A Fluorescent Cyclotriveratrylene: Synthesis, Emission properties and Acetylcholine recognition in water

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1/ Synthesis of Ethyl \(n\)-Butylphosphonochloridoate 2

Diethyl \(n\)-Butylphosphonate \(^1\): \[\text{P} \begin{array}{c} \begin{array}{c} \text{OEt} \\ \text{EtO} \end{array} \end{array} \text{Et} \]

A mixture of triethylphosphite (19.1 mL, 110 mmol) and \(n\)-butyl bromide (10.8 mL, 100 mmol) were heated at 120 °C for 72 h. After cooling at room temperature, water (50 mL) was added to the reaction mixture which was then extracted with diethyl ether (2 \(\times\) 50 mL), washed with water (4 \(\times\) 100 mL), dried over magnesium sulphate, filtered and concentrated \(^{\text{in vacuo}}\). Diethyl \(n\)-Butylphosphonate 5 (6.077 g, 31%) was isolated as a colourless oil; \(\nu_{\text{max}}\)(NaCl)/cm\(^{-1}\) (2988, 2875, 2352, 1469, 1390, 1024, 963); \(\delta_1\)(300.13 MHz; CDCl\(_3\)) 0.89 (3H, t, \(J\) 7.2, \(H_2\)); 1.30 (6H, t, \(J\) 7.2, OCH\(_2\)C\(_3\)H\(_7\)); 1.39 (2H, m, \(J\) 7.2, \(H_3\)); 1.49-1.74 (4H, m, \(J\) 7.2, \(H_{4,5}\)); 4.06 (2H, m, \(J\) 7.2, OCH\(_2\)CH\(_3\)); \(\delta_p\)(120.1 MHz; CDCl\(_3\)) 32.43 (s).

Ethyl \(n\)-Butylphosphonochloridoate 2:

To a solution of 3 (3.884 g, 20 mmol) in dry dichloromethane (100 mL) at 0 °C was added dropwise oxalyl chloride (4.4 mL, 50 mmol) under inert conditions. The mixture was stirred for 20 minutes at 0 °C and 16 h at room temperature. The crude liquid was concentrated under reduced pressure. Dry dichloromethane (50 mL) was added and evaporated \(^{\text{in vacuo}}\) to remove the oxalyl chloride excess (repeated twice). The residual yellow oil 2 (3.602 g, 98%) was used without further purification; \(\delta_1\)(300.13 MHz; CDCl\(_3\)) 0.93 (3H, t, \(J\) 7.2, \(H_4\)), 1.38
(3H, t, J 7.2, OCH$_2$CH$_3$), 1.46 (2H, m, J 7.2, H$_b$), 1.70 (2H, m, J 7.2, H$_a$), 2.16 (2H, m, J 7.2, H$_a$), 4.24 (2H, m, J 7.2, OCH$_2$CH$_3$); $\delta$C (75.5 MHz; CDCl$_3$) 13.42 (s, J 1.1, C$_d$), 15.88 (d, J 7.3, OCH$_2$CH$_3$), 23.19 (d, J 20, C$_c$), 24.35 (d, J 6.1, C$_b$), 33.33 (d, J 123, C$_a$), 62.97 (d, J 8.2, OCH$_2$CH$_3$); $\delta$P (120.1 MHz; CDCl$_3$) 45.19.

2/ UV-Vis absorption and fluorescence emission of Probe 1

![Normalized UV-Vis absorption and fluorescence emission of Probe 1](image.png)

**Figure S1**: Normalized UV-Vis absorption and fluorescence emission of Probe 1
3/ NMR Spectra:

$^1$H and $^{31}$P NMR of compound 5 (CDCl$_3$)

$^{13}$C NMR of compound 5 (CDCl$_3$)
$^1$H and $^{31}$P NMR of compound 2 (CDCl$_3$)

$^{13}$C NMR of compound 2 (CDCl$_3$)
$^1$H NMR of CTV 4 (CDCl$_3$)

$^{31}$P NMR of CTV 4 (CDCl$_3$)
**13C NMR of CTV 4 (CDCl₃)**

![13C NMR spectrum of CTV 4](image)

**1H and 31P NMR of Probe 1 (CD$_3$OD)**

![1H and 31P NMR spectrum of Probe 1](image)
$^{13}$C NMR of Probe 1 (CD$_3$OD)

$^1$H and $^{31}$P NMR of Probe 1 (D$_2$O)
$^{13}$C NMR of Probe 1 (D$_2$O)
4/ $^1$H NMR Titration of ACh

![Graph](image)

**Figure S2:** $^1$H NMR chemical shift variation of probe 1 ($10^{-3}$ M) upon titration with ACh (●). Data fitting with a 1:1 binding model is shown as dotted lines.

**References**