabilize the significantly more developed crystal network of 3D COFs rely solely on covalent interactions [29]. 3D COFs appear to have a better-developed specific surface area than 2D COFs, due to their larger spatial dimension. The higher porosity of 3D COFs makes them more volumetric and lighter than 2D COFs, which should increase their application in areas such as gas storage and separation, or catalysis. However, it is 2D COFs that enjoy more widespread identification and are much more widely used, in contrast to 3D COFs. There are a number of reasons for this, the most important of which is the lack of readily available building blocks with the right structures to form a 3D network and the complex topology of the spatial network itself [24,25]. In addition, obtaining 3D COFs in an interpretable crystalline form is a significant problem. Most of the 3D COFs obtained are in amorphous form and have much lower stability due to the lack of additional p-p interactions that stabilize the crystal structure (as in the case of 2D COFs) [30]. As a result, since 2007, 3D COF materials have been obtained only in one-element topologies, i.e., dia [31], ctn, bor [32], pts [33], ffc [9], rra [34], srs [35], lon [36], stp [28], acs [37], tbo [27], bcu [38], and fjh [39]. Between 2020 and 2021, five new topologies for 3D COF materials were documented. Li et al. [40] obtained a 3D COF (3D-hea-COF) material exhibiting a hea-type topology through a reaction between the precursor [2,3,6,7,14,15-hexakis(4-formylphenyl)] triptycene (HFPTP) and [tetrakis(4-amino biphenyl)methane (TABPM)]. X. Xu et al. performed a reaction between 5,10,15,20-tetra(4-aminophenyl)porphyrin (TAPP) and hexa(4-formylphenyl) benzene (HFPB), resulting in a porphyrin-based 3D COF (TAPP-HFPB-COF) with an she-type topology [41]. A paper by Xie et al. was also published, in which they obtained two highly crystalline 3D COF-type materials (3D-TPB-COF-OMe and 3D-TPB-COF-Ph) from their sterically controlled synthesis, designed using electron diffraction techniques. The latter, 3D-TPB-COF-Ph, exhibited an ljh-type topology not previously documented in the ToposPro database [42]. Wang et al., through a stratigraphic strategy, obtained a 3D COF (SPB-COF-DBA), constructed from flat square units of cobalt (II) phthalocyanate (PcCo), which also exhibited an nbo-type topology that was not yet documented [43]. The first 3D COF-type material based on anionic titanium (Ti-COF-1) was also obtained [44]. A highly crystalline material with remarkable stability, Ti-COF-1 was obtained from octahedral Ti (IV) complex units and exhibited an soc-type topology. However, despite promising results and simulation calculations, new topologies of three-dimensional covalent organic structures still remain a synthetic challenge to realize, despite obtaining and designing them.

2. Triptycene in Polymeric Materials

Triptycene is an aromatic hydrocarbon, belonging to the triptycene group. It consists of three aromatic rings condensed into a [2,2,2] bicyclooctatriene grouping resembling a paddle wheel (Figure 2). Due to this unique form, the triptycene molecule exhibits considerable rigidity and provides a good base for the synthesis of polymers.

The presence of triptycene in the structure of polymeric materials increases their thermal strength. Triptycene polymers begin to degrade mostly at about 400 °C and retain more than 50% of their weight even at 800 °C. R. Bera et al., obtained nanoporous azopolymers (NAPs) whose thermal degradation occurs between 528–531 °C. Moreover, at 800 °C, the char yield of these polymers was greater than 67%. The authors justify the thermal stability of NAPs with the presence of triptycene fragments in the structure of azopolymers. [45] Nanoporous networks based on triptycene and amine bonds obtained by A. Alam et al. (TBOSBLs), showed similar charring efficiency to NAPs at 800 °C (<50%), which the authors also justify with the presence of triptycene units in the polymer structure [46].

Triptycene-based microporous polymers (TMPs) degraded at a lower temperature range, 397–460 °C, but their carbon yield at 800 °C was in the 56–68% range. In the results of measuring the thermal stability of TMPs, the authors explain both the triptycene molecules embedded in the structure of the polymers and their crosslinking [47]. On the other hand, T_COPs (covalent-organic polymers based on hydroxy-functionalized triptycene) had the highest thermal stability compared to the previously mentioned triptycene-based polymeric materials—thermal degradation occurred only at 600 °C, retaining a carbon yield of more than 60% up to that point [48]. In all of the aforementioned examples of triptycene-based polymeric materials, they were found to be mainly in amorphous form, although there are reports of such materials in graphite-like form [49,50]. Polyphenylene networks containing triptycene units (TPPs), obtained by S. Shetty et al., exhibited very high thermal stability, as they began to degrade in the 558–604 °C range, losing only 10% of their weight [49]. Polymeric materials based on triptycene are characterized by a high specific surface area. The presence of triptycene fragments contributes to the formation of meso- and micro-pores in the spatial network of the polymer molecule, as triptycene units are characterized by the phenomenon of so-called “internal molecular free volume” (IMFV) [51,52]. This means that in addition to the spaces formed initially between the joined building blocks of the polymer, the triptycene fragments present in the structure provide additional volume due to their three-dimensional structure. A summary of the specific surface area values along with the maximum pore volume of some polymeric materials containing triptycene is shown in Table 2. The large specific surface areas as well as the presence of more than one type of porosity in them, give triptyc polymer materials very good adsorption properties. Hence, many of these types of materials perform well in gas storage (especially for CO₂, H₂, and CH₄) [45,46,49,53], selective gas separation, as well as in the adsorption of dyes [50]. A. Hassan et al. show that polymeric triptycene materials (T_COPs) can also be used to absorb radioactive iodine from the environment [48].

Table 2. Properties of triptycene based materials.

Polymer	S _{ABET} (m ² g ⁻¹)	S _{ALANG} (m ² g ⁻¹)	V _{total} (cm ³ g ⁻¹)	Reference
NAP 1	1095	1622	1.060	[45]
NAP 2	923	1353	0.690	
TMP1	923	1211	0.490	[47]
TMP2	1094	1457	0.700	
TMP3	1372	1817	0.860	
TAP1	474	736	0.740	[53]
TAP2	772	1173	1.410	
TAP3	729	1093	1.040	
TBPAL1	775	1036	0.401	[54]
TBPAL2	729	945	0.369	
TBPAL3	602	942	0.446	
TBPAL4	620	1027	0.529	
TBPAL5	815	1411	0.760	
T_COP-1	206		0.218	[48]
T_COP-2	259	-	0.320	
T_COP-3	826		0.533	
TPP1	380		0.250	[49]
TPP2	468	-	0.290	
TPP3	240		0.250	
STP-2	541	736	0.320	[55]
STP-3	378	515	0.340	
TBOSBL1	649	1051	0.527	
TBOSBL2	570	810	0.384	[46]
TBOSBL3	493	817	0.467	

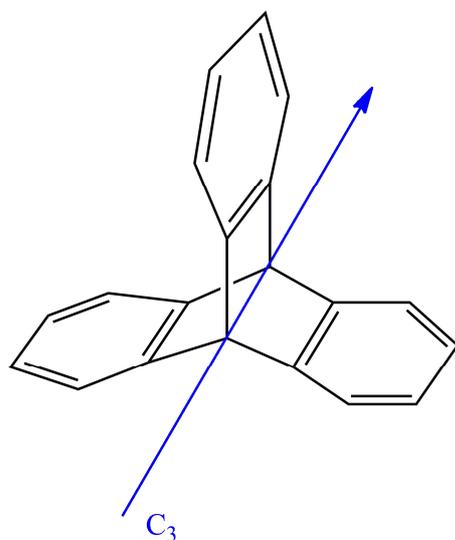


Figure 2. Triptycene structure with the three-fold symmetry axis.

Triptycene in 3D COFs

The addition of triptycene fragments makes it possible to improve the stability and strength parameters of polymeric materials. However, despite the reported use of triptycene for the synthesis of polymeric materials, there are not many reports on the use of triptycene for analogous purposes in the synthesis of COFs. The reason for this phenomenon is most likely due to the fact that the class of porous COF-type materials was established relatively recently (2005) [56] and is only beginning to develop. Moreover, of the COF structures obtained so far, 2D structures predominate, while 3D COF structures are more difficult to obtain. Based on publications on the addition of triptycene fragments to polymeric materials, it can be expected that the introduction of these fragments into crystalline structures increases the crystallinity of COF materials, enriches the specific surface area with additional internal volume (IMFV), and the incorporation of a rigid triptycene backbone guarantees the stability and resistance of the system to thermal and chemical effects. Between 2020 and 2021, five articles were published in which the authors describe the synthesis of 3D COFs based on triptycene. All of the published syntheses are based on the same starting reagent: (six-connected) [2,3,6,7,14,15-hexakis(4-formylphenyl)Triptycene] (HFPTP), whose spatial structure resembles a triangular prism. In 2020, H. Liu et al. published the reaction between HFPTP and synergistic 4-connected 2D D_{2h} monomer 1,3,6,8-tetrakis(4-aminophenyl)pyrene (TAPPy) which resulted in the first 3D COF material based on triptycene with stp topology, JUC-564 (Figure 3) [57]. It is the only example of such a material to date.

The material was characterized by high thermal stability (TGA: ~ 450 °C), very well-developed specific surface area, and low density (0.108 g/cm³); BET analysis results confirmed a surface area of 3383 m²/g, and N₂ adsorption measurements showed the presence of two types of porosity, with pore diameters of 15 Å and 41 – 43 Å. In the case of the second value, it is the largest obtained so far for 3D COF-type materials (in comparison, the previously largest values for 3D COFs were 15.4 Å for JUC-518 [58] and 28 Å for DBA-3DCOF [29]). A material with such large pores provides an opportunity for the development of 3D COF structures and increases the potential applicability in biomedicine, among other fields, as the authors also found that large biologically active molecules, such as proteins, can be adsorbed in the pores of the materials [57]. In 2021, four more publications were published on newly-obtained triptycene-based 3D COF structures.

H. Liu et al. obtained two new 3D COF materials by reacting HFPTP sequentially with 6- and 1,3,5-tris(4-aminophenyl)triazine (TAPT) JUC-568 with a ceq topology (Figure 3) connected 2,3,6,7,14,15-hexa(3',5'-diisopropyl-4'-amino) Triptycene (HDIATP) JUC-569 with an acs topology (Figure 4) [28]. JUC-569 exhibited good thermal stability (TGA: ~ 400 °C).

BET analysis and measurement of N_2 adsorption showed that the specific surface area was equal to $1254 \text{ m}^2/\text{g}$ and was mainly rich in micropores with a diameter of about 13 \AA (1.27 nm). JUC-568 was obtained in an analogous manner to the material published in the same year by Z. Liu et al. [3D-ceq-COF] [59], which showed similar structural parameters and a ceq topology (Figure 5).

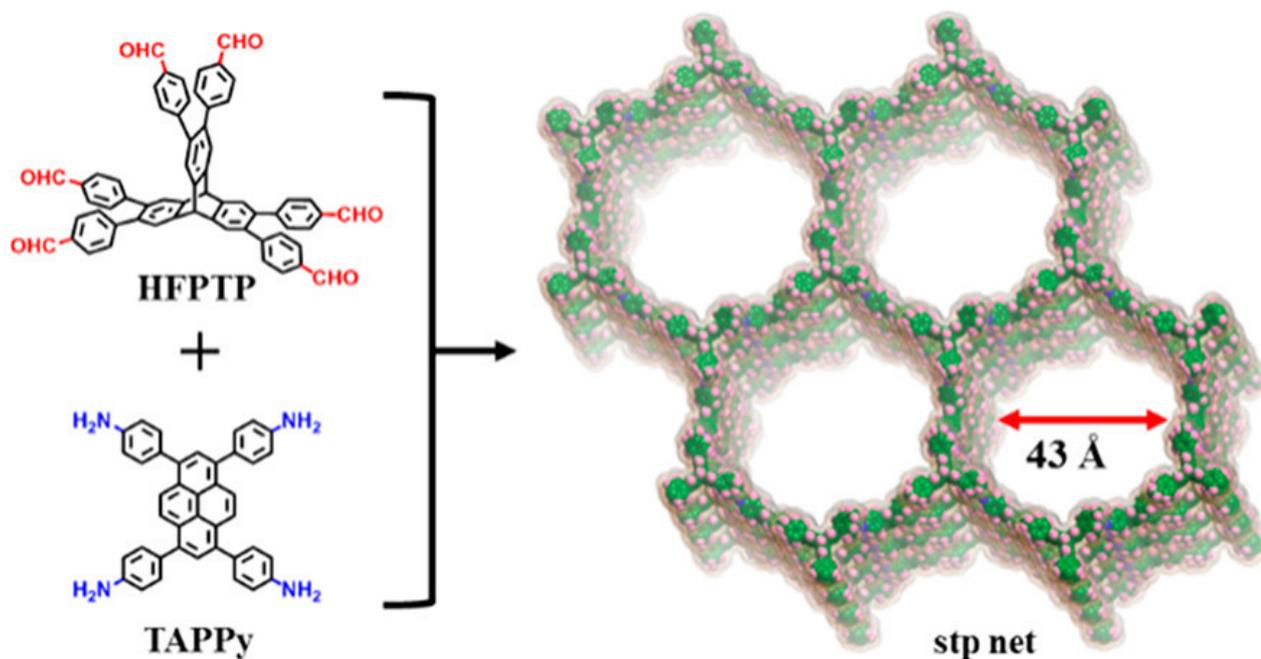
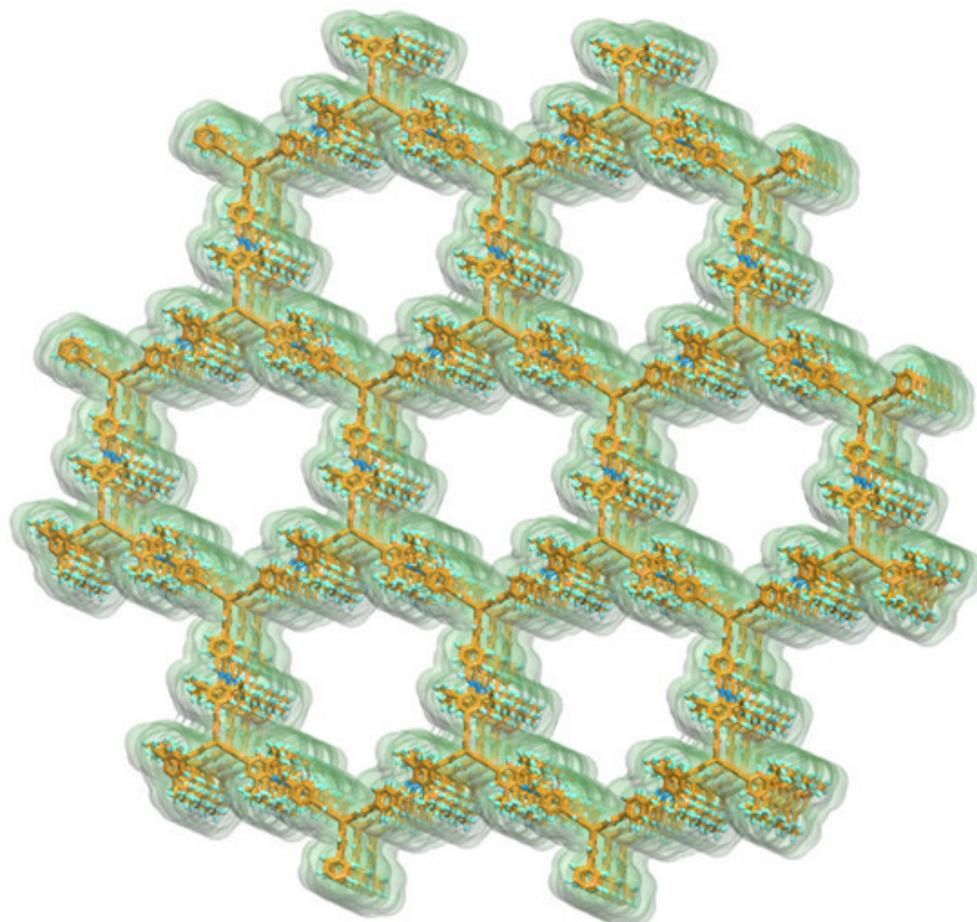


Figure 3. The new COF (termed JUC-564) has a high specific surface area (up to $3300 \text{ m}^2\text{g}^{-1}$), the largest pore size among 3D COFs (43 \AA), and record-breaking low density among crystalline materials reported to date (0.108 gcm^{-3}) [56].

The material had a higher thermal stability than JUC-568 (TGA $\sim 550 \text{ }^\circ\text{C}$). Its specific surface area was equal to $1148.6 \text{ m}^2/\text{g}$, and it was also rich in micropores with diameters between $10\text{--}16 \text{ \AA}$. The obtained 3D COF materials [28,59] were investigated for adsorption of gases such as CO_2 , CH_4 , and H_2 (see Table 3). The adsorption levels of both 3D-ceq-COF and its analogue JUC-568 for CO_2 and CH_4 at two different temperatures (273 and 298 K) proved to be extremely high, especially for H_2 adsorption (JUC-568— $274 \text{ cm}^3/\text{g}$ at 77 K , 3D-ceq-COF— $178.49 \text{ cm}^3/\text{g}$ at 77 K and $131.27 \text{ cm}^3/\text{g}$ at 87 K), which is significantly higher than for other materials of this type such as PPN-3 (1.58 wt\%) [60], PAF-1 (1.66 wt\%) [61], SPT-CMP1 (1.72 wt\%) [62], and DL-COF-1 (2.09 wt\%) [63]. The adsorption values of CO_2 , CH_4 , and H_2 also compare favorably to the results obtained for JUC-569: CO_2 ($98 \text{ cm}^3/\text{g}$ at 273 K and $81 \text{ cm}^3/\text{g}$ at 298 K); CH_4 ($48 \text{ cm}^3/\text{g}$ at 273 K and $32 \text{ cm}^3/\text{g}$ at 298 K); and H_2 ($274 \text{ cm}^3/\text{g}$ at 77 K). In the same year, the team of Z. Li et al. published another new structure in addition to 3D-ceq-COF. The 3D-hea-COF material was obtained using a reaction between HFPTP and [tetrakis(4-amino-biphenyl)methane] (TABPM) and had an hea topology not yet reported for 3D COF materials (Figure 5) [40].

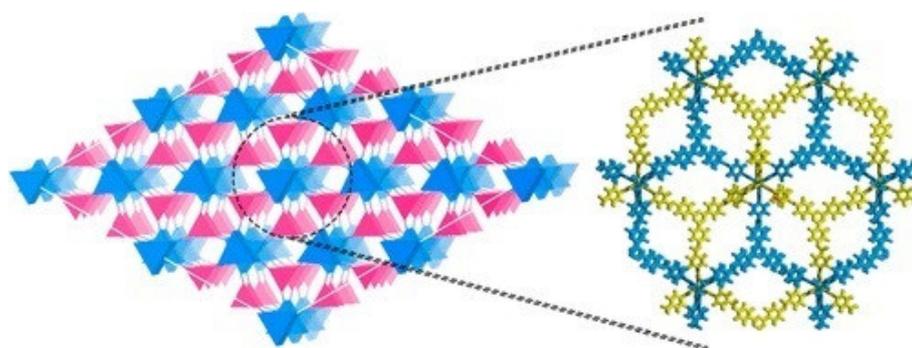
Like the previously described structures, 3D-hea-COF exhibited good thermal stability properties (TGA: $\sim 480 \text{ }^\circ\text{C}$) as well as specific surface area (BET: $1804.0 \text{ m}^2/\text{g}$). Its surface area, like that of JUC-568-569 and 3D-ceq-COF, was mainly rich in micropores with a diameter of about 16 \AA . The paper mentions that 3D-hea-COF was tested mainly for H_2 adsorption. The 3D COF material shows good hydrogen adsorption ($193.48 \text{ cm}^3/\text{g}$ at 77 K and $131.03 \text{ cm}^3/\text{g}$ at 87 K), which is comparable to the results obtained with PAF-1 ($186 \text{ cm}^3 \text{ g}^{-1}$) [61], Trip-PIM ($185 \text{ cm}^3 \text{ g}^{-1}$) [64], and SPT-CMP1 ($193 \text{ cm}^3 \text{ g}^{-1}$) [62]. According to the authors, such a high adsorption value is due to the presence of triptycene fragments and aromatic systems in the 3D-hea-COF structure, which, by forming an internal microstructure in the material, cause greater gas adsorption [40]. The use of triptycene,

as a building block that provides a stable framework for the crystal structure, was also presented in an article published in 2021 by Y. Wang et al. Two different 3D COF materials were obtained using an imine condensation reaction [6 + 4]: Trip-COF-1 and Trip-COF-2 with stp topologies [65]. Both materials had good crystalline properties, with each forming a structure that resembled a honeycomb (Figures 6 and 7).



acs net

Figure 4. A 3D triptycene-based COF, JUC-569, with an acs topology [27].



ceq net

Figure 5. A 3D-COF with a ceq topology utilizing a D_3h -symmetric triangular prism vertex with a planar triangular linker [58].

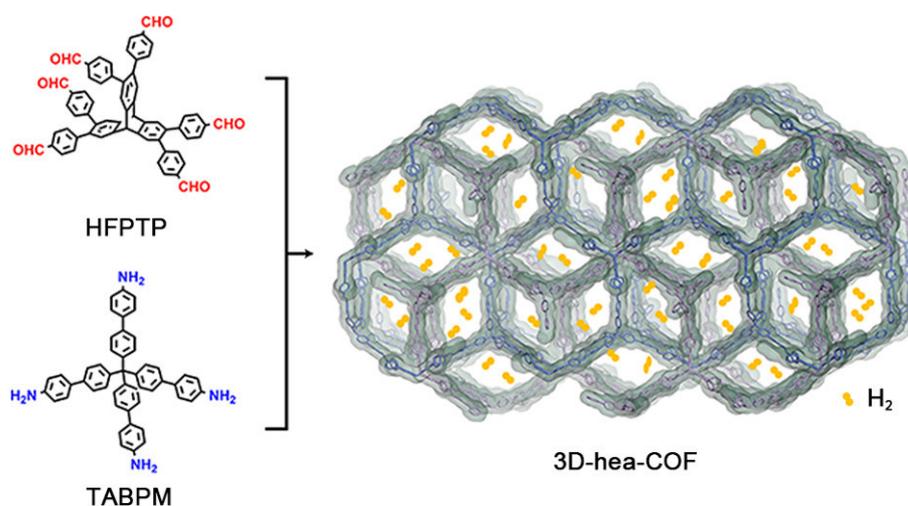


Figure 6. A 3D COF with an hea topology [39].

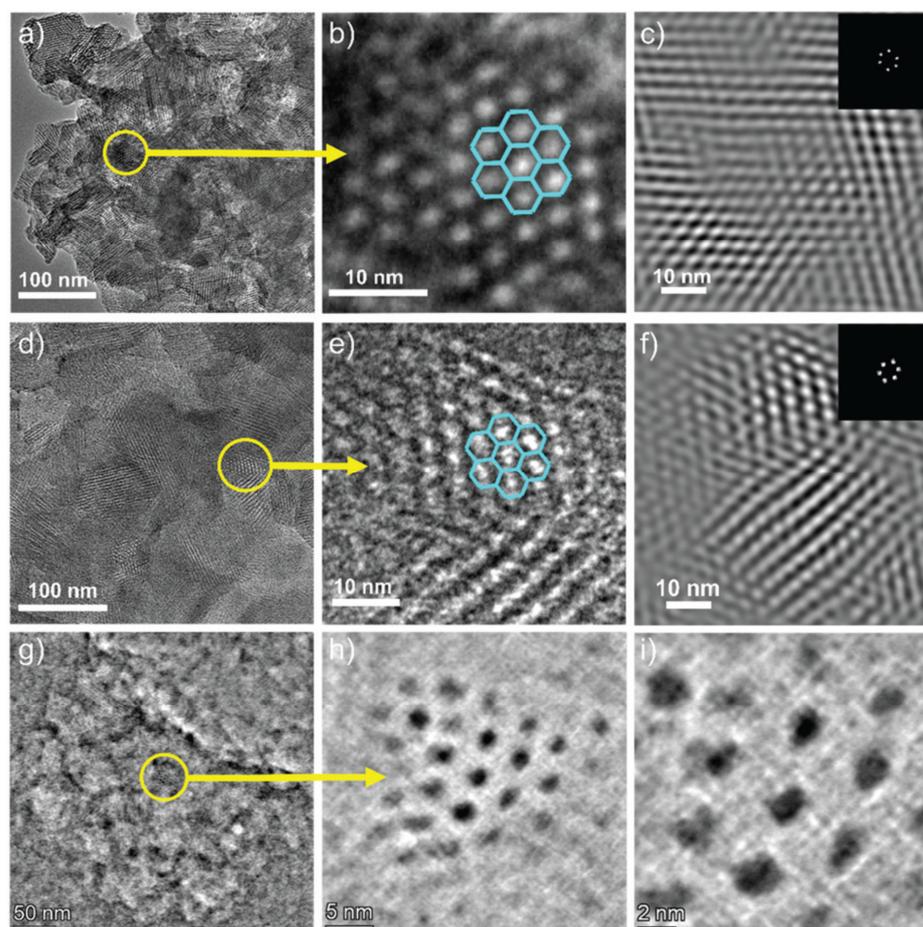


Figure 7. (a) TEM image of Trip-COF 1; (b) TEM image of Trip-COF 1 giving an enlarged view of the selected area in panel (a); (c) Fourier-filtered image of selected areas of Trip-COF 1; inset: fast Fourier transform (FFT) from the selected areas; for Trip-COF 2 see (d–f), respectively; (g) iDPC image of Trip-COF 1; (h,i) enlarged views of a selected area in panel (g) [65].

The surface areas for Trip-COF-1 and Trip-COF-2 were determined by measuring the adsorption of gaseous N₂, obtaining values of 1474 m²/g and 1624 m²/g, respectively. For Trip-COF-1, BET analysis showed the presence of three types of porosity: micro-, meso- and macro-porosity. The pore values occurred in the ranges of about 13 Å, 30 Å, and 40 Å.

Trip-COF-2 had two types of porosity, with pore diameters of about 13 Å and 29 Å. The authors explain the differences in the BET analysis as due to the presence of the 2-fold interpenetrating structure in Trip-COF-1, which causes the phenomenon of interpenetration and, consequently, greater variation in porosity. This structural feature is missing in Trip-COF-2, resulting in the structure forming only two types of porosity [65]. In this way, the authors show how, by handling the size and interpenetration of each reactant and reaction conditions, the structural properties of 3D COF materials can be influenced, which can contribute to a better understanding of their complexity. In addition, materials in which it is possible to design and control the formation of pores of a specific size represent a good application potential in the catalysis, separation and adsorption of large molecules. The authors also believe that the unusual honeycomb structure of Trip-COFs can be used for optoelectronic applications, due to the delocalization of p-electrons along the wall of 1D nanowires [65].

Table 3. Triptycene based 3D COF properties.

Name	Topology	TGA (°C)	S _{BET} (M ⁻¹ g ⁻¹)	Pore Size Distribution (Å)	CO ₂ Uptake (cm ³ g ⁻¹)	CH ₄ Uptake (cm ³ g ⁻¹)	H ₂ Uptake (cm ³ g ⁻¹)	Reference
Trip-COF 1 Trip-COF 2	stp	-	1473.00 1624.00	12.6, 29.6, 39.9 12.6, 29.3	-	-	-	[65]
JUC-568 JUC-569	ceq/acs	~520 ~400	1433.00 1254.00	~19.2 ~18.7	98.00 (273 K), 81.00 (298 K) 47.00 (273 K), 31.00 (298 K)	48.00 (273 K), 32.00 (298 K) 19.00 (273 K), 11.00 (298 K)	274.00 (77 K) 167.00 (77 K)	[28]
3D-ceq-COF	ceq	~550	1148.6	10, 16	91.27 (273 K), 330.33 (298 K)	36.28 (273 K), 23.22 (298 K)	178.49 (77 K), 131.27 (98 K)	[59]
3D-hea-COF JUC-564	hea stp		1804.00 3383.00	16 15, 43	80.01 (273 K)	21.77 (273 K)	193.48 (77 K)	[40] [57]

3. Future Perspectives

3D COF materials, in which it is possible to design and control pore formation to a specific size, represent a good application potential in the catalysis, separation, and adsorption of large molecules. The promising results of these structures in gas adsorption measurements demonstrate the possible potential of using triptycene-based 3D COF materials for environmental action in the adsorption of heating gases from the atmosphere [40,59] as well as in the development of work on the acquisition and storage of hydrogen-based renewable fuels [40]. In addition, obtained 3D COFs in the form of unusual structures, such as the honeycomb structure of Trip-COFs, can be used for optoelectronic applications due to the delocalization of p-electrons along the wall of 1D nanochannels [65]. Therefore, the field of 3D triptycene based COFs is an unexplored area and requires further studies in terms of controlled synthesis of such structures. An important issue that has not arisen in the literature is the toxicity of triptycene based COFs, which is of high importance in the case of their application in the medical, biological, and environmental fields. These studies are crucial to understand the biological and environmental fates of these 3D structures and their impacts on living organisms. In particular, the medical applications of triptycene-based structures seem to be underappreciated and almost unexplored, but these materials might be used as platforms for a drug delivery system with a high loading capacity, biocompatibility and straightforward surface functionalization.

4. Conclusions

Covalent Organic Frameworks are a new class of crystalline porous materials showing great application potential due to their physicochemical properties. Due to their high specific surface areas, porosities, crystallinities, chemical-thermal stabilities, and biocompatible morphologies, COFs find applications not only in industrial areas, but also in biomedical areas. 3D COFs are characterized by better physical parameters than 2D-COFs, but are less frequently used, due to the difficulty of synthesizing them and finding suitable building blocks for their construction.

The triptycene skeleton addition to 3D COF structures enhances their chemical and physical properties. The rigid, three-paddle-wheel triptycene form provides 3D COFs with architectural stability, extra volume (IMFV), and lower density, which results in high thermal stability (up to 500 °C) and good adsorption of gases such as CO₂, H₂, and CH₄. In addition, some of them have a specific surface area rich in pores of more than one type, with some macro-scale CFOs able to adsorb not only gases but also large biomolecules the size of proteins (JUC-564). Moreover, the addition of the triptycene building block not only enriches the library of 3D COF building blocks, but also extends new application possibilities for these materials. The impressive adsorption properties of gases, including heating gases such as CO₂ and CH₄, allow these types of materials to be used in environmental rescue applications. The presence of pores with a diameter of more than 41 Å, capable of adsorbing large molecules, makes 3D COF materials a good alternative in the design of nanocarriers with therapeutic applications. In order to develop triptycene 3D COFs and explore their great application potential, further investigations and analyses are required. Moreover, the development of COF databases and their theoretical tailoring seems to be an area of high interest and importance for the development of 3D COFs and 3D COFs based on triptycene.

Author Contributions: Conceptualization, R.M. and M.B.; writing—original draft preparation, M.B. and R.M.; writing—review and editing, M.B. and R.M.; supervision, R.M.; project administration, R.M.; funding acquisition, R.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Sciences Centre, grant number UMO-2018/31/B/ST8/02460.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Zhao, F.; Liu, H.; Mathe, S.; Dong, A.; Zhang, J. Covalent Organic Frameworks: From Materials Design to Biomedical Application. *Nanomaterials* **2017**, *8*, 15. [[CrossRef](#)]
2. Abuzeid, R.; EL-Mahdy, A.F.M.; Kuo, S.-W. Covalent organic frameworks: Design principles, synthetic strategies, and diverse applications. *Giant* **2021**, *6*, 100054. [[CrossRef](#)]
3. Deng, L.; Zhang, J.; Gao, Y. "Synthesis, Properties, and Their Potential Application of Covalent Organic Frameworks (COFs)", *Mesoporous Materials—Properties and Applications*; IntechOpen: London, UK, 2018. [[CrossRef](#)]
4. Guan, Q.; Zhou, L.; Li, W.; Li, Y.; Dong, Y. Covalent Organic Frameworks (COFs) for Cancer Therapeutics. *Chem. A Eur. J.* **2020**, *26*, 5583–5591. [[CrossRef](#)] [[PubMed](#)]
5. Yaghi, O.M. Reticular Chemistry—Construction, Properties, and Precision Reactions of Frameworks. *J. Am. Chem. Soc.* **2016**, *138*, 15507–15509. [[CrossRef](#)] [[PubMed](#)]
6. Mercado, R.; Fu, R.-S.; Yakutovich, A.V.; Talirz, L.; Haranczyk, M.; Smit, B. In Silico Design of 2D and 3D Covalent Organic Frameworks for Methane Storage Applications. *Chem. Mater.* **2018**, *30*, 5069–5086. [[CrossRef](#)]
7. Martin, R.L.; Simon, C.M.; Medasani, B.; Britt, D.K.; Smit, B.; Haranczyk, M. In Silico Design of Three-Dimensional Porous Covalent Organic Frameworks via Known Synthesis Routes and Commercially Available Species. *J. Phys. Chem. C* **2014**, *118*, 23790–23802. [[CrossRef](#)]
8. Martin, R.L.; Simon, C.M.; Smit, B.; Haranczyk, M. In silico Design of Porous Polymer Networks: High-Throughput Screening for Methane Storage Materials. *J. Am. Chem. Soc.* **2014**, *136*, 5006–5022. [[CrossRef](#)]
9. Lan, Y.; Han, X.; Tong, M.; Huang, H.; Yang, Q.; Liu, D.; Zhao, X.; Zhong, C. Materials genomics methods for high-throughput construction of COFs and targeted synthesis. *Nat. Commun.* **2018**, *9*, 5274. [[CrossRef](#)]
10. Ongari, D.; Yakutovich, A.V.; Talirz, L.; Smit, B. Building a Consistent and Reproducible Database for Adsorption Evaluation in Covalent–Organic Frameworks. *ACS Cent. Sci.* **2019**, *5*, 1663–1675. [[CrossRef](#)]
11. Tong, M.; Lan, Y.; Yang, Q.; Zhong, C. Exploring the structure-property relationships of covalent organic frameworks for noble gas separations. *Chem. Eng. Sci.* **2017**, *168*, 456–464. [[CrossRef](#)]
12. De Vos, J.S.; Borgmans, S.; Van Der Voort, P.; Rogge, S.M.J.; Van Speybroeck, V. ReDD-COFFEE: A ready-to-use database of covalent organic framework structures and accurate force fields to enable high-throughput screenings. *J. Mater. Chem. A Mater.* **2023**, *11*, 7468–7487. [[CrossRef](#)]
13. Wu, M.-X.; Yang, Y.-W. Applications of covalent organic frameworks (COFs): From gas storage and separation to drug delivery. *Chin. Chem. Lett.* **2017**, *28*, 1135–1143. [[CrossRef](#)]

14. Ma, H.; Chen, J.J.; Tan, L.; Bu, J.H.; Zhu, Y.; Tan, B.; Zhang, C. Nitrogen-Rich Triptycene-Based Porous Polymer for Gas Storage and Iodine Enrichment. *ACS Macro Lett.* **2016**, *5*, 1039–1043. [[CrossRef](#)]
15. Wang, C.; Wang, Y.; Ge, R.; Song, X.; Xing, X.; Jiang, Q.; Lu, H.; Hao, C.; Guo, X.; Gao, Y.; et al. A 3D Covalent Organic Framework with Exceptionally High Iodine Capture Capability. *Chem. A Eur. J.* **2018**, *24*, 585–589. [[CrossRef](#)] [[PubMed](#)]
16. Konavrapu, S.K.; Biradha, K. Luminescent Triazene-Based Covalent Organic Frameworks Functionalized with Imine and Azine: N₂ and H₂ Sorption and Efficient Removal of Organic Dye Pollutants. *Cryst. Growth Des.* **2019**, *19*, 362–368. [[CrossRef](#)]
17. Yu, S.B.; Lyu, H.; Tian, J.; Wang, H.; Zhang, D.W.; Liu, Y.; Li, Z.T. A polycationic covalent organic framework: A robust adsorbent for anionic dye pollutants. *Polym. Chem.* **2016**, *7*, 3392–3397. [[CrossRef](#)]
18. Liu, Y.; Dikhtiarenko, A.; Xu, N.; Sun, J.; Tang, J.; Wang, K.; Xu, B.; Tong, Q.; Heeres, H.J.; He, S.; et al. Triphenylphosphine-Based Covalent Organic Frameworks and Heterogeneous Rh-P-COFs Catalysts. *Chem. A Eur. J.* **2020**, *26*, 12134–12139. [[CrossRef](#)]
19. Li, Y.; Pei, B.; Chen, J.; Bing, S.; Hou, L.; Sun, Q.; Xu, G.; Yao, Z.; Zhang, L. Hollow nanosphere construction of covalent organic frameworks for catalysis: (Pd/C)@TpPa COFs in Suzuki coupling reaction. *J. Colloid Interface Sci.* **2021**, *591*, 273–280. [[CrossRef](#)]
20. Yang, Q.; Luo, M.; Liu, K.; Cao, H.; Yan, H. Covalent organic frameworks for photocatalytic applications. *Appl. Catal. B* **2020**, *276*, 119174. [[CrossRef](#)]
21. Yazdani, H.; Shahbazi, M.-A.; Varma, R.S. 2D and 3D Covalent Organic Frameworks: Cutting-Edge Applications in Biomedical Sciences. *ACS Appl. Bio. Mater.* **2022**, *5*, 40–58. [[CrossRef](#)]
22. Chen, S.; Yuan, B.; Liu, G.; Zhang, D. Electrochemical Sensors Based on Covalent Organic Frameworks: A Critical Review. *Front. Chem.* **2020**, *8*, 601044. [[CrossRef](#)]
23. Gan, S.; Tong, X.; Zhang, Y.; Wu, J.; Hu, Y.; Yuan, A. Covalent Organic Framework-Supported Molecularly Dispersed Near-Infrared Dyes Boost Immunogenic Phototherapy against Tumors. *Adv. Funct. Mater.* **2019**, *29*, 1902757. [[CrossRef](#)]
24. Ma, X.; Scott, T.F. Approaches and challenges in the synthesis of three-dimensional covalent-organic frameworks. *Commun. Chem.* **2018**, *1*, 98. [[CrossRef](#)]
25. Huang, N.; Wang, P.; Jiang, D. Covalent organic frameworks: A materials platform for structural and functional designs. *Nat. Rev. Mater.* **2016**, *1*, 16068. [[CrossRef](#)]
26. Zhu, D.; Zhu, Y.; Chen, Y.; Yan, Q.; Wu, H.; Liu, C.Y.; Wang, X.; Alemany, L.B.; Gao, G.; Senftle, T.P.; et al. Three-dimensional covalent organic frameworks with pto and mhq-z topologies based on Tri- and tetrapopic linkers. *Nat. Commun.* **2023**, *14*, 2865. [[CrossRef](#)] [[PubMed](#)]
27. Kang, X.; Han, X.; Yuan, C.; Cheng, C.; Liu, Y.; Cui, Y. Reticular Synthesis of tbo Topology Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2020**, *142*, 16346–16356. [[CrossRef](#)]
28. Li, H.; Chen, F.; Guan, X.; Li, J.; Li, C.; Tang, B.; Valtchev, V.; Yan, Y.; Qiu, S.; Fang, Q. Three-Dimensional Triptycene-Based Covalent Organic Frameworks with ceq or acs Topology. *J. Am. Chem. Soc.* **2021**, *143*, 2654–2659. [[CrossRef](#)]
29. Baldwin, L.A.; Crowe, J.W.; Pyles, D.A.; McGrier, P.L. Metalation of a Mesoporous Three-Dimensional Covalent Organic Framework. *J. Am. Chem. Soc.* **2016**, *138*, 15134–15137. [[CrossRef](#)]
30. Gui, B.; Lin, G.; Ding, H.; Gao, C.; Mal, A.; Wang, C. Three-Dimensional Covalent Organic Frameworks: From Topology Design to Applications. *Acc. Chem. Res.* **2020**, *53*, 2225–2234. [[CrossRef](#)]
31. Uribe-Romo, F.J.; Hunt, J.R.; Furukawa, H.; Klöck, C.; O’Keeffe, M.; Yaghi, O.M. A Crystalline Imine-Linked 3-D Porous Covalent Organic Framework. *J. Am. Chem. Soc.* **2009**, *131*, 4570–4571. [[CrossRef](#)]
32. El-Kaderi, H.M.; Hunt, J.R.; Mendoza-Cortés, J.L.; Côté, A.P.; Taylor, R.E.; O’Keeffe, M.; Yaghi, O.M. Designed Synthesis of 3D Covalent Organic Frameworks. *Science* **2007**, *316*, 268–272. [[CrossRef](#)]
33. Lin, G.; Ding, H.; Yuan, D.; Wang, B.; Wang, C. A Pyrene-Based, Fluorescent Three-Dimensional Covalent Organic Framework. *J. Am. Chem. Soc.* **2016**, *138*, 3302–3305. [[CrossRef](#)]
34. Zhang, Y.; Duan, J.; Ma, D.; Li, P.; Li, S.; Li, H.; Zhou, J.; Ma, X.; Feng, X.; Wang, B. Three-Dimensional Anionic Cyclodextrin-Based Covalent Organic Frameworks. *Angew. Chem. Int. Ed.* **2017**, *56*, 16313–16317. [[CrossRef](#)]
35. Yahiaoui, O.; Fitch, A.N.; Hoffmann, F.; Fröba, M.; Thomas, A.; Roeser, J. 3D Anionic Silicate Covalent Organic Framework with srs Topology. *J. Am. Chem. Soc.* **2018**, *140*, 5330–5333. [[CrossRef](#)]
36. Ma, T.; Kapustin, E.A.; Yin, S.X.; Liang, L.; Zhou, Z.; Niu, J.; Li, L.H.; Wang, Y.; Su, J.; Li, J.; et al. Single-crystal X-ray diffraction structures of covalent organic frameworks. *Science* **2018**, *361*, 48–52. [[CrossRef](#)] [[PubMed](#)]
37. Zhu, Q.; Wang, X.; Clowes, R.; Cui, P.; Chen, L.; Little, M.A.; Cooper, A.I. 3D Cage COFs: A Dynamic Three-Dimensional Covalent Organic Framework with High-Connectivity Organic Cage Nodes. *J. Am. Chem. Soc.* **2020**, *142*, 16842–16848. [[CrossRef](#)] [[PubMed](#)]
38. Gropp, C.; Ma, T.; Hanikel, N.; Yaghi, O.M. Design of higher valency in covalent organic frameworks. *Science* **2020**, *370*, eabd6406. [[CrossRef](#)] [[PubMed](#)]
39. Nguyen, H.L.; Gropp, C.; Ma, Y.; Zhu, C.; Yaghi, O.M. 3D Covalent Organic Frameworks Selectively Crystallized through Conformational Design. *J. Am. Chem. Soc.* **2020**, *142*, 20335–20339. [[CrossRef](#)] [[PubMed](#)]
40. Li, Z.; Sheng, L.; Hsueh, C.; Wang, X.; Cui, H.; Gao, H.; Wu, Y.; Wang, J.; Tang, Y.; Xu, H.; et al. Three-Dimensional Covalent Organic Frameworks with hea Topology. *Chem. Mater.* **2021**, *33*, 9618–9623. [[CrossRef](#)]
41. Xu, X.; Cai, P.; Chen, H.; Zhou, H.-C.; Huang, N. Three-Dimensional Covalent Organic Frameworks with she Topology. *J. Am. Chem. Soc.* **2022**, *144*, 18511–18517. [[CrossRef](#)]

42. Xie, Y.; Li, J.; Lin, C.; Gui, B.; Ji, C.; Yuan, D.; Sun, J.; Wang, C. Tuning the Topology of Three-Dimensional Covalent Organic Frameworks via Steric Control: From pts to Unprecedented ljh. *J. Am. Chem. Soc.* **2021**, *143*, 7279–7284. [[CrossRef](#)]
43. Wang, X.; Bahri, M.; Fu, Z.; Little, M.A.; Liu, L.; Niu, H.; Browning, N.D.; Chong, S.Y.; Chen, L.; Ward, J.W.; et al. A Cubic 3D Covalent Organic Framework with nbo Topology. *J. Am. Chem. Soc.* **2021**, *143*, 15011–15016. [[CrossRef](#)]
44. Lu, H.; Han, W.; Yan, X.; Chen, C.; Niu, T.; Gu, Z. A 3D Anionic Metal Covalent Organic Framework with soc Topology Built from an Octahedral Ti^{IV} Complex for Photocatalytic Reactions. *Angew. Chem. Int. Ed.* **2021**, *60*, 17881–17886. [[CrossRef](#)]
45. Bera, R.; Ansari, M.; Alam, A.; Das, N. Nanoporous azo polymers (NAPs) for selective CO₂ uptake. *J. CO₂ Util.* **2018**, *28*, 385–392. [[CrossRef](#)]
46. Alam, A.; Mishra, S.; Hassan, A.; Bera, R.; Dutta, S.; Das Saha, K.; Das, N. Triptycene-Based and Schiff-Base-Linked Porous Networks: Efficient Gas Uptake, High CO₂/N₂ Selectivity, and Excellent Antiproliferative Activity. *ACS Omega* **2020**, *5*, 4250–4260. [[CrossRef](#)] [[PubMed](#)]
47. Bera, R.; Mondal, S.; Das, N. Triptycene based microporous polymers (TMPs): Efficient small gas (H₂ and CO₂) storage and high CO₂/N₂ selectivity. *Microporous Mesoporous Mater.* **2018**, *257*, 253–261. [[CrossRef](#)]
48. Hassan, A.; Alam, A.; Ansari, M.; Das, N. Hydroxy functionalized triptycene based covalent organic polymers for ultra-high radioactive iodine uptake. *Chem. Eng. J.* **2022**, *427*, 130950. [[CrossRef](#)]
49. Shetty, S.; Baig, N.; Hassan, A.; Al-Mousawi, S.; Das, N.; Alameddine, B. Polyphenylene networks containing triptycene units: Promising porous materials for CO₂, CH₄, and H₂ adsorption. *Microporous Mesoporous Mater.* **2020**, *303*, 110256. [[CrossRef](#)]
50. Preet, K.; Gupta, G.; Kotal, M.; Kansal, S.K.; Salunke, D.B.; Sharma, H.K.; Chandra Sahoo, S.; Van Der Voort, P.; Roy, S. Mechanochemical Synthesis of a New Triptycene-Based Imine-Linked Covalent Organic Polymer for Degradation of Organic Dye. *Cryst. Growth Des.* **2019**, *19*, 2525–2530. [[CrossRef](#)]
51. Luo, S.; Zhang, Q.; Bear, T.K.; Curtis, T.E.; Roeder, R.K.; Doherty, C.M.; Hill, A.J.; Guo, R. Triptycene-containing poly(benzoxazole-co-imide) membranes with enhanced mechanical strength for high-performance gas separation. *J. Memb. Sci.* **2018**, *551*, 305–314. [[CrossRef](#)]
52. Zhang, Y.; Zhu, Y.; Guo, J.; Gu, S.; Wang, Y.; Fu, Y.; Chen, D.; Lin, Y.; Yu, G.; Pan, C. The role of the internal molecular free volume in defining organic porous copolymer properties: Tunable porosity and highly selective CO₂ adsorption. *Phys. Chem. Chem. Phys.* **2016**, *18*, 11323–11329. [[CrossRef](#)]
53. Bera, R.; Ansari, M.; Alam, A.; Das, N. Triptycene, Phenolic-OH, and Azo-Functionalized Porous Organic Polymers: Efficient and Selective CO₂ Capture. *ACS Appl. Polym. Mater.* **2019**, *1*, 959–968. [[CrossRef](#)]
54. Alam, A.; Bera, R.; Ansari, M.; Hassan, A.; Das, N. Triptycene-Based and Amine-Linked Nanoporous Networks for Efficient CO₂ Capture and Separation. *Front. Energy Res.* **2019**, *7*, 141. [[CrossRef](#)]
55. Zhang, C.; Zhai, T.L.; Wang, J.J.; Wang, Z.; Liu, J.M.; Tan, B.; Yang, X.L.; Xu, H.B. Triptycene-based microporous polyimides: Synthesis and their high selectivity for CO₂ capture. *Polymer* **2014**, *55*, 3642–3647. [[CrossRef](#)]
56. Co, A.P.; Benin, A.I.; Ockwig, N.W.; O’Keeffe, M.; Matzger, A.J.; Yaghi, O.M. Porous, Crystalline, Covalent Organic Frameworks. *Science* **2005**, *310*, 1166–1170. [[CrossRef](#)]
57. Li, H.; Ding, J.; Guan, X.; Chen, F.; Li, C.; Zhu, L.; Xue, M.; Yuan, D.; Valtchev, V.; Yan, Y.; et al. Three-Dimensional Large-Pore Covalent Organic Framework with stp Topology. *J. Am. Chem. Soc.* **2020**, *142*, 13334–13338. [[CrossRef](#)] [[PubMed](#)]
58. Li, H.; Chang, J.; Li, S.; Guan, X.; Li, D.; Li, C.; Tang, L.; Xue, M.; Yan, Y.; Valtchev, V.; et al. Three-Dimensional Tetrathiafulvalene-Based Covalent Organic Frameworks for Tunable Electrical Conductivity. *J. Am. Chem. Soc.* **2019**, *141*, 13324–13329. [[CrossRef](#)]
59. Li, Z.; Sheng, L.; Wang, H.; Wang, X.; Li, M.; Xu, Y.; Cui, H.; Zhang, H.; Liang, H.; Xu, H.; et al. Three-Dimensional Covalent Organic Framework with ceq Topology. *J. Am. Chem. Soc.* **2021**, *143*, 92–96. [[CrossRef](#)]
60. Lu, W.; Yuan, D.; Zhao, D.; Schilling, C.I.; Plietzsch, O.; Muller, T.; Brase, S.; Guenther, J.; Blumel, J.; Krishna, R.; et al. Porous Polymer Networks: Synthesis, Porosity, and Applications in Gas Storage/Separation. *Chem. Mater.* **2010**, *22*, 5964–5972. [[CrossRef](#)]
61. Ben, T.; Ren, H.; Ma, S.; Cao, D.; Lan, J.; Jing, X.; Wang, W.; Xu, J.; Deng, F.; Simmons, J.M.; et al. Targeted Synthesis of a Porous Aromatic Framework with High Stability and Exceptionally High Surface Area. *Angew. Chem. Int. Ed.* **2009**, *48*, 9457–9460. [[CrossRef](#)]
62. Jiang, J.X.; Laybourn, A.; Clowes, R.; Khimyak, Y.Z.; Bacsá, J.; Higgins, S.J.; Adams, D.J.; Cooper, A.I. High Surface Area Contorted Conjugated Microporous Polymers Based on Spiro-Bipropylenedioxythiophene. *Macromolecules* **2010**, *43*, 7577–7582. [[CrossRef](#)]
63. Li, H.; Pan, Q.; Ma, Y.; Guan, X.; Xue, M.; Fang, Q.; Yan, Y.; Valtchev, V.; Qiu, S. Three-Dimensional Covalent Organic Frameworks with Dual Linkages for Bifunctional Cascade Catalysis. *J. Am. Chem. Soc.* **2016**, *138*, 14783–14788. [[CrossRef](#)] [[PubMed](#)]
64. Ghanem, B.S.; Msayib, K.J.; McKeown, N.B.; Harris, K.D.; Pan, Z.; Budd, P.M.; Butler, A.; Selbie, J.; Book, D.; Walton, A. A triptycene-based polymer of intrinsic microporosity that displays enhanced surface area and hydrogen adsorption. *Chem. Commun.* **2007**, *1*, 67–69. [[CrossRef](#)] [[PubMed](#)]
65. Wang, Y.; Wu, C.; Sun, W.; Pan, Q.; Hao, W.; Liu, H.; Sun, J.; Li, Z.; Sun, J.; Zhao, Y. Triptycene-based three-dimensional covalent organic frameworks with stp topology of honeycomb structure. *Mater. Chem. Front.* **2021**, *5*, 944–949. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.