Supporting Information

Hydrolase-Like Activity Provided by Zinc(II) and Oleoyl-Histidine at Liposome Membrane Surface

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Keywords: Artificial Enzyme, Liposome, Membrane Interface, Histidine, Zinc(II)

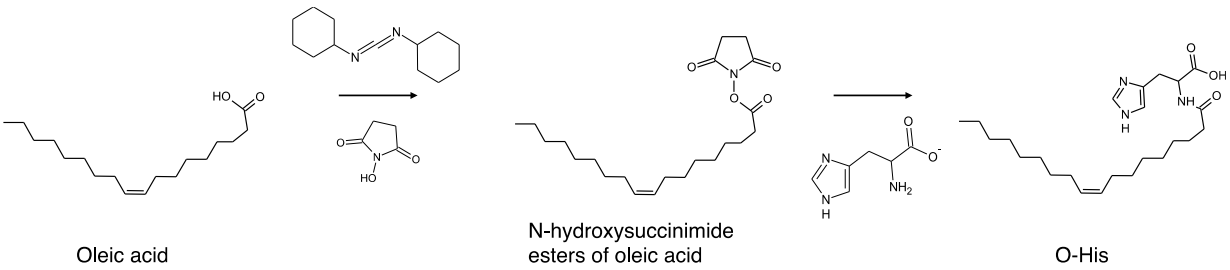
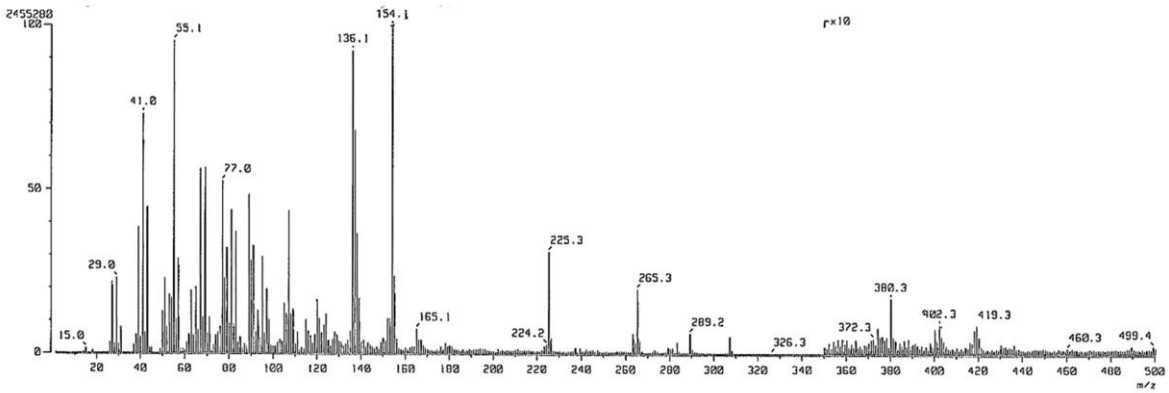


Figure S1. Synthesis scheme for O-His. Yield was 55.9%.

(a)



(b)

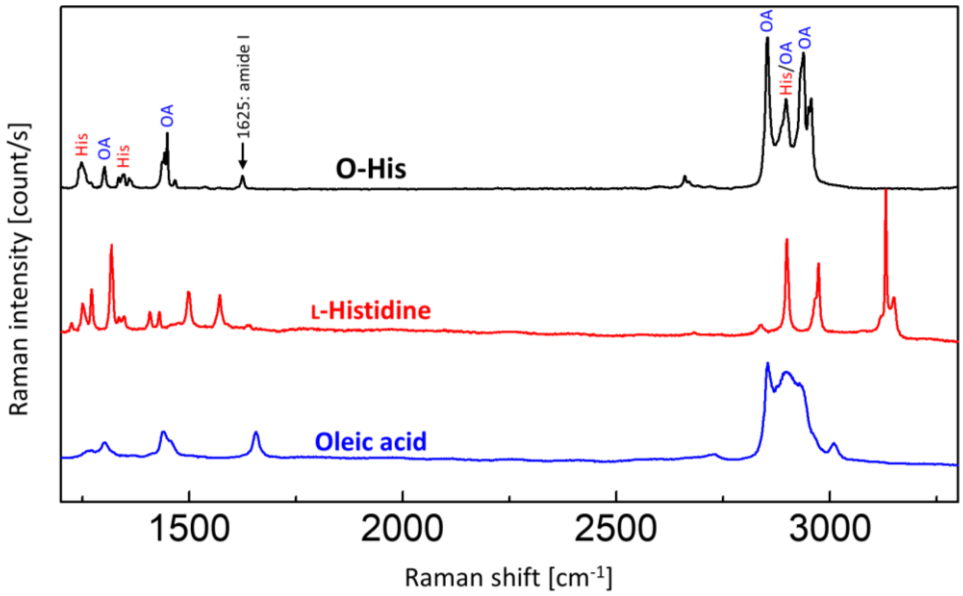


Figure S2. (a) MS spectrum of synthesized O-His (M_w: 419.6). (b) Raman spectra of O-His (solid powder: *black line*), L-Histidine (His) (solid powder: *red line*), and Oleic acid (OA) (liquid: *blue line*). In O-His spectrum, the peak at 1625 cm^{-1} (amide I) was generated, while the peak at 3100-3150 cm^{-1} (terminal amino group) was disappeared. The assignments of His and OA were as follows: 1248 (δC-N (His)), 1301 (CH_2, twist (OA)), 1347 (ν ring (C-N) (His)), 1440 (CH_2, bent (OA)), 2855 (ν CH_2 (OA)), 2855 (ν CH_2 (OA)), 2928 (ν CH_3 (OA)).

Peak assignments were taken from literature:

Mesu, J.G.; Visser, T.; Soulimani, F.; Weckhuysen, B.M. Infrared and Raman spectroscopic study of pH-induced structural changes of L-histidine in aqueous environment. *Vibrational Spectrosc.* **2005**, *39* (1), 114-125.

Czamara, K.; Majzner, K.; Pacia, M. Z.; Kochan, K.; Kaczor, A.; Baranska, M. Raman spectroscopy of lipids: A review. *J. Raman Spectrosc.* **2015**, *46* (1), 4−20.

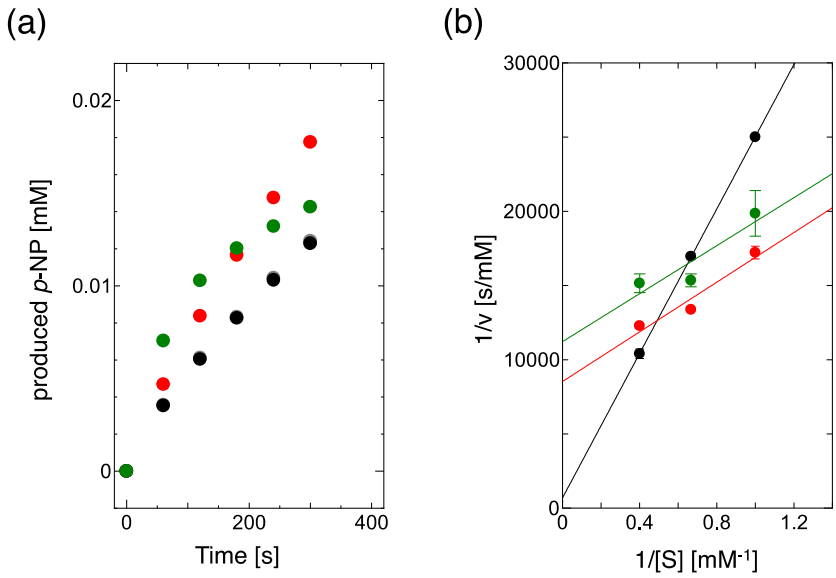


Figure S3. (a) Time course of *p*-NP production in the presence of DPPC (O-His 20mol%) (*green*). (b) Lineweaver-Burk plot for DPPC (O-His 20mol%). [O-His] = 0.3 mM, [O-His]/[Zn^{2+}] = 3/1. Experiments were conducted at 25 ℃.

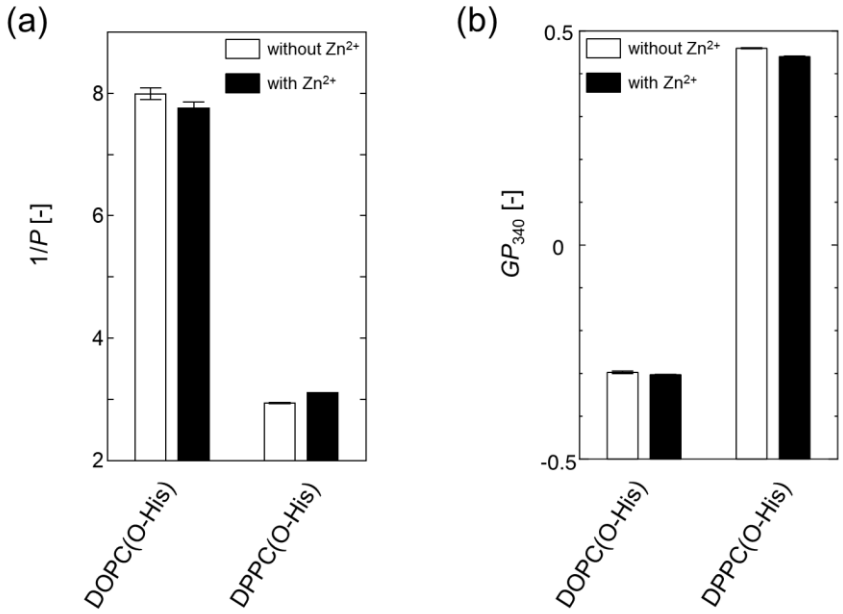


Figure S4. (a) Inner membrane fluidities (1/*P*) of liposomes. A lower 1/*P* indicates a decrease of fluidity. (b) Inner membrane polarities (GP_{340}) of liposomes. A lower GP_{340} indicates an increase of polarity. [Total amphiphile] = 100 μM, [DPH] = 0.4 μM, [Laurdan] = 1 μM, [O-His] = 20 μM, [O-His]/[Zn^{2+}] = 3/1. Experiments were conducted at 25 ℃. When the domain (e.g., lipid raft composed of cholesterol and sphingomyelin) is formed, drastic changes in inner membrane properties (1/*P* and GP_{340} values) can be observed. Herein, inner membrane properties were not significantly changed by the presence of Zn^{2+}, suggesting that the addition of Zn^{2+} could hardly induce the domain formation (no raft-like ordered domain of O-His/Zn^{2+} can be formed).