A radical polymer for highly efficient solar evaporation and gas separation

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A radical polymer for highly efficient solar evaporation and gas separation

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Abstract

The unique magnetic, electronic and optical features derived from their unpaired electrons have made radical polymers an attractive material platform for various applications. Here, we report solution-processable radical polymer membranes with multi-level porosities and study the impact of free radicals on important membrane separation processes including solar vapor generation, hydrogen separation and CO\textsubscript{2} capture. The radical polymer is a supreme light absorber over the full solar irradiation range with sufficient water transport channels, leading to a highly efficient solar evaporation membrane. In addition, the radical polymer with micropores and adjustable functional groups are broad-spectrum gas separation membranes for both hydrogen separation and CO\textsubscript{2} capture. First principle calculations indicate that the conjugated polymeric network bearing radicals is more chemically reactive with CO\textsubscript{2}, compared with H\textsubscript{2}, N\textsubscript{2} and CH\textsubscript{4}. This is evidenced by a high CO\textsubscript{2} permeability in gas separation membranes made of the conjugated radical polymer.
Introduction

Membrane separation provides energy-efficient and environmentally sustainable solutions to clean water stresses, hydrogen economy and decarbonization.\(^1,^2\) The design of membrane materials with good processability, controllable high porosity at different levels and suitable functionalities is critical to realize effective separations, and is yet challenging. One example is solar-powered desalination membrane. Though a variety of traditional polymers, such as polyvinyl alcohol and cellulose, have been employed for solar evaporation, they mainly constitute the hydrophilic matrix for water transport without desirable photothermal response.\(^2,^4\) Additional solar absorbers including carbon nanotubes (CNTs),\(^5\) plasmonic Au nanorods,\(^6\) graphene sheets\(^7\) and solar interactive conjugated polymers\(^11\) (conductive or metallic, which are typically hydrophobic and difficult to process) need to be blended with the polymer matrix to enable sufficient solar energy utilization.\(^4,^8\) Thus, traditional polymer-based membranes for solar vapor generation require complicated design to achieve optimal performance. A polymer with broad solar absorption capacity and efficient water transporting ability is highly desirable for solar evaporation.

Another example is gas separation, including hydrogen purification and carbon capture. Current commercial gas separation membranes are fabricated from a few polymers with low permeability and high selectivity for the easy processability of such polymers.\(^9,^10\) The low gas permeability of commercial membranes requires large membrane size for sufficient production, which is a critical cost challenge for
industrial applications. Recently, polymers of intrinsic microporosity (PIMs) membranes have been reported as promising candidates for CO$_2$ separation due to their good solution processability and high CO$_2$ permeability.$^{11,12}$ In addition to their pore size-exclusive effect, the functionality of pore surface in PIMs also plays an important role in enhancing CO$_2$ transport. In particular, the adsorption of CO$_2$ molecules is favored on pore surface with high polarities because of the van der Waals interaction between CO$_2$ molecules and polar groups, such as –OH, -NH$_2$ or –COOH, which increases the CO$_2$ adsorption concentration, and thus an enhancement in CO$_2$ permeability. However, one drawback of PIMs is that they suffer a substantial plasticization effect from CO$_2$, leading to performance decay.$^{13,14}$ Post membrane treatments such as cross-linking are proposed for improving the performance at the expense of compromised permeability.$^{14}$ Crosslinking is also demonstrated as an effective approach to maintain stable H$_2$/CO$_2$ selectivity at industrial relevant high temperature for hydrogen purification.$^{10,15}$ Therefore, a covalently cross-linked polymer with high porosity at sub-angstrom level and processability are ideal candidates for gas separation. In addition, CO$_2$-philic functionalities within the polymer can enable better separation performances for carbon capture.

Radical polymers have been developed as an emerging material platform for a plethora of advanced applications such as energy storage,$^{16,17}$ plastic magnetics$^{18,19}$ and photothermal therapy,$^{20,21}$ owing to their unique magnetic, electronic and optical properties derived from their unpaired electrons.$^{22,23}$ Here, we report
solution-processable radical polymer membranes with multi-level porosities, which can serve as a versatile platform for multiple separations. The radical polymer was prepared via self-polymerization of 7,7,8,8-tetracyanoquinodimethane (TCNQ) in a strong acid. We investigate how the free radicals impact on the solar vapor generation and the gas separation performances of the membranes. When the membrane is used as a solar vapor generation membrane, it shows a water evaporation rate of 1.68 kg m$^{-2}$ h$^{-1}$ via a 92% solar energy efficiency under 1-sun irradiation. These values are achieved because the inherent water transport channel and free radicals which facilitate the light absorption and photothermal effect. Theoretical calculation shows that the existence of free radicals largely expands the absorption spectrum range, thus enhancing the solar irradiation utilization. In addition, the porous radical polymer membrane can be employed as gas separation membranes. The membrane with unreacted $-$CN groups shows H$_2$ and CO$_2$ permeabilities of 1351 barrer and 751 barrer, respectively, with ideal H$_2$/CH$_4$ and CO$_2$/CH$_4$ selectivities of 75 and 42, respectively. After transferring $-$CN groups into CO$_2$-affinitive $-$COOH groups, the CO$_2$ permeability experienced a sharp enhancement to 1462 barrer, leading to high performance CO$_2$ capture membrane with a CO$_2$/CH$_4$ selectivity of 34. First-principles calculations suggest that radicals are more chemically reactive with CO$_2$, compared with H$_2$, N$_2$ and CH$_4$, which contribute to the high CO$_2$ permeability.
Results and discussions

The self-polymerization of 7,7,8,8-tetracyanoquinodimethane (TCNQ) was conducted in a Brønsted superacid, trifluoromethanesulfonic acid (TFMSA), in an autoclave, which serves as both the solvent and catalyst. After heating the autoclave at 170 °C for 15 hours, the yellow TCNQ/TFMSA (1:34 in weight ratio) solution was transformed into a black gel membrane. Figure 1a shows schematically the
polymerization process. The formation of the cross-linked polymeric gel membrane, rather than insoluble powder or bulk morphology for other triazine-based polymers, can be ascribed to the strong interaction between the basic triazine rings of as-synthesized polymer and the superacidic TFMSA. Such effects have also been utilized to process nitrogen-rich engineering plastics and other graphite-like materials in concentrated sulfuric acid. In the as-prepared radical polymer/TFMSA gel membrane, TFMSA accounts for 97.15% of the total weight. The chemical composition of the radical polymer (denoted as RP-CN) after removing TFMSA was investigated by X-ray photoelectron spectroscopy (XPS) study. As shown in Figure 1c, the N1s spectra of RP-CN shows two distinct peaks at ~398.7 eV and ~401.4 eV. The first peak can be assigned to the –C=N-C- of formed triazine rings. The second peak is associated with unreacted nitrile group, which accounts for 20.5% of whole N content. This was also observed in covalent triazine-based framework prepared under ionthermal conditions.
Figure 2 | First-principles calculations on f-RP without/with the radical state. 

a, Optimized atomic structure of the f-RP molecule in the ground state, and f-RP with one-radical state, in which the spin-density is visualized by using green color with an iso-surface value of $3.0 \times 10^{-3} \text{e/Å}^3$. b, The calculated adsorption energies between gas molecules and f-RP with (red column) and without (blue column) radical. c, The density of states (DOS) of the f-RP without (upper figure) and with (lower figure) the radical state, where the Fermi level is shifted to 0 eV, and the magenta dash line denotes the band gap. d, The calculated optical adsorption spectra of the f-RP without (upper figure) and with (lower figure) the radical state, where xx and yy denote the incident light polarization directions.

An intense electron paramagnetic resonance (EPR) spectrum in Figure 1d demonstrates the presence of free radicals in RP membrane with a $g$ value of 2.0036,
which are normally assigned to carbon-based radicals with some spin densities associated with nitrogen atoms.\textsuperscript{18} We further employ first-principles calculations to investigate the effect of radical state on the electronic and optical properties of the radical polymer. A fragment containing a triazine ring formed \textit{via} the trimerization of three \textendash CN groups from three TCNQ molecules is used as a simplified model structure (denoted as \textit{f}-RP). The atomic structure of \textit{f}-RP in the ground state (no radical state) is shown in Figure 2a, which is a planar structure. To simulate the radical state, one possible way is to rotate the TCNQ side chains by 90°, as suggested in the previous studies.\textsuperscript{18} We can see that after the rotation, the \textit{f}-RP becomes spin-polarized, which is the feature of the radical state. The calculated magnetic moment is about 1.97 μB. This is because that the side chain is distorted when forming the radical state. This distorted structure could reduce the electronic coupling with other side chains, thus introducing singly occupied molecular orbital (SOMO) near Fermi level. The electrons occupied in localized SOMO states are associated with large effective mass, which can interact with photons more effectively. This is beneficial to convert the photon energy to thermal energy.

On the other hand, the localized electronic states near Fermi level are energetically unstable, and they can be spontaneously split and form the spin-polarized states (Stoner magnetism) (see Supplementary Fig. 11). It turns out that this radical state favours the spin-polarization, as its energy is about 0.36 eV lower than that of the non-polarized state for the distorted structure. The formation of radical state in the
f-RP has significant impact on the electronic and optical properties. For example, the band gap of the f-RP with the radical state is much smaller than that of the f-RP in the ground state. As the DOSs shown in Figure 2c, the PBE band gap of the f-RP with the radical state is about 0.33 eV, in contrast with 1.22 eV in the non-radical state. This would extend the absorption of the irradiation light into higher wavelength, resulting in a much broader light adsorption in the f-RP with the radical state. By comparing the optical adsorption spectra of f-RP with (lower figure in Figure 2d) and without (upper figure in Figure 2d) the radical state, it is evident that with the formation of the radical state, the optical adsorption is extended from ~1020 nm into ~1642 nm. More importantly, the adsorption in the visible light range (from 400 nm to 700 nm) is also much enhanced. All these results suggest that the formation of the radical state in the f-RP is beneficial to the interaction with the irradiation light, enabling a higher efficiency for the adsorption of the visible light. The excellent absorption features of RP are confirmed experimentally with UV–vis–NIR absorption spectra. As shown in Figure 3b, RP showed an average light absorption of 97.8% and a solar absorption of 99.5% at a wide wavelength range from 250 to 2500 nm, enabling high solar energy harvesting over full solar spectrum.
Figure 3 | Solar evaporation performance of RP-water/GF membrane. a, Schematic of solar vapour generation based on radical polymer membrane. b, UV–vis–NIR spectrum of RP-water membrane. The normalized spectral solar irradiance density of air mass 1.5 global tilt solar spectrum is shown by the blue dotted line. c, Infrared image showing the temperature distribution after irradiation time of 180 s under 1-sun irradiation. d, Surface temperature variation of RP-water/GF over time under 1-sun irradiation. e, Mass loss of water with and without the RP-water/GF membrane over time under 1-sun irradiation.
As discussed, the strong interaction between the Brønsted superacid TFMSA and basic triazine rings expanded the cross-linked polymer skeleton, resulting in a polymeric gel membrane. After immersing the RP/TFMSA in ultrapure water, TFMSA was exchanged with water molecules to form a water swollen RP membrane. In this way, a single polymer that efficiently absorbs solar irradiation and transports water simultaneously was obtained, which is unusual for polymer-based solar vapor generation membranes. The weight percentage of RP is increased from 2.85 wt% in the RP/TFMSA gel membrane to 15.1 wt% in RP/water membrane, while the RP/TFMSA gel membrane shrunk to ~25% of its original volume after transforming to RP/water membrane. Such a dramatic change in volume results in a twisted membrane shape. To prepare the RP/water membrane for solar vapor generation test, a glass-fiber filter membrane was used as a scaffold to improve the mechanical strength and achieve a flat gel membrane (Supplementary Fig. 5). The obtained membrane was denoted as RP-water/GF. Though RP-water has a water content of ~85 wt%, one should note that water desorption-adsorption in RP-water is irreversible. Once water molecules are expelled, the cross-linked RP polymer skeleton will form a compact structure with insignificant water swelling ratio.

Figure 3a illustrates schematically the solar vapor generation based on radical polymer membrane. The surface temperature of RP-water/GF membrane quickly rises under sun irradiation. The infrared image of the hydrogel membrane irradiated for 3 minutes under 1-sun illumination demonstrates equilibrium surface temperature of
around 37.2 °C (Figure 3c). The plateaued surface temperatures are ~40 °C for 1-sun irradiations, as shown in Figure 3d. After the evaporation rate reaches the steady state, the mass changes with and without RP-water/GF membrane over time under 1-sun irradiation are recorded and shown in Figure 3e. The evaporation rates with the membrane are around 1.68 kg m\(^{-2}\) h\(^{-1}\), which are much higher than that of pure water. The solar–vapor conversion efficiency can be calculated by the following formula:

\[
\eta = \frac{\dot{m}h_{LV}}{C_{opt}P_0}
\]  

in which \(\dot{m}\) is the mass flux, \(h_{LV}\) is the latent enthalpy of the liquid-vapour phase change, \(P_0\) is the solar irradiation power of one sun (1 kW m\(^{-2}\)), and \(C_{opt}\) refers to the illumination intensity on the membrane surface\(^{32}\). We measured the vaporization enthalpy of water in RP-water by differential scanning calorimetry (DSC) experiment (Supplementary Fig. 6). The calculated vaporization enthalpy of water is around 1972 J g\(^{-1}\), which is smaller than the theoretical value for bulk water (2444 J g\(^{-1}\))\(^{4,33,34}\). This observation is also reported in hydrogel membranes, in which confined water molecules may escape the polymer network as small clusters\(^{4}\). The calculated energy efficiency for RP-water/GF is ~92% for 1-sun irradiation. Such a high energy efficiency can be ascribed to the excellent absorption features of the radical polymer membrane not only in visible light range, but also in NIR window due to the SOMO energy level arise from free radicals. The energy for electron transition from HOMO to SOMO matches with NIR light. The surface morphology of the RP-water/GF membrane show no obvious change before and after 1-sun irradiation (Supplementary Fig. 7), indicating that the water transport in the membrane is efficient. This is
benefited from the high water content in the porous polymeric network (~84.9 wt% in RP-water and ~70.0 wt% in RP-water/GF).

Figure 4 | Gas separation performances of RP-CN and RP-COOH. a, schematic illustration of synthesis of RP-COOH from RP-CN. b, Surface SEM images of RP-CN membrane. Inset: Optical image of a RP-CN membrane. c, Single-gas permeabilities (H₂, CO₂, N₂, and CH₄) through RP-CN and RP-COOH membranes at 30 °C and a transmembrane pressure of 1 bar. d, CO₂ sorption isotherms of RP-CN and RP-COOH obtained at 35 °C over a range of pressures from 0 to 10 bar. e, The o-positron lifetime (and hence free volume diameter) distribution in RP-CN and
RP-COOH at 30 °C based on PALS measurements. Robeson plots for H₂/CH₄ gas pairs with the 1991 upper bounds indicated by a pink line and 2008 upper bounds by a blue line. The single-gas permeation data of RP-CN membrane (red star) were compared with accumulated literature data for state-of-the-art ultrapermeable PIMs (yellow squares), microporous solids (zeolites, MOFs, POPs and inorganic 2D material, blue triangles) and commercial polymer membranes (green triangles). Robeson plots for CO₂/CH₄ gas pairs with the 1991 upper bounds indicated by a pink line and 2008 upper bounds by a blue line. The single-gas permeation data of RP-COOH membrane (blue star) was compared with accumulated literature data of PIM-PIs (green diamond) and ladder PIMs (purple triangles).

Further, we investigate how the radicals impact the transportation of gas molecules through the radical membrane. The prepared dense and homogeneous radical polymer membrane was denoted as RP-CN, see Method for preparation details. RP-CN has a smooth surface under scanning electron microscopy as shown in Figure 4b. It is well known that nitrile groups can be further oxidized to form carboxyl groups under basic environment. When RP-CN membrane was treated in 10 mM NaOH/IPA solution for 24 hours at 70 °C, the N1s XPS peak at ~401.4 eV disappears, indicating that the nitrile groups is transformed (Supplementary Fig. 8a). This is further confirmed by FTIR study. Though nitrile group is not detected for RP membrane, the base treated membrane shows an additional peak at ~1722 cm⁻¹ associated with –COOH group (Supplementary Fig. 8b). The EPR signals remains in RP-COOH membrane after
Gas permeation studies through the homogenous and free-standing RP membranes were carried out in a permeation cell at 30 °C and a transmembrane pressure of 1 bar with industrially important gases including H₂ over CO₂, N₂ and CH₄. Figure 4c shows the permeability of various gases as a function of their kinetic diameter. RP-CN membrane shows impressive permeabilities for H₂ (1351 barrer) and CO₂ (751 barrer), while much lower values are observed for N₂ (83 barrer) and CH₄ (18 barrer). The ideal selectivities of H₂ over N₂ and CH₄ are ~16 and ~75, respectively. This is explained by the small free volume of RP-CN of 4.92 Å as is detected by position annihilation lifetime spectroscopy (PALS, Figure 4e) and the low tendency of CH₄ to interact with nitrogen-rich RP-CN polymer. The separation performances for H₂/CH₄ are demonstrated in the Robeson upper bound plot (Figure 4f). It shows that the separation performance of RP-CN for H₂/CH₄ surpasses both the 1991 and 2008 Robeson upper bounds, and is comparable to recently reported state-of-art materials, including ultrapermeable PIMs, microporous frameworks and inorganic 2D materials, suggesting the high porosity of RP-CN polymer at sub-nanometer level that facilitates hydrogen transport while blocking the permeation of CH₄.

We also notice that RP-CN shows considerable CO₂ permeability (751 barrer) at excellent CO₂/CH₄ selectivity (42). To gain more insights, the interactions of radicals with gas molecules are studied by first-principles calculations. The calculated
adsorption energies between gas molecules and f-RP with (red column) and without (blue column) radical are shown in Figure 2b, from which we can see a relatively large increment in the adsorption energy for CO$_2$ adsorbed on f-RP with radical, compared with that of other molecules (H$_2$, N$_2$ and CH$_4$) and without the radical. It can be understood that the f-RP with radical is more chemically reactive than the f-RP without radical. It is noted that the orbital polarization in CO$_2$ induced by the external influence might be slightly easier compared with other molecules studies, which thus leads to stronger adsorption. In addition, the affinity between the nitrogen-rich characteristics of triazine rings and CO$_2$ may also contribute to the considerable CO$_2$ uptake in RP-CN (Figure 4d).$^{35}$

It is interesting to note that after converting the remaining nitrile groups to carboxyl groups, a slight drop in H$_2$ permeability is observed with a sharp increase in CO$_2$ permeability for RP-COOH membrane, when compared with the original RP-CN membrane. The permeabilities of RP-COOH membrane are 1278 barrer for H$_2$, 1462 barrer for CO$_2$, 77 barrer for N$_2$ and 43 barrer for CH$_4$. The ideal selectivities of CO$_2$ over N$_2$ and CH$_4$ of are $\sim$19 and $\sim$34, respectively. The separation performances for CO$_2$/CH$_4$ are demonstrated in the Robeson upper bound plot (Figure 4g). It surpasses both the 1991 and 2008 Robeson upper bounds, and exceeds most of the recently reported state-of-art PIMs. In addition to the radicals and triazine rings, the −COOH groups in RP-COOH favorably interacts with CO$_2$ $\textit{via}$ hydrogen bonding and electrostatic interactions.$^{36-38}$ Specifically, the oxygen in CO$_2$ forms hydrogen bond
with the acidic hydrogen in the –COOH group, while the electrostatic interaction is derived from the partial polarization of the positive carbon in CO₂ and the negative oxygen of carbonyl in the –COOH group.⁶,⁷ Thus, RP-COOH shows higher CO₂ sorption over the full range of pressure than RP-CN (Figure 4d), enhancing the permeability of the RP-COOH membrane. The slight drop of H₂ permeability maybe contributed by the lower fractional free volume and tighter average chain spacing after carboxyl functionalization in RP-COOH,⁹ evidenced by PALS study (Figure 4e).

In summary, we report a radical polymer for solar vapor generation and gas separation. The pronounced solar vapor generation performances are attributed to the expanded conjugated polymeric network bearing radicals. It is a highly efficient light absorber over the full solar irradiation range with sufficient water transport channels, which is unusual for polymer-based membranes. In addition, the radical polymer is composed of micropores and adjustable functional groups, which can be employed as broad-spectrum gas separation membranes for both hydrogen purification and carbon capture. We expect that such a processable conjugated radical polymers with controllable multi-level high porosity will open up exciting new opportunities for scalable and high-performance separation schemes for energy-efficient and environmentally benign separation processes.

Methods
Preparation of RP/TFMSA gel membrane and RP-water membranes

Briefly, 1.6 mL of Trifluoromethanesulfonic acid (TFMSA, Sigma-Aldrich, reagent grade) was added to 0.08 g of 7,7,8,8-tetracyanoquinodimethane (TCNQ, >98%, TCI) in a glass vial at room temperature in a glove bag filled with nitrogen. After stirring for 1 minute, the yellow solution was transferred into a glass dish, which was sealed in a 100 mL autoclave and heated at 170 °C for 15 hours. After slowly cooling down to room temperature, RP/TFMSA gel membrane was obtained. RP-water membrane was prepared from RP/TFMSA gel membrane by solvent exchange with N-methyl-2-pyrrolidone (NMP) for 3 days and ultrapure water for 3 days, subsequently. The obtained RP hydrogel membrane was stored in DI water before use.

Preparation of RP-water/GF composite membrane for solar evaporation

Briefly, 1.6 mL of TFMSA was added to 0.08 g of TCNQ in a glass vial at room temperature in a glove bag filled with nitrogen. After stirring for 1 minute, the yellow solution was drop-cast onto a GF/F glass-fiber filter membrane (4.7 cm in diameter, 0.67 mm in thickness, Whatman) in a flat glass dish (5.0 cm in diameter). The glass dish was sealed in a 100 mL autoclave and heated at 170 °C for 15 hours. After slowly cooling down to room temperature, the obtained gel-like membrane was immersed in NMP for 3 days to remove TFMSA, followed by immersion in DI water to remove NMP. Normally, no sulfur signal which is characteristic of TFMSA can be detected by XPS study after 3 days of solvent exchange with NMP. The obtained black gel
membrane was stored in DI water before solar evaporation measurements.

**Preparation of RP-CN and RP-COOH membranes for gas separation**

1.6 mL of TFMSA was added to 0.08 g of TCNQ in a glass vial at room temperature in a glove bag filled with nitrogen. After stirring for 1 minute, the yellow solution was transferred into a flat glass dish (5.0 cm in diameter) and allowed to spread into a thin layer. The glass dish was sealed in a 100 mL autoclave and heated at 170 °C for 15 hours. After slowly cooling down to room temperature, the obtained gel-like membrane was sandwiched between two glass plates to protect the nitrile groups from moisture exposure and maintain its flat configuration. The sandwiched structure was heated at 150 °C for 4 days to slowly remove most of CF₃SO₃H. Then the membrane was immersed in NMP for 3 days to remove the excess CF₃SO₃H. Normally, no sulfur signal can be detected by XPS study after 3 days of solvent exchange. The obtained black RP-CN membrane was stored in DI water. RP-COOH membrane was fabricated by heating RP-CN membrane in a 10 mM NaOH solution in isopropanol at 70 °C for 24 hours, followed by immersing in a 1 M aqueous HCl solution, to allow the transformation of –CN groups into –COOH groups.

**Solar vapor generation measurements**

The steam generation studies were performed in a constant temperature (25 °C) and relative humidity (55%) atmosphere with a sun simulator (Solar-500, NBet, China). A homemade real-time monitoring device was employed to evaluate the photothermal
water evaporation performance. In each experiment, the light intensity on the absorber was monitored using an optical power meter (Newport, 843-R) with a thermopile sensor (Newport, 919P-010-6), while the water evaporation rate was recorded in real time with an electronic analytical balance with 0.1 mg resolution (ATX224, SHIMADZU Co., Japan). The sample membranes were cut into circles with 20 mm diameters for performance evaluation.

Gas permeation measurements

Gas permeation properties of pure gases were tested with a variable-pressure constant-volume gas permeation cell. The membrane was mounted onto the permeation cell and vacuumed overnight before tests. Pure gas permeability was tested following the order of H₂, N₂, CH₄, and CO₂. The cell temperature was kept constant at 30 °C. The gas permeability through the membrane was calculated according to the steady state pressure increment (dp/dt) as given by the following equation:

\[
P = \frac{273 \times 10^{10}}{760} \frac{Vl}{AT(P_2 \times \frac{T}{14.7})} \frac{dp}{dt}
\]

(2)

where \(P\) denotes the gas permeability in Barrer (1 Barrer=1×10⁻¹⁰ cm³ (STP)·cm cm⁻² s⁻¹ cmHg⁻¹), \(V\) refers to the volume of the downstream reservoir (cm³), \(A\) is the effective membrane area (cm²), \(l\) represents the membrane thickness (cm), \(T\) is the testing temperature (K) and \(P_2\) is defined as the upstream pressure of the system.

The ideal gas selectivity (\(\alpha\)) between two different gases across a membrane is the
ratio of their single gas permeability as described in the following Equation:

$$\alpha_{A/B} = \frac{P_A}{P_B}$$

(3)

where $P_A$ and $P_B$ refer to the permeabilities of gases $A$ and $B$, respectively.

**First-principles calculations**

All the first-principles calculations were carried out using density-functional theory based Vienna *ab initio* simulation package (VASP 5.4.4.18) with the spin-polarization, in which the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional and projector augmented-wave (PAW) method based pseudopotentials were used. The cut-off energy for the electronic plane-wave expansion was set to 400 eV, and $\Gamma$-center single $k$-point was applied for sampling the first Brillouin zone. For all the calculations, the energy and force on each atom were converged to smaller than $10^{-8}$ eV and 0.01 eV/Å, respectively.

The radical state in the f-RP was simulated by rotating the side chain by $90^\circ$, as suggested in the previous study. The optical spectra of f-RP in the ground and radical state were calculated at the PBE level using random phase approximation (RPA), where 360 unoccupied states, and six lowest unoccupied and highest occupied states were included in the calculations. For the $\text{H}_2$, $\text{N}_2$, $\text{CO}_2$ and $\text{CH}_4$ molecules on the ground state and radical state of f-RP, we considered all the possible high-symmetric adsorption configurations, and the relevant adsorption energies $E_a$ were calculated by the equation below with the Van der Waals effect (DFT-D3):
\[ E_a = E_{M+TCNQ} - E_M - E_{TCNQ} \]  \hspace{1cm} (4)

where \( E_{M+TCNQ} \) is the total energy of the adsorbed molecule and the adsorbent f-RP, and \( E_M \) and \( E_{TCNQ} \) are the total energies of the isolated molecules (\( M=\text{H}_2, \text{N}_2, \text{CO}_2 \) or \( \text{CH}_4 \)) and the f-RP, respectively.

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**Author contributions**

S.Z. supervised the project. W.L. synthesized the materials and conducted the gas separation experiment. M.Y. performed the theoretical calculations. W.L. and J.L. performed solar vapor generation measurements. M.J.Y helped with solid-state NMR. J.L. helped with DSC test. Y.Q.L and F.L helped with PALS test. Z.X.C helped with UV-vis-NIR spectra. S.J. and J.W helped with CO2 sorption study. W.L. and S.Z. analyzed the data and wrote the manuscript with contributions from all the authors.

**Competing financial interests**

The authors declare no competing financial interests.
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