The ability to precisely monitor temperature at a high resolution is an important task, particularly in terms of safety. Inspired by natural thermosensitive transient receptor potential cation channels, we developed a temperature sensor based on thermal-driven ionic charge separation. To mimic the function of nature, an ionic covalent organic framework-based nanofluidic membrane was fabricated. By engineering the membrane to separate two electrolyte solutions, the temperature difference across the membrane can synchronously induce a potential. The high charge density and narrow channel size render extraordinary permselectivity to the membrane, thus offering a thermosensation selectivity of up to 1.25 mV K⁻¹, superior to that of any known natural system. Additionally, the generated potential is linearly related to the introduced temperature gradient, thus allowing for precise detection. With these attributes, an alarm device with high thermosensation sensitivity was constructed, demonstrating great promise for environmental temperature monitoring.

**Keywords:** covalent organic framework, nanofluidic membrane, thermosensation, ionic charge separation, temperature monitoring

# Introduction

Temperature is one of the fundamental parameters in science and engineering.¹⁻³ Respective sensors are ubiquitous in daily life and in almost all industrial processes. It is estimated that temperature sensors occupy ~80% of the worldwide sensor market.⁴⁻⁶ The physicochemical underpinnings of the current thermal sensation systems include (1) thermometers based on the thermal expansion of encased liquids, (2) optical sensors...
Covalent organic frameworks (COFs) are regular open matrices linked by organic struts. In two-dimensional (2D) COFs, the layered sheets are stacked face-to-face in the third dimension, forming continuous transport channels. With such stunning structures, these materials have received considerable attention in the material community. The practicality of COFs in comparison with other materials for the design of nanofluidic membranes comes from their purely organic composition, which provides stability. Additionally, the monomer design can be fine-tuned due to the endless number of organic reactions at a chemist’s disposal, resulting in a material that retains its robustness while providing a large number of available functional groups in nanospaces. In this contribution, we demonstrate that COFs possess all the necessary traits for the design of high-performance thermosensation devices based on thermal-driven ionic charge separation. To address this challenging topic, a carboxylic acid-functionalized COF membrane (COF-COOH) was fabricated by pairing 1,3,5-triformylphloroglucinol (Tp) and 2,5-diaminobenzoic acid (Db). Owing to its ultrasmall one-dimensional channel size (1.2 nm) and highly negatively charged surface, the resulting membrane was highly permselective, screening the transport of anions while favoring that of cations, thereby leading to significant transmembrane potentials in response to temperature gradients with a sensitivity of up to 1.25 mV K⁻¹ (Figure 1). In addition, the thermoelectric response was rapid, stable, reproducible, and reversible, thus providing an alternative option for constructing a temperature monitoring system.

**Experimental Methods**

**Fabrication of the free-standing COF-COOH membrane**

The free-standing COF-COOH membrane was synthesized via interface condensation of Tp and Db. The Db (36.0 mg, 0.236 mmol) dispersed in a p-toluene sulfonic acid (TsOH, 89.8 mg, 0.472 mmol) aqueous phase (20 mL) was gently placed on top of the Tp (33.1 mg, 0.157 mmol) dichloromethane (20 mL) solution. The system was kept at 35 °C for 3 days. The free-standing COF-COOH was obtained as a brown powder after being washed thoroughly with water and ethanol in sequence and then dried under vacuum for further characterization.

**Fabrication of COF-COOH/PAN**

COF active layers were formed via interface polymerization on the surface of an asymmetric polyacrylonitrile
The PAN support was vertically placed in the middle of a homemade diffusion cell, resulting in a volume of 7 cm³ in each cell (Supporting Information Figure S1). An aqueous solution of Dba (12.6 mg, 0.083 mmol) and TsOH (31.5 mg, 0.165 mmol) (7 mL) and the CH₂Cl₂ solution (7 mL) of Tp (11.6 mg, 0.055 mmol) were separately introduced into the two sides of the diffusion cell. The reaction mixture was kept at 35 °C for 3 days. The resulting membrane was rinsed with methanol to remove any residual monomers and catalyst. Finally, each membrane was rinsed with water for 24 h and then used for tests or air-dried for physicochemical characterization.

Results and Discussion

Nanofluidic membrane fabrication and characterization

The free-standing COF-COOH membrane was synthesized by interfacial polymerization, as depicted in Figure 2a, whereby the Dba dispersed in the TsOH aqueous phase was gently placed on top of the Tp dichloromethane solution (Figure 2b). The structure and crystallinity of the resulting COF membrane were scrutinized by powder X-ray diffraction (PXRD). The diffraction peak of 4.54° at 2θ is ascribed to the (100) plane of COF-COOH. The appearance of a characteristic peak of 26.6° at 2θ, attributable to the (001) plane, suggests the preferential planar orientation of the 2D sheets in the membrane (Supporting Information Figure S2). The experimental PXRD profile displays only limited deviations from the eclipsed stacking mode (Supporting Information Figure S3). The Brunauer–Emmett–Teller (BET) surface area was estimated to be 399 m² g⁻¹. Fitting of the sorption isotherms using the nonlocal density functional theory (NLDF) model resulted in a pore size distribution centered at 1.2 nm, in conformity with the predicted value of the eclipsed stacking model. The zeta potential of COF-COOH is −11.6 ± 2.4, validating its highly negatively charged surface.

To increase the operability and stability of the COF membrane, we grew the COF layer on PAN ultrafiltration membranes. PAN was selected because of its flexibility and hydrophilicity, which is not only easy to handle but also highly permeable to ions. To control the COF active layers exclusively on the PAN support, the Tp-dichloromethane solution and the Dba-TsOH aqueous solution were separately introduced into a homemade diffusion cell segregated by PAN into two chambers (Supporting Information Figure S1). Over 3 days, a vermilion film was formed on PAN facing the organic phase (COF-COOH/PAN, Supporting Information Figure S4). Primary characterization of the resulting membrane was thoroughly performed prior to the thermoelectric response study.

The Fourier-transform infrared (FT-IR) spectrum of COF-COOH/PAN revealed that the adsorption features of −NH₂ (≈ 3300 cm⁻¹) and −CHO (≈2880 and ≈1650 cm⁻¹) for the monomers disappeared with concomitant emergence of a peak for C≡C at 1562 cm⁻¹, indicating a high condensation degree of the membrane and no monomer being trapped in the pore channel (Supporting Information Figure S5). Scanning electron microscopy (SEM) images revealed continuous film surfaces that contoured the underlying PAN support with a thickness of approximately 220 nm (Supporting Information Figures S6 and S7). Contact angle measurements revealed that COF-COOH/PAN was hydrophilic with a water contact angle of 52° ± 4° (Supporting Information Figure S8). Dye molecule exclusion tests indicated that the COF active layer is porous but without large defects because the negatively charged thymol blue, with size (1.0 × 1.1 nm), characteristic of a microporous structure (Supporting Information Figure S3).
penetrated the membrane, whereas methyl blue, with a greater size (1.5 x 2.0 nm), was fully withheld (see details in the Experimental Section in the Supporting Information Figure S9).

**Ion permselectivity evaluation**

Encouraged by these characterization results, we next investigated the ion transport properties of COF-COOH/PAN. Given the similar bulk diffusivities of K\(^{+}\) and Cl\(^{-}\), KCl was the electrolyte of choice (unbuffered KCl was used unless otherwise specified). COF-COOH/PAN was located between the two chambers of a conductivity cell. The transmembrane current was recorded using symmetric KCl solutions with concentrations ranging from 0.01 mM to 3 M (Supporting Information Figure S10). The variation of the normalized transmembrane conductance derived from the slope of the current–voltage (I–V) curve versus KCl concentrations confirmed the nanoscale channels and the absence of KCl leakage through large cracks (Figure 3a). Ions were transported across COF-COOH/PAN in a fashion parallel to that in the bulk electrolyte at high electrolyte concentrations (>100 mM). At lower ionic strengths (<100 mM), the ion conductivity of COF-COOH/PAN deviated from the bulk behavior and demonstrated saturation, which is typical of surface-charge-governed ionic transport. Under such circumstances, the electrostatic force of the overlapped EDL could screen ions, repel co-ions, and attract counter-ions. Moreover, considering that the surface-charge-governed regime of COF-COOH/PAN extended above 100 mM, the x-intercepts (V\(_i\)) of the I–V plots exhibited average reversal potentials (three times) of −58.4, −112.4, and −109.6 mV for cis/trans = 1.0/0.1, 10/0.1, and 100/0.1 mM KCl, respectively (Figure 3b). The permeability ratios of K\(^{+}\)/Cl\(^{-}\) calculated based on the Goldman equation (eq 1) were 449, 416, and 78, respectively, confirming the preferential passage of cations over a wide range of concentration gradients.\(^{57}\)

\[
\frac{P_{K^+}}{P_{Cl^-}} = \frac{a_{Cl^-}}{a_{K^+}} \cdot \exp\left(-\frac{V_i F}{RT}\right) \cdot \exp\left(-\frac{V_r F}{RT}\right)
\]

To gain additional insight into the ion transport profiles inside the nanopores, theoretical calculations using a continuum approach based on the Nernst–Planck–Poisson equations were performed using COMSOL. The calculation model is illustrated in the Supporting Information Figure S11, whereby a negatively charged nanochannel separates KCl solutions with different concentration gradients. The dimension of the nanochannel was set according to the characterization results (200 nm length and 1.2 nm diameter). To gain affordable computation scale, a 2D model was employed and the fluidic pathway was simplified to be a 200 nm long single channel with a width of 1.2 nm. The radial ion distribution from the channel axis to the channel wall was calculated, which revealed the presence of high concentration of K\(^{+}\) ions throughout the channel, even at low bath concentrations. Moreover, the concentration of Cl\(^{-}\) ions was always lower than that of K\(^{+}\) ions, although the discrepancy decreased with an increase in the concentration gradient, consistent with the

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**Figure 3** Investigation of transmembrane ion transport. (a) Measured steady-state ionic conductance of COF-COOH/PAN, as well as a bulk prediction for KCl solutions (dashed line). The bulk conductivity represents the conditions where the effect of the surface charge can be neglected. (b) I–V curves recorded under various KCl concentration gradients separated by COF-COOH/PAN. (c) Numerical simulation of the distributions of K\(^{+}\) (solid line) and Cl\(^{-}\) (dashed line) with various concentration gradients (the left side was fixed at 0.1 mM, while the right side increased from 0.1 mM to 1 M) inside the nanochannels of COF-COOH.

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experimental results (Figure 3c). These phenomena can be rationalized by the high negative charge density and ultrasmall channel size of COF-COOH that produce co-ion exclusion.58,59

Theoretical principle of biomimetic thermosensation

Developments in the principles of nanofluidic transport allow us to mimic the function of biological pores. It is established that the transmembrane diffusion potential ($\Delta \phi_{\text{diff}}$) is a function of temperature and salt activity of the electrolytes (eq 2 and see detailed derivation process in the Supporting Information), where $t_i$ is the transference number of cations, $T$ is temperature, and $a$ is the electrolyte activity.

\[
\Delta \phi_{\text{diff}} = \phi_{\text{cis}} - \phi_{\text{trans}} = (2t_i - 1) \frac{R}{F} (T_{\text{trans}} \ln a_{\text{trans}} - T_{\text{cis}} \ln a_{\text{cis}}) \quad (2)
\]

Experimentally, we can measure the open-circuit potential ($V_{\text{oc}}$) directly. According to the equivalent circuit of our experimental setup, $V_{\text{oc}}$ is the sum of $\Delta \phi_{\text{diff}}$, the redox potential of the Ag/AgCl electrodes ($E_{\text{redox}}$), and the voltage drops across the membrane ($iR_{\text{membrane}}$) and solution ($iR_{\text{solution}}$), where $i$ is the ionic current, and $R_{\text{membrane}}$ and $R_{\text{solution}}$ are the internal resistance of the membrane and the solution resistance, respectively (eq 3).

\[
V_{\text{oc}} = V_{\text{cis}} - V_{\text{trans}} = -(\Delta \phi_{\text{diff}} + E_{\text{redox}} + iR_{\text{membrane}} + iR_{\text{solution}}) \quad (3)
\]

$E_{\text{redox}}$ can be calculated using eq 4.

\[
E_{\text{redox}} = E_{\text{cis}} - E_{\text{trans}} = \frac{R}{F} (T_{\text{trans}} \ln a_{\text{trans}} - T_{\text{cis}} \ln a_{\text{cis}}) \quad (4)
\]

Under open-circuit conditions, $i$ is close to 0 and the drops in $iR$ can be ignored. Therefore, the equation $V_{\text{oc}}$ relating to the solution temperature and concentration can be established as eq 5.

\[
V_{\text{oc}} = -(\Delta \phi_{\text{diff}} + E_{\text{redox}}) = -2t_i \frac{R}{F} (T_{\text{trans}} \ln a_{\text{trans}} - T_{\text{cis}} \ln a_{\text{cis}}) \quad (5)
\]

To study the potential changes in response to the temperature gradients between the two electrolytes, we used symmetric solutions ($\alpha_{\text{cis}} = \alpha_{\text{trans}} = a$). Both $\Delta \phi_{\text{diff}}$ and $V_{\text{oc}}$ are equal to zero at the initial state ($T_{\text{cis}} = T_{\text{trans}}$). Upon introducing a temperature gradient, $\Delta T$ ($\Delta T = |T_{\text{trans}} - T_{\text{cis}}|$), the magnitude of the potential changes can be derived from eqs 6 and 7.

\[
\Delta V_{\text{oc}}(T) = -2t_i \frac{R}{F} \Delta T \ln a \quad (6)
\]

\[
\Delta \phi_{\text{diff}}(T) = (2t_i - 1) \frac{R}{F} \Delta T \ln a \quad (7)
\]

Thermoelectric response evaluation

Once we confirmed the high permselectivity of COF-COOH/PAN, we proceeded to study its thermoelectric response properties. To investigate the influence of the temperature gradient between the two chambers on the transmembrane potential, COF-COOH/PAN was placed in contact with symmetric KCl solutions (1 mM). In the steady state, negligible zero-voltage currents were detected. When a slight temperature gradient was induced by briefly heating or cooling one end of the solution, an apparent voltage was observed, suggesting the remarkable sensitivity of temperature-driven ion transport (Supporting Information Figure S12). To quantitatively study the thermoelectric response, a customized setup was engineered, whereby $\Delta T$ was recorded by a pair of immersed microthermometers, and the changes in voltage ($\Delta V_{\text{oc}}$) were monitored by Ag/AgCl electrodes, which were output by an electrochemical workstation (Supporting Information Figure S13). Figure 4a depicts the time evolution curves of $\Delta T$ and $\Delta V_{\text{oc}}$ recorded with COF-COOH/PAN, during which the temperature of the trans side increased from 25 °C to approximately 35 °C and then returned naturally to thermal equilibrium, whereby $\Delta V_{\text{oc}}$ synchronously changed in response to temperature changes. In the cooling stage, both $\Delta V_{\text{oc}}$ and $\Delta T$ decreased with time, and vice versa. A linear dependence with a correlation coefficient ($R^2$) value greater than 0.99 was obtained by plotting the variation of $V_{\text{oc}}$ against temperature changes, in line with the theoretical derivation (eq 6 and Figure 4a, inset). Averaging over three different batches, the thermosensation sensitivity derived from the slope of the aforementioned plots was 1.17 mV K$^{-1}$ for COF-COOH/PAN, far outcompeting the thermosensation sensitivity of organisms as well as the reported systems (Supporting Information Table S3).60-64 Moreover, this temperature-induced potential change was reversible and instantaneous, and no degradation of performance was observed for at least eight cycles, indicating a stable linear correlation between the temperature gradient and ion transport potential (Figure 4b and Supporting Information Table S4). Impressively, the device showed instantaneous response to the temperature stimuli, with an average relative sensitivity of 97% (see details in the Supporting Information Figure S14).

Given that $\Delta V_{\text{oc}}$ is independent of the initial temperature but not $\Delta T$, we further investigated the thermosensation capability of COF-COOH/PAN. Initially, we evaluated the thermoelectric responses of the developed thermosensation system toward other temperature windows. The permselectivity of COF-COOH/PAN was retained in response to both hot and cold stimuli. For example, the $t_i$ values for the systems within the temperature ranges of 15–25 °C and 35–45 °C were calculated to be 0.968 and 0.951, respectively. Moreover, linear
The thermoelectric sensitivities gradient under various ionic strengths (Supporting Information Table S5). The sensitivities decreased with increasing electrolyte concentration, which can be reasonably explained by eq 6; the slope decreased as ln a increased. Furthermore, to evaluate the thermosensation properties of COF-COOH/PAN in the presence of salt concentration gradients, 0.5 M and 0.01 M KCl were used as electrolytes, which acted as surrogates of seawater and river water, respectively. After a brief heating was imposed on the low-salt side, a maximum power density was calculated to be 156.7 mV and 13.8 μA, respectively. Calculated according to $P_{\text{out}} = V_{\text{oc}} \times I_{\text{sc}}/4$, a power density of 68.7 W m$^{-2}$ was obtained. After introducing a temperature gradient of approximately 15 K, the $V_{\text{oc}}$ and $I_{\text{sc}}$ values increased to 169.0 mV and 16.9 μA, respectively, and the power density was calculated to be 91.0 W m$^{-2}$ (Supporting Information Figure S21).

### Temperature alarm device

The high tolerance toward various conditions in terms of salt concentrations and temperature windows, as well as the ultrahigh thermosensation sensitivity of COF-COOH/PAN, motivated us to explore the possibilities of designing a temperature alarm system (Supporting Information Figure S22). As the magnitude of the voltage increases linearly with an increase in the temperature gradient, we could precisely set an alarm limit. To visualize the alarm signal, we assembled an integral system that can translate information about temperature gradient into voltage signals that are then taken up and amplified by a microcontroller unit (Figure 5a). The light-emitting diodes

![Figure 4](image-url)

**Figure 4** | Thermosensation performance evaluation of COF-COOH/PAN. (a) The synchronous time evolution of $\Delta V_{\text{oc}}$ in response to the solution temperature change with the initial temperatures of 25 and 35 °C, respectively, inset: The linear fits of $\Delta V_{\text{oc}}$ against $\Delta T$ according to eq 6. (b) Comparison of thermosensation sensitivity for COF-COOH/PAN with those of other benchmark systems, ZnHAB$^{40}$ Shark$^{31}$ poly(ethylene terephthalate) PET$^{62}$ silica isoporous nanochannels (SIM)/PET$^{62}$ asy-AAO-Au$^{63}$ (c) Continuous and synchronous time evolution curves of $\Delta V_{\text{oc}}$ (blue) and $\Delta T$ (red) recorded with COF-COOH/PAN membrane in 1 mM KCl for eight cycles.

| Electrolyte   | Mean $\Delta V_{\text{oc}}$ (mV K$^{-1}$) | Mean $\Delta I_{\text{sc}}$ (μA K$^{-1}$) |
|---------------|------------------------------------------|------------------------------------------|
| KCl 0.5 M     | 1.17 mV K$^{-1}$                         | 0.90 mV K$^{-1}$                         |
| NaCl 0.01 M   | 0.90 mV K$^{-1}$                         | 0.85 mV K$^{-1}$                         |
| LiCl 0.5 M    | 0.85 mV K$^{-1}$                         | 0.80 mV K$^{-1}$                         |

This can be rationalized by their difference in diffusion coefficient of cations, decreasing in the order $K^+ > Na^+ > Li^+$ (Supporting Information Figures S19 and S20). The faster the cation diffuses, the more efficient the charge separation will occur, which is a typical behavior of cation-selective membranes. The high thermosensation sensitivity of COF-COOH/PAN shows potential in harvesting low-quality temperature gradient into electricity. To do so, COF-COOH/PAN was placed between the asymmetric NaCl aqueous solutions (0.5/0.01 M) to mimic the salinity gradient at a river mouth. Given that the concentration gradient and hot stimulation drive the ion transport in opposite directions, the temperature gradient was imposed on the low-salt concentration side. The initial $V_{\text{oc}}$ and $I_{\text{sc}}$ values were measured to be 156.7 mV and 13.8 μA, respectively. Calculated according to $P_{\text{out}} = V_{\text{oc}} \times I_{\text{sc}}/4$, a power density of 68.7 W m$^{-2}$ was obtained. After introducing a temperature gradient of approximately 15 K, the $V_{\text{oc}}$ and $I_{\text{sc}}$ values increased to 169.0 mV and 16.9 μA, respectively, and the power density was calculated to be 91.0 W m$^{-2}$ (Supporting Information Figure S21).
(LEDs) responded spontaneously when the change in temperature exceeded the predetermined alarm limit. Figure 5b shows a digital photograph of the experimental setup. To use as a sensor for monitoring the changes in the surrounding temperature, a conductivity cell made from different materials and volume was employed. Owing to the different thermal conductivities of aluminum and plastic materials, the temperature of electrolyte (0.1 mM KCl) in the plastic cell with large volume can be considered as unchanged in a short time when the surrounding environment temperature changes, but that in the aluminum cell with small volume does not. In a steady state, the potential between the two cells remains the same; thus, the output voltage is zero at the load resistance. When the surrounding temperature changes, a temperature gradient between the two chambers is formed, and the sensor outputs a voltage, which activates the alarm circuit that lights the LED after overriding the set limit. Given that the magnitude of the temperature gradient determines the value of the pulse voltage, the gating temperature can be precisely set by manipulating the circuit. Additionally, the ultrahigh thermosensation selectivity of the developed system allows a tiny temperature variation to be detected. To demonstrate a showcase study, we set the temperature gradient around 1 K as a safe variation. We heated or cooled the sensor and measured the temperature gradients to test the feasibility of the device. It was shown that when the temperature gradient of the electrolytes exceeded the safe value, the LED was lighted. Upon further increasing the temperature gradient, the lamp light intensity increased within a specific range (Figure 5c and Supporting Information Movies S1 and S2).

**Conclusions**

This work demonstrates one of the very first examples of using temperature as a precision input in a responsive membrane-based ionic charge separation system to obtain stable, reversible, and instant electrochemical signal output, with the attributes of ultrasensitivity and high tolerance toward various operating conditions. We advanced COF as a customized platform to mimic the function of thermo-transient receptor potential channels in nature with high performance; a thermosensation sensitivity of up to 1.25 mV K$^{-1}$ was obtained, placing it within striking distance of the all-time temperature sensor record. We believe that introducing the developed thermosensation system to the compendium of realized temperature sensors can fill the current gap in temperature-responsive materials.

**Supporting Information**

Supporting Information is available and includes materials syntheses, characterization details, and supporting figures.

**Conflict of Interest**

There is no conflict of interest to report.

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