Electronic supplementary information (ESI)

Weak Hydrogen Bonding Competition between O−H···π and O−H···Cl

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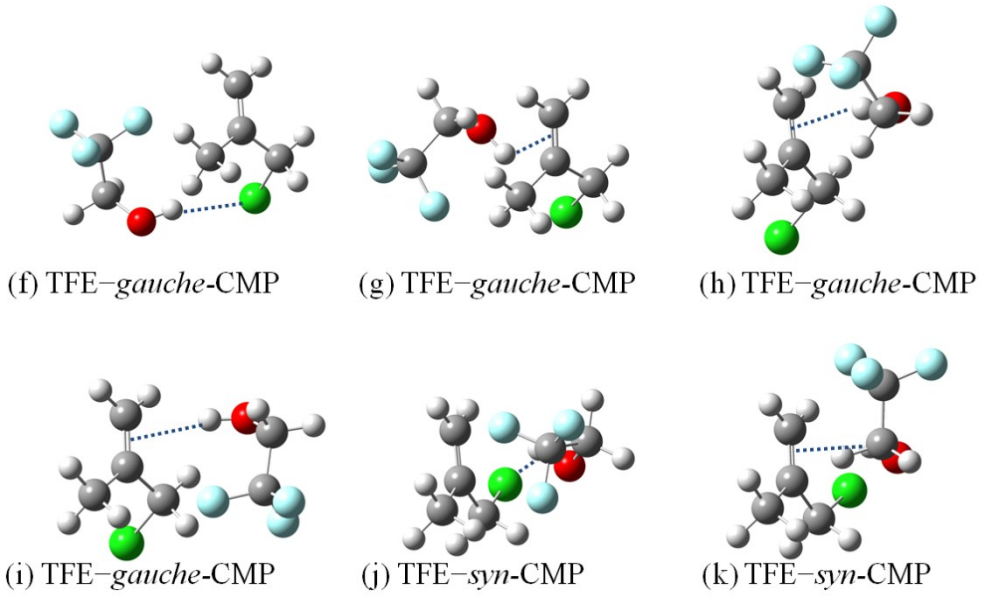

Fig. S1. The high-lying structures of the TFE−CMP complexes obtained at the B3LYP-D3/aug-cc-pVTZ level. The dashed lines denote the O−H···π and O−H···Cl hydrogen bonds.

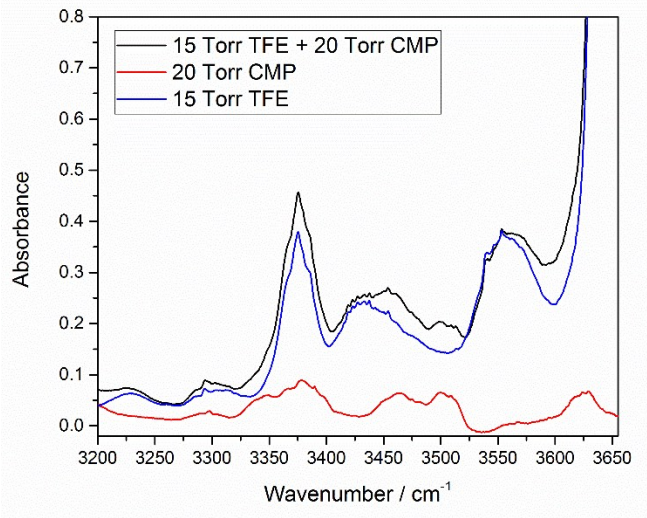

Fig. S2. Spectra of TFE, CMP, and their mixture in the 3200-3650 cm^{-1} region. A 6 m path length cell was used.

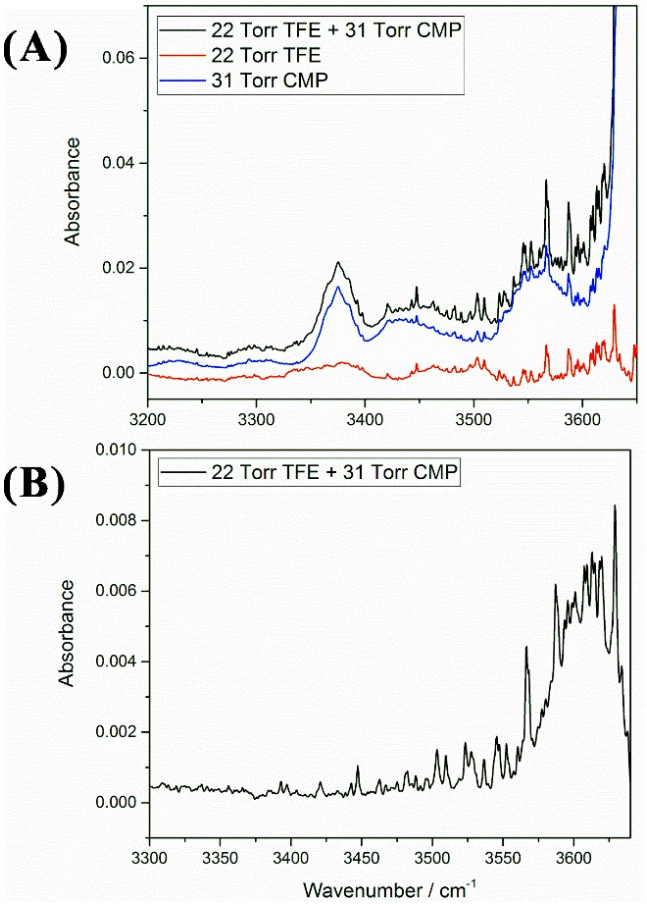

Fig. S3. (A) Spectra of TFE, CMP, and their mixture in the 3200-3650 cm^{-1} region. A 20 cm path length cell was used. (B) Spectra of the TFE−CMP complex in the ν_{OH} band region.

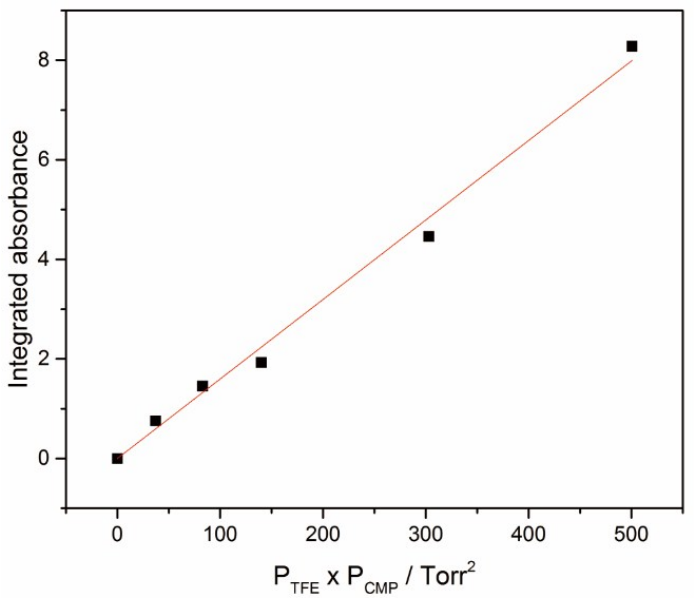

Fig. S4. The integrated absorbance of the OH-stretching band in the TFE−CMP complex as a function of the product of the TFE and CMP pressures. The integration region for TFE−CMP is 3525-3632 cm^{-1}.

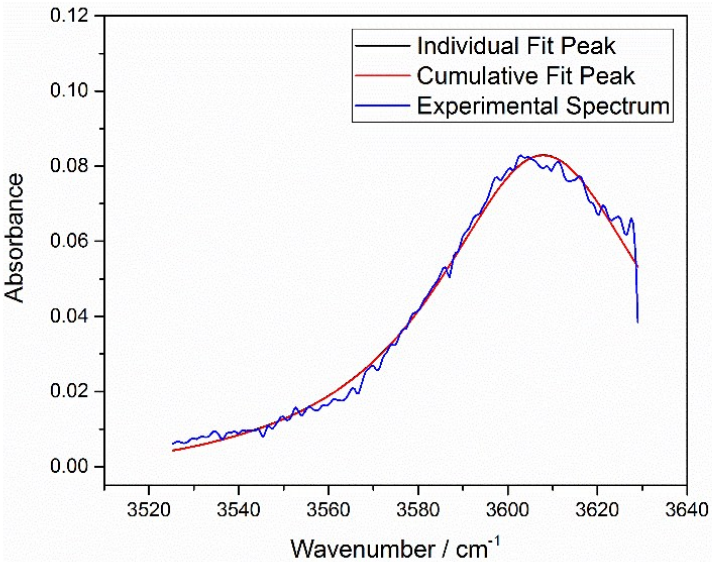

Fig. S5. The deconvolution fitting of the OH-stretching fundamental transition band of TFE−CMP.

Table S1. Selected geometric parameters of the most stable TFE−CMP structures at the MP2/aug-cc-pVTZ level (angles in degrees; lengths/distances in Å)

structures	O−H···π/Cl			C=C
	Δr_{OH} [a]	r_{HB} [b]	θ [c]	$\Delta r_{C=C}$ [d]
TFE−*gauche*-CMP (a)	0.0051	--	--	0.0028
TFE−*gauche*-CMP (b)	0.0066	--	--	0.0035
TFE−*gauche*-CMP (c)	0.0061	2.2952	152.8	0.0004
TFE−*syn*-CMP (d)	0.0055	--	--	0.0039
TFE−*syn*-CMP (e)	0.0046	2.3871	174.1	0.0014

[a] $\Delta r_{OH} = r_{complex} - r_{monomer}$, is the change in the OH bond length upon complexation. [b] Intermolecular hydrogen bond distance. [c] Intermolecular hydrogen bond angle. [d] $\Delta r_{C=C} = r_{complex} - r_{monomer}$, is the change in the C=C bond length upon complexation.

Table S2. Comparison of the calculated BE (not corrected) and BSSE of the most stable TFE−CMP structures with B3LYP-D3 and MP2 methods (kJ mol^{-1})

structures	B3LYP-D3/aug-cc-pVTZ		MP2/aug-cc-pVTZ	
	BE	BSSE	BE	BSSE
TFE−*gauche*-CMP (a)	-26.1	0.9	-29.5	6.4
TFE−*gauche*-CMP (b)	-23.7	1.2	-28.3	7.0
TFE−*gauche*-CMP (c)	-25.7	1.0	-28.3	6.3
TFE−*syn*-CMP (d)	-30.4	1.1	-33.4	7.3
TFE−*syn*-CMP (e)	-28.7	1.1	-32.3	7.4