

1 **Electronic Supplementary Information (ESI)**

2 **Poly(methyl methacrylate) grafted imogolite nanotubes prepared**
3 **through surface-initiated ARGET ATRP**

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5 **Materials.** Imogolite was synthesized according to the method introduced by Farmer et al.⁶
6 The reagents, tetraethyl orthosilicate and aluminium chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), used for
7 synthesizing imogolite were purchased from Tokyo Chemical Industry and Sigma Aldrich,
8 respectively. 1,8-Octanediol and 2-bromoisobutyric acid were purchased from Tokyo Chemical
9 Industry. P-toluenesulfonic acid monohydrate, phosphoryl chloride, and cyclohexane were
10 purchased from WAKO Pure Chemical Industries. All of the above chemicals were used as
11 received. Copper(II) bromide (99.999%, Aldrich), N,N,N',N'',N''-pentamethyldiethylenetriamine
12 (PMDETA, TCI), and ascorbic acid (WAKO) were used as received without purification.
13 Methyl methacrylate was distilled under vacuum before polymerization.

14 **Instrumentation.** Fourier transform infrared (FT-IR) spectroscopic measurements were
15 carried out on a Spectrum One (Perkin Elmer Japan Co., Ltd.) using KBr pellets. ^1H nuclear
16 magnetic resonance (NMR) spectra were measured by a JEOL JNM-AL300 spectrometer (JEOL,
17 Tokyo, Japan). Gel permeation chromatographic (GPC) analysis was carried out at 40 °C on a
18 TOSOH HLC-8220GPC with a RI detector. The thermogravimetric analysis (TGA) was
19 performed on a SII-EXSTAR 6000 TG/DTA 6200 thermobalance (SII Nano Technology Inc.)
20 with a heating rate of 10 °C min^{-1} under nitrogen. The SFM images were taken with a SPI3800N
21 probe station (SII Nano Technology Inc., Japan) operated in a dynamic force mode. A 20×20
22 μm^2 scanner and a diamond-like carbon (DLC) tip on a cantilever (resonance frequency 115-190

1 kHz, spring constant $2.5\text{-}10\text{ Nm}^{-1}$) were used. The samples for SFM measurement were prepared
2 by dip-coating from a dilute solution onto a freshly cleaved mica surface. Wide angle X-ray
3 diffraction (WAXD) measurements were carried out at the BL02B2 beam line of SPring-8 using
4 the powder products packed in a quartz glass capillary. The WAXD used incident X-rays with
5 the wavelength $\lambda = 0.10\text{ nm}$. Scattering vector $q\text{ [nm}^{-1}\text{]}$ is defined as $q = (4\pi/\lambda)\sin\theta$, where θ is
6 the scattering angle.

7 **Synthesis of ammonium salt of 8-(2-bromo-2-methylpropanoyloxy) octyl phosphate**
8 **(BMPOPO₄(NH₄)₂)**

9 BMPOPO₄(NH₄)₂ was synthesized by a three-step reaction. First step: A 300 mL round bottom
10 flask, attached to a Dean Stark apparatus was charged with 2-bromoisobutyric acid (16.7 g, 100
11 mmol), 1,8-octanediol (22.0 g, 150 mmol), p-toluenesulfonic acid monohydrate (1.2 g, 6.3
12 mmol), and 100 mL cyclohexane. The reaction was heated in an oil bath thermostated at 95 °C.
13 The azeotrope from the cyclohexane with water was separated in the Dean Stark collector. After
14 6 h, the reaction was stopped and allowed to cool, followed by filtration and rinse with Et₂O. The
15 filtrate was dried by rotavap. The product, 8-hydroxyoctyl 2-bromoisobutyrate, was separated
16 through a silica chromatographic column using chloroform as the eluent and concentrated by
17 rotary evaporation (yield: 71%). ¹H NMR (300 MHz, CDCl₃): δ 4.16 (t, 2H, -CH₂CH₂O-CO-),
18 3.63 (t, 2H, HOCH₂CH₂-), 1.93 (s, 6H, -COC(CH₃)₂Br), 1.68 (m, 2H, -CH₂CH₂O-CO-), 1.57 (m,
19 2H, HOCH₂CH₂-), 1.33 (m, 8H, HOCH₂CH₂-(CH₂)₄-CH₂CH₂O-).

20 Second step: Synthesis of 8-(2-bromo-2-methylpropanoyloxy) octyl phosphoric acid. In an
21 ice bath, THF (40 mL) solution of 8-hydroxyoctyl 2-bromoisobutyrate (18.0 g, 61.0 mmol) and
22 pyridine (7.9 g, 100 mmol) was added to a stirred mixture of phosphoryl chloride (15.3 g, 100
23 mmol) and THF (100 mL) via a dropping funnel under N₂ atmosphere. The solution was allowed

1 to stir at room temperature for 3 hours. The reaction was quenched by adding 80 mL water into
2 the above solution, and the resultant mixture was stirred in a 40 °C water bath for 2 hours. The
3 product was extracted with Et₂O for several times. The combined extracts were dried with
4 anhydrous MgSO₄, and Et₂O was removed by rotary evaporation. The oil product was purified
5 by dissolution (with chloroform) and precipitation (with hexane) for several times, and the
6 hexane phase was removed by a glass dropper each time. (yield: 50%). ¹H NMR (300 MHz,
7 CDCl₃): δ 9.40 (s, 2H, (HO)₂PO-O-), 4.16 (t, 2H, -CH₂CH₂O-CO-), 4.02 (q, 2H, (HO)₂PO-
8 OCH₂CH₂-), 1.93 (s, 6H, -COC(CH₃)₂Br), 1.67 (m, 4H, (HO)₂PO-OCH₂CH₂(CH₂)₄-CH₂CH₂O-
9 CO-), 1.33 (m, 8H, -OCH₂CH₂-(CH₂)₄-CH₂CH₂O-).

10 Third step: precipitation of ammonium salt BMPOPO₄(NH₄)₂. A quantity (10.0 g) of 8-(2-
11 bromo-2-methylpropanoyloxy) octyl phosphoric acid was dissolved in 200 mL 2-propanol, and
12 NH₃ was bubbled through the solution for 15 min. NH₃ was obtained from a hot 25% aqueous
13 ammonia solution and transferred into the amphiphile solution via a glass pipet fixed onto a
14 plastic tube. The precipitated ammonium salt was separated from the solvent by centrifugation
15 and removal of the solvent. The product was dried under vacuum at 50 °C for 6 hours (yield:
16 91%). ¹H NMR (300 MHz, D₂O): δ 4.09 (t, 2H, -CH₂CH₂O-CO-), 3.62 (m, 2H, (NH₄O)₂PO-
17 OCH₂CH₂-), 1.79 (s, 6H, -COC(CH₃)₂Br), 1.56 (m, 2H, -CH₂CH₂O-CO-), 1.44 (m, 2H,
18 (NH₄O)₂PO-O-CH₂CH₂-), 1.19 (m, 8H, -OCH₂CH₂-(CH₂)₄-CH₂CH₂O-).

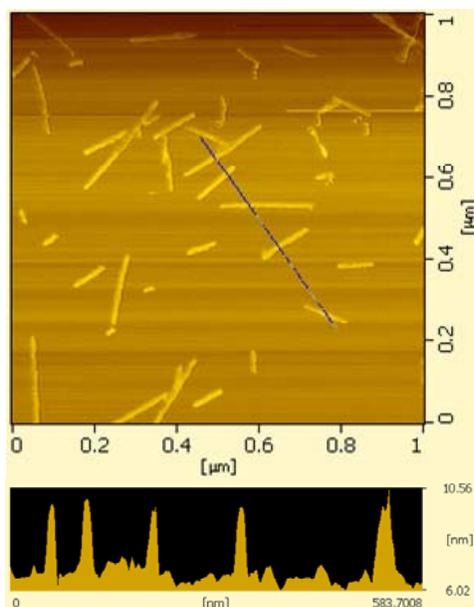
19 **Surface modification of imogolite with BMPOPO₄(NH₄)₂**

20 Imogolite solution (2.6 mg mL⁻¹, 200 mL, pH = 5.0) was mixed with the aqueous solution of
21 BMPOPO₄(NH₄)₂ (1.6 g in 50 mL 0.1 M acetate buffer, pH = 5.0) under magnetic stirring and
22 stirred at room temperature for 48 hours. The white product was collected by filtration and

1 washed with THF/H₂O (volume ratio of 1:1) by several dispersion-centrifugation cycles,
2 followed by freeze-drying with benzene to give a white powder of (2-bromo-2-methylpropanoate)
3 octyl phosphate modified imogolite (BMPOPO₄-imogolite).

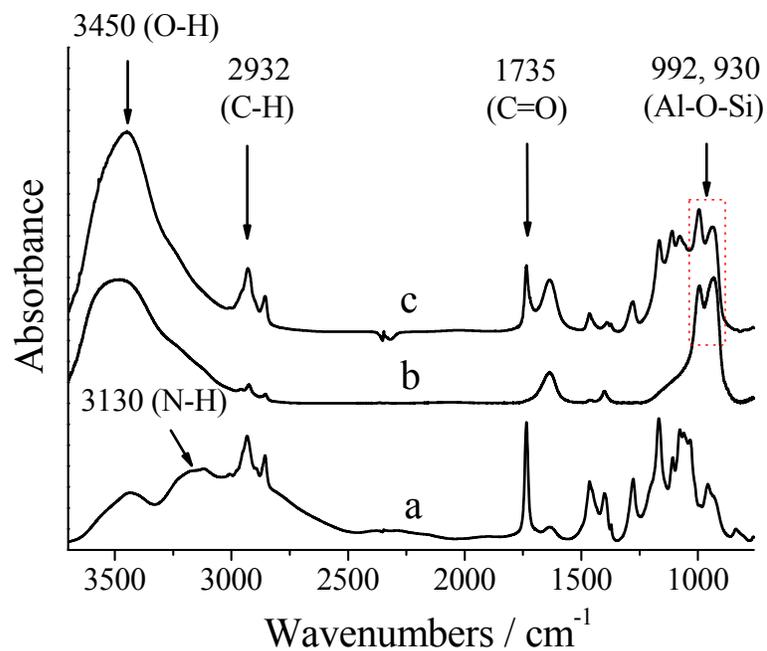
4 **Surface-initiated ARGET ATRP of MMA from imogolite surface**

5 A process called activators regenerated by electron transfer for atom transfer radical
6 polymerization (ARGET ATRP)²⁴ was employed for surface initiated polymerization. In a
7 typical recipe, CuBr₂ (3.0 mg, 0.0134 mmol) and PMDETA (23.2 mg, 0.134 mmol) were
8 dissolved in anisole (10.0 mL). After the formation of Cu(II) complex, BMPOPO₄-imogolite
9 (50.0 mg), ascorbic acid (21.8 mg, 0.124 mmol) and MMA (10.0 g, 100 mmol) were added. The
10 above mixture was sealed with a rubber septum and deoxygenated by argon bubbling for 5 min
11 at room temperature and subsequently placed in an oil bath thermostated at 40 °C. The
12 polymerization was stopped by opening the flask and exposing the catalyst to air. Polymeric
13 products were isolated by precipitation from methanol and finally dried under vacuum at 50 °C
14 for 6 hours.

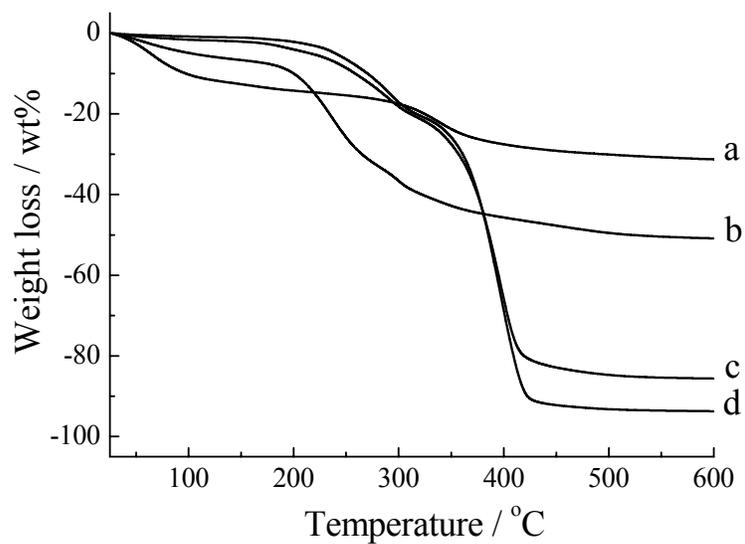


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2 **Figure S1.** SFM height images of the diluted as-prepared synthetic imogolite. The bottom one
3 shows the cross-section analysis.

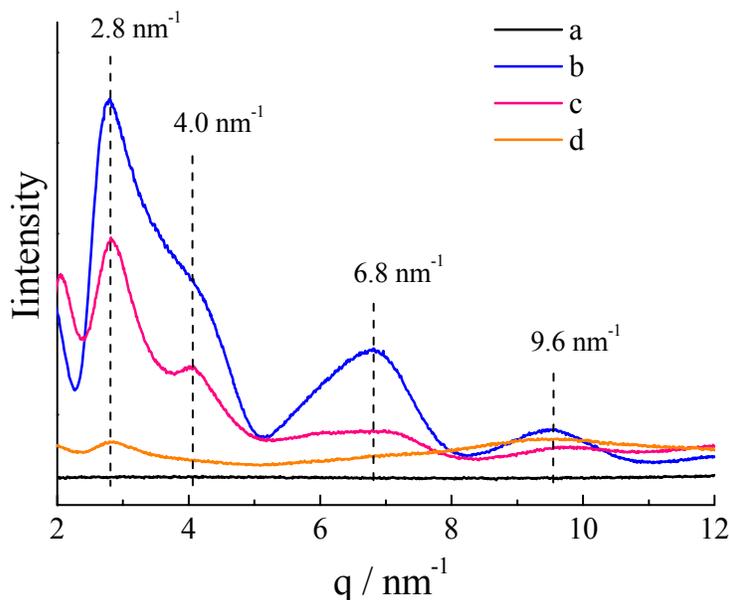
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6 **Figure S2.** FT-IR spectra of (a) $\text{BMPOPO}_4(\text{NH}_4)_2$, (b) bare imogolite, and (c) BMPOPO_4 -
7 imogolite.



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- 2 **Figure S3.** TGA thermograms for (a) bare imogolite, (b) BMPOPO₄-imogolite, (c) PMMA-g-
- 3 imogolite with $M_n = 26600$ and $M_w/M_n = 1.22$, and (d) PMMA-g-imogolite with $M_n = 32700$ and
- 4 $M_w/M_n = 1.33$ under nitrogen atmosphere.



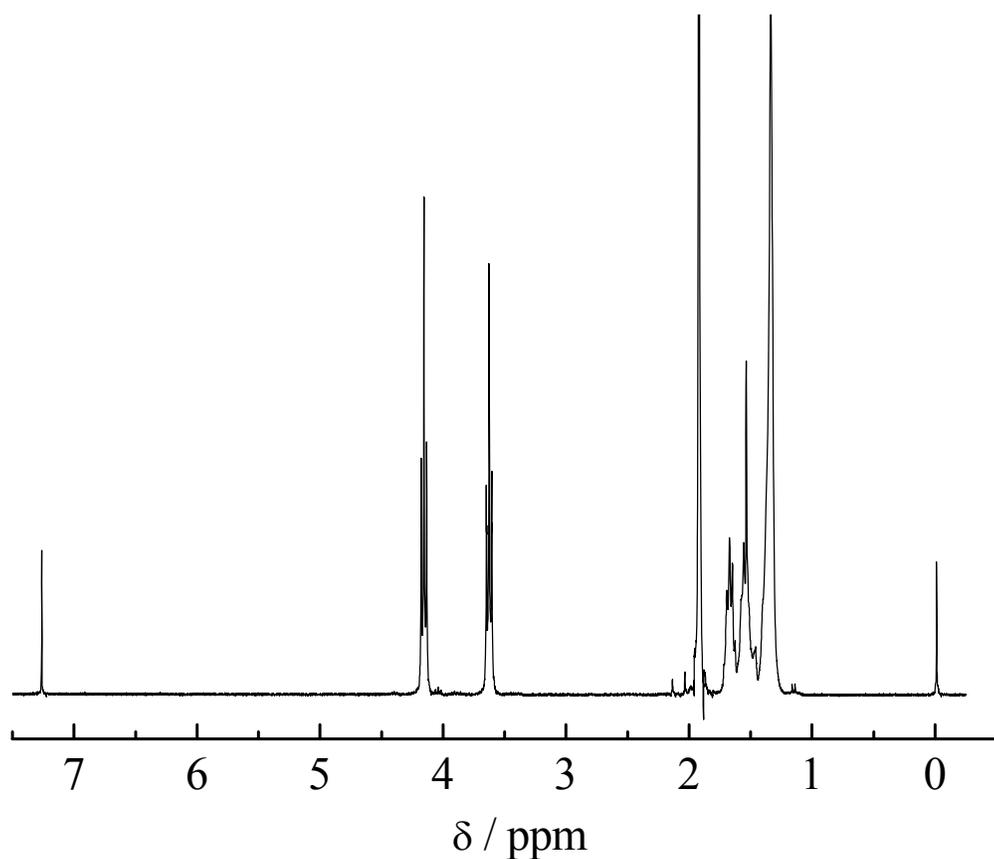
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2 **Figure S4.** WAXD profiles of (a) quartz glass capillary background, (b) bare imogolite, (c)
3 BMPOPO₄-imogolite, and (d) PMMA-g-imogolite with $M_n = 32700$ and $M_w/M_n = 1.33$.

4 The diffraction peaks at $q = 2.8, 4.0, 6.8,$ and 9.6 nm^{-1} can be assigned to the (100), (110),
5 (001), and (211) planes of the parallel bundles of the imogolite nanotubes, respectively.⁴ For
6 BMPOPO₄ modified imogolite, those four diffractions still exist, suggesting the presence of
7 imogolite bundles. On the other hand, the peaks at around $q = 2.8$ and 4.0 nm^{-1} become sharper
8 than those of the bare imogolite, as a result, can easily be distinguished from their overlapped
9 profile, indicating the higher regularity of those bundles than that of the bare imogolite. Hence it
10 is reasonable to conclude that during the modification process only highly ordered imogolite
11 bundles can remain. In addition, the diffraction from (001) plane at *ca.* $q = 6.8 \text{ nm}^{-1}$ becomes
12 much weaker and broader, suggesting the bundle size significantly decreased along the (001)
13 plane direction. The above results indicate that small sized imogolite bundles with high
14 regularity form the rigid core of BMPOPO₄-imogolite during the modification process. After

1 surface-initiated polymerization of MMA, these small sized imogolite bundles become the cores
2 of PMMA-g-imogolite, and the diffraction of (100) plane at around $q = 2.8 \text{ nm}^{-1}$ still can be
3 observed. This result is consistent with the explanation for SFM observation.

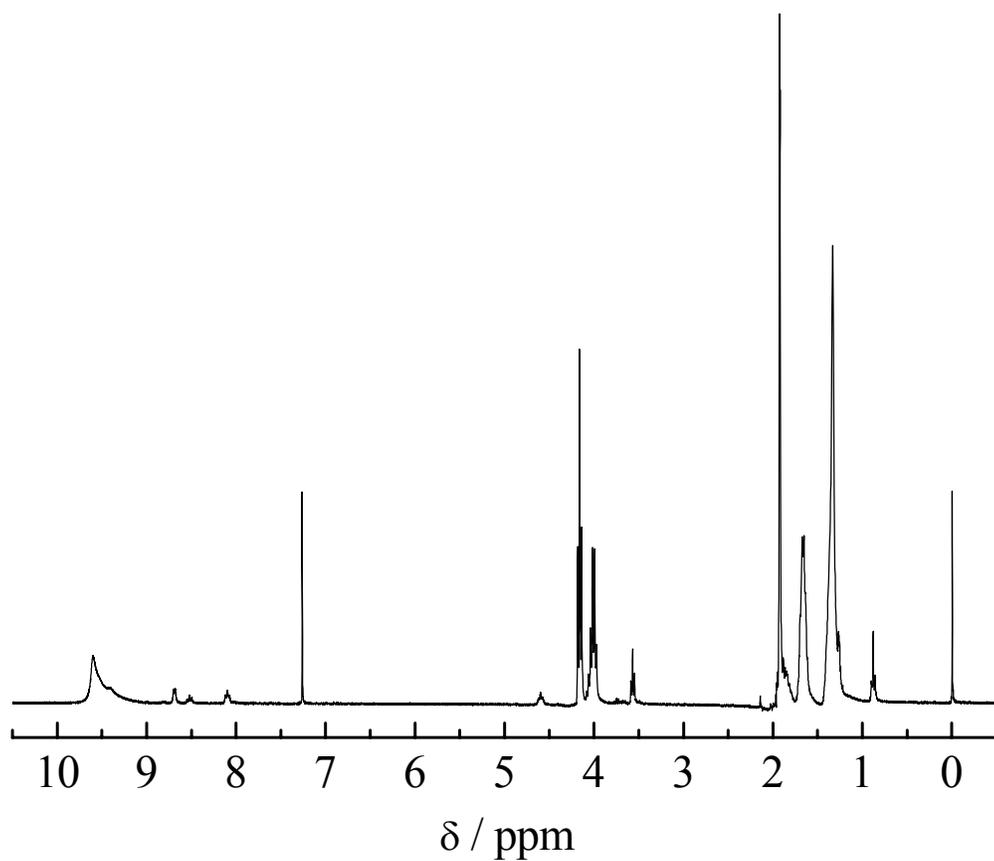
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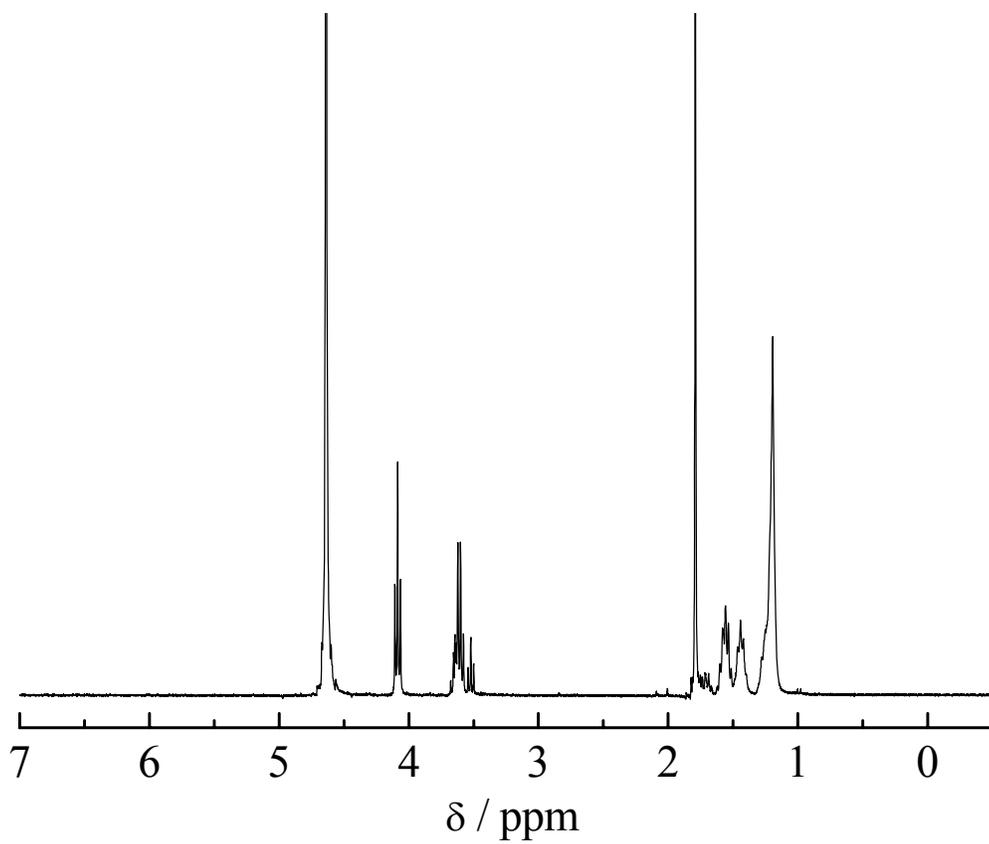


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7 **Figure S5.** ^1H NMR spectrum of 8-hydroxyoctyl 2-bromoisobutyrate in CDCl_3 .



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2 **Figure S6.** ^1H NMR spectrum of 8-(2-bromo-2-methylpropanoyloxy) octyl phosphoric acid in
3 CDCl_3 .



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2 **Figure S7.** ¹H NMR spectrum of ammonium salt of 8-(2-bromo-2-methylpropanoyloxy) octyl
3 phosphate (BMPOPO₄(NH₄)₂) in D₂O.