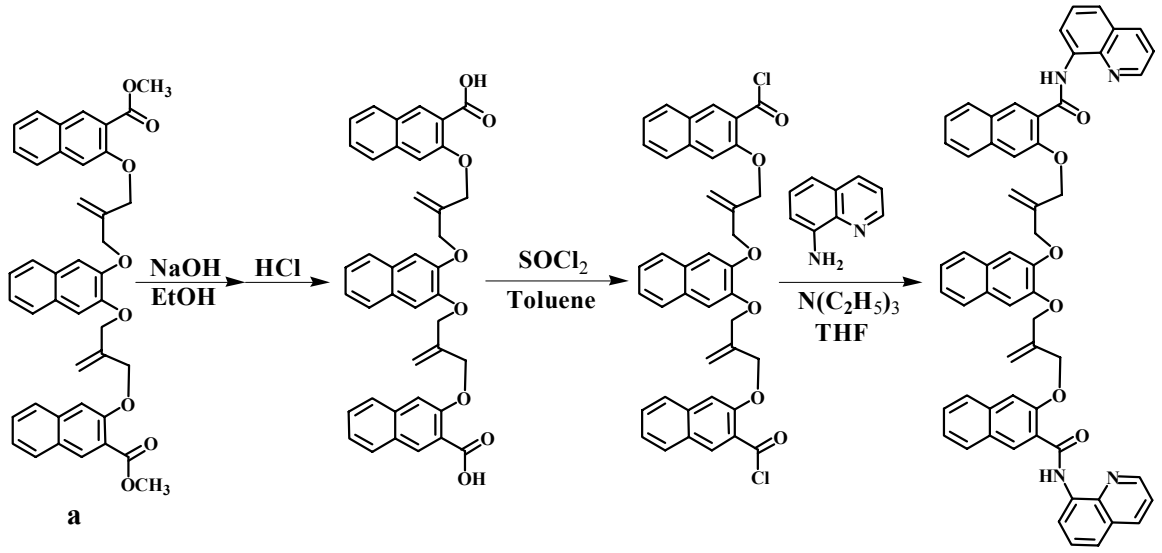
Supplementary Material (ESI) for Chemical Communications

Electronic Supplemental Information

Title: Phosphate anion-selective recognition by boron complex having plural hydrogen bonding sites

Author: Naohiro Kameta and Kazuhisa Hiratani*

Content



Scheme: Synthesis of polyether **1**. Synthetic method of compound **a** was described in Ref.6

Polyether **1**: 1H NMR ($CDCL_3$) δ4.86 (s, 4H, Ar-CH_2), 5.13 (s, 4H, Ar-CH_2), 5.53 (s, 2H, CH_2=C), 5.58 (s, 2H, CH_2=C), 6.85 (s, 2H, Ar), 7.19 (dd, 2H, Ar), 7.21 (t, 2H, Ar), 7.29 (s, 2H, Ar), 7.28 (dd, 2H, Ar), 7.35 (t, 2H, Ar), 7.41 (t, 2H, Ar), 7.43 (dd, 2H, Ar), 7.54 (t, 2H, Ar), 7.58 (d, 2H, Ar), 7.89 (d, 2H, Ar), 7.98 (dd, 2H, Ar), 8.67 (dd, 2H, Ar), 8.82 (s, 2H, Ar), 9.04 (dd, 2H, Ar), 12.1 (s, 2H, NH). IR (KBr) 1662 cm^{-1}, 1530 (CONH). ESI-MS (CH_3CN) m/z = 893 (H^+).

Ligand **2**: ^{1}H NMR ($CDCl_3$) δ4.02 (s, 8H, Ar-CH_2), 4.60 (s, 2H, CH_2=C), 4.66 (s, 2H, CH_2=C), 7.28 (dd, 2H, Ar), 7.35 (t, 2H, Ar), 7.46 (t, 2H, Ar), 7.53 (dd, 2H, Ar), 7.62 (d, 2H, Ar), 7.63 (d, 2H, Ar), 7.77 (d, 2H, Ar), 7.84 (dd, 2H, Ar), 7.95 (d, 2H, Ar), 8.23 (dd, 2H, Ar), 8.35 (s, 2H, Ar), 8.89 (dd, 2H, Ar), 8.94 (dd, 2H, Ar), 6.26 (s, 2H, OH), 11.2 (s, 2H, OH), 12.2 (s, 2H, NH). IR (KBr) 3447 cm^{-1} (O-H, broad), 1654, 1537 (CONH). ESI-MS (CH_3CN) m/z = 893 (H^+).

Boron complex: ^{1}H NMR ($CDCl_3$) δ3.94 (s, 8H, Ar-CH_2), 3.97 (s, 8H, Ar-CH_2), 4.43 (s, 4H, CH_2=C), 4.61 (s, 4H, CH_2=C), 7.18 (dd, 4H, Ar), 7.23 (t, 4H, Ar), 7.33 (t, 4H, Ar), 7.45 (dd, 4H, Ar), 7.49 (d, 4H, Ar), 7.51 (d, 4H, Ar), 7.75 (d, 4H, Ar), 7.74 (dd, 4H, Ar), 7.82 (d, 4H, Ar), 8.13 (dd, 4H, Ar), 8.22 (s, 4H, Ar), 8.78 (dd, 4H, Ar), 8.84 (dd, 4H, Ar), 11.1 (s, 4H, OH), 11.9 (s, 4H, NH), 0.96 (t, 9H, NEt_3), 2.78 (q, 6H, NEt_3). IR (KBr) 3444 cm^{-1} (O-H, broad), 1653, 1534 (CONH). Elemental analysis, found (calc.), C, 77.79 (77.72); H, 4.73 (4.69); N, 6.20 (6.25).

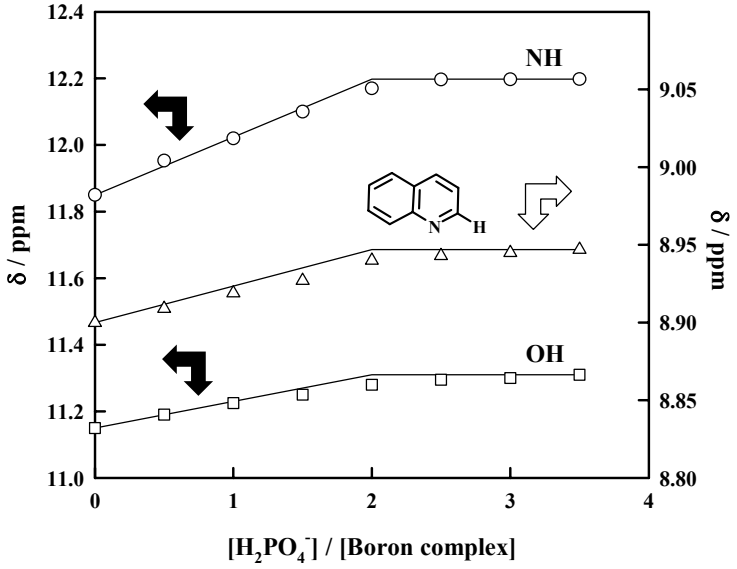


Figure: ^{1}H-NMR titration plots of the hydroxy (OH), the amide (NH), and the quinoline (2-position) in the boron complex on the complexation with $H_2PO_4^-$ in CD_3CN. □δ / ppm values indicate the apparent chemical shifts of those protons.

Derivation of equation for determination of binding constants (K_1 and K_2).

K_1 = [Boron–Anion] / ([Boron][Anion])
K_2 =[Boron–2 Anion] / [Boron–Anion][Anion]

$[\text{Anion}]_{\text{total}} = [\text{Anion}] + [\text{Boron–Anion}] + [\text{Boron–2 Anion}]$

$$K_1K_2[\text{Anion}]^3 + (2K_1K_2[\text{Boron}]_{\text{total}} - K_1K_2[\text{Anion}]_{\text{total}} + K_1)[\text{Anion}]^2 + (K_1[\text{Boron}]_{\text{total}} - K_1[\text{Anion}]_{\text{total}} + 1)[\text{Anion}] - [\text{Anion}]_{\text{total}} = 0$$

$$\Delta\delta_{obs} = \frac{K_1[Anion](\delta_1 - \delta_{Boron}) + K_1K_2[Anion]^2(\delta_2 - \delta_{Boron})}{1 + K_1[Anion] + K_1K_2[Anion]^2}$$

δ_{Boron} is the chemical shifts of the amide NH proton in the boron complex. δ_1 and δ_2 are the chemical shifts of the amide NH proton in the boron complex captured with a anion and two anions respectively.