Supporting information

For the manuscript

Novel Triphosphorylation Polyurethane Nanoparticles for Blood-contacting Biomaterials' Coating

Jun Zhang[a], Zhijun Sun[a], aomiao Zhu[a], Qiaochu Guo[b], hengai He[a], Ao Xia[a]*, Hong Mo[a], Xiaohua Huang[a]*, Jian Shen[a]

a. Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, Jiangsu Key Laboratory of Biomedical Materials & College of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210029, People's Republic of China. Fax: +86 25 83599188,

b. Nanjing Foreign Languages School, Nanjing 210029, People's Republic of China.

*Author to whom all correspondence should be addressed

E-mail Address: aoxia@njnu.edu.cn

huangxiaohuabio@hotmail.com

Tel: +86-25-83598031, Fax: +86-25-83716813

Quantum chemistry calculation of $NH^+(C_2H_5)_3–P_3O_{10}^{5-}$

All the molecules were completely optimized using the DFT/B3LYP method with the 6-31+g(df,p) basis set. All the theoretical calculations were carried out using the GAUSSIAN 03 program package with the default convergence criteria.

Interaction energy is defined as $E_b = E_{(product)} - E_{(reactant)}$. In this study, $E_{(reactant)}$ is the sum energy of constituent molecules in a pair including the cationic quaternary ammonium salt $NH^+(C_2H_5)_3$ and PO_4^{3-}/or $P_3O_{10}^{5-}$, each of which were previously optimized independently. Then, the pair of constituent molecules being placed together in a proper position was optimized to generate a final geometry, and the corresponding energy minima could be considered as $E_{(product)}$.

From Table 1, the E_b of the $NH^+(C_2H_5)_3–P_3O_{10}^{5-}$ pair is -0.6857720 a.u., which is lower than that of the $NH^+(C_2H_5)_3–PO_4^{3-}$ pair (-0.5710717 a.u.). The ΔE_b is about -301.58 kJ/mol, which could explain the stronger interaction of $NH^+(C_2H_5)_3$ and $P_3O_{10}^{5-}$ than the pair of $NH^+(C_2H_5)_3–PO_4^{3-}$.

Supplementary Table 1. The corresponding energy of each individual molecule and pair

|	Energy (a.u.) calculated at B3LYP/6-31+g(df,p) level
Individual PO_4^{3-}	-642.002181748
Individual $P_3O_{10}^{5-}$	-1775.89352468
Individual $NH^+(C_2H_5)_3$	-292.833437537
Pair of $NH^+(C_2H_5)_3$—PO_4^{3-}	-935.406691004
Pair of $NH^+(C_2H_5)_3$—$P_3O_{10}^{5-}$	-2069.41273429
E_b of $NH^+(C_2H_5)_3$—PO_4^{3-}	-0.571071719
E_b of $NH^+(C_2H_5)_3$—$P_3O_{10}^{5-}$	-0.685772073
$\Delta E_b = E_b(NH^+(C_2H_5)_3$—$P_3O_{10}^{5-}) - E_b(NH^+(C_2H_5)_3$—$PO_4^{3-}) = -301.5778$ KJ/mol	

A proton transfer could be observed from the optimized geometry of both pairs. As demonstrated in Figure 1, the optimized structure of the $NH^+(C_2H_5)_3–PO_4^{3-}$ pair was characterized by the plane P25–O26–O25 (plane POO, for short) in the HPO_4^{2-} molecule, being parallel with the plane C2–C4–C6 (plane CCC, for short) of the $N(C_2H_5)_3$ molecule, and the two negatively charged oxygen atoms pointing to the

hydrogen atoms of the $N(C_2H_5)_3$ molecule. It turned out that the planes POO and CCC nearly coincided However, a similar situation was not found in $NH^+(C_2H_5)_3–P_3O_{10}^{5-}$ in which the center of the $P_3O_{10}^{5-}$ molecule was apart from the plane CCC of the $N(C_2H_5)_3$ in the perpendicular direction to the plane CCC (Figure 2). The analysis showed that $P_3O_{10}^{5-}$ can receive a proton from $NH^+(C_2H_5)_3$ and locate the minima without too much structural adjustment, whereas the HPO_4^{3-} needed to consume some of the energy to translate to a similar height of the plane CCC, and to hold a specified orientation towards the $N(C_2H_5)_3$ upon receiving a proton.
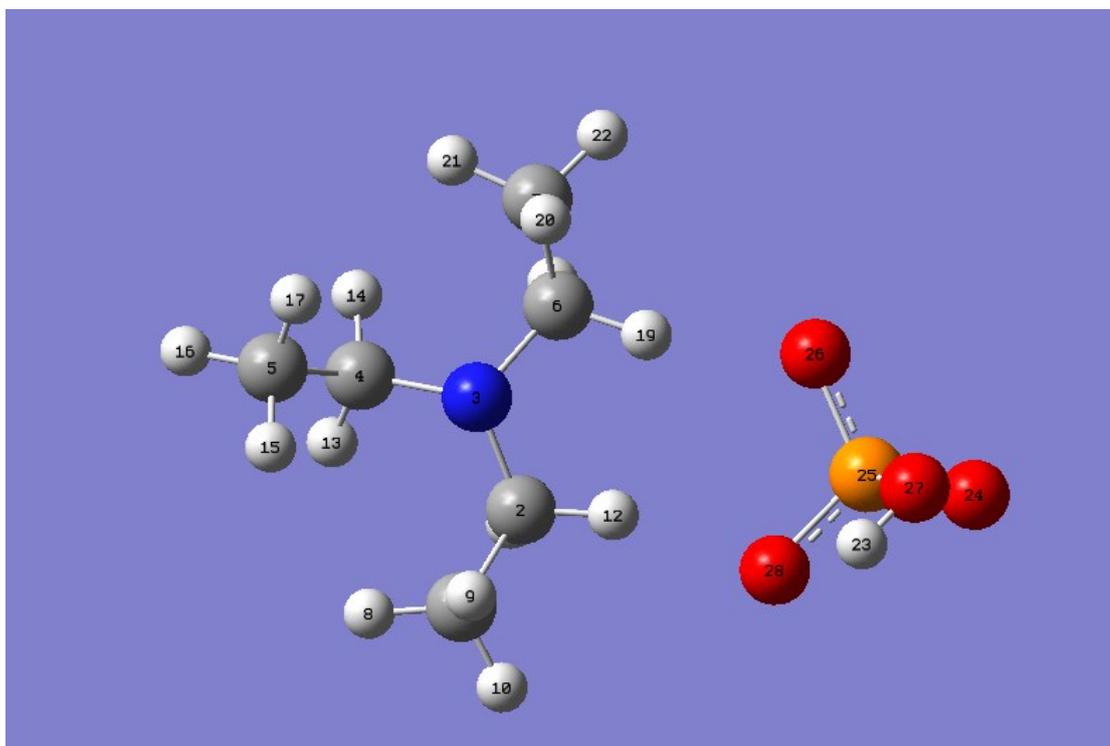
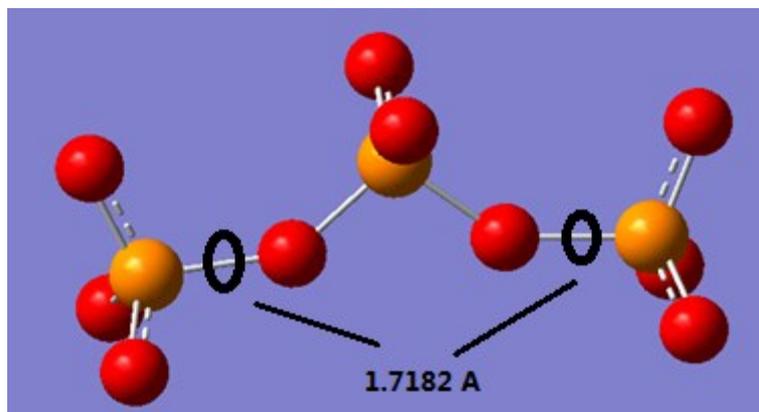**Supplementary Figure 1. The optimized geometry of $NH^+(C_2H_5)_3—PO_4^{3-}$ pair.**
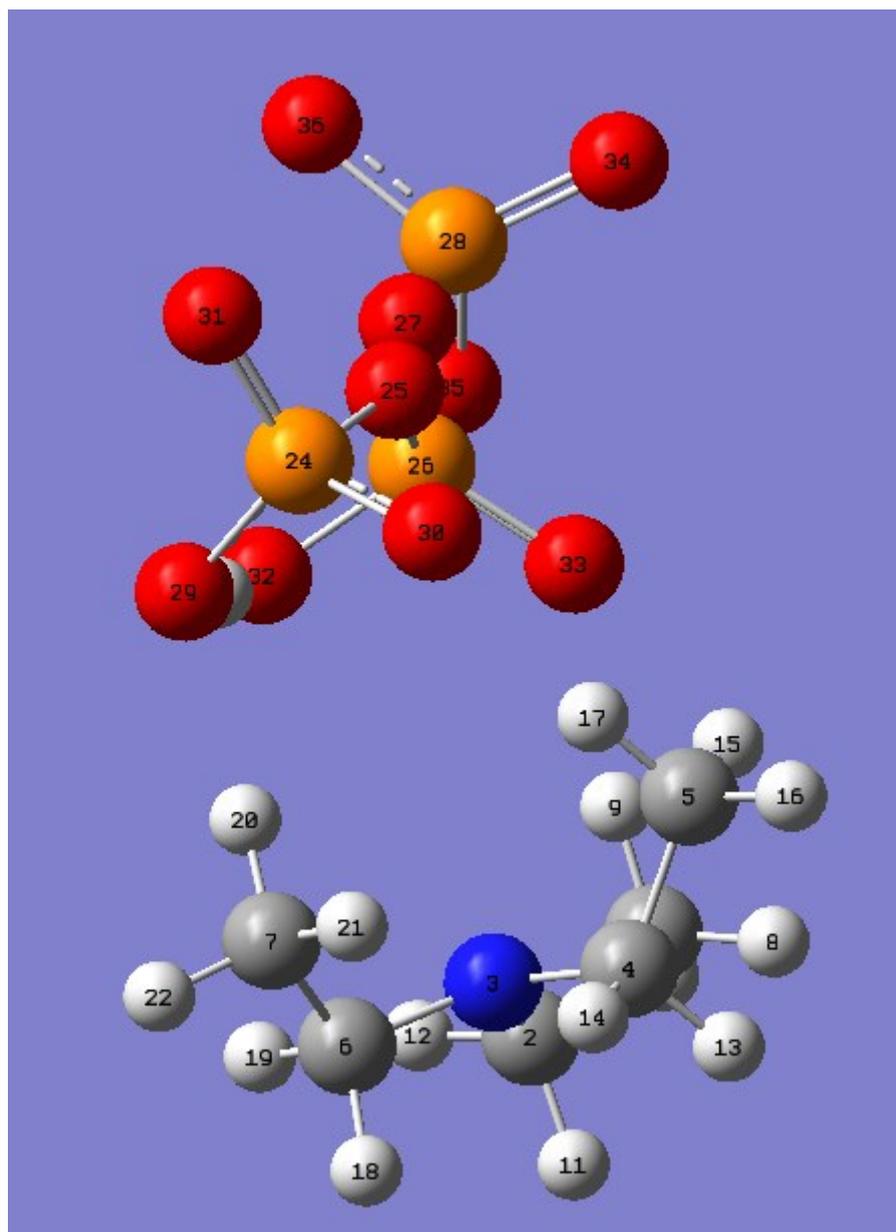
Supplementary Figure 2. The optimized geometry of $NH^+(C_2H_5)_3$—$P_3O_{10}^{5-}$ pair

For $P_3O_{10}^{5-}$, the bond connecting the bridge oxygen atom and the terminal phosphorus atom is marked in Figure 3. With an equal length of 1.7182 Å for both of the marked bonds provided by an independent optimization process seemed reasonable because of molecular symmetry. However, by reacting with $NH^+(C_2H_5)_3$, one of the above bond lengths became longer than before, with a value of 1.8489 Å in the final optimized $N(C_2H_5)_3$–$HP_3O_{10}^{5-}$ structure, and the other one remained nearly

at the original value. By receiving a proton, $P_3O_{10}^{5-}$ might have a tendency to bonding with $NH^+(C_2H_5)_3$ center.

Supplementary Figure 3. The optimized of $P_3O_{10}^{5-}$ molecule individually.