

Electronic Supplementary Information

Investigation of Adsorptive Orientation State Change of Anionic Porphyrin with Hydrolysis Reaction of α -Tricalcium Phosphate

Daichi Noda,¹ Norio Saito,² Iori Yamada,¹ Motohiro Tagaya^{1,*}

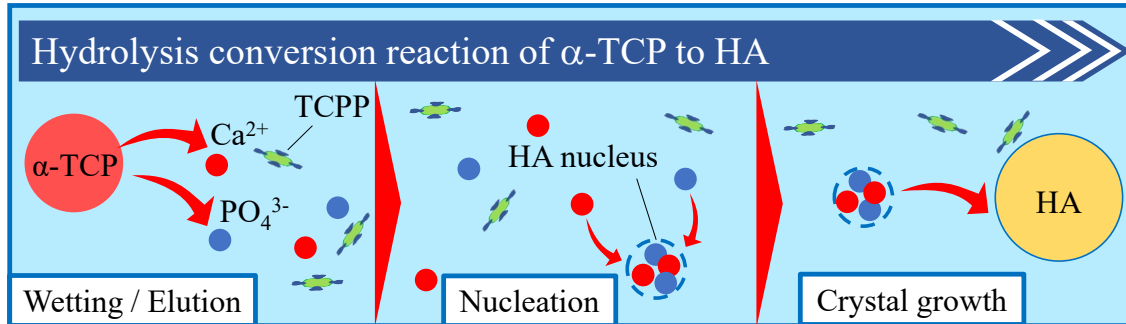
*¹ Department of Materials Science and Technology, Nagaoka University of Technology,
1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan*

*² Department of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science,
1-3 Kagurazaka, Shinjuku, Tokyo 162-8601, Japan*

*** Author to whom correspondence should be addressed:**

Tel: +81-258-47-9345; Fax: +81-258-47-9300, E-mail: tagaya@mst.nagaokaut.ac.jp

Scheme S1



Scheme S1. Illustration of hydrolysis conversion reaction from α -TCP to HA in this study.

Experimental Procedure S1

The Soret band of samples were separated into peak I–III. The position of peak I, peak II and peak III were 411–414 nm, 421–427 nm and 375–380 nm. All the deconvolutions were performed by fitting the Gaussian function using the software SOLVER option (Excel 2016). In the SOLVER calculation, the generalized reduced gradient method was used until all the constraints were satisfied. The deconvolutions were optimized until the sum of the residual squares of the measured and synthesized data was minimized. The error was within 3% in all samples.

The peak I position (411–414 nm) is close to the Soret band (B(0,0)) of TCPP (410 nm) and TCPP⁴⁻ (413 nm). Accordingly, TCPP was considered to be present as the mono-anion to tri-anion adsorption state on HA/TC. Thus, the peak I could be assignable to the vertically-adsorbed TCPP, taking into account that the carboxylate ion of citric acid can vertically be replaced with PO₄ site on HA.^{S1}

The peak II position (421–427 nm) is close to the Soret band (B(0,0)) of TCPP²⁺ (430 nm). Here, TCPP²⁺ does not exist in the aqueous solution at pH 7.0 in this study. The peak II seems to be due to the TCPP with an electronic state similar to the TCPP²⁺ owing to the interacting with Ca²⁺ site at the porphyrin ring. Moreover, as a result of the assuming of the interaction state between Ca²⁺ site and the porphyrin ring on the HA surface, we speculated that the peak II was assignable to TCPP adsorbed in the horizontal state by the interaction of Ca²⁺ ion and carboxylate ion at diagonal two end groups.

The peak III was assignable to the electronic transition of B(1,0).²

Reference

- S1 M. R. T. Filgueiras, D. Mkhonto and N. H. de Leeuw, *J. Cryst. Growth*, 2006, **294**, 60–68.
S2 S. E. Clarke, C. C. Wamser and H. E. Bell, *J. Phys. Chem. A*, 2002, **106**, 3235–3242.

Figure S1

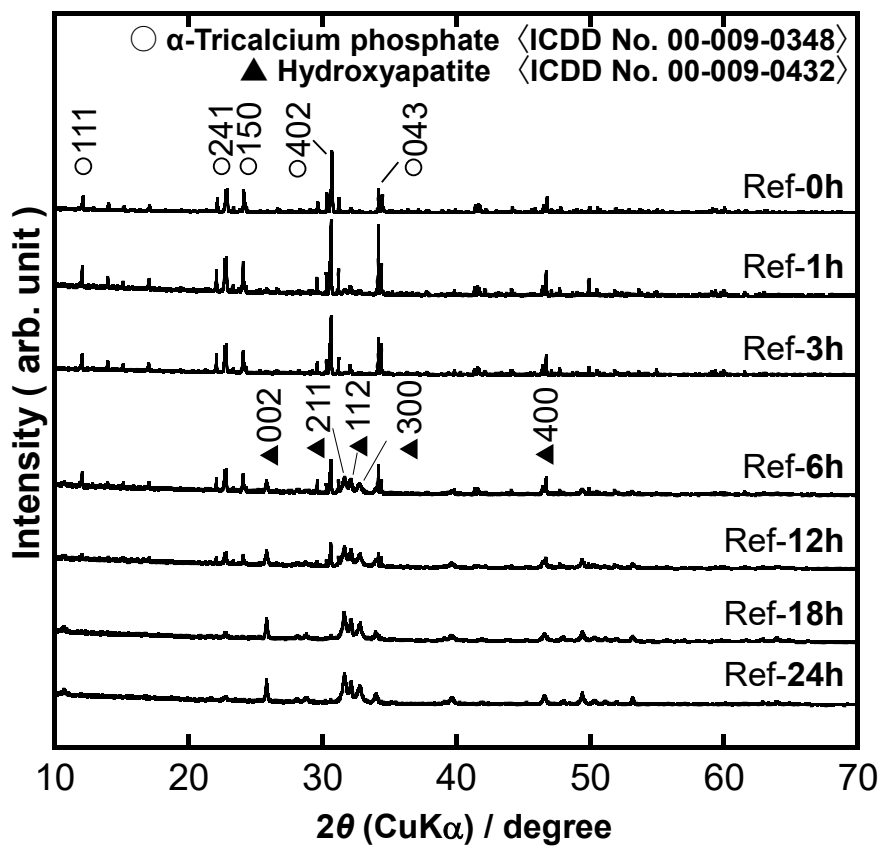


Figure S1. XRD patterns of Ref- X h ($X = 0, 1, 3, 6, 12, 18, 24$), and all the patterns can be attributed to α -TCP or HA.

Figure S2

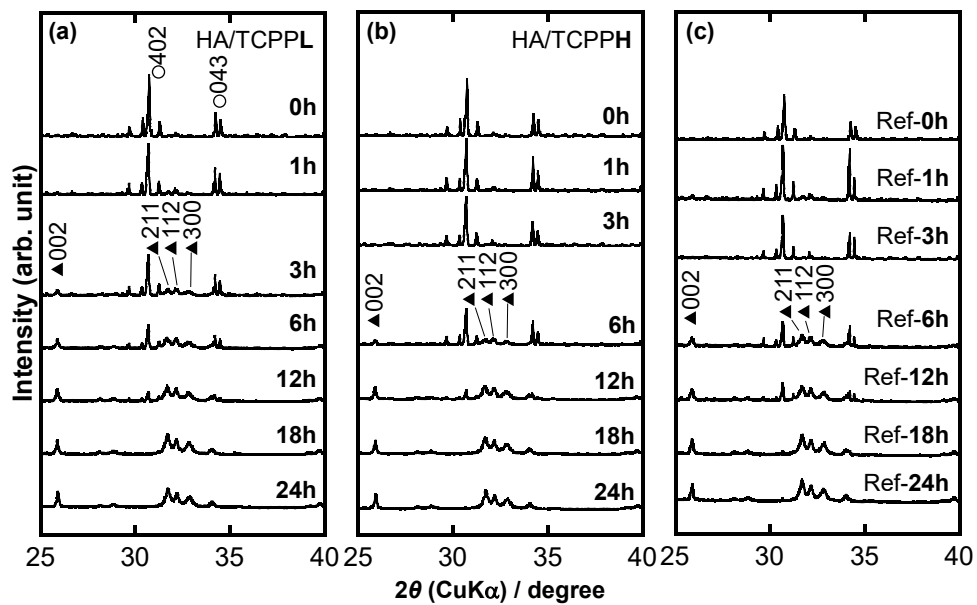


Figure S2. XRD patterns of (a) HA/TCPPL-Xh, (b) HA/TCPPH-Xh and Ref-Xh ($X = 0, 1, 3, 6, 12, 18, 24$) at the range of 25-40 degree, and all the patterns can be attributed to (○) α -TCP (ICDD No. 00-009-0348) and/or (▲) HA (ICDD No. 00-009-0432).

Figure S3

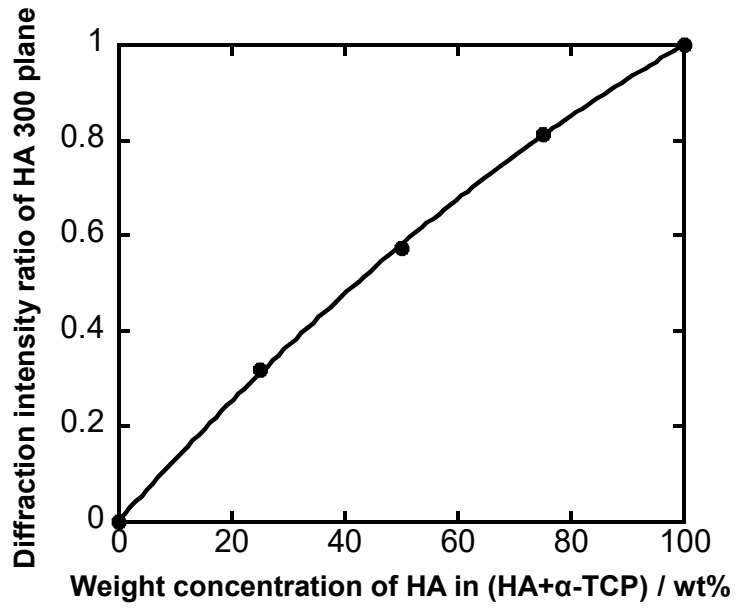


Figure S3. Diffraction intensity ratio of HA 300 plane with the HA content in the mixture of HA with α -TCP, where the relationship was regarded as the quadratic approximation equation ($y = -3 \times 10^{-5}x^2 + 0.0132x + 0.0024$, $R^2=0.9999$).

Figure S4

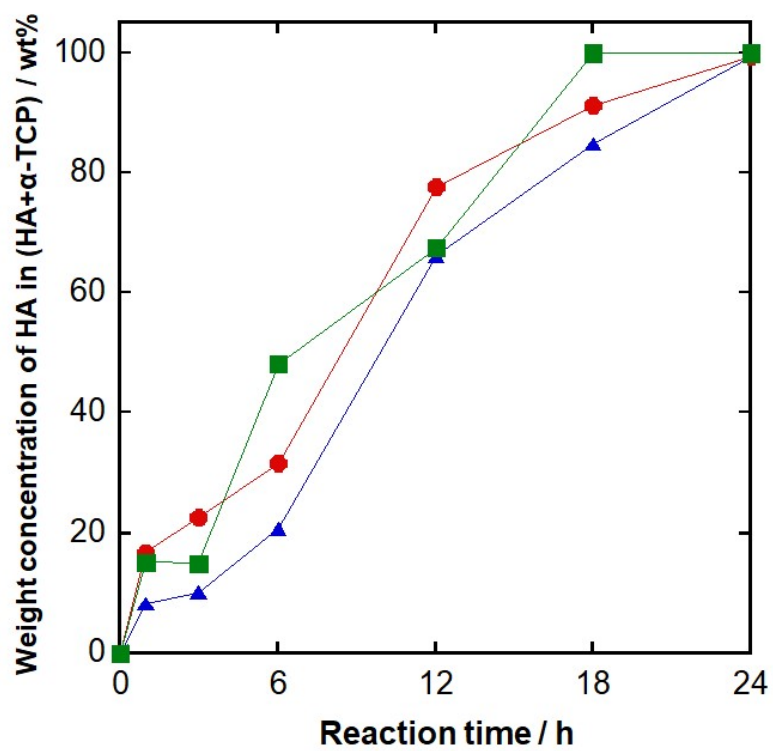


Figure S4. Weight concentration of HA in (●) HA/TCPPL, (▲) HA/TCPPH and (■) Ref. from the calibration curve (Fig. S3, ESI).

Figure S5

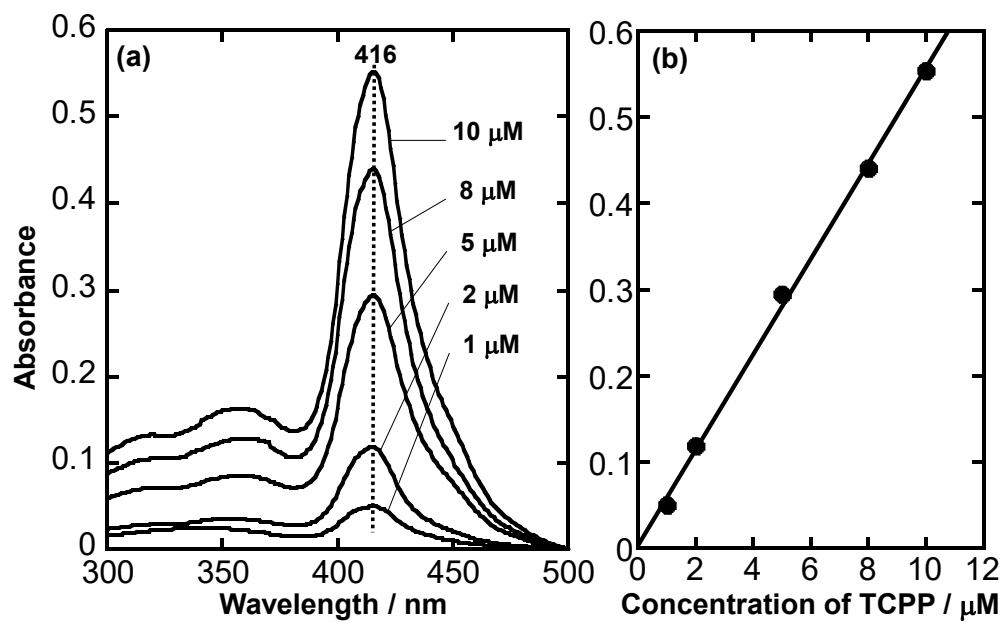


Figure S5. (a) UV-Visible absorption spectra in the HCl aqueous solution with the different concentrations of TCPP, and (b) the calibration curve between the concentration and absorbance ($y=0.0551x + 0.0044$, $R^2=0.9981$).

Figure S6

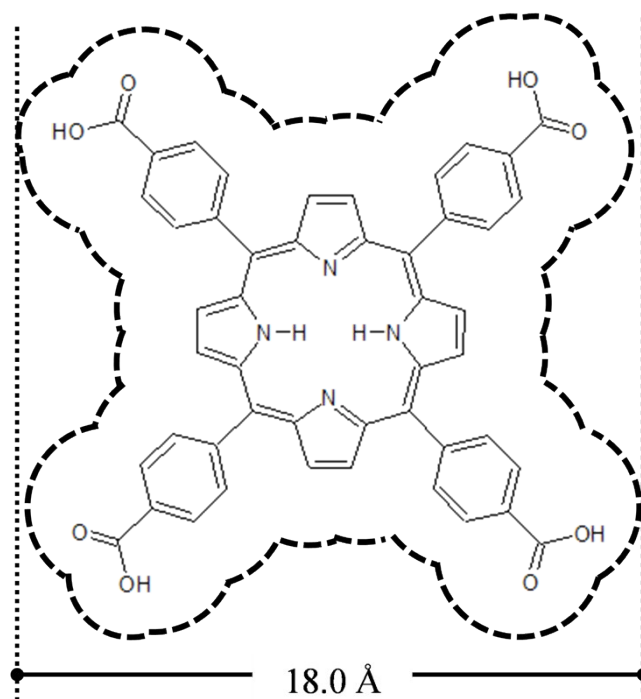


Figure S6. Molecular structure and diameter of TCPP.

Figure S7

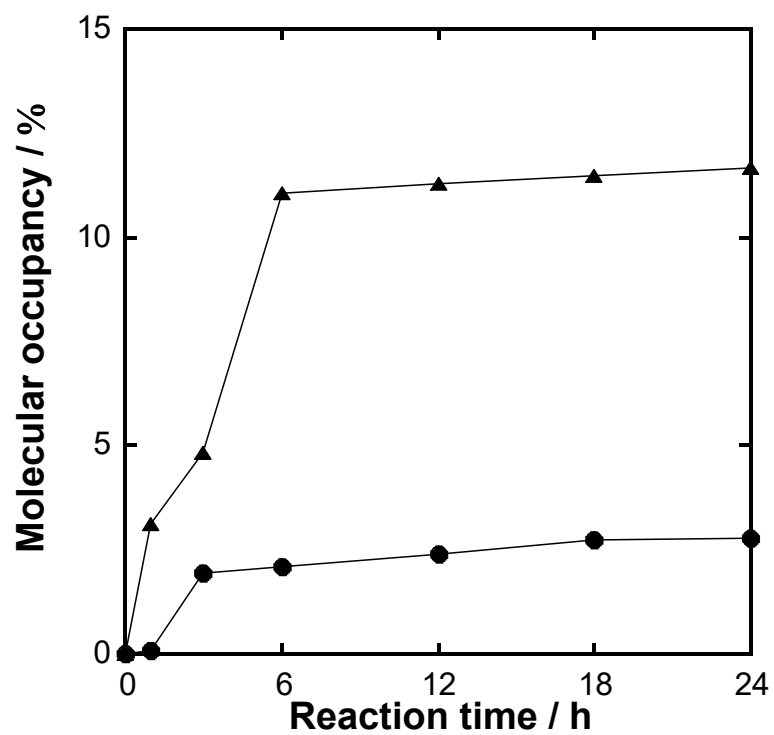


Figure S7. TCPP molecular occupancy adsorbed on (●) HA/TCPPPL and (▲) HA/TCPPH.

Equation (S1)

The molecular occupied cross-sectional area of TCPP was calculated as a square shape with a side length of 18.8 Å in **Figure S5, ESI**. The TCPP molecular occupancy on the particle surface was calculated by the following equation (2).

$$\text{Molecular occupancy} = \frac{3.24 \times 10^{-18} \cdot M_a \cdot N_A}{2.27 \cdot (1 - R_{HA}) + 29.0 \cdot R_{HA}} \quad (\text{S1})$$

Here, the N_A is Avogadro's constant, M_a is the adsorbed amount of TCPP, and R_{HA} is the volume ratio of HA on the produced particles.

Figure S8

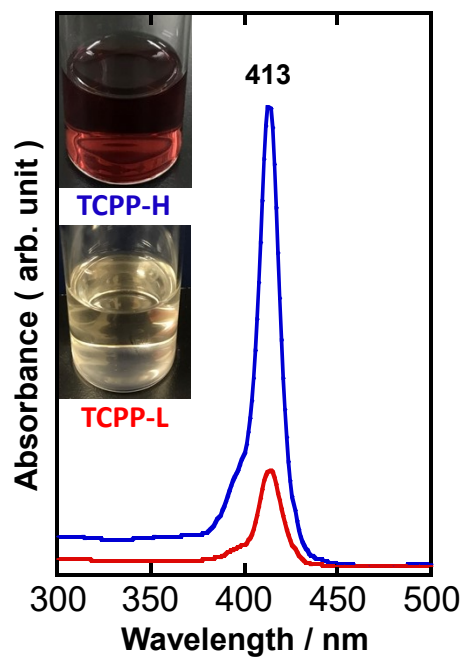


Figure S8. UV-Visible absorption spectra of (red line) TCPP-L (conc. 1 μM) and (blue line) TCPP-H (conc. 100 μM), and (inset) their apparent solution photographs.

Figure S9

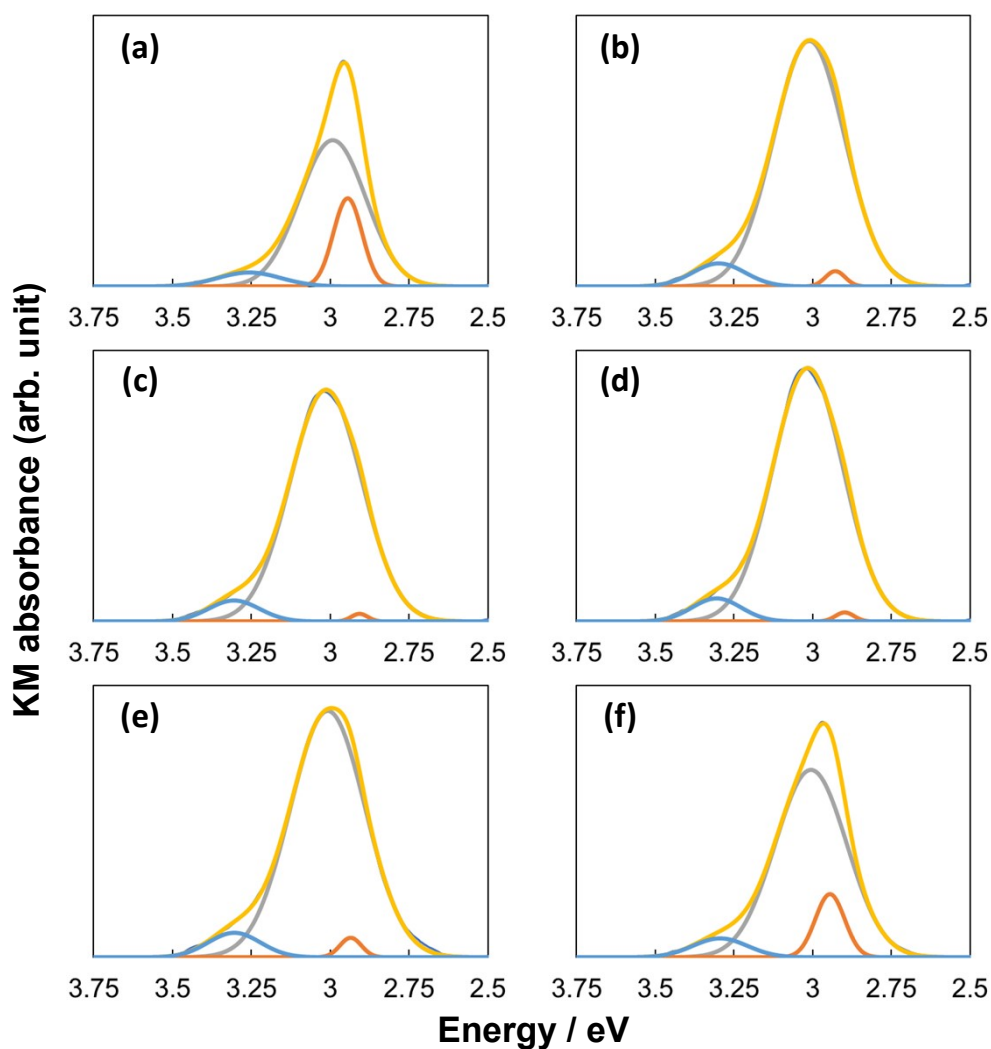


Figure S9. Deconvolution results of UV-Visible absorption spectra attributed to the Soret band of HA/TCPPL- X h (X = (a) 1, (b) 3, (c) 6, (d) 12, (e) 18, (f) 24). The spectra were separated and fitted to horizontal and vertical molecular adsorption states of TCPPL, and the electronic transition (B(1,0)), which were represented by orange and gray, and light-blue colored lines. Here, the raw and summation spectra were represented by blue and yellow colored lines, respectively.

Figure S10

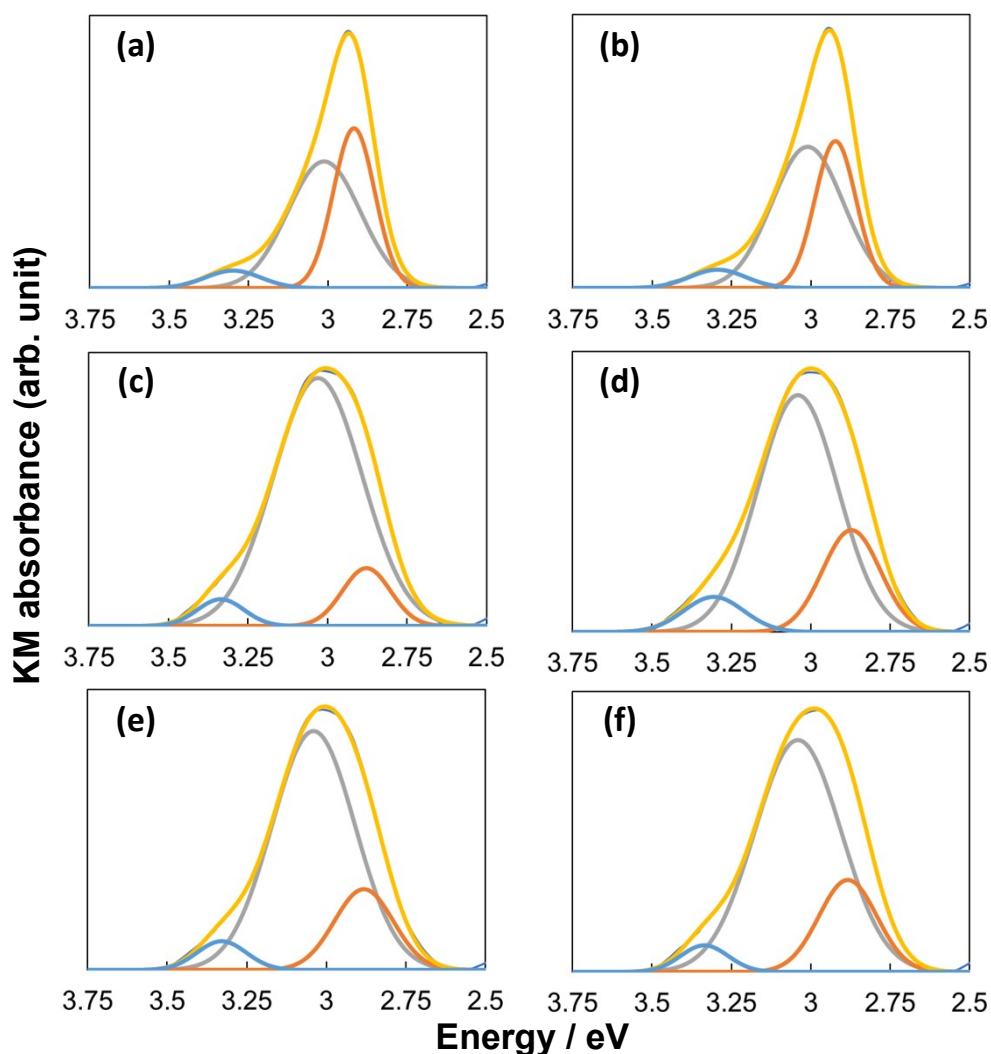


Figure S10. Deconvolution results of UV-Visible absorption spectra attributed to the Soret band of HA/TCPPH-**X**h (**X** = (a) 1, (b) 3, (c) 6, (d) 12, (e) 18, (f) 24). The spectra were separated and fitted to horizontal and vertical molecular adsorption states of TCPP, and the electronic transition (B(1,0)), which were represented by orange and gray, and light-blue colored lines. Here, the raw and summation spectra were represented by blue and yellow colored lines, respectively.