Aqueous Suspensions of GdPO4 Nanorods: a Paramagnetic Mineral Liquid Crystal

Supplementary Materials

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Synthesis of sodium 1-hydroxy-2-(2-(2-hydroxyethoxy)ethoxy)ethoxyethane-1,1-diylbis(hydrogenphosphonate) PEG 200-HMBP (f)
i) BrBn, NaH, THF, -70°C; ii) DMSO, DCM, (CO)$_2$Cl$_2$, -55°C, TEA; iii) CHCN, H$_5$IO$_6$, PCC, 0°C; iv) DCM, (CO)$_2$Cl$_2$, 0°C; v) P(OSiMe$_3$)$_3$, 0°C, MeOH; vi) activated charcoal (10%), H$_2$O, H$_2$.

1-phenyl-2, 5, 8, 11-tetraoxatridecan-13-ol (a)

In a 250 mL round bottom three neck flask, fitted with mechanical stirrer, a thermometer, an addition funnel and a gas inlet tube, 1.1 equivalent of sodium hydride (56.1 mmol, 1.3 g) in dry THF (40 mL) were introduced under inert atmosphere. 1 equivalent of PEG 200 (51 mmol, 10 g) in dry THF (60 mL) was added at -70°C. The reaction mixture was stirred at room temperature overnight. Benzyl bromide (51 mmol, 6.1 mL) was added dropwise. The solution was stirred at room temperature and the evolution of the reaction was followed by TLC and $^1$H NMR. The solution is then filtered and evaporated under reduced pressure. The residue was dissolved in dichloromethane (70 mL) of and then extracted three times with water (20 mL). The organic layer was dried with MgSO$_4$. After filtration, the solvent was evaporated under reduced pressure.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49–7.11 (m, 5H), 4.55 (s, 2H), 3.78–3.45 (m, 16H), 3.11 (s, 1H).
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 138.1, 128.2, 127.6, 127.6, 127.5, 73.1, 72.4, 70.5, 70.4, 70.3, 70.2, 70.1, 69.3, 61.5. IR (KBr, cm$^{-1}$): v$_{O-H}$ = 3424; v$_{C-Haro}$ = 3005-3087; v$_{C=Halip}$ = 2867; v$_{C=O}$ = 1454-1495; v$_{C-O}$ = 1141. Yield: 77%. Yellow oil.

{2-[2-(2-Benzylxy-ethoxy)-ethoxy]-ethoxy}-acetaldehyde (b)

In a 100 mL round bottom three neck flask, fitted with mechanical stirrer, a thermometer, an addition funnel and a gas inlet tube, a solution of DMSO (21.8mmol, 1.7 g) diluted in 4.4 mL of dichloromethane is added dropwise at -55°C to a solution of oxalyl chloride (17.2mmol, 2.2 g) in dichloromethane (22.6 mL) under an argon stream. After two minutes of mechanical stirring, a solution of a (10mmol, 2.84 g) in dichloromethane (9 mL) is added dropwise. After 15 minutes of stirring, the mixture was warmed to -30°C. Then, dry triethylamine (50.4mmol, 5.1 g) was added dropwise. After 12 hours at room temperature, the mixture was hydrolyzed with water (20 mL). The aqueous phase was extracted twice with dichloromethane (20 mL). The combined organic phases were washed successively with HCl (20%) and NaHCO$_3$ (5%). The organic layer was dried with MgSO$_4$. After filtration, the solvent was evaporated under reduced pressure.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.51–6.98 (m, 5H), 4.48 (s, 2H), 4.04 (d, J = 5.3 Hz, 2H), 3.70–3.22 (m, 13H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 200.4, 137.9, 128.0, 127.9, 127.4, 127.3, 127.2, 127.1, 76.3, 72.7, 70.6, 70.3, 70.1, 69.0. IR (KBr, cm$^{-1}$): v$_{C=H}$ = 2832; v$_{C=O}$ = 1707. Yield: 74%. Yellow oil.

{2-[2-(2-Benzylxy-ethoxy)-ethoxy]-ethoxy}-acetic acid (c)

In a 100 mL round bottom three neck flask, fitted with mechanical stirrer, a thermometer, an addition funnel and a gas inlet tube, acetonitrile (64.4 mL) is added to 1,1 equivalent (8.85mmol, 2.02g) of periodic acid H$_5$IO$_6$ and the mixture was stirred at room temperature for 15 minutes. The corresponding aldehyde b (8.05mmol, 2.27 g) in acetonitrile (8 mL) and (0.1625mmol, 0.035 g) of pyridinium chlorochromate PCC in acetonitrile were added at T=0°C dropwise successively. The reaction was monitored by TLC (solvent: 95% DCM, 5% EtOH). At the end of the reaction, ethyl acetate (20 mL) was added and the solution was washed with brine, an aqueous solution of NaHSO$_3$ then brine, and then dried with MgSO$_4$. After filtration, the volatile fractions were evaporated under reduced pressure.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.46–7.00 (m, 5H), 4.54 (s, 2H), 4.36–3.91 (m, 2H), 3.62 (m, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.5, 138.1, 137.9, 128.3, 127.8, 127.7, 127.6, 127.5, 73.1, 70.1, 69.8, 69.4, 69.3, 69.2, 68.5. IR (KBr, cm$^{-1}$): v$_{C-OH}$ = 3062; v$_{C=O}$ = 1757; v$_{C=H}$ = 1110, v$_{C=H}$ anh = 3029; v$_{C=O}$ anh = 1352. Yield: 72%. Brown oil.
{2-[2-(2-Benzylxoy-ethoxy)-ethoxy]-ethoxy}-acetyl chloride (d)

In a 100 mL round bottom three neck flask, fitted with mechanical stirrer, a thermometer, an addition funnel and a gas inlet tube, carboxylic acid e (1 mmol, 0.298 g) in dichloromethane (25 mL) was introduced. The flask is placed in an ice bath (0°C). Oxalyl chloride (5mmol, 0.63 g) in dichloromethane (10 mL) was added dropwise. The reaction mixture was stirred at room temperature for 24 hours and was then evaporated under reduced pressure and washed twice with both dichloromethane and ether.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43–7.12 (m, 5H), 4.70 (s, 2H), 4.57–4.41 (m, 2H), 3.71–3.30 (m, 12H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.8, 138.2, 128.4, 127.8, 127.7, 127.6, 127.4, 73.2, 71.3, 70.6, 70.6, 70.5, 70.4, 69.4, 68.8. IR (KBr, cm$^{-1}$): $\nu$C=O = 1801; $\nu$C-Cl = 748; $\nu$C-O = 1029-1352; $\nu$C=C = 1455. Quantitative Yield. Brown oil.

(2-{2-[2-(2-Benzylxoy-ethoxy)-ethoxy]-ethoxy}-1-hydroxy-1-phosphono-ethyl)-phosphonic acid (e)

In a 25 mL round bottom three neck flask, fitted with thermometer, an addition funnel and a gas inlet tube, acid chloride d (5mmol, 1.58 g) was introduced and 2 equivalents of tris(trimethyl silyl) phosphite (10mmol, 2.98 g) are added dropwise under argon at 0°C. Once the addition is complete, the reaction mixture was left under magnetic stirring at room temperature for 1h. The progress of the reaction is then followed by $^{31}$P {$^1$H} NMR. Volatile fractions were then evaporated under reduced pressure. The resulting oil was hydrolyzed in methanol at room temperature for 4 hours. After solvent evaporation, dark oil was obtained. The product was precipitated three times in ether to obtain a pure product.

$^{31}$P NMR (162 MHz, D$_2$O) $\delta$ 16.8 (t, $J$ = 11.8Hz).$^1$H NMR (400 MHz, D$_2$O) $\delta$ 7.55–7.08 (m, 5H), 4.54 (s, 2H), 4.01–3.84 (m, 2H), 3.83–3.55 (m, 12H). $^{13}$C NMR (125 MHz, D$_2$O) $\delta$ 137.1, 128.3-127.5 (m), 73.4 (t, $J$ =117, 8 Hz), 72.6-69.5 (m), 60.2. IR (KBr, cm$^{-1}$): $\nu$O-H= 3400; $\nu$P=O= 1103; $\nu$P-O= 945; $\nu$C-O= 1246; $\nu$C=C= 1232. Yield: 78%. Brown oil.

1-hydroxy-2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)ethane-1,1-diylidiphosphonic acid (f)

In a 50 mL round bottom flask, Bisphosphonate e (2.25mmol, 1 g) was dissolved in water (25 mL), then palladium on activated charcoal 10% (0.3 g) was added. The mixture was purged three times. The resulting mixture was stirred for 12 h under H$_2$ atmosphere (1 atm, balloon), filtered. The solution was filtered through celite, the pH is adjusted to 6 and the product was freeze dried.
\[ ^{31}\text{P NMR (162 MHz, D}_2\text{O)} \delta 16.2 \text{ (t, } J = 12.4\text{Hz).} \]
\[ ^{1}\text{H NMR (400 MHz, D}_2\text{O)} \delta 3.86-3.77 \text{ (m, 2H), 3.72-3.53 \text{ (m, 12H).} \]
\[ ^{13}\text{C NMR (101 MHz, D}_2\text{O)} \delta 72.5 \text{ (t, } J = 116.5\text{ Hz), 70.9-68.9 \text{ (m), 60.3 \text{ (d, } J = 10.6\text{ Hz).} \]

IR (KBr, cm\(^{-1}\)):
\[ \nu_{\text{O-H}} = 3426; \nu_{\text{P=O}} = 1117; \nu_{\text{P-O}} = 975. \text{ Yield: 72 %. Brown solid. Melting point: 235 °C.} \]

**Diffraction pattern of GdPO\(_4\)_ nanorods**

![Diffraction pattern](image)

JCPDS card number (Gadolinium phosphate hydrate): 00-039-0232

**Zeta potential of the GdPO4 nanorods as a function of pH**

![Zeta potential graph](image)

As pointed out in green the isoelectrical point is at a pH = 6.43