

Electronic Supplementary Information for:

Comparing a mononuclear Zn(II) complex with hydrogen bond donors with a dinuclear Zn(II) complex for catalysing phosphate ester cleavage

Guoqiang Feng, Juan C. Mareque-Rivas and Nicholas H. Williams

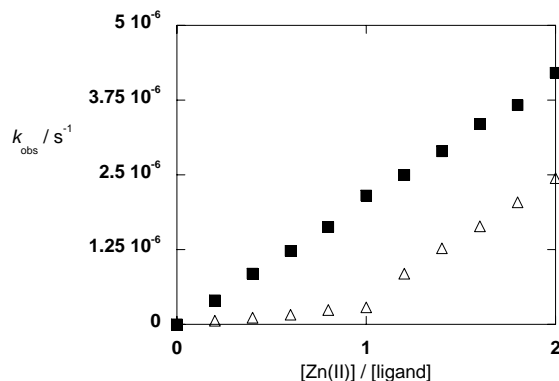


Fig. S1 Dependence of the rate of HPNPP transesterification at pH 7.1 (50 mM HEPES) and 25 °C on (a) the ratio of Zn(II) to **2** (Δ ; **2** is constant at 1 mM - this expands the data for **2** shown in figure 1) and (b): Zn(II) only (\blacksquare ; x-axis scale: mM). These data also show the reactions are first order in Zn(II) and **Zn-2** under these conditions, with free Zn(II) more active than the **Zn-2** complex.

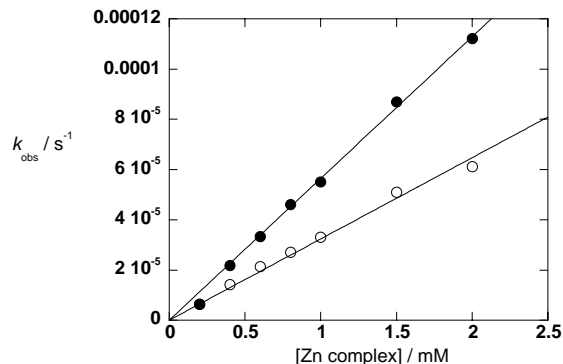


Fig. S2 Dependence of the rate of HPNPP transesterification on the concentration of **Zn-3** and **Zn₂-4** at pH 7.1 (50 mM HEPES) and 25 °C. **Zn-3** (\circ); **Zn₂-4** (\bullet).

We note that the ^{31}P NMR experiments shown below show that 5 mM HPNPP is turned over in an approximately first order fashion and similar rate by both complexes, whereas the kinetic experiments shown in fig. S2 predict **Zn₂-4** to be about 50% more reactive. The ^{31}P NMR experiment were run under less temperature controlled conditions than the kinetic experiments as they were designed primarily to identify the products that form and whether the complexes undergo turnover. Hence, they cannot be analysed as accurately in terms of rates; however, we explain the apparent discrepancy as follows: the higher concentration of substrate used (5 mM cf. 1 mM) will lead to partial saturation of **Zn₂-4** by substrate, which binds diesters more tightly, and to product inhibition as the reaction proceeds; overall, as the product will have a very similar binding constant to the substrate, this will lead to first order changes in substrate concentration (as observed for the changes in the ^{31}P NMR signals), but at a reduced rate relative to the plot in fig. S2. **Zn-3**, which binds diesters more weakly, will not be affected in this way (and the usual first order behaviour is still expected) and so will show a rate closer to that observed with **Zn₂-4**. Simulating the reaction progress using our kinetically determined parameters supports this interpretation. This is a manifestation of what we describe in the penultimate paragraph – the mononuclear complex will reach a higher limiting rate as substrate or complex concentration is raised.

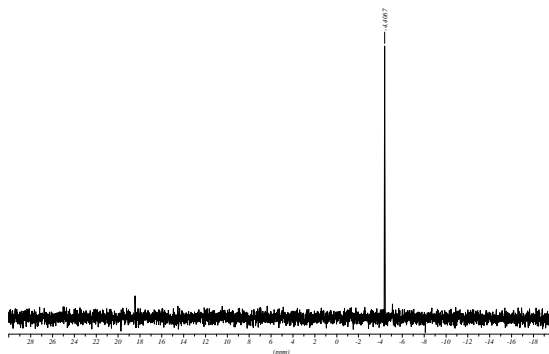


Fig. S3 ^{31}P NMR spectra of HPNPP solution (5mM, 10% D_2O in H_2O) at pH 7.1 (50 mM HEPES) and 22 °C.

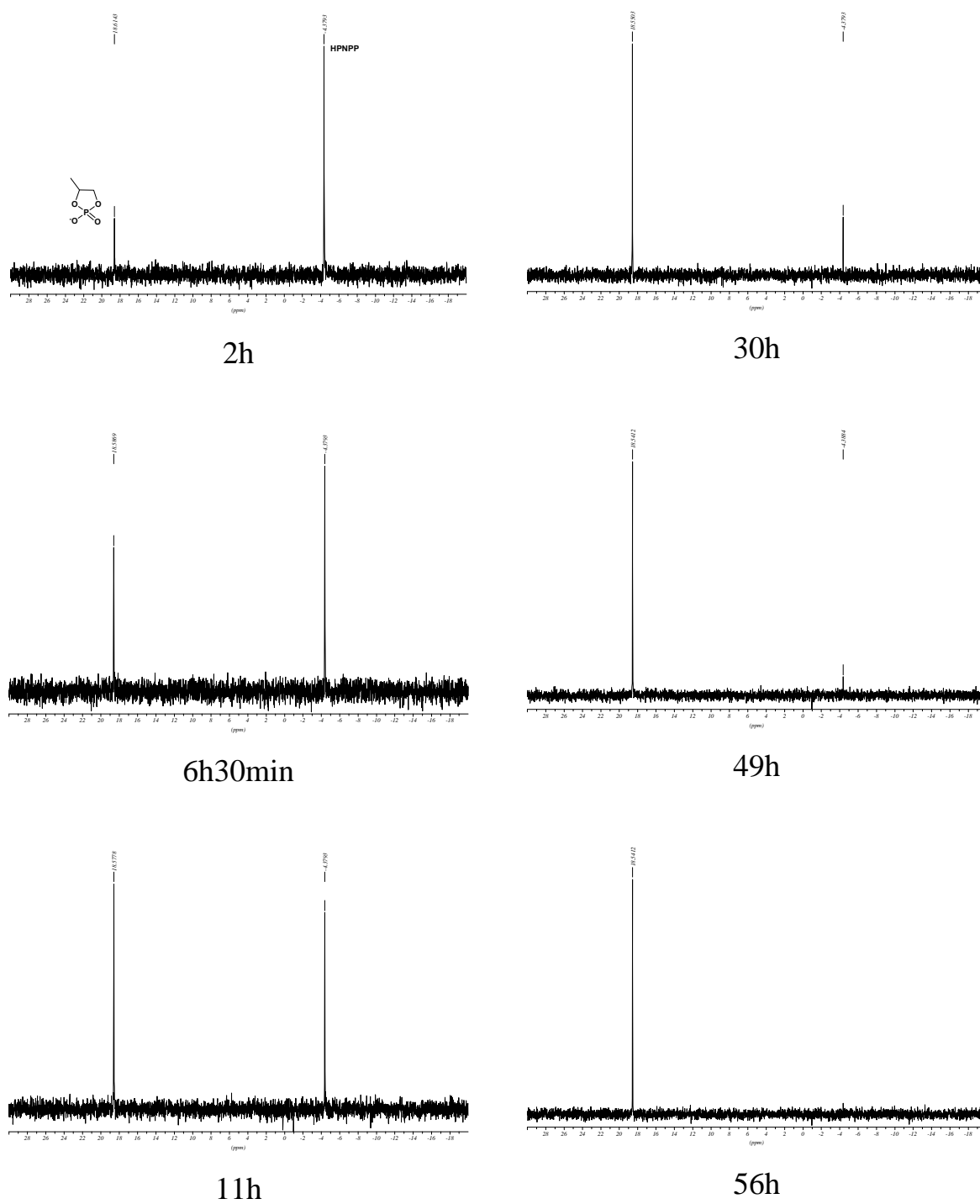


Fig. S4 ^{31}P NMR spectra of HPNPP solution (5mM, 10% D_2O in H_2O) in the presence of $\text{Zn}_2\text{-4}$ (1mM) at pH 7.1 (50 mM HEPES) and 22 °C

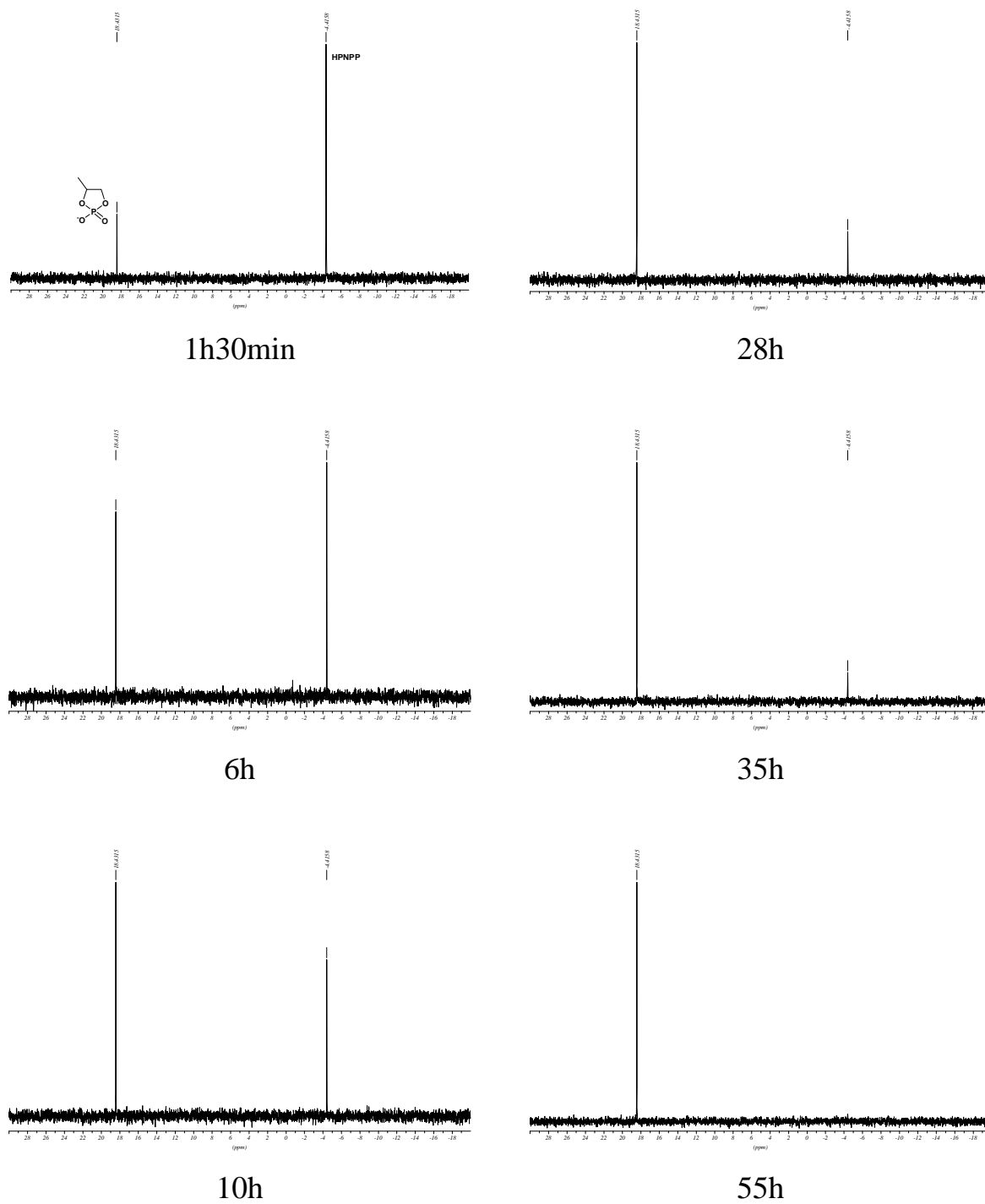


Fig. S5 ^{31}P NMR spectra of HPNPP solution (5mM, 10% D_2O in H_2O) in the presence of Zn-3 (1mM) at pH 7.1 (50 mM HEPES) and 22 °C.