Supporting information

Humidity-Responsive Molecular Gate-Opening Mechanism for Gas Separation in Ultraselective Nanocellulose/IL Hybrid Membranes

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Surface analysis

Surface analysis of hybrid NFC/IL films was performed by XPS, and corresponding spectra are displayed in Figure S1. The relative atomic ratios reported in the main text are obtained from the areas under the individual element-specific ionization peaks.

![XPS spectra](image)

**Figure S1.** XPS spectra acquired from neat NFC and hybrid NFC/IL films (labeled). Also identified are the C 1s, N 1s and O 1s ionization peaks (labeled with dashed vertical lines).
Dynamic mechanical analysis (DMA)

Free-standing NFC and NFC/IL films with different IL loading levels, prepared according to the procedure in the main text and cut into strips measuring 2 cm x 1 cm with a laser cutter, have been analyzed by DMA in a TA Instruments RSA III instrument operated in tensile mode at a strain amplitude of 0.5%. The dynamic storage and loss moduli (E' and E", respectively) have been measured as a function of frequency at ambient temperature. The frequency spectra presented in Figure S2 confirm that the membranes behave as solid-like materials wherein E' > E" over the entire frequency range examined. Moreover, the two IL-containing specimens can, for the most part, be considered physical gels, since E' and E" are parallel (the increases in the low-frequency results for the film with 35 wt% IL suggest that a crossover might occur at lower frequencies, indicating a long, but not infinite, relaxation time).

![Frequency spectra of the dynamic tensile moduli (E', filled symbols, and E", open symbols) for neat NFC and hybrid NFC/IL films (see legend for specimen details) at ambient temperature.](image)

Figure S2. Frequency spectra of the dynamic tensile moduli (E', filled symbols, and E", open symbols) for neat NFC and hybrid NFC/IL films (see legend for specimen details) at ambient temperature.

X-ray diffractometry (XRD)
Free-standing NFC and NFC/IL films with different IL loading levels have also been examined by XRD at ambient temperature in a Bruker D8 A25 DaVinci X-ray diffractometer equipped with a rotating CuKα anode. The Crystallinity Index (CrI) of all the materials investigated is calculated according to the method proposed by Segal et al.\textsuperscript{1} The results of this analysis are summarized in Figure S3. The inherent NFC crystallinity due to interfibrillar H-bonding appears to be disrupted due to the addition of IL that orients along the nanofibrillar surfaces.

![Figure S3](image)

**Figure S3.** XRD profiles collected from neat NFC and hybrid NFC/IL films (see legend for specimen details) at ambient temperature. Calculated CrI values are included for comparison.

**Gas sorption**

Gravimetric sorption analysis conducted on pre-dried and desorbed self-standing films employ dry gases instead of humidified gases since the presence of water induces membrane swelling and specimen volume changes at different experimental conditions.\textsuperscript{2} A series of CO\textsubscript{2} sorption isotherms is displayed as a function of pressure for NFC and NFC/IL films in Figure
S4A and confirms, as implied by the permeabilities included in Figure 6, that the CO\textsubscript{2} sorption capacity increases with increasing IL loading level. Differences in CO\textsubscript{2} sorption become pronounced at high pressures where the NFC acts as a typical polymeric matrix exhibiting dual-mode sorption behavior.\textsuperscript{3} Incorporation of [Emim][OAc] into NFC visibly alters the curvature of the isotherms.\textsuperscript{4}

![Figure S4.](image)

**Figure S4.** (A) Dry-gas CO\textsubscript{2} sorption isotherms and (B) solubility selectivity for neat NFC and hybrid NFC/IL films (see legend for specimen details) at 35°C. The solid lines serve to connect the data, and the error bars correspond to the standard error in the data.

Similarly, the sorption capacity of N\textsubscript{2} has been measured so that the corresponding CO\textsubscript{2}/N\textsubscript{2} solubility selectivity could be directly ascertained (cf. Figure S4B). Contrary to expectation, addition of IL to NFC appears to have a relatively small influence on solubility selectivity in hybrid NFC/IL films, increasing CO\textsubscript{2}/N\textsubscript{2} from *ca.* 2 to 4 in NFC and from *ca.* 4 to 11 in films containing 35 wt% [Emim][OAc]. Although the effect of IL loading on CO\textsubscript{2}/N\textsubscript{2} solubility selectivity is not clear at very low pressures (due to low uptake of N\textsubscript{2}), the overall trend remains evident at higher pressures.

**Permeation stability test**

Results from the stability analysis mentioned as a requirement for commercial application
in the main text are provided over the course of 30 h at 35°C in Figure S5A. Complementary SEM images of the surface and cross-section of the corresponding membrane after long-time testing are displayed together in Figure S5B and indicate no obvious morphological changes after the permeation tests, as expected.

Figure S5. (A) Stability analysis of humidified mixed-gas CO₂ permeability (black, left axis) and CO₂/N₂ separation factor (blue, right axis) for NFC/IL membranes with 50 wt% [Emim][OAc] measured at 35°C and 1.7 bar. (B) SEM images of the membrane surface (left of white dashed line) and cross-section (right of white dashed line) acquired from the membrane after testing.

References