

Electronic Supplementary Information (ESI)

Flame retardance-donated lignocellulose nanofibers (LCNFs) by Mannich reaction with (amino-1,3,5-triazinyl)phosphoramidates and their properties

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1. Materials and chemicals.

LCNF (CellFim L-45TM) manufactured from cypress, fiber width of 50–300 nm and fiber length of 45 μm or less, is provided as an aqueous 90~95% dispersion from the Cellulose Development Division of Mori Machinery Corp. (Okayama, Japan).



Polypropylene pellet (MA3, 0.5 mm under) from Japan Polypropylene Co. was used.

2. Measurements and Instruments.

Differential scanning calorimetry (DSC) for M.p. was determined with SII EXSTAR6000 at a heating rate of 10 °C/min, data are shown in ESI. TGA measurements were carried out with a Thermo Plus TG 8120, Rigaku Corp. FT-IR (ATR method) was taken with Perkin Elmer spotlight 300. ¹H, ¹³C NMR, and ³¹P NMR were taken with a JEOL LNM-ECS-400. The samples were characterized by scanning electron microscopy (SEM), using FE-SEM (JSM-6701F, JEOL) operated at 5kV, in which specimens were coated with a thin layer of osmium (Neoc-STB, Meiwafoysis). EA was performed on a PE 2400 II (PerkinElmer) elemental analyser. MALDI-TOF mass was taken by Shimadzu AXIMA Performance.

LOI (Limited Oxygen Index) measurements were achieved with Suga flammability test device ON-1. The test pieces were prepared as follows: the aqueous dispersions of Mannich adducts, obtained by the reaction of LCNFs (CellFim L-45™) with phosphoramidated melamines **4** or **5** under varying their ratio (mmol/g), were molded using appropriate amount to a small vessel (100 x 15 x 15 mm) and shaped to a thin plate, which was followed by air-drying and the vacuum drying.

UL94V test method: Laboplast mill gels PP resin (prime polymer homo PP/prime polypro J-106), calcium stearate (used as an acid adsorbent and dispersant), and antioxidant at 200 °C, and then gradually flame retardant sample of the Mannich adduct was kneaded for 5 min at 50 rpm. The obtained compound was set in a cold press to form a sheet having a predetermined thickness. UL94V test pieces were cut out from the sheet and evaluated for flame retardance.

UL-94V flame retardant evaluation:

Results by using Sample A: Dripping occurred in the test piece of 3.0 mm thickness within 2~3 seconds after the first flame contact, and in about 20 seconds a large drop occurred and the fire was extinguished at the same time. The appearance of extinguishing

as well as falling off was observed even during the second flame contact, and it was rated V-2 (Table 3). With the 1.5 mm thick test piece, a drip occurred 0 to 1 second after the first flame contact, and a large dropout occurred in about 5 seconds, and the fire was extinguished at the same time. At the second flame contact, it sometimes extinguished itself, but the flame reached the clamp in about 20 seconds, so the test failed.

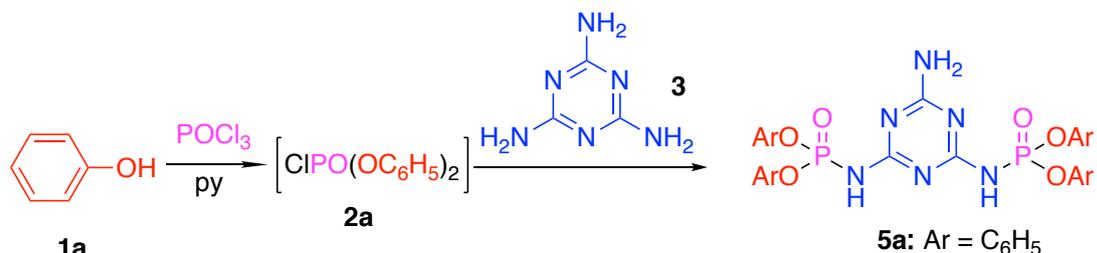
Results by using Sample B: With a 3 mm thick test piece, a drip occurred within 2 to 3 seconds after the first flame contact, and a large dropout occurred in about 25 seconds, and the fire was extinguished at the same time. Although it was possible to extinguish itself during the second flame contact, it was rejected because there was an after flame for more than 30 seconds. With the 1.5 mm thick test piece, there was a tendency for a drip to occur 0 to 1 second after the end of the first flame contact, and a large dropout to occur at the same time for about 8 seconds, as well as a tendency to extinguish the fire, but at the time of the second flame contact, the It did not extinguish, and the flame reached the clamp in about 15 seconds, so the test failed. In addition, even after the first contact with flame, there was a case where after flame was generated for 30 seconds or longer without self-extinguishing.

In the UL94V test, the sample A had better drip and release of the fire when dropped, and good results were obtained, but the LOI showed no difference. It is considered that the UL94V rating was improved by the addition of maleic anhydride-modified PP, which resulted in a better dispersion state or a greater drip and dropout property (fluidity during melting).

Cone calorimeter combustion experiments were performed with a Toyo Seiki Seisakusho, Cone calorimeter C3.

3. Synthesis of Retardant Compounds.

Tetraphenyl (6-Amino-1,3,5-triazine-2,4-diyl)diphosphoramidate (5a); Method A from PhOH (**1a**):



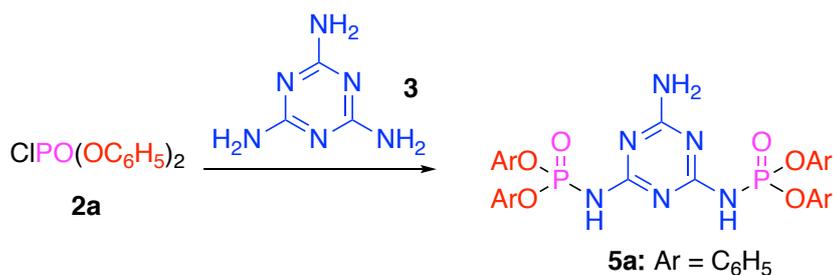
In a three-necked round-bottomed flask (500 mL) were placed THF (100 mL), pyridine (200 mL), and POCl_3 (59 mL, 632 mmol) under N_2 . To the cooled mixture in an ice-water bath (0–4 °C) was added dropwise a solution of phenol (**1a**, 113 g, 1.2 mol) in THF (20 mL) over 80 min. The mixture was allowed to warm gradually to room temperature and stirred overnight and then heated at 45 °C for 7 h. The resulting white suspension was diluted with THF (200 mL) and transferred to a cooled (0–4 °C) mixture of melamine (**3**, 40 g, 317 mmol), pyridine (60 mL), and MgCl_2 (550 mg) in THF (100 mL). Remaining solids in the flask were transferred by washing with THF (100 mL). The resulting mixture was allowed to warm to room temperature, and stirred overnight, and then heated at 60 °C for 17 h.

Workup procedure: The whole reaction mixture was transferred into a one-necked round flask (1 L) with toluene (100 mL) and most of solvents were removed on a rotary evaporator to dryness. The residue was co-evaporated with toluene (50 mL x 2) to remove remaining pyridine. The residual solids were partitioned with hot water (1 L) and filtered off while it is hot, and washed with hot water, and then with MeOH. Solids obtained were dried on a rotary evaporator at ~60 °C under vacuum to afford the crude **5a** (71.2 g, 38% based on melamine **3**). Recrystallized from pyridine- H_2O (4:1). **5a**: Chemical Formula: $\text{C}_{27}\text{H}_{24}\text{N}_6\text{O}_6\text{P}_2$, MW: 590.5.

5a: mp 260 °C (DSC) (ref. (1): 275–276°C); IR(ATR) : 3288, 1617, 1587, 1567, 1527, 1488, 1427, 1324, 1254, 1213, 1181, 1155, 1097, 1070, 1026, 1010, 969, 950, 906,

897, 869, 822, 778, 767, 752, 686, 616, 592, 568, 530, 516, 491, 479 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, DMSO-d_6) δ 7.13–7.18 (m, 4H), 7.22–7.24 (m, 8H), 7.26–7.31 (m, 8H), 10.1 (brs, 2H); $^{13}\text{C-NMR}$ (100 MHz, DMSO-d_6) δ 120.98 (d, $J = 4.8$ Hz), 125.75, 130.18, 150.63 (d, $J = 6.7$ Hz), 165.87 (one absorption peak based on the triazine core could not be detected in the $^{13}\text{C-NMR}$); $^{31}\text{P NMR}$ (162 MHz, DMSO-d_6) δ -9.32; MALDI-TOF (MS) for $\text{C}_{27}\text{H}_{24}\text{N}_6\text{O}_6\text{P}_2$: Calcd 590.12; found 590.75[M]⁺, 612.93[M+Na]⁺, 628.90[M+K]⁺; Anal. Calcd for $\text{C}_{27}\text{H}_{24}\text{N}_6\text{O}_6\text{P}_2$: C, 54.92; H, 4.10; N, 14.23%; Found: C, 55.11; H, 4.11; N, 14.44%.

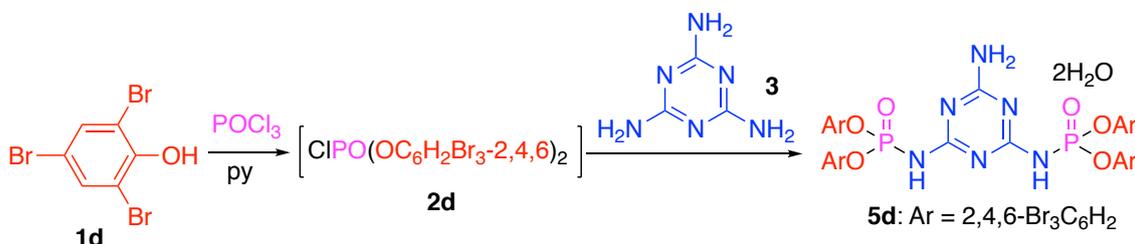
Tetraphenyl (6-amino-1,3,5-triazine-2,4-diyl)diphosphoramidate 5a; Method B from $\text{ClPO}(\text{OPh})_2$, **2a**):



To a suspension of melamine (**3**, 63 g, 500 mmol) in pyridine (800 mL) was added under cooling at 0–4 °C diphenyl chlorophosphate (**2a**, 297 g, 1.1 mol) dropwise over 60 min. The resulting mixture was stirred at room temperature for 3 h and at 60 °C for one day. The whole mixture was transferred to a one-necked round flask using toluene (300 mL) and most of solvent was evaporated on a rotary evaporator to dryness. The residual solids were co-evaporated with toluene (200 mL x 2) to remove remaining pyridine. To the residual materials was added hot water (500 mL) and the resulting suspension was heated at ~100 °C and filtered off while it is hot, and solids were washed with hot water. Solid obtained was dried at 90 °C under high vacuum to afford **5a** (238 g, 80% based on melamine **3**).

Tetrakis(2,4,6-tribromophenyl)

(6-amino-1,3,5-triazine-2,4-diyl)diphosphoramidate (**5d**); Method A from 2,4,6-tribromophenol (**1d**):



In a three-necked round-bottomed flask (500 mL) were placed MgCl₂ (530 mg), pyridine (60 mL), and POCl₃ (10.6 mL, 113.6 mmol) under N₂. To the cooled mixture in an ice-water bath (0–4 °C) was added dropwise a solution of 2,4,6-tribromophenol (**1d**, 76.6 g, 231.6 mmol) in THF (65 mL) over 80 min. The mixture was allowed to warm gradually to room temperature and stirred overnight and then heated at 50 °C for 12 h. The mixture was diluted with pyridine (70 mL) and cooled in an ice-water bath, and added to a melamine-powdery slurry (**3**, 13.7 g, 108.3 mmol) in THF (30 mL). The resulting mixture was allowed to warm to room temperature, and stirred overnight, and then heated at 60 °C for 24 h. The whole mixture was transferred to a one-necked round flask with toluene (100 mL) and most of solvent was evaporated on a rotary evaporator to dryness. The residual solids were co-evaporated with toluene (100 mL x 2) to remove remaining pyridine, which was followed by addition of hot water (500–700 mL) and the resulting suspension was heated at ~95 °C, and filtered off while it is hot, and solids were washed with hot water. Solids on a Büchner funnel were dried at 90 °C under high vacuum to afford the crude **5d**•2H₂O (89.54 g).

The whole of this solid was suspended in a mixed solution of MeOH (300 mL) and AcOEt (10 mL), and heated at reflux for 3 h. After being cooled to room temperature, the mixture was filtered and dried at 90 °C under vacuum to give the desired diphosphoramidate dihydrate **5d**•2H₂O, 83.42 g (53.0 mmol, 22.9% yield based on 2,4,6-tribromophenol (**1d**) or 46% yield based on melamine), purity ca. 96% by ¹H NMR analysis. The filtrate portion contained a mixture of tris(2,4,6-tribromophenyl)

phosphate (main) and unknown products (6.1 g), determined by ^1H NMR analysis.

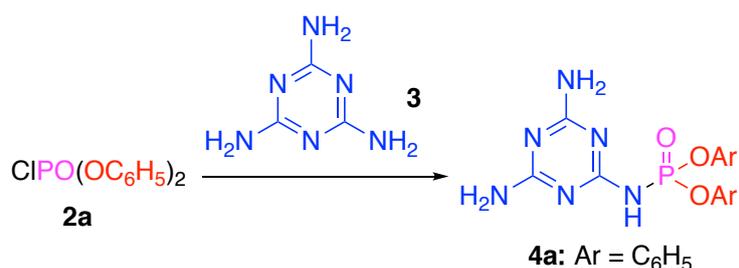
The diphosphoramidate **5d** can be recrystallized from DMSO-THF or Pyridine- H_2O .

5d: Chemical Formula $\text{C}_{27}\text{H}_{12}\text{Br}_{12}\text{N}_6\text{O}_6\text{P}_2 \cdot 2\text{H}_2\text{O}$, MW: 1573.2.

Mp 274 °C (DSC); IR(ATR): 3414, 1665, 1547, 1510, 1434, 1371, 1258, 1232, 1214, 1160, 1083, 1060, 916, 857, 739,728, 687, 645, 579, 553, 519, 481 cm^{-1} ; ^1H -NMR (400 MHz, DMSO- d_6) δ 4.55 (br), 7.51 (s, 8H, ArH), 7.81 (s, 2H, NH_2); ^{13}C -NMR (100 MHz, DMSO- d_6) δ 117.02, 118.75 (d, $J = 3.8$ Hz), 135.07, 148.96 (d, $J = 7.6$ Hz), 160.16 (one absorption peak based on the triazine core could not be detected in the ^{13}C -NMR); ^{31}P NMR (162 MHz, DMSO- d_6) δ -13.69. Anal. Calcd for $\text{C}_{27}\text{H}_{12}\text{Br}_{12}\text{N}_6\text{O}_6\text{P}_2 \cdot 2\text{H}_2\text{O}$: C, 20.61; H, 1.03; N, 5.34%. Found: C, 20.72; H, 0.92; N, 5.59%.

Tris(2,4,6-tribromophenyl) phosphate; ref. (2) : mp 257.9°C (DSC); ^1H -NMR (400 MHz, DMSO- d_6) δ 7.84 (s, 6H, ArH); ^{13}C -NMR (100 MHz, DMSO- d_6) δ 117.54, 118.63 (d, $J = 6.7$ Hz), 135.21, 148.39 (d, $J = 7.6$ Hz); ^{31}P NMR (162 MHz, DMSO- d_6) δ -14.92.

Diphenyl (4,6-diamino-1,3,5-triazin-2-yl)phosphoramidate (4a), ref. (3).



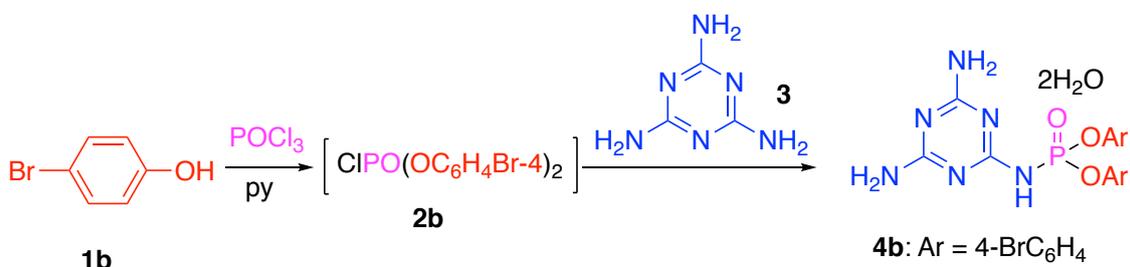
To a suspension of melamine (**3**, 8.3 g, 65.5 mmol) in THF (30 mL) containing pyridine (5 mL) and triethylamine (2 mL) was added dropwise with cooling at 0–4 °C diphenyl chlorophosphate (**2a**, 13.3 g, 49.5 mmol) over 30 min. The resulting mixture was allowed to warm to room temperature and stirred for 24 h and heated at 45 °C for 24 h. The whole mixture was transferred to a one-necked round flask using toluene (50

mL) and most of the solvent was evaporated on a rotary evaporator to dryness. To the residual materials was added hot water (200 mL) and the resulting mixture was agitated at ~80 °C to form a dispersion solution. The solids were filtered off while it is hot and washed with hot water. Solid obtained was dried under a high vacuum to afford **4a** (4.23 g, 24% based on diphenyl chlorophosphate **2a**). **4a**: Chemical Formula C₁₅H₁₅N₆O₃P, MW: 358.3.

4a: mp 217.2 °C (DSC); ¹H-NMR (400 MHz, DMSO-d₆) δ 6.92–6.95 (m, 2H), 7.10–7.12 (m, 4H), 7.17–7.21 (m, 4H), 7.37 (brs, 4H); ¹³C-NMR (100 MHz, DMSO-d₆) δ 120.43 (d, *J* = 4.8 Hz), 123.26, 129.59, 153.48 (d, *J* = 6.6 Hz), 160.51 (one absorption peak based on the triazine core could not be detected in the ¹³C-NMR); ³¹P NMR (162 MHz, DMSO-d₆) δ -9.91. MALDI-TOF (MS) for C₁₅H₁₅N₆O₃P: Calcd 358.09; found 381.15 m/z [M+Na]⁺;

Bis(4-bromophenyl) (4,6-diamino-1,3,5-triazin-2-yl)phosphoramidate (**4b**);

Method A from 4-bromophenol (**1b**):



In a similar manner as above, the title compound was prepared by addition of 4-bromophenol (**1b**, 39.15 g, 226 mmol) in THF (50 mL) to a solution of POCl₃ (11 mL, 118 mmol) in pyridine (28 mL) and THF (50 mL) with cooling at 0–4 °C over 60 min under N₂. Stirring was continued at room temperature overnight and at 40 °C for 3 h. The resulting mixture was transferred drop by drop to a cooled (0–4 °C) suspension of melamine (**3**, 21.5 g, 170 mmol) in pyridine (12 mL) and THF (80 mL), and the remaining white precipitates were thoroughly transferred with THF (50 mL), and the resulting mixture was stirred at room temperature overnight and at 40 °C for 3 h. The

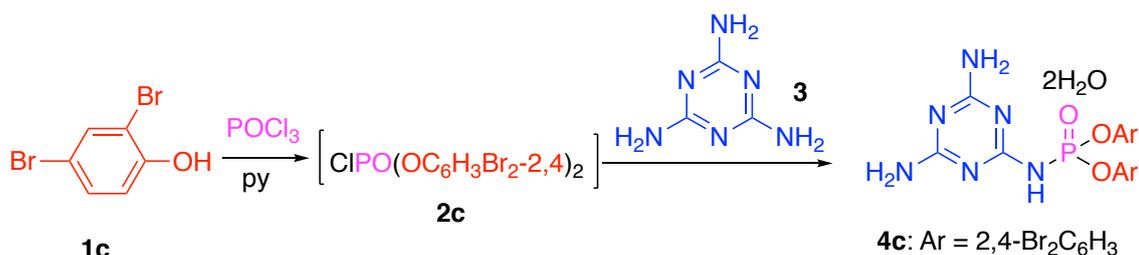
reaction mixture was worked up in a similar manner as the case of **5d**, which was followed by washing with hot water, and then filtrated to give the desired monophosphoramidate **4b**•2H₂O, 54.82 g (41% yield based on **1b**, purity 94%), contaminated with a small amount of tris(4-bromophenyl) phosphate (ca. 6%). The washing of this crude product in hot MeOH (ca. 500 mL) and filtration gave pure **4b**•2H₂O (36.46 g, more than 96% pure by ¹H NMR analysis). **4b**: Chemical Formula C₁₅H₁₃Br₂N₆O₃P•2H₂O, MW: 552.1.

4b: mp 220.3 °C (DSC); IR (ATR): 3438, 3409, 1666, 1464, 1273, 1220, 1199, 1088, 1074, 1040, 946, 929, 913, 817, 800, 789, 771, 666, 632, 568, 546, 538, 523, 506, 494, 473 cm⁻¹; ¹H-NMR (400 MHz, DMSO-d₆) δ 3.16 (brs, 1H, NH), 7.10 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.68 (brs, 4H, NH₂); ¹³C-NMR (100 MHz, DMSO-d₆) δ 115.0, 122.65 (d, *J* = 4.8 Hz), 132.38, 152.98 (d, *J* = 7.6 Hz), 160.41 (one absorption peak based on the triazine core could not be detected in the ¹³C-NMR); ³¹P NMR (162 MHz, DMSO-d₆) δ -10.55. Anal. Calcd for C₁₅H₁₃Br₂N₆O₃P•2H₂O: C, 32.63; H, 3.10; N, 15.22%. Found: C, 32.86; H, 2.73; N, 15.50%.

Tris(4-bromophenyl) phosphate: mp 109.8 °C (DSC); IR (ATR): 3412, 1718, 1676, 1581, 1513, 1480, 1400, 1298, 1230, 1199, 1174, 1090, 1066, 1010, 979, 929, 912, 822, 766, 740, 634, 621, 545, 525, 493, 482 cm⁻¹; ¹H-NMR (400 MHz, DMSO-d₆) δ 7.27 (d, *J* = 9.0 Hz, 2H), 7.64 (d, *J* = 9.0 Hz, 2H); ¹³C-NMR (100 MHz, DMSO-d₆) δ 118.42, 122.27 (d, *J* = 4.8 Hz), 133.23, 148.92 (d, *J* = 6.7 Hz); ³¹P NMR (162 MHz, DMSO-d₆) δ -17.296.

Bis(4,6-dibromophenyl) (4,6-diamino-1,3,5-triazin-2-yl)phosphoramidate (4c);

Method A from 2,4-dibromophenol (**1c**):



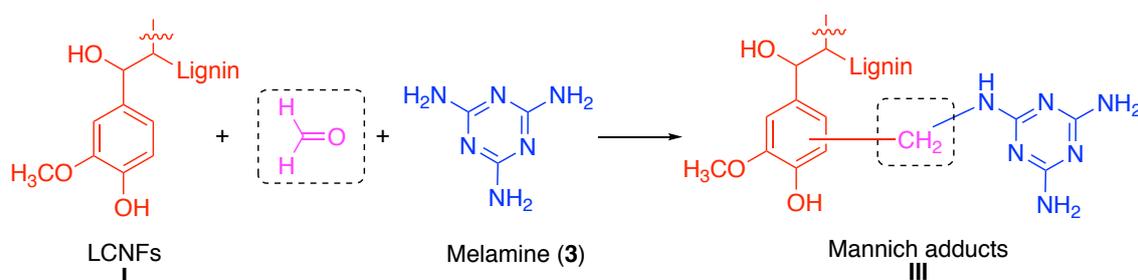
A solution of 2,4-dibromophenol (**1c**, 25.3 g, 100.4 mmol) in THF (25 mL) was added to a mixture of POCl₃ (5.0 mL, 53.5 mmol), pyridine (15 mL), and THF (50 mL) with cooling at 0–4 °C under N₂, and the stirring was continued at room temperature overnight and at 40 °C for 5 h. The resulting white suspension was transferred to a cooled (0~4 °C) mixture of melamine (**3**, 9.45 g, 74.9 mmol), pyridine (5 mL, 62 mmol), and THF (50 mL). Solids remaining in the flask were transferred using THF (50 mL). The mixture was allowed to warm to room temperature and stirred overnight, and then heated at 40 °C for overnight. Workup as above followed by the partition of the solids with hot water (500 mL), and filtration gave the phosphoramidate dihydrate **4c**•2H₂O (29.3 g, 39% yield based on **1c**) (purity 94%), contaminated with a small amount of tris(2,4-dibromophenyl) phosphorate (ca. 5%). The product was further purified by heating in AcOEt followed by filtration and washing with MeOH (400 mL) with heating to give pure **4c**•2H₂O (15.72 g). **4c**: Chemical Formula

C₁₅H₁₁Br₄N₆O₃P•2H₂O, MW: 709.9.

4c: mp 208.8 °C (DSC); IR (ATR): 3438, 3409, 1666, 1464, 1273, 1220, 1199, 1088, 1074, 1040, 946, 913, 817, 789, 666, 633, 629, 568, 546, 523 cm⁻¹; ¹H-NMR (400 MHz, DMSO-d₆) δ 3.50 (br, 1H, NH), 7.48 (d,d, *J* = 8.4, 2.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.71 (brs, 4H, NH₂), 7.75 (d, *J* = 2.4 Hz, 2H); ¹³C-NMR (100 MHz, DMSO-d₆) δ 115.0, 115.1 (d, *J* = 8.6 Hz), 122.7, 131.4, 134.7, 149.6 (d, *J* = 5.8 Hz), 159.5 (one absorption peak based on the triazine core could not be detected in the ¹³C-NMR); ³¹P-NMR (162 MHz, DMSO-d₆) δ -11.81; Anal. Calcd for C₁₅H₁₁Br₄N₆O₃P•2H₂O: C, 25.38; H, 2.13; N, 11.84%. Found: C, 25.62; H, 1.84; N, 11.63%.

4. Mannich Reactions of LCNFs.

Mannich reaction of LCNFs with melamine (2,4,6-triamino-1,3,5-triazine, **3) and HCHO, leading to **III**:**



In a 1 L cylindrical flask, were placed LCNFs (CellFim L-45TM) (aq. 94.68% dispersion 97 g, dry weight 5.2 g), melamine **3** (2,4,6-triamino-1,3,5-triazine, MW: 126.12) (767 mg, 6.08 mmol), cetyltrimethylammonium bromide (105 mg), and H₂O (500 mL). The mixture was swirled and sonicated for several minutes before the reaction, and then formalin (5 mL) was added. The entire mixture was stirred at room temperature for 3 h, at 50 °C for 3 h, and at 70 °C for 33 h. After cooling to room temperature, the mixture was filtered and washed with hot water to give the three-component products **III** as an aqueous 79.8% dispersion (dry weight 5.3 g). EA of **III**: C, 48.49; H, 6.34; N, 3.24.

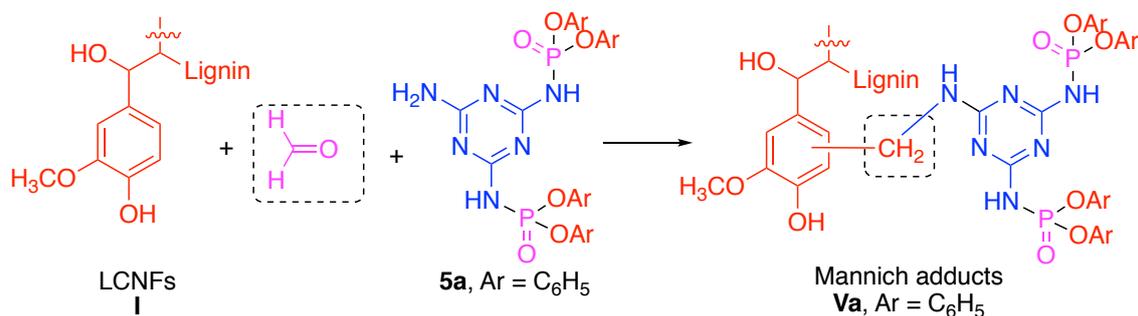
EA of virgin freeze-dried LCNFs: C, 48.33; H, 6.38; N, --.

IR (ATR) of melamine (**3**): 3467, 3416, 3318, 3112, 2343, 2118, 1997, 1907, 1626, 1524, 1464, 1429, 1169, 1019, 873, 809, 760, 728, 686, 672, 608, 581, 455 cm⁻¹.

IR (ATR) of virgin freeze-dried LCNFs (CellFim L-45TM): 3339, 2903, 2110, 1638, 1509, 1452, 1424, 1370, 1316, 1266, 1160, 1111, 1058, 1033, 897, 664, 594, 560, 519, 494, 479, 457 cm⁻¹.

IR (ATR) of freeze-dried Mannich products **III** (**3**/LCNFs = 2 mmol/g): 3339, 2903, 1589, 1509, 1453, 1424, 1369, 1335, 1317, 1265, 1160, 1110, 1058, 1033, 898, 813, 663, 611, 559, 522, 487, 466, 455 cm⁻¹.

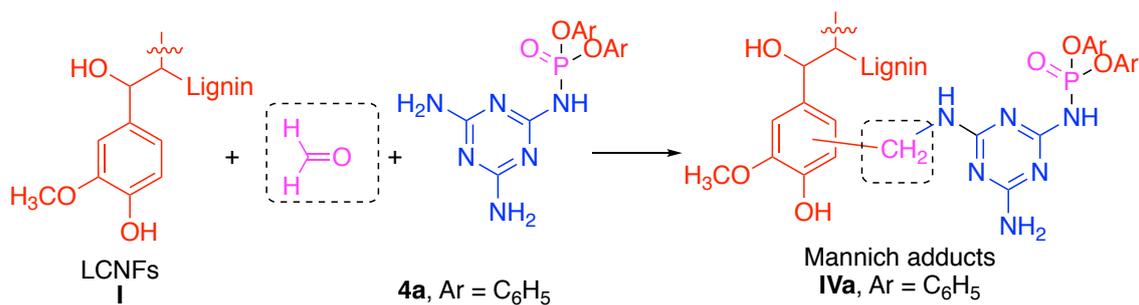
Mannich reaction of LCNFs with 5a (Ar = C₆H₅) and HCHO, leading to Va:



Typical experimental procedure for Mannich reaction of LCNFs with **5a** (Ar = C₆H₅) and HCHO: In a 2 L cylindrical flask were placed LCNFs (CellFim L-45™) (aq. 94.97% dispersion, 268 g, dry weight: 13.4 g), **5a** (Ar = C₆H₅) (tetraphenyl (6-amino-1,3,5-triazine-2,4-diyl)diphosphoramidate, MW: 590.47) (11 g, 18.6 mmol), cetyltrimethylammonium bromide (191 mg), and H₂O (1 L). The mixture was swirled and sonicated for several minutes before the reaction, and then formalin (13 mL) was added. The entire mixture was stirred at room temperature for 3 h, at 50 °C overnight, and the additional formalin (3 mL) was added and stirred at 70 °C for 3 h. During the reaction, when white small particles due to unreacted **5a** were preserved, sonication was repeated. After cooling to room temperature, the mixture was filtered and washed with water to give the three-component products **Va** (Ar = C₆H₅) as an aqueous 70.9% dispersion (89.3 g, dry weight 26 g).

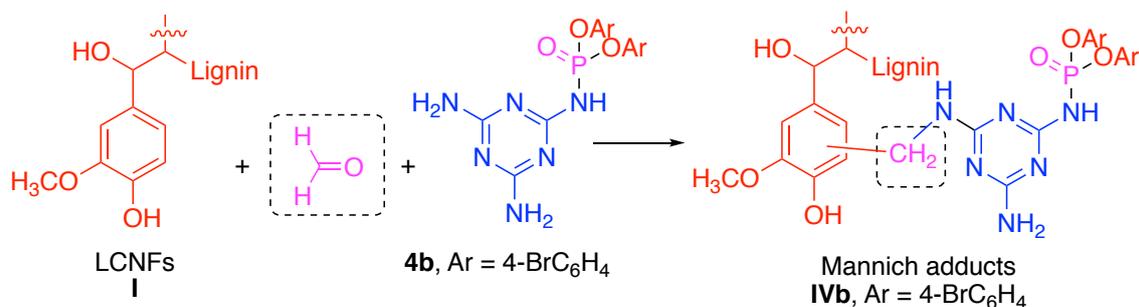
Va: FT-IR (ATR) of **Va** (Ar = C₆H₅), freeze-dried (**5a**/LCNFs = 1.05 mmol/g): 3339, 2901, 1589, 1488, 1448, 1371, 1336, 1246, 1209, 1185, 1159, 1104, 1059, 1033, 1011, 971, 939, 905, 870, 823, 777, 766, 753, 686, 616, 593, 568, 536, 517, 503, 495, 481 cm⁻¹; EA: C, 51.77; H, 5.41; N, 3.64; P, 3.36.

Mannich reaction of LCNFs with 4a (Ar = C₆H₅) and HCHO, leading to IVa:



In a 100 mL round-bottomed flask, were placed consecutively LCNFs (CellFim L-45™) (aqueous 88.5% dispersion, 8.9 g, dry weight 1 g), **4a** (Ar = C₆H₅) (bisphenyl(4,6-diamino-1,3,5-triazine-2-yl)phosphoramidate, MW: 358.3) (487 mg, 1.36 mmol), cetyltrimethylammonium bromide (42 mg), and H₂O (80 mL). The mixture was sonicated several minutes with swirling before the reaction, and then formalin (1 mL) was added. After stirring at 50 °C for 21 h and at 70 °C for 5 h, the mixture was cooled to room temperature, filtered and washed consecutively with water, acetone, and water, giving **IVa** (Ar = C₆H₅), an aqueous 72.1% dispersion 5.0 g, dry weight 1.4 g. EA: C, 50.65; H, 5.97; N, 2.76.

Mannich reaction of LCNFs with 4b (Ar = 4-BrC₆H₄) and HCHO, leading to IVb:

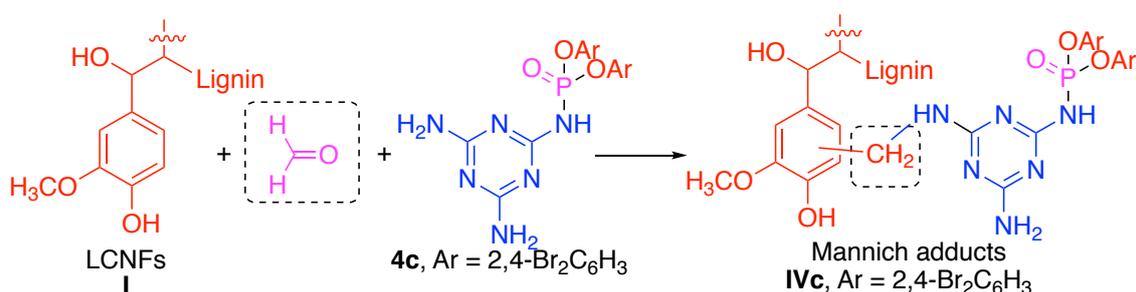


In a 200 mL round-bottomed flask, were placed consecutively LCNFs (CellFim L-45™) (aqueous 88.5% dispersion, 26.5 g, dry weight 3 g), **4b**•2H₂O (Ar = 4-BrC₆H₄) (bis(4-bromophenyl)(4,6-diamino-1,3,5-triazine-2-yl)phosphoramidate•dihydrate, MW: 552.1144) (2.16 g, 3.9 mmol), cetyltrimethylammonium bromide (113 mg), and H₂O (170 mL). The mixture was sonicated several minutes with swirling before the reaction, and then formalin (3 mL) was added. After stirring at 50 °C for 17 h, additional formalin (1 mL) was added and stirred at 70 °C for 5 h. After cooling to room

temperature, the mixture was filtered and washed consecutively with water, acetone, and water, giving the Mannich adducts **IVb** (Ar = 4-BrC₆H₄), an aqueous 76.2% dispersion, 15.65 g, dry weight 3.7 g.

EA: C, 49.27; H, 6.09; N, 2.25.

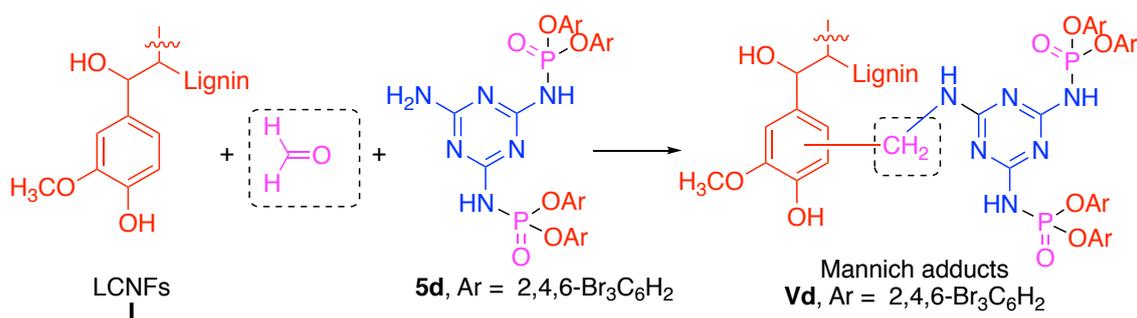
Mannich reaction of LCNFs with 4c (Ar = 2,4-Br₂C₆H₃) and HCHO, leading to IVc:



In a 200 mL round-bottomed flask, were placed consecutively LCNFs (CellFim L-45™) (aqueous 88.5% dispersion, 26.6 g (dry weight: 3 g), **4c**•2H₂O (Ar = 2,4-Br₂C₆H₃) (bis(2,4-dibromophenyl)(4,6-diamino-1,3,5-triazine-2-yl) phosphoramidate•dihydrate, MW: 709.9066) (2.81 g, 3.96 mmol), cetyltrimethylammonium bromide (92 mg), and H₂O (170 mL). The mixture was sonicated several minutes with swirling before the reaction, and then formalin (3 mL) was added. After being stirred at 50 °C for 18 h, the mixture was sonicated and formalin (1 mL) was added, then heating was continued at 70 °C for. After cooling to room temperature, the mixture was filtered and washed consecutively with water, acetone, and water, giving the Mannich adducts **IVc** (Ar = 2,4-Br₂C₆H₃), an aqueous 71.9% dispersion, 17.6 g, dry weight 4.8 g.

EA: C, 42.80; H, 4.56; N, 4.98.

Mannich reaction of LCNFs with 5d (Ar = 2,4,6-Br₃C₆H₂) and HCHO, leading to Vd:



In a 100 mL round-bottomed flask, were placed consecutively LCNFs (CellFim L-45™) (aqueous 89.3% dispersion 9.38 g, dry weight 1 g), **5d**•2H₂O (Ar = 2,4,6-Br₃C₆H₂) (755 mg, 0.48 mmol), cetyltrimethylammonium bromide (41 mg), and H₂O (70 mL). The mixture was sonicated several minutes with swirling before the reaction, and then formalin (1 mL) was added. The entire mixture was stirred at 50 °C for 12 h and at 70 °C overnight. After cooling to room temperature, the mixture was filtered and washed consecutively with water, acetone, and water. The solid obtained was dried at 90 °C under high vacuum to give **Vd** (Ar = 2,4,6-Br₃C₆H₂), 1.58 g, as a hard mass.

FT-IR (ATR) of freeze-dried **Vd** (**5d**/LCNFs = 1 mmol/g): 3413, 3341, 2903, 1714, 1665, 1548, 1510, 1435, 1372, 1257, 1234, 1212, 1160, 1112, 1082, 1059, 1034, 918, 859, 792, 739, 728, 687, 672, 643, 580, 553, 521, 481 cm⁻¹; EA: Found: C, 38.37; H, 4.14; N, 2.46.

Large scale procedure (5 g): In a 1 L cylindrical flask, were placed consecutively LCNFs (CellFim L-45™) (aqueous 91.5% dispersion 58 g, dry weight 5 g), **5d**•2H₂O (MW: 1573.2469) (5.08 g, 3.2 mmol), cetyltrimethylammonium bromide (168 mg), and H₂O (800 mL). The mixture was sonicated several minutes with swirling, and then formalin (5 mL) was added. The entire mixture was stirred at room temperature and warmed gradually to 50 °C. When the mixture was stirred for 12 hours, sonication was repeated to ensure that the mass of **5d** was broken. Additional formalin (2 mL) was added and heating was continued at 70 °C overnight and at 80 °C for 4 h. After cooling to room temperature, the mixture was filtered and washed with water to give **Vd** (Ar = 2,4,6-Br₃C₆H₂), 33.1 g (aqueous 69.1% dispersion, dry weight 10.2 g).

Larger scale procedure (28 g): In a 3L tall flask, were placed consecutively LCNFs (CellFim L-45) (aqueous 94.7% dispersion, 518 g (anhydrous weight 27.55 g), **5d**•2H₂O (MW: 1573.2469) (22.76 g, 14.47 mmol), cetyltrimethylammonium bromide (490 mg), and H₂O (the mixture was adjusted to a total amount of ca. 2.2 L). This mixture was sonicated for several minutes with swirling, and then formalin (30 mL) was added. The entire mixture was stirred at 48 °C for 15 h and at 65 °C overnight. Additional formalin (5 mL) and cetyltrimethylammonium bromide (50 mg) were added and heating was continued at 75 °C for 7 h. After cooling to room temperature, the mixture was filtered and washed consecutively with water, acetone, and water to give the three-component reaction products **Vd** as an aqueous 77.5% dispersion, 221 g (dry weight: 49.7 g).

5. Fabrication and Characterization of the Modified LCNFs Composites.

Preparation of PP/flame retardant LCNF composite material. The freeze-dried flame-retardant-treated LCNF and powdered PP (Novatec MA 3, manufactured by Japan Polypropylene Corporation) were mixed together at a ratio of 10:90 and blended using an extreme mill (MX-1100 XTS manufactured by WARING). This mixture was subjected to solid phase shearing treatment with a kneader (Roller Mixer R60 manufactured by Toyo Seiki Seisaku-sho, Ltd.). Subsequently, 10% of maleic acid-modified PP (Kayabrid 002PP manufactured by Kayaku Akzo Chemical Co., Ltd.) was added to the total amount of the recovered mixture, and after thorough stirring, melting was performed using a twin-screw extruder (2D 15 W made by Toyo Seiki Seisaku-sho, Ltd.) And kneading was carried out. The obtained strand was pelletized with a pelletizer and a test piece for strength test was prepared using an injection-molding machine (Babyplast 6/10 P made by Rambaldi). The test piece was allowed to stand at room temperature for 1 week and sufficiently crystallized before use in the strength test.

Dispensability of PP/flame retarded LCNF composite.

The pellets prepared in the above item 2 were formed into a film by a press machine and observed under natural light and polarized light (crossed Nicole). As a result, aggregates derived from LCNF and bubbles due to poor interfacial adhesion (compatibility) were not visually confirmed, suggesting that the dispensability of flame retardant LCNF in the resin is relatively good.



For measurement of tensile strength and bending strength, AGS-5 kNG made by Shimadzu was used. For Izod impact strength measurement, No. 258-D manufactured by Yasuda Seiki Seisakusho was used.

Cone Calorimeter Combustion:

Water-based paint comprised of acrylic urethane emulsion, 34.3% (Gen Gen Corporation, Japan, SC-91™) was used for formulation with LCNFs fabric. Blended sample was prepared by mixing an equal amount of SC-91™ (100 g) and aqueous 3.87% NPCM-treated LCNFs fabric **Vd (5d)**/untreated LCNFs = 0.63 mmol/g, 100 g). This mixed material was sprayed on an iron plate (10 x 10 cm²) to 30 μm (thin film when dried) and air-dried.

	SC-91™ (aqueous 34.3%)	LCNFs fabric Vd (5d) /untreated LCNFs = 0.63 mmol/g, aqueous 3.87%)
Reference	100 g	0
Blended sample	100 g	100 g

Cone Calorimeter Combustion: each specimen is wrapped in aluminium foil and

exposed horizontally to the external heat flux, e.g. 35 kW/m². Results are given in Table.

Heat release experiment using cone calorimeter.^{a)}

	SC-91™	Blended SC-91™ with Vd
Total calorific value ^{b)}	1.12	0.69

^{a)}Painting process: Spray 30 µm (thin film when dried) on an iron plate. ^{b)} Combustion test: total calorific value (MJ/m²) for 20 min.

6. Supplementary Figures, Tables, Pictures, and Videos.

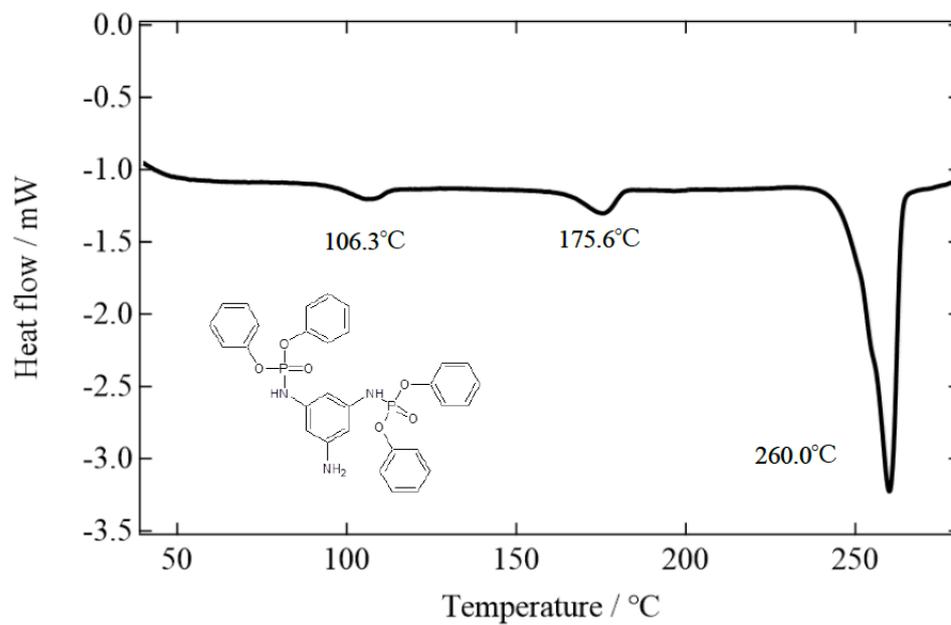


Fig.S1 The Differential scanning calorimetry (DSC) of **5a**.

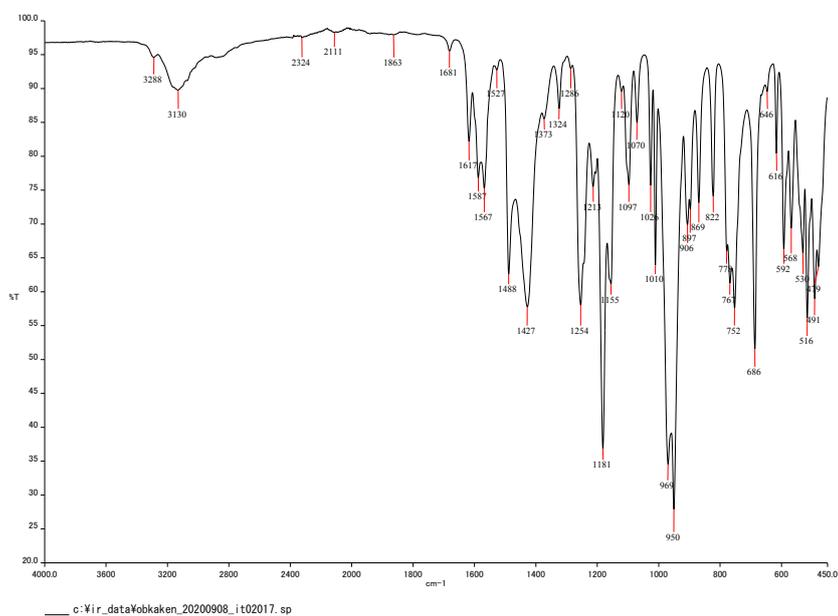


Fig.S2 The FT-IR (ATR) of **5a**.

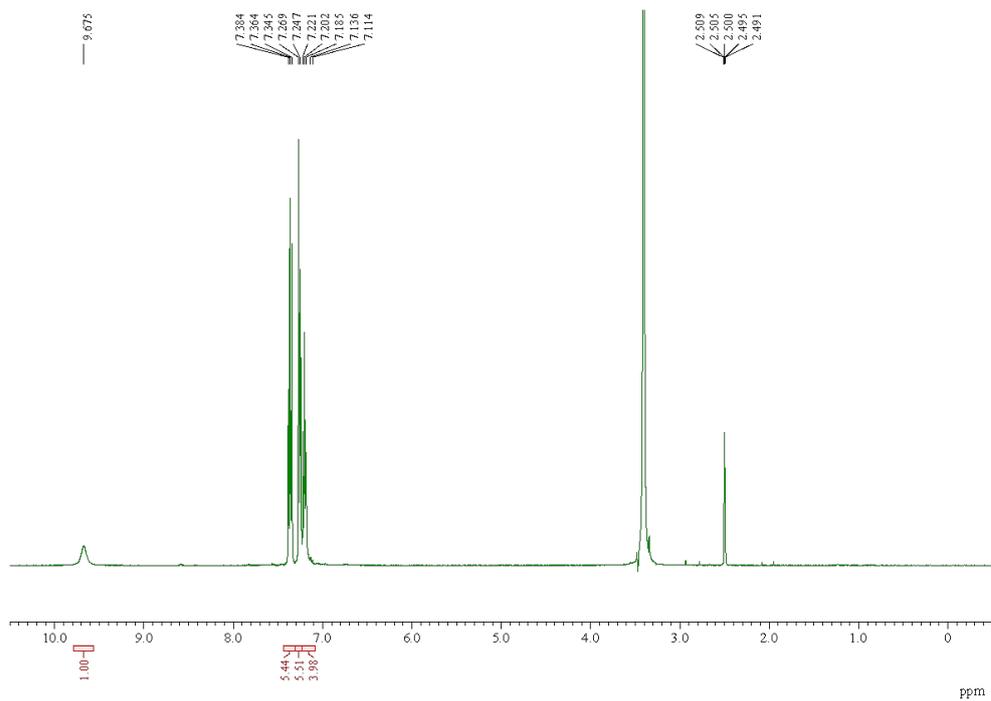


Fig.S3a The ¹H-NMR spectrum of **5a**.

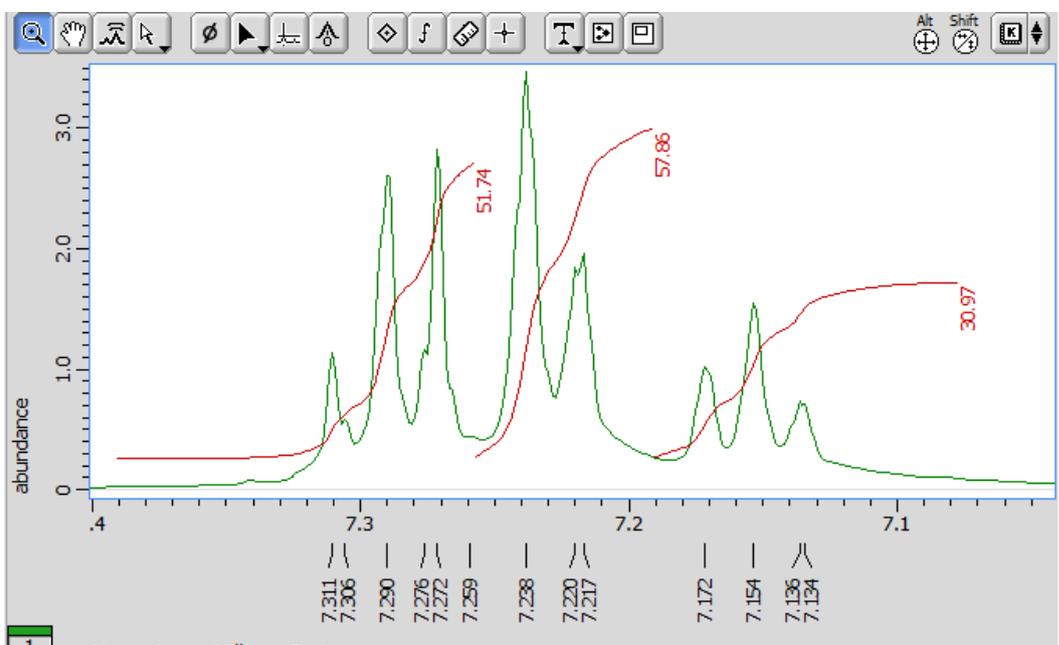


Fig.S3b The ¹H-NMR spectrum (expanded) of **5a**.

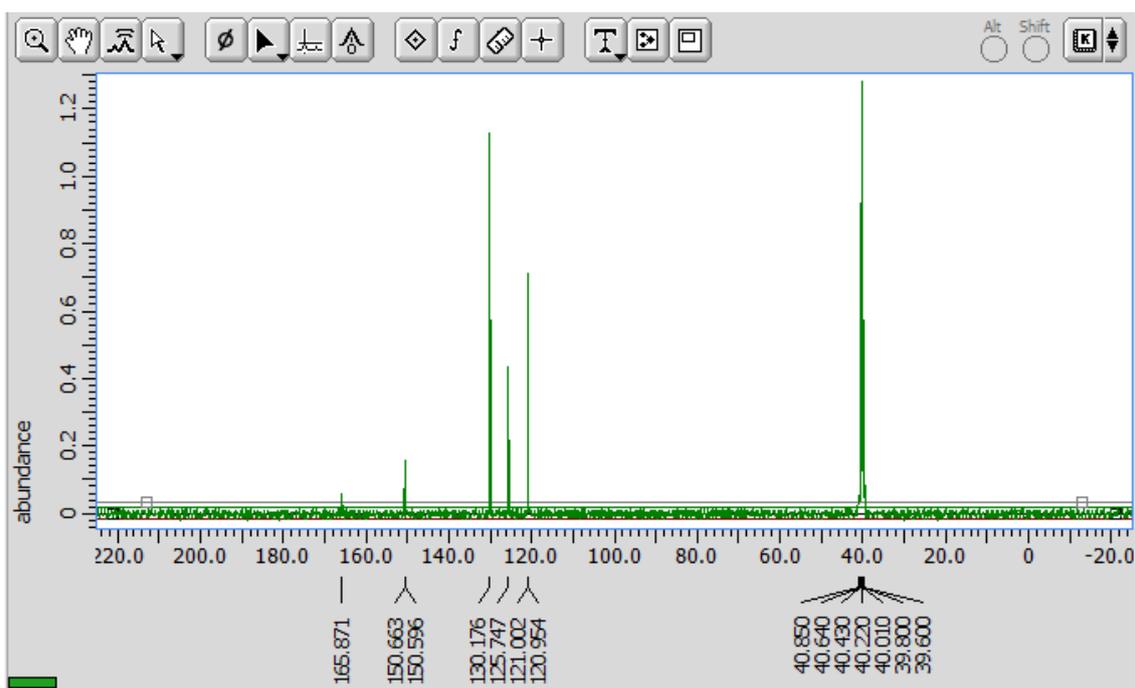


Fig.S4 The ^{13}C -NMR spectrum of 5a.

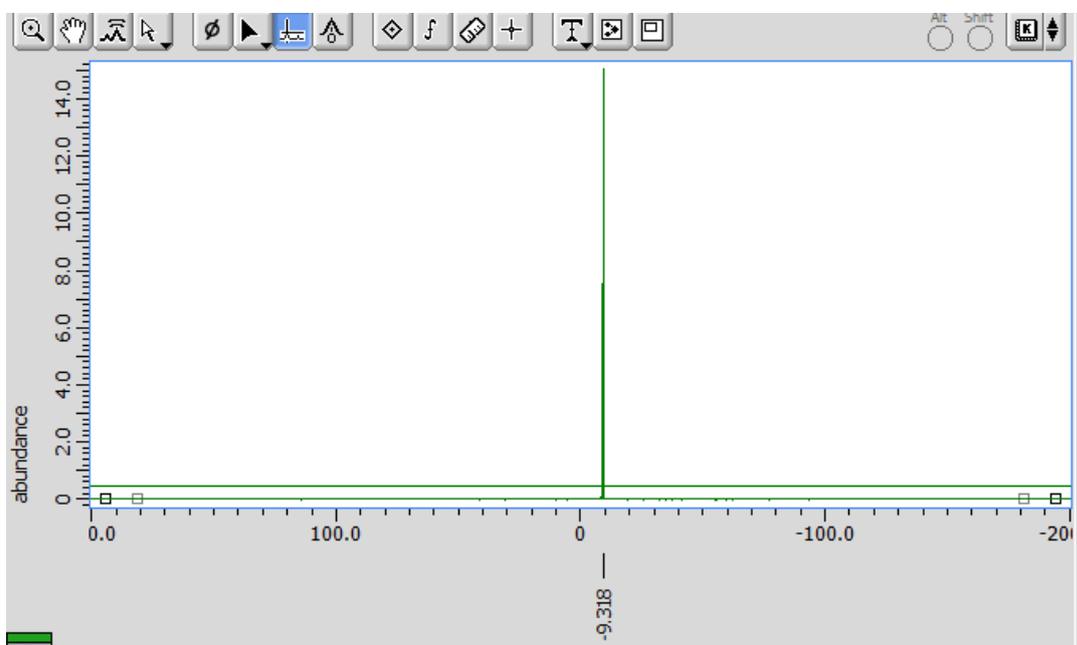


Fig.S5 The ^{31}P NMR spectrum of 5a.

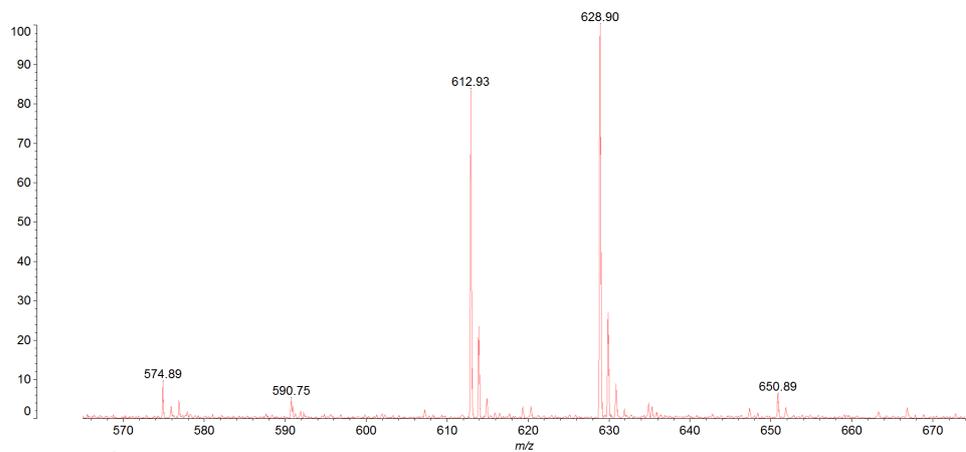


Fig.S6 The MALDI-TOF result of **5a**.

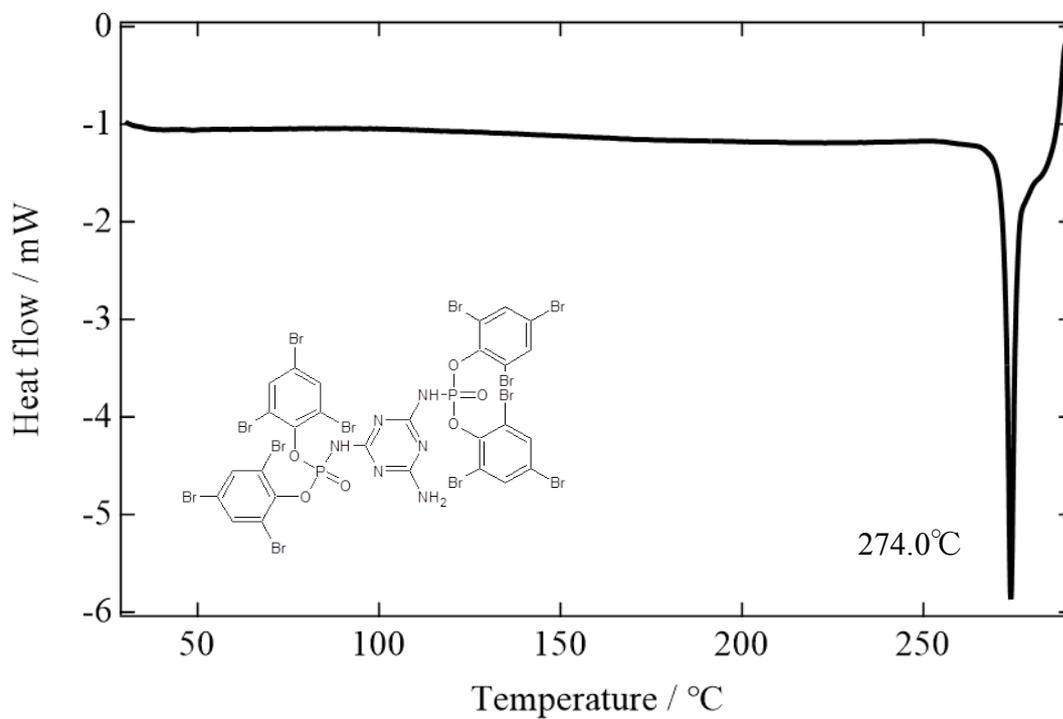


Fig.S7 The DSC of **5d**.

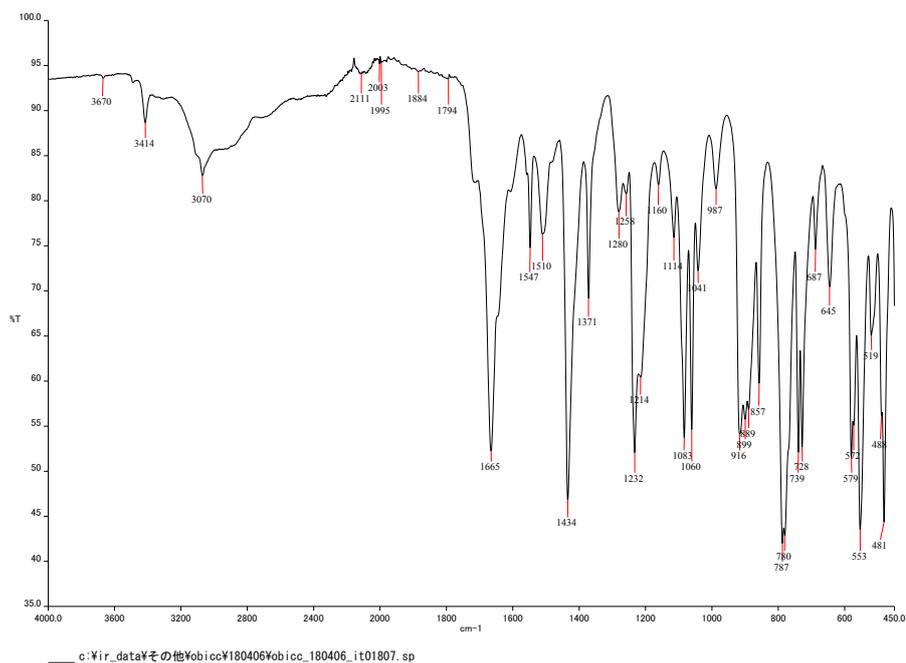


Fig.S8 The FT-IR (ATR) of **5d**.

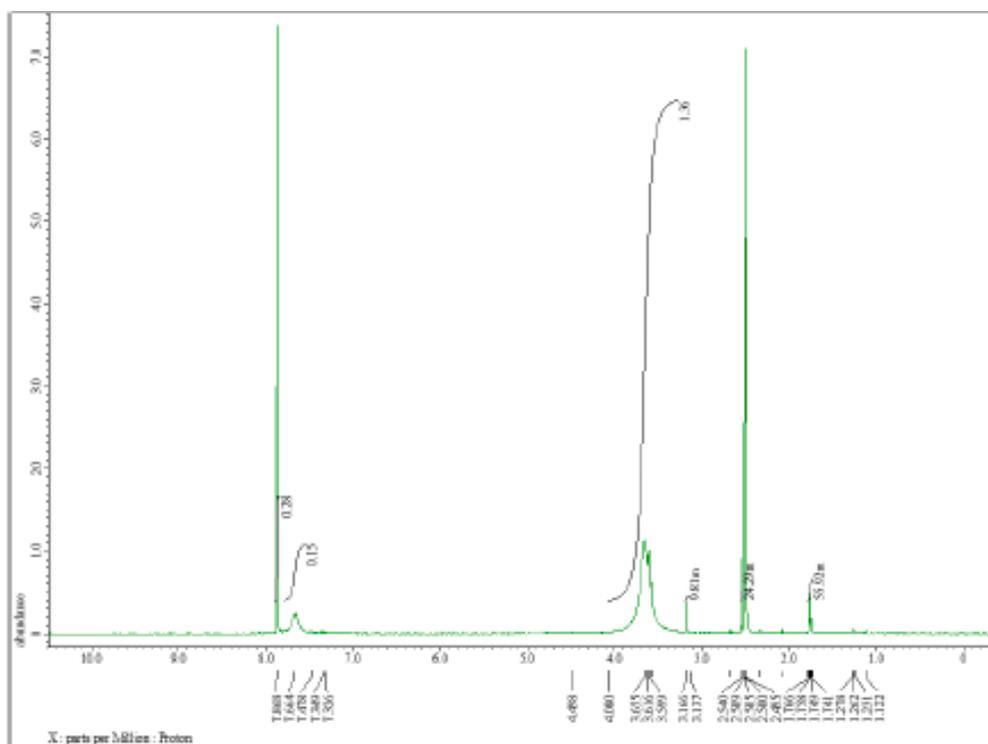


Fig.S9 The ¹H-NMR spectrum of **5d**.

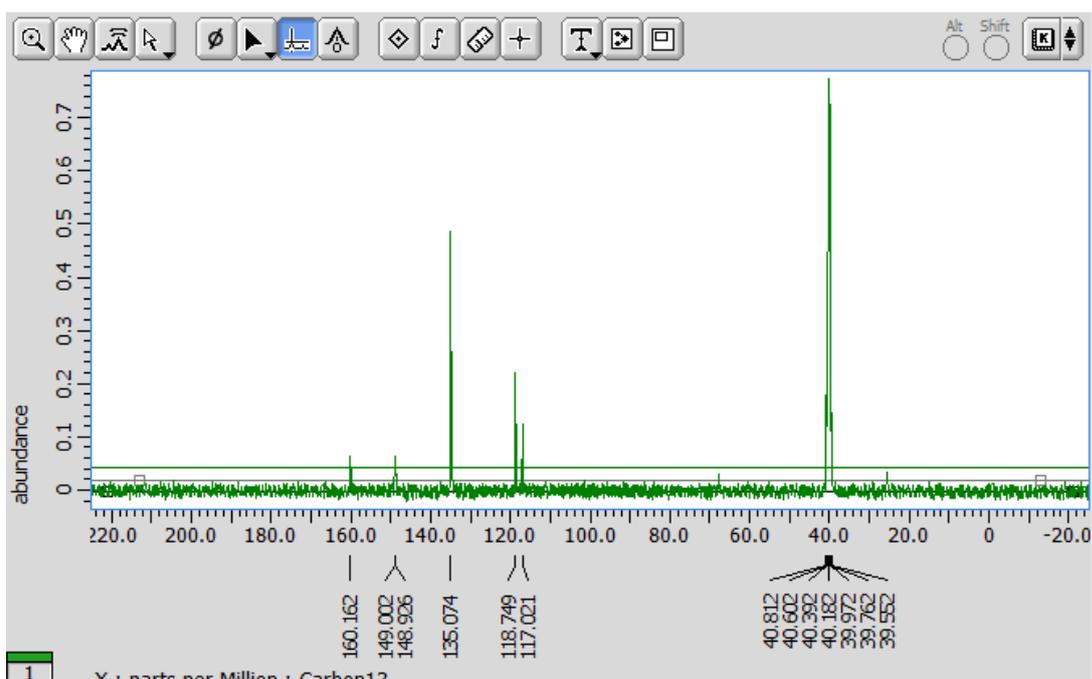


Fig.S10 The ^{13}C -NMR spectrum of 5d.

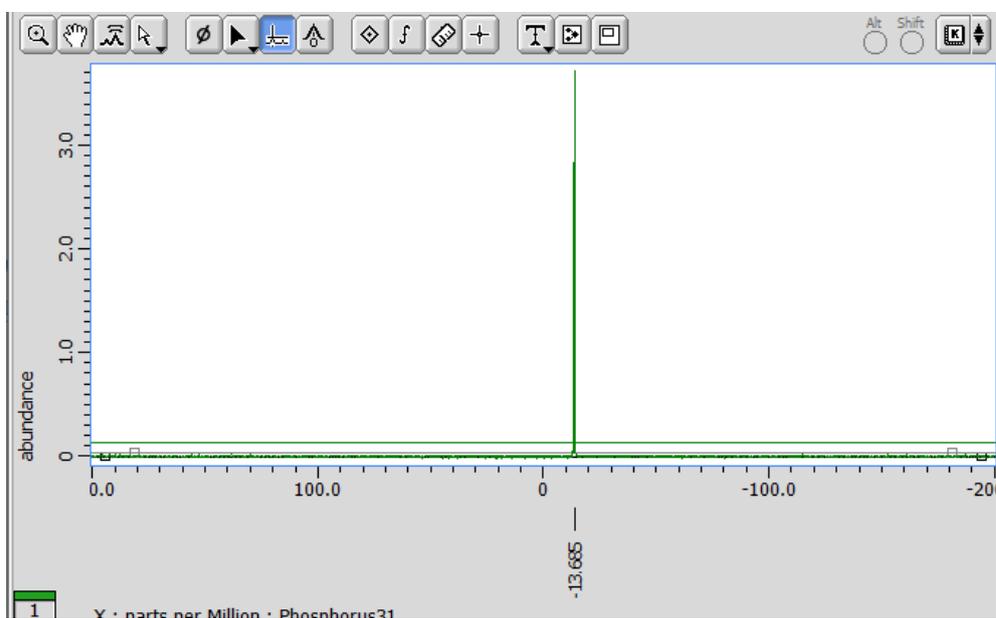


Fig.S11 The ^{31}P NMR spectrum of 5d.

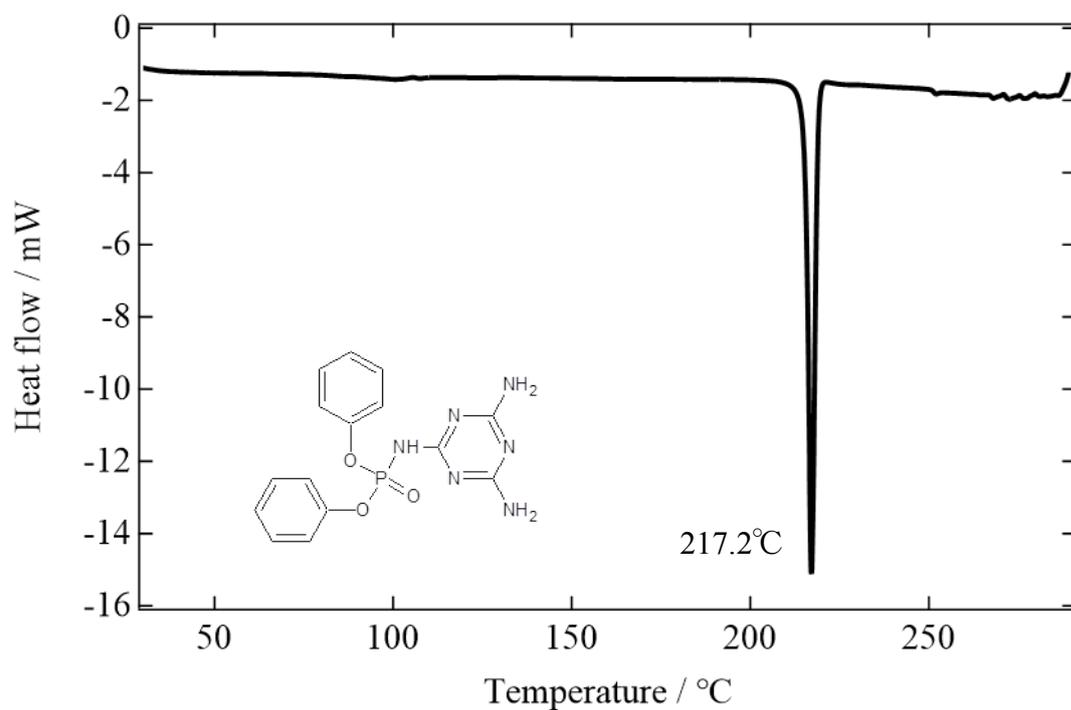


Fig.S12 The DSC of 4a.

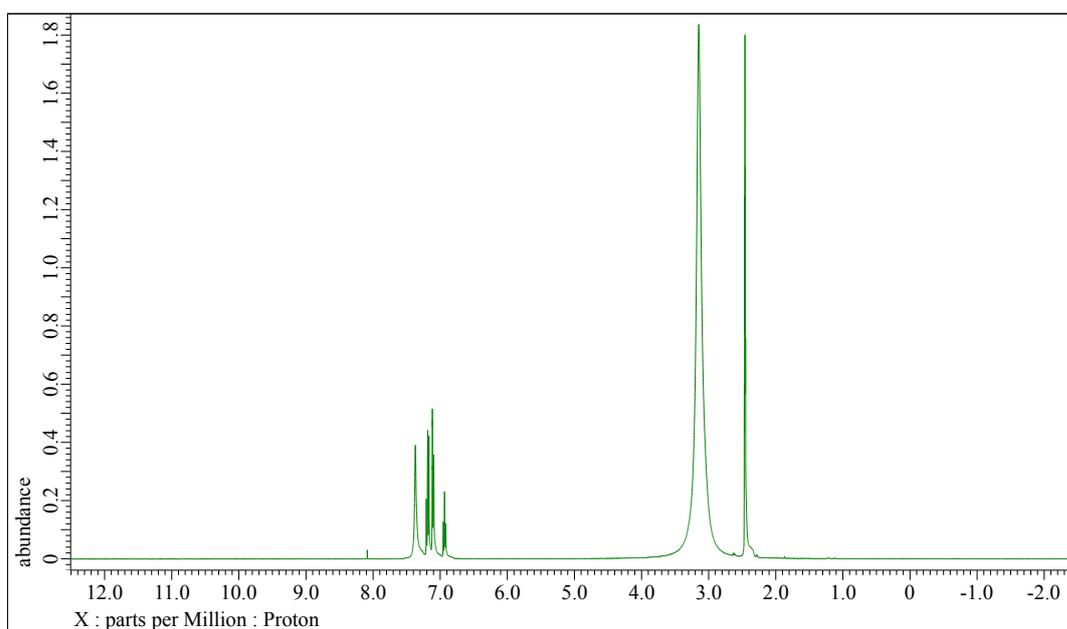


Fig.S13a The ¹H-NMR spectrum of 4a.

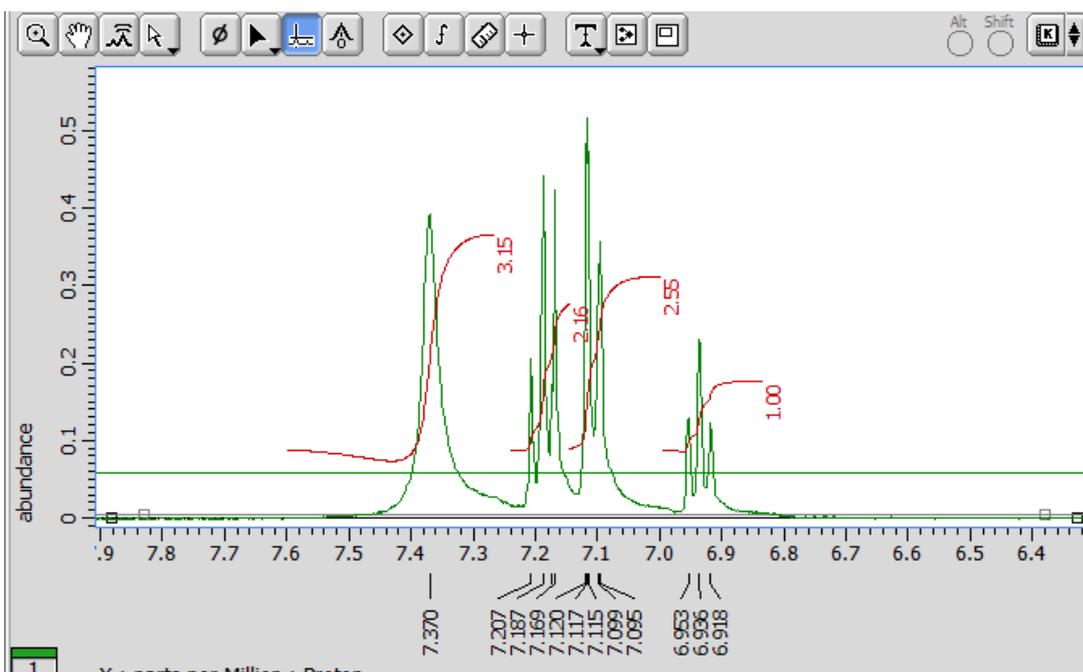


Fig.S13b The ^1H -NMR spectrum (expanded) of 4a.

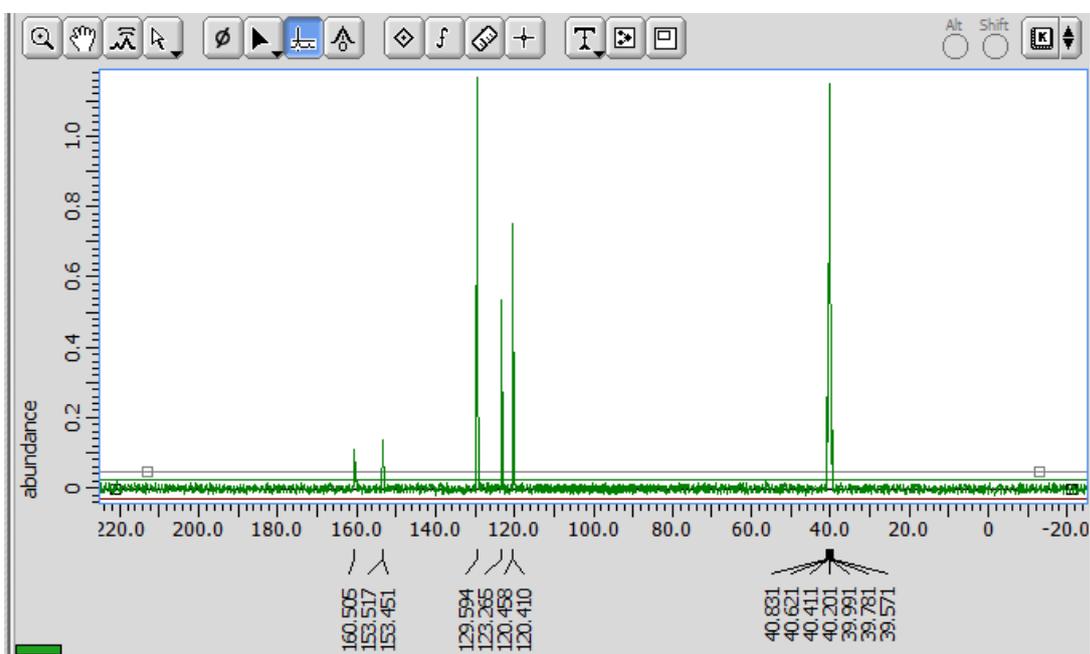


Fig.S14 The ^{13}C -NMR spectrum of 4a.

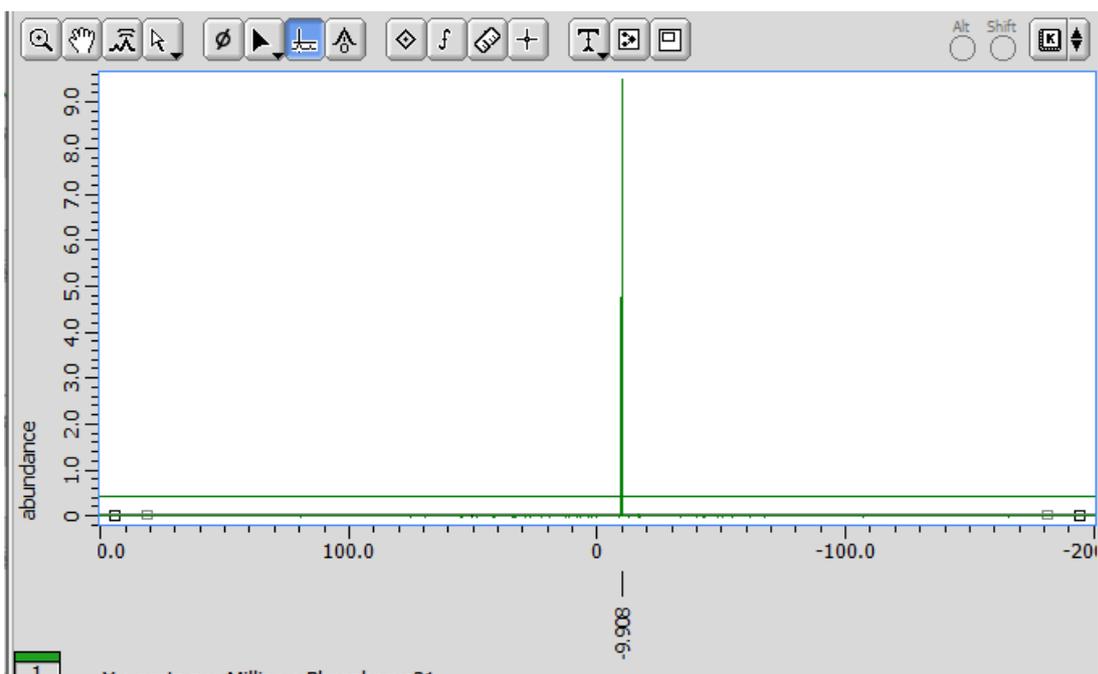


Fig.S15 The ^{31}P NMR spectrum of **4a**.

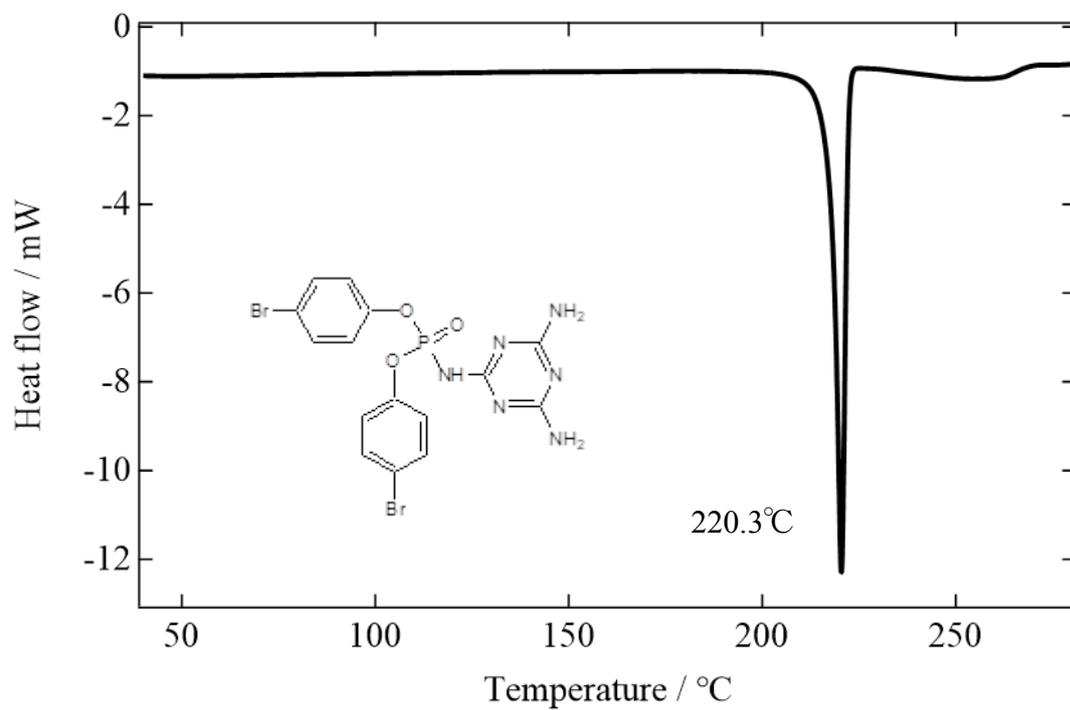


Fig.S16 The DSC of **4b**.

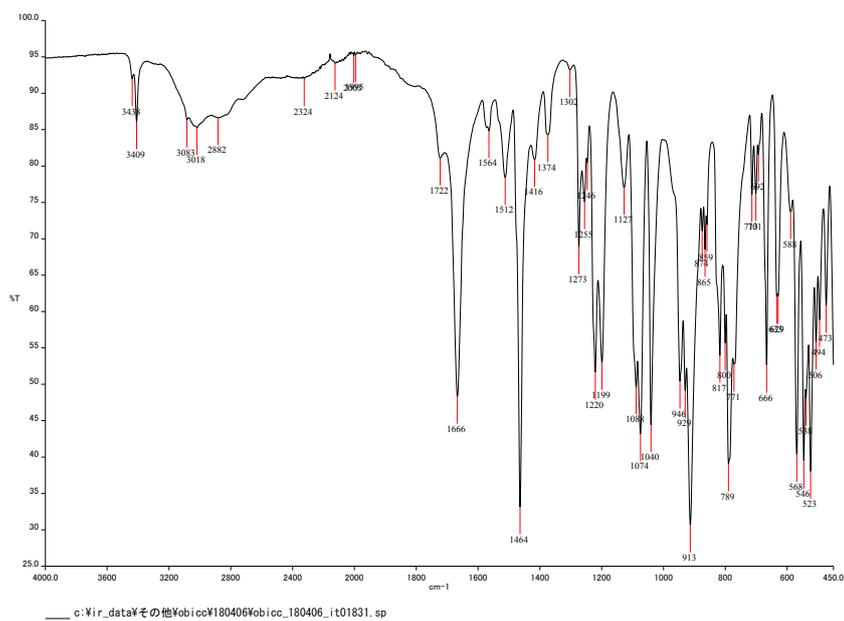


Fig.S17 The FT-IR (ATR) of 4b.

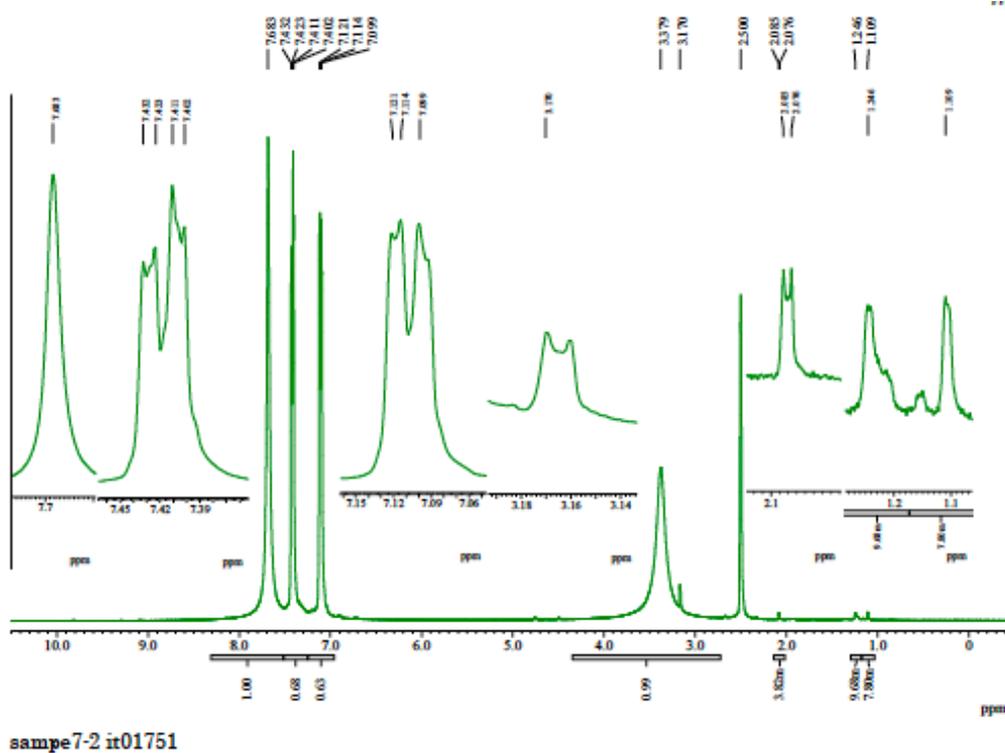
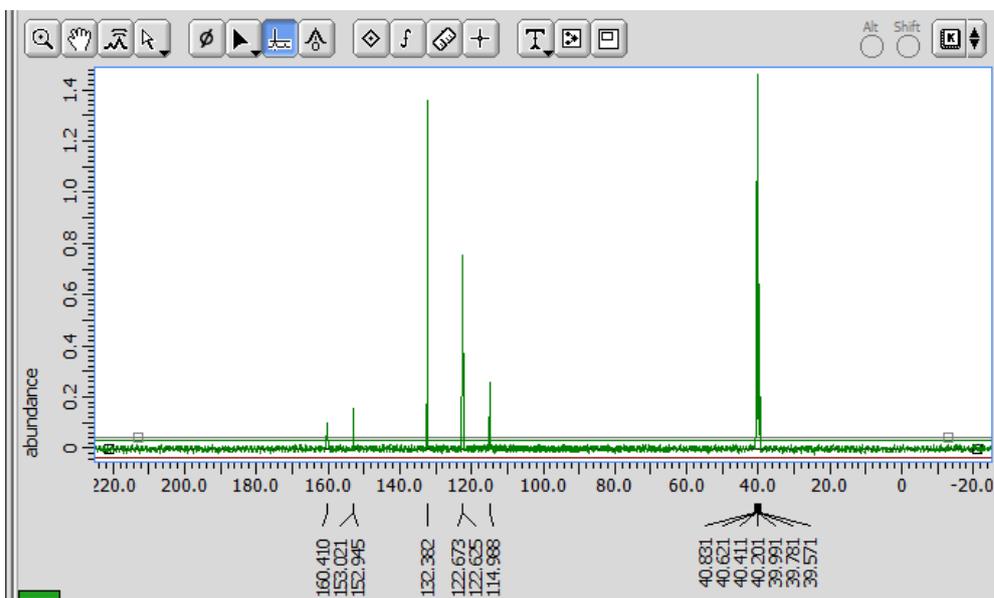


Fig.S18 The ¹H-NMR spectrum of 4b.



07-26 13C

Fig.S19 The ^{13}C -NMR spectrum of **4b**.

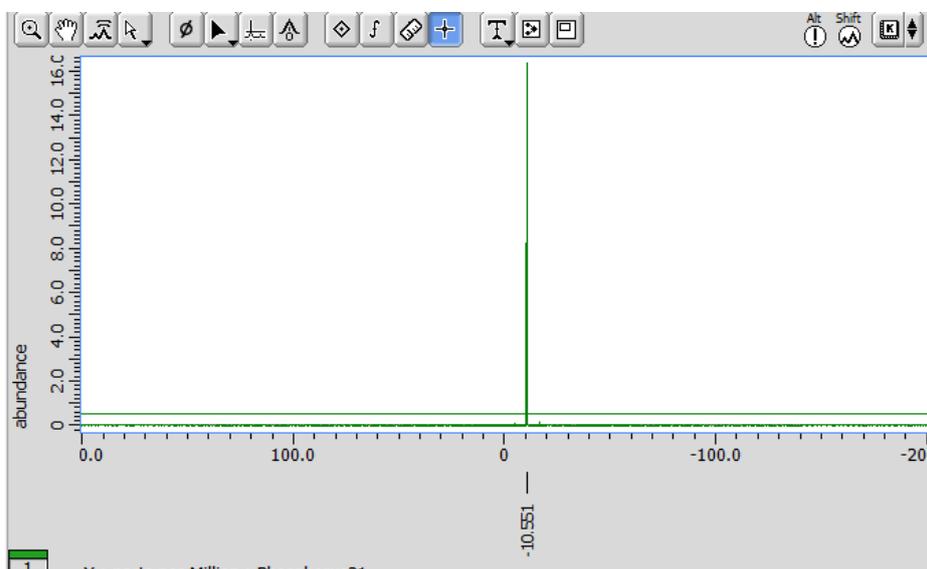


Fig.S20 The ^{31}P NMR spectrum of **4b**.

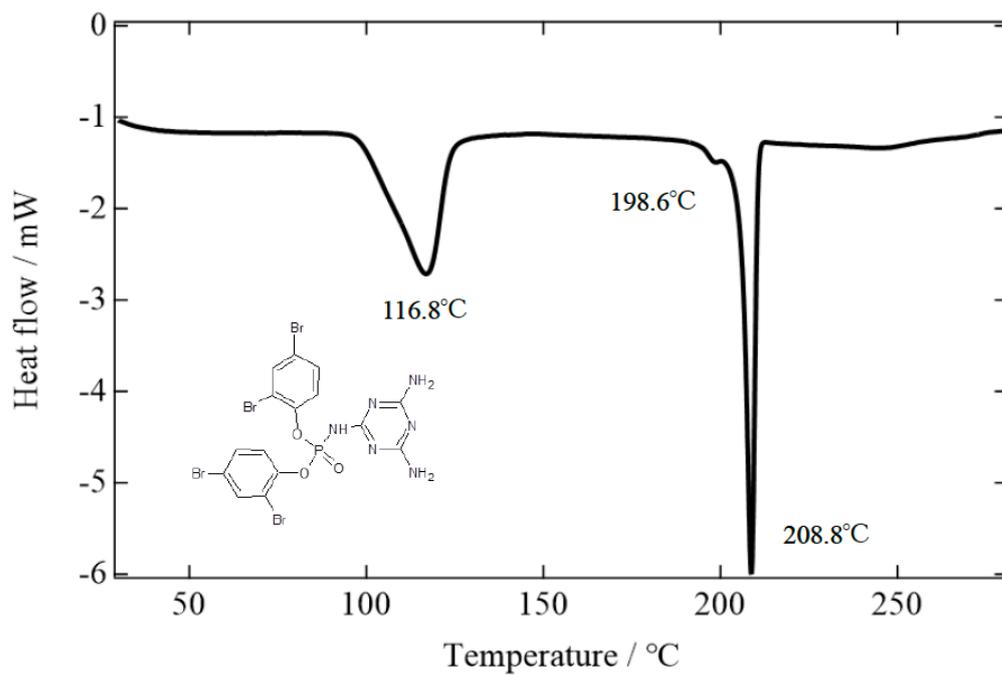


Fig.S21 The DSC of 4c.

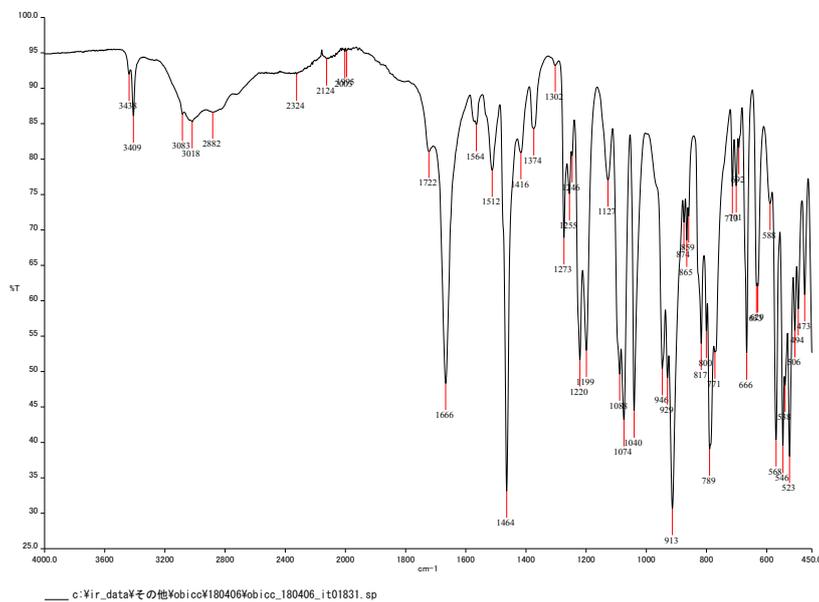


Fig.S22 The FT-IR (ATR) of 4c.

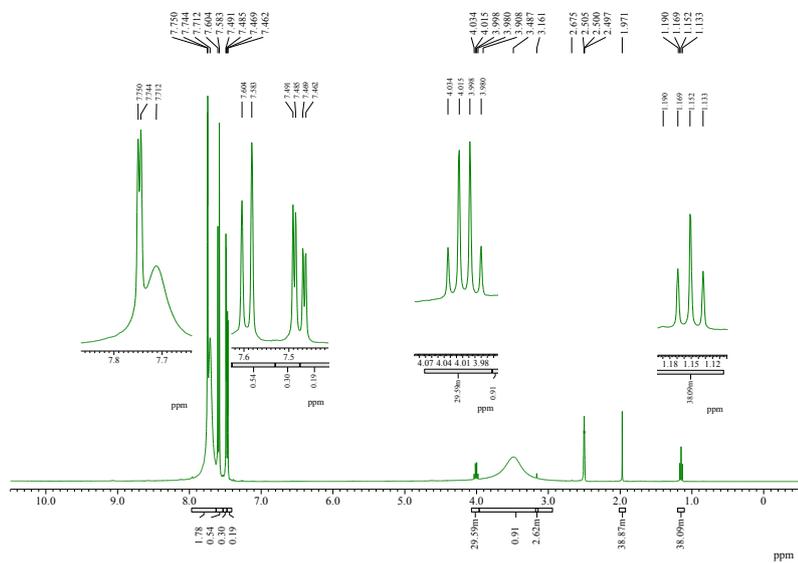
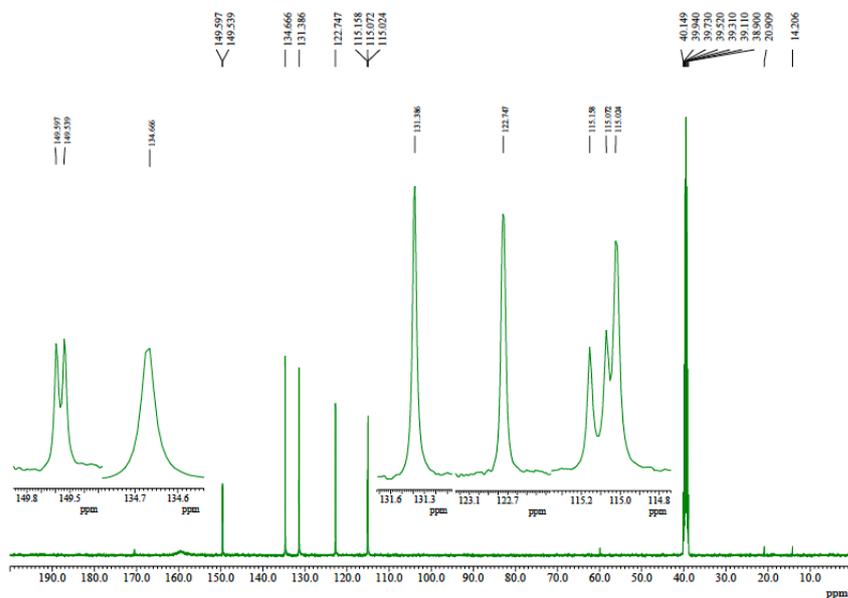


Fig.S23 The ^1H -NMR spectrum of **4c**.



sample4 it1811 CNMR

Fig.S24 The ^{13}C -NMR spectrum of **4c**.

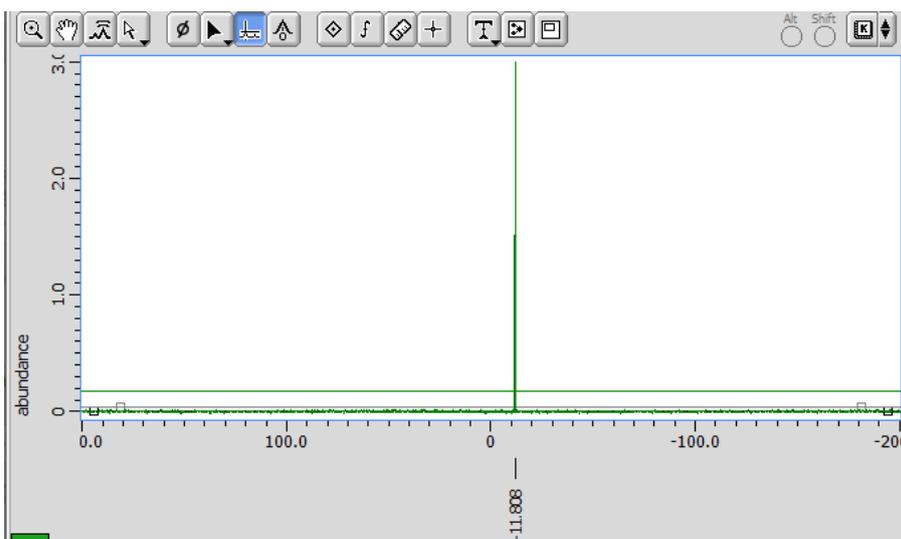


Fig.S25 The ^{31}P NMR spectrum of **4c**.

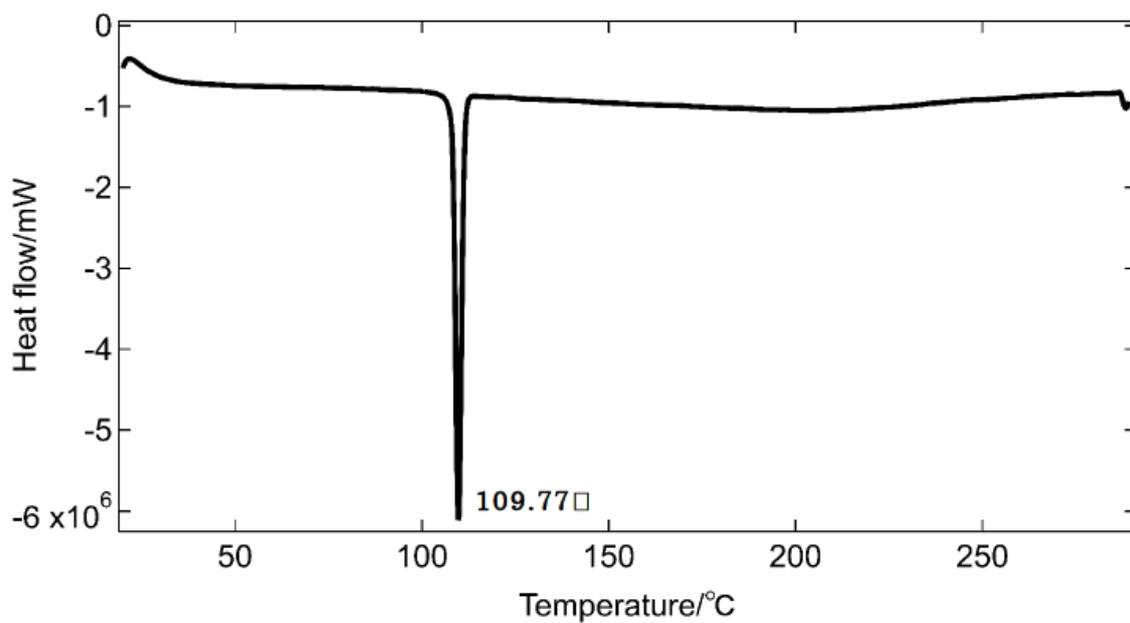
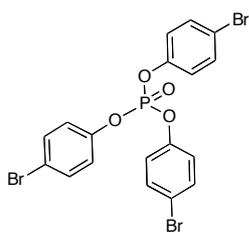


Fig.S26 The DSC of tris(4-bromophenyl) phosphate.

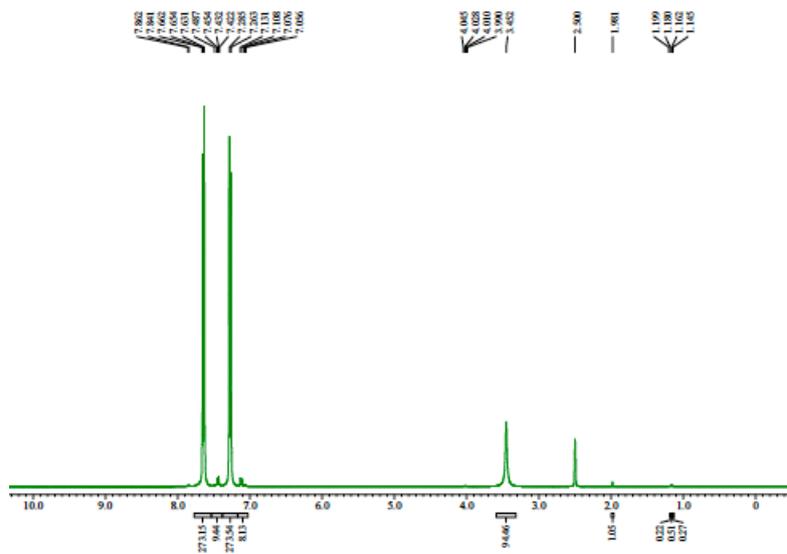


Fig.S27 The ^1H -NMR spectrum of tris(4-bromophenyl) phosphate.

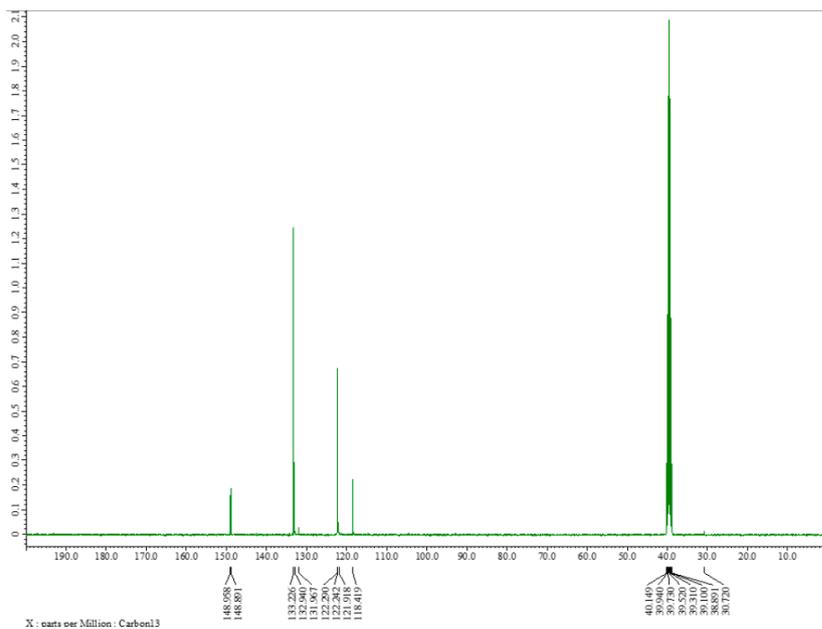


Fig.S28 The ^{13}C -NMR of tris(4-bromophenyl) phosphate.

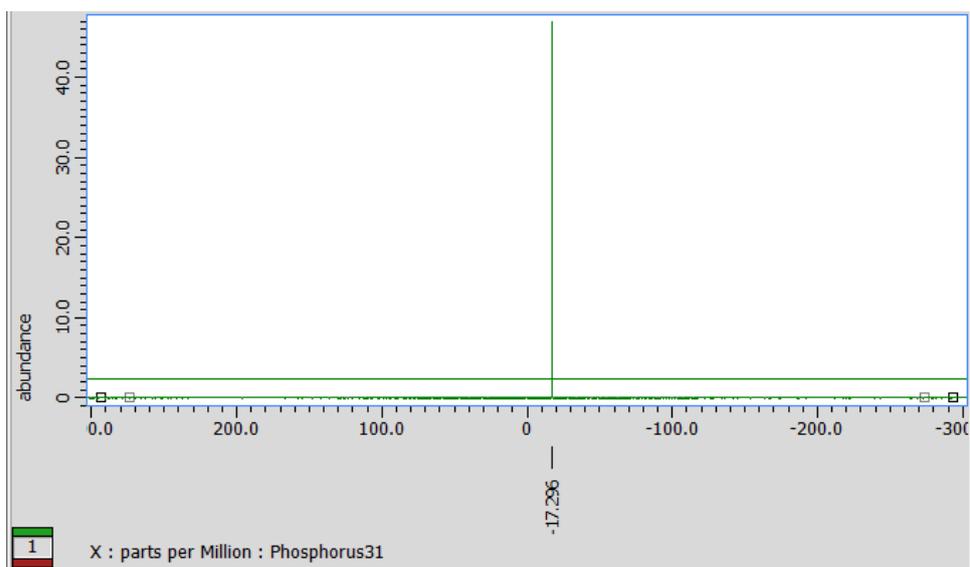


Fig.S29 The ^{31}P NMR spectrum of tris(4-bromophenyl) phosphate.

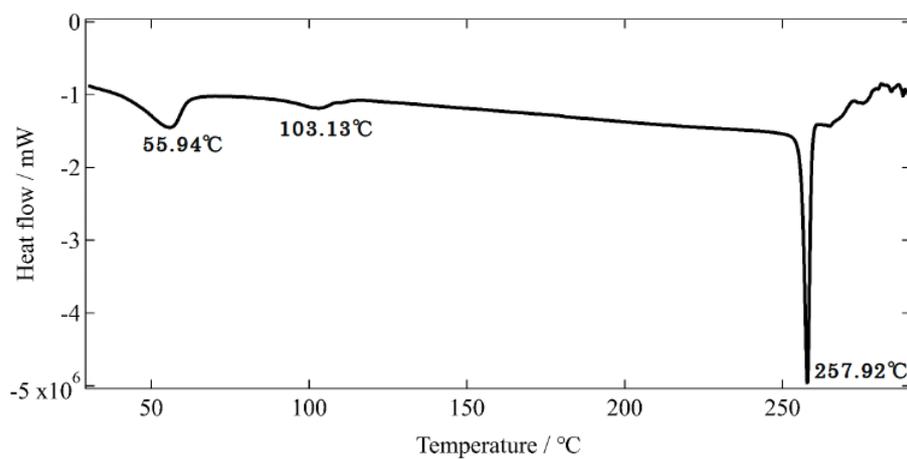
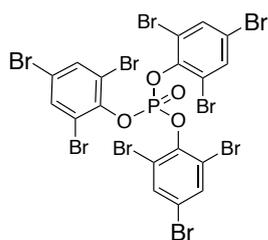


Fig.S30 The DSC of tris((2,4,6-tribromophenyl) phosphate.

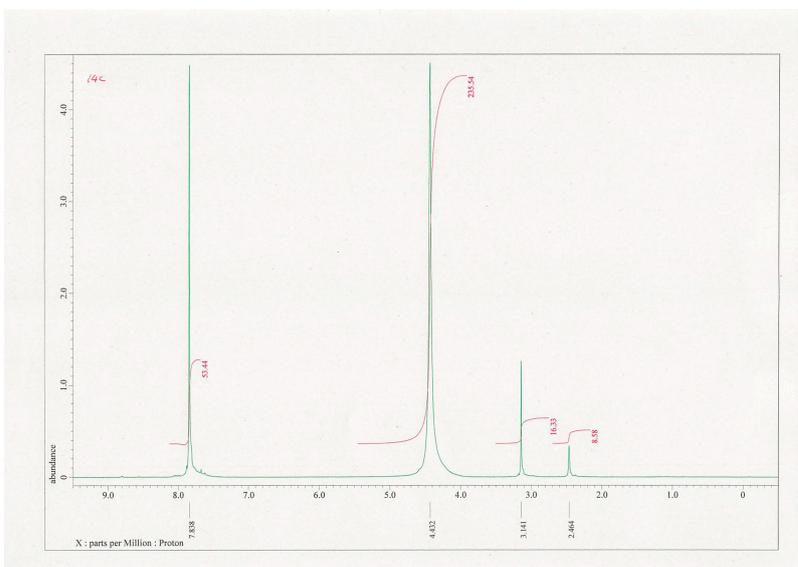


Fig.S31 The ¹H-NMR spectrum of tris((2,4,6-tribromophenyl) phosphate).

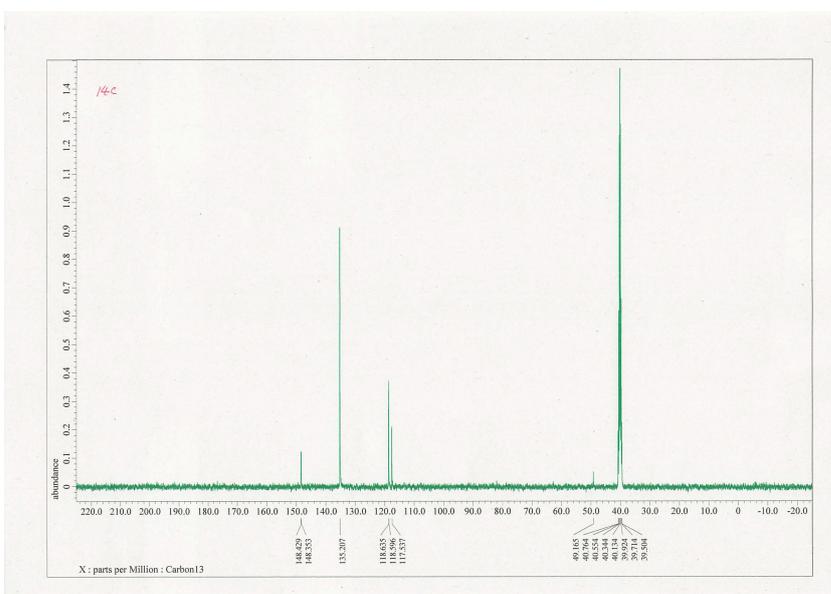


Fig.S32 The ¹³C-NMR of tris((2,4,6-tribromophenyl) phosphate).

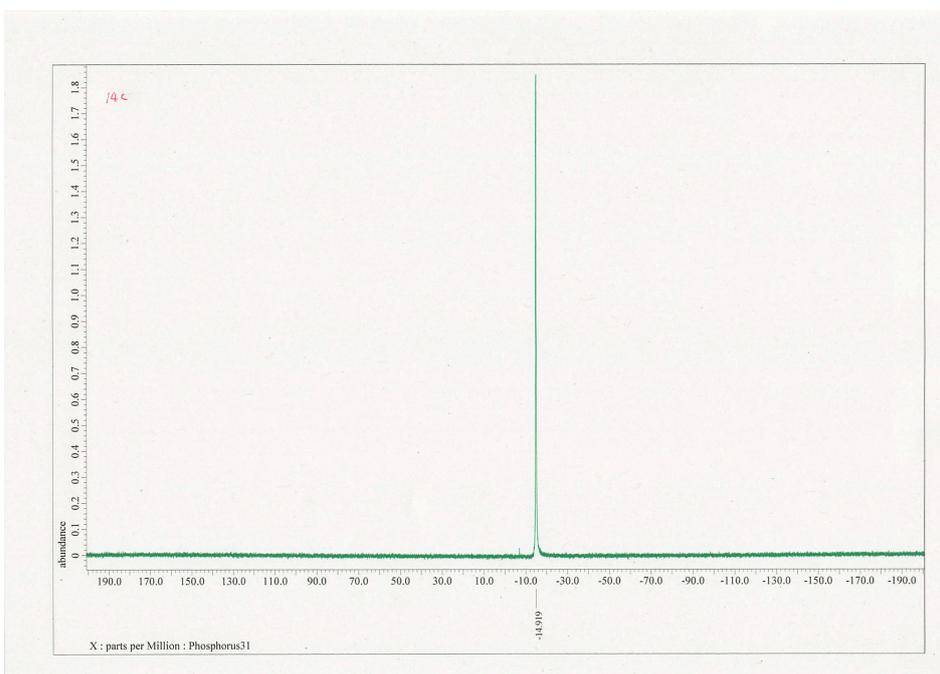


Fig.S33 The ^{31}P NMR spectrum of tris(2,4,6-tribromophenyl) phosphate.

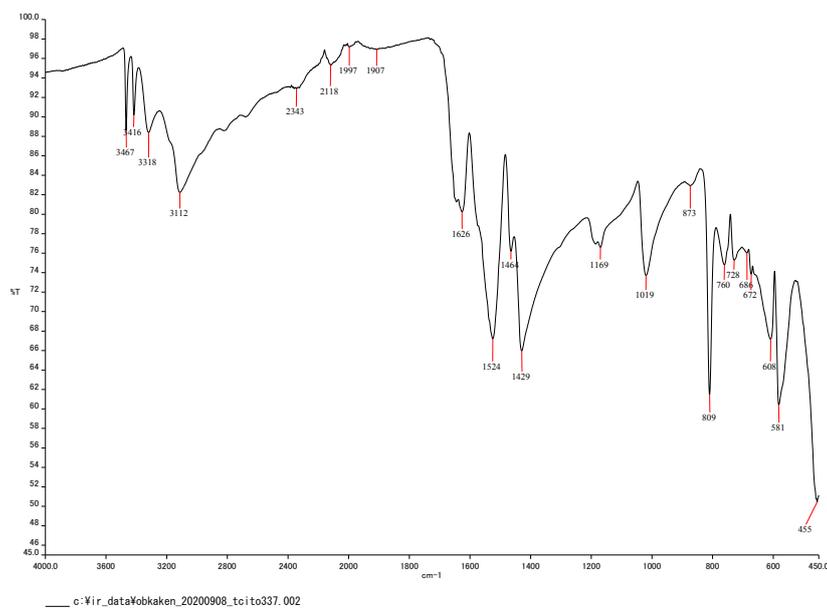


Fig.S34 The FT-IR (ATR) of Melamine **3**.

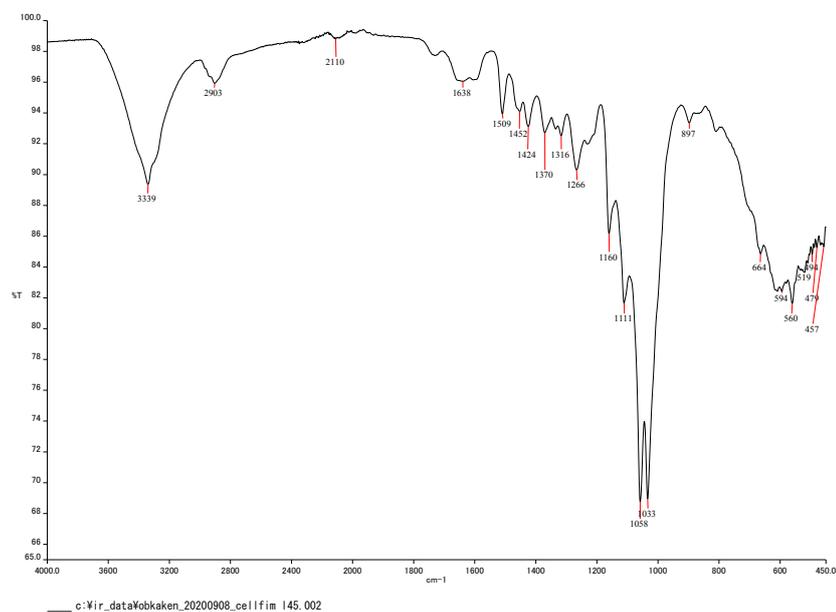


Fig.S35 The FT-IR (ATR) of LigCNFs (CellFim L-45™) (Freeze-dried).

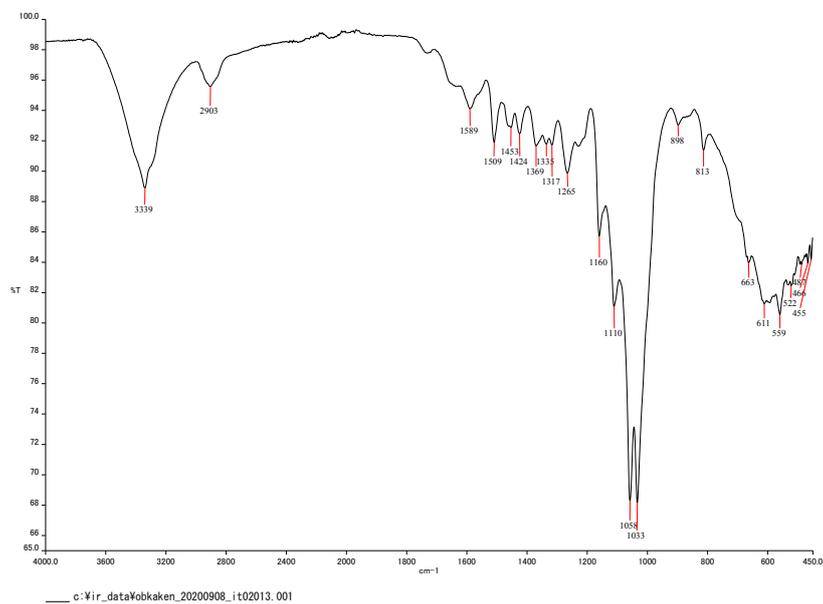


Fig.S36 The FT-IR (ATR) of Mannich adduct **III** from melamine (**3**) and HCHO, **3**/LCNFs (2 mmol/g).

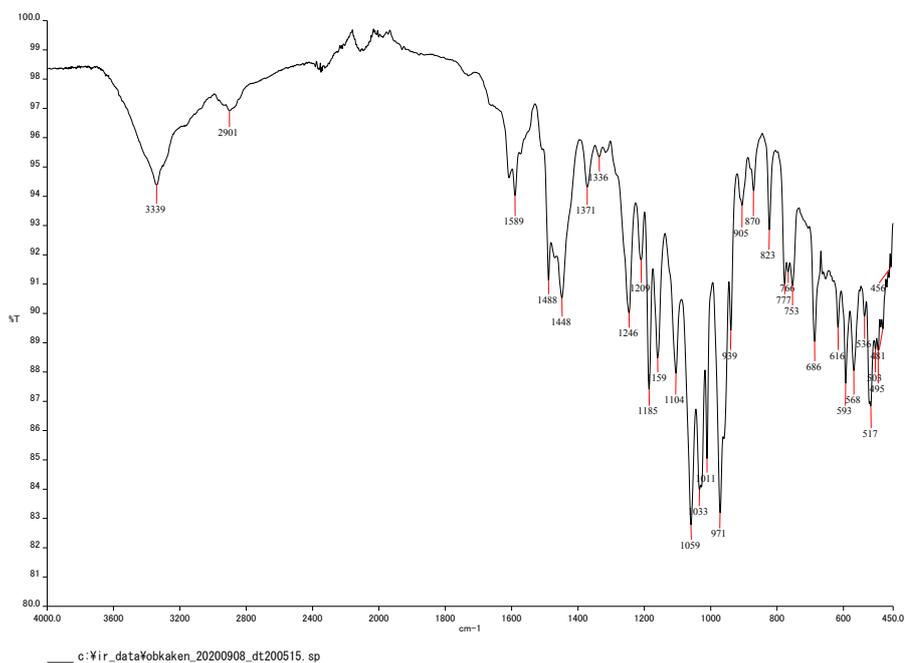


Fig.S37 The FT-IR (ATR) of Mannich adduct **Va** ($\text{Ar} = \text{C}_6\text{H}_5$) from **5a/LCNFs** (1.0 mmol/g), and HCHO.

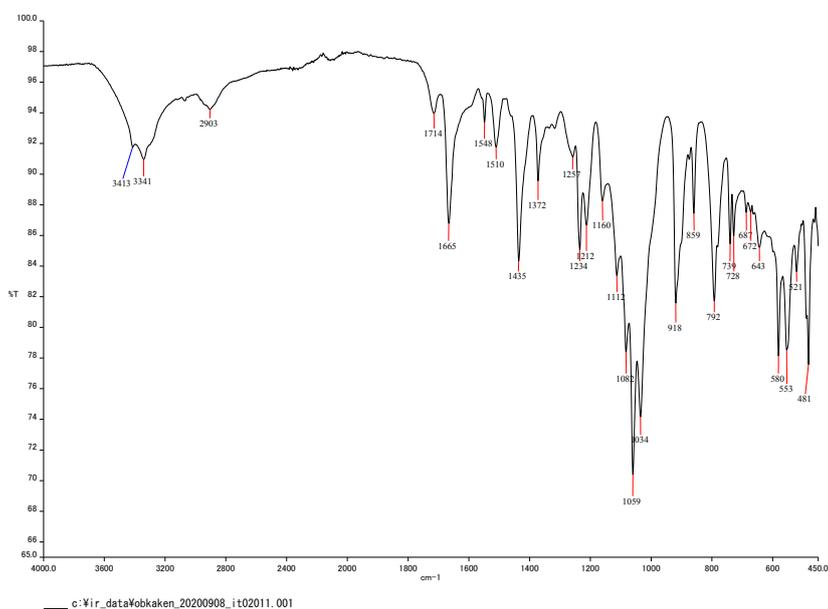


Fig.S38 The FT-IR (ATR) of Mannich adduct **Vd** ($\text{Ar} = 2,4,6\text{-Br}_3\text{C}_6\text{H}_2$) from **5d/LCNFs** (1.0 mmol/g), and HCHO.

Table S1. Evaluation of Mannich reaction based on the weight change of adducts the **III** under the varying **3**/LCNFs ratio.^{a)}

Run	3 , g	3 /LCNFs (mmol/g)	Products, g
1	0.266	0.7	3.098
2	0.379	1.0	3.119
3	0.495	1.3	3.243
4	0.609	1.6	3.319
5	0.72	1.9	3.417
6	0.836	2.2	3.498
7	0.95	2.5	3.499

a) Carried out using LCNFs (aq. 91.15% dispersion 34 g, dry weight 3 g), HCHO (3 mL), cetyltrimethylammonium bromide (30~50 mg), and **3** in H₂O (130 mL), at 55 °C for 24 h.

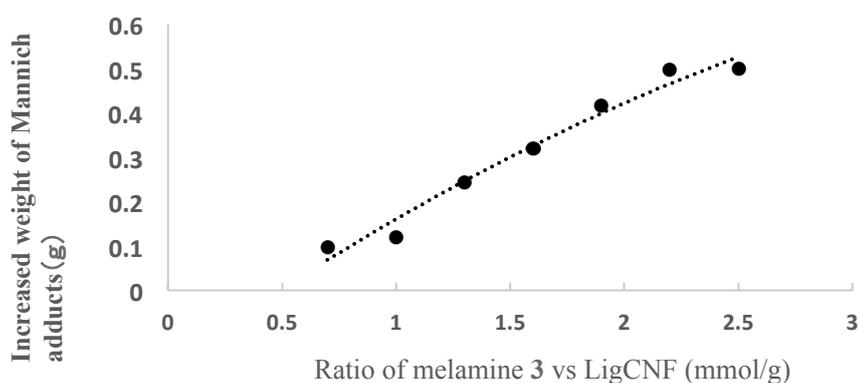


Fig. 1 Recovery amount of the Mannich adducts under increasing the Melamine/LCNFs (mmol/g) ratio.

Fig.S39 The amount of the Mannich adducts under varying the ratio of **3** vs. LCNFs (3 g).

Table S2. Evaluation of Mannich reaction on basis of the adducts **Va** (Ar = C₆H₅) under the varying ratio of **5a**/LCNFs.^{a)}

Run	5a , g	5a /LCNFs (mmol/g)	Va , dried, g
1	0.76	0.4	3.362
2	1.32	0.7	3.869
3	1.89	1.0	3.994
4	2.44	1.3	4.569
5	3.01	1.6	4.993
6	3.58	1.9	5.32
7	4.15	2.2	5.59

^{a)} Carried out using LCNFs (3 g), **5a**•2H₂O (MW: 626.49), cetyltrimethylammonium bromide (60~80 mg), and HCHO (3 mL) in H₂O (130 mL) at 55 °C for 20 h, 70 °C for 2 h.

Table S3. EA data of Mannich products **Va** (Ar = C₆H₅) under varying the ratios of **5a**/LCNFs.

Run	5a /LCNFs mmol/g.	EA of Va (Ar = C ₆ H ₅)		
		Carbon (%)	Hydrogen (%)	Nitrogen (%)
1	0	48.33	6.38	-
2	0.4	49.80	5.79	1.11
3	1	50.41	5.56	2.31
4	1.6	51.77	5.41	3.64
5	1.9	52.41	5.25	4.88
6	2.2	51.46	5.16	5.37

Table S4. Evaluation of Mannich reaction on the basis of adduct **Vd** (Ar = 2,4,6-Br₃C₆H₂) under varying the ratio of **5d**/LCNFs.^{a)}

Run	5d , g	5d /LCNFs (mmol/g)	Product, dried, g
1	0.48	0.1	3.162
2	1.89	0.4	4.558
3	3.36	0.7	5.945
4	4.77	1.0	7.283
5	6.15	1.3	8.566
6	7.58	1.6	10.459

^{a)} Carried out using LCNFs (3 g), **5d**•2H₂O (MW: 1573.2469), cetyltrimethylammonium bromide (60~80 mg), and HCHO 3~4 mL in H₂O (170 mL) at 55 °C, 20 h, 70 °C, 12 h.

Table S5. The LOI testing of the Mannich adducts of LCNFs with retardant agents under varying their ratio.

Run	Triazine phosphoramidates	Mannich adducts	Ratio of retardant vs. LCNFs (mmol/g)	Br content, %	P content, %	LOI
1	None		--	--		19.5
2	Melamine	III	1.2	--	--	21.0
3	4a	IVa	0.68	ND	1.16	25.2
4	4a	IVa	0.82	ND	ND	26.5
5	4a	IVa	1.1	ND	ND	27.5
6	5a	Va	0.91	ND	2.54	28.7
7	5a	Va	1.35	ND	3.36	30.2
8	5a	Va	2.15	ND	4.52	27.3

9	4b	Vb	0.26	ND	ND	22.5
10	4b	Vb	0.49	ND	ND	24.2
11	4b	Vb	0.83	ND	ND	28.3
12	4b	Vb	1.14	ND	ND	32.8
13	4b	Vb	1.5	ND	ND	33.3
14	4c	Vc	1.14	ND	ND	43.3
15	5d	Vd	0.48	28	ND	39.3
16	5d	Vd	0.63	33	ND	46
17	5d	Vd	0.79	ND	ND	47

Picture S1. Combustion test of the LCNFs and Mannich adducts **Vd**: Starting Material LCNFs.



Before ignition



After ignition, the flame burned throughout and the specimen burned mostly.

Picture S2. Combustion test of the LCNFs and Mannich adducts **Vd**: Flame retardant-treated LCNFs **Vd** (**5d**/LCNFs 0.63 mmol/g).



Before ignition



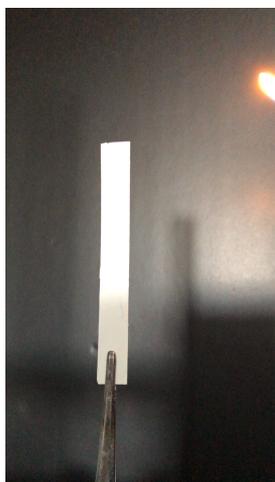
After ignition, a char layer was formed promptly, the test piece hardly burned

Video S1. Combustion test of the Mannich adducts **Va** of **5a**/LCNFs (1.3 mmol/g).



(TD20200515#2 1.3 mmol/g).

Video S2. Combustion test of the Mannich adducts **Vd** of **5d**/LCNFs (0.9 mmol/g).



(it01825#2 0.9 mmol/g)

Picture S3. Combustion test of the Mannich adducts **Va** under various ratio of **5a**/LCNFs.

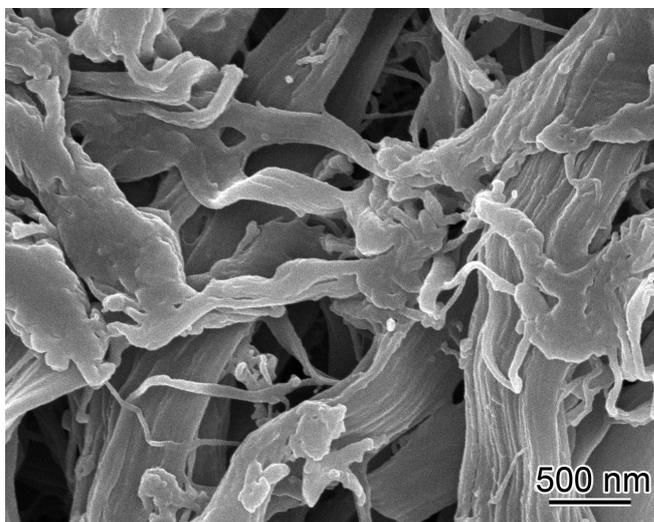


5a/LCNFs = 1.2 mmol/g

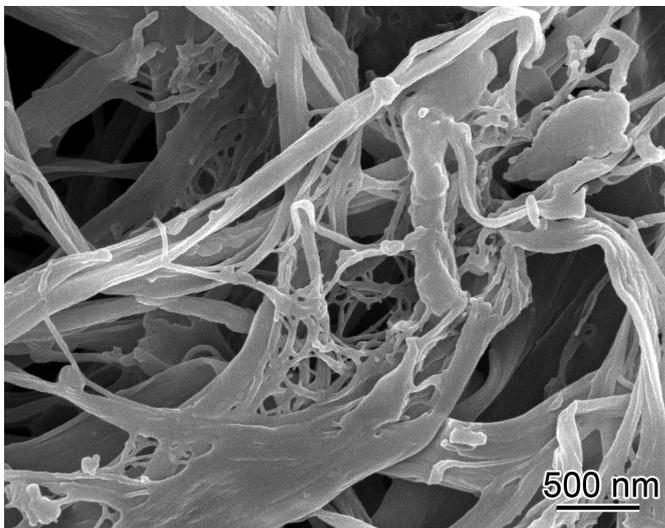


5a/LCNFs = 2.5 mmol/g

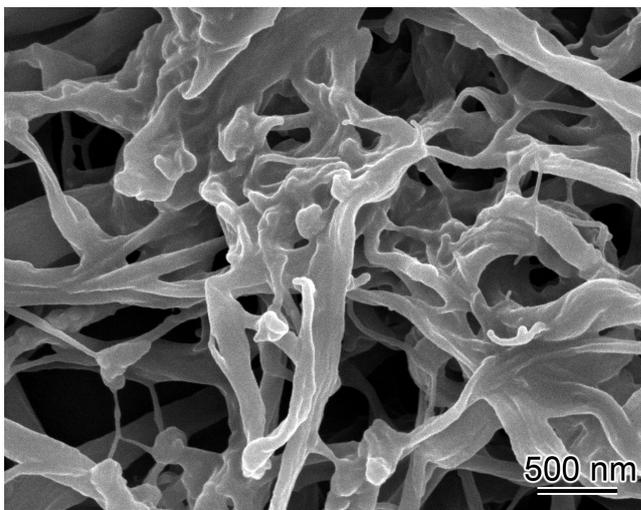
Fig.S40 The SEM images of the TG thermolysis-burnt samples.



(a) The untreated LCNFs, produced from Japanese cypress (soft wood).



(b) The treated LCNFs by Mannich reaction with melamine **3**.



(c) The treated LCNFs by Mannich reaction with diphosphoramidate **5d**.

7. References

- (1) N. Zhang, C.-M. Cheng, R.-J. Wang, *Chinese J. Struct. Chem.*, 2012, **31**, 1042–1046.
- (2) A. P. K. Sodhi, M. S. Bhatia, *Chemical & Environmental Research*, 2005, **14**, 161–170.
- (3) K. Matsubara and T. Katsumata, *Jpn. Kokai Tokkyo Koho*, 1996, JP 08012692 A 19960116.