

Electronic Supporting Information

Naphthalene-based linkers for metal phosphonates. Synthesis, structure, and interesting conformational flexibility influence on final lanthanum hybrids

Michał J. Bialek^{,a}, Jan Janczak^b, Jerzy Zon^{*,c}*

a) Department of Chemistry, University of Wrocław, 14 F. Joliot-Curie Street, 50-383 Wrocław, Poland

b) Institute of Low Temperature and Structural Research, Polish Academy of Sciences, 2 Okolna Street, P.O. Box 1410, 50-950 Wrocław, Poland

c) Department of Chemistry, Wrocław University of Technology, 27 Wybrzeże Wyspińskiego Street, 50-370 Wrocław, Poland

* (M.J.B.) michal.bialek@chem.uni.wroc.pl

* (J.Z.) jerzy.zon@pwr.wroc.pl

Detailed synthetic procedures for ligands

All chemicals used in the synthesis were readily available from commercial sources (Sigma Aldrich, Merck) and were used as received. Infrared absorption spectra of solids were measured on a Perkin–Elmer FT-IR 1600 spectrophotometer in KBr discs. NMR spectra for ^1H , ^{31}P and ^{13}C were recorded with a Bruker Avance DRX 300 instrument at the indicated frequencies. Melting points were determined using a Boetius apparatus and were uncorrected. Elemental analyses for C and H were performed with Elementar vario EL III analyzer and for P by ICP-OES method.

Naphthalene-1,4-diphosphonic acid, [**1**, H_4 NDP(1,4)]

Tetraethyl naphthalene-1,4-diphosphonate (1b)

1,4-dibromonaphthalene (1.70 g, 5.94 mmol, **1a**), obtained by the literature procedure,¹ was placed in a two-necked round-bottom flask and heated to 160 °C under argon atmosphere. After 1,4-dibromonaphthalene melted NiBr_2 (0.160 g, 0.732 mmol) was added and next triethyl phosphite (2.60 cm³, 16.7 mmol) was added dropwise over 7 h. After 3 h second portion of NiBr_2 (0.100 g, 0.458 mmol) was added. The mixture was heated at the same temperature and stirred under argon overnight. Dark to orange viscous oil was obtained and was purified by column chromatography on silica gel 60 (32–63 μm) using a 9:1 v/v mixture of ethyl acetate/ethanol. As less polar compound, first diethyl 4-bromonaphthalene-1-phosphonate is eluted ($R_f = 0.45$, silica gel on PET foils with fluorescent indicator 254 nm, UV lamp for visualization, AcOEt : EtOH in ratio 9:1 v/v). Target compound (**1b**) was isolated in yield 1.19 g (50 %) in form of a light oil, which can solidified upon standing giving a colorless crystalline solid, mp. 57–59 °C, $R_f = 0.29$ (silica gel on TLC-PET foil with fluorescent indicator 254 nm, UV lamp for visualization, AcOEt : EtOH in ratio 9:1 v/v).

^1H NMR (300 MHz, CDCl_3) δ 8.74 – 8.52 (m, 2H), 8.31 – 8.19 (m, 2H), 7.70 – 7.62 (m, 2H), 4.40 – 3.88 (m, 8H), 1.32 (t, $J = 7.1$ Hz, 12H); $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_3) δ 18.03 (s) (18.85 (s) for diethyl 4-bromonaphthalene-1-phosphonate); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 132.94 – 132.28 (imposition of signals of two carbon atoms), 130.42 (dd, $J = 180.9, 3.4$ Hz), 127.65 (s), 127.37 (s), 62.55 (d, $J = 5.1$ Hz), 16.37 (d, $J = 7.3$ Hz).

Naphthalene-1,4-diphosphonic acid (1)

Tetraethyl naphthalene-1,4-diphosphonate (1.40 g, 3.50 mmol, **1b**), concentrated hydrochloric acid (8.0 cm³) and water (8.0 cm³) were mixed together. Obtained solution was heated at reflux for 20 h. Then white precipitate was filtered and dried providing pure acid **1c**. Additional amount of the product was acquired after evaporation of the residual solution and crystallization of obtained solid from distilled water. Total yield of compound **1**: 0.959 g (95 %), mp. 265 – 275 °C (softening of crystals).

^1H NMR (300 MHz, d_6 -DMSO) δ 8.65 (dd, $J = 5.9, 2.8$ Hz, 2H), 8.03 (dd, $J = 13.2, 5.6$ Hz, 2H), 7.63 (dd, $J = 6.5, 3.3$ Hz, 2H), 7.10 (br s, 4H); $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, d_6 -DMSO) δ 11.74 (s); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, d_6 -DMSO) δ 134.88 (dd, $J = 176.4, 3.1$ Hz), 132.83 (dd, $J = 11.0, 11.0$ Hz), 130.93 – 130.31 (m), 128.32 (s), 126.97 (s); IR (KBr, cm⁻¹) ν_{max} 3220 (br s), 2706 (br s), 2285 (br s), 1928 (m), 1715 (m), 1514 (s), 1452 (m), 1423 (w), 1358 (w), 1305 (m), 1216 (vs), 1169 (s), 1109 (s), 1015 (vs), 974 (s), 936 (s), 858 (s), 815 (s), 761 (vs), 681 (m), 624 (s), 560 (m), 533 (s), 506 (m), 482 (s), 459 (m), 440 (s), 415 (m); Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{O}_6\text{P}_2 \cdot 2\text{H}_2\text{O}$ (324.16): C, 37.05; H, 4.35; P, 19.11. Found: C, 37.12; H, 4.08; P, 19.13.

¹ O. Cakmak, I. Demirtas, H. T. Balaydin, *Tetrahedron* 2002, **133**, 20048–20051

1-(phosphono)naphthalene-4-(methylphosphonic) acid, [2, H₄NDP(1,4C)]

1-bromo-4-(bromomethyl)naphthalene (**2a**) was obtained in two steps, according to known procedures, from 1-methylnaphthalene.²

Diethyl 1-bromonaphthalene-4-(methylphosphonate) (2b)

1-bromo-4-(bromomethyl)naphthalene (8.0 g, 25.4 mmol, **2a**) and triethyl phosphite (5.32 cm³, 30.6 mmol) were added to round-bottom flask equipped with a short distillation set. Mixture was slowly heated and after short time clear solution was obtained. Reaction started when was heated to about 100 °C and what was indicated by evolving EtBr, a volatile by-product. It was condensed and collected (2.36 g, 85 %). Temperature of an oil bath rose to 150 °C and solution was mixed and heated for 2 h in total. Completeness of conversion was also monitored by TLC. Obtained orange oil was additionally heated for 30 min under reduced pressure to remove all volatile substances. The crude product was used in the next step without further purification. For spectral characterization of ester **2b**, a sample was purified by column chromatography on silica gel 60 (32–63 μm) using ethyl acetate as eluent.

1.21 g (98 % after column chromatography), R_f = 0.21 (silica gel on PET foils with fluorescent indicator 254 nm, UV lamp for visualization, ethyl acetate). ¹H NMR (300 MHz, CDCl₃) δ 8.31 – 8.25 (m, 1H), 8.14 – 8.07 (m, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.33 (dd, *J* = 7.7, 3.8 Hz, 1H), 4.06 – 3.85 (m, 4H), 3.60 (d, *J* = 22.0 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 6H); ³¹P{¹H} NMR (121 MHz, CDCl₃) δ 25.99 (s); ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 133.21 (d, *J* = 5.1 Hz), 132.19 (d, *J* = 2.7 Hz), 129.52 (d, *J* = 4.1 Hz), 128.75 (d, *J* = 7.6 Hz), 128.44 (d, *J* = 9.9 Hz), 127.85 (s), 127.24 (s), 126.89 (s), 125.03 (d, *J* = 1.3 Hz), 122.40 (d, *J* = 5.4 Hz), 62.29 (d, *J* = 6.8 Hz), 30.81 (d, *J* = 139.5 Hz), 16.36 (d, *J* = 6.0 Hz).

Diethyl 1-(diethoxyphosphoryl)naphthalene-4-(methylphosphonate) (2c)

Diethyl 1-bromonaphthalene-4-(methylphosphonate) (1.56 g, 4.36 mmol, **2b**) and 1,3-diisopropylbenzene (2 cm³) was placed in a two-necked round-bottom flask and heated to 160 °C under argon atmosphere. After that, NiBr₂ (0.048 g, 0.22 mmol) was added and next addition of triethyl phosphite (0.92 cm³, 5.30 mmol) was started dropwise over 5 h. There were two more portions of NiBr₂ (0.096 g, 0.44 mmol) added to the mixture after 1.5 and 3 h from start of the reaction. The mixture was heated at the same temperature and stirred under argon overnight. Orange solution was obtained and evaporated under reduced pressure and heating. Product was purified by column chromatography on silica gel 60 (32–63 μm) using a 9:1 v/v mixture of ethyl acetate/ethanol as eluent. Target compound (**2c**) was isolated in yield 62 % (1.12 g) in form of light oil, which can solidified upon standing giving a colorless crystalline solid, mp. 52-54 °C, R_f = 0.20 (silica gel on PET foils with fluorescent indicator 254 nm, UV lamp for visualization, using a 9:1 v/v mixture of ethyl acetate/ethanol).

¹H NMR (300 MHz, CDCl₃) δ 8.53 (dd, *J* = 6.3, 3.6 Hz, 1H), 8.22 – 8.11 (m, 2H), 7.59 (dd, *J* = 6.6, 3.3 Hz, 2H), 7.54 – 7.49 (m, 1H), 4.26 – 3.87 (m, 8H), 3.66 (d, *J* = 22.5 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 6H), 1.15 (t, *J* = 7.1 Hz, 6H); ³¹P{¹H} NMR (121 MHz, CDCl₃) δ 25.68 (d, *J* = 4.9 Hz), 19.76 (d, *J* = 4.9 Hz); ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 134.43 (dd, *J* = 9.7, 3.6 Hz), 133.98 (dd, *J* = 8.9, 4.0 Hz), 133.12 (dd, *J* = 11.4, 2.6 Hz), 132.21 (dd, *J* = 12.9, 5.0 Hz), 127.24 (s), 127.45 – 127.07 (m), 127.02 (s), 126.49 (s), 125.14 (s), 124.09 (dd, *J* = 184.1, 4.1 Hz), 62.29 (d, *J* = 7.0 Hz), 62.18 (d, *J* = 5.4 Hz), 31.40 (d, *J* = 138.4 Hz), 16.33 (d, *J* = 2.8 Hz), 16.25 (d, *J* = 2.3 Hz).

² a) M. C. Carreno, R. Hernandez-Sanchez, J. Mahugo, A. Urbano, *J. Org. Chem.* 1999, **64**, 1387-1390; b) G. Yang, C. Shen, L. Zhang, W. Zhang, *Tetrahedron Lett.* 2011, **52**, 5032-5035

1-(phosphono)naphthalene-4-(methylphosphonic) acid (2)

Diethyl 1-(diethoxyphosphoryl)naphthalene-4-(methylphosphonate) (1.12 g, 2.70 mmol, **2c**) was placed in round-bottom flask and dissolved in dry CH₂Cl₂ (8 cm³). Next, trimethylsilyl bromide (2.14 cm³, 16.2 mmol) was added to the solution and flask was closed, wrapped with parafilm and put on magnetic stirrer at room temperature for 24 h. Subsequently, the solution was evaporated under reduced pressure at a bath, which temperature was below 70 °C. Light, viscous oil of **2d** was obtained. Methanol (8 cm³) was added to the oil and obtained solution was mixed for 24 h. After that, solution was evaporated and distilled water was added and again evaporated. This operation was repeated twice. Cream precipitate of pure acid (**2**) was obtained (0.805 g, 98 %), mp. 247-252 °C.

¹H NMR (300 MHz, d₆-DMSO) δ 8.59 (dd, *J* = 5.6, 4.1 Hz, 1H), 8.61 (br s, 4H), 8.22 – 8.18 (m, 1H), 7.94 (dd, *J* = 15.7, 7.3 Hz, 1H), 7.61 – 7.49 (m, 2H), 7.49 – 7.41 (m, 1H), 3.51 (d, *J* = 22.2 Hz, 2H); ³¹P{¹H} NMR (121 MHz, d₆-DMSO) δ 21.07 (d, *J* = 4.6 Hz), 13.32 (d, *J* = 4.6 Hz); ¹³C{¹H} NMR (75 MHz, d₆-DMSO) δ 135.66 (dd, *J* = 9.5, 3.2 Hz), 133.14 (dd, *J* = 11.2, 2.3 Hz), 132.40 (dd, *J* = 12.0, 4.6 Hz), 131.60 (dd, *J* = 8.3, 3.4 Hz), 129.38 (dd, *J* = 180.5, 3.9 Hz), 128.08 (d, *J* = 5.0 Hz), 127.43 (dd, *J* = 15.6, 7.1 Hz), 126.53 (s), 126.18 (s), 126.13 (s), 33.24 (d, *J* = 131.3 Hz); IR (KBr, cm⁻¹) ν_{max} 3414 (br m), 2916 (br s), 2358 (br s), 1906 (m), 1622 (m), 1582 (m), 1514 (m), 1422 (m), 1392 (m), 1322 (m), 1212 (s), 1128 (vs), 1094 (vs), 1012 (vs), 976 (vs), 944 (s), 910 (s), 852 (m), 758 (s), 718 (m), 672 (m), 634 (m), 604 (m), 550 (m), 504 (s), 480 (s), 450 (m). Anal. Calcd for C₁₁H₁₂O₆P₂ (302.16): C, 43.72; H, 4.00; P, 20.50. Found: C, 43.92; H, 3.98; P, 20.52.

The obtainment of ligands single crystals

Naphthalene-1,4-diphosphonic acid [NDP(1,4)hydr, (**1**)]

Obtained crystals were air sensitive due to loss of crystal water. Suitable single crystal was obtained from a diluted solution slightly acidified with hydrochloric acid. The solution was prepared by dissolving of the acid sample in acidified water in high temperature. After cooling small needles precipitated. The solution was being diluted until a small amount of bigger needles was obtained after cooling.

1-(phosphono)naphthalene-4-(methylphosphonic) acid [NDP(1,4C)hydr, (**2a**); NDP(1,4C), (**2b**)]

Good quality crystal of hydrate was obtained by crystallization from distilled water. Concentrated solution was prepared in elevated temperature and then cooled slowly. Polycrystalline precipitate was removed and after a few days suitable single crystals appeared.

Anhydrous crystals were isolated from a residue of starting materials in the room temperature reaction of ligand with samarium chloride (0.1 : 0.1 mmol) in water solution (6 cm³).

pH-potentiometry

The protonation constants were determined by pH-potentiometric titrations of 2 cm³ samples at ligand concentration of 1·10⁻³ mol/dm³ for H₄NDP(1,4), and 2·10⁻³ mol/dm³ for H₄NDP(1,4C). The measurements were carried out in argon atmosphere at 298 K at constant ionic strength (0.10 M KNO₃) with a MOLSPIN pH-meter equipped with a Russel CMAW 711 semi-micro combined electrode and a 0.250 cm³ micrometer syringe containing base solution at 0.103084 M concentration, which was assigned by the titration of potassium hydrogen phthalate with well-known concentration. The samples were titrated from pH = 2 (coordination reactions mixtures pH). The protonation constants of ligands were calculated by means of a general computational program, SUPERQUAD 5.20.³ Standard deviations quoted were computed by SUPERQUAD and refer to random errors only.

³ P. Gans, A. Sabatini, A. Vacca, *J. Chem. Soc., Dalton Trans.* 1985, 1195-1200

Table S1. Selected bond lengths [Å] and angles [°] in the structures **1 - 4**

NDP(1,4)hydr (1)					
P1-O1	1.4867(14)	P2-O5	1.5435(16)	O2-P1-C1	105.50(9)
P1-O2	1.5417(16)	P2-C4	1.795(2)	O3-P1-C1	107.07(10)
P1-O3	1.5456(17)	O1-P1-O2	114.28(9)	O3-P1-C1-C2	-1.9(2)
P1-C1	1.794(2)	O1-P1-O3	109.17(9)	O5-P2-C4-C3	3.3(2)
P2-O4	1.4892(14)	O2-P1-O3	108.28(9)	P2-C4-C5-C6	-0.3(3)
P2-O6	1.5408(17)	O1-P1-C1	112.21(9)	P1-C1-C10-C9	1.0(3)
NDP(1,4C)hydr (2a)					
P1-O1	1.4863(10)	P2-C11	1.7935(14)	C5-C4-C3-C2	4.8(3)
P1-O2	1.5469(10)	O1-P1-O2	112.71(6)	C10-C1-C2-C3	-4.3(3)
P1-O3	1.5638(11)	O1-P1-O3	113.76(7)	P1-C1-C10-C9	6.9(3)
P1-C1	1.7853(13)	O2-P1-O3	105.20(6)	C11-C4-C5-C6	-6.3(3)
P2-O4	1.4993(10)	O1-P1-C1	113.81(6)	O2-P1-C1-C2	-12.12(16)
P2-O5	1.5402(10)	O2-P1-C1	106.65(6)	O5-P2-C11-C4	166.57(13)
P2-O6	1.5454(11)	O3-P1-C1	103.88(6)		
NDP(1,4C) (2b)					
P1-O1	1.4941(17)	P2-C11	1.773(2)	C5-C4-C3-C2	1.7(3)
P1-O2	1.5248(19)	O1-P1-O2	110.62(10)	C10-C1-C2-C3	-1.6(3)
P1-O3	1.537(2)	O1-P1-O3	113.40(12)	P1-C1-C10-C9	-1.5(3)
P1-C1	1.779(2)	O2-P1-O3	109.18(14)	C11-C4-C5-C6	-2.9(3)
P2-O4	1.4809(17)	O1-P1-C1	111.60(10)	O1-P1-C1-C2	-8.1(2)
P2-O5	1.5441(16)	O2-P1-C1	108.98(11)	O6-P2-C11-C4	168.55(14)
P2-O6	1.5496(15)	O3-P1-C1	102.73(10)		
La-NDP(1,4) (3)					
La1-O21	2.4253(14)	P11-O11	1.4921(15)	P21-O23	1.5694(16)
La1-O24 ⁱ	2.4321(13)	P11-O12	1.5402(17)	P22-O24	1.4930(14)
La1-O11	2.4885(16)	P11-O13	1.5602(16)	P22-O25	1.5167(14)
La1-O22 ⁱⁱ	2.5315(14)	P12-O14	1.4944(16)	P22-O26	1.5835(15)
La1-O2W	2.5372(18)	P12-O15	1.5133(15)	O1W-La1-O21	118.78(5)
La1-O15 ⁱⁱⁱ	2.5528(16)	P12-O16	1.5722(15)	O11-O25 ^{iv} -O15 ⁱⁱⁱ -O22 ⁱⁱ	1.9(5)
La1-O25 ^{iv}	2.5819(14)	P21-O21	1.4892(15)	O11-O22 ⁱⁱ -O24 ⁱ -O2W	1.9(5)
La1-O1W	2.6225(17)	P21-O22	1.5208(14)	O2W-O24 ⁱ -O15 ⁱⁱⁱ -O25 ^{iv}	2.4(5)
(i) -x, -y, 1-z; (ii) -x, -0.5+y, 0.5-z; (iii) -x, -y, -z; (iv) x, 0.5-y, -0.5+z					
La-NDP(1,4C) (4)					
La-O1	2.4447(16)	La-O5W	2.669(3)	P2-C4	1.800(2)
La-O1 ⁱ	2.4447(16)	P1-O1	1.4976(16)	O5W-La-O4W	120.49(11)
La-O3W	2.5541(17)	P1-O2	1.535(6)	O5W-La-O1W	107.67(13)
La-O3W ⁱ	2.5541(17)	P1-O3	1.556(6)	O4W-La-O1W	131.84(11)
La-O2W ⁱ	2.5758(18)	P1-C11	1.782(2)	O2W-O1-O1 ⁱ -O2W ⁱ	0.00
La-O2W	2.5758(18)	P2-O4	1.521(4)	O3W ⁱ -O1-O1 ⁱ -O3W	0.00
La-O1W	2.588(3)	P2-O5	1.528(5)	O3W ⁱ -O2W-O2W ⁱ -O3W	0.00
La-O4W	2.612(3)	P2-O6	1.533(6)		
(i) x, -y, z					

Table S2. Hydrogen bonds in the structures **1 - 4**

D-H...A	D-H [Å]	H...A [Å]	D...A [Å]	D-H...A [°]
NDP(1,4)hydr (1)				
O2-H2O...O8 ⁱ	0.84(2)	1.73(2)	2.564(2)	168(3)
O3-H3O...O1 ⁱⁱ	0.70(2)	1.89(2)	2.577(2)	170(3)
O5-H5O...O4 ⁱⁱⁱ	0.79(2)	1.77(2)	2.5550(19)	169(3)
O6-H6O...O7 ⁱⁱⁱ	0.83(2)	1.75(3)	2.581(2)	177(3)
O7-H71...O7 ^{iv}	0.89(3)	1.94(3)	2.8303(18)	172(2)
O7-H72...O4	0.77(2)	1.98(3)	2.735(2)	168(3)
O8-H81...O1 ^v	0.84(2)	1.89(3)	2.721(2)	175(3)
O8-H82...O8 ^v	0.88(3)	1.98(3)	2.8519(18)	173(2)
C2-H2...O3	0.93	2.47	2.923(3)	110
C3-H3...O5	0.93	2.48	2.925(3)	110
(i) x, 0.5-y, -0.5+z; (ii) x, -1+y, z; (iii) 1-x, 1-y, -z; (iv) 1-x, -0.5+y, 0.5-z; (v) -x, -0.5+y, 0.5-z				

NDP(1,4C)hydr (2a)				
O2-H2O...O4 ⁱ	0.87(2)	1.63(2)	2.4942(14)	171(2)
O3-H3O...O1W ⁱⁱ	0.83(2)	1.81(2)	2.6353(16)	175(2)
O5-H5O...O2W ⁱⁱⁱ	0.79(2)	1.79(2)	2.5671(16)	171(2)
O6-H6O...O1 ⁱ	0.76(2)	1.83(2)	2.5912(15)	177(2)
O1W-H1W1...O4 ^{iv}	0.76(2)	2.02(2)	2.7532(15)	162(2)
O1W-H2W1...O1 ^v	0.81(2)	1.95(2)	2.7551(15)	176(2)
O2W-H1W2...O2 ^{vi}	0.80(2)	2.07(2)	2.8558(16)	172(2)
O2W-H2W2...O1W	0.88(2)	1.98(2)	2.8489(18)	169(2)
C2-H2...O2	0.93	2.48	2.9011(18)	108
(i) 0.5-x, 0.5+y, 0.5-z; (ii) 1-x, 1-y, -z; (iii) -0.5+x, 0.5+y, z; (iv) 0.5-x, 0.5-y, -z; (v) x, 1-y, -0.5+z; (vi) x, -1+y, z				
NDP(1,4C) (2b)				
O2-H2O...O1 ⁱ	0.8200	1.8100	2.582(2)	156.700
O3-H3O...O4 ⁱⁱ	0.8200	1.9300	2.592(2)	137.200
O5-H5O...O4 ⁱⁱⁱ	0.8200	1.7900	2.565(2)	155.700
O6-H6O...O1 ^{iv}	0.8200	1.7700	2.575(2)	166.000
C2-H2...O1	0.93	2.52	2.960(3)	109
C9-H9...O2	0.93	2.52	3.133(3)	124
(i) -x, -y, -z; (ii) 0.5-x, -y, -0.5+z; (iii) 0.5-x, 0.5+y, z; (iv) x, 0.5-y, 0.5+z				
La-NDP(1,4) (3)				
O12-H12O...O14 ⁱ	0.82(3)	1.65(3)	2.458(2)	168.(3)
O13-H13O...O25 ⁱⁱ	0.82(2)	1.746(7)	2.557(2)	170.(3)
O16-H16O...O22 ⁱⁱ	0.82(2)	1.800(7)	2.612(2)	171.(3)
O23-H23O...O3W ⁱⁱⁱ	0.82(2)	1.93(2)	2.694(3)	156.(3)
O26-H26O...O15 ⁱⁱⁱ	0.817(8)	1.801(6)	2.618(2)	177.(3)
O1W-H11W...O26 ^{iv}	0.82(2)	1.958(19)	2.722(2)	154.(2)
O1W-H12W...O3W	0.82(2)	2.06(2)	2.838(3)	160.(2)
O2W-H21W...O16 ^v	0.82(2)	1.900(15)	2.681(2)	159.(3)
O3W-H31W...O14 ⁱ	0.82(2)	1.97(3)	2.788(2)	174.(4)
O3W-H32W...O12 ^{vi}	0.82(2)	2.31(3)	2.991(3)	142.(3)
C12-H12...O11	0.93	2.47	2.908(3)	109
C13-H13...O15	0.93	2.54	2.950(3)	107
C16-H16...O14	0.93	2.55	3.228(3)	130
C22-H22...O22	0.93	2.49	2.929(2)	109
C23-H23...O25	0.93	2.48	2.928(2)	110
C26-H26...O24	0.93	2.36	3.060(2)	132
C29-H29...O23	0.93	2.53	2.116(3)	121
(i) 1-x, -y, -z; (ii) x, 0.5-y, -0.5+z; (iii) -x, 0.5+y, 0.5-z; (iv) -x, -y, 1-z; (v) x, 0.5-y, 0.5+z; (vi) 1-x, -0.5+y, 0.5-z				
La-NDP(1,4C) (4)				
O1W-H1O1...O4 ⁱ	0.819(5)	2.14(2)	2.863(3)	147.(4)
O2W-H1O2...O4 ⁱ	0.819(5)	1.870(7)	2.685(2)	174.(4)
O2W-H2O2...O3 ⁱⁱ	0.820(5)	2.038(12)	2.835(3)	164.(4)
O3W-H1O3...O2 ⁱⁱⁱ	0.819(5)	2.104(9)	2.913(3)	170.(4)
O3W-H2O3...O6W ^{iv}	0.819(5)	1.971(11)	2.774(3)	166.(4)
O4W-H1O4...O6 ^{iv}	0.821(5)	2.030(6)	2.850(2)	177.(4)
O5W-H1O5...O1 ⁱⁱ	0.8200	2.507(6)	2.917(3)	112.1(5)
O6-H61...O2 ⁱ	0.8200	1.7600	2.493(3)	147.400
O3-H31...O5 ⁱ	0.8200	1.7700	2.550(3)	158.700
O6W-H2O6...O4	0.79(4)	1.98(4)	2.732(3)	159.(4)
O6W-H1O6...O5 ⁱⁱ	0.76(4)	1.97(5)	2.722(3)	170.(5)
C2-H2...O2	0.93	2.55	3.265(4)	134
C3-H3...O5	0.93	2.49	2.936(3)	109
(i) 0.5+x, 0.5-y, z; (ii) x, y, -1+z; (iii) x, -y, -1+z; (iv) -0.5+x, -0.5+y, z				

Table S3. Crystal data and structure refinement for crystals **1 - 4**

	Symbol of the structure				
	NDP(1,4)hydr (1)	NDP(1,4C)hydr (2a)	NDP(1,4C) (2b)	La-NDP(1,4) (3)	La-NDP(1,4C) (4)
empirical formula	C ₁₀ H ₁₄ O ₈ P ₂	C ₁₁ H ₁₆ O ₈ P ₂	C ₁₁ H ₁₂ O ₆ P ₂	C ₂₀ H ₂₃ LaO ₁₅ O ₄	C ₂₂ H ₃₉ LaO ₂₁ P ₄
formula weight	324.15	338.18	302.15	766.17	902.32
crystal size [mm ³]	0.36 x 0.26 x 0.21	0.36 x 0.29 x 0.24	0.28 x 0.22 x 0.16	0.29 x 0.22 x 0.19	0.35 x 0.33 x 0.12
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	P2 ₁ /c	C2/c	Pbca	P2 ₁ /c	Cm
a [Å]	23.267(4)	22.492(3)	16.2835(5)	10.614(2)	9.2113(2)
b [Å]	4.886(1)	8.066(1)	7.8798(2)	12.316(3)	26.5836(5)
c [Å]	12.329(2)	15.534(2)	19.1588(5)	20.809(4)	6.8556(10)
β [°]	93.18(1)	91.50(1)	90	104.34(3)	96.740(2)
V [Å ³]	1399.4(4)	2817.2(6)	2458.3(1)	2635.4(9)	1667.1(1)
Z	4	8	8	4	2
density (calcd) [Mg·m ⁻³]	1.539	1.595	1.633	1.931	1.798
F(000)	672	1408	1248	1520	912
θ range [°]	3.31 - 29.48	2.98 - 29.29	3.06 - 29.44	2.94 - 29.39	2.99 - 29.40
coeff, μ [mm ⁻¹]	0.344	0.345	0.374	1.938	1.560
T [K]	293(2)	295(2)	295(2)	295(2)	295(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
reflections coll., independ., obs.	11572, 3577, 2027	18874, 3243, 2018	31447, 3610, 2879	35427, 6785, 5900	11315, 3506, 3464
R _{int}	0.0446	0.0612	0.0183	0.0204	0.0189
data/parameters	3577/205	3610/215	3243/176	6785/394	3506/252
final R indices (I > 2σ(I))	R ₁ = 0.0441, wR = 0.0783	R ₁ = 0.0275, wR = 0.0648	R ₁ = 0.0447, wR = 0.0648	R ₁ = 0.0193, wR = 0.0277	R ₁ = 0.0173, wR = 0.0413
R indices (all data)	R ₁ = 0.1113, wR = 0.0947	R ₁ = 0.0434, wR = 0.0759	R ₁ = 0.1058, wR = 0.1271	R ₁ = 0.0483, wR = 0.0543	R ₁ = 0.0181, wR = 0.0417
GOF on F ²	1.016	1.024	1.002	1.009	1.026
peak, hole [e·Å ⁻³]	0.367, -0.341	0.287, -0.259	0.478, -0.453	0.806, -0.404	0.354, -0.312
CCDC number	895377	895374	895375	895373	895376

Table S4. Results of continuous shape measures analysis for lanthanum centers

	S _{SAPR, 1}	S _{TDD, 2}	S _{BTTPR, 3}	Δ _(1,2)	Δ _(1,3)	Δ _(2,3)	φ _(1→2)	φ _(2→1)	φ _(1→3)	φ _(3→1)	φ _(2→3)	φ _(3→2)
La-NDP(1,4)	0.936	1.584	1.621	31.6	48.6	53.3	57.1	74.4	64.1	84.5	76.2	77.1
	S _{CSAPR, 1}	S _{TCTTPR, 2}	S _{JCSAPR, 3}	Δ _(1,2)	Δ _(1,3)	Δ _(2,3)	φ _(1→2)	φ _(2→1)	φ _(1→3)	φ _(3→1)	φ _(2→3)	φ _(3→2)
La-NDP(1,4C)	0.174	0.896	1.097	26.1	37.6	30.8	38.5	87.5	39.1	98.4	62.1	68.7

S - the shape measure relative to the: SAPR - square antiprism (D_{4d}); TDD - triangular dodecahedron (D_{2d}); BTTPR - biaugmented trigonal prism (C_{2v}); JCSAPR - capped square antiprism J10 (C_{4v}); CSAPR - spherical capped square antiprism (C_{4v}); TCTTPR - spherical tricapped trigonal prism (D_{3h})
 Δ_(1,2) - the deviation from the shape 1→2 interconversion path; φ_(1→2) - generalized interconversion coordinates (the sum φ_(1→2) + φ_(2→1) is greater than 100% due to non-zero value of Δ_(1,2))

Scheme S1. Description of the naphthalene aromatic system. (Cg) - ring centroid, (A) - a distance between ring centroids, (B) - a distance between molecular planes, (C) - slippage, (α) - an offset shift angle

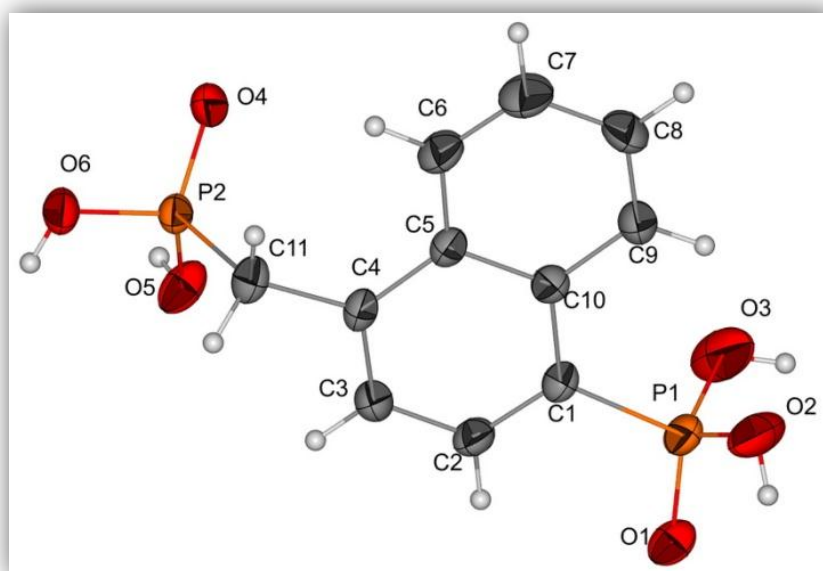
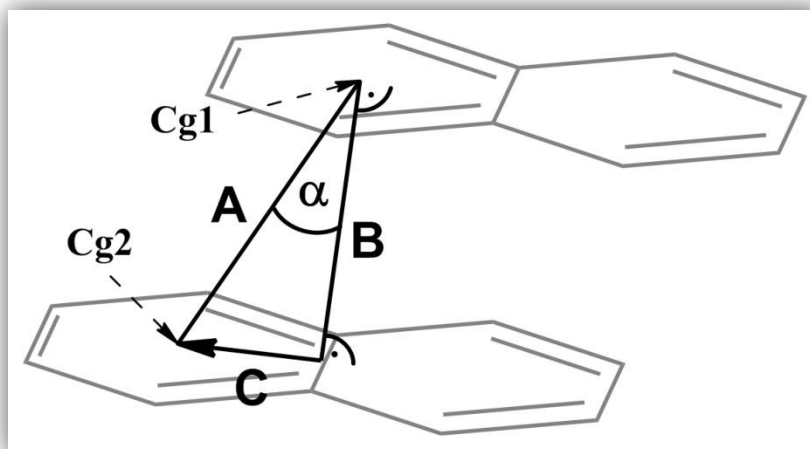


Figure S1. Asymmetric unit of NDP(1,4C). Displacement ellipsoids are drawn at the 50 % probability level

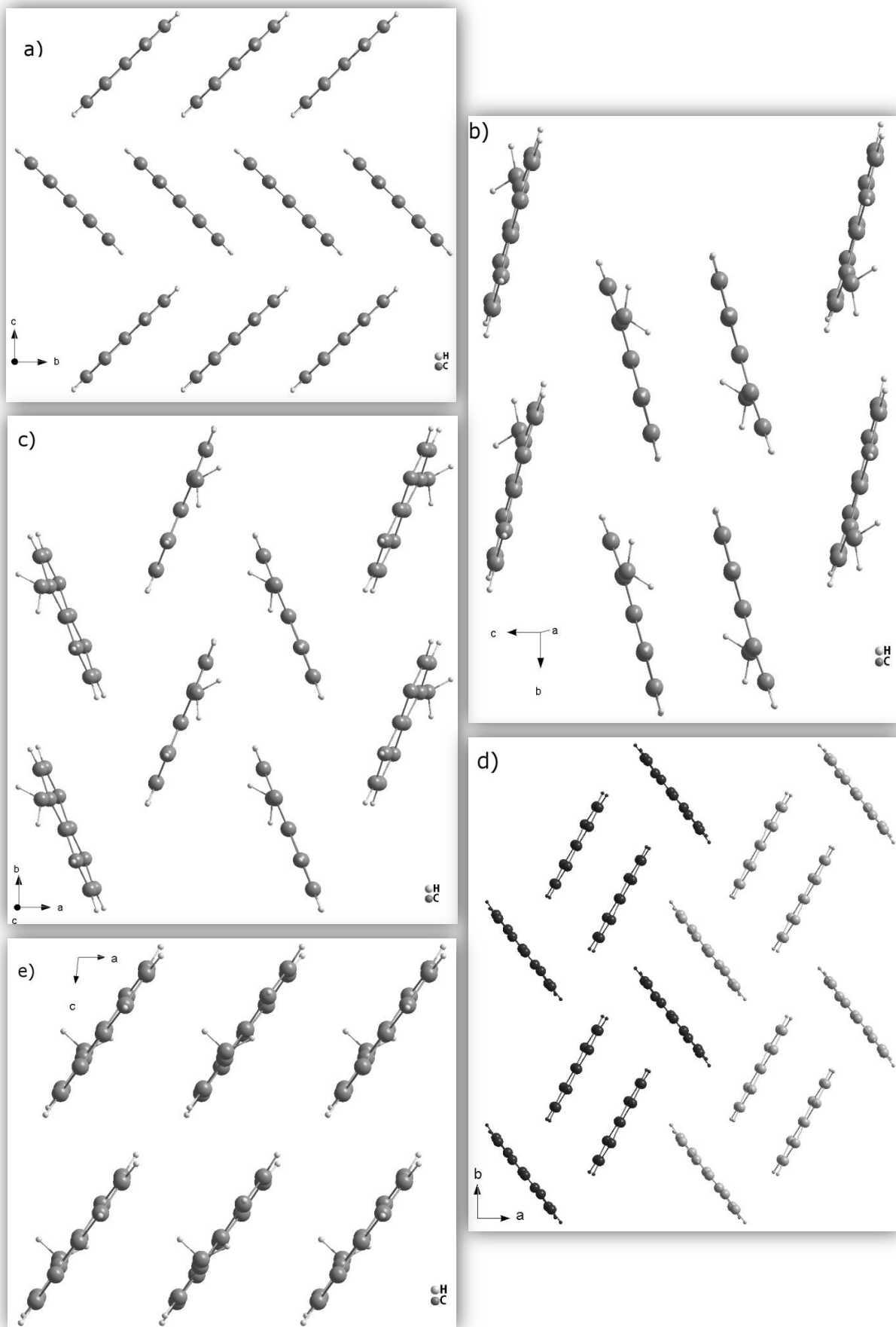


Figure S2. Naphthalene rings arrangement in organic layers in the structure a) NDP(1,4)hydr (**1**), b) NDP(1,4C)hydr (**2a**), c) NDP(1,4C) (**2b**), d) La-NDP(1,4) (**3**) - uniform color of the rings within coordination layer, e) La-NDP(1,4C) (**4**)

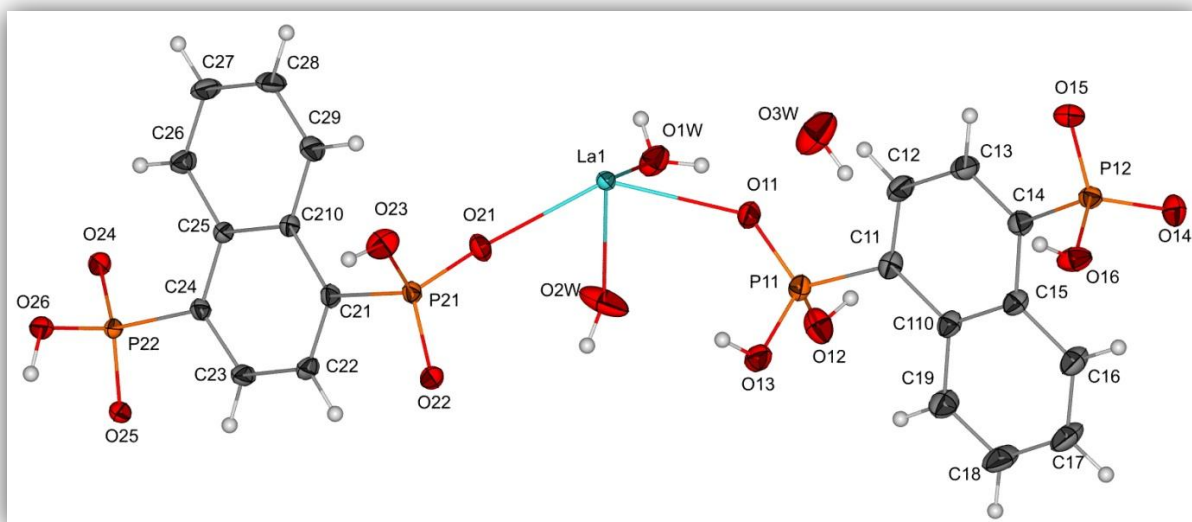


Figure S3. Asymmetric unit of La-NDP(1,4). Displacement ellipsoids are drawn at the 50 % probability level

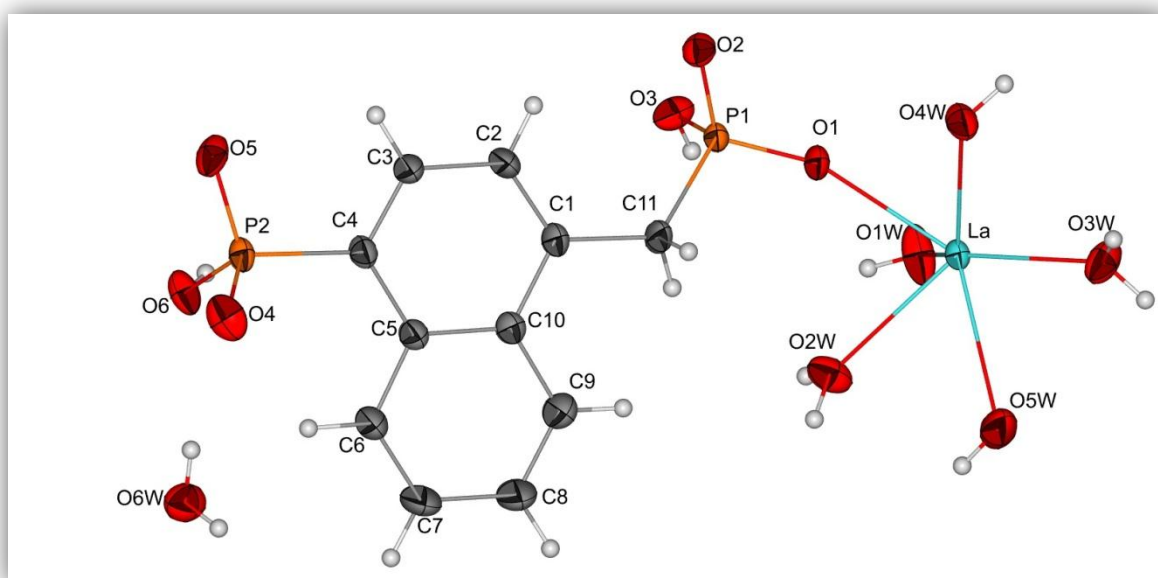


Figure S4. Asymmetric unit of La-NDP(1,4C). Displacement ellipsoids are drawn at the 50 % probability level

Spectroscopic analysis

^1H , ^{31}P , ^{13}C NMR spectra of phosphonic acids (**1** and **2**).

In the case of symmetrically disubstituted $\text{H}_4\text{NDP}(1,4)$ (**1**), there is a minimum number of ^1H NMR signals from aromatic hydrogen atoms. Apart from this, $^1\text{H}_{\text{Ar}}-^1\text{H}_{\text{Ar}}$ and $^1\text{H}_{\text{Ar}}-^{31}\text{P}$ couplings complicate the spectrum. In $\text{H}_4\text{NDP}(1,4\text{C})$ (**2**) spectrum, it is even more apparent. In this case, there is also a characteristic signal from the methylene bridge. It is doublet with clearly marked coupling constant, $^2J_{\text{H,P}}$ equals ~ 22 Hz. Depending on an NMR solvent and pH, there can be also very broad signal with various chemical shift from protons of the phosphonic group.

$^{31}\text{P}\{^1\text{H}\}$ NMR spectra are simple. There is one singlet for symmetrical ligand and two doublets for asymmetrical one with $^{31}\text{P}-^{31}\text{P}$ coupling through six bonds, $^6J_{\text{P,P}}$ equals about 5 Hz. Signals of phosphorous atoms connected directly to the aromatic rings are upfield shifted.

^{13}C NMR spectra are more complex due to the $^{13}\text{C}-^{31}\text{P}$ couplings. Signals are usually doublets or doublets of doublets, unless they overlap to give triplet-like signals. The most characteristic signal comes from the carbon atom connected to the phosphorous one. Obtained doublet has a large coupling constant ($^1J_{\text{C,P}}$). For aromatic carbon atoms, it is about 180 Hz (for **1** and **2**) and lower, 131 Hz (for **2**), in the case of aliphatic ones.

IR of phosphonic acids (**1** and **2**) and lanthanum phosphonates (**3** and **4**)

Region between 4000 and about 1500 cm^{-1} contains broad bands from hydroxyl groups involved in hydrogen-bond networks especially broad for free $\text{H}_4\text{NDP}(1,4)$ (**1**), and $\text{H}_4\text{NDP}(1,4\text{C})$ (**2**). Bands about 1514 cm^{-1} arisen due to skeleton vibrations. In **2**, there are also bands from deformations of methylene bridge around 1400 cm^{-1} . Fingerprint region comprises bands from the phosphonic group. Hence for **1**, there is $\nu(\text{P}=\text{O})$ band at 1216 cm^{-1} , $\nu_{\text{as}}(\text{PO}_3)$ at 1109, and $\nu_{\text{s}}(\text{PO}_3)$ at 1015 cm^{-1} . For the second ligand (**2**) it is: 1211, 1127, and 1012 cm^{-1} , respectively. Out-of-plane deformation C-H vibrations are located in the region 860 - 815 cm^{-1} . Band centered at 760 cm^{-1} is attributed to P-C stretching vibration.

For coordination compounds **3** and **4**, there are also visible $\delta(\text{HOH})$ vibration bands of the lattice and coordination water molecules present in the region 1650 - 1630 cm^{-1} broadened by hydrogen bonding. There are also La-O(H) and La-O(P) stretching vibration bands located, for 2D coordination polymer, at 467 and 367 cm^{-1} ; and at 495 and 337 cm^{-1} for discrete complex. Spectra in 4000 - 400 cm^{-1} region for all compounds are shown in Fig. S5 and S6.

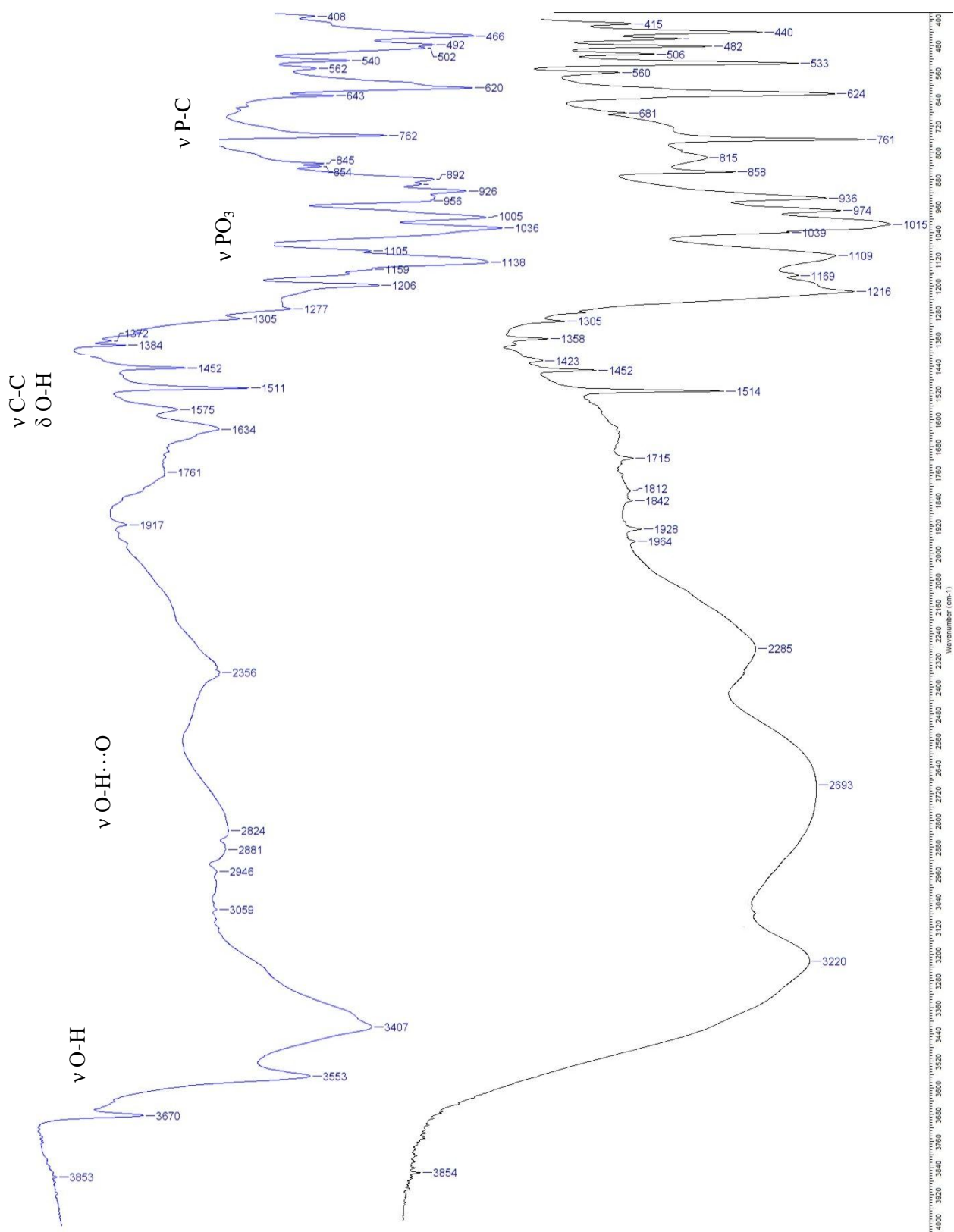


Figure S5. IR spectra of H₄NDP(1,4) (black) and La-NDP(1,4) (blue)

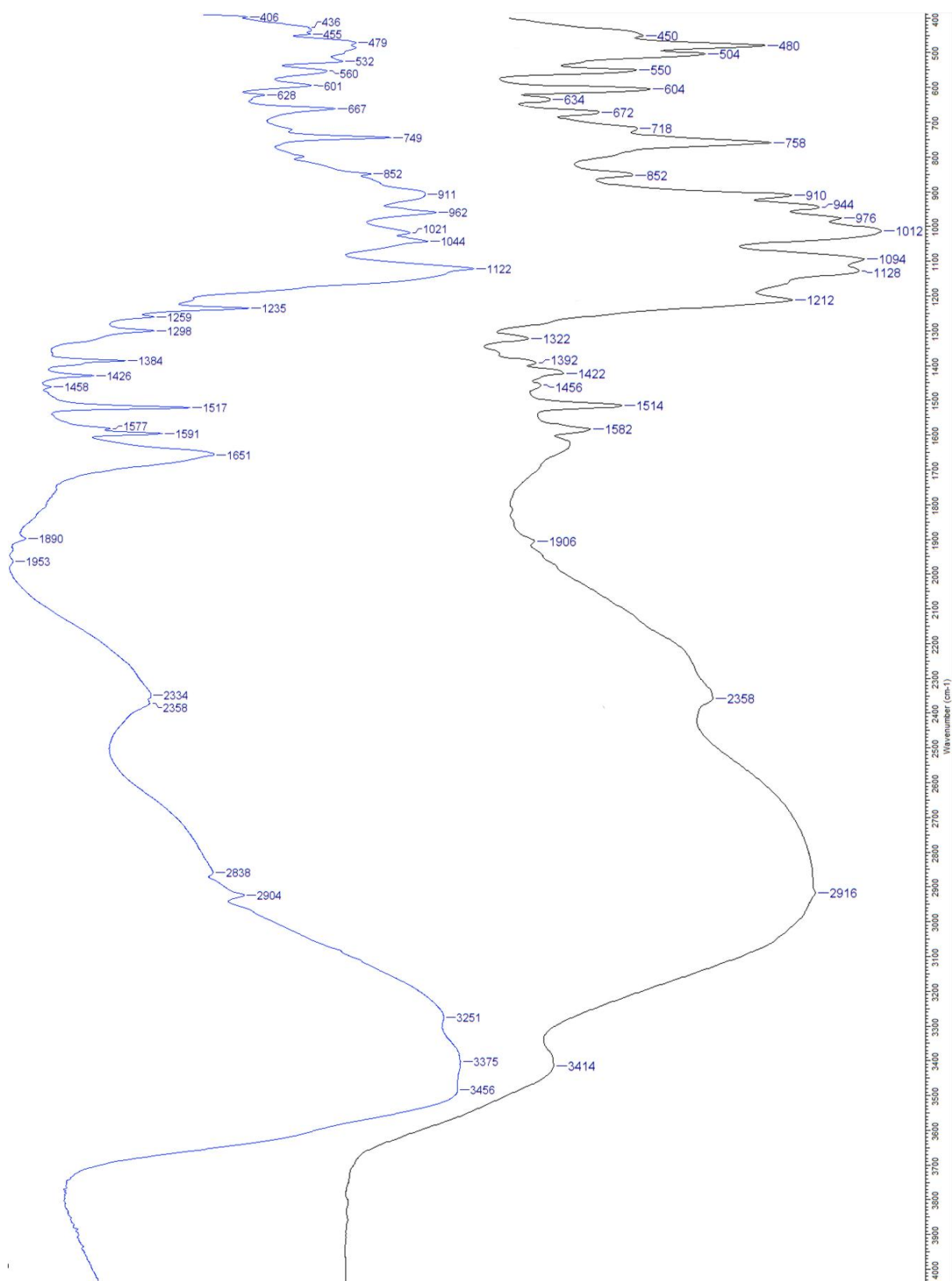


Figure S6. IR spectra of H₄NDP(1,4C) (black) and La-NDP(1,4C) (blue)