



Supporting Information

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Protonation-induced transition between two distinct
helical conformations of a synthetic oligomer *via* a
linear intermediate**

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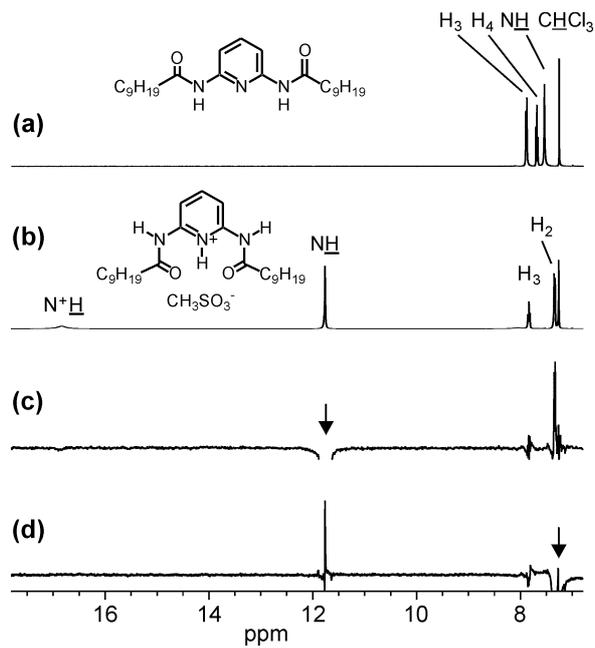


Figure S11. Part of the 400 MHz ^1H NMR spectra of 20 mM CDCl_3 solutions of: (a) **1**; and (b) **1-H⁺CH₃SO₃⁻**; and NoeDIFF spectra of **1-H⁺** (c) and (d). The arrows indicate the signals of the irradiated protons. Note the absence of correlation with N^+H .

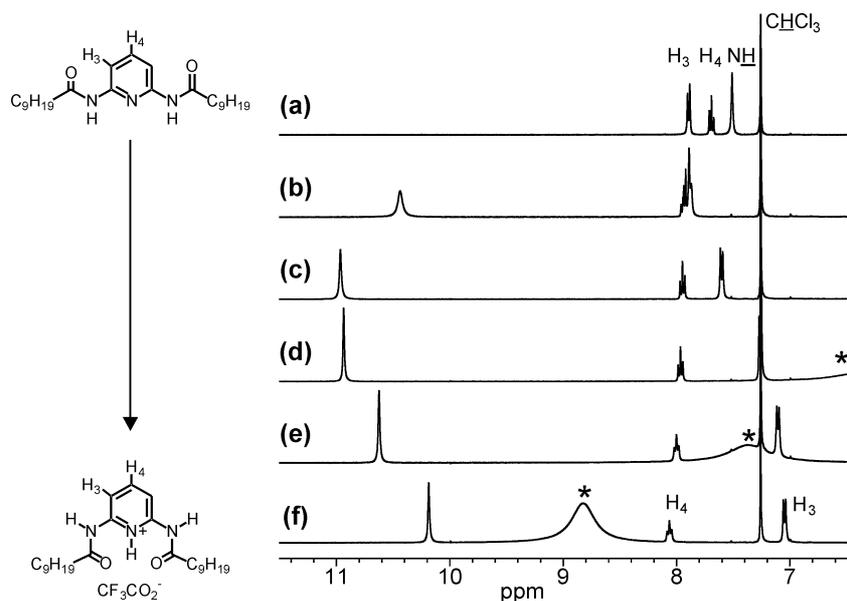


Figure SI2. Part of the 400 MHz ^1H NMR spectra of **1** in CDCl_3 in the presence of increasing amounts of $\text{CF}_3\text{CO}_2\text{H}$: (a) 0 eq.; (b) 0.5 eq.; (c) 1 eq.; (d) 2 eq.; (e) 4 eq.; (f) 10 eq. The asterisks mark the average signal between $\text{CF}_3\text{CO}_2\text{H}$ and H_2O . The protonation and subsequent conformational change result in an upfield shift of H_3 that reaches a limit at *ca* 4 eq. of TFA.

At low concentration of TFA, the carboxylate function is presumably solvated by the amide NH resulting in a strong deshielding of the latter; at high concentration of TFA, the carboxylates are solvated by other TFA molecules resulting in an upfield shift of the NH signal. All three crystal structures of 2,6-bis(carboxylamino)-pyridinium available in the CCDB show such hydrogen bonding between the anion and the amide NH.

Unlike with MsOH , the protonation is not quantitative because of the lower acidity of TFA. Note that in the presence of TFA, the pyridinium proton exchanges rapidly and its NMR signal coalesces with the signals of H_2O and TFA.

NoeDIFF experiments on $\mathbf{1-H}^+ \text{CH}_3\text{CO}_2^-$ show the same correlations as in $\mathbf{1-H}^+ \text{CH}_3\text{SO}_3^-$ indicating a similar conformational change.

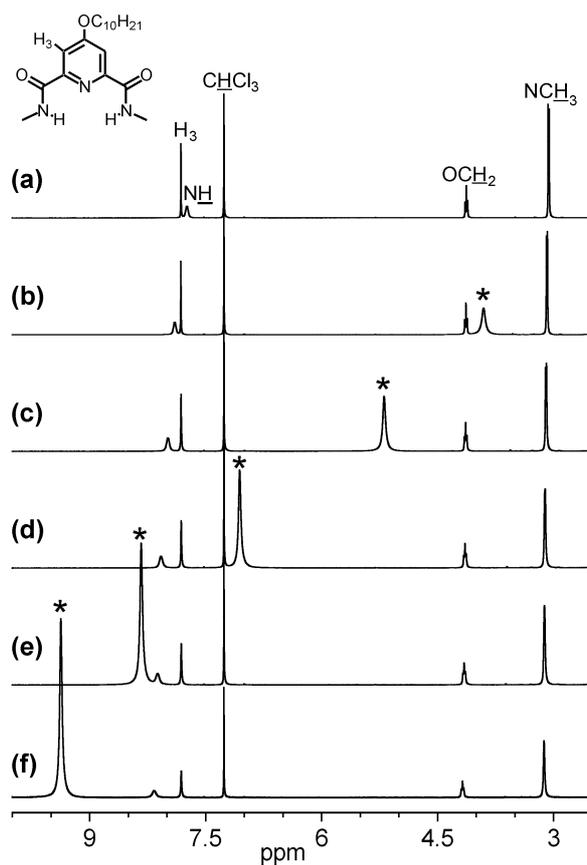


Figure S13. Part of the 400 MHz ^1H NMR spectra of **2** in CDCl_3 in the presence of increasing amounts of $\text{CF}_3\text{CO}_2\text{H}$: (a) 0 eq.; (b) 1 eq.; (c) 2 eq.; (d) 5 eq.; (e) 10 eq.; (f) 20 eq. The asterisks mark the average signal between $\text{CF}_3\text{CO}_2\text{H}$ and H_2O . No indication of protonation at the pyridine nitrogen is observed.

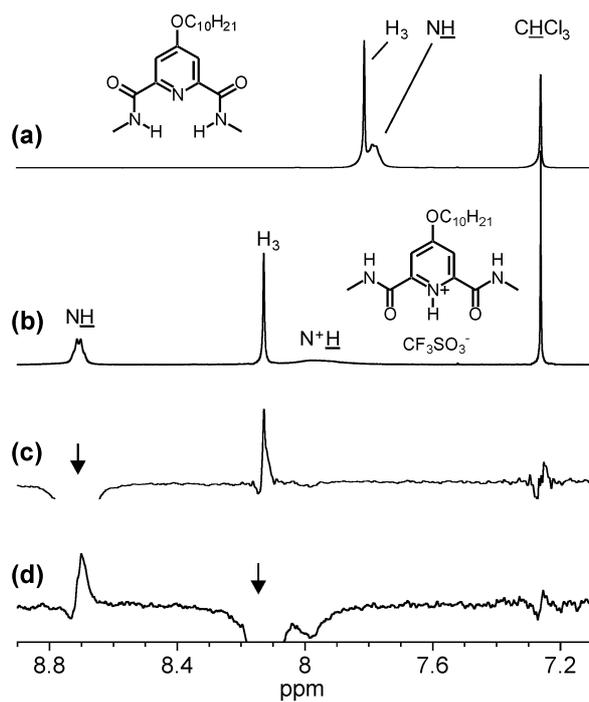


Figure SI4. Part of the 400 MHz ^1H NMR spectra of 20 mM CDCl_3 solutions of: (a) **2**; and (b) 2-H^+ CF_3SO_3^- ; and NOE-DIFF spectra of 2-H^+ (c) and (d). The arrows indicate the signals of the irradiated protons.