Supporting Information

Can the presence of a fluorine-containing functional group in eutectic mixtures indeed bring fluorous affinity for fluorotelomer alcohol?

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The geometries of all initial DES materials were fully optimized using Grimme's DFT-D3 empirical dispersion correction with Tmolex (version 21.0.0) at the B3LYP/aug-cc-pVTZ level. Moreover, vibrational frequency calculations were carried out to confirm the optimized geometries as true minima. The properties of the considered solvent systems were investigated by analyzing minimal HBA:HBD clusters at a 1:1 ratio. The DES simulation systems with fluorotelomer alcohol (6:2 FTOH as representatives) contained 65 molecules (HBA:HBD:target = 6:6:1). The initial conformations were initially generated via Packmol, where the solvent molecules were randomly and loosely packed into a cube (4 × 4 × 4 nm). Periodic boundary conditions were implemented for cubic boxes in all directions, with the addition of box sides of 1.2 Å and a tolerance of 2.0 Å. In all instances, long-range Coulomb interactions were computed using the particle-mesh Ewald (PME) method, with a grid spacing of 0.16 nm and interpolation order of 4. These systems were then equilibrated classically in Gromacs 2022 package for 20 ns under canonical (NVT) and isothermal-isobaric (NPT) ensemble dynamics at 298.15 K and 1 atm. The molecules were treated using the general Amber force field (GAFF). The final frame obtained from the classical NPT run was utilized as the input for the ab initio molecular dynamics (AIMD) simulations. The AIMD simulations were carried out in CP2K package, using the TZVP basis set to describe the valence electrons and GTH core potential for different atom types. Furthermore, the simulations employed the B3LYP exchange-correlation functional with Grimme's DFT-D3 empirical dispersion correction, and a timestep of 1.0 fs. The system underwent an initial equilibration with AIMD under NPT procedures for 10 ps, followed by a production level run of 40 ps. The following analyses conducted with the program TRAVIS. Local structure and microscopic interactions were analyzed by Multiwfn.
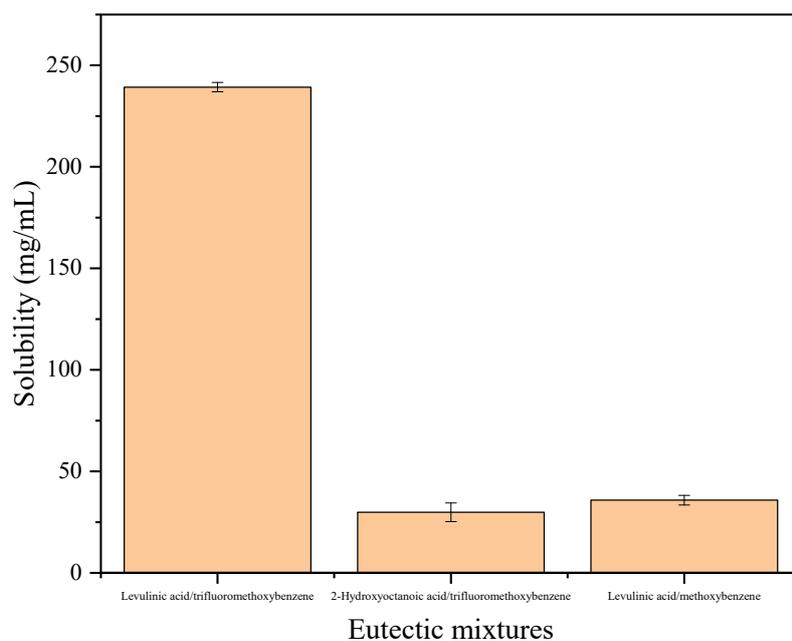
Figure S1. Solubility of 1H,1H,2H,2H-perfluoro-1-octanol (6:2 FTOH) in the

trifluoromethoxybenzene-based deep eutectic solvents (HBD: HBA = 1:1, molar ratio) at 298.15 K
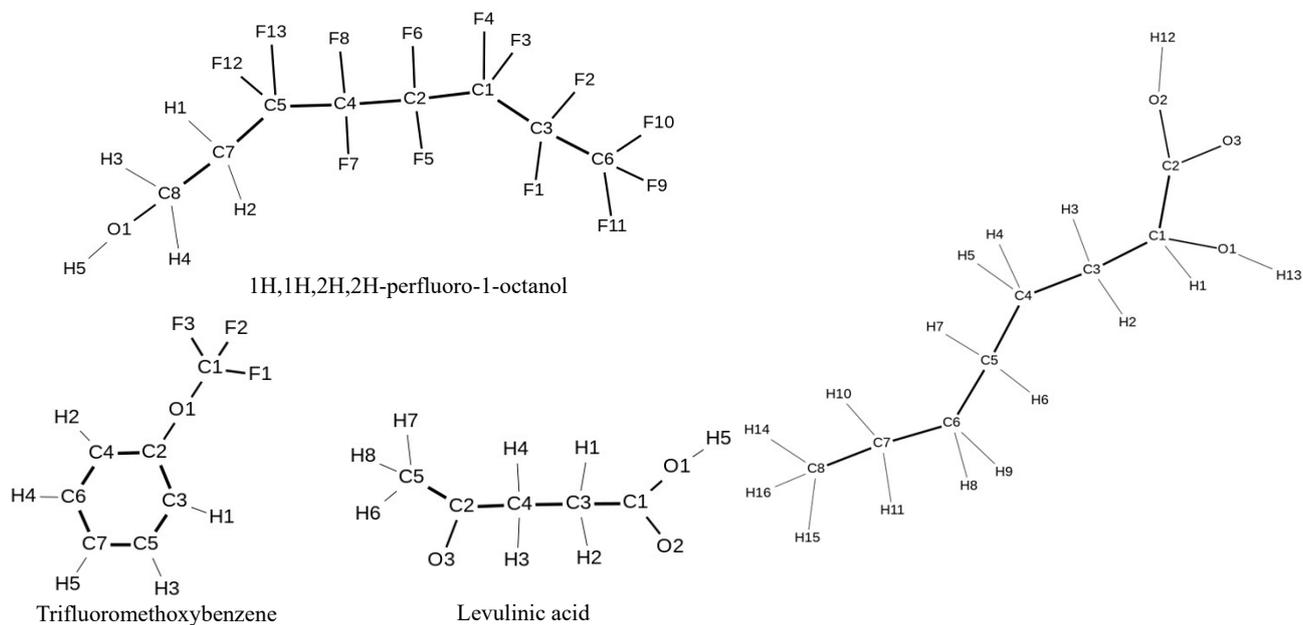
and 1 atm.

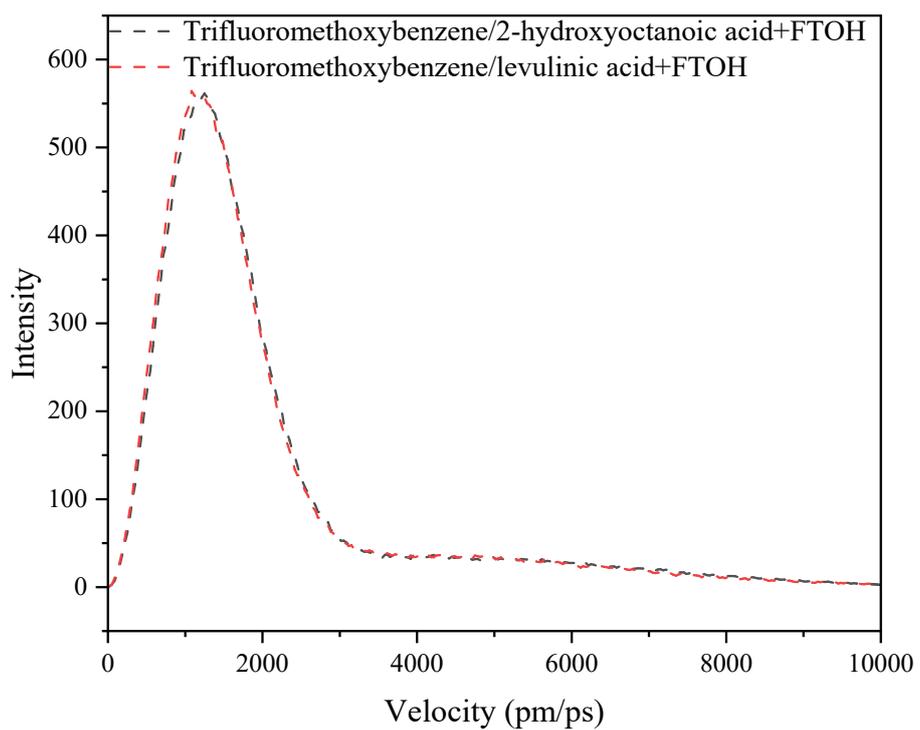**Figure S2**. Atom numbering of different compounds.

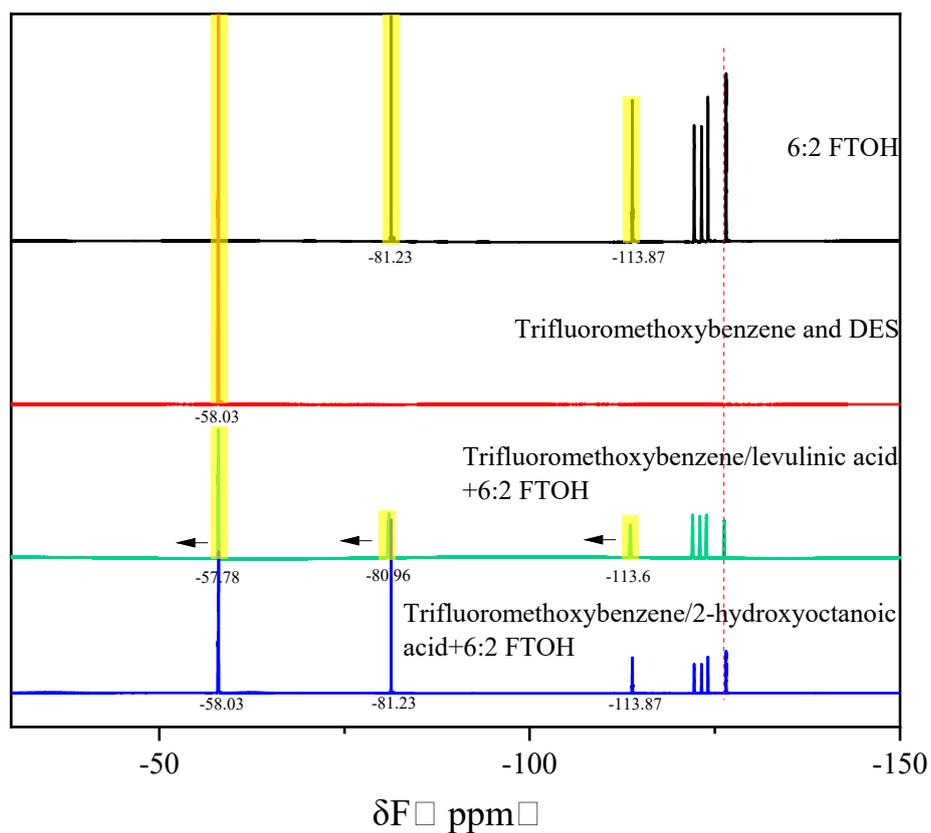**Figure S3**. Velocity distribution function for the mass center of 6:2 FTOH in the eutectic solvents.

Figure S4. ^{19}F NMR chemical shifts of the starting materials and the obtained eutectic solvent systems with and without 6:2 FTOH.

Table S1. Th activity coefficient of target in different eutectic systems.

DES	Activity coefficient
Lev-Tfb	3.732394557
2-Hyd-Tfb	3.333357319