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Room temperature sensing of CO₂ using C3-symmetry pyridinium-based porous ionic polymers with triazine or benzene cores†

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A new class of ionic polymers tethering triazine (benzene) core hybrids with three dipyridinium as cationic counterparts combined with bromide and/or chloride anions PPyBz-O_{Br} and PPyTri-O_{Cl} were successfully prepared via the alkylation of 4,4'-dipyridyl derivatives 4,4'-bp-O with 1,3,5-tris(bromomethyl)benzene BB and/or cyanuric chloride CC. The precursor, 4,4'-bp-O, was synthesized through the condensation of 4-pyridine carboxaldehyde and 4,4'-oxydianiline. The resulting ionic polymers, PPyBz-O_{Br} and PPyTri-O_{Cl}, underwent metathetical anion exchange, forming new ionic polymers bearing LiTFSI and KPF₆ as anions. Characterization of the synthesized hybrid molecules was performed through FTIR, ¹H NMR, and ¹³C NMR analyses. PXRD and SEM showed semi-crystalline structures and a homogenous distribution of micro-/or nanoparticles. TGA and DTA displayed high thermal stability of the synthesized polymer. The sensing activity of the modified ionic polymers was examined using a quartz crystal nanobalance (QCN) for CO₂ detection. The resulting sensor demonstrated the ability to provide precise, selective, and reproducible CO₂ measurements.

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1. Introduction

The detection of carbon dioxide (CO₂) is pivotal across diverse domains, including fire detection,¹ greenhouse gas surveillance,² air-quality monitoring,^{3,4} health,⁵⁻⁷ marine and environmental studies,⁸ and food supply chain management.^{9,10} Traditional CO₂ sensing methods, such as gas chromatography,¹¹ infrared spectrometry,¹² fluorescence,¹³⁻¹⁵ photoacoustic spectroscopy,¹⁶ and severinghaus electrodes,¹⁷ offer high selectivity and sensitivity. However, they often suffer from drawbacks such as high costs, bulkiness, elevated power consumption, and susceptibility to electromagnetic interference.^{16,18} The development of highly sensitive, efficient, and cost-effective sensors is critical for on-site analysis and reducing CO₂ emissions. The quartz crystal nanobalance (QCN) is a device that utilizes a quartz crystal microbalance (QCM) to

detect mass changes at the nanogram level by measuring changes in the resonator frequency. By incorporating an appropriate chemical interface layer or recognition element, the QCN exhibits significant potential for CO₂ sensing.¹⁹

CO₂-responsive polymers have garnered significant attention due to their high flexibility and sensitivity at room temperature.²⁰⁻²⁴ These polymers undergo changes in physical attributes, such as electrical resistance, volume, and transparency, when exposed to CO₂.²⁵ Among the functional groups in these polymers, amidine,^{26,27} guanidine,²⁸ and amines,^{29,30} especially tertiary amines, have been extensively studied for their CO₂ responsiveness. Tertiary amines, with moderate base properties, exhibit good switchability between neutral and charged states. In contrast, primary and secondary amines form carbamate salts in the presence of CO₂, making them less suitable for sensing applications.³¹⁻³³

In recent years, considerable efforts have been made dedicated to the design, synthesis, and development of focused macromolecules with significant electrochemical features, which are the aims associated with various applications in organic synthesis. A wide range of porous materials such as covalent organic frameworks (COFs),³⁴ porous organic polymers (POPs),³⁵ metal-organic frameworks (MOFs),³⁶ organic-inorganic hybrid materials³⁷ etc., are attractive scaffolds for designing and developing various applications such as gas storage,³⁸⁻⁴¹ photovoltaics,⁴² conductivity,⁴³⁻⁴⁵ batteries,⁴⁶⁻⁵⁰ catalysis,⁵¹⁻⁵⁴ optoelectronic devices,⁵⁵ and electrochemical sensing.⁵⁶

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While various advanced porous materials such as zeolites,⁵⁷ metal-organic frameworks (MOFs),⁵⁸ ionic liquids,^{59,60} phenolic resins, activated carbons, and carbon composites⁶¹ have been explored, POPs, particularly those with porous frameworks containing C-N linkages, have emerged as promising candidates for CO₂ sensing. The dipole-dipole interaction between CO₂ and N atoms in these frameworks enhances their effectiveness.⁶²⁻⁶⁴ One of the effective methods for incorporating C-N functional groups is to synthesize triazine with the rigid-shaped structure and C3-symmetry, utilizing a simple synthetic method not only without the formation of byproducts but also without the need for any kind of catalyst. Moreover, the other N-rich functionalities, such as pyridine, amine, amide, carbazole, or porphyrin units, need to be designed and synthesized reasonably, which have been proven to be efficient functional materials for gas storage/separation, heterogeneous catalysis, and sensing.^{65,66}

However, the performance of QCM sensors depends significantly on the properties of the coating material used. Previous studies have explored a range of materials, including acrylonitrile-styrene copolymers (AS), tetramethylammonium fluoride tetrahydrate (TMAF), and polyethyleneimine (PEI) coatings. For example, AS-coated QCM sensors showed sensitivity to CO₂ but were also highly affected by humidity, limiting their specificity for CO₂ in mixed-gas environments.⁶⁷ Similarly, TMAF-coated QCM sensors demonstrated sensitivity to multiple gases such as SO₂, NH₃, and CO₂, with limited selectivity for CO₂.⁶⁸ More recently, multilayered systems involving materials such as PEI and nitrogen-doped tungsten carbide (WC@NC) have shown promise in mixed-gas classification but are complex to fabricate and optimize.⁶⁹ Despite these advances, challenges remain in achieving high sensitivity, selectivity, and thermal stability for CO₂ detection using QCM-based sensors. In this context, the design of porous materials with tailored functionalities presents a promising approach. Porous ionic polymers (PIPs), particularly those combining nitrogen-rich frameworks and electrostatic interaction sites, offer significant potential for CO₂ sensing. However, previous work in this area has been limited by the lack of synergistic design elements that enhance both adsorption and sensor performance. In this study, we report a new class of porous ionic polymers (PIPs) designed for CO₂ sensing, incorporating triazine (benzene) cores and pyridinium cations with PF₆⁻ and TFSI anions. The unique combination of triazine and pyridinium units introduces several advantages. The triazine core provides a nitrogen-rich, semi-crystalline framework with high thermal stability, enabling robust performance in harsh conditions. Pyridinium cations introduce electrostatic interaction sites, increasing affinity for CO₂ molecules while maintaining selectivity over NH₃ and H₂S. Furthermore, the incorporation of PF₆⁻ and TFSI anions influences the material's morphology and crystallinity, optimizing gas diffusion and adsorption.

2. Experimental

2.1. Synthesis of *N,N'*-(oxybis(4,1-phenylene))bis(1-(pyridin-4-yl)methanimine) 4,4'-bp-O

A mixture of 4-pyridine carboxaldehyde (2 mmol) and 4,4'-oxydianiline (1 mmol) was dissolved in ethanol (25 mL) with drops of

conc. HCl as a catalyst. The reaction mixture was heated under reflux for 3 h. Then, the precipitate formed was filtered, washed thoroughly with ethanol, dried, and recrystallized from acetone to give the desired Schiff bases **4,4'-bp-O**. It was obtained as white crystals in 90%, Mp = 250 °C. FTIR (ν , cm⁻¹): 3016 (s, Ar-H stretch), 1622 (C=N, imine), 1596 (C=N, pyridine), 1460 (Ar C=C bending), 1082 (Ar C-N bending), 829 (Ar C=C bending). ¹H NMR (400 MHz, DMSO-*d*₆): δ_{H} = 7.14 (d, 4H, *J* = 5.48 Hz, Ar-H), 7.45 (d, 4H, *J* = 5.84 Hz, Ar-H), 7.86 (d, 4H, *J* = 3.96 Hz, Ar-H), 8.75 (s, 2H, HC=N), 8.76 (d, 4H, *J* = 3.96 Hz, Ar-H). ¹³C NMR (DMSO-*d*₆, 200 MHz): δ_{C} = 158, 156, 150, 146, 143, 123, 122, 119.

2.2. Synthesis of dipyrindinium cationic polymers-based triazine and/or benzene core PPyBz-O_{Br} and PPyTri-O_{Cl}

To a solution of 4,4'-dipyridyl, **4,4'-bp-O** (1.5 mmol) in acetonitrile (20 mL) was added dropwise a solution 1,3,5-tris(bromomethyl)benzene **BB** and/or cyanuric chloride **CC** in acetonitrile (20 mL) under stirring. The reaction mixture was then refluxed for 72 h. The precipitate formed was collected by filtration, washed with chloroform (3 × 15 mL) dried to the desired ionic polymers **PPyBz-O_{Br}** and **PPyTri-O_{Cl}**.

2.2.1 Characterization of polymer PPyBz-O_{Br}. PPyBz-O_{Br} was obtained as a yellow powder in 95% yield, FTIR: ν [cm⁻¹]: 3385 (pyridinium salt stretch), 3116 (alkenyl C-H stretch), 3016 (Ar C-H stretch), 2970 (Alkyl C-H stretch), 1636 (pyridinium salt ring vibration), 1460 (Ar C=C bending), 1160 (Ar C-N bending), 829 (Ar C-C bending). ¹H NMR (850 MHz, DMSO): δ (ppm) 8.77 (s, 1H), 8.49 (m, 2H), 8.29 (m, 2H), 8.02 (s, 1H), 7.94-7.33 (m, 4H), 5.80 (m, 2H). ¹³C NMR (400 MHz, DMSO): δ (ppm) 160.21, 149.96, 147.92, 145.22, 144.47, 140.07, 134.23, 132.76, 130.71, 129.54, 126.76, 66.06.

2.2.2 Characterization of polymer PPyTri-O_{Cl}. PPyTri-O_{Cl} was obtained as a brown powder in 75% yield, FTIR: ν [cm⁻¹]: 3423 (pyridinium salt stretch), 3116 (alkenyl C-H stretch), 3016 (Ar C-H stretch), 1636 (pyridinium salt ring vibration), 1593 (triazine C=N), 1384 (C-N bending) 1460 (Ar C=C bending), 1160 (Ar C-N bending), 829 (Ar C-C bending). ¹H NMR (850 MHz, DMSO): δ (ppm) 8.81 (m, 2H), 8.59 (m, 2H), 8.34 (m, 1H), 8.25-8.01 (m, 2H), 7.62-7.28 (m, 2H). ¹³C NMR (400 MHz, DMSO): δ (ppm) 171.86, 166.97, 155.94, 152.24, 141.35, 138.27, 133.66, 122.06.

2.3. Metathesis synthesis of ionic polymers PPyBz-O_{PF₆}, PPyBz-O_{TFSI}, PPyTri-O_{PF₆} and PPyTri-O_{TFSI}

To a solution of ionic polymers **PPyBz-O_{Br}** and **PPyTri-O_{Cl}** (1 mmol) in acetonitrile was added a solution of lithium bis(trifluoromethane)sulfonimide (LiTFSI) and/or potassium hexafluorophosphate (KPF₆) (1.2 mmol) and the solution was refluxed for 24 h. The solid formed was collected by filtration, washed with deionized water and dried at 100 °C.

2.3.1 Characterization of polymer PPyBz-O_{PF₆}. PPyBz-O_{PF₆} was obtained as a yellowish-orange powder in 90% yield, FTIR: ν [cm⁻¹]: 3423 (pyridinium salt stretch), 3116 (alkenyl C-H stretch), 3016 (Ar C-H stretch), 2970 (Alkyl C-H stretch), 1636 (pyridinium salt ring vibration), 1460 (s, Ar C=C bending), 1160 (Ar C-N bending), 829 (Ar C-C bending), 863 (PF₆⁻). ¹H NMR (850 MHz, DMSO): δ (ppm) 8.85 (s, 1H), 8.59 (m, 2H), 8.41 (m,



2H), 8.15 (s, 1H), 8.03–7.37 (m, 4H), 5.92 (m, 2H). ^{13}C NMR (400 MHz, DMSO): δ (ppm) 160.21, 148.24, 147.71, 145.16, 144.92, 140.31, 134.28, 132.98, 130.84, 129.83, 128.49, 126.87, 67.06. ^{31}P NMR (162 MHz, DMSO) δ –131.01 to –157.36 (sep). ^{19}F NMR (377 MHz, DMSO) δ –69.18 (s), –71.07 (s).

2.3.2 Characterization of polymer PPyBz-O_{TFSI}. PPyBz-O_{TFSI} was obtained as a light orange powder in 90%, FTIR: ν [cm^{-1}]: 3423 (pyridinium salt stretch), 3116 (alkenyl C–H stretch), 3016 (Ar C–H stretch), 2970 (alkyl C–H stretch), 1636 (pyridinium salt ring vibration), 1460 (Ar C=C bending), 1160 (Ar C–N bending), 829 (Ar C–C bending), 1207 (SO_2 , TFSI) and 1353 (CF_3 , TFSI). ^1H NMR (850 MHz, DMSO): δ (ppm) 8.85 (s, 1H), 8.59 (m, 2H), 8.41 (m, 2H), 8.15 (s, 1H), 8.03–7.37 (m, 4H), 5.92 (m, 2H). ^{13}C NMR (400 MHz, DMSO): δ (ppm) 160.05, 148.16, 147.81, 145.36, 144.64, 140.23, 134.16, 132.74, 130.03, 128.65, 126.76, 66.98. ^{19}F NMR (377 MHz, DMSO): δ (ppm) –73.49 (s).

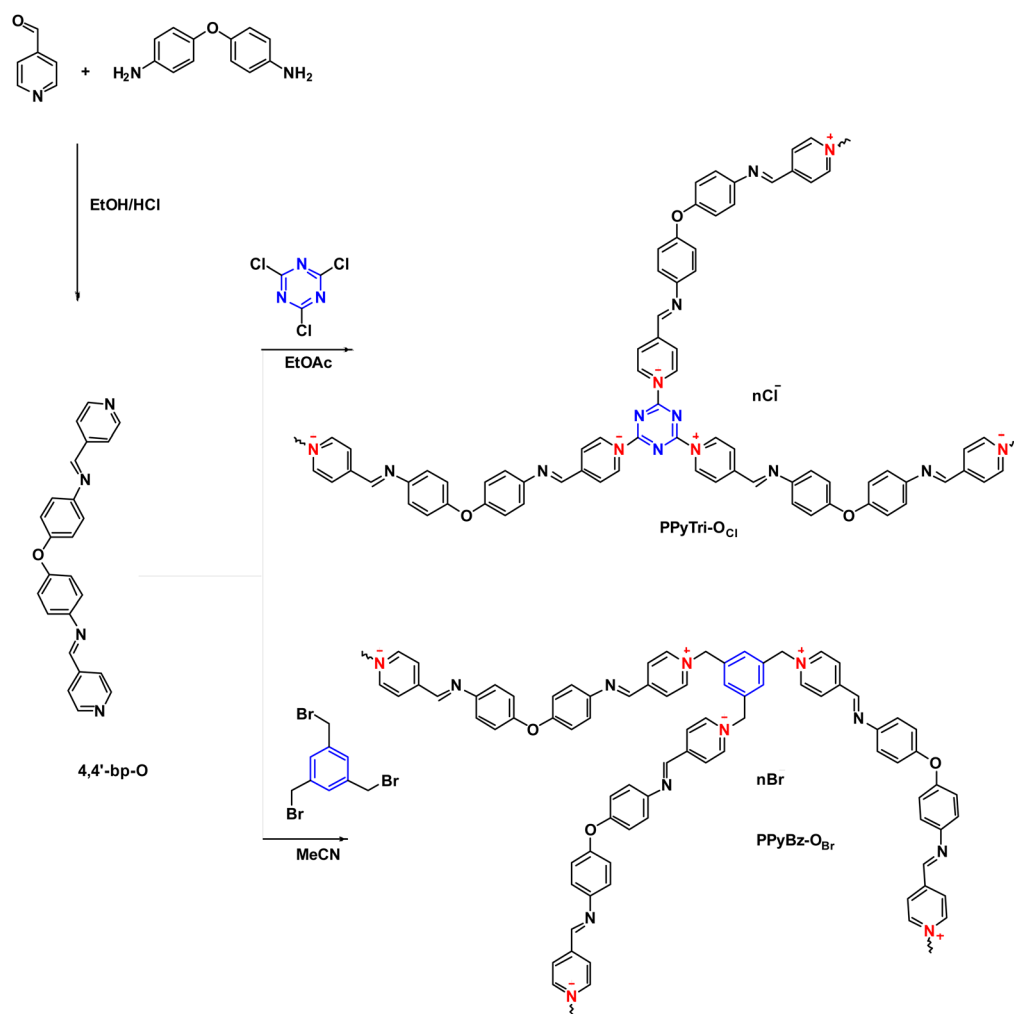
2.3.3 Characterization of PPyTri-O_{PF6}. PPyTri-O_{PF6} was obtained as a reddish-brown powder in 90% yield, FTIR: ν [cm^{-1}]: 3423 (pyridinium salt stretch), 3116 (alkenyl C–H stretch), 3016 (Ar C–H stretch), 1636 (pyridinium salt ring vibration), 1593 (triazine C=N), 1384 (C–N⁺ bending) 1460 (Ar C=C bending), 1160 (Ar C–N bending), 829 (Ar C–C bending), 863 (PF_6^-). ^1H

NMR (850 MHz, DMSO): δ (ppm) 8.87 (m, 2H), 8.67 (m, 2H), 8.39 (s, 1H), 8.33–8.19 (m, 2H), 7.73–7.38 (m, 2H). ^{13}C NMR (400 MHz, DMSO): δ (ppm) 171.79, 167.11 154.94, 152.24, 141.18, 138.41, 133.76, 121.99. ^{31}P NMR (162 MHz, DMSO) δ –131.01 to –157.36 (sep). ^{19}F NMR (377 MHz, DMSO) δ –69.17 (s), –71.06 (s).

2.3.4 Characterization of polymer PPyTri-O_{TFSI}. PPyTri-O_{TFSI} obtained as a brown powder in 95% yield, FTIR: ν [cm^{-1}]: 3423 (s, pyridinium salt stretch), 3116 (w, alkenyl C–H stretch), 3016 (s, Ar C–H stretch), 1636 (vs., pyridinium salt ring vibration), 1593 (s, triazine C=N), 1384 (s, C–N⁺ bending) 1460 (s, Ar C=C bending), 1160 (s, Ar C–N bending), 829 (vs., Ar C–C bending), 1207 (SO_2 , TFSI) and 1353 (CF_3 , TFSI). ^1H NMR (850 MHz, DMSO): δ (ppm) 8.77 (m, 2H), 8.55 (m, 2H), 8.30 (s, 1H), 8.21–8.06 (m, 2H), 7.60–7.25 (m, 2H). ^{13}C NMR (400 MHz, DMSO): δ (ppm) 171.93, 167.04 155.94, 152.31, 141.03, 138.41, 133.76, 122.06. ^{19}F NMR (377 MHz, DMSO) δ –73.49 (s).

2.4. Fabrication of PPyTri-O and PPyBz-O CO₂ sensors

The QCN was used to evaluate the PPyTri-O and PPyBz-O activity toward CO₂ detection. In order to ensure a clean surface, the piranha solution (a blend of sulfuric acid and hydrogen peroxide) was used to clean the QCN chips, and the samples



Scheme 1 Synthesis of the precursor Schiff base 4,4'-bp-O and targeted C3-symmetry porous ionic polymers PPyBz-O_{Br}, PPyTri-O_{Cl}.



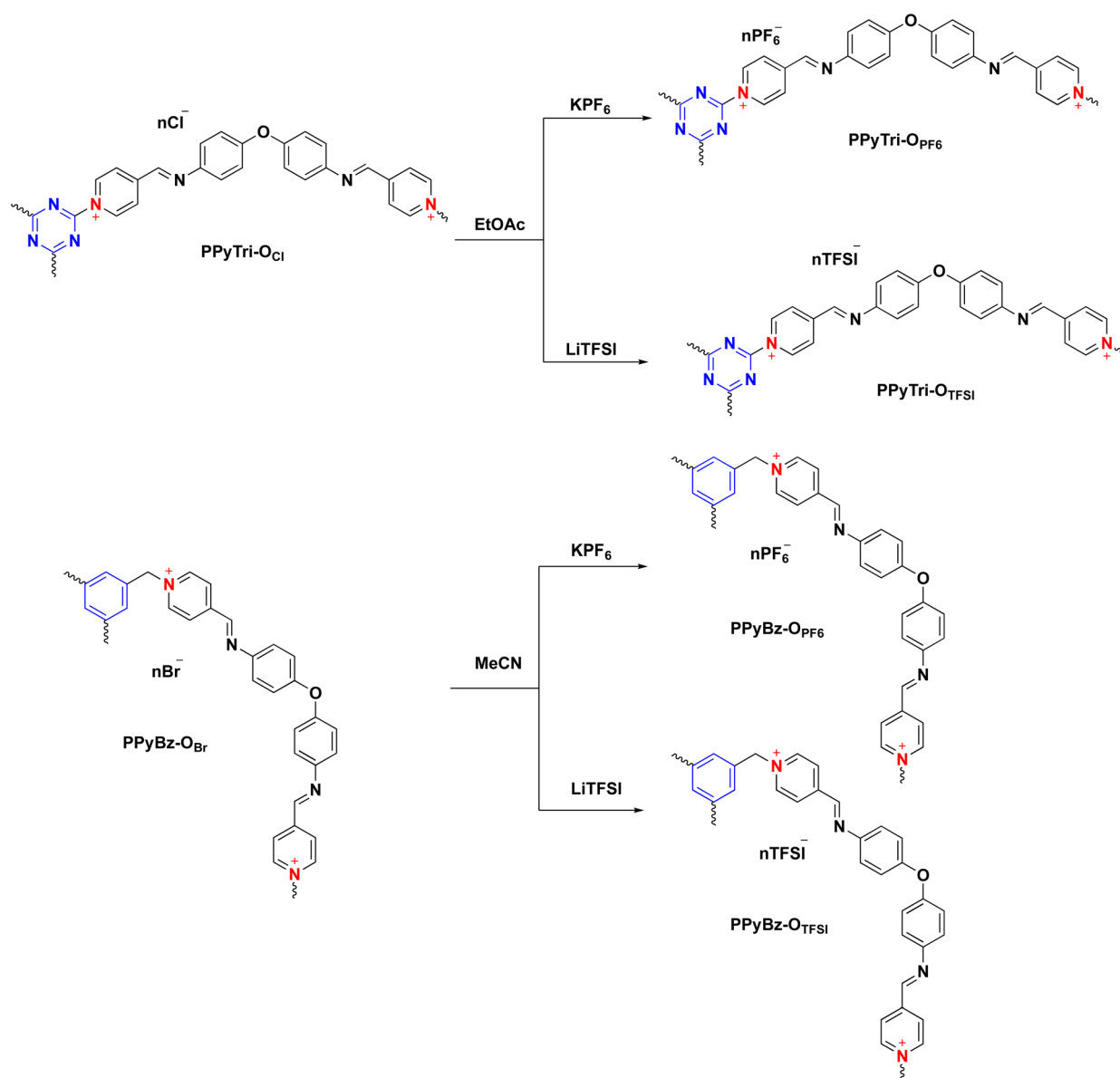
were rinsed with deionized water and dried using nitrogen. To create conductive pathways for the PIP sensors, the gold electrode was deposited on the QCN chip using a sputtering deposition method. The PIP layers were then applied using the spin coating technique and connected to the measurement system using bond wires. The CO₂ chamber was prepared by installing inlets and outlets for gas flow and a temperature control system of 20 °C, 25 °C, and 30 °C using Peltier temperature baths. CO₂ gas was then introduced into the chamber, and the sensor responses were analyzed to evaluate the performance of the PIP sensors under different temperature conditions.

3. Results and discussion

3.1. Synthesis and characterization

The design of C₃-symmetry porous ionic polymers (PIPs) involved careful consideration of the core structure and linkers.

Thus, in the present work, new ionic polymers with a C₃-symmetry structure were synthesized and investigated for their CO₂ detection. The benzene and/or triazine core, viologen as linkers, and PF₆⁻ and TFSI⁻ as counter anions were combined in the same framework of the tailored polymers in order to improve the electrostatic and aromatic properties impacting their overall behavior as well as CO₂ sensing. The synthesis of the targeted C₃-symmetry pyridinium ionic polymers **PPyBz-O_{Br}**, **PPyBz-O_{PF6}**, **PPyBz-O_{TFSI}**, **PPyTri-O_{Cl}**, **PPyTri-O_{PF6}**, and **PPyTri-O_{TFSI}** was accomplished using the synthetic methodology depicted in Schemes 1 and 2. The first step involved the synthesis of the precursor's Schiff base **4,4'-bp-O** through thermal condensation of the 4-pyridine carboxaldehyde with 4,4'-oxydianiline in refluxing ethanol and in the presence of the catalytic amount of acid. The ¹H NMR spectra of the monomer **4,4'-bp-O** showed characteristic signals at 7.14–8.76 ppm and 7.09–8.76 ppm attributed to the aromatic protons of the phenyl



Scheme 2 Metathesis of C₃-symmetry porous ionic polymers.



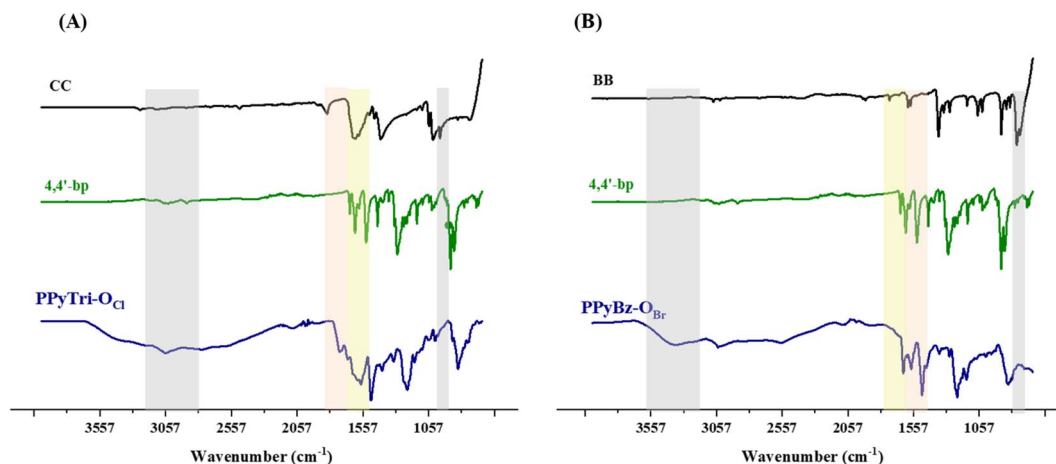


Fig. 1 FTIR spectra of the precursor Schiff base 4,4'-bp-O and targeted C3-symmetry porous ionic polymers. (A) Triazine core and (B) benzene core.

and pyridine rings, respectively. While the imine proton (HC=N) appeared as a distinct singlet at 8.75 ppm.

The Menshutkin reaction was adopted as a common method for generating polymers-based quaternary pyridinium as ammonium salt. Thus, the appropriate 1,3,5-tris(bromomethyl) benzene **BB** and/or cyanuric chloride **CC** were used in the polymerization process through their conjunction with the synthesized bis(1-(pyridin-4-yl)methanimine) Schiff base 4,4'-bp-O as linkers to furnish the desired cationic polymers **PPyBz-OB_r** and **PPyTri-O_{Cl}** bearing chloride and bromide as counter anions, as elucidated in Scheme 1. The success of the synthesis of the targeted C3-symmetry ionic polymers was supported by the investigation of their spectral data based on FTIR and NMR results. Thus, the FTIR spectrum of the polymer **PPyTri-O_{Cl}** (Fig. 1(A)) clearly showed the disappearance of the stretching vibration near 850 cm⁻¹ attributed to the C-Cl band of the starting material **CC**, supporting the quaternization of pyridine ring in the monomer 4,4'-bp-O. A new intense band was observed near 1645 cm⁻¹ belonging to pyridinium cations, which is another piece of evidence for the success of the quaternization reaction and formation of the targeted ionic

polymers **PPyTri-O_{Cl}**. The spectra also showed a shift of the C=N absorption bands of the triazine ring (1508 cm⁻¹) compared to their precursor **CC**. The C=N absorption of the azomethine linkage and pyridine ring were observed at 1630 and 1650 cm⁻¹, respectively. Similarly, no stretching bands near 690 cm⁻¹ were recorded in the FTIR spectra of the polymers tethering to the benzene core **PPyBz-OB_r** (Fig. 1(B)), confirming the absence of the C-Br bond in their structure and confirming their involvement in the alkylation of the pyridine nucleus yielding the desired adduct **PPyBz-OB_r**, with the quaternary nitrogen atoms (N⁺) exhibiting an intense band around 1645 cm⁻¹, evidencing the proposed structures. In addition, the band observed at 1640 cm⁻¹ confirmed the presence of the imine linkage in the framework of the resulting **PPyBz-OB_r** ionic polymer.

On the other hand, the structures of the synthesized polymers **PPyBz-OB_r**, **PPyBz-OPF₆**, **PPyBz-OTFSI**, **PPyTri-O_{Cl}**, **PPyTri-OPF₆**, and **PPyTri-OTFSI** were elucidated based on their NMR spectra. The ¹H NMR spectra of the developed polymers-based triazine core **PPyTri-O_{Cl}** and their analogs **PPyTri-OPF₆** and **PPyTri-OTFSI** (Fig. 2(A)) exhibited a broad signal in the aromatic

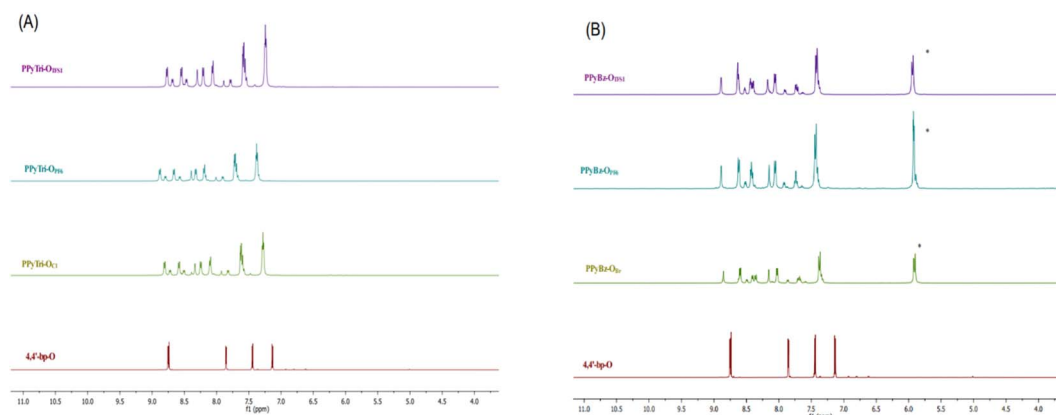


Fig. 2 ¹H NMR spectra of the precursor Schiff base 4,4'-bp-O and the targeted C3-symmetry porous ionic polymers. (A) Triazine core and (B) benzene core.

area ranging from 7.25 to 8.87 ppm due to the polymeric backbone effect. The imine protons resonated around 8.30–8.39 ppm. Moreover, the carbons of the triazine ring and imine were recorded at 171.86–171.93 ppm and 166.97–167.04 ppm, respectively, in their ^{13}C NMR spectra. The remaining aromatic carbons were observed in their appropriate area (121.80 to 155.94 ppm) and are detailed in the experimental section.

The ^1H NMR of the polymers comprising the benzene nucleus, **PPyBz-O_{Br}**, **PPyBz-O_{PF₆}**, and **PPyBz-O_{TFSI}** (Fig. 2(B)), revealed additional signals at 5.80 to 5.94 ppm attributed to methylene protons (CH_2), confirming the incorporation of the benzene core in the polymer structures resulting from the quaternization reaction. Their NMR spectra revealed the same broadness as appeared on the first set of the triazine-ionic polymers. The spectra also displayed characteristic singlets at 8.02, 8.19, and 8.15 ppm belonging to the imine protons ($\text{CH}=\text{N}$) with the same shift impact that seemed in the triazine core results. Extra aromatic protons resonated at 8.77 and 8.85 ppm confirming the presence of the benzene rings. The ^{13}C NMR spectra showed new signals ranging from 66.06 to 66.98 ppm, revealing the presence of the methylene carbons (CH_2).

The resulting cationic polymers, **PPyBz-O_{Br}** and **PPyTri-O_{Cl}**, which incorporate chloride (Cl^-) and bromide (Br^-) as counter anions, undergo a metathesis reaction. This anion exchange process occurs when the polymers are treated with a saturated brine solution of LiTFSI and KPF_6 , yielding the cationic polymers with PF_6^- and TFSI^- as counter anions: **PPyBz-O_{PF₆}**, **PPyBz-O_{TFSI}**, **PPyTri-O_{PF₆}** and **PPyTri-O_{TFSI}**. The success of the metathesis reaction was confirmed and supported by the investigation of the spectral data of the resulting polymers **PPyBz-O_{PF₆}**, **PPyBz-O_{TFSI}**, **PPyTri-O_{PF₆}** and **PPyTri-O_{TFSI}** tethering the PF_6^- and TFSI^- as counter anions. Their FTIR spectra (Fig. S1 †) showed the appearance of the absorption bands at 863 cm^{-1} , 1207 cm^{-1} , and 1353 cm^{-1} , confirming the presence of PF_6^- , SO_2 , and CF_3 , respectively, of TFSI^- anions. The analysis of ^{19}F NMR and ^{31}P NMR (Fig. S2 †) of the polymers **PPyBz-O_{PF₆}**, **PPyBz-O_{TFSI}**, **PPyTri-O_{PF₆}**, and **PPyTri-O_{TFSI}** were in accordance with their structures. The polymers **PPyBz-O_{PF₆}** and **PPyTri-O_{PF₆}** displayed distinguished two singlets at -69.17 and -71.06 ppm and -69.18 and -71.07 ppm, respectively. In addition, the PF_6^- anion exchange was also confirmed from the resonance of distinct septet in the range of -131.01 to -157.36 ppm appearing in the ^{31}P NMR spectra of **PPyBz-O_{PF₆}** and **PPyTri-O_{PF₆}** polymers. The TFSI^- anions appeared as a singlet near -73.49 ppm in the ^{19}F NMR spectra of **PPyBz-O_{TFSI}** and **PPyTri-O_{TFSI}** polymers supporting their structures (Fig. S2 †).

3.2. Morphology study

Powder X-ray diffraction (PXRD) was utilized to analyze the crystalline nature of the synthesized polymers (Fig. 3). The PXRD patterns showed semi-crystalline behavior for all formed polymers, with four main characteristic peaks at $2\theta = 19.3^\circ$, 26.4° , 54.4° , and 72.9° . The diffraction peaks at $2\theta = 10^\circ$ – 30° and $2\theta = 35^\circ$ – 50° were the confirmation of the (002) and (101) planes of the carbon materials, respectively. The peak at 10° – 30° indicated the fragmented and devolved crystallite aromatic

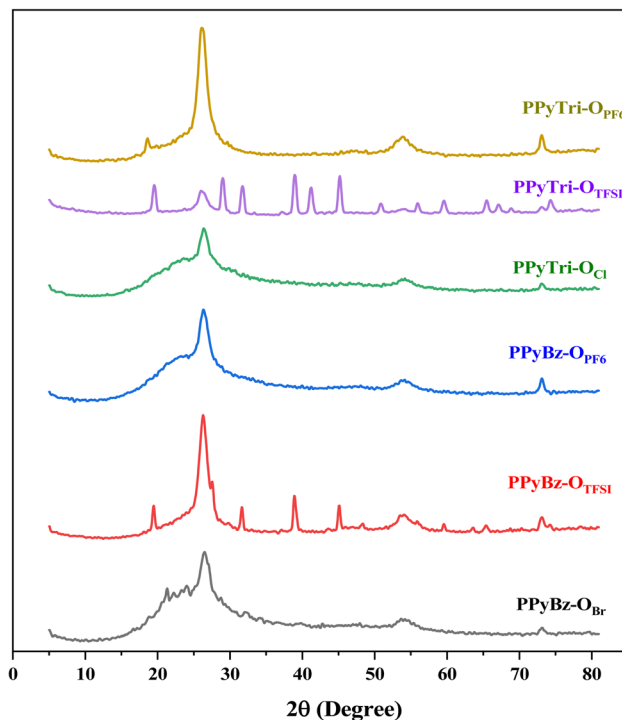


Fig. 3 PXRD patterns of the synthesized C3-symmetry porous ionic polymers.

structure, while a broad and weak peak at 35° – 50° indicated an amorphous structure with minimal graphitization degree.⁷⁰

The exchange anions affected the crystallinity of the designed two core polymers due to the flexible structure *via* the imine and aliphatic bridges between the rigid aromatic rings. The anions displacement by the TFSI^- anion in **PPyBz-O_{TFSI}** and **PPyTri-O_{TFSI}** polymers caused an increase in the crystallinity in the PXRD patterns and showed diffraction peaks at 19.5° , 28.9° , 31.7° , 39.0° , 45.1° that matched (201), (114), (015), (116), (125) crystal planes, respectively, and were consistent with the data from the JCPDS card (no: 01-082-2341) of TFSI^- . The bulky size of the TFSI^- ion affected the natural crystal packing due to the formation of the bilayer structure with no significant change in the crystallinity of PF_6^- . This structural flexibility has also been reported in porous materials.^{71–73}

To obtain in-depth insight into the impact of the anions on the morphology of the C3-symmetry porous ionic polymers, the synthesized polymers were examined using scanning electron microscopy (SEM) at a magnification of 20 kx, as shown in (Fig. 4(A–F)). In the case of the polymers **PPyTri-O** and **PPyBz-O**, distinct and well-defined morphologies were observed, featuring sphere-shaped structures with sizes ranging from nanosized. Conversely, both **PPyTri-O_{PF₆}** and **PPyBz-O_{PF₆}** exhibited aggregated clusters, coarse surfaces, and loosely arranged irregular particles. Similarly, the polymers **PPyTri-O_{TFSI}** and **PPyBz-O_{TFSI}** showed aggregated and irregular particles in the micron-scale dimensions. These SEM images vividly depict the significant impact of bulky anions on the polymer morphology. This observation aligns with findings reported by E. Maya *et al.*⁷⁴



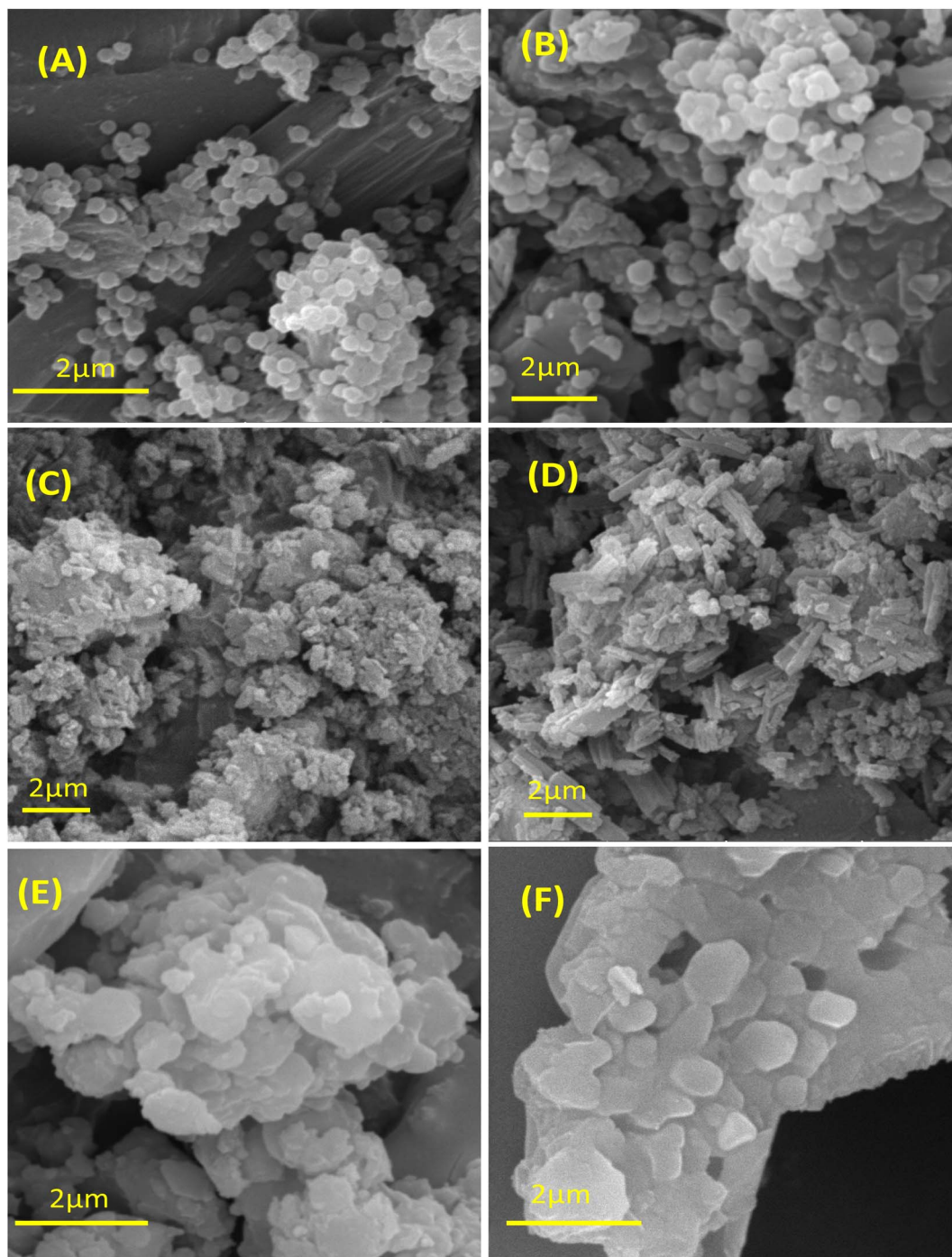


Fig. 4 SEM images of the synthesized porous ionic polymers with C3-symmetry (A) PPyBz-O_{Br}, (B) PPyTri-O_{Cl}, (C) PPyBz-O_{PF₆}, (D) PPyTri-O_{PF₆}, (E) PPyBz-O_{TFSI} and (F) PPyTri-O_{TFSI}.

3.3. Thermal study

The thermal properties of the synthesized C₃-symmetry ionic polymers were studied using thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) in the temperature range of 25–1000 °C at a heating rate of 10 °C min⁻¹ (Fig. S3†). The TGA/DTG curves exhibited three-step weight loss. Most synthesized polymers were not hygroscopic in nature, and the first stage of weight loss occurred between 200 °C and 600 °C,

while the second stage was observed between 630 °C and 840 °C owing to the degradation of the polymer backbone.^{70,75–77}

Table 1 presents a comprehensive comparison of T_{10} , T_{25} , and T_{50} , illustrating thermal decomposition at 10%, 25%, and 50%, respectively, for the polymers. The values of T_{10} , T_{25} , and T_{50} in the case of triazine core, the polymer with PF₆ anion has the highest thermal stability, while in the case of benzene core, the anion with TFSI has the highest thermal stability. Moreover, Table 1 outlines the final temperature for the polymer



Table 1 Thermal behavior of the synthesized C3-symmetry porous ionic polymers

	$T_{10\%}$	$T_{25\%}$	$T_{50\%}$	T_{final}	T_{max}
PPyTri-O _{Cl}	280	320	380	740	690
PPyTri-O _{PF6}	270	370	470	680	700
PPyTri-O _{TFSI}	220	360	400	830	800
PPyBz-O _{Br}	230	275	360	765	730
PPyBz-O _{PF6}	160	190	300	685	670
PPyBz-O _{TFSI}	300	370	460	770	720

degradation (PDT_{final}) and the maximum polymer decomposition temperature (PDT_{max}). As exemplified by Table 1, the PDT_{final} values ranged from 680 °C to 830 °C, while the DTG revealed PDT_{max} in the range of 670–800 °C. The bulky anion TFSI with triazine core shows the highest lowest values of PDT_{final} and PDT_{max} in comparison with the other anions. While the polymers with PF6 anion have the same value of PDT_{final} in two cores; however, the PDT_{max} value shows the highest thermal stability in the triazine core. From the polymers under investigation, it was found that the triazine core had more thermal stability, which may be due to less flexibility, and the bulky anion TFSI also increases the thermal stability by increasing the electrostatic effect.

3.4. Nitrogen adsorption analysis

Nitrogen adsorption–desorption isotherms, as shown in Fig. S4,† were taken to characterize the pores in the C3-symmetry ionic polymer. All the polymers exhibited type IV nitrogen adsorption–desorption isotherms.⁷⁸ The adsorption equilibrium leads to the growth of the H3 hysteresis loop, associated with capillary condensation in mesoporous structures, including the accumulation of the slit pore formation.⁷⁹ Table 2 shows the specific surface area calculated using the Bruner–Emmett–Teller (BET) theory model and density functional theory (DFT), as well as pore volume and average pore size calculated using the BJH model and DFT. Accordingly, the pore-size distributions were evaluated through BJH and DFT, approved mesopores character (more than 2 nm pores) for all the pore-size distribution patterns (Fig. S4†). Table 2 shows that the polymers with the triazine core have a higher specific surface area when compared with polymers with benzene cores

Table 2 Surface area, pore volume, and pore size for synthesized C3-symmetry ionic polymers

Sample code	Surface area ($m^2 g^{-1}$)			Pore volume ($cm^3 g^{-1}$)		Pore size (nm)	
	BET	BJH	DFT	BJH	DFT	BJH	DFT
PPyTri-O _{Cl}	54.73	58.40	52.83	0.17	0.17	5.7	6.9
PPyTri-O _{PF6}	60.57	64.66	57.73	0.18	0.18	5.7	6.3
PPyTri-O _{TFSI}	35.00	26.76	33.78	0.11	0.10	5.7	6.3
PPyBz-O _{Br}	50.76	34.18	54.49	0.19	0.19	5.7	6.3
PPyBz-O _{PF6}	53.84	56.30	56.61	0.21	0.19	5.7	6.3
PPyBz-O _{TFSI}	46.15	37.60	46.35	0.15	0.15	5.7	6.3

for the same anion. That may be due to the flexibility of methylene in the benzene core that reduces the surface area.⁸⁰ However, when the anion is exchanged by PF₆ or TFSI for the same core, it is found that TFSI has a lower surface area compared to PF₆. The same pattern is found in the benzene and triazine cores, and that may affect the bulky anions to reduce the surface area. Notably, the counter anions occupy some spaces within the networks of these porous polymers, more or less leading to reduced surface areas.⁸¹ On the other hand, for the ionic porous polymers with C3-symmetry, the rigidity of skeletons was more or less weakened by the tritopic building blocks comprising phenyl and/or triazine rings, which could create much more complex conformational torsions by free rotation around single carbon–carbon bonds, and also tends to cause the interpenetration of chain segments. Correspondingly, these three porous polymers show lower specific surface areas.^{82,83}

3.5. QCN study

3.5.1 Sensor activity of PPyTri-O and PPyBz-O derivatives on QCN chips for CO₂ gas sensing. The detection of CO₂ on the surface of porous ionic polymers (PIPs) sensors was performed and measured using QCN. A comparative frequency shift (Δf) analysis of CO₂ gas exposure across PPyTri-O and PPyBz-O derivatives films at 20 °C, 25 °C, and 30 °C was performed. The process was conducted sequentially at each temperature, providing sufficient time for the QCN chips to stabilize after each temperature adjustment, and the baseline frequency (f_0) for each PIP sensor was recorded before CO₂ gas exposure.^{84–86} Fig. 5 illustrates the monitoring of the frequency shift (Δf) for each individual PIPs sensor while the CO₂ gas is introduced into the chamber. The (Δf) values and the average of (Δf) were recorded for every CO₂ concentration level ranging from low to hundreds of ppm. Upon the introduction of CO₂ gas to the sensors, it was observed that the frequency decreased rapidly, and the response time of the PPyTri-O and PPyBz-O derivatives was established as the time required for the frequency shift to reduce by ~85% upon activation of the gas. The polymers PPyTri-O_{PF6} and PPyBz-O_{PF6} displayed the highest adsorption of CO₂ on their surfaces, followed by PPyTri-O_{Cl} and PPyBz-O_{Br}, while the PPyBz-O_{TFSI} and PPyTri-O_{TFSI} recorded the least

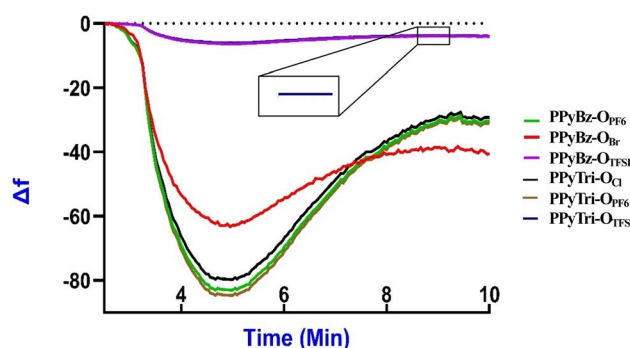


Fig. 5 QCN sensorgram curves of PPyTri-O and PPyBz-O thin film derivatives showing the response to CO₂ gas at 25 °C.



response. The response time for the four polymers was between 4 to 5 min. As the gas molecules were adsorbed onto the surface of the sensitive film, the sensors reached a steady state. When the CO₂ gas was purged from the sensors using clean N₂, the frequency returned to its original level, and the sensors demonstrated quick recovery with approximately 2 min. These data demonstrated that the type of counter anion significantly influences the CO₂ adsorption capacity of PIPs. Among the four polymers, the ionic polymers with PF₆ as the counter anion attained the best results, followed closely by PIPs containing halogens and those with TFSI were the last. These results were consistent with the surface area findings derived from the BET model theory, where the PIPs displayed a surface area in the same order as their response to CO₂ adsorption, PF₆ > Cl, Br > TFSI. The obtained results are in agreement with those from the prior research on polymerization-derived PIPs,^{81,82} which indicated that inorganic anions such as halogens and PF₆ provided the most effective CO₂ adsorption. This concludes that selecting the right anion is crucial for achieving high CO₂ detection performance and increasing the CO₂ adsorption on the surface of the formed sensor. Furthermore, the influence of the cations on the CO₂ detection comes right after the anions impact and can be observed in the difference responses between PIPs with triazine and benzene cores in PPyTri-O_{PF6} and PPyBz-O_{PF6} as well as in PPyTri-O_{Cl} and PPyBz-O_{Br}. The ionic polymers with triazine entities showed a higher affinity for CO₂ than those with a benzene core, which can be predicted by the effect of C-N linkages on attractive CO₂ adsorption.⁸⁷

3.5.2 Precision analysis. The precision of the PIP sensors was assessed by calculating the standard deviations of the Δf values after 25 minutes of gas exposure for the PIP sensors on the QCN chips (Fig. 6). The analysis confirmed that the mean frequency shifts of the sensors were consistent with 25 minutes CO₂ gas exposure experiments at different temperatures (Fig. 7).

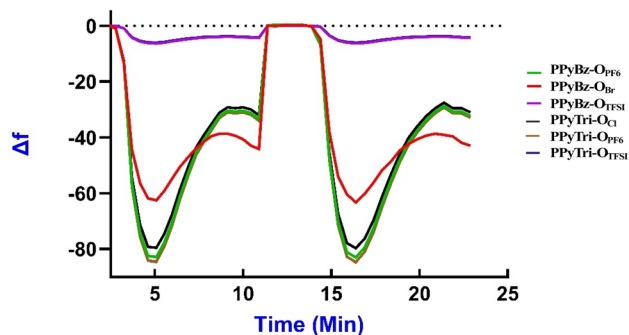


Fig. 7 Sensorgram curves of PIPs after 25 minutes of exposure showing a high level of precision of the sensors.

Fig. 6 and 7 depict the mean Δf values for the sensors, and the standard deviation of the repeated exposures ranged from 8.98 to 9.65 Hz, indicating a high level of precision and repeatability. These results demonstrate the exceptional precision and reliability of the PIP sensors for CO₂ gas detection at temperatures between 20 °C and 30 °C. According to the data in Fig. 6, it can be observed that the impact of the temperature on the frequency shift becomes more pronounced as the temperature rises from 20 °C to 30 °C.

3.5.3 Selectivity, reproducibility, and sensitivity. The selectivity of the fabricated PIP sensors on QCN chips for CO₂ gas sensing at varying temperatures was studied in comparison to non-targeted gases such as NH₃ and H₂S (Fig. 6 and S5[†]). The obtained sensors outperformed the selectivity toward CO₂ gas in comparison with NH₃ and H₂S as the Δf values decreased, indicating CO₂ gas adsorption on the surface. In contrast, the decrease in Δf values for NH₃ and H₂S indicates the non-sensing of these gases (Fig. S5[†]). These findings demonstrate the exceptional CO₂ selectivity of the sensors at different

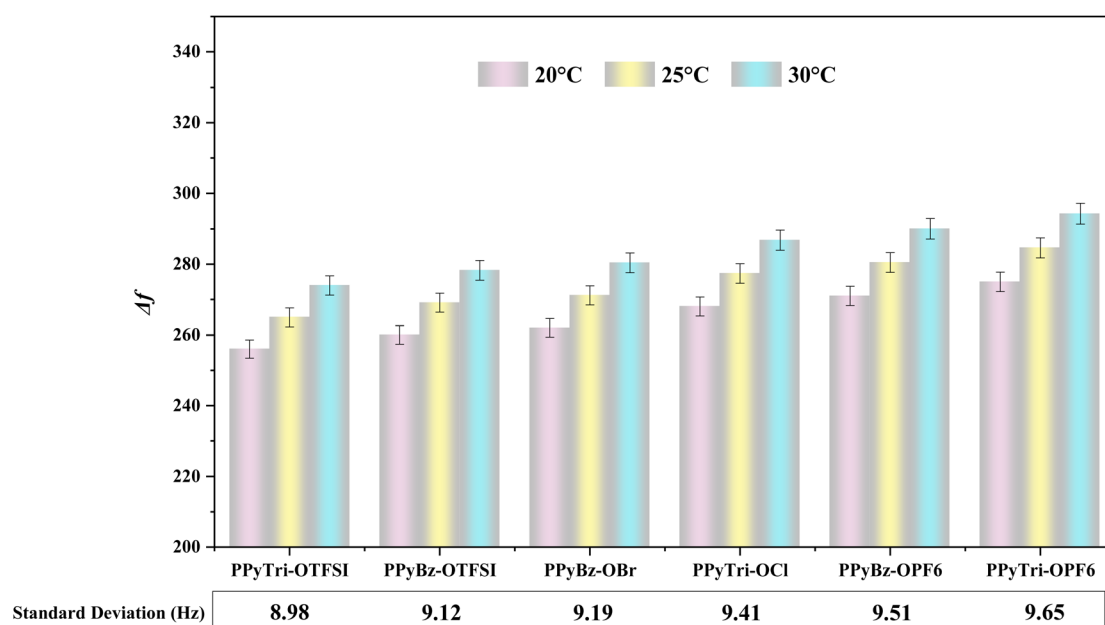


Fig. 6 The average frequency shift (Δf) and standard deviation for each PIP sensor at 20 °C, 25 °C, and 30 °C.



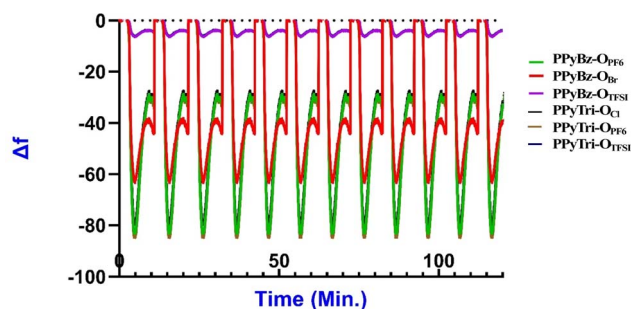


Fig. 8 The repeatability response sensorgram curves of PIPs for multiple cycles.

temperatures, making them a suitable choice for CO₂ detection applications.

The reproducibility test was undertaken through multiple repeated measurements of the frequency shift (Δf) for randomly chosen PIPs at three temperatures (20 °C, 25 °C, and 30 °C). The relative standard deviations (RSD) of the Δf values were computed to evaluate the sensors' reproducibility. Table S1† and Fig. (8) exhibit the frequency shift measurements (Δf) and RSD (%) values for the samples, respectively. The RSD values in the table indicate that the frequency shifts between the triplicate measurements demonstrate a high level of reproducibility, and the outcomes in the figures for each run were stable and indistinguishable, as there were no noticeable differences in the response. These results demonstrate the dependability of the designed sensors when exposed to CO₂ gas under various temperature conditions.

Evaluating the efficiency of the formed sensors on the QCN chips as CO₂ gas sensors at various temperatures provides vital information regarding the capabilities of the sensors. Sensitivity can be represented as the change in the frequency (Δf) per unit concentration of CO₂ and can be calculated by dividing the average frequency shift (Δf) by CO₂ concentration.

3.5.4 Mechanism of action. The fabricated PIP sensors on quartz crystal nanobalance (QCN) chips detected CO₂ gas by

leveraging the CO₂ affinity of Lewis acidic groups within the PIPs. When CO₂ molecules permeate the sensor phase, the polymer chains undergo structural changes, increasing rigidity. This rigidification due to CO₂ adsorption causes a steady frequency shift. The primary transduction mechanism involves depositing polymer film layers containing CO₂-philic moieties (e.g., PF₆) onto the piezoelectric quartz crystal surface. When CO₂ gas interacts with the PIP sensor, the polar moieties of the porous ionic polymer form host-guest complexes with CO₂ molecules, increasing the overall mass and reducing conformational chain flexibility, which stiffens the PIP film. Consequently, the frequency shift (Δf) is directly proportional to mass change (Δm) and inversely proportional to the square of the base resonance frequency (f_0), as described by the Sauerbrey equation:

$$\Delta f = -(2 \cdot f_0^2 \cdot \Delta m) / (A \cdot \rho \cdot \sqrt{\mu})$$

where A is the electrode area, ρ is the density of quartz, and μ is the shear modulus.

The designed PIP sensors on QCN chips enable precise, selective, and reproducible CO₂ measurements due to the stability of the physisorption process. This process forms weak intermolecular bonds between the CO₂ molecules and the PIP-coated QCN chip surface, ensuring stable and continuous linkages during gas adsorption and desorption.

To contextualize the performance of the synthesized porous ionic polymers for CO₂ sensing, a comparison was made with the previously reported QCM-based sensing materials. Table 3 summarizes the frequency shifts observed for CO₂ detection using various materials, alongside their selectivity toward interfering gases such as NH₃ and H₂S. Ethyl cellulose (EC) exhibited strong CO₂ responsiveness, while polypyrrole (PPy) demonstrated limited sensitivity. Tetramethylammonium fluoride tetrahydrate (TMAF) and polyethyleneimine (PEI) showed substantial CO₂ responses; however, their cross-sensitivity to NH₃ and SO₂ limits their practical applicability. Similarly, nitrogen-doped tungsten carbide (WC@NC) provided excellent

Table 3 Sensing of CO₂ and selectivity over H₂S and NH₃ in PIPs and some reported materials

Material	Frequency shift for CO ₂ (Hz)	Selectivity CO ₂ over H ₂ S	Selectivity CO ₂ over NH ₃	Notes	Ref.
Ethyl cellulose (EC)	438.95	Moderate	Low	Strong CO ₂ response; limited cross-responsiveness	88
Polypyrrole (PPy)	59.00	Low	Low	Modest sensitivity to CO ₂ , mainly used in gas mixture detection	
Tetramethylammonium fluoride (TMAF)	300.80	Moderate	Low	Good CO ₂ sensitivity but notable responses to SO ₂ and NH ₃	
Polyethyleneimine (PEI)	980.78	Low	Low	Exceptional response to NH ₃ , making it less selective for CO ₂	
WC@NC (nitrogen-doped tungsten carbide)	11.78	Low	Low	Excellent H ₂ S selectivity but minimal CO ₂ sensitivity	
PPyTri-OTFSI	264.96	High	High	High CO ₂ sensitivity with excellent selectivity over H ₂ S and NH ₃ ; thermally stable	This work
PPyBz-OTFSI	269.10	High	High		
PPyBz-OBz	271.17	High	High		
PPyTri-OC1	277.38	High	High		
PPyBz-OPF6	280.49	High	High		
PPyTri-OPF6	284.63	High	High		



selectivity for H₂S but showed minimal sensitivity to CO₂. In comparison, the newly developed porous ionic polymers (e.g., **PPyTri-O_{TFSI}**, **PPyBz-O_{TFSI}**, and **PPyTri-O_{PF6}**) exhibited high CO₂ sensitivity with frequency shifts ranging from 264.96 Hz to 284.63 Hz, demonstrating superior performance compared to the previously reported materials. Furthermore, these polymers exhibited exceptional selectivity for CO₂, with minimal interference from NH₃ and H₂S, which is critical for real-world applications. The tunable performance of these polymers, achieved through structural modifications and tailored anion incorporation, further underscores their potential as next-generation materials for precise and selective CO₂ sensing.

4. Conclusions

An efficient quaternization of the designed 4,4'-dipyridyl derivative **4,4'-bp-O** with the appropriate 1,3,5-tris(-bromomethyl)benzene **BB** and/or cyanuric chloride **CC** resulted in the effective synthesis of a new class of porous ionic polymers tethering triazine (benzene) nucleus conjugated to three pyridiniums as cationic counterparts tethered bromide/chloride anions **PPyBz-O** and **PPyTri-O**. LiTFSI and KPF₆ anions were incorporated into the core of such polymers through a metathesis protocol furnished on the formation of new ionic polymers. The structures of the formed polymers were investigated by FTIR, ¹H NMR, and ¹³C NMR analyses. The synthesized polymer was analyzed using PXRD, which showed the presence of semi-crystalline structures. The SEM examination demonstrated that micro or nanoparticles were uniformly distributed within the polymer. Furthermore, the TGA and DTA analyses indicated that the synthesized polymers exhibited good thermal stability. The modified porous ionic polymer was tested for CO₂ gas sensing using quartz crystal nanobalance (QCN), which demonstrated precise, selective, and reproducible measurements.

Data availability

The authors confirm that all data are included in the manuscript.

Conflicts of interest

There are no conflicts to declare.

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