

Predicting and Screening High-Performance Polyimide Membranes Using Negative Correlation Based Deep Ensemble Methods

- Supplementary Documents

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Tab. S1 List of materials used in this paper

Item Name	Specification/Model	Manufacturer
3,5-Diaminobenzoic acid (DABA)	Purity 98%	J&K Scientific
4,4'-(Hexafluoroisopropylidene)-phthalic anhydrides (6FDA)	Purity 98%	J&K Scientific
N-Methyl pyrrolidone (NMP)	Analytically pure	Sinopharm Chemical Reagent Co., Ltd.
N, N-Dimethylacetamide (DMAc)	Analytically pure	Sinopharm Chemical Reagent Co., Ltd.
N, N-Dimethylformamide (DMF)	Analytically pure	Sinopharm Chemical Reagent Co., Ltd.
Dimethyl sulfoxide (DMSO)	Analytically pure	Sinopharm Chemical Reagent Co., Ltd.
Tetrahydrofuran (THF)	Analytically pure	Sinopharm Chemical Reagent Co., Ltd.
Graphics processing unit (GPU)	GeForce RTX3070	NVIDIA

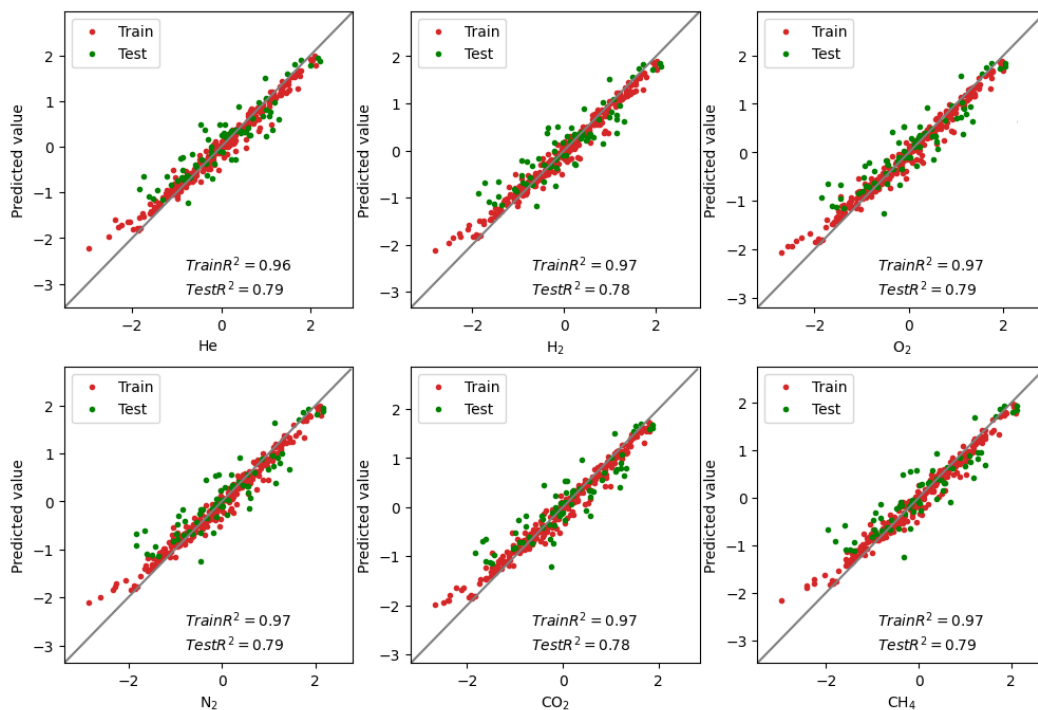


Fig. S1 Gaussian Regression scatter plot of R^2 prediction results

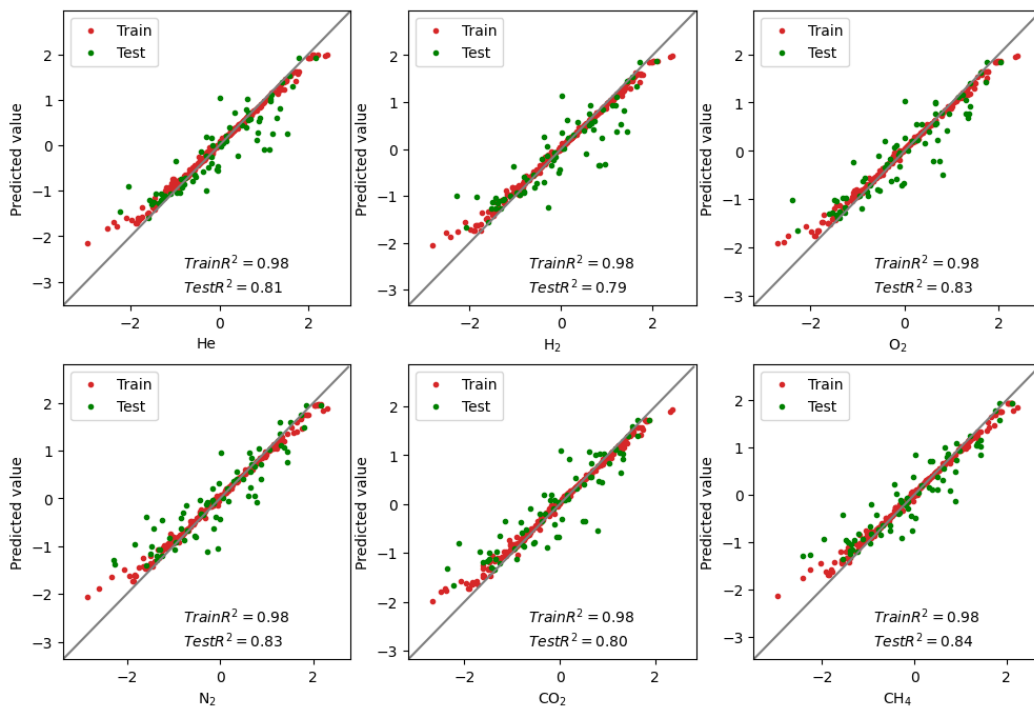


Fig. S2 Random Forest scatter plot of R² prediction results

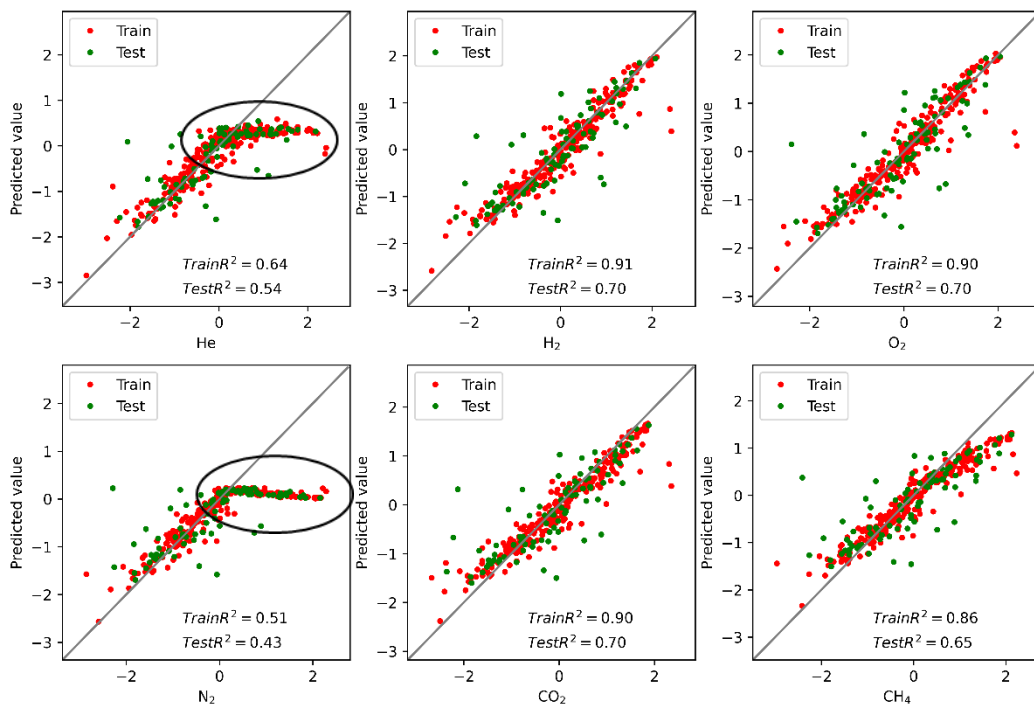


Fig. S3 DNN model scatter plot of R² prediction results

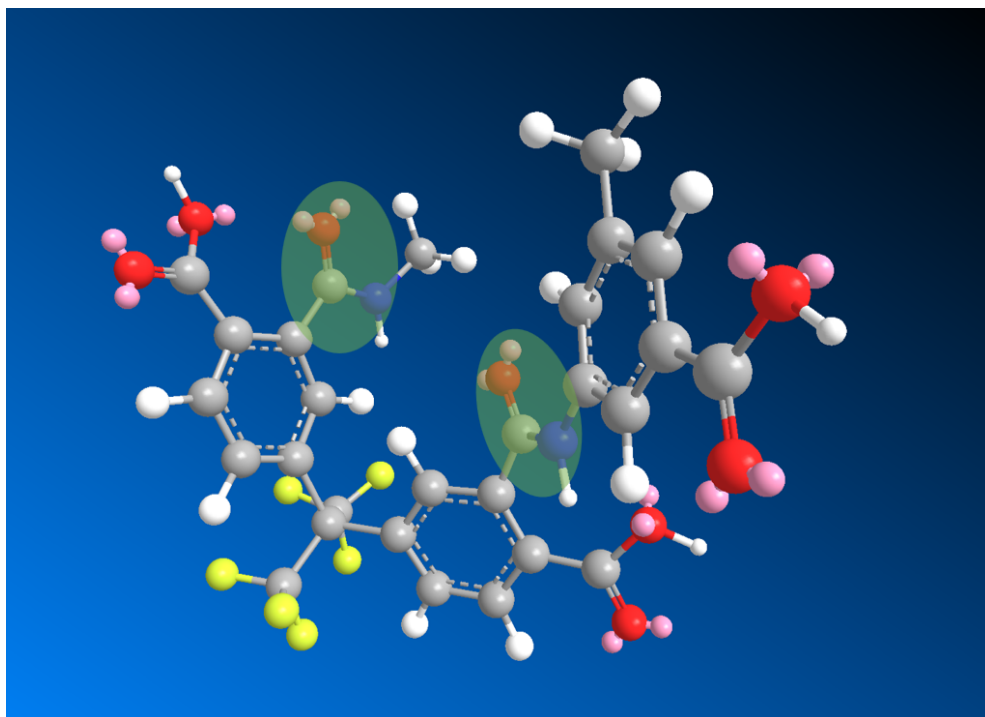
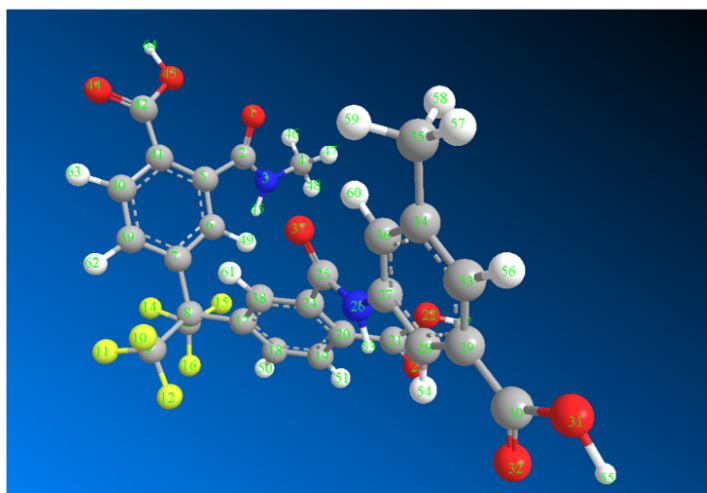


Fig. S4 Polyimide 6FDA-DABA, the carbonyl group of the amide part is connected to the nitrogen atom



Atom	Atom Type (MM2)	Charge (Huckel)
O(1)	O Carbonyl	-0.822463
C(2)	C Carbonyl	0.396361
N(3)	N Amide	0.252951
C(4)	C Alkane	-0.0482796
O(37)	O Carbonyl	-0.793682
C(25)	C Carbonyl	0.0700975
N(26)	N Amide	0.336989
F(10)	F	-0.255833

Fig. S5 Polyimide 6FDA-DABA, atomic charge of carbonyl group

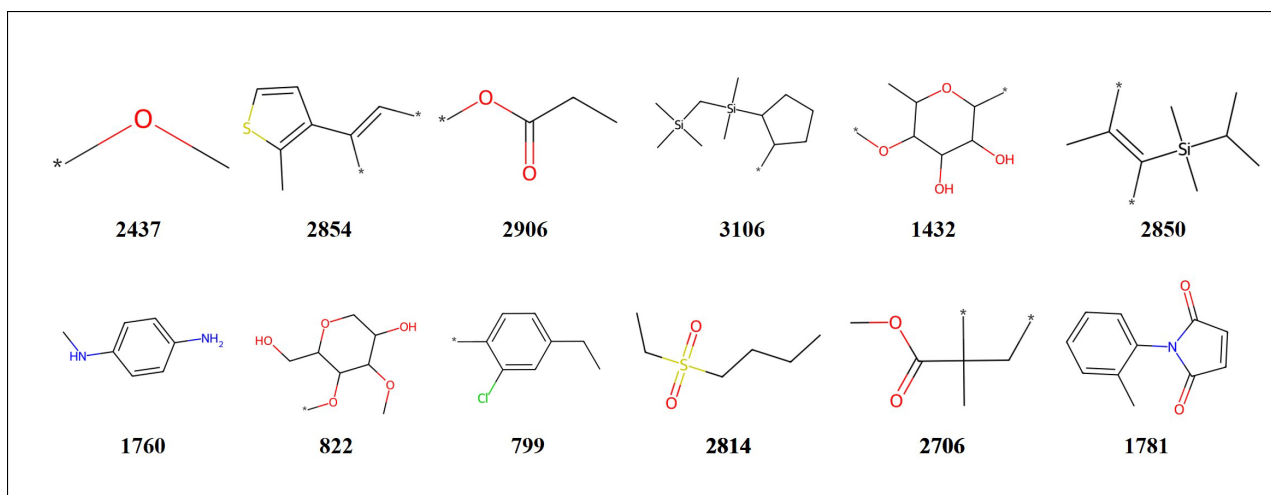


Fig. 11 Visualization of the most important substructures calculated using the SHAP method on the DNN-NCL model

The second most significant substructure is feature 2854, which represents the thiophene group. This substructure comprises a five-membered ring with a sulfur atom, which is characteristic of the thiophene ring. The presence of sulfur in the thiophene ring renders it aromatic and electron-rich. The introduction of a cyclic structure, such as thiophene, generally increases the rigidity of the polymer chain and reduces its flexibility, thereby reducing the free volume within the polymer matrix¹.

A further illustrative example is that of feature 2906, which represents an ester group.

In reality, esters are polar due to the presence of carbonyl (C=O) and ether (C-O-C) bonds². The transport behavior of gases in polymer membranes can be influenced by polar groups, although the extent of this influence varies depending on the nature of the gas in question. In the case of polar gases (e.g. H₂O, NH₃), the ester groups are capable of significantly increasing their affinity for the polymer through dipole-dipole interactions or hydrogen bonding³. This results in an enhanced solubility of these gases in the membrane. Despite CO₂ being a non-polar molecule, it interacts more strongly with ester groups than other non-polar gases (e.g. N₂ or CH₄) due to its

significant quadrupole moment and higher polarizability, resulting in higher solubility and permeability for CO₂⁴.

In the case of typical non-polar gases such as N₂ and CH₄, the influence of the ester group is primarily manifested in its impact on the polymer structure. Should the ester group facilitate further physical cross-linking within the polymer matrix or enhance crystallinity, thereby creating a more rigid polymer structure, this will result in a reduction in free volume and, consequently, a decrease in the permeability of the gas⁵. The impact of this structural alteration may differ depending on the specific gas in question. For instance, it may lead to a more pronounced reduction in the diffusion rate of larger molecules (e.g., CH₄) compared to smaller molecules (e.g., He, H₂).

The impact of the ester group on gas permeability can be attributed to a complex interplay between solubility and diffusivity. For polar gases and CO₂ the increase in solubility may be the dominant factor, leading to an increase in permeability. In contrast, for other non-polar gases the decrease in diffusivity due to structural factors is more significant, resulting in a decrease in permeability. This differential effect can be employed to adjust the selectivity of the membrane, for instance to enhance the separation efficiency of CO₂/N₂ or H₂O/CH₄.

The SHAP analysis provides an explanation for the dominant effect of the ester group on the increase in solubility and the decrease in diffusion rate of polyimide. The blue data points situated close to zero within the right-hand cluster in Figure 9E represent instances with low eigenvalues. The clustering of these low values near zero indicates that they exert a weak positive (or at least non-negative) effect on the model output. The warm points on the left represent instances with high eigenvalues, which exert a negative effect on the model output. This distribution indicates that the machine learning model considers the reduced diffusion rate

due to the structural changes in the polymer caused by the increased ester content to be of greater consequence than the increased solubility.

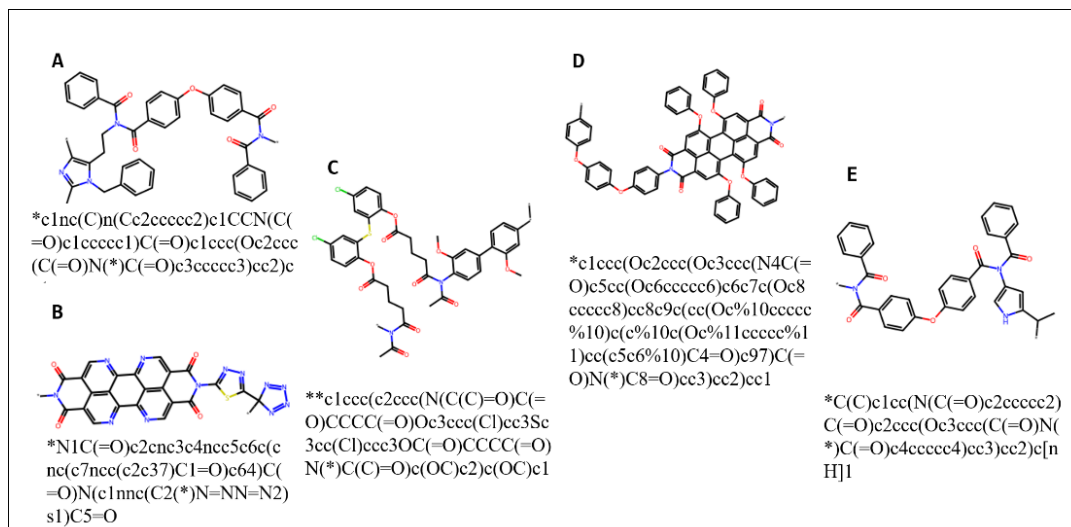


Fig. S6 Representative structural visualization in O₂/N₂ separation predictions

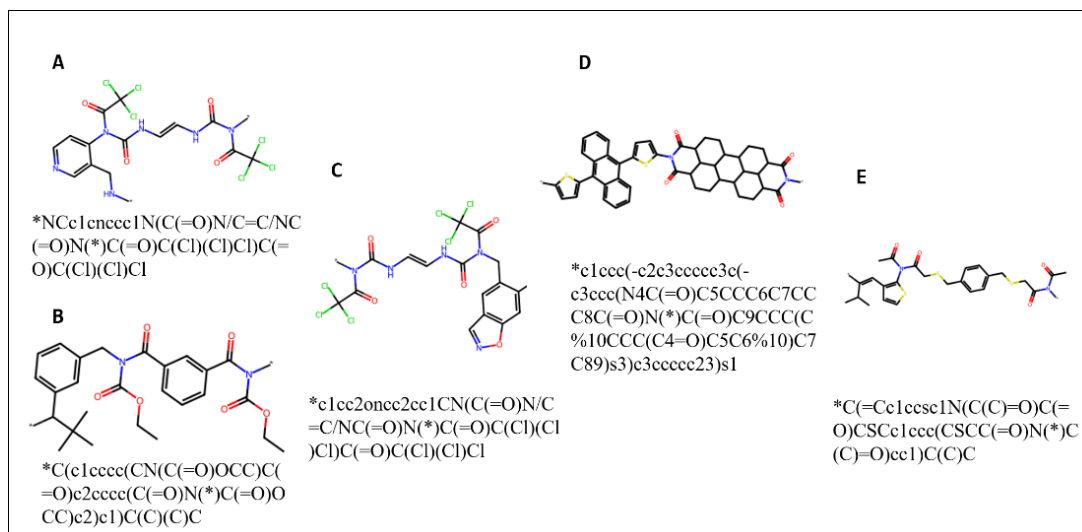


Fig. S7 Representative structural visualization in H₂/CO₂ separation predictions

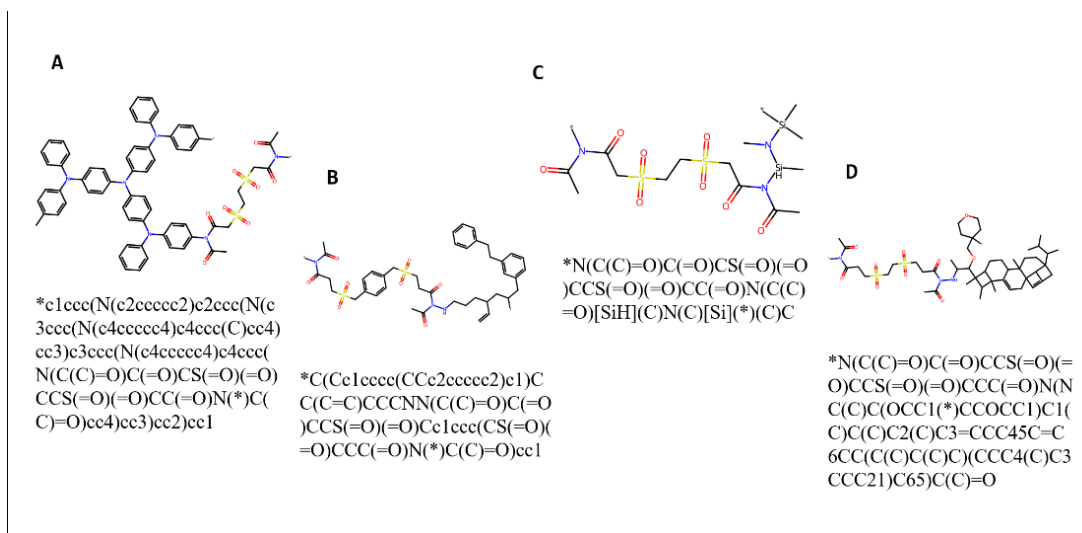


Fig. S8 Representative structural visualization in CH₄/CO₂ separation predictions

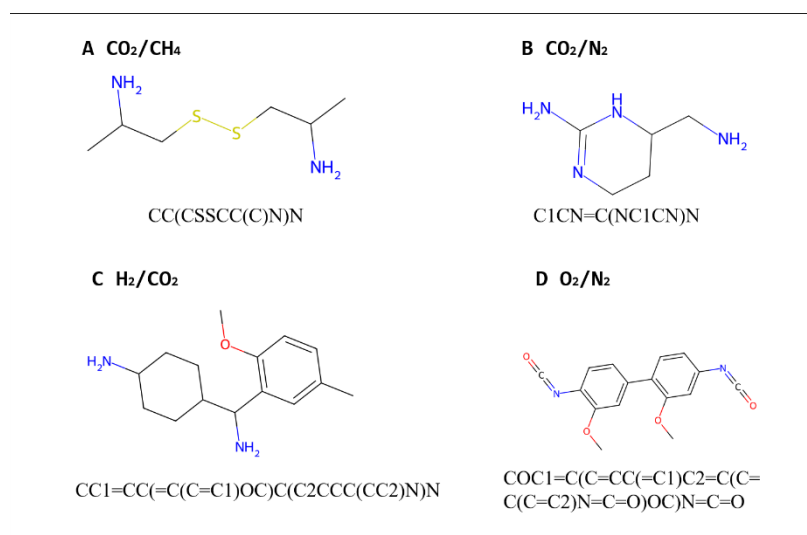


Fig. S9 Common features of model-predicted polyimide separation membrane structures that exceed existing Robeson limits

As illustrated in Figure S9A, in CO₂/CH₄ separation systems, the polyimide structure that exceeds the Robeson upper limit is distinguished by the presence of disulfide bonds (-S-S-) and amino groups (NH₂). The amino groups can facilitate the interaction between the two by forming hydrogen bonds with CO₂ molecules, thereby increasing the solubility and permeability of CO₂ in the membrane material⁶. Furthermore, the presence of disulfide bonds in the membrane

material enhances the membrane's flexibility and chemical stability⁷. The distribution of the disulfide bonds creates channels that are favorable for the diffusion of CO₂ molecules, whereas CH₄ molecules have a lower ability to pass through these channels due to their larger size.

As illustrated in Figure S9B, one of the common characteristics of polyimide structures that can exceed the Robeson upper bound in CO₂/N₂ separation systems are the presence of multiple amino (NH₂) and heterocyclic amine groups. The heterocyclic amine groups can provide additional adsorption sites in the polyimide membrane structure, thus promoting the adsorption of CO₂ molecules⁸. Moreover, the heterocyclic amine groups can enhance the solubility and diffusion rate of CO₂ in the membrane material by forming analogous interactions with the amine groups⁹.

As illustrated in Figure S9C, one of the defining characteristics of polyimides that exceed the Robeson upper bound in CO₂/H₂ separation systems is the presence of amino (NH₂) and benzene rings. The presence of benzene rings not only increases the rigidity and stability of the membrane material, but also facilitates the π - π interaction of the benzene ring with CO₂ molecules, thereby further enhancing the solubility of CO₂ in the membrane material¹⁰. In contrast, the interaction between H₂ molecules and the amino groups, oxygen atoms and benzene rings in the membrane material is relatively weak, which results in H₂ being adsorbed or chemically reacted with the membrane material to a limited extent¹¹. This weak interaction facilitates the rapid passage of H₂ through the membrane, preventing its retention by the membrane material.

As illustrated in Figure S9D, one of the defining characteristics of polyimides that exceed the Robeson upper bound in O₂/N₂ separation is the presence of benzene rings and methoxy groups (-OCH₃). The π -electron cloud of the benzene ring can form weak π - π interactions with the unpaired electrons in the O₂ molecule, thereby increasing the solubility of O₂ in the membrane.

Furthermore, the presence of methoxy groups affects the interaction of the polyimide structure with O₂ and N₂ molecules. Although both O₂ and N₂ are non-polar molecules, O₂ exhibits a slightly higher quadrupole moment and polarizability than N₂¹². The polar and electron-withdrawing effect of the methoxy groups enhances the interaction with O₂, thereby increasing the material's selectivity for O₂ relative to N₂.

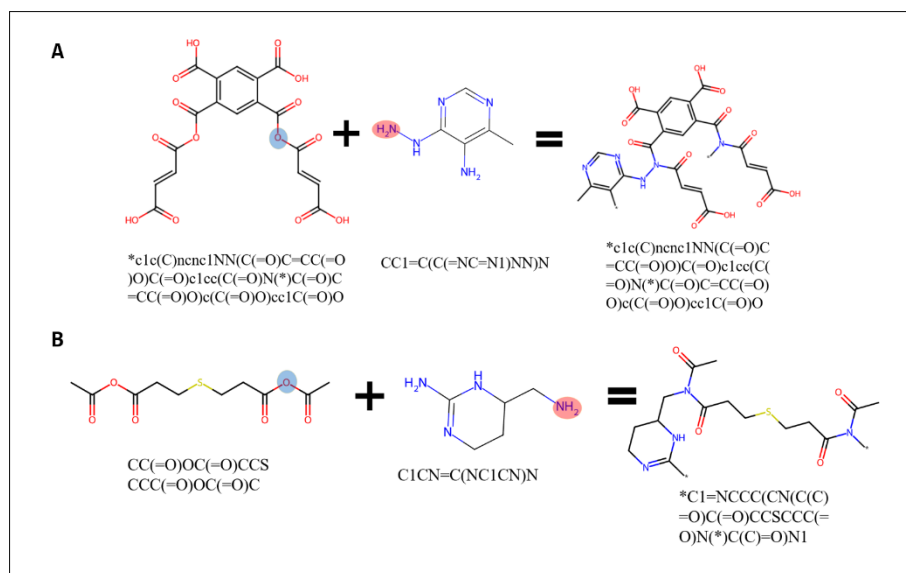


Fig. S10 The selective prediction results of the DNN-bagging model are mapped on previous research **A** Polyimide modified with methyl pyrimidine **B** Polyimide modified with tetrahydropyrimidin

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