In situ polymerization approach to the synthesis of superhydrophobic and superoleophilic nanofibrous membranes for oil/water separation

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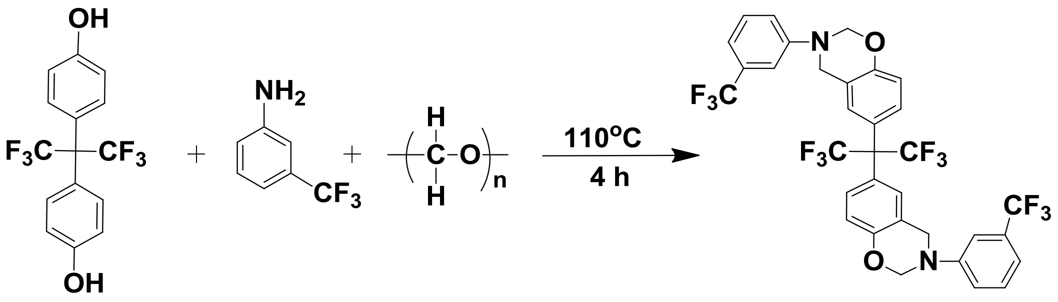
Supporting Information



BAF **tfa** **paraformaldehyde** **BAF-tfa**

Fig. S1. Chemical synthetic route of BAF-tfa monomer.

Structural confirmation of BAF-tfa

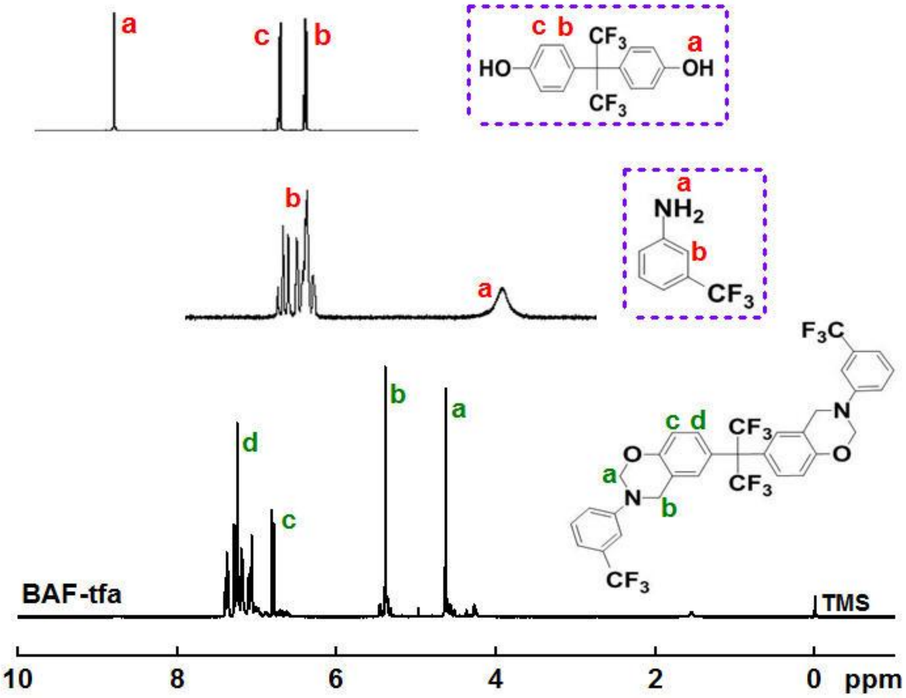


Fig. S2 ^{1}H NMR spectrograph of fluorinated bisphenol A, *m*-(trifluoromethyl) aniline (above), and the reaction product of BAF, tfa and paraformaldehyde (BAF-tfa) (below).

The as-synthesized BAF-tfa monomer after purification and crystallization was subjected to nuclear magnetic resonance (NMR) spectroscopic analysis. Fig. S2 illustrates the ^{1}H NMR spectrum of BAF-tfa. For pure BAF, the peak for Ar-OH appeared at 9.16 ppm, while signals for aromatic protons appeared at 6.98 and 6.64 ppm. In case of pure tfa, the proton for amine group has given chemical shift at 3.7 ppm while aromatic protons have given signals around 6.8-7.2 ppm (Fig. S2 above). Specific for oxazine ring, the peaks for Ar-CH_2-N and N-CH_2-O are observed in ^{1}H NMR, which are distinctive of benzoxazine monomers.[1] For BAF-tfa monomer, the characteristic protons of Ar-CH_2-N and N-CH_2-O appeared at 4.63 ppm, and 5.46 ppm. Moreover, aromatic protons have given their chemical shift in the range of 6.81-7.46 ppm (Fig. S2 below).

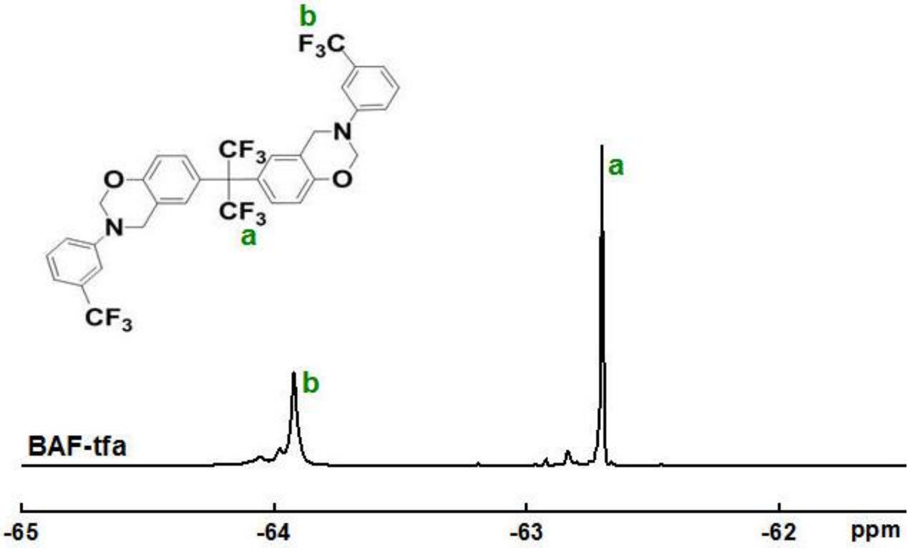


Fig. S3 ^{19}F NMR spectrograph of BAF-tfa monomer.

^{19}F NMR has given further structural affirmation of BAF-tfa monomer (Fig. S3). The chemical shift for N-Ar-CF_3 is appeared at 120.26 ppm, while for C-CF_3 at 63.92 ppm.[2] Acquisition of quantitative results from all NMR analysis has confirmed the chemical structure of BAF-tfa.

FT-IR spectroscopic analysis of pure and modified membranes

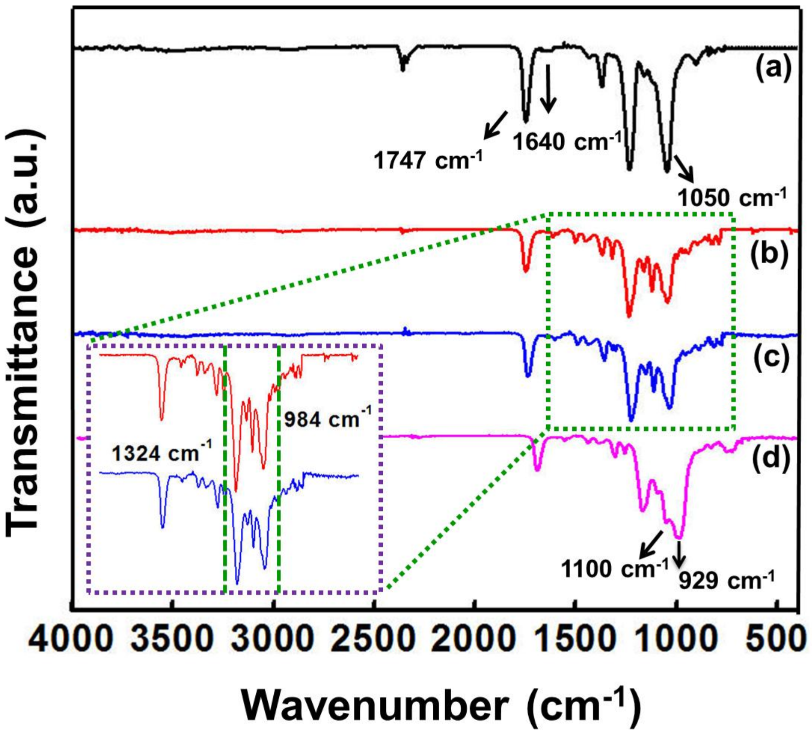


Fig. S4 FT-IR spectrograph of (a) CA, (b) FCA-1 before curing, (c) FCA-1 after curing and (d) FCA-1/SNP-2 nanofibrous membranes. Inset is the characteristics peaks specific for benzoxazine monomer.

Incorporation of low surface energy F-PBZ to the CA nanofibrous membranes have been analyzed by FT-IR spectroscopic analysis. Fig. S4 shows the typical FT-IR spectrum of pure and modified CA nanofibrous membranes. The pure CA nanofibrous membranes exhibited a number of absorption features below 2000 cm^{-1} with the characteristic peaks at 1747 and 1640 cm^{-1} which were attributed to the C=O and C-O-C, respectively (Fig. S4a). Moreover, the peak at 1050 cm^{-1} was assigned to symmetrical C-O stretching of CA nanofibers.[3, 4] The decrease in adsorption bands for CA and the presence of characteristic bands specific for benzoxazine monomer have confirmed the incorporation of cross-linked structure of F-PBZ within the CA nanofibers. FCA-1 nanofibrous membrane has shown the typical distinguishing bands for oxazine ring at 830 cm^{-1} and for C-O-C at 945 cm^{-1} along with an adsorption band for trisubstituted benzene ring at 1320 cm^{-1} (Fig. S4b).[5, 6] The decrease in peak resolution of the band for trisubstituted benzene ring have pointed out the in situ polymerization of oxazine ring on the surface of CA and thus validated the transformation of monomers into oligomers and polymers (Fig. S4c). In the Fig. S4d, the appearance of characteristic adsorption peaks at 1100 for Si-O-Si and at 929 cm^{-1} for Si-OH bond have confirmed the incorporation of SiO_2 nanoparticles within the FCA-1/SNP-2 nanofibrous membranes.[7, 8]

Oil contact angle measurements

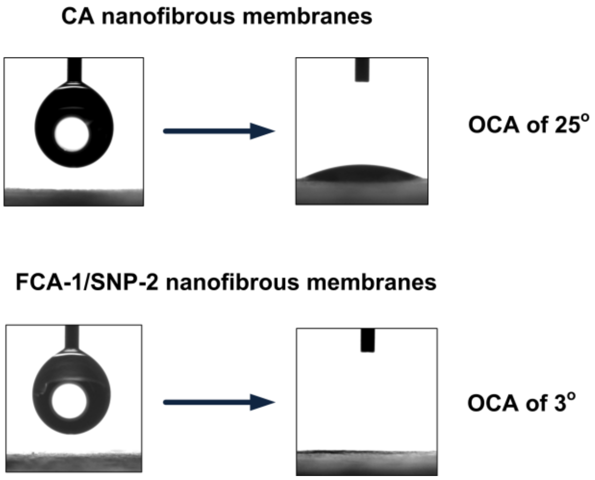


Fig. S5 Photographs showing the OCAs of CA and FCA-1/SNP2 nanofibrous membranes.

References

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