Electronic supplementary materials *Mendeleev Commun.*, 2025, **35**, 119–121

A chemical approach for probing the interphase boundary between polymer-electrolyte membrane and HT-PEM fuel cell carbon nanofiber anode

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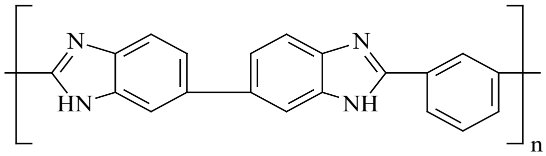
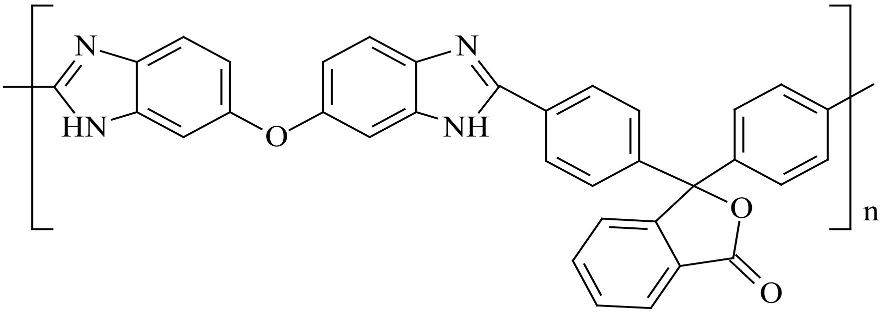


***m*-PBI**



PBI-O-PhT

Figure S1 Chemical structures of *m*-PBI and PBI-O-PhT.

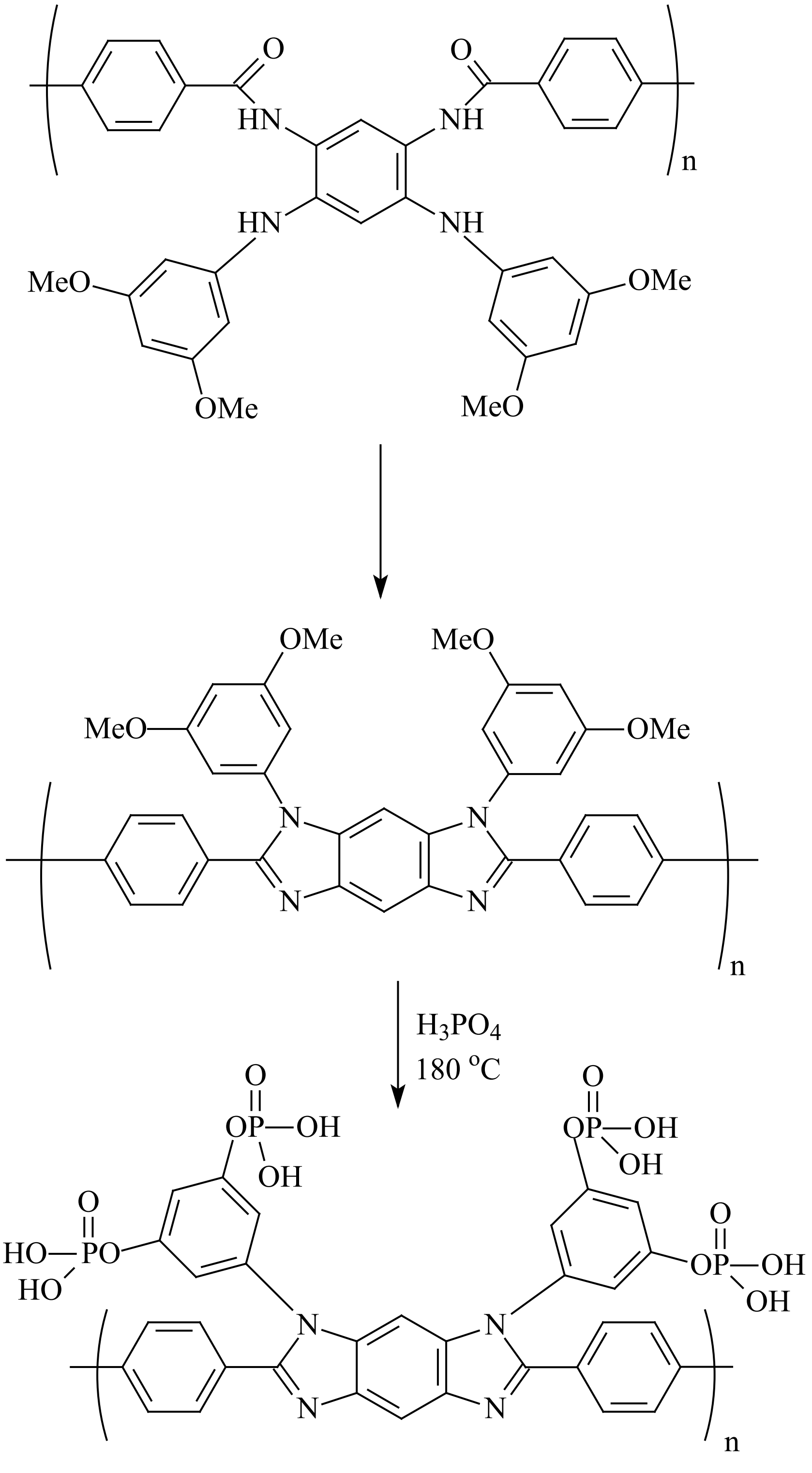


Figure S2 Thermal cyclization for the PBI-4MeO-BP membrane obtaining followed by its self-phosphorylation.

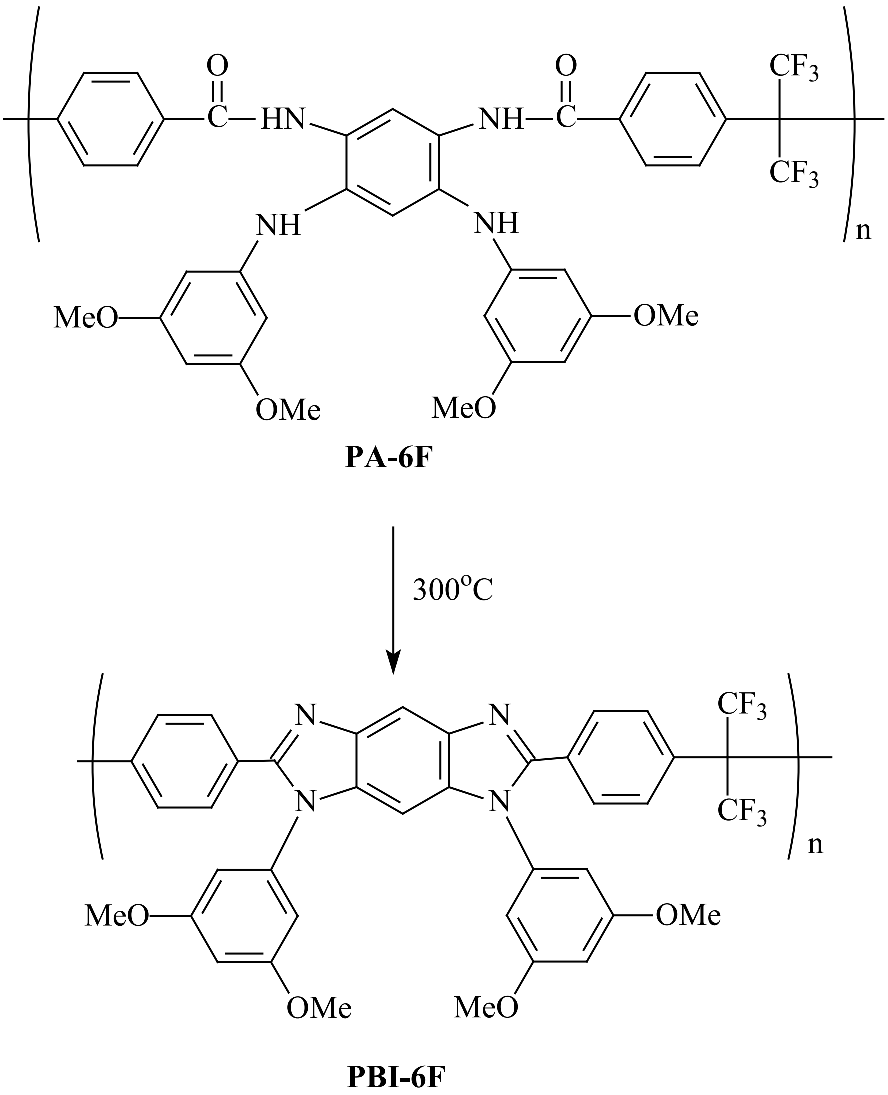


Figure S3 Thermal cyclization for the PBI-6F formation.

Additional experimental details

Pt/CNF electrode obtaining

Polyacrylonitrile (PAN)-based composite nanofibers were obtained by the needle-free electrospinning according to the Nanospider^{TM} technology (a method of electrospinning from a free surface) on a NS Lab Nanospider^{TM} setup (Elmarco, Czechia) at relative humidity of 8 % and voltage of 69 kV (distance between electrodes was 190 mm). The electrospinning polymer solution contained 3.25 g of PAN (M_w $150 \cdot 10^3$ Da), 0.1 g of Vulcan®XC-72 (Cabot, USA) carbon black (~3 wt.% relative to PAN) and 0.03 g of $ZrCl_4$ dispersed in 50 mL of DMF for 3 h in ultrasonic bath. The resulting PAN/Vulcan/Zr composite nanofiber mat was stabilized (oxidized) at 250 °C in air for 2 h. The resulting material (PAN/Vulcan/Zr-250) was immersed into 0.5 wt.% solution of $Zn(NO_3)_2$ in water/ethanol (1:3 v/v) mixture for ~24 h. Then, the material was dried at 100 °C for 2 h and pyrolyzed under vacuum (with heating rate of 3 K min^{-1}) at 1000 °C for 2 h. Since T_b (Zn) is 907 °C, it evaporates during the pyrolysis step providing extra surface for CNF. The resulting material (here and further it is called as CNF mat) saved its form after pyrolysis (elemental analysis data: C 88.5%; N 6.2%; Zr 0.2%). Pt was deposited onto CNF mats with a surface area of 6.76 cm^2 separately for each mat. The Pt deposition was carried out in 10 mL of aqueous solution containing the calculated amount of $H_2[PtCl_6] \cdot 6H_2O$ and 0.5 g of HCOOH (reducing agent) for 3 days to obtain Pt/CNF with Pt concentration of 1.2 mg$_{Pt}$ cm^{-2}. For

MEA 2 and MEA 3, the self-phosphorylating polymer coating PBI-6F [S1] was deposited onto Pt/CNF mat surface by immersing of Pt/CNF into 0.1 wt.% solution of PA-6F (Figure S3) in hexafluoroisopropanol for 10 min, then, the coated mats were dried in air for 1 h at 300 °C. As a result, PA-6F converted into PBI-6F on the Pt/CNF anode surface at 300 °C. All Pt/CNF electrocatalysts were washed with distilled water and dried under vacuum for 2 h at 100 °C.

MEA assembling

For MEA assembling, the resulting anodes (pure Pt/CNF or Pt/CNF with PBI-6F coating) were assembled with the proton-conducting membranes (PBI-O-PhT [S2] or PBI-4OMe-BP) and Celtec®-P Series 1000 cathodes [S2] and placed between two graphite flow field plates (Arbin Instruments, USA). Particularly, MEA 1 included pure Pt/CNF anode and the PBI-O-PhT membrane. MEA 2 included the Pt/CNF anode coated with the self-phosphorylating PBI-6F coating and the PBI-O-PhT membrane. MEA 3 included both, the Pt/CNF anode coated with the self-phosphorylating PBI-6F coating and the self-phosphorylating PBI-4OMe-BP membrane.

HT-PEM fuel cell operation

The hydrogen-air HT-PEM fuel cell MEA (5 cm^2 working area) performance was studied using a standard test fuel cell with two graphite flow field plates (Arbin Instruments, USA) using standard gas diffusion cathodes Celtec®-P Series 1000 [S3], Pt/CNF-based anodes and PBI-O-PhT or PBI-4OMe-BP membranes depending on MEA. HT-PEMFC MEA polarization curves were recorded at 180 and 200 °C and ambient pressure, FC voltage was scanned at a rate of 5 mV/s using an Elins P-200X Potentiostat (Electrochemical Instruments, Russia). The anode and cathode were supplied with H_2 and air at rates of 100 and 800 mL/min, correspondingly.

References

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