pH-Independent Recognition of Polyhydroxy Compounds by Niobium(V) Porphyrin Complex with Unique Sugar Selectivity

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The niobium(V) complex with tetraphenylporphin having OH⁻ as an auxilliary ligand exists as a dimeric complex, \([\text{Nb}_2(\text{tpp})_2\text{O}_3]^{-}\) at a total concentration \(>10^{-4}\) mol dm⁻³, and reacts with an aliphatic or aromatic polyhydroxy compound to form a monomeric complex containing chelate rings by coordination of the deprotonated species, and to cause an appreciable UV-Vis spectral change. In contrast to phenylboronic acid (PBA), the reactivity of \([\text{Nb}_2(\text{tpp})_2\text{O}_3]^{-}\) is independent of pH at least between 4 and 8. Aliphatic comounds are more reactive than aromatic compounds in dioxane-water, while the reactivity order is reversed in the two-phase reaction. The sugar selectivity order of \([\text{Nb}_2(\text{tpp})_2\text{O}_3]^{-}\) in dioxane-water (10:1) (sorbose > fructose >> mannose > arabinose, galactose > glucose) is appreciably different from that of PBA (fructose > sorbose >> arabinose > galactose > mannose > glucose). This may be related to the difference in size of the Lewis acidic center.

Keywords Polyol, niobium(V) porphyrin complex, optical detection, sugar selectivity, pH-independency

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Introduction

Polyhydroxy compounds abound in various biological systems and are widely used in various industries, so their quantitation is required in various fields.1–3 Since aliphatic compounds (polyols) are much less reactive than aromatic compounds (polyphenols), quantitation of the aliphatic compounds by use of some chemical reaction is limited.4 A unique exception is a reaction with an organic boronic acid. For example, phenylboronic acid (PBA) reacts with polyols to form diesters containing chelate rings. This reaction has been extensively developed for optical recognition of sugars by introduction of a chromophore or fluorophore.5–8 Simple derivatives of PBA have the following characteristics, which may occasionally be drawbacks. First, the reaction product is involved in an acid-base equilibrium in neutral aqueous media, so that the reactivity with a polyol becomes pH dependent under physiological conditions. Second, simple derivatives show rather similar selectivities; e.g., 1,3-diols are more favored than 1,2-diols and \(\alpha\)-fructose is most favored among sugars. With a view to reducing the pH dependence of the reactivity, an electron-withdrawing substituent was proposed to increase the acidity of BA.9,10 A special host containing two boronic acids or a supramolecular assembly system was proposed to enhance the selectivity to \(\alpha\)-glucose.11–13 For further development towards various analytes, the hosts based on Lewis acids other than boron may be promising but have scarcely been explored; only Co(II) and Cu(II) complexes were examined for sugar sensing.14,15

We have successfully used the porphyrin complexes of zirconium(IV) for recognition and potentiometric detection of hard bases such as citrate and triphosphate.16,17 Preliminary examinations indicated that the Zr(IV) porphyrin complexes react with polyphenols but not with polyols. Since vanadium(V) complexes are known to react even with simple alcohols in organic solvents,18,19 a porphyrin complex of a metal center with a higher oxidation number than four is expected to be promising for recognition of polyhydroxy compounds. Since the tetravalent porphyrin complexes of vanadium are more stable than the pentavalent ones and since the interaction with more than two hydroxy groups is expected for a larger metal center on a porphyrin ring, we have adopted the niobium(V) porphyrin complex and evaluated its performances in recognition and optical detection of polyhydroxy compounds. As a result, pH independence of recognition is achieved along with a different sugar selectivity from that of PBA.

Experimental

One of the niobium(V) complexes with tetraphenylporphin (TTP, H₂tpp), \([\text{Nb}_2(\text{tpp})_2\text{O}_3]^{-}\) (abbreviated as Nb-TPP-OH based on the monomer-dimer equilibrium described below; \(O^−\) anion is equivalent to two OH⁻ as the hydrolysis degree) was prepared as described previously \([\chi_{\text{max}}: 418 \text{ nm}; \log\varepsilon: 5.64 \text{(chloroform)}; \nu(\text{Nb-O}): 668 \text{ cm}^{-1} \text{(KBr disk)}; \Delta: 7.7 \text{ ppm, } 

99.7\% \text{ H}_{\text{p,p,p}}: 7.7 - 7.6 \text{ ppm, } 

\text{H}_{\text{p,p,o}}: 7.9 - 7.7 \text{ ppm (chloroform)}])20 In the case of two-phase reactions, a 1-cm³ aliquot of a chlorobenzene solution of Nb-TPP-OH at 3.3 × 10⁻⁵ mol dm⁻³ (hereinafter expressed as a monomer) was shaken with 1 cm³ aliquots of aqueous solutions of a polyhydroxy compound at 2 × 10⁻⁶ – 2 mol dm⁻³ for 3 h. After phase separation, the absorption spectrum of the chlorobenzene phase was recorded with a cell of 1 mm length. In the case of reactions in dioxane-water
(10:1 - 10:3), a 1-cm³ aliquot of a dioxane solution of Nb-TPP-OH was reacted with 0.1 – 0.3 cm³ aliquots of aqueous solutions of a polyhydroxy compound at various concentrations. In the case of reactions in benzene, a 1-cm³ aliquot of a benzene solution of Nb-TPP-OH was reacted with 1 cm³ aliquots of benzene solutions of glycerin. Chloroform solutions of complexes were diluted with acetone and were subjected to ESI-MS (Synapt G2 HDMS, Waters). 1H NMR spectra were recorded by dissolving the isolated complexes in deuterated chloroform (AV 400N, Bruker).

Results and Discussion

Previous work and strategy

The niobium(V) complex with TPP has a dimeric structure of [Nb₂(tpp)₂O₃] bridged by three O²⁻ in the absence of any special auxiliary ligand,²⁰–²² while having a monomeric structure such as [Nb(tpp)OX] or [Nb(tpp)X₃] in the presence of some coordinating anion (X–), in the solid states (Scheme 1).²¹,²³ Thus, an appreciable change in the UV-Vis spectrum is expected by the reaction of [Nb₂(tpp)₂O₃] with a protic compound of HX to give [Nb(tpp)OX] or [Nb(tpp)X₃], due to the disappearance of π–π stacking of porphyrin rings. A preliminary study on the reaction of [Nb₂(tpp)₂O₃] with hydrochloric acid just showed such a change, which was used for optical detection of phosgene, which hydrolyzes to form HCl, in chlorohydrocarbons.²⁴ Since auxiliary ligands such as O²⁻ and X⁻ are located on an identical side of the porphyrin ring,²⁰–²³ high reactivity to polyhydroxy compounds is expected due to chelate ring formation with deprotonated polyols.

Dissolution state of Nb-TPP-OH in organic solvents

When UV-Vis spectra were recorded for a series of benzene solutions of Nb-TPP-OH at [C₆H₅-TBP-OPH] = 10⁻³.⁹ – 10⁻⁶.⁹ mol dm⁻³ using optical cells of various lengths, a systematic shift of a Soret band from 418 to 430 nm was observed with an isosbestic point at 424 nm; only the spectrum at [C₆H₅-TBP-OPH] = 10⁻⁶.⁹ mol dm⁻³ showed a slight downward deviation, which is probably attributed to partial adsorption of the complex to a quartz cell (Fig. 1(a)). A further deviation was observed in chlorobenzene. The species with λₘₚ = 430 nm was predominant in less polar solvents such as dimethylformamide and dimethyl sulfoxide. This change is attributable to the monomer (λₘₚ = 430 nm)–dimer (418 nm) equilibrium given by Eq. (1), based on the similar changes of the Zr-TPP complex and others.¹⁶

\[
2[Nb(tpp)O(OH)] = [Nb₂(tpp)₂O₃] + H₂O \quad (1)
\]

Under the present experimental conditions (in water-saturated benzene), the water concentration was in large excess relative to the concentration of the complex and was kept substantially constant. Thus, the equilibrium constant could be expressed by Eq. (2).

\[
K_{dim} = [Nb₂(tpp)₂O₃]/[Nb(tpp)O(OH)]^2 \quad (2)
\]

The mass balance about niobium(V) is expressed as Eq. (3).

\[
C_{Nb-TPP-OH} = [Nb(tpp)O(OH)] + 2[Nb₂(tpp)₂O₃] \quad (3)
\]

The dimerization constant was optimized to give a minimum error square sum with respect to the apparent molar absorption coefficients at 418 nm as a function of [C₆H₅-TBP-OPH] (Fig. 1(b)). The obtained constant, \(K_{dim} = 10^{6.35±0.02} \text{ mol}^{-1} \text{ dm}^3\), was appreciably larger than that of Zr-TPP-OH (10⁵.₅ₐ mol⁻¹ dm³ in chlorobenzene).¹⁶ This difference of the constant is attributed to the difference in the number of bridging oxide anions (3 for Nb-TPP-OH; 2 for Zr-TPP-OH). The dimeric species is predominant at \(C_{Nb-TPP-OH} ≥ 10^{-4.5} \text{ mol dm}^{-3}\) in benzene as well as in chlorobenzene. Such a condition is adopted for recognition of polyhydroxy compounds as described below.

Acid-base properties of Nb-TPP-OH

The reaction of Nb-TPP-OH at \(C_{Nb-TPP-OH} = 10^{-4.5} \text{ mol dm}^{-3}\) with MOH (M⁺: Na⁺ or tetrabutylammonium (TBA⁺)) in dioxane–water (10:1) respectively showed a shift of a Soret band to 429 nm or to 431.5 nm (Fig. S-1a, Supporting Information). The molar ratio plot indicates the reaction stoichiometry of \(C_{Nb-TPP-OH} = 1\) : 1 (Fig. S-1b, Supporting Information). The negative mode ESI-MS spectrum of the reaction product with NaOH has a peak at \(m/z = 737.1279\), which corresponds to \([Nb(tpp)O]^-\) (Fig. S-2, Supporting Information). Thus, the reaction is expressed as:

\[
Scheme 1 Chemical structures of Nb-TPP-OH and schematic illustration of the reactions with protic compounds.
\[ \text{[Nb}_2(\text{tp})_2\text{O}_3] + 2\text{MOH} = 2\text{M}^+.[\text{Nb}(\text{tp})\text{O}_2]^- + \text{H}_2\text{O} \quad (4) \]

The difference in absorption maximum between the products by the respective reactions with two MOHs is attributable to the difference in electrostatic interaction between \([\text{Nb}(\text{tp})\text{O}_2]^-\) and the counter cation \(\text{M}^+\) in this solvent of relatively low polarity.

The reaction of Nb-TPP-OH with an acid of HA (A\(^-\): CH\(_3\)COO\(^-\) or Cl\(^-\)) between chlorobenzene/water respectively showed a shift of a Soret band to 430 nm or to 424 nm with an isosbestic point at 423 or 420 nm (Figs. S-3a, 3b, Supporting Information).\(^{16}\) The spectral characteristic of the reaction product with CH\(_3\)COOH agreed with that of the structurally characterized species of \([\text{Nb}(\text{tp})\text{O}(\text{CH}_3\text{COO})]^{2+}\).\(^{21}\) Thus, the reaction is expressed by Eq. (5):

\[ \text{[Nb}_2(\text{tp})_2\text{O}_3] + 2\text{H}^+ + 2\text{A}^- = 2[\text{Nb}(\text{tp})\text{OA}] + \text{H}_2\text{O} \quad (5) \]

The changes in absorbance at the respective absorption maxima shown in Fig. S-3c (Supporting Information) could be reproduced using an equilibrium constant given by Eq. (6) as in the case of \([\text{Sn}(\text{tp})(\text{OH})_2]^{2+}\):\(^{25}\)

\[ K_{\text{HA}} = \frac{[\text{Nb}(\text{tp})\text{OA}]^2/[\text{[Nb}_2(\text{tp})_2\text{O}_3][\text{H}^+][\text{A}^-]^2]}{\text{log}(K_{\text{HA}}/\text{mol}^{-3}\text{dm}^9) = 9.77 \pm 0.02 \text{ for HA = CH}_3\text{COOH; and } -5.26 \pm 0.04 \text{ for HCl. The reactivity with acetic acid of the lower acidity is much higher than that with hydrochloric acid.}} \]

Reactions of Nb-TPP-OH with polyols

The reactions of Nb-TPP-OH with two trihydroxy compounds (glycerin [hereinafter glc; the hydroxy compounds are expressed by their initials without explicit indication of the number of hydroxy protons] and trimethylol ethane), two dihydroxy compounds (1,3-propanediol and 1,2-ethyleneglycol), and ethanol were examined in dioxane-water (10:1) by UV-Vis spectroscopy. Glycerin caused a spectral shift of a Soret band to 423 nm at 10\(^{-2}\) – 1 mol dm\(^{-3}\) (Fig. 2(a)). Since a decrease in total concentration of unreacted Nb-TPP-OH shifted the monomer-dimer equilibrium given by Eq. (1), a slight but systematic shift of the intersection of absorption spectra was observed at around 415 nm. In contrast to PBA, the reactivity of Nb-TPP-OH with glc was independent of pH at least between 4 and 8 (Fig. S-4, Supporting Information). Trimethylol ethane showed only a slight change, while neither 1,3-propanediol nor 1,2-ethyleneglycol nor ethanol caused any change.

The reactivity of Nb-TPP-OH to glycerin was extremely enhanced in benzene; the molar ratio plot clearly indicated the reaction stoichiometry of \(C_{\text{Nb-TPP-OH}}:C_{\text{glc}} = 1:1\) (Fig. S-5, Fig. 2).
Supporting Information). The positive mode ESI-MS of the reaction product with glycerin has a peak at m/z = 817.1512, which corresponds to [Nb(tpp)(H$_3$glc)]Na$^+$, where H$_3$glc$^-$ indicates a species formed by deprotonation of three hydroxy groups (Fig. S-6, Supporting Information). Thus, the reaction with glycerin is expressed as Eq. (7) that gives three water molecules as a byproduct:

$$[\text{Nb}_2(\text{tpp})_2\text{O}_3] + 2\text{glc} = 2[\text{Nb}(\text{tpp})(\text{H}–3\text{glc})] + 3\text{H}_2\text{O} \quad (7)$$

The changes in absorbance as a function of the free glc concentration shown in Fig. 2(b) could be reproduced using the equilibrium constant given by Eq. (8):

$$K_{3W} = [\text{Nb}(\text{tpp})(\text{H}–3\text{glc})]^2/[\text{Nb}_2(\text{tpp})_2\text{O}_3][\text{glc}]^2 \quad (8)$$

log $K_{3W}$ = –2.7 in dioxane-water (10:1); –2.9 in (10:2); and –3.1 in (10:3). The equilibrium constant was smaller in the medium of the higher water content, although the decrements were less than those expected by Eq. (7). This is probably attributed to the enhanced hydration and the stabilization of free glycerin in the water-rich medium. The constant in the two-phase system (chlorobenzene/water) was slightly small: log $K_{3W}$ = –3.5 ± 0.2.

The $^1$H NMR spectra of H$_2$tpp, [Nb$_2$(tpp)$_2$O$_3$], [Nb(tpp)O(OAc)], and [Nb(tpp)(H$_3$glc)] at 9.5 – 7.5 ppm are shown in Fig. S-7 (Supporting Information). The pyrrole protons of H$_2$tpp were shifted to the higher field in [Nb$_2$(tpp)$_2$O$_3$] due to the ring current effect of one porphyrin to the other, while being shifted only slightly to the lower field in [Nb(tpp)O(OAc)] and [Nb(tpp)(H$_3$glc)]. The $^1$H NMR spectra of glc and [Nb(tpp)(H$_3$glc)] at 4.2 – 1.8 ppm are shown in Fig. S-8 (Supporting Information). Three signals for [Nb(tpp)(H$_3$glc)] observed at 2.9, 2.3, and 1.8 ppm had a peak area ratio of 1:2:2, and the ratio of the total area of these peaks to the total area of pyrrole protons was 5:8; three hydroxy protons were not observed. Appreciable shifts of the original signals of glc at 3.8 – 3.6 ppm to the higher fields indicate that H$_3$glc$^-$ is located just on the porphyrin plane. All these results indicate that glycerin is recognized through three deprotonated hydroxyl groups above the porphyrin plane.

Reactions of Nb-TPP-OH with sugars

The reactions of Nb-TPP-OH with six sugars (sorbose, fructose, mannose, arabinose, galactose, glucose) were examined in the two-phase system by UV-Vis spectroscopy. Sorbose and fructose caused appreciable spectral shifts to the longer wavelengths at 10$^{-2}$ – 1 mol dm$^{-3}$, whereas other compounds showed no changes. The spectral change, however, suggests a reduction in total concentration of the complexes that is caused by precipitation of some product. The same reaction was clearly observed, on the other hand, for all the sugars in dioxane-water (10:1); for example, for fructose at a lower concentration of 10$^{-4}$ – 10$^{-3}$ mol dm$^{-3}$ (Fig. S-9, Supporting Information). The reactivities to ketohexoses are higher than those to aldohexoses due to the high distribution constants of these compounds. The reactivity was independent of pH between 4 and 8 (Fig. S-13, Supporting Information). Thus, the reaction with sorbose is similar to the reaction with glycercin expressed by Eq. (7).

Although the TOF-MS spectrum of the reaction product with mannose has a peak at m/z = 905.1647, which corresponds to [Nb(tpp)(H$_3$.sor)]Na$^+$ (Fig. S-10, Supporting Information). The reactivity was independent of pH between 4 and 8 (Fig. S-11, Supporting Information). Thus, the reaction product between fructose and sorbose is reversed.

The equilibrium constants obtained from the changes of the absorbance (Fig. S-9, Supporting Information) are summarized in Table 1. The equilibrium constant for the reaction with sorbose in dioxane-water (10:1) is 10$^{13}$ times larger than that with glycerin. This is attributable to the fact that three OH groups on sorbose are favorably preorganized to react with Nb-TPP-OH.

Reactions of Nb-TPP-OH with polyphenols

The reactions of Nb-TPP-OH with three polyphenols (catechol, resorcinol, phenol) were examined both in the two-phase system and dioxane-water (10:1) by UV-Vis spectroscopy. All the polyphenols showed appreciable shifts of the band to the longer wavelengths accompanied with broadening (Fig. S-12, Supporting Information). The reactivities in the two-phase system were much higher than those in dioxane-water (10:1), due to the high distribution constants of these compounds. The reactivity was independent of pH between 4 and 8 (Fig. S-13, Supporting Information). The reactivity order between fructose and sorbose is reversed.

The equilibrium constants obtained from the changes of the absorbance (Fig. S-9, Supporting Information) are summarized in Table 1. The equilibrium constant for the reaction with sorbose in dioxane-water (10:1) is 10$^{13}$ times larger than that with glycerin. This is attributable to the fact that three OH groups on sorbose are favorably preorganized to react with Nb-TPP-OH.

Reactions of Nb-TPP-OH with polyhydroxy compounds

<table>
<thead>
<tr>
<th>Polyhydroxy compound</th>
<th>log($K_{3W}$/mol$^{-1}$ dm$^3$)$^a$</th>
<th>n</th>
<th>Two-phase$^b$</th>
<th>Dioxane-water (10:1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glycerin</td>
<td>3</td>
<td>–3.5</td>
<td>–2.7</td>
<td></td>
</tr>
<tr>
<td>Sorbose</td>
<td>3</td>
<td>c</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Fructose</td>
<td>3</td>
<td>c</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Mannose</td>
<td>2</td>
<td>d</td>
<td>–2.0</td>
<td></td>
</tr>
<tr>
<td>Arabinose</td>
<td>2</td>
<td>d</td>
<td>–2.7</td>
<td></td>
</tr>
<tr>
<td>Galactose</td>
<td>2</td>
<td>d</td>
<td>–3.0</td>
<td></td>
</tr>
<tr>
<td>Glucose</td>
<td>2</td>
<td>d</td>
<td>–3.7</td>
<td></td>
</tr>
<tr>
<td>Polyphenol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catechol</td>
<td>2</td>
<td>3.0</td>
<td>–2.0</td>
<td></td>
</tr>
<tr>
<td>Resorcinol</td>
<td>1</td>
<td>1.0</td>
<td>–2.7</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>1</td>
<td>–0.6</td>
<td>d</td>
<td></td>
</tr>
</tbody>
</table>

a. ±0.1.

b. Water/chlorobenzene.

c. Precipitation.
d. Negligibly small.

The positive mode TOF-MS spectrum of the reaction product with sorbose has a peak at m/z = 905.1647, which corresponds to [Nb(tpp)(H$_3$.sor)]Na$^+$ (Fig. S-10, Supporting Information). The reactivity was independent of pH between 4 and 8 (Fig. S-11, Supporting Information). Thus, the reaction with sorbose is similar to the reaction with glycerin expressed by Eq. (7).

The reactions of Nb-TPP-OH with three polyhydroxy compounds (catechol, resorcinol, phenol) were examined both in the two-phase system and dioxane-water (10:1) by UV-Vis spectroscopy. All the polyphenols showed appreciable shifts of the band to the longer wavelengths accompanied with broadening (Fig. S-12, Supporting Information). The reactivities in the two-phase system were much higher than those in dioxane-water (10:1), due to the high distribution constants of these compounds. The reactivity was independent of pH between 4 and 8 (Fig. S-13, Supporting Information). The reactivity order between fructose and sorbose is reversed.

The equilibrium constants obtained from the changes of the absorbance (Fig. S-9, Supporting Information) are summarized in Table 1. The equilibrium constant for the reaction with sorbose in dioxane-water (10:1) is 10$^{13}$ times larger than that with glycerin. This is attributable to the fact that three OH groups on sorbose are favorably preorganized to react with Nb-TPP-OH.
of [Nb(tpp)(H-cat)(H-cat)], which had been isolated by the reaction with large excess catechol and had been structurally characterized, was not detected in this study.

Although the TOF-MS spectra of the reaction products with resorcinol (res) and phenol have no assignable peaks, the reactions expressed by Eqs. (11) and (12) as well as others are expected:

\[
\text{[Nb}_2(tpp)_2O_3] + \text{res} = 2\text{[Nb(tpp)O(H-res)]} + \text{H}_2\text{O} \quad (11)
\]

\[
K_{1W} = \frac{[\text{Nb(tpp)O(H-res)}]^2/([\text{Nb}_2(tpp)_2O_3][\text{res}]^2)} \quad (12)
\]

Summary of reactivities and spectral characteristics

The equilibrium constants obtained from the changes of the absorbance are summarized in Table 1. The equilibrium constant for the reaction with acetic acid in the two-phase system \((K_{1W} = 10^{-17} \text{ mol}^{-1} \text{ dm}^3)\) given by Eq. (6) may be recalculated using the protonation constant, as a constant with the neutral species serving as a reactant to be \(K_{1W} = 10^{13} \text{ mol}^1 \text{ dm}^{-3}\). The value is comparable to those for the reactions with resorcinol and phenol of \(n = 1\), so that the reaction is expressed as Eq. (11). The reactivity order of polyhydroxy compounds are as follows: catechol > sorbose, fructose > glycerin in the two-phase system; sorbose, fructose > glycerin, catechol in dioxane-water. The difference in the reactivity order is attributable to the difference in lipophilicity and thereby to the difference in the distribution constant of polyhydroxy compounds.

The absorption spectra of the representative species are shown in Fig. 3, where the molar extinction coefficient is normalized by the number of the niobium(V) complex unit involved. The absorption maximum of the dimeric species is located at the shortest wavelength, while those of the monomeric species containing one monodentate ligand are at the longest wavelength; the molar absorptivity of the anionic species is about twice that of the neutral one. The absorption maxima of the species reacted with polyhydroxy compounds are located between these two extremes. The reaction product with catechol shows extremely broadened absorption.

Conclusions

The Nb-TPP-OH complex, which exists as \([\text{Nb}_2(tpp)_2O_3] \text{ at } C_{\text{Nb-TPP-OH}} > 10^{-4.5} \text{ mol dm}^{-3}\), reacts with a polyhydroxy compound to form a monomeric complex containing chelate rings by coordination of the deprotonated species and to cause an appreciable UV-Vis change. In contrast to phenylboronic acid, the reactivity of \([\text{Nb}_2(tpp)_2O_3]\) is independent of pH under physiological conditions. The sugar selectivity order of \([\text{Nb}_2(tpp)_2O_3]\) (sorbose > fructose >> mannose > arabinose, galactose > glucose) is appreciably different from that of PBA (fructose > sorbose >> arabinose > galactose > mannose > glucose). This may be related to the difference in size of the Lewis acidic center.

Acknowledgements

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Supporting Information

Additional figures showing the UV-Vis changes by the reactions of Nb-TPP-OH with acids, bases, sugars, and polyphenols and the NMR and TOF-MS spectra of the reaction products. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

References