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.

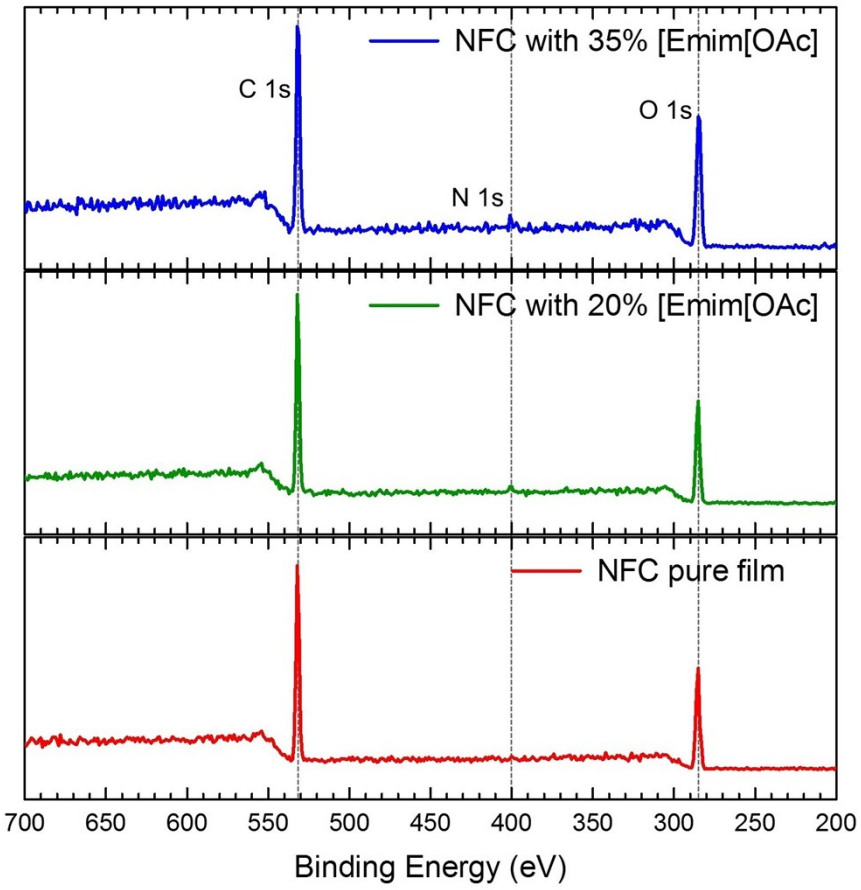

Figure S1. XPS spectra acquired from neat NFC and hybrid NFC/IL films (labeled). Also identified are the C 1s, N 1s and O 1s ionization peaks (labeled with dashed vertical lines).

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).

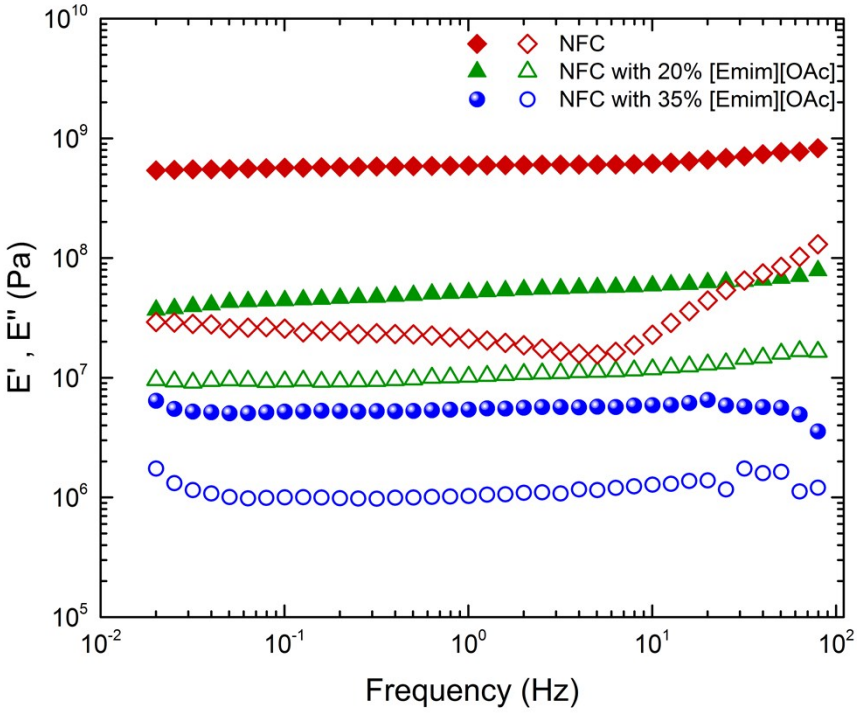

Figure S2. Frequency spectra of the dynamic tensile moduli (E', filled symbols, and E", open symbols) for neat NFC and hybrid NFC/IL films (see legend for specimen details) at ambient temperature.

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*.[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.

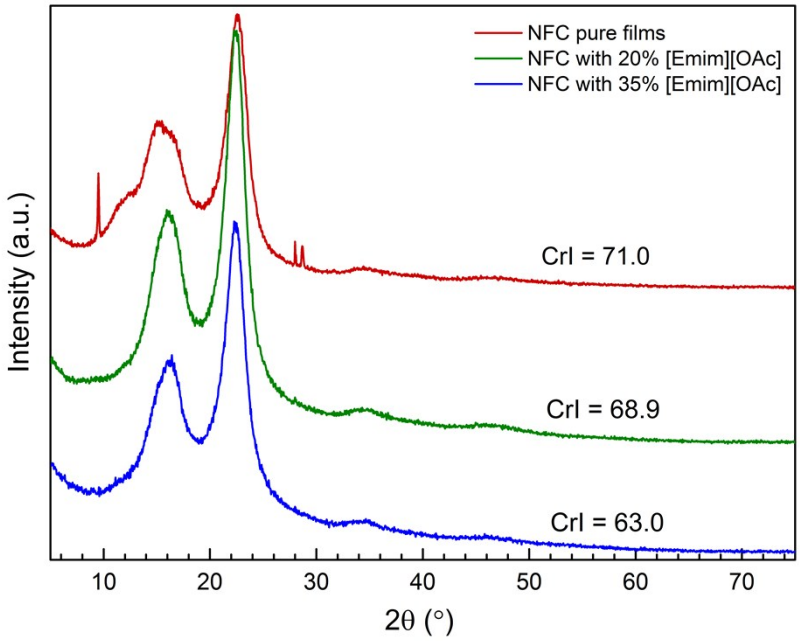

Figure S3. XRD profiles collected from neat NFC and hybrid NFC/IL films (see legend for specimen details) at ambient temperature. Calculated CrI values are included for comparison.

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.[2] A series of CO_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_2 sorption capacity increases with increasing IL loading level. Differences in CO_2 sorption become pronounced at high pressures where the NFC acts as a typical polymeric matrix exhibiting dual-mode sorption behavior.[3] Incorporation of [Emim][OAc] into NFC visibly alters the curvature of the isotherms.[4]

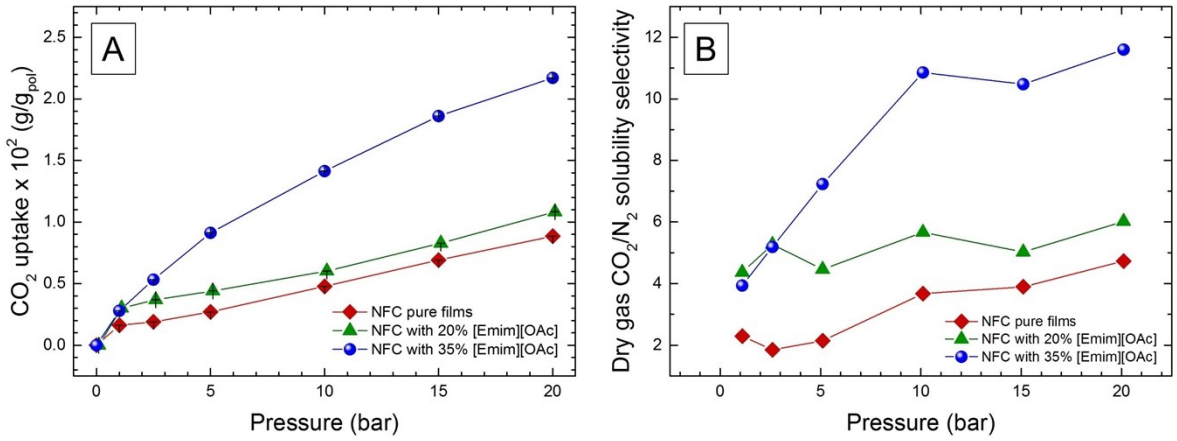

Figure S4. (A) Dry-gas CO_2 sorption isotherms and (B) solubility selectivity for neat NFC and hybrid NFC/IL films (see legend for specimen details) at 35°C. The solid lines serve to connect the data, and the error bars correspond to the standard error in the data.

Similarly, the sorption capacity of N_2 has been measured so that the corresponding CO_2/N_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_2/N_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_2/N_2 solubility selectivity is not clear at very low pressures (due to low uptake of N_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**.**

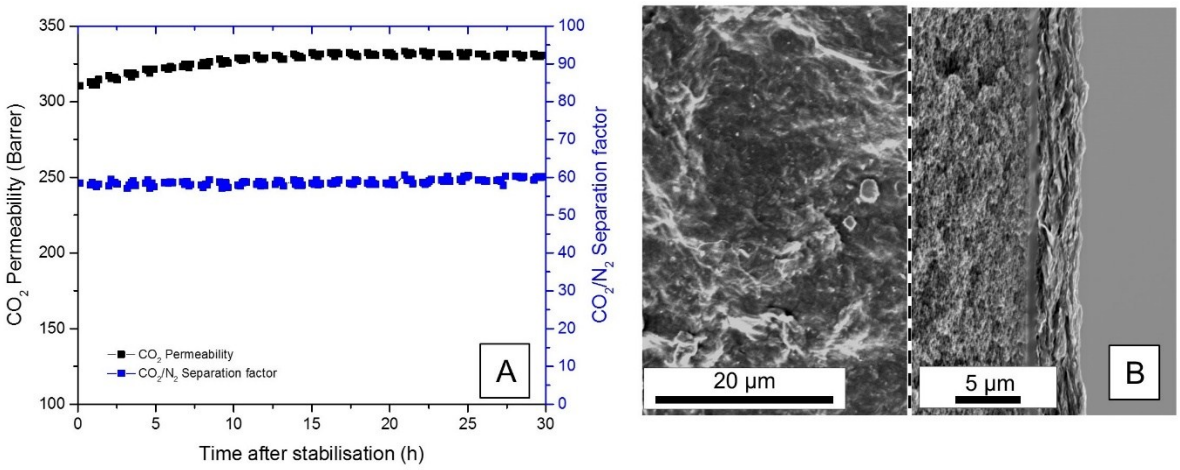

Figure S5. (A) Stability analysis of humidified mixed-gas CO_2 permeability (black, left axis) and CO_2/N_2 separation factor (blue, right axis) for NFC/IL membranes with 50 wt% [Emim][OAc] measured at 35°C and 1.7 bar. (B) SEM images of the membrane surface (left of white dashed line) and cross-section (right of white dashed line) acquired from the membrane after testing.

References

1 L. Segal, J. J. Creely, A. E. Martin Jr. and C. M. Conrad, *Text. Res. J.*, 1959, 786–794.

2 H. Bux, C. Chmelik, J. M. Van Baten, R. Krishna and J. Caro, *Adv. Mater.*, 2010, **22**, 4741–4743.

3 I. Kikic, M. Lora, A. Cortesi and P. Sist, *Fluid Phase Equilib.*, 1999, **158**, 913–921.

4 A. Yokozeki, M. B. Shiflett, C. P. Junk, L. M. Grieco and T. Foo, *J. Phys. Chem. B*, 2008, **112**, 16654–16663.