# Electronic supplementary information for the manuscript

## "Arbuzov chemistry with chlorofullerene C<sub>60</sub>Cl<sub>6</sub>: a powerful method for selective synthesis of highly functionalized [60]fullerene derivatives"

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### **Experimental procedures**

#### 1. Synthesis of $C_{60}[P(O)(OEt)_2]_5H$ (1a)

Chlorofullerene  $C_{60}Cl_6$  (933 mg, 1 mmol) was dissolved in 800 mL of toluene under stirring in air for 1 h. Triethyl phosphite (1.66 g, 10 mmol) was added in one portion to the chlorofullerene solution. The reaction mixture changed the color from bright red to dark brown (immediately after addition of triethyl phosphite) and then to wine red (within 5-10 minutes after the triethyl phosphite addition). The course of the reaction was monitored by HPLC (C18 reversed phase, Phenomenex Luna C18 5 um). Typically, the reaction was accomplished in 10-15 minutes after addition of triethyl phosphite. It was also observed that larger excess of the reagent (up to 50 mmol) improves the selectivity of the reaction with respect to the formation of the target  $C_{60}[P(O)(OEt)_2]_5H$ . The reaction mixture was concentrated at the rotary evaporator. The viscous red-orange oily residue was dissolved in deionized water and the resulting aqueous solution was filtered a tight paper filter ("blue tape"). It seems that byproducts through  $C_{60}[P(O)(OEt)_2]_nH_m$  (n=3 and m=1; n=2 and m=0; n=1 and m=1) formed in small amounts are not soluble in water and can be separated by filtration procedure. The aqueous filtrate was extracted several times with ethyl acetate until inorganic phase became almost colorless. The combined organic extracts were dried over anhydrous MgSO<sub>4</sub> and concentrated to dryness at the rotary evaporator. The obtained red glassy residue was further dried in vacuum (10<sup>-3</sup> mbar) at room temperature until the sample reached a constant weight.

Alternatively, the reaction mixture obtained after the addition of triethyl phosphite to  $C_{60}Cl_6$  was poured on the top of silica gel (Acros Organics, 40-60 um, 60 A). Following elution with toluene-ethanol mixtures (toluene/EtOH v/v ratio was gradually changed from 10:1 to 1:10) produced trace amounts of brown and reddish byproducts followed by bright orange-red fraction of the target  $C_{60}[P(O)(OEt)_2]_5H$ . The solution of  $C_{60}[P(O)(OEt)_2]_5H$  eluted from the column was concentrated to dryness at the rotary evaporator and then further dried in vacuum  $(10^{-3} \text{ mbar})$  at room temperature until the sample reached a constant weight. The isolated yield of **1a** was 1.125-1.294 g (80-92%).

#### 2. Synthesis of 1b-d, 2b and 3c

Chlorofullerene  $C_{60}Cl_6$  (933 mg, 1 mmol) was dissolved in 800 mL of toluene under stirring in air for 1 h. A corresponding trialkyl phosphite (10-50 mmol) was added in one portion to the chlorofullerene solution. The reaction mixture changed the color from bright red to dark brown (immediately after addition of trialkyl phosphite) and then to wine red (within 10-120 minutes after the trialkyl phosphite addition). To ensure completion of the reaction, the reagent mixtures were stirred for 2-3 hrs or left overnight at room temperature. Afterwards, the reaction mixtures were poured on the top of silica gel (Acros Organics, 40-60 um, 60 A) column. Following elution with toluene-ethanol mixtures (toluene/EtOH v/v ratio was gradually changed from 99:1 to 1:1) produced trace amounts of brown (3c and similar compounds) and reddish (2b and similar compounds) byproducts followed by bright orange-red fraction of the target  $C_{60}[P(O)(OR)_2]_5H$ . The solution of  $C_{60}[P(O)(OR)_2]_5H$  eluted from the column was concentrated to dryness at the rotary evaporator and then further dried in vacuum  $(10^{-3} \text{ mbar})$  at room temperature until the sample reached a constant weight. The isolated yields of **1b-d** were 75-94%.

#### 3. Synthesis of 4

Compound **1a** (1.4 g, 1 mmol) was dissolved in anhydrous dichloromethane in argon atmosphere. The reagent TMSBr (4.59 g, 30 mmol) was added in one portion. The resulting mixture was heated at reflux for 80 hrs and then was concentrated to dryness at the rotary evaporator. The oily residue was dissolved in methanol-toluene mixture (1 : 1 v/v). Solid cesium fluoride (800 mg) was added to

the solution and the mixture was sonicated for 30 min. The precipitated cesium salt of **4** was separated by centrifugation, dissolved in deionized water and precipitated with addition of 40 ml of 8M hydrochloric acid. The precipitate of **4** was separated by centrifugation, dissolved in water and concentrated to dryness at the rotary evaporator. The dissolving-concentration cycle was repeated four times to ensure complete removal of hydrochloric acid. The obtained residue was dried in vacuum  $(10^{-3} \text{ mbar})$  at room temperature until the sample reached a constant weight. The isolated yield of **4** was 50-65%.

#### 4. Proton conductivity measurements for compound 4

The powder of **4** was molded in a pellet with the diameter of 5 mm and the thickness of 0.6 mm under the pressure of 30 MPa at room temperature. The pellet was sandwiched between two carbon electrodes to form symmetrical C/compound **4**/C diode cell suitable for the measurements. The cell with the film of compound **4** was stored at a certain value of ambient humidity and at a certain temperature. The temperature control was provided by Huber CC2 Thermostat ( $\pm$  0.1°C). The frequency response was obtained in the frequency range 1.0 Hz – 2.0 MHz using Z-2000 (LLS "Elins") impedance meter. The frequency dependence of impedance was analyzed using a previously reported graphical analytical procedure [N.G. Bukun, A.E. Ukshe, E.A. Ukshe. *Russ. J. Electrochem.*, 1993, **29**, 146.].

#### Selected spectroscopic data:

**1a.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ, ppm): 1.28-1.38 (m, 30H), 4.19-4.28 (m, 2H), 4.28-4.44 (m, 18H), 5.57-5.65 (m, 1H).

<sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>, δ, ppm, *J*/Hz): 15.73-15.9 (m, 2P), 16.07-16.21 (m, 2P), 21.03 (t, 1P, <sup>5</sup>J<sub>P-P</sub>=4.4).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, δ, ppm): 16.41-16.45 (m, <u>C</u>H<sub>3</sub>), 16.63-16.82 (m, <u>C</u>H<sub>3</sub>), 54.73 (m, <u>C</u><sub>sp3</sub> fullerene cage-H), 57.55 (d, <u>C</u><sub>sp3</sub> fullerene cage-P, <sup>1</sup>J<sub>P-P</sub>=142.8), 58.40 (d, <u>C</u><sub>sp3</sub> fullerene cage-P, <sup>1</sup>J<sub>P-P</sub>=148.4), 59.92 (d, <u>C</u><sub>sp3</sub> fullerene cage-P, <sup>1</sup>J<sub>P-P</sub>=148.0), 63.93-64.00 (m, <u>C</u>H<sub>2</sub>), 64.27-64.33 (m, <u>C</u>H<sub>2</sub>), 64.39-64.45 (m, <u>C</u>H<sub>2</sub>), 64.60-64.66 (m, <u>C</u>H<sub>2</sub>), 138.69, 143.34, 143.36, 143.46, 144.04, 144.07, 144.47, 144.50, 144.57, 144.59, 144.95, 145.00, 145.52, 145.54, 145.81, 146.75, 146.97, 147.06, 148.16, 148.23, 148.31, 148.39, 148.47, 148.74, 148.77, 149.10, 149.34, 150.83.

FTIR (KBr pellet, v, cm<sup>-1</sup>): 428 (VW), 448 (VW), 502 (W), 540 (M), 558 (S), 570 (M), 606 (M), 636 (S), 658 (VW), 744 (W), 758 (W), 772 (W), 790 (W), 862 (VW), 970 (S), 1018 (VS), 1048 (VS), 1098 (S), 1162 (M), 1200 (W), 1254 (S), 1368 (W), 1390 (M), 1418 (W), 1440 (W), 1460 (W), 1474 (W), 2338 (W), 2360 (W), 2864 (W), 2906 (M), 2928 (M), 2978 (M).

ESI MS: m/z=1405 ([M-H]<sup>-</sup>). m.p.>250 °C (with decomposition)

**1b.** <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD:CDCl<sub>3</sub> 4:1, δ, ppm): 1.28-1.40 (m, 30H), 1.43-1.53 (m, 30H), 5.00-5.07 (m, 4H), 5.07-5.16 (m, 4H), 5.16-5.22 (m, 2H).

<sup>31</sup>P{1H} NMR (202 MHz, CD<sub>3</sub>OD:CDCl<sub>3</sub> 4:1, δ, ppm, *J*/Hz): 13.71 (d, 2P, <sup>5</sup>J<sub>P-P</sub>=24.4), 14.95 (dd, 2P, <sup>5</sup>J<sub>P-P</sub>=24.4, <sup>5</sup>J<sub>P-P</sub>=3.8), 17.99 (t, 1P, <sup>5</sup>J<sub>P-P</sub>=3.8).

<sup>13</sup>C{1H} NMR (126 MHz, CD<sub>3</sub>OD:CDCl<sub>3</sub> 4:1, δ, ppm, *J*/Hz): 24.34 (<u>C</u>H<sub>3</sub>), 24.38 (<u>C</u>H<sub>3</sub>), 23.51-23.62 (m, <u>C</u>H<sub>3</sub>), 24.72-24.89 (m, <u>C</u>H<sub>3</sub>), 24.99-25.00 (m, <u>C</u>H<sub>3</sub>), 55.80 (m, <u>C</u><sub>sp3</sub> fullerene cage<sup>-</sup>H), 58.83 (d, <u>C</u><sub>sp3</sub> fullerene cage<sup>-</sup>P, <sup>1</sup>J<sub>P-P</sub>=141.6), 59.87 (d, <u>C</u><sub>sp3</sub> fullerene cage<sup>-</sup>P, <sup>1</sup>J<sub>P-P</sub>=151.2), 61.22 (d, <u>C</u><sub>sp3</sub> fullerene cage<sup>-</sup>P, <sup>1</sup>J<sub>P-P</sub>=152.2), 74.28-74.34 (m, <u>C</u>H), 74.56-74.76 (m, <u>C</u>H), 74.89-74.96 (m, <u>C</u>H), 140.25, 143.96, 143.97, 144.32, 144.75, 144.76, 144.91, 145.27, 145.30, 145.65, 145.66, 145.73, 145.81, 146.58, 146.89, 147.75, 147.93, 148.02, 149.02, 149.07, 149.27, 149.33, 149.35, 149.60, 149.88, 149.94, 150.07, 151.76.

FTIR (KBr pellet, v, cm<sup>-1</sup>): 530 (W), 541 (M), 558 (M), 572 (M), 607 (M), 637 (M), 896 (W), 939 (M), 998 (VS), 1103 (M), 1143 (W), 1176 (W), 1250 (M), 1375 (W), 1386 (M), 1419 (VW), 1461 (W), 2851 (W), 2928 (M), 2979 (M).

ESI MS: m/z=1548 ([M+H]<sup>+</sup>). m.p.>250 °C (with decomposition)

**1c.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ, ppm): 0.80-0.90 (m, 30H), 1.23-1.41 (m, 20H), 1.58-1.74 (m, 20H), 4.14-4.36 (m, 20H), 5.62-5.67 (m, 1H).

<sup>31</sup>P{1H} NMR (202 MHz, CDCl<sub>3</sub>, δ, ppm, *J*/Hz): 15.46 (d, 2P, <sup>5</sup>J<sub>P-P</sub>=25.2), 15.93 (dd, 2P, <sup>5</sup>J<sub>P-P</sub>=25.2, <sup>5</sup>J<sub>P-P</sub>=4.1), 20.49 (t, 1P, <sup>5</sup>J<sub>P-P</sub>=4.1).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, δ, ppm, *J*/Hz): 13.77 (<u>C</u>H<sub>3</sub>), 13.85 (<u>C</u>H<sub>3</sub>), 13.88 (<u>C</u>H<sub>3</sub>), 18.80 (<u>C</u>H<sub>2</sub>), 18.84 (<u>C</u>H<sub>2</sub>), 32.74-32.78 (m, <u>C</u>H<sub>2</sub>), 32.88-32.94 (m, <u>C</u>H<sub>2</sub>), 33.00-33.05 (m, <u>C</u>H<sub>2</sub>), 54.84 (<u>C<sub>sp3</sub> fullerene cage</sub>-H), 57.71 (d, <u>C<sub>sp3</sub> fullerene cage</u>-P, <sup>1</sup>J<sub>P-P</sub>=142.7), 58.48 (d, <u>C<sub>sp3</sub> fullerene cage</sub>-P, <sup>1</sup>J<sub>P-P</sub>=146.2), 59.88 (d, <u>C<sub>sp3</sub> fullerene cage</u>-P, <sup>1</sup>J<sub>P-P</sub>=146.5), 68.03-68.07 (m, O<u>C</u>H<sub>2</sub>), 68.20-68.37 (m, O<u>C</u>H<sub>2</sub>), 68.43-68.49 (m, O<u>C</u>H<sub>2</sub>), 138.84, 143.23, 143.25, 143.42, 143.96, 144.01, 144.45, 144.50, 144.59, 144.60, 144.88, 144.97, 145.56, 145.65, 146.78, 146.98, 147.08, 148.16, 148.23, 148.35, 148.41, 148.46, 148.74, 148.76, 148.89, 149.15, 149.41, 150.60.</u></u>

FTIR (KBr pellet, v, cm<sup>-1</sup>): 490 (M), 507 (M), 510 (M), 520 (W), 540 (M), 558 (M), 571 (M), 606 (M), 636 (M), 664 (VW),), 700 (W), 724 (W), 780 (W), 832 (W), 998 (VS),), 1026 (VS),), 1063 (S), 1119 (M), 1149 (M), 1233 (S), 1380 (W), 1461 (M), 2295 (W), 2348 (W), 2388 (W), 2871 (S), 2931 (S), 2959 (S).

ESI MS: m/z=1687 ([M-H]<sup>-</sup>). m.p.=127-129 °C.

**1d.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ, ppm): 3.75-3.93 (m, 20H), 4.46-4.67 (m, 20H), 5.70-5.77 (m, 1H).

<sup>31</sup>P{1H} NMR (202 MHz, CDCl<sub>3</sub>, δ, ppm, *J*/Hz): 16.00 (d, 2P, <sup>5</sup>J<sub>P-P</sub>=26.0), 16.55 (dd, 2P, <sup>5</sup>J<sub>P-P</sub>=26.0, <sup>5</sup>J<sub>P-P</sub>=4.9), 21.04 (t, 1P, <sup>5</sup>J<sub>P-P</sub>=4.9).

<sup>13</sup>C{1H} NMR (126 MHz, CDCl<sub>3</sub>, δ, ppm, *J*/Hz): 43.17-43.22 (m, <u>C</u>H<sub>2</sub>Cl), 43.30-43.45 (m, <u>C</u>H<sub>2</sub>Cl), 43.63-43.67 (m, <u>C</u>H<sub>2</sub>Cl), 54.65 (<u>C</u><sub>sp3</sub> fullerene cage</sub>-H), 57.47 (d, <u>C</u><sub>sp3</sub> fullerene cage-P, <sup>1</sup>J<sub>P-P</sub>=143.6), 58.18 (d, <u>C</u><sub>sp3</sub> fullerene cage-P, <sup>1</sup>J<sub>P-P</sub>=147.2), 59.62 (d, <u>C</u><sub>sp3</sub> fullerene cage-P, <sup>1</sup>J<sub>P-P</sub>=148.3), 67.66-67.72 (m, O<u>C</u>H<sub>2</sub>), 68.00-68.13 (m, O<u>C</u>H<sub>2</sub>), 68.24-68.30 (m, O<u>C</u>H<sub>2</sub>), 138.82, 143.09, 143.63, 143.65, 144.12, 144.27, 144.29, 144.33, 144.56, 144.63, 144.75, 145.25, 145.50, 146.78, 147.01, 147.09, 147.47, 147.57, 147.90, 148.35, 148.38, 148.44, 148.51, 148.60, 148.97, 149.00, 149.12, 150.09.

FTIR (KBr pellet, v, cm<sup>-1</sup>): 538 (M), 558 (M), 564 (M), 628 (W), 636 (M), 671 (M), 698 (S), 758 (M), 836 (W), 922 (M), 967 (S), 1029 (VS), 1084 (S), 1161 (W), 1196 (M), 1254 (S), 1263 (S), 1305 (M), 1383 (W), 1426 (M), 1452 (M), 1493 (M), 1737 (W), 1806 (W), 1871 (W), 1944 (W), 2851 (M), 2922 (S), 3002 (W), 3026 (M), 3060 (M), 3083 (W).

ESI MS: m/z=1751 ([M-H]<sup>-</sup>). m.p.>250 °C (with decomposition)

**2b.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ, ppm, *J*/Hz): 1.30-1.31 (d, 6H), 1.40-1.51 (m, 27H), 1.58 (d, 3H, <sup>3</sup>J<sub>H-H</sub>=6.1), 4.90-5.11 (m, 4H), 5.20-5.26 (m, 1H), 5.40-5.46 (m, 1H), 6.04-6.12 (m, 1H).

<sup>31</sup>P{1H} NMR (202 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm, *J*/Hz): 12.50 (dd, 2P, <sup>5</sup>J<sub>P-P</sub>=33.0, <sup>5</sup>J<sub>P-P</sub>=4.7), 13.33 (d, 2P, <sup>5</sup>J<sub>P-P</sub>=33.0), 18.88 (d, 1P, <sup>5</sup>J<sub>P-P</sub>=4.7).

<sup>13</sup>C{1H} NMR (126 MHz, CDCl<sub>3</sub>, δ, ppm, *J*/Hz): 23.82-23.89 (m, <u>C</u>H<sub>3</sub>), 24.06-24.11 (m, <u>C</u>H<sub>3</sub>), 24.22-24.56 (m, <u>C</u>H<sub>3</sub>), 56.37 (<u>C</u><sub>sp3</sub> fullerene cage</sub>-H), 59.00 (d, <u>C</u><sub>sp3</sub> fullerene cage</sub>-P, <sup>1</sup>J<sub>P-P</sub>=152.6), 60.87 (d, <u>C</u><sub>sp3</sub> fullerene cage</sub>-P, <sup>1</sup>J<sub>P-P</sub>=148.0), 73.52-73.68 (m, <u>C</u>H), 73.77-73.83 (m, <u>C</u>H), 74.00-74.06

(m, <u>C</u>H), 74.14-74.20 (m, <u>C</u>H), 134.13, 134.71, 134.76, 136.27, 136.30, 137.05, 139.39, 140.98, 141.08, 141.57, 141.59, 141.83, 142.00, 142.74, 142.90, 143.86, 143.95, 144.33, 144.46, 144.70, 144.76, 144.86, 144.99, 145.17, 145.24, 145.31, 145.42, 145.64, 145.68, 145.71, 145.78, 145.99, 146.00, 146.02, 146.40, 146.61, 146.70, 146.76, 146.86, 147.08, 147.14, 147.31, 147.66, 147.73, 147.96, 148.22, 148.38, 149.13, 149.44, 149.47, 149.72, 150.16, 150.73, 154.49, 156.12.

FTIR (KBr pellet, v, cm<sup>-1</sup>): 1010 (VS), 2924 (S), 2852 (M), 2956 (M), 566 (M), 1102 (M), 528 (M), 638 (M), 1458 (M), 1238 (M), 1228 (M), 1176 (W), 1142 (W), 1380 (W), 468 (W), 668 (W), 2364 (W), 888 (W), 628 (W), 2350 (W), 764(VW), 788(VW).

ESI MS: m/z=1215 ([M-H]<sup>-</sup>). m.p.>250 °C (with decomposition)

**3c.** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, δ, ppm): 0.98-1.02 (m, 12H), 1.48-1.58 (m, 8H), 1.84-1.94 (m, 8H), 4.51-4.59 (m, 8H).

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>, δ, ppm): 14.40 (s, 2P).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, δ, ppm): 13.75 (<u>C</u>H<sub>3</sub>), 13.78(<u>C</u>H<sub>3</sub>), 18.82 (<u>C</u>H<sub>2</sub>), 18.85 (<u>C</u>H<sub>2</sub>), 32.87-32.96 (m, <u>C</u>H<sub>2</sub>), 61.94 (<u>C<sub>sp3</sub> fullerene cage</u>-P), 62.02 (<u>C<sub>sp3</sub> fullerene cage</u>-P), 62.99 (<u>C<sub>sp3</sub> fullerene cage</sub>-P), 63.07 (<u>C<sub>sp3</sub> fullerene cage</u>-P), 68.45-68.55 (m, O<u>C</u>H<sub>2</sub>), 137.51, 139.17, 139.56, 141.26, 142.00, 142.23, 142.50, 142.94, 143.11, 143.18, 143.29, 143.42, 143.46, 144.31, 144.46, 144.47, 144.57, 144.82, 144.84, 145.13, 145.48, 145.69, 145.74, 147.01, 147.31, 147.65, 147.70, 148.82, 149.75, 155.47.</u>

FTIR (KBr pellet, v, cm<sup>-1</sup>): 1024 (VS), 1060 (S), 2926 (S), 2956 (M), 526 (M), 1256 (M), 2868 (M), 2856 (M), 562 (M), 1230 (M), 624 (M), 1460 (M), 902 (W), 1426 (W), 540 (W), 548 (W), 1378 (W), 1116 (W), 1148 (W), 2364 (W), 2332 (W), 476 (W), 776 (W), 726 (W), 820 (W), 670 (W), 706 (VW), 660 (VW).

ESI MS: m/z=1132 ([M+CN]<sup>-</sup>). m.p.>250 °C (with decomposition)

**4.**  ${}^{1}H{}^{31}P{}$  NMR (600 MHz, acetone-D6,  $\delta$ , ppm): 4.62 (s, 1H).

<sup>31</sup>P NMR (120 MHz, acetone-D6, δ, ppm): 0.66 (s, 2P), 10.57-10.88 (m, 2P), 16.57 (s, 1P).

<sup>13</sup>C NMR (150 MHz, acetone-D6, δ, ppm): 56.84 (<u>C</u><sub>sp3</sub> fullerene cage</sub>-H), 57.54 (<u>C</u><sub>sp3</sub> fullerene cage</sub>-P), 58.37 (<u>C</u><sub>sp3</sub> fullerene cage</sub>-P), 59.03 (<u>C</u><sub>sp3</sub> fullerene cage</sub>-P), 59.90 (<u>C</u><sub>sp3</sub> fullerene cage</sub>-P), 60.67 (<u>C</u><sub>sp3</sub> fullerene cage</sub>-P), 61.55 (<u>C</u><sub>sp3</sub> fullerene cage</sub>-P), 138.55, 143.32, 143.95, 143.98, 144.37, 144.91, 145.04, 145.16, 145.18, 145.64, 146.30, 146.32, 146.53, 146.59, 146.64, 147.94, 148.09, 148.25, 148.47, 148.54, 148.83, 148.91, 149.08, 149.13, 149.43, 149.49, 151.06, 151.10.

FTIR (KBr pellet, v, cm<sup>-1</sup>): 450 (W), 496 (W), 528 (W), 596 (M), 638 (W), 664 (W), 834 (W), 880 (M), 988 (S), 1006 (S), 1054 (S), 1120 (S), 1182 (S), 1204 (S), 1230 (S), 3420 (S).

ESI MS: m/z=1125 ([M-H]<sup>-</sup>), 562 ([M-2H]<sup>2-</sup>). m.p.>250 °C (with decomposition)

#### X-ray crystallography for 1a·0.19H<sub>2</sub>O

Data collection for single crystal of  $1a \cdot 0.19 H_2O (0.06 \times 0.02 \times 0.01 \text{ mm}^3)$  was carried out with a MAR225 CCD detector at 100 K using synchrotron radiation at the BESSY storage ring, BL 14.2 ( $\lambda = 0.83774$  Å, PSF of the Free University of Berlin, Germany). The structure was solved using direct methods (SHELXS97) and refined against  $|F^2|$  with SHELXL97. Absorption correction was not applied. There are two crystallographically independent molecules of 1a and a water molecule with the partial occupacy of 0.382. Each 1a molecule show a disorder of phosphonate groups with the second components (10 - 13%) oriented in opposite directions respective to the phosphonate groups of the main components. Due to low abundances of the second components, only P and some O atoms were located and refined with isotropic thermal parameters. All other non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed into geometrically calculated positions and refined in the riding mode. Crystal data for  $1a \cdot 0.19H_2O$ : M = 1410.48, monoclinic,  $P2_1/n$ , a = 20.628(1), b = 16.0821(7), c = 35.467(1)Å,  $\beta = 93.954(3)^{\circ}$ , V = 11740.6(8) Å<sup>3</sup>, Z = 8,  $D_{calc} = 1.596$  g cm<sup>-3</sup>. LS refinement with 30243 reflections and 1915 parameters yielded a conventional  $R_1 = 0.088$  for 24124 reflections with I > $2\sigma$  (I) and  $wR_2 = 0.223$  for all reflections. For more details see CCDC – (the number should be inserted!).



Fig. S1. ESI MS spectrum of compound 1a



Fig. S2. <sup>1</sup>H NMR spectrum of compound 1a

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Fig. S4 <sup>31</sup>P NMR spectrum of compound 1a

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Fig. S6. High-field part of the <sup>13</sup>C NMR spectrum of compound 1a



Fig. S7. Low-field part of the <sup>13</sup>C NMR spectrum of compound 1a



Fig. S8. H-H COSY NMR spectrum of compound 1a



Fig. S9. H-P HMBC NMR spectrum of compound 1a



Fig. S10. H-C HSQC NMR spectrum of compound 1a

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Fig. S11. ESI mass spectrum of compound 1b



Fig. S12. <sup>1</sup>H NMR spectrum of compound 1b

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Fig. S13 <sup>31</sup>P{1H} NMR spectrum of compound 1b



Fig. S14. High-field part of the <sup>13</sup>C NMR spectrum of compound 1b



Fig. S15. Low-field part of the <sup>13</sup>C NMR spectrum of compound 1b



Fig. S16. H-P HMBC NMR spectrum of compound 1b



bpm

Fig. S17. H-C HSQC NMR spectrum of compound 1b



Fig. S18. H-C HMBC NMR spectrum of compound 1b



Fig. S19. ESI mass spectrum of compound 1c



Fig. S20. <sup>1</sup>H NMR spectrum of compound 1c

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Fig. S21.  ${}^{1}H{}^{31}P{}$  NMR spectrum of compound 1c

UA-12c\_005001r



Fig. S22 <sup>31</sup>P NMR spectrum of compound 1c

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Fig. S24. High-field part of the <sup>13</sup>C NMR spectrum of compound 1c



Fig. S25. A part of the high-field part of the <sup>13</sup>C NMR spectrum of compound 1c



Fig. S26. Low-field part of the <sup>13</sup>C NMR spectrum of compound 1c



Fig. S27. H-H COSY NMR spectrum of compound 1c



Fig. S28. H-P HMBC NMR spectrum of compound 1c



Fig. S29. <sup>31</sup>P-<sup>31</sup>P COSY NMR spectrum of compound 1c



Fig. S30. ESI mass spectrum of compound 1d

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Fig. S31. <sup>1</sup>H NMR spectrum of compound 1d



Fig. S32.  ${}^{1}H{}^{31}P{}$  NMR spectrum of compound 1d

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Fig. S34 <sup>31</sup>P{1H} NMR spectrum of compound 1d



**Fig. S35**. High-field part of the <sup>13</sup>C NMR spectrum of compound **1d** 



Fig. S36. Low-field part of the <sup>13</sup>C NMR spectrum of compound 1d

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Fig. S37. H-H COSY NMR spectrum of compound 1d



mdd

Fig. S38. H-P HMBC NMR spectrum of compound 1d



Fig. S39. H-C HSQC NMR spectrum of compound 1d



Fig. S40. ESI MS spectrum of compound 2b

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Fig. S41. <sup>1</sup>H NMR spectrum of compound 2b





**Fig. S42**.  ${}^{1}H{}^{31}P{}$  NMR spectrum of compound **2b** 

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Fig. S43 <sup>31</sup>P NMR spectrum of compound 2b



Fig. S44 <sup>31</sup>P{1H} NMR spectrum of compound 2b

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Fig. S45. High-field part of the <sup>13</sup>C NMR spectrum of compound 2b



Fig. S46. Low-field part of the <sup>13</sup>C NMR spectrum of compound 2b



bpm

Fig. S47. H-H COSY NMR spectrum of compound 2b



Fig. S48. H-H NOESY NMR spectrum of compound 2b



Fig. S49. H-P HMBC NMR spectrum of compound 2b



Fig. S50. H-C HSQC NMR spectrum of compound 2b



Fig. S51. H-C HMBC NMR spectrum of compound 2b



**Fig. S52**. ESI MS spectrum of compound **3c** (m/z=1132 corresponds to the [M+CN]<sup>-</sup> anion)



Fig. S53. <sup>1</sup>H NMR spectrum of compound 3c



Fig. S54 <sup>31</sup>P NMR spectrum of compound 3c



Fig. S55. High-field part of the <sup>13</sup>C NMR spectrum of compound 3c



Fig. S56. Low-field part of the <sup>13</sup>C NMR spectrum of compound 3c



bpm

Fig. S57. H-H COSY NMR spectrum of compound 3c



Fig. S58. H-C HSQC NMR spectrum of compound 3c



Fig. S59. ESI mass spectrum of compound 4



**Fig. S60**.  ${}^{1}H{}^{31}P{}$  NMR spectrum of compound 4





Fig. S62. Low field part of the <sup>13</sup>C NMR spectrum of compound 4



Fig. S63. High field part of the <sup>13</sup>C NMR spectrum of compound 4



Fig. S64. Optical absorption spectra of compounds 1a-d and 4



Fig. S65. Optical absorption spectra of compounds 2b and 3c



Fig. S66. Cole-cole diagram of impedance for compound 4 measured under different relative humidity values. Inset shows impedance locus for compound 4 under RH=15 %. (The frequencies are shown on the graph; the pellet area was 0.196 cm<sup>2</sup>, the pellet thickness was 0.06 cm)

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Fig. S67. Temperature dependences of the specific conductivity of compound 4 under different relative humidity values



**Fig. S68.** TG/DSC decomposition curves for compound **4** along with the mass spectrometric profiles confirming liberation of water at 120-220 °C. (Heating rate 10 °C /min, argon atmosphere.)