## Electronic Supplementary Information (ESI) for CrystEngComm

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Figure S2:  ${}^{31}P$ -CP/MAS NMR spectrum of  $[Ba(CH_3PO_3CCl_2PO_2NC_4H_8O)(H_2O)_2]_n$  (2)

**Figure S3:** <sup>31</sup>P-CP/MAS NMR spectrum of [Sr<sub>2</sub>(CH<sub>3</sub>PO<sub>3</sub>CCl<sub>2</sub>PO<sub>2</sub>NC<sub>4</sub>H<sub>8</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>3.5</sub>]<sub>n</sub> (**3**)

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**Figure S8:** A thermogravimetric curve of the starting material  $(C_4H_8NH_2)_2CH_3PO_3C-Cl_2PO_2NC_4H_8$  performed in nitrogen atmosphere in a temperature range of 25–600 °C and at a heating rate of 5 °C /min.

**Figure S9:** A thermogravimetric curve of  $[Mg(CH_3PO_3CCl_2PO_2NC_4H_8O)(H_2O)_3]_n$  (1) performed under synthetic air in a temperature range of 25–700 °C and at a heating rate of 5 °C /min.

**Figure S10:** A thermogravimetric curve of  $[Ba(CH_3PO_3CCl_2PO_2NC_4H_8O)(H_2O)_2]_n$  (2) performed under synthetic air in a temperature range of 25–900 °C and at a heating rate of 5 °C /min.

**Figure S11:** A thermogravimetric curve of  $[Sr_2(CH_3PO_3CCl_2PO_2NC_4H_8)_2(H_2O)_{3.5}]_n$  (3) performed under synthetic air in a temperature range of 25–900 °C and at a heating rate of 5 °C /min.



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