Data-Driven Evaluation as a Preliminary Tool to Judiciously Choose Covalent Organic Frameworks to be used as Fillers in Mixed Matrix Membranes for Hydrogen Separation

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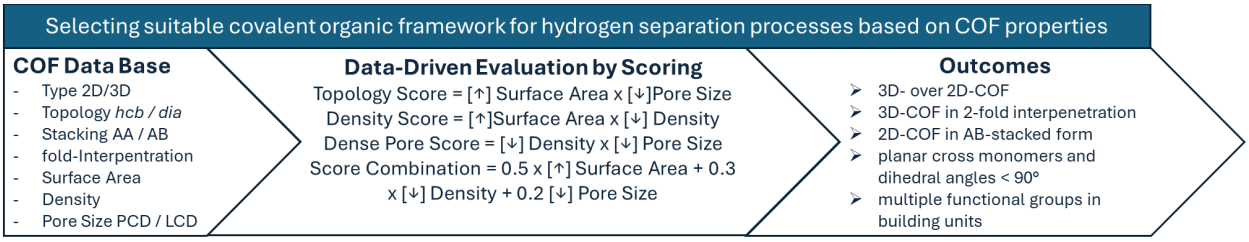
Abstract

Hydrogen counts as the fuel of the future for the decarbonization of industry and the transport sector. A membrane that contains porous materials as a filler can be used for energy transformation to gain hydrogen from different gas mixtures. The variety of porous materials makes it difficult to select a specific one for hydrogen separation. Covalent Organic Frameworks (COFs) are becoming increasingly popular for gas separation processes, especially for applications at high temperatures. The properties of a COF depend on the configuration of the various building units. Especially topologies containing the assembly of a planar cross are suitable for the desired properties of large surface area in combination with low density and small pores. Data-driven evaluation is provided to select the most promising COF features and topologies from the CoRE-COF database of 1242 reported COFs based on quantification using the scoring model approach. The result of the scoring model shows that 3D COFs on average have higher potential compared to 2D COFs. Four different normalized scores describe the configuration with the highest potential. The simple quantification approach of the preferred properties enables the selection of a specific topology from 2D or 3D covalent organic frameworks and serves as an indication for further advantageous features for a selective hydrogen separation material.

Keywords: covalent organic frameworks, scoring model, mixed matrix membranes, hydrogen separation

Graphical Abstract



Scientific Contribution Statement

This study contributes to the field of porous materials for gas separation by developing a simple approach to evaluating the properties of covalent organic frameworks (COF) to identify suitable COF which have promising potentials as filers in mixed matrix membranes (MMM) for hydrogen separation. Unlike other studies, this approach focuses rather on the methodology simplicity to screen the COF that does not require high computational demand such as molecular simulation but rather focusing on their physical properties.

1. Introduction

An urgent need to accelerate the energy transition process from a fossil fuel-based economy to a sustainable one increases with the consequences of climate change. In this perspective, the use of hydrogen as one of the sustainable energy carriers becomes crucial. There are several ways to produce hydrogen. For example, hydrogen can be produced from the steam reforming of methane, which is currently one of the most common ways to produce hydrogen. Another possibility is to produce hydrogen from biomass pyrolysis, which could also be coupled with the production of other functional materials such as carbon nanotubes. Regardless of the path chosen for hydrogen production, it must usually be followed by the process of hydrogen purification, where hydrogen is separated from other gases. The hydrogen purification process also plays an important role when considering the hydrogen transport process. For example, the use of natural gas pipelines could be considered as one of the most promising alternatives for the distribution of hydrogen. Hydrogen can be mixed with natural gas and thus a separation process is required before the final user can use purified. Another example is the transport of hydrogen by first converting it into ammonia or methanol, which is quite attractive and promising from the point of view of safety and sustainability [1]. Hydrogen can be transported in form of one of the mentioned derivates like ammonia between various hydrogen valleys [2]. The derivative can be cracked in the valley to release energy or hydrogen gas as needed. However, as in the previous case, this approach also requires a separation process before the purified hydrogen can be used, since ammonia must first be cracked and thus separated from nitrogen.

Hydrogen separation process can be carried out by various methods such as cryogenic distillation and pressure swing adsorption. The main drawback of these conventional technologies is their high energy consumption. Membrane technology is a promising alternative to replace conventional separation technologies. There are several advantages associated with the use of membranes for hydrogen separation, such as high separation performance, low carbon footprint and low energy consumption. [3]. To date, most membranes used in industry are made of polymeric materials. Despite their advantages in terms of economics and fabrication, their performance is always limited by the trade-off between productivity and selectivity, usually represented by the Robeson plot. Therefore, different strategies have been proposed to overcome this challenge and one of them is the construction of a mixed matrix membrane.

A mixed matrix membrane (MMM) is a membrane composed of at least two different materials: polymers and fillers. The former acts as a continuous phase while the latter acts as a discrete phase. The incorporation of fillers into the polymer matrix is then expected to increase the separation performance of polymer membranes and thus exceed the upper limit. To date, various fillers such as zeolite, graphene oxide, metal organic frameworks (MOF) and covalent organic frameworks (COF) have been investigated for the preparation of MMM for hydrogen separation [4]. Among all these possibilities, COF may be one of the most promising fillers because of their customizable architecture and high porosity, they are built by covalent bonding and thus have better framework stability [5] making COFs favorable fillers for processes with high temperatures stable requirements [6].

Data based analysis or machine learning have been used in various studies to select MOFs with a specific target or for a specific application [7]. Despite promising potential of COF, there are only a few studies using COF as fillers in MMM for hydrogen separation. One of the main reasons for this lack of studies may be due to the large number of COFs that have been reported, which is clearly reflected by the number of COFs published in the last decade [8]. This makes it difficult to rationally select the COF to be used as fillers in MMM. This study aims to provide preliminary evaluations of the COF that have high potential to be used

as fillers in MMM. For the evaluation criteria of the COF, there are three properties that will be evaluated in this study, namely the gravimetric surface area, the pore size, and the density of each COF. The three properties are chosen because they can represent different influences on the gas separation performance, such as adsorption and interaction ability, geometric separation ability, and increasing free volume [9,10]. The unitless scores of these parameters quantify the COFs based on grouped properties such as topology to evaluate the hypothetical hydrogen separation performance, which can be used as a guideline to evaluate their suitability as fillers in MMM used for hydrogen separation. Scoring is commonly in management to evaluate unrelated characteristics as a supporting tool to find the most promising option. This study aims to show that simple methods can also be established in engineering or materials science. For example MolScore proves that normalized scoring with values between 0 and 1 enable the comparison of multiple parameters [11].

1. Materials and methods

2.1 Dataset and Approach

The data used in this study was obtained from the CoRE COF database. The dataset includes all published COFs with their name, topology, type, reference, simulated or measured surface area, pore limiting diameter (PLD), largest cavity diameter (LCD), density, void fraction and functional volume of each material [12]. To learn from previously published COFs, materials must be reported to a database that stores the data in a standardized way that allows comparison of individual properties and features. Updating the data-driven evaluation with new materials shows different results due to changes in scores. Evaluation of the data-driven output by researchers results in simulated materials that are used for various purposes in the application. The next step is to physically synthesize the selected COF. Adjustments and optimizations during synthesis can result in different crystallinity and therefore different properties compared to the ideal simulated ones. Analysis of the physical COF in combination with optimized synthesis conditions [13], leads to new Covalent Organic Frameworks that can be evaluated in the following analysis approach (see figure 1).

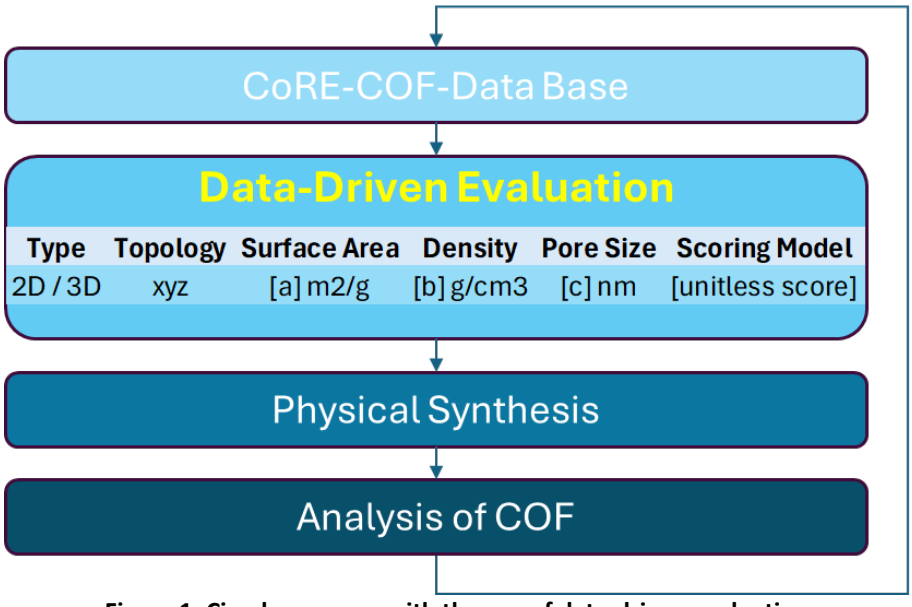


Figure 1: Circular process with the use of data-driven evaluation

Previous simulations from Koc University have shown that hypothetical COFs that do not match the kinetic diameter of hydrogen are promising materials for hydrogen purification processes [14].

2.2 Scoring model

In general, a scoring model comprises of three essential elements: input variables, scoring algorithms, and scoring outputs [15]. Input variables are the data points which are then processed using various scoring algorithms, which are developed based on mathematical models, to produce scores as the output.

In this study three different parameters of the COF are used as the input variables, namely the gravimetric surface area, the density and the pore size. The gravimetric surface area can be correlated with the gas adsorption performance of the COF since in general, higher surface area leads to higher gas adsorption capacity. Meanwhile, the density parameter can be associated with the porosity that gives an indication of the unoccupied space inside the material [16]. This could then be related to the permeability improvement of polymeric membranes when such COF are incorporated into polymeric matrices. Finally, the pore size parameter is related to the ability of the COF to perform molecular sieving for hydrogen separation, which could improve the hydrogen selectivity of the resulting MMM. In addition, it should be noted that the input variables used in this study do not consider the functional groups that can be incorporated within the COF. The selected three main characteristics of the COF (e.g., surface area, density, and pre-size) are already sufficient to provide a preliminary evaluation of the COF that could be used as fillers in MMM for hydrogen separation. This contributes to simplification without sacrificing the effectiveness of this approach.

First, we analyze the output score based on the combination of the gravimetric surface area and the density of the COF. The gravimetric surface area represents the interaction of the material with the gas molecules as well as the adsorbing performance. The density represents the porosity that gives an indication of unoccupied space or free volume inside the material [16]. The result of this combination represents a material with high free volume and high interaction between gas molecules and framework. This value is normalized using the min-max normalization against the ideal condition, where the highest surface area in combination with the lowest reported density and pore size is targeted [17]. The output score for this combination analysis is given as the density score (DS) which is the result of the multiplication product of the normalized S_{Bet}, representing the gravimetric surface area, with the normalized inverse of density, representing the unoccupied space.

A multiplication by 10 results in values between 0 and 10, where 0 represents a non-porous material and 10 an ideal material for both features. The higher the value, the closer the combination comes to the ideal. Equation 1 shows the calculation of DS:

$$\boldsymbol{Density\ Score\ (DS)} = \frac{Surface\ Area\left[SBet\ in\frac{m2}{g}\right]}{Max.\ \ Surface\ Area\left[in\frac{m2}{g}\right]} * \left(1 - \frac{Density\ \left[in\frac{g}{cm3}\right]}{Max.\ \ Density\left[in\frac{g}{cm3}\right]}\right) * 10 \quad (1)$$

The second analysis is carried out by combining the surface area parameter and pore size. Assuming a large diameter can form channels where the gas molecules can penetrate through in a strait way, smaller channels and micropores are advantageous [18]. The combination of both parameters represents a material with a high accessible surface area in the form of small pores. The equation to calculate the TS is then given in equation 2:

$$\boldsymbol{Topology\ Score\ (TS)} = \frac{Surface\ Area\left[SBet\ in\frac{m2}{g}\right]}{Max.\ \ Surface\ Area\left[in\frac{m2}{g}\right]} * \left(1 - \frac{Pore\ Size\ LCD\ [in\ nm]}{Max.\ \ Pore\ Size[in\ nm]}\right) * 10 \quad (2)$$

The third combination analysis the combination of the density and pore size. This score describes the distribution of a small pore size with respect to the porosity of the material. A high score is representative of a light atomic structure that forms small pores. For efficient use in a MMM the aim is to divide the free volume into the smallest possible pores. The equation 3 shows the formula to calculate the DPS score:

$$\boldsymbol{Dense\ Pore\ Score\ (DPS)} = \left(1 - \frac{Density\ \left[in\frac{g}{cm3}\right]}{Max.\ \ Density\left[in\frac{g}{cm3}\right]}\right) * \left(1 - \frac{Pore\ Size\ LCD\ [in\ nm]}{Max.\ \ Pore\ Size\ [in\ nm]}\right) * 10 \quad (3)$$

The last formula combines all three features. In addition, the normalized features are weight, to manage the influence of the property on the gas separation performance.

$$\boldsymbol{Score\ Combi\ (SC)} = \left(\begin{array}{l} 0.5 * \frac{Surface\ Area\left[SBet\ in\frac{m2}{g}\right]}{Max.\ \ Surface\ Area\left[in\frac{m2}{g}\right]} + \\ 0.3 * \left(1 - \frac{Pore\ Size\ LCD\ [in\ nm]}{Max.\ \ Pore\ Size\ [in\ nm]}\right) + \\ 0.2 * \left(1 - \frac{Density\ \left[in\frac{g}{cm3}\right]}{Max.\ Density\left[in\frac{g}{cm3}\right]}\right) \end{array}\right) * 10 \quad (4)$$

The influence of the Surface Area represents the interaction between gas molecule and framework; therefore, the gravimetric surface area influences the SC with 50%. Representing the Knudsen Effect and respecting the kinetic diameter of hydrogen the pore size weighs in with 30%. The density of the material represents the unoccupied volume that provides free volume to take the potential permeation into account.

All scores are equivalent to rankings where 0 is the least and 10 the highest score. The quantification allows to rank the COFs based on different combinations of features. Furthermore, comparison between different similarities like stacking of 2D-COFs or interpenetrated 3D-frameworks can be quantified.

3. Results and Discussions

3.1 Comparison of Density, Topology and Dense Pore Score

First, based on the maximum values of materials in the COF database the maximum boundary values for the surface area, the density and the pore size are defined as 10.000 m^2/g, 2 g/cm^3 and 10 nm, respectively. In this study, COF with higher surface area, low density and small pore size are preferable. COF with high surface area might be beneficial to increase the gas interaction to the framework resulting in higher selectivity [19]. Meanwhile, COF with low density property is preferable since it is directly related to the material porosity and represents both the void fraction and the functional volume [21]. As in the case of

gravimetric surface area, COF with lower density is preferable since it correlates with their high porosity and thus could contribute to increasing the MMM gas permeability. Meanwhile, with respect to the pore size, a small pore of around 0.289 nm is preferable, due to the kinetic size of hydrogen [22]. In this case, choosing COF with small pore size might then contribute to enhancing the MMM hydrogen gas selectivity.

We analyze the correlation between the DS, TS and DPS representing the favorable properties based on the distribution in the Figure 2. In the three figures, we split the result based on the COF main morphology, namely 2D and 3D, which are colored in blue or yellow, respectively, to gain a deeper understanding of the impact of different COF morphology on each score. Figure 2A shows the correlation between DS and TS.

The relation between the two scores DS and TS tends to show a linear correlation with an increasing variance as either the DS or TS gets higher. However, the non-straight linearity, for example at a DS of 6, shows that the scores do not directly correlate to each other influenced by the pore size effecting the TS. Only 27 COFs reach scores above 6 in both scores. After splitting the data set based on the dimension into 2D and 3D materials, the first trend indicates that 3D-COFs in general show higher potential based on the twenty materials in the targeted area representing 13% of the 3D data points, even though there exist seven 2D-Frameworks with equally high scores that are in the same area of figure 2A. The seven data points representing only 0.6 % of the 2D data are closer to each other and trend to show a linear correlation. The deviation of the twenty 3D COFs expresses more flexibility when it comes to designing a favorable structure. In general, the 3D COFs show potential to reach higher scores, but the researcher must differentiate in the selection due to the higher variance.

We then analyze the correlation in figure 2B and 2C, between the DS and DPS as well as TS and DPS, respectively. In Comparison to the relation of the two other scores the DPS shows a non-linear trend. The DPS values increase exponentially at DS and TS scores between 0 and 1. COFs with a DS or TS score between one and two show a high DPS but a low DS and TS. The highest value of with a high point at DS and TS around 2 followed by decreasing DS and TS with increasing DPS. Due to the opposite ratio, the course of the curve shows that the database does not include materials with high DPS as well as high DS or TS. Therefore, it looks like COFs with high values for all three scores cannot be manufactured. In figure 2B and 2C the target area can be defined by a line between the maximum scores of 10. The line depicts the border of possible and physically impossible materials. The area with no reported materials in both figures point out that the individual desired targets are contradictory. In conclusion a high DS or TS results in a low DPS, if the Density or Topology Score is above 2. Because of the relation between DPS and the other scores, an ideal material, which meets all desired requirements, has not been reported yet and may not exist. For the selection of one specific material respecting a combination of the three favorable properties the Score Combi (SC) is introduced. Both COF types are evaluated individually in terms of dimension based on the SC.

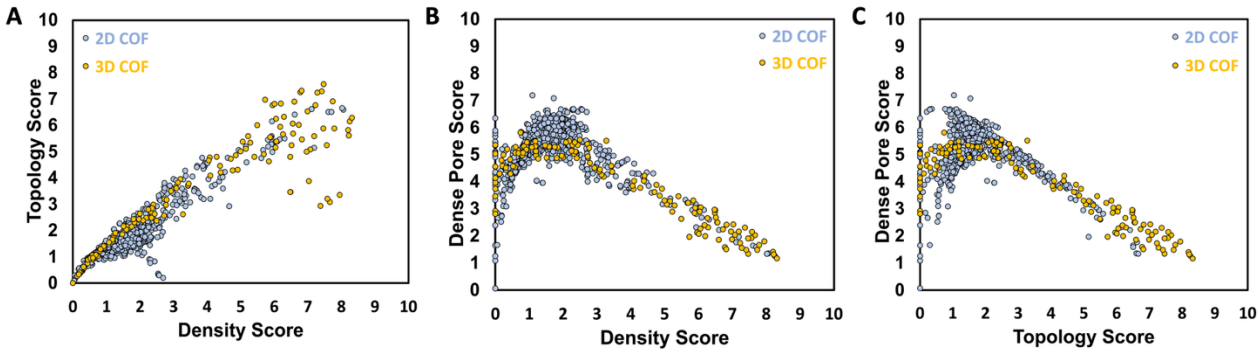


Figure 2: Comparison of A Density and Topology Score, B Density and Dense Pore Score, and C Topology and Dense Pore Score

3.2 2D Covalent Organic Framework

After analyzing the general trend of TS, DS and DPS, we further analyze the results based on the COF morphology which will be initialized by discussing the 2D COF in this section. The analysis is carried out based on the variety of different topologies of 2D COF which describes the possible configurations of different geometric building unit [23].

First, as presented in Table 1, around 88% of all reported 2D COF are in *hcb* topology which represents the formation of hexagonal pore channels. Even though it constitutes the majority of 2D COF, iIt seems that the COF with this topology is not the best option to be used as fillers in MMM used for hydrogen separation. This can be reflected through its SC score which could be considered as average in comparison to other 2D COF topologies. For example, 2D COF with *sql* topology with a square geometry exhibits higher average scores compared to 2D COF with *hcb* topology. The *sql* 2D COF are synthesized by combining a planar cross monomer containing four functional groups with a linear unit containing two functional groups. Among the various examples of 2D COF with *hcb* topology, both TAPP-BDP and CCOF-2 exhibit the highest potential. The former, which is reported to be used for photocatalysis [24], reaches the SC score of more than 7. Meanwhile, the latter reaches SC score above 8, which is the highest individual score out of the 2D COFs. Another case can also be seen in 2D COF with *fxt* topology, where a double wall forms the main pores. For the formation of the pores a double number of atoms stabilize the mesopores. The mesopores enable a high void fraction. However, pores with more than 2 nm in combination with a low density are not suitable for the targeted application.

Table 1. Average TS, DS, DPS and SC of 2D COFs based on their topologies

Topology	Topology Score	Density Score	Dense Pore Score	Score Combi	Reported materials
3D	3,67	3,98	3,63	6,36	143
2D	1,68	1,57	5,36	4,86	1099
htb	2,30	2,06	5,31	5,25	2
bex	1,90	1,51	5,35	5,06	5
sql	1,87	1,68	5,22	5,02	260
kgm	1,73	1,84	5,71	4,88	41
mtf	1,59	1,10	5,13	4,84	2
fes	1,50	1,27	5,41	4,82	6

hcb	**1,62**	**1,53**	**5,39**	**4,81**	**770**
hxl	**1,53**	**1,07**	**5,17**	**4,77**	**5**
tri	**1,50**	**1,05**	**5,19**	**4,76**	**1**
kgd	**1,09**	**0,73**	**5,03**	**4,50**	**5**
fxt	**1,19**	**1,32**	**6,13**	**4,40**	**2**
Grand Total	**1,91**	**1,85**	**5,16**	**5,03**	**1242**

In addition to the evaluation of the 2D COF topology, we analyze the results based on the different stacking configurations existing in the 2D COF. In general, the stacking in 2D COF can be classified either as AA or AB stacking. AA stacking means that the layers of the 2D-COF sheets are directly aligned on top of each other, with atoms or molecules in each layer positioned exactly above those in the layer below. AB stacking refers to layers arranged that the atoms or molecules of the second layer fit into the gaps of the first layer, resulting in an offset stacking [25]. The result of the analysis based on the 2D COF stacking is depicted in the Figure 3. As can be expected, shifted AB-stacked materials reach slightly higher Density, Topology Scores and a higher Score Combination compared to the AA alternative. The slight shift of one layer enables the surface area to increase. The stability of the structure increases too [26]. In contrast a high Dense Pore Score prefers AA-stacked COFs. The space between the layers decreases in AB-Stacking. This formation reaches higher packed density, resulting in a worse DPS while the maximum pore size stays the same. The data is supplemented by another column in which the form of stacking is manually entered. Only COFs with reported entries of AA and AB of the same material are considered.

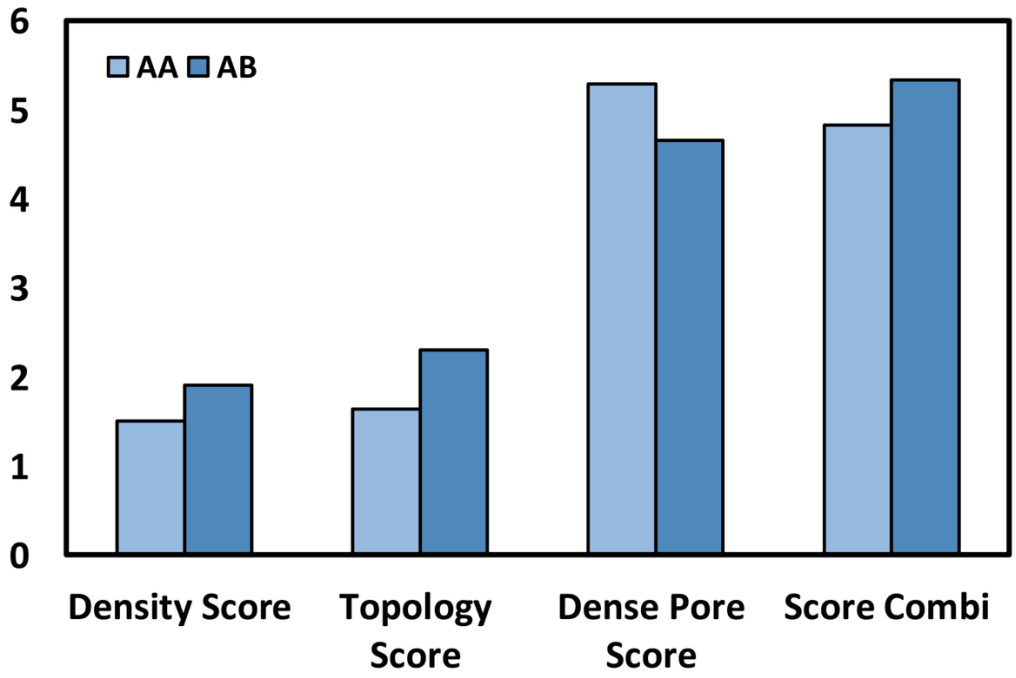


Figure 3: Influence of AA- and AB-Stacking on all four scores

3.3 3D Covalent Organic Framework

After analyzing the 2D COF, we continue the analysis on the 3D COF with the same approach. As in the case of the 2D COF, the scores in the 3D COF are also grouped based on the COF topologies and the result

is presented in the Table 2. As has been previously mentioned, in general, COFs with 3D morphology achieve higher scores compared with their 2D COF counterpart which might be contributed from the establishment of the interconnections within the 3D COF frameworks that enables to use the third dimension as void fraction. The impact on the surface area and density improves the scores compared to 2D COF, as reflected in higher DS and TS. The increasing number of options to connect different building units do not show a specific trend and tend to vary depending on the topology of the 3D COF. Compared to the positive impact, a high DPS results in a low score combination like in 2D stacked COF. It follows that the DPS influences the combined score SC negatively.

The most common three-dimensional organic configuration is the diamond. 55% of the 3D COF data are reported in *dia* topology, characterized by tetrahedral linkage connected in a diamond-like arrangement. Table 2 shows the *dia*-group averages in the lower half of topologies. The variance of DS, TS and DPS for the dia group is more balance around values of 3 to 4 than in topologies with higher SC. Other topologies with a high TS like *cut*, *fjh* and *pts* have in common that they contain a planar cross building unit. For the design of the desired properties, this building unit shows more potential. From each of the top three topologies only one or two simulated COFs are reported resulting in less evidence for a general trend. The group with the highest SC and more than three reported materials is the *fjh* topology. These COFs are formed by linking trigonal-planar and square-planar building units. The dihedral angles below 90° result in a highly crystalline structure with significant porosity and surface area [27].

Table 2. Average TS, DS, DPS and SC of 3D COFs based on their topologies

Topology	Topology Score	Density Score	Dense Pore Score	Score Combi	Reported materials
3D	3,67	3,98	3,63	6,36	143
cut	5,69	6,56	2,50	7,79	1
lvt	5,66	6,26	2,66	7,72	1
hea	5,36	6,67	2,55	7,68	2
fjh	5,25	6,47	2,65	7,60	3
bcu	5,43	5,77	2,91	7,51	3
tbo	4,27	7,57	1,96	7,48	4
tty	5,34	5,29	3,12	7,38	1
pcb	4,85	5,55	3,34	7,23	2
ffc	4,00	6,80	2,52	7,19	5
pts	4,78	5,39	2,83	7,14	7
ctn	4,88	4,66	3,55	7,07	8
sqc	4,96	4,26	3,09	6,94	3
stp	3,94	5,40	3,39	6,81	7
acs	3,61	3,08	4,46	6,20	1
bor	3,24	3,47	4,17	6,08	5
dia	3,30	3,27	3,78	6,02	79
ceq	2,94	2,71	5,03	5,79	2
spn	2,62	3,28	5,52	5,73	1

soc	2,62	2,35	5,41	5,66	3
ljh	2,17	1,51	4,89	5,21	1
scu	1,87	1,53	5,43	5,11	2
ion	1,07	0,68	5,06	4,45	1
hcb	0,66	0,29	3,97	4,12	1
2D	1,68	1,57	5,36	4,86	1099
Grand Total	1,91	1,85	5,16	5,03	1242

In addition to the COF topology, we also discuss the result in the 3D COF based on the interpenetrated structure of the framework whose result is presented in the Figure 4. Interpenetration in COF framework refers to a structure where multiple independent networks are interwoven within a single material. In the context of COFs, this means that two or more distinct frameworks are intertwined, creating a more complex and stable structure. The numbers in the Figure 4 show the level of interpenetration, 1 stands for non-fold interpenetrated. This interpenetration can enhance the mechanical strength, stability, and functional properties of the material [28]. In general, two- or three interpenetrated 3D-COFs show higher scores to non- or higher-fold-interpenetrated options of the same type of material. Figure 4 shows that 3-fold interpenetrated materials are the most promising COFs on average. The material with the highest individual SC above 8.5 belongs to the *dia* topology, a two-fold interpenetrated 3D-Sp COF containing a hindered rotation tetrahedral monomer [29].

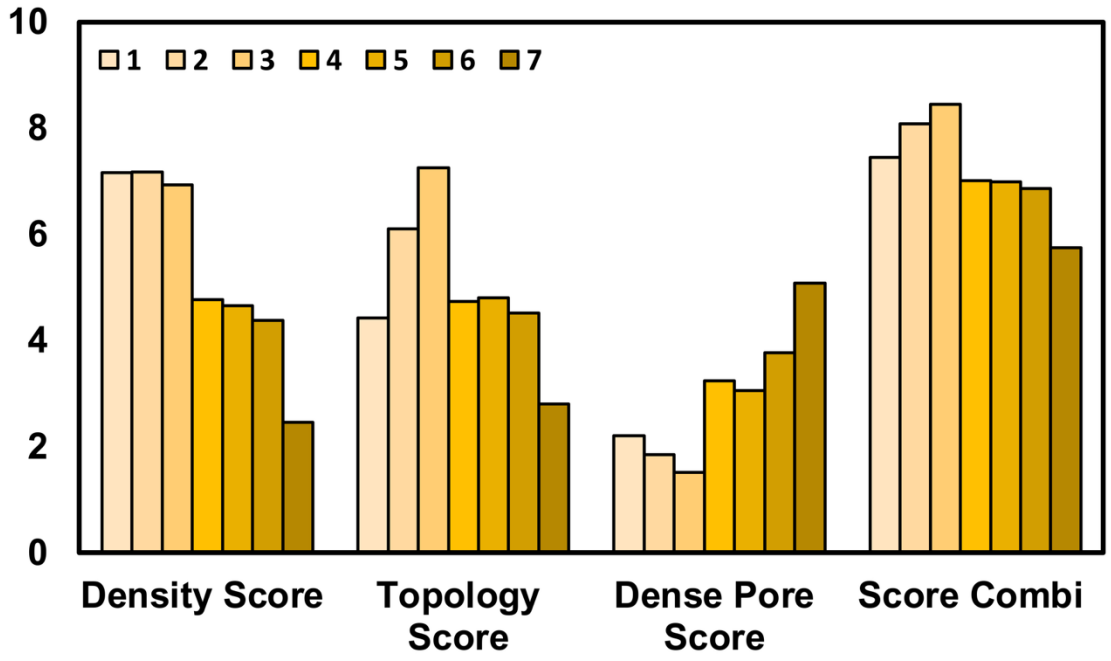


Figure 4: The effect of fold-interpenetration in 3D-COFs on all four scores

Lastly, we also analyze the result of the 3D COF based on the number of the functional groups of the building blocks and the result is presented in the Figure 5. Compared to planar 2D-COFs the third dimension offers more options for combination and an increasing number of functional groups of the building units. In Figure 5, the the colour represents the sum of the functional groups and forms the number of monomer combination. For example, in the case of dia, it represents [4 + 2], a monomer with 4 functional groups reacts with the partner monomer of 2 functional groups. Since multiple configuration options are possible in 3D space, the sum of the functional groups contained of both monomer building units forming the framework increases up to 12 in case of [8 + 4]-combination. The trend shows that as the number of functional groups increases, the SC tents also to increase. Exceptions like for the *scu* topology refute this. This means that selected highly interconnected frameworks show a high potential for hydrogen separation. The most well-known synthesis for 3D-COFs is the Schiff-based reaction, a primary amine reacts with a primary aldehyde to generate a covalent -C=N- bonding and water. With every imine connection there is a chance of a cis- or trans- configuration. A favorable trans-imine generates a linear connection resulting in higher crystallinity. With every interconnection the chance of forming cis-imine products increases affecting the crystallinity of the final material [30]. Therefore, the number of monomer combinations can also be seen as degree of complexity for the crystallization process. A high value means high complexity for the synthesis. The lowest number of reacting functional groups is 5. A value of 4 would represent a polymer chain. The number represents the difficulty of manufacturing a high crystallin COF. A high number represents high interconnection inside the framework.

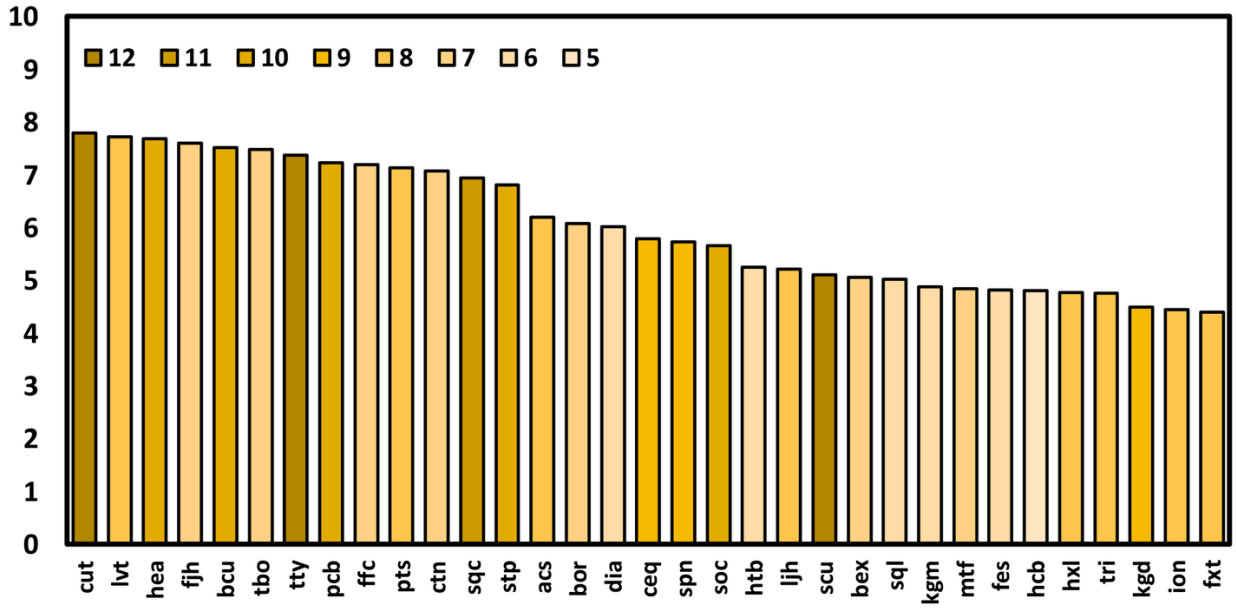


Figure 5: Ranking of Score Combi and Sum of functional groups in 3D COFs

A higher number of reacting functional groups of the monomers tend to reach higher scores. However, the number of reported materials containing a monomer combination higher than nine reacting functional groups by polycondensation reaction is limited to twenty-five reported COFs that are meanly only simulated ones. One idea to achieve higher interconnection is to add one functional group to the monomer building unit. This effect can also be described as “cantellation” reported on Metal Organic Frameworks in

2020 [31] and can also be considered for COF synthesis. Instead of a para-functional group that is aligned straight, the meta or ortho-monomer can be used to increase the score. The change also doubles the number of functional groups for one monomer building unit.

4. Conclusion

This study has shown that the scoring model method can be used as a simple effective tool for the preliminary evaluation of COF that can be used as fillers in MMM for hydrogen separation. In this case, the scoring model allows to find the trends of COF based on the important parameters for gas separation processes, namely surface area, density and pore size. Our evaluation study then showed that, in general, 3D COF could be more promising as fillers in MMM for hydrogen separation than their 2D counterparts. This is because their interconnection enables the formation of frameworks with higher surface area, lower density and smaller pore size. In particular, the 3D COF built with planar cross building unit, high interconnectivity and with interpenetrated framework are desirable to be used as fillers in MMM for hydrogen separation. This can be exemplified as in the case of 3D COF with *cut* or *fjh* topology. However, this does not exclude the fact that some of the 2D COF may also be promising to be used as fillers in the MMM for hydrogen separation. For example, the evaluation results of 2D COF show that planar cross-linked monomers as in *sql* topology have a high potential in the form of AB stacking, which can be beneficial to increase the hydrogen selectivity in MMM due to the reduction of the pore aperture of the COF.

Although this simple approach is remarkably effective, its effectiveness is highly dependent on the input variables. The CoRE-COF database needs to be updated regularly. Unfortunately, the dataset does not contain COFs reported in the last five years, and several 3D topologies are represented by only one material in the available dataset, so the trends shown by only one data point must be evaluated critically. Nevertheless, we have successfully demonstrated in this study that this simple tool can be effectively used as a preliminary evaluation tool for the judicious selection of COF as fillers in MMM for hydrogen separation.

Availability of data and materials

The database used in this study is available as supplementary information.

Competing interests

The authors declare no competing interests.

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Authors' contributions

K. H: Conceptualization, Methodology, Software, Formal analysis, Investigation, Writing - Original Draft, Visualization

B. P. L: Resources, Writing - Review & Editing, Supervision, Project administration, Funding acquisition

N. P: Validation, Writing - Original Draft, Writing - Review & Editing, Visualization, Supervision, Project administration

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