Supporting Information

Stoichiometry of Lanthanide–Phosphate Complexes at Water Surface Studied Using Vibrational Sum Frequency Generation Spectroscopy and DFT Calculation

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1. Fitting results

The bands observed in the VSFG spectra in Figure 3 and Figure 4 in the main text were fitted with a Lorentzian function:

$$I_{VSFG} \propto \left|\chi_R^{(2)}\right|^2 = \left|\frac{A_{POO}}{\omega - \omega_{POO} + i\Gamma_{POO}}\right|^2,$$

where $\chi_R^{(2)}$ is the second-order resonant nonlinear susceptibility element. A_{POO}, ω_{POO}, and Γ_{POO} are the amplitude, center frequency, and width of the resonance of symmetric POO^- stretch, respectively. The spectra were fitted well, indicating that the VSFG spectra have small nonresonant background. The parameters obtained from the fitting analysis are presented in Table S1. The VSFG spectrum of the surface

of aqueous solution dissolving DBP and $Eu(NO_3)_3$ (DBP: 1.25 mM, Figure 4) was fitted by two Lorentzian functions.

Table S1. Fitting parameters for the VSFG spectra in the symmetric POO^- stretch region.

Sample	ω_{POO} / cm^{-1}	Γ_{POO} / cm^{-1}
HDEHP, $Lu(NO_3)_3$	1127	26
HDEHP, $Tm(NO_3)_3$	1118	28
HDEHP, $Er(NO_3)_3$	1124	28
HDEHP, $Dy(NO_3)_3$	1119	25
HDEHP, $Eu(NO_3)_3$	1118	23
HDEHP, $Sm(NO_3)_3$	1117	22
HDEHP, $La(NO_3)_3$	1111	22
HDEHP, NaOH	1098	20
DBP(1.25 mM), $Eu(NO_3)_3$	1110, 1167	28, 28
DBP(0.625 mM), $Eu(NO_3)_3$	1116	26

2. VSFG spectrum for diisooctylphosphinic acid

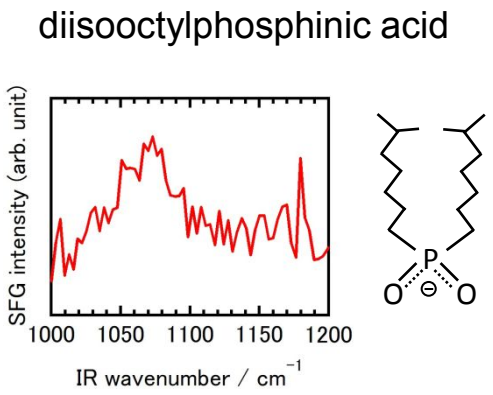

Figure S1. VSFG spectrum of the surface of an aqueous solution dissolving a small amount of diisooctylphosphinic acid (~90%, Sigma-Aldrich) and 50 mM $Eu(NO_3)_3$.