Electronic Supplementary Material (ESI) for Dalton Transactions.

# Supplementary Information

# $Ti_7$-Containing, Tetrahedral 36-Tungsto-4-Arsenate(III) $[Ti_6(TiO_6)(AsW_9O_{33})_4]^{20-}$

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## Experimental details

### 1. General methods and materials

The reagents were used as purchased without further purification. FT-IR spectra (KBr pellets) were recorded on a Nicolet-Avatar 370 spectrometer. Thermogravimetric analyses were carried out with a TA Instruments Q 600 device at a heating rate of 5 ºC/min under a nitrogen atmosphere. The $^{183}$W NMR spectrum was recorded on a JEOL ECX 400 instrument using a 10 mm tube. Mass spectra were obtained in the negative ion mode by direct injection using an Agilent 6520 Q-TOF LC/MS mass spectrometer. The general strategy includes assignment of the polyanion species and determination of the clusters stability in aqueous solution. Elemental analyses for Na, Ti, As, and W (ICP-OES), as well as Cs (ICP-MS) were performed at Central Institute for Engineering, Electronics and Analytics (ZEA-3), Forschungszentrum Jülich, 52425 Jülich. The C analysis was performed in the Ocean Lab, School of Engineering and Science, Jacobs University.

### 2. Synthesis

**Synthesis of $Na_{20}[Ti_6(TiO_6)(AsW_9O_{33})_4]\cdot 63H_2O$ (Na-1):**

$TiOSO_4$ (0.128 g, 0.80 mmol) was dissolved in 20 mL of sodium acetate buffer (1 M, pH 4.6) followed by addition of $Na_9[B\text{-}\alpha\text{-}AsW_9O_{33}]\cdot 27H_2O$ (1.10 g, 0.37 mmol). The solution was kept at room temperature for 1 h with constant stirring. Then the solution was filtered and allowed to evaporate in an open beaker. Colourless crystals of **Na-1** started to appear after one day and were collected after ten days (yield: 0.105 g, 10%, based on $Na_9[B\text{-}\alpha\text{-}AsW_9O_{33}]\cdot 27H_2O$). The **Na-1** can be prepared in sodium acetate buffer (1M) with variable pH range from 4.2 to 5. As an optimum condition, the procedure at pH 4.6 is described in detail. IR of **Na-1**: 1619(m), 966 (m), 898 (m), 823 (s), 763 (s), 729 (m), 662 (m), 475 (w), 453 (m) cm$^{-1}$. Anal. Calcd (Found) for **Na-1**: Na 4.16 (4.02), W 59.86 (59.90), As 2.71 (2.68), Ti 3.03 (2.99).

### Synthesis of $Na_{17.5}Cs_{2.5}[Ti_6(TiO_6)(AsW_9O_{33})_4]\cdot72H_2O\cdot2NaCH_3COO$ (NaCs-1)

The procedure was analogous to that of **Na-1**, but the pH of the 1M sodium acetate buffer used was 5.0 instead of 4.6, and 40 μL of 1 M CsCl was added to the reaction solution after stirring. Colourless crystals of **NaCs-1** started to form after one day and were collected after ten days. (yield: 0.030 g, 3%, based on $Na_9[B\text{-}\alpha\text{-}AsW_9O_{33}]\cdot27H_2O$). IR of **NaCs-1**: 1623(m), 1559(w), 1411(w), 958 (m), 890 (m), 820 (s), 764 (s), 728 (m), 667 (m), 474 (w), 452 (m) cm$^{-1}$. Anal. Calcd (Found) for **NaCs-1**: Na 3.85 (4.29), Cs 2.85 (2.91), W 56.8 (56.7), As 2.57 (2.68), Ti 2.87 (2.53), C 0.41 (0.24).

## 3. X-ray diffraction

A colorless block crystal of **NaCs-1** with dimensions 0.08 * 0.06 * 0.05 mm$^3$ was mounted on a Hampton cryo-loop for indexing and intensity data collection at 100 K on a Bruker D8 APEX II CCD using Mo-Kα radiation ($\lambda$ = 0.71073 Å). Lorentz and polarization corrections were applied, and an absorption correction was performed using the SADABS program (G. M. Sheldrick, Siemens Analytical X-ray Instrument Division: Madison, WI, 1995). The structures of **NaCs-1** was solved by direct methods using the SHELXS-97 program and refined by full-matrix least-squares on $F^2$ using the SHELXL-2013 program. The refinement suggests an occupancy of 0.16667 on Cs atom at special position, resulting in 4 Cs atoms in the formula, whereas the elemental analysis shows that the bulk material contains only 2.5 Cs in the formula. Herein, the latter formula is shown throughout the paper due to the bulk material was used for all further characterizations. The relevant crystallographic data and structure refinement details, and the selected bond lengths and angles of **NaCs-1** can be found in Tables S1 and S2, respectively.

**Table S1.** Crystal data for $Na_{17.5}Cs_{2.5}[Ti_6(TiO_6)(AsW_9O_{33})_4]\cdot 72H_2O\cdot 2NaCH_3COO$ (**NaCs-1**).

| Compound | **NaCs-1** |
|---|---|
| Empirical formula | $C_4H_{150}As_4Cs_{2.5}Na_{19.5}O_{214}Ti_7W_{36}$ |
| Formula weight | 11657.39 |
| Crystal system | Cubic |
| Space group | *Fd*-3*m* |
| $T$/ K | 100 |
| $\lambda$/ Å | 0.71073 |
| $a$/ Å | 38.955(2) |
| $V$/ Å$^3$ | 59114(9) |
| Z | 8 |
| $D_{calc}$/ g·cm$^{-3}$ | 2.620 |
| Absorption coefficient/ mm$^{-1}$ | 14.985 |
| $F$(000) | 41504 |
| Crystal size/ mm | 0.08*0.06*0.05 |
| Theta range for data collection/ ° | 3.429-24.711 |
| Reflections collected | 199037 |
| Independent reflections | 2403 |
| $R_{\text{int}}$ | 0.2058 |
| No. of parameters | 69 |
| $T_{\min}$ / $T_{\max}$ | 0.1346/0.1887 |
| Goodness-of-fit on F2 | 1.013 |
| $R_1{}^a$, w$R_2$ [$I > 2\sigma(I)$]: | 0.0482, 0.1217 |
| $R_1$, w$R_2{}^b$ (all data) | 0.0839, 0.1524 |
| Largest diff. peak and hole/ e. Å$^{-3}$ | 2.903 and -4.064 |

$^aR_1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$, $wR_2 = \{\Sigma w[(Fo)^2 - (Fc)^2]^2/\Sigma w[(Fo)^2]^2\}^{1/2}$

**Table S2.** Selected bond lengths (Å) and angles (°) for compound **NaCs-1** $^a$

| | | | |
|---|---|---|---|
| W(1)-O(1A) | 1.718(17) | Ti(1)-O(12T)#5 | 1.90(2) |
| W(1)-O(1B) | 1.893(12) | Ti(1)-O(12T)#6 | 1.90(2) |
| W(1)-O(1B)#1 | 1.893(12) | Ti(1)-O(12T)#7 | 1.90(2) |
| W(1)-O(1C) | 1.916(4) | Ti(1)-O(12T)#8 | 1.90(2) |
| W(1)-O(1C)#2 | 1.916(4) | Ti(1)-O(12T)#2 | 1.90(2) |
| W(1)-O(1AS) | 2.363(15) | Ti(2)-O(12T) | 1.75(2) |
| W(2)-O(2C) | 1.708(13) | Ti(2)-O(22T)#9 | 1.945(11) |
| W(2)-O(22T) | 1.832(11) | Ti(2)-O(22T)#10 | 1.945(11) |
| W(2)-O(2A) | 1.913(5) | Ti(2)-O(22T)#11 | 1.945(11) |
| W(2)-O(2B) | 1.934(8) | Ti(2)-O(22T) | 1.945(11) |
| W(2)-O(1B)#1 | 1.969(12) | O(1C)-W(1)#3 | 1.916(4) |
| W(2)-O(1AS) | 2.326(11) | O(1B)-W(2)#1 | 1.969(12) |
| As-O(1AS)#3 | 1.792(15) | O(1AS)-W(2)#1 | 2.326(10) |

| | | | |
|---|---|---|---|
| As-O(1AS)#4 | 1.792(15) | O(2B)-W(2)#1 | 1.934(8) |
| As-O(1AS) | 1.792(15) | O(2A)-W(2)#9 | 1.913(5) |
| Ti(1)-O(12T) | 1.90(2) | | |
| | | | |
| O(1A)-W(1)-O(1B) | 100.4(5) | O(12T)#5-Ti(1)-O(12T)#6 | 90.0 |
| O(1A)-W(1)-O(1B)#1 | 100.4(5) | O(12T)-Ti(1)-O(12T)#7 | 180.0 |
| O(1B)-W(1)-O(1B)#1 | 89.6(7) | O(12T)#5-Ti(1)-O(12T)#7 | 90.000(1) |
| O(1A)-W(1)-O(1C) | 101.6(6) | O(12T)#6-Ti(1)-O(12T)#7 | 90.0 |
| O(1B)-W(1)-O(1C) | 158.0(6) | O(12T)-Ti(1)-O(12T)#8 | 90.0 |
| O(1B)#1-W(1)-O(1C) | 87.6(6) | O(12T)#5-Ti(1)-O(12T)#8 | 90.000(1) |
| O(1A)-W(1)-O(1C)#2 | 101.6(6) | O(12T)#6-Ti(1)-O(12T)#8 | 180.0 |
| O(1B)-W(1)-O(1C)#2 | 87.6(6) | O(12T)#7-Ti(1)-O(12T)#8 | 90.000(1) |
| O(1B)#1-W(1)-O(1C)#2 | 158.0(6) | O(12T)-Ti(1)-O(12T)#2 | 90.0 |
| O(1C)-W(1)-O(1C)#2 | 86.9(9) | O(12T)#5-Ti(1)-O(12T)#2 | 180.0 |
| O(1A)-W(1)-O(1AS) | 169.9(7) | O(12T)#6-Ti(1)-O(12T)#2 | 90.000(1) |
| O(1B)-W(1)-O(1AS) | 72.7(4) | O(12T)#7-Ti(1)-O(12T)#2 | 90.0 |
| O(1B)#1-W(1)-O(1AS) | 72.7(4) | O(12T)#8-Ti(1)-O(12T)#2 | 90.000(1) |
| O(1C)-W(1)-O(1AS) | 85.6(5) | O(12T)-Ti(2)-O(22T)#9 | 105.2(4) |
| O(1C)#2-W(1)-O(1AS) | 85.6(5) | O(12T)-Ti(2)-O(22T)#10 | 105.2(4) |
| O(2C)-W(2)-O(22T) | 103.5(6) | O(22T)#9-Ti(2)-O(22T)#10 | 149.5(7) |
| O(2C)-W(2)-O(2A) | 102.3(6) | O(12T)-Ti(2)-O(22T)#11 | 105.2(4) |
| O(22T)-W(2)-O(2A) | 89.5(6) | O(22T)#9-Ti(2)-O(22T)#11 | 86.6(7) |
| O(2C)-W(2)-O(2B) | 98.2(6) | O(22T)#10-Ti(2)-O(22T)#11 | 85.5(7) |
| O(22T)-W(2)-O(2B) | 90.8(6) | O(12T)-Ti(2)-O(22T) | 105.2(4) |
| O(2A)-W(2)-O(2B) | 158.8(6) | O(22T)#9-Ti(2)-O(22T) | 85.5(7) |
| O(2C)-W(2)-O(1B)#1 | 97.5(6) | O(22T)#10-Ti(2)-O(22T) | 86.6(7) |
| O(22T)-W(2)-O(1B)#1 | 159.1(5) | O(22T)#11-Ti(2)-O(22T) | 149.5(7) |
| O(2A)-W(2)-O(1B)#1 | 85.3(6) | W(1)#3-O(1C)-W(1) | 150.0(9) |
| O(2B)-W(2)-O(1B)#1 | 87.0(6) | W(1)-O(1B)-W(2)#1 | 122.5(6) |
| O(2C)-W(2)-O(1AS) | 166.8(6) | As-O(1AS)-W(2)#1 | 117.5(5) |
| O(22T)-W(2)-O(1AS) | 87.1(5) | As-O(1AS)-W(2) | 117.5(5) |
| O(2A)-W(2)-O(1AS) | 85.4(5) | W(2)#1-O(1AS)-W(2) | 92.5(5) |
| O(2B)-W(2)-O(1AS) | 73.4(5) | As-O(1AS)-W(1) | 134.5(8) |
| O(1B)#1-W(2)-O(1AS) | 72.3(5) | W(2)#1-O(1AS)-W(1) | 92.5(5) |
| O(1AS)#3-As-O(1AS)#4 | 97.0(6) | W(2)-O(1AS)-W(1) | 92.5(5) |
| O(1AS)#3-As-O(1AS) | 97.0(6) | W(2)#1-O(2B)-W(2) | 120.6(9) |
| O(1AS)#4-As-O(1AS) | 97.0(6) | W(2)#9-O(2A)-W(2) | 145.8(9) |

|  |  |  |  |
|---|---|---|---|
| O(12T)-Ti(1)-O(12T)#5 | 90.0 | Ti(2)-O(12T)-Ti(1) | 180.0 |
| O(12T)-Ti(1)-O(12T)#6 | 90.000(2) | W(2)-O(22T)-Ti(2) | 145.1(7) |

[a]Symmetric codes: #1 *x*, *z*, *y*; #2 *z*, *x*, *y*; #3 *y*, *z*, *x*; #4 *y*, *x*, *z*; #5 *x*, -*z*+1/4, -*y*+1/4; #6 *y*, -*x*+1/4, -*z*+1/4; #7 -*x*+1/4, -*y*+1/4, *z*+0; #8 -*y*+1/4, *x*, -*z*+1/4; #9 *z*, *y*, *x*; #10 -*z*+1/4, *y*, -*x*+1/4; #11 -*x*+1/4, *y*, -*z*+1/4.

## 4. Bond valence sum calculations

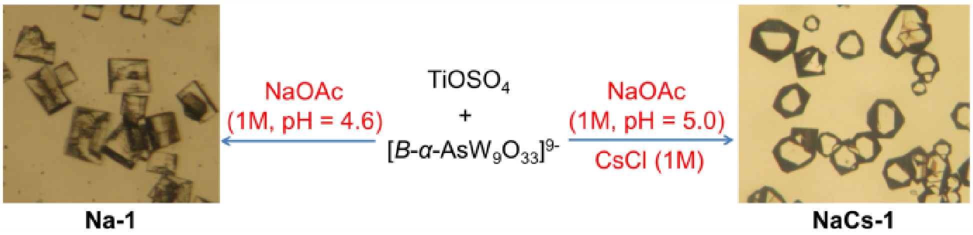
Bond valence sum (BVS) calculations were performed on the Bond Valence Calculator (Version 2.00) copyrighted by Chris Hormillosa & Sean Healy and distributed by I. D. Brown (I. D. Brown, D. Altermatt, Acta Crystallogr. 1985, B41, 244-247.). The BVS values for different atoms in **NaCs-1** are presented in **Table S3**.

**Table S3**. Bond valence sum values for oxygen atoms in **NaCs-1**.

| Atom | BVS value | Atom | BVS value |
|---|---|---|---|
| O1C | -2.01 | O2B | -1.91 |
| O1B | -1.94 | O2A | -2.02 |
| O1A | -1.71 | O12T | -2.00 |
| O1AS | -1.96 | O22T | -1.96 |
| O2C | -2.00 |  |  |

## 5. Toxicity test of Na-1

The A431 cell line was purchased from CLS Cell Lines Service GmbH (Eppelheim, Germany) and maintained in Dulbecco's modified Eagle's medium (DMEM) supplemented with 10% standardized fetal bovine serum (FBS), at 37 °C in a humidified atmosphere enriched with 5% $CO_2$. Cells were seeded in 96-well plates (3000 cells well$^{-1}$, Cellstar, Greiner Bio-One GmbH, Frickenhausen, Germany) with $4 \times 10^4$ cells well$^{-1}$. After 24 h, the culture medium was substituted by fresh medium (without FBS) containing varying concentrations of $[Ti_6(TiO_6)(AsW_9O_{33})_4]^{20-}$ (0/ 0.1/ 0.25/ 0.5/ 0.75/ 1.0 mg ml$^{-1}$). The 96-well plates were incubated at 37 °C in a humidified atmosphere enriched with 5% $CO_2$ for the indicated time points. For determination of cytotoxicity, commercially available kits were used according to the manufactures instructions. Briefly, quantitative estimations of lactate dehydrogenase (CytoScan™-LDH assay, G-Biosciences, St Louis, MO, USA) were done upon cell lysis by measurements of the absorption of the resulting formazan at 492 nm using a micro-plate reader (VarioskanFlash, Thermo Fisher Scientific, Bonn, Germany). The XTT (2,3-Bis-(2-methoxy-4-nitro-5-sulfophenyl)-2H-tetrazolium-5-carboxanilide salt) assay (Cell Proliferation Kit XTT, AppliChem GmbH, Darmstadt, Germany) was read out at 450 nm. For a better comparison of the obtained values, the amount of cellular proteins in each well was determined by sulforhodamine B (CytoScan™-SRB Cell assay, G-Biosciences, St Louis, MO, USA) at 560 nm. The protein content was related to the data from the LDH and XTT test. All calculations were performed using OriginPro 8.6 (OriginLab Corporation, Northampton, MA, USA).



**Scheme S1. Reaction scheme and single crystal pictures for Na-1 and NaCs-1, respectively.**

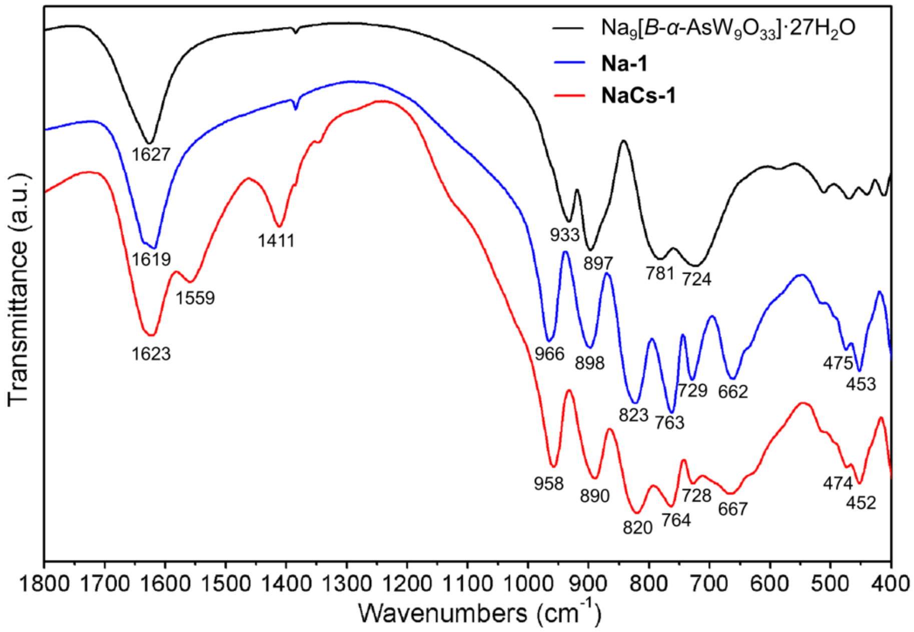


**Fig. S1** IR spectra of Na$_9$[$B$-$\alpha$-AsW$_9$O$_{33}$]·27H$_2$O (black), **Na-1** (blue), and **NaCs-1** (red).

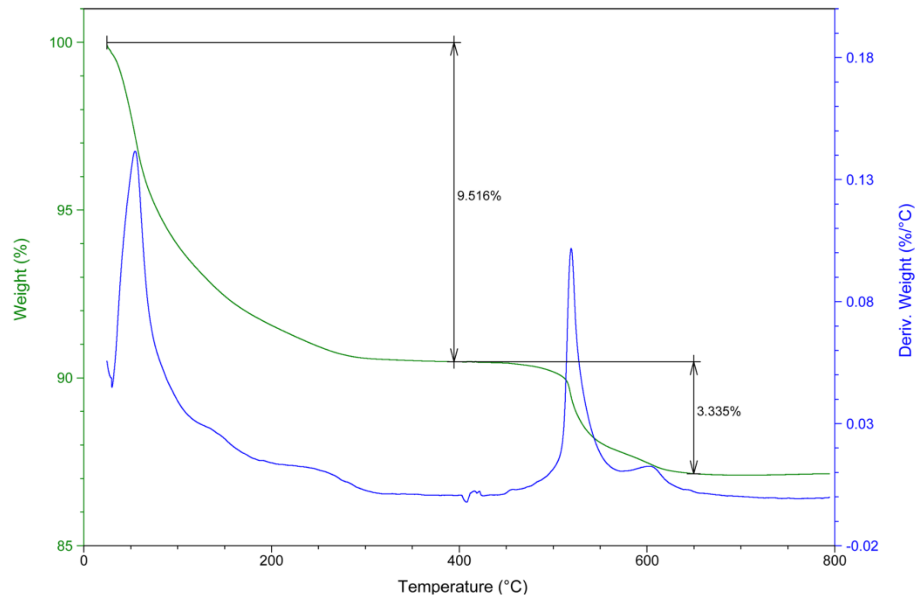


**Fig. S2** Thermogram of **Na-1** from room temperature to 800 °C under N2 atmosphere. The blue curve shows the derivative profile.

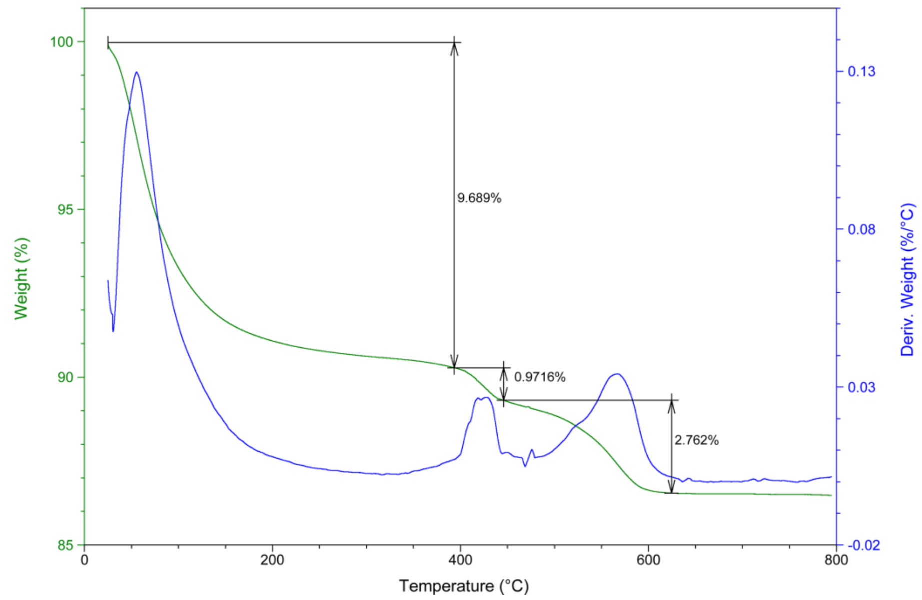


**Fig. S3** Thermogram of **NaCs-1** from room temperature to 800 °C under N2 atmosphere. The blue curve shows the derivative profile.

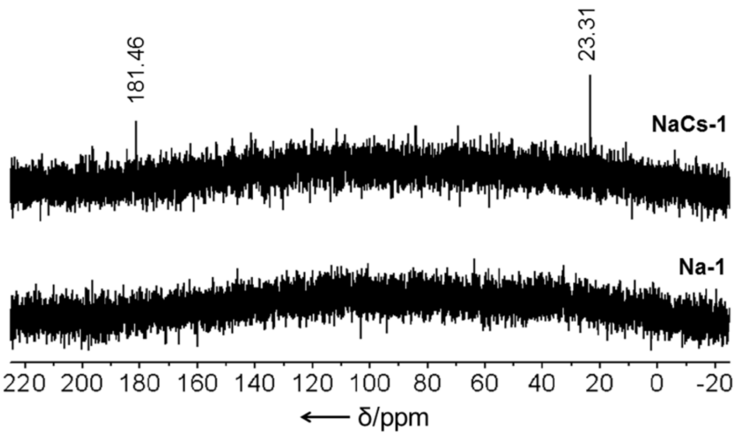


**Fig. S4** Room temperature $^{13}$C NMR spectra of **NaCs-1** and **Na-1** in $D_2O/H_2O$.

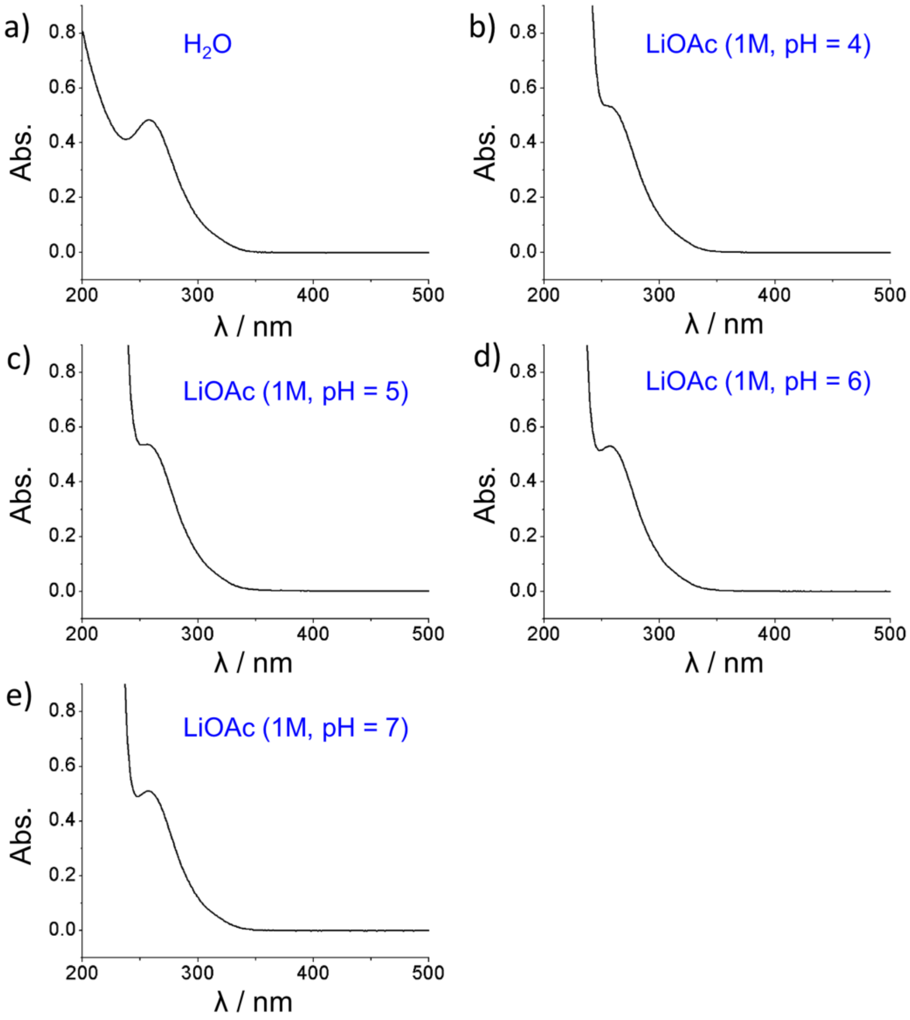


**Fig. S5** UV-vis spectra of **Na-1** in (a) $H_2O$, (b) $LiCH_3COO/CH_3COOH$ (1M, pH = 4), (c) $LiCH_3COO/CH_3COOH$ (1M, pH = 5), (d) $LiCH_3COO/CH_3COOH$ (1M, pH = 6) and (e) $LiCH_3COO/CH_3COOH$ (1M, pH = 7). The concentrations was $2.5\times10^{-6}$ M for **1**. Time-dependent UV-vis spectra (10 min, 2 h, 4 h and 24 h) recorded in each solvent showed identically overlap, suggesting the stability of **1** in the above-mentioned solvents.