Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

Molecular transport in ionic liquid/nanomembrane hybrids

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XPS spectra

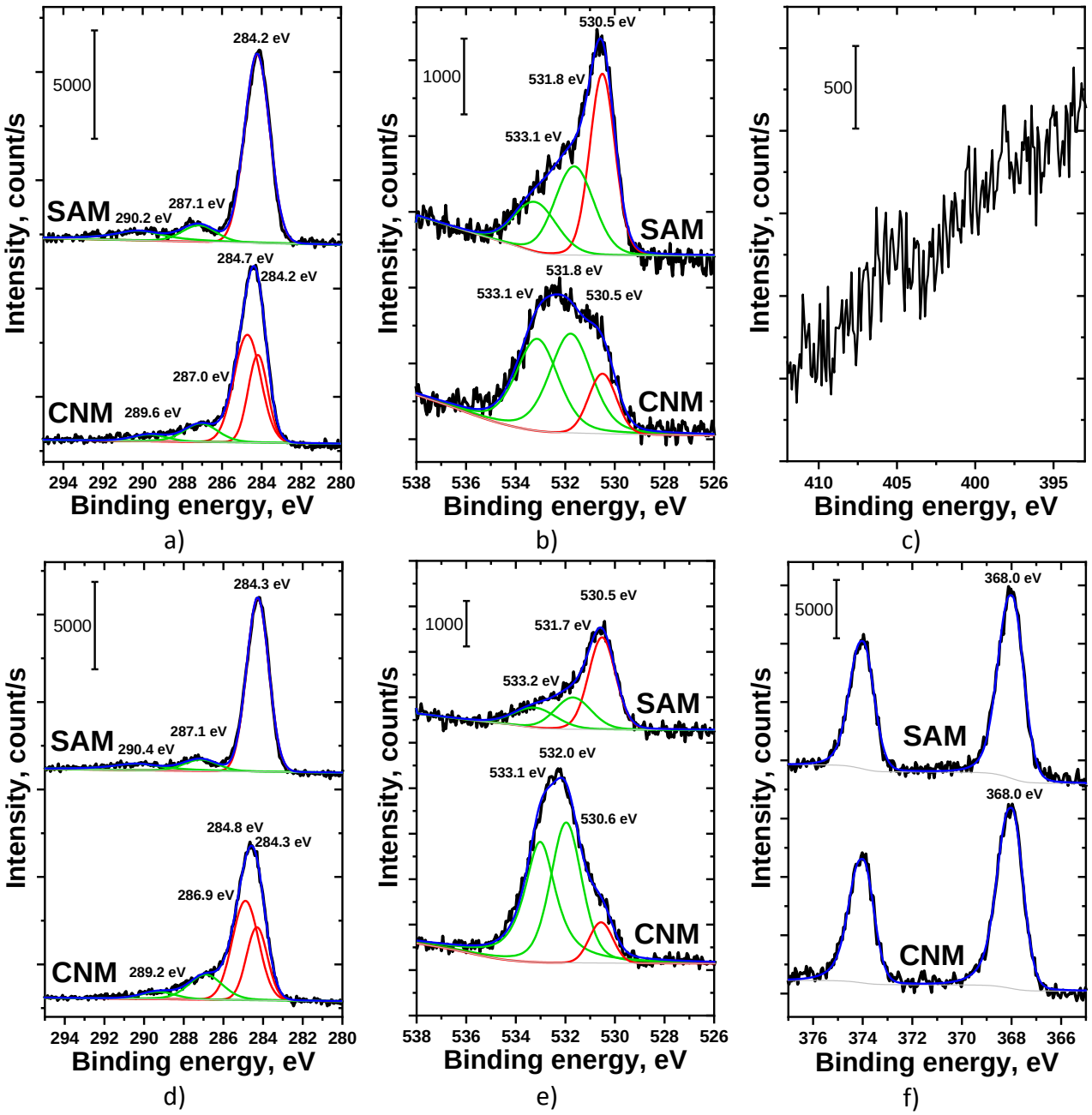

Figure S1. XP spectra. a) C1s for SAM and CNM prepared from biphenyl-4-carboxylic acid; b) O1s for SAM and CNM prepared from biphenyl-4-carboxylic acid; c) N1s for bare silver surface without molecules; d) C1s for SAM and CNM prepared from p-(terphenyl)-4-carboxylic acid; e) O1s for SAM and CNM prepared from p-(terphenyl)-4-carboxylic acid; f) Ag3d for SAM and CNM prepared from p-(terphenyl)-4-carboxylic acid.

Transformation of aromatic carbon (284.2–284.3 eV) with π-π* satellite (290.2-290.4 eV) in self-assembled monolayers to sp^3 carbon (284.7–284.8 eV) and oxidized carbon (286.9–287.0 eV, 289.2–289.6 eV) can be seen after electron irradiation of both BPC and TPC SAMs (Fig. S1a, Fig. S1d).[1] Carbon component 287.1 eV in SAMs corresponds to carbon atoms in the carboxylate groups. Cross-linking of SAM leads to destruction of the carboxylate moiety as evidenced by reduced content of oxygen bonded to silver surface (530.5–530.6 eV) and increase of signals from C=O (531.7–532.0 eV) and C-O (533.1–533.2 eV) functionalities (Fig. S1b, Fig. S1e). XP spectrum in Fig. S1c demonstrates absence of nitrate species in the silver bilayer substrates upon electrodeposition. The chemical state of silver (368.0 eV) remains stable after electron irradiation (Fig. S1f).

PM-IRRAS spectra

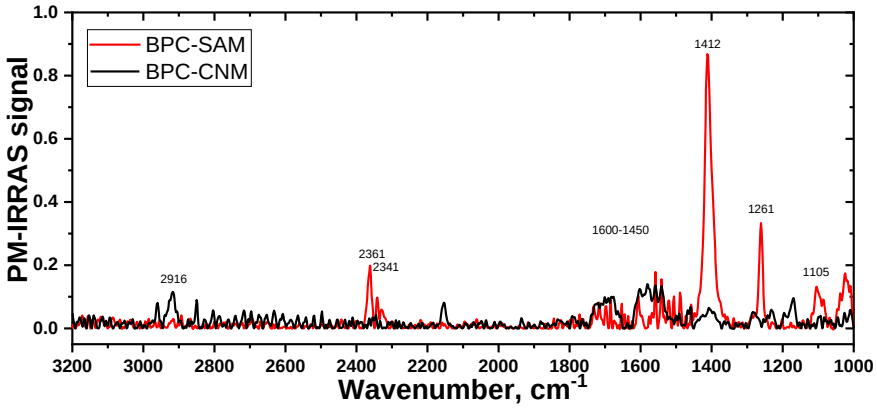

Figure S2. PM-IRRAS spectra. a) SAM and CNM prepared from biphenyl-4-carboxylic acid; b) SAM and CNM prepared from from p-(terphenyl)-4-carboxylic acid.

Surface-bound carboxylate groups are known to be IR active (1412 cm^{-1} for BPC-SAM and 1406 cm^{-1} for TPC-SAM).[2-4] Their decomposition upon irradiation is confirmed by IR-spectra (Fig. S2). Degradation of aromatic structure is also observed in 1600-1450 cm^{-1} region.

References

1. NIST X-Ray Photoelectron Spectroscopy Database, NIST SRD 20, Version 4.1 (http://srdata.nist.gov/xps/).

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3. N. E. Schlotter, M. D. Porter, T. B. Bright, D. L. Allara, *Chem. Phys. Lett.*, 1986, **132**, 93-98.

4. E. L. Smith, M. D. Porter, *J. Phys. Chem.*, 1993, **97**, 8032-8038.