Supplementary Material (ESI) for *PCCP*

Probing the microscopic hydrophobicity of smectite surfaces. A vibrational spectroscopic study of dibenzo-p-dioxin sorption to smectite

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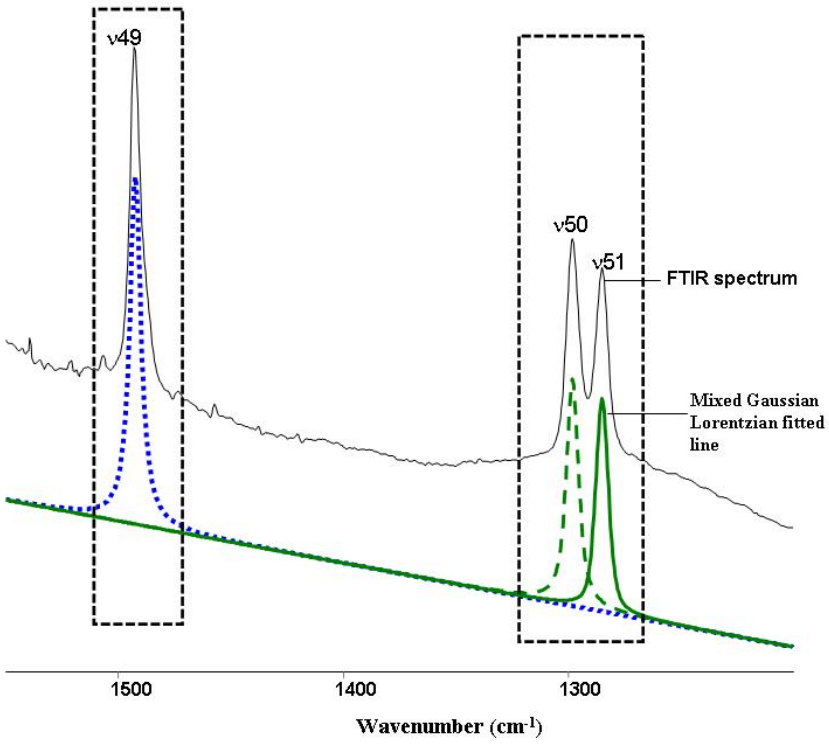

Fig. S1. Peak-fitted spectra of DD –Cs-saponite complex in the region of 1520- 1270 cm^{-1}. Peak fitting was done using mixed Gaussian-Lorentzian function. Peak intensity and Peak area of fitted spectra were used for quantitative and qualitative analysis of DD sorbed to smectite clay with different exchangeable cations.

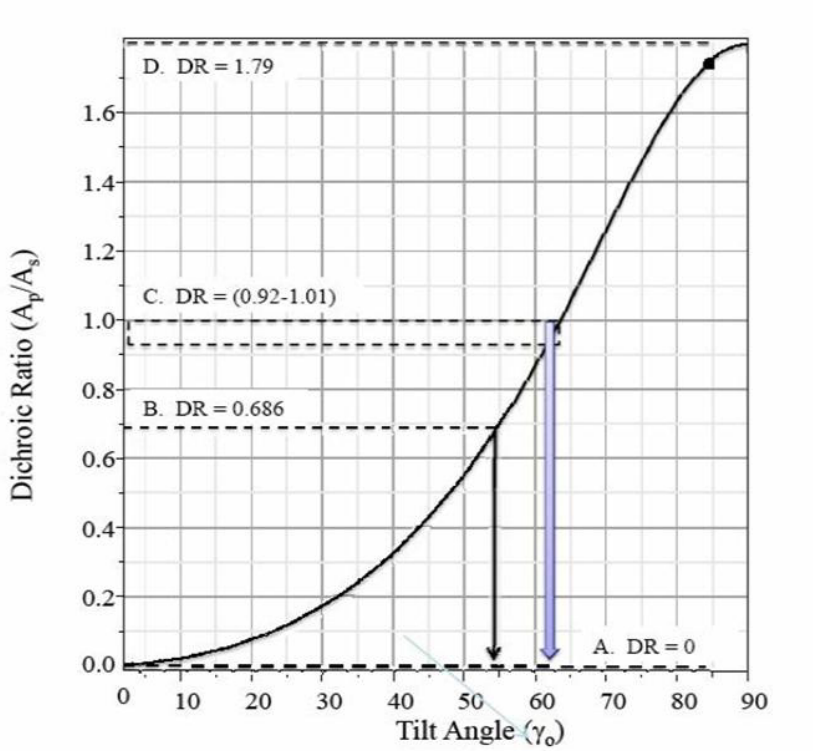

Fig. S2. Relationship between ATR dichroic ratios (D) and tilt angle (γ) of solute with respect to the surface of IRE. A, B, and D indicate the solute is oriented perpendicular, parallel, and isotropically to the IRE surface, respectively. The relationship between the dichroic ratio and tilt angle of DD sorbed on Cs-saponite are shown in C. Average tilt angle (γ) of the IR transition dipole moment was calculated using the refractive index of ZnSe (2.406), Clay: Saponite (1.504) and water (1.333) and angle of incidence 45^o.

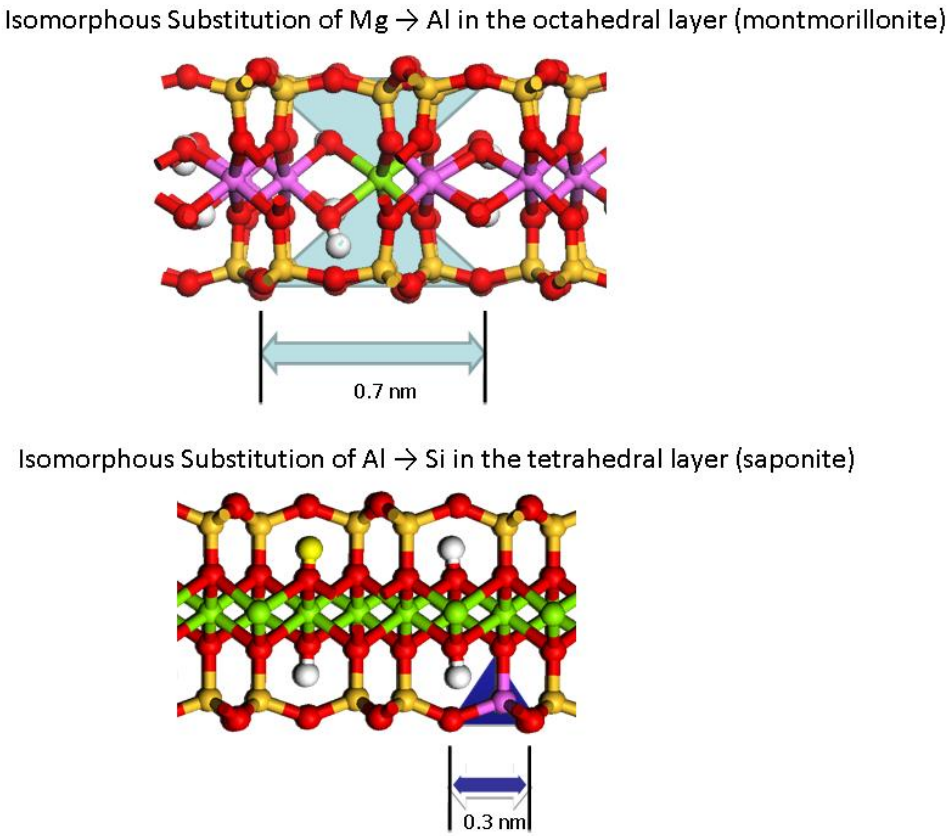

Fig. S3. Ball and stick representation of charge distribution on smectite clay with isomorphic substitution in octahedral sheet (top) and tetrahedral sheet (bottom) representing the approximate charge distribution for montmorillonite and saponite, respectively.

Table S 1. Observed and calculated Raman and IR vibrational frequencies (cm-1) of dibenzo-p-dioxin in crystalline and a polar solvents

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Experimental				N	Theoretical‡	Band Assignment
Raman frequency (cm^{-1})		IR frequency (cm^{-1})			predicted by	
Crystalline DD	DD solution (in CCl_4)	Crystalline DD (in KBr Pellet)	DDsolution (in $CHCl_3$)		BLYP/631G^{++}	
242	233			ν_{20}	239	C-O-C oop def
267	271			ν_{15}	286	$^{\delta}$CH oop , skel def oop
399	395			ν_{11}	390	skel def
441	438			ν_{30}	433	$^{\delta}$C-O-C,skel def
450	459	450		ν_{14},ν_{58}	450	skel def oop
534	531			ν_{29}	534	skel def
552				ν_{49}	551	$^{\delta}$CH oop
565				ν_{10}	564	$^{\delta}$C-O-C,skel def
		609		ν_{55}	610	skel def
		668		ν_{44}	667	$^{\delta}$C-O-C,skel def
725	731			ν_{9}	713	benzene ring breth
749	747	746		$\nu_{18,}\nu_{57}$	738	$^{\delta}$CH oop
762				ν_{43}	753	$^{\delta}$CH oop
		831	830	ν_{54}	837	ring breath
		851		ν_{43}	851	$^{\delta}$C-O-C,skel def
		858				
897	895			ν_{19}	906	skel def
		908				
927	928	925	928	$\nu_{42,}\nu_{56}$	928	$^{\delta}$CH oop
980				ν_{16}	1013	$^{\delta}$CH oop
		966				
1030	1030	1030	1030	$\nu_{8,}\nu_{53}$	1032	$^{\delta}$CH ,skel def , benzene ring breath
1095				ν_{27}	1077	$^{\delta}$CH , skel def
		1116	1113	ν_{28}	1112	$^{\delta}$CH ,skel def , benzene ring breath
1153	1151	1150		$\nu_{7,}\nu_{52}$	1157	$^{\delta}$CH
1191	1186	1195		$\nu_{26,}\nu_{41}$	11671203	$^{\delta}$CH, $^{\nu}$ C-O-C, skel def
1225	1227	1225		ν_{6}	1241, 1203	$^{\nu}$C-C, $^{\nu}$ C-O-C
1278				ν_{25}	1246	$^{\delta}$CH
		1287	1288	ν_{40}	1267	$^{\nu}$C-C, $^{\nu}$ C-O-C
		1295	1296	ν_{51}	1285	$^{\nu}$C-C, $^{\delta}$ CH
		1303		ν_{50}	1296	$^{\nu}$ C-O-C, skel def
1317	1315			ν_{5}	1311	$^{\nu}$ C-O-C, skel def
		1339				
		1396				
1416		1412				
1464		1465		$\nu_{24,}\nu_{39}$	1441, 1463	$^{\nu}$C-C
		1489	1489	ν_{35}	1481	$^{\delta}$CH,skel def
1502		1498		ν_{4}	1497	$^{\nu}$C-C, $^{\nu}$ C-O-C, $^{\delta}$ CH
		1512				
		1553				
		1567				
1587	1588	1591	1591	$\nu_{23,}\nu_{48}$	15641596	$^{\delta}$CH,skel def
1622	1623	1626		$\nu_{3,}\nu_{38,}$	1608	$^{\delta}$CH,skel def
	3022		3075	$\nu_{32,}$	3075	$^{\nu}$CH
	3041		3086	ν_{12}	3086	$^{\nu}$CH
	3059		3094	ν_{33}	3094	$^{\nu}$CH
	3088		3100	ν_{13}	3100	$^{\nu}$CH

‡ = normalized by factor 0.9628, ν = stretching, δ=bending, Skel= skeleton, oop= out of plane, def= deformation

Table S2. Observed Raman and IR vibrational modes of dibenzo-p-dioxin (DD) in a polar solvents and in DD-Cs-saponite complex

Ref DD solution‡	Cs-saponite-DD complex			Ref DD solution§	Band Assignment
IR	ATR-FTIR	FTIR-SSCF	Raman-SSCF	Raman§	
				233	C-O-C oop def
				271	$^{\delta}$CH oop, skel def oop
			361	395	skel def
				438	skel def
				459	skel oop def
		493			Mg–OH or $^{\delta}$Si–O of clay
		482			Mg–OH or $^{\delta}$Si–O of clay
			566	531	skel def
		660			Mg–O of clay
	720		676	731	benzene ring breath
	746		729	747	skel def ,$^{\delta}$CH oop
830	828				ring breath
928					$^{\delta}$ CH oop
	974	942			$^{\nu}$ Si-O of clay
	1016	1014			$^{\nu}$ Si-O oop of clay
1030	1019	1067	1019	1030	$^{\delta}$CH ,skel def, ring breath
1113	1128	1121	1130		$^{\delta}$ CH , skel def
	1195	1181		1151	$^{\delta}$CH
		1227		1186	$^{\delta}$CH
				1227	$^{\nu}$C-O-C, skel def
1288	1285	1285	1266		$^{\nu}$C-O-C, $^{\nu}$C-C
1296	1298	1297	1293		$^{\nu}$C-C ,$^{\delta}$ CH
			1363	1315	$^{\delta}$CH, skel def
1489	1493	1491	1491		$^{\delta}$CH, skel def
				1588	$^{\delta}$CH, skel def
1591	1542		1586		$^{\delta}$CH, skel def
			1616	1623	$^{\delta}$CH, skel def
			1696		
	1639	1628			$^{\delta}$H-O-H band of water
	2119				Sym $^{\nu}$O-H of clay and water
	3504	3677			Asym $^{\nu}$O-H of clay

‡ = $CHCl_3$, § = CCl_4, ν = stretching, ν = stretching, δ=bending, Skel= skeleton, def= deformation, Sym= symmetric Asym= asymmetric, oop= out of plane