Supporting Information for

Partitioning of the Vibrational Free Energy

Dmitri G. Fedorov,

Research Center for Computational Design of Advanced Functional Materials (CD-FMat), National Institute of Advanced Industrial Science and Technology (AIST), Central 2, Umezono 1-1-1, Tsukuba, 305-8568, Japan.

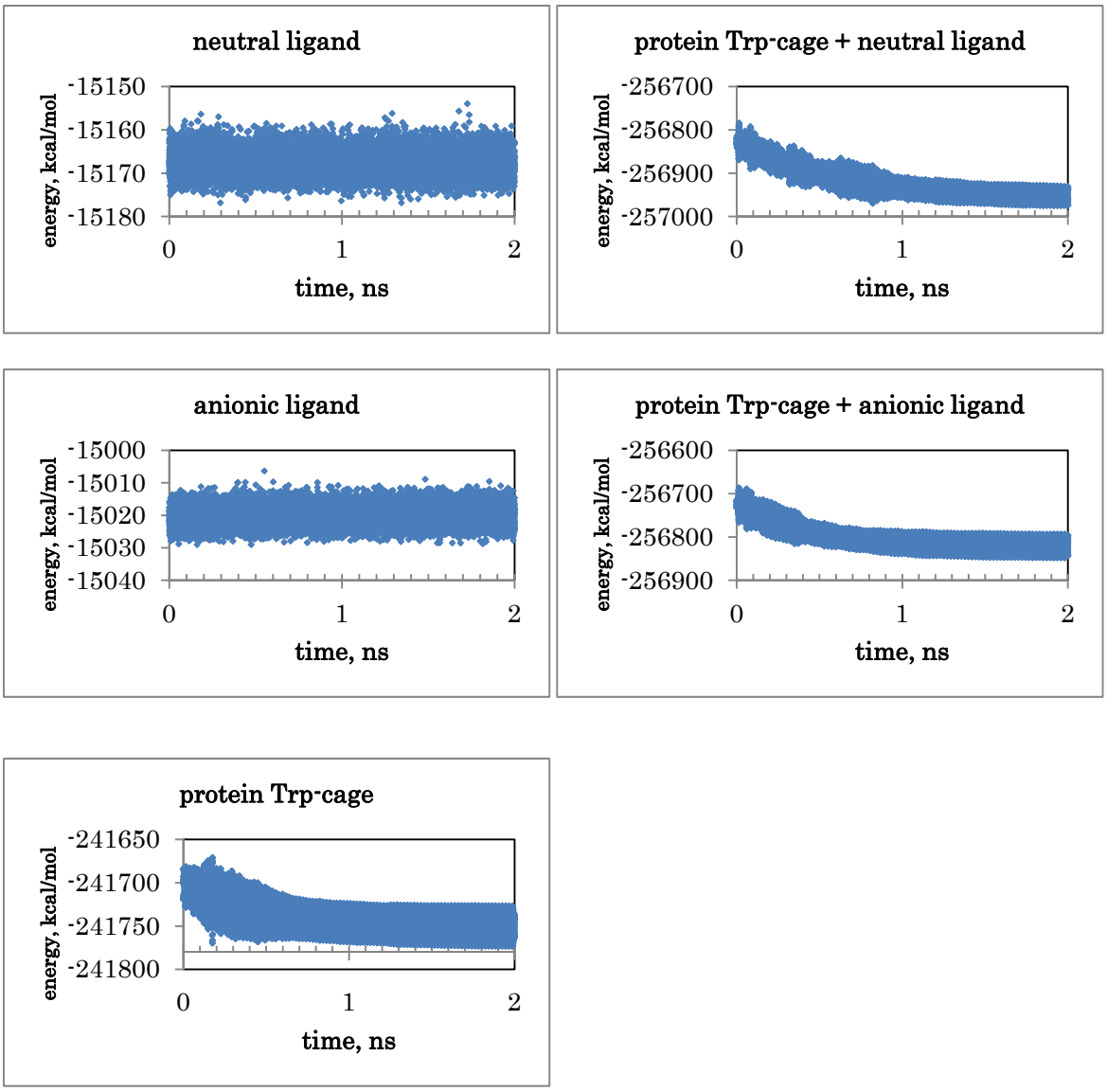

Figure S1. Fluctuations of the potential energies in FMO2-DFTB3 NVT MD simulations.

The derivation of eq 19 is as follows.

$$F_a^{\text{vib}} = \frac{Rhv_a}{2k} + RT\ln\left(1-\exp\left(-hv_a/kT\right)\right) = 0$$

Introducing $x = \frac{hv_a}{kT}$,

$$-\frac{x}{2} = \ln\left(1-\exp\left(-x\right)\right) = 0$$

$$\exp\left(-x/2\right) = 1-\exp\left(-x\right)$$

Introducing $y = \exp\left(-x/2\right)$,

$$y = 1-y^2$$

$$y = \frac{-1+\sqrt{5}}{2}$$

$$\ln y = -\frac{x}{2} = \ln\left(\frac{\sqrt{5}-1}{2}\right)$$

$$x = -2\ln\left(\frac{\sqrt{5}-1}{2}\right) = \frac{hv_a}{kT}$$

$$v_a = \frac{2kT}{h}\ln\left(\frac{2}{\sqrt{5}-1}\right)$$