Modes of Binding Interaction Between Viologen Guests and the Cucurbit[7]uril Host

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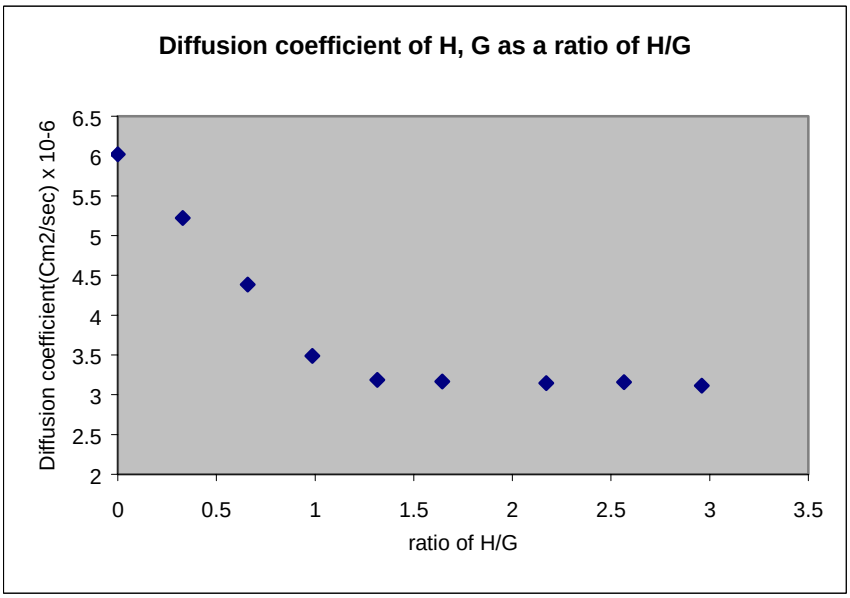
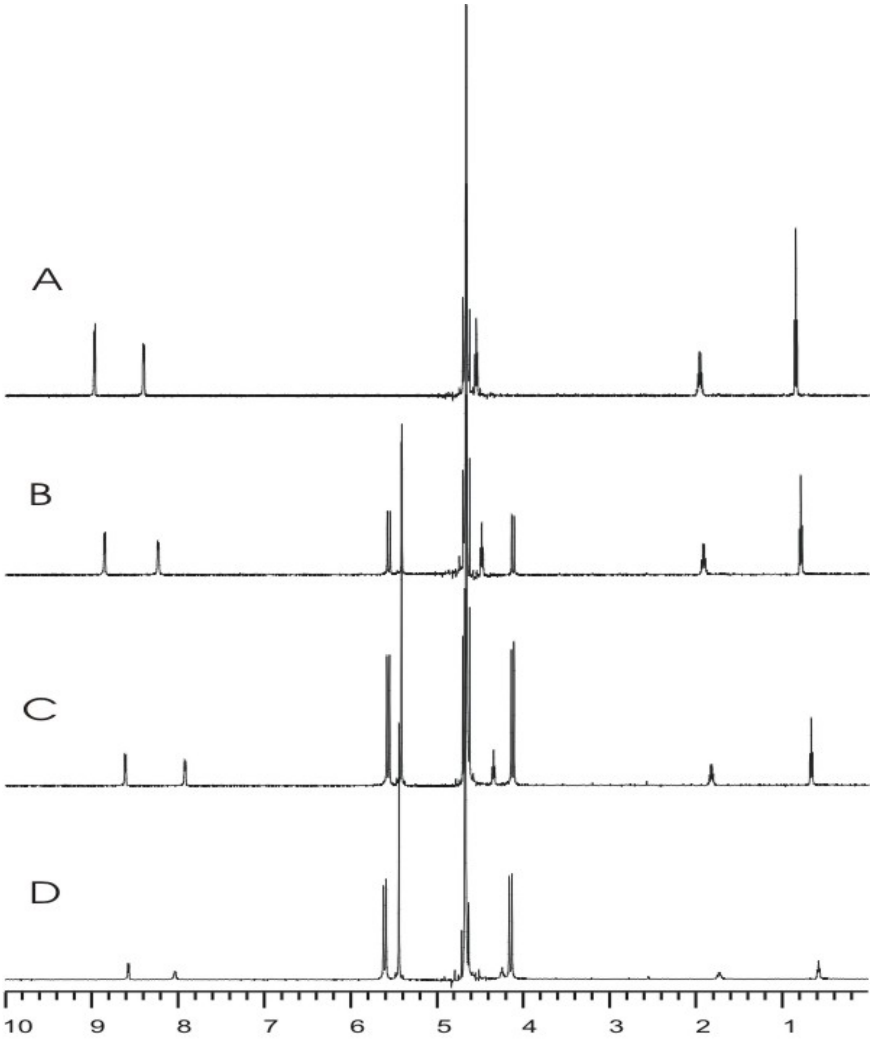
Supporting information

Diffusion coefficient of guest molecule
Guest : Ethylviologen
Host: CB7
Solvent: 0.2 M NaCl in D_2O
Instrument: 500MHz NMR

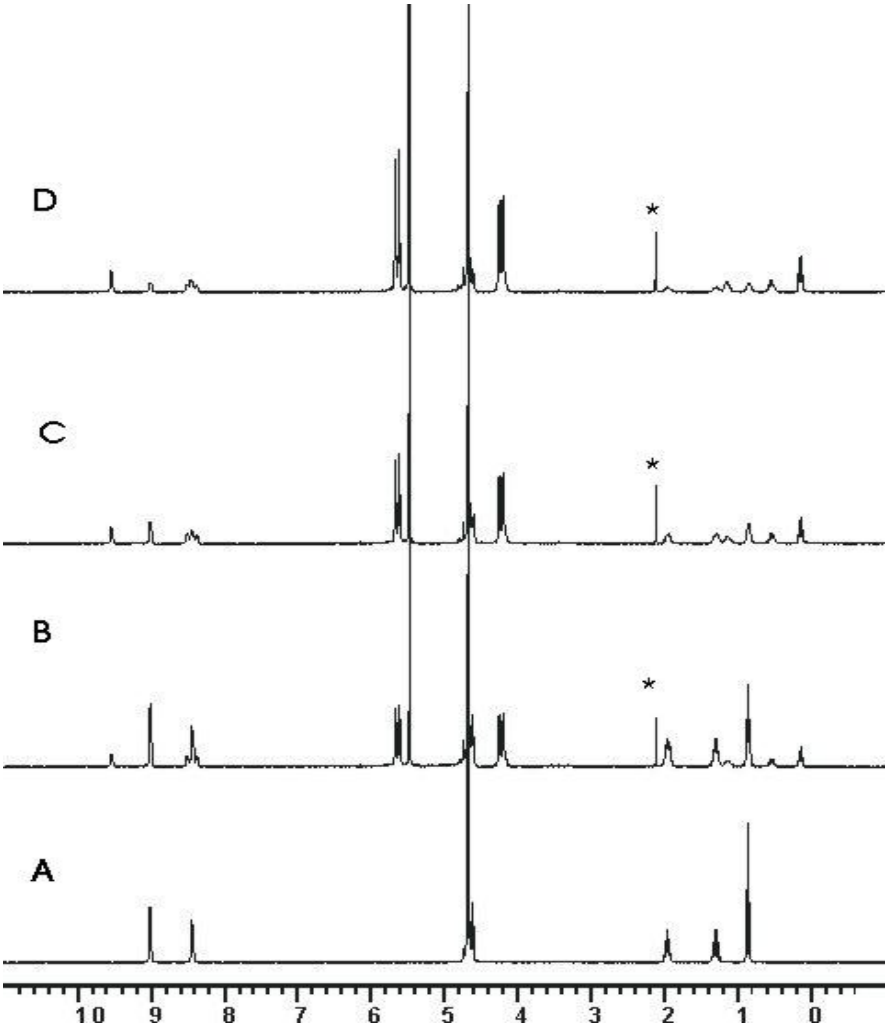


NMR titration of propylviologen with CB7



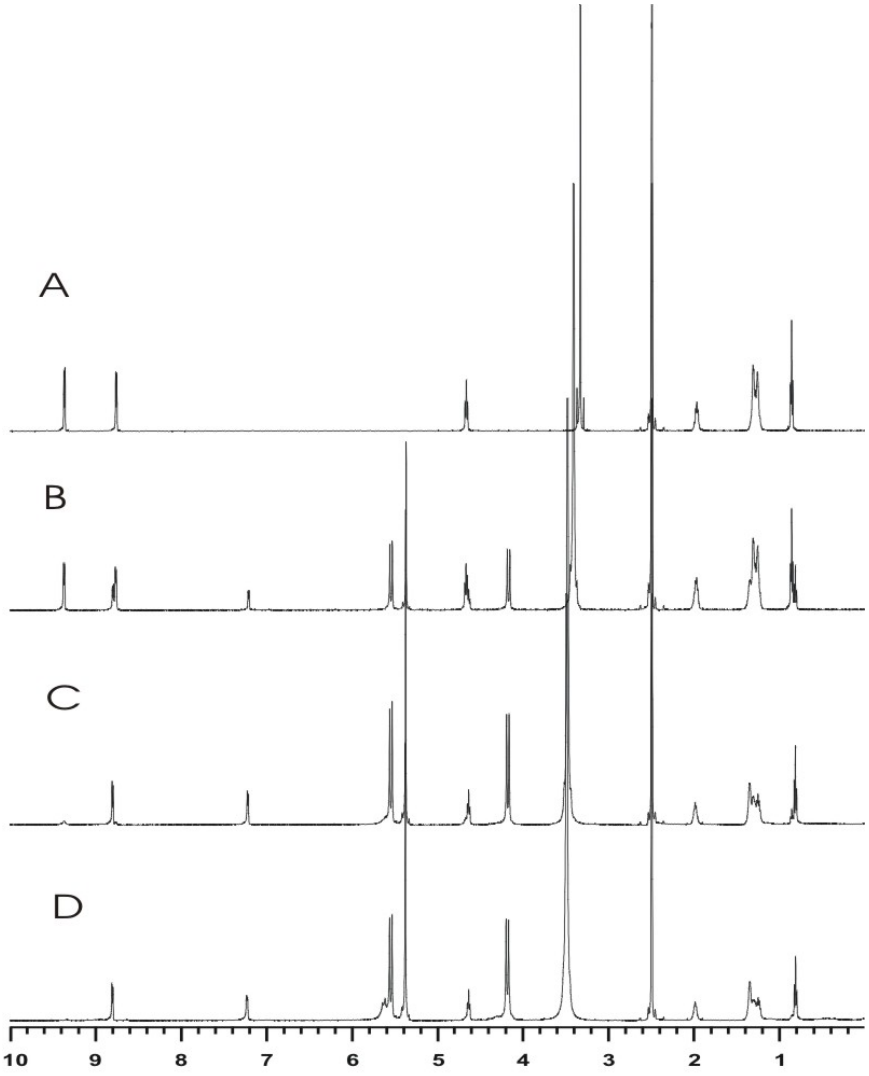
Solvent : 0.2 M NaCl in D_2O, 500MHz
A: propylviologen
B: addition of CB7 (0.34eq)
C: addition of CB7 (1.03eq)
D: addition of CB7 (1.72eq)

NMR titration of butyl viologen with CB6



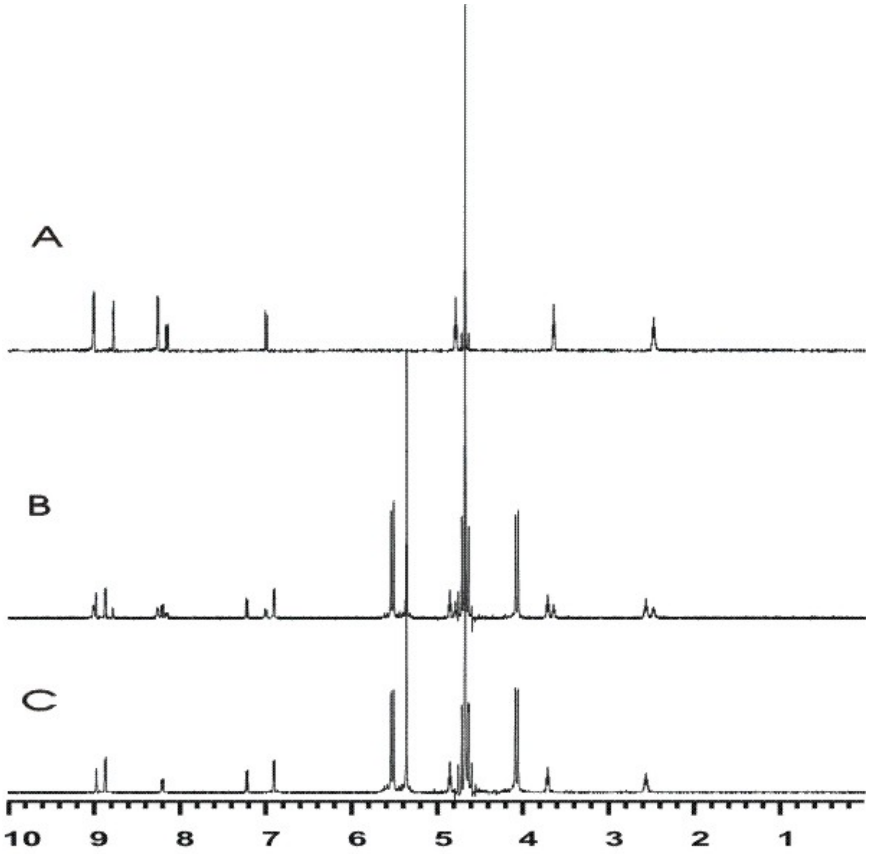
Solvent : 0.2M NaCl in D_2O, 300MHz
A : butyl viologen
B : addition of CB6 (0.5eq)
C : addition of CB6 (1.0eq)
D : addition of CB6 (1.5eq)
Asteric is a solvent (acetone)

NMR titration of heptylviologen with CB7



Solvent : DMSO-d_6, 500MHz
A: heptyl viologen
B: addition of CB7 (0.4eq)
C: addition of CB7 (1.05eq)
D: addition of CB7 (1.4eq)

NMR titration of amino-dinitrophenyl-propyl viologen with CB7



Solvent : D_2O, 500MHz
A: amino-dinitrophenyl-propyl viologen
B: addition of CB7 (0.66eq)
C: addition of CB7 (1.09eq)

General procedure for the synthesis of bis(alkyl)viologens

A mixture of 4,4'-dipyridyl (1.0 equiv) and the corresponding alkyl bromide (8 equiv) in CH_3CN was refluxed for 3days. The resulting precipitate was filtered, washed with hot chloroform to remove monoalkylated product and dried under vacuum.

^{1}H NMR of **EV^{2+}**(500MHz, 0.2M NaCl-D_2O) δ (ppm) 8.99 (d, J=5Hz, 4H, α of viologen), 8.40 (d, J=5Hz, 4H, β of viologen), 4.61 (q, 4H, CH_2), 1.55(t, 6H, CH_3), MASS (FAB): 214 ($M^{+\cdot}$)

^{1}H NMR of **PV^{2+}**(500MHz, 0.2M NaCl-D_2O) δ (ppm) 8.98 (d, J=6Hz, 4H, α of viologen), 8.41 (d, J=6Hz, 4H, β of viologen), 4.56 (t, 4H, CH_2), 1.96 (m, 4H, CH_2), 0.85(t, 6H, CH_3), MS (FAB): 242 ($M^{+\cdot}$)

^{1}H NMR of **BV^{2+}**(300MHz, 0.2M NaCl-D_2O) δ (ppm) 9.01 (d, J=6.3Hz, 4H, α of viologen), 8.44 (d, J=6.3Hz, 4H, β of viologen), 4.60 (t, 4H, CH_2), 1.95 (m, 4H, CH_2), 1.30 (m, 4H, CH_2), 0.85(t, 6H, CH_3), MS (FAB): 270 ($M^{+\cdot}$)

Synthesis of NHV•$(PF_6)_2$

A mixture of 4,4'-dipyridyl (2g, 12.8mmol) and 3-bromopropylamine hydrobromide (7g, 52mmol) in CH_3CN was refluxed for 3days. . The resulting precipitate was filtered and dissolved in water. The solution was treated with NaOH solution until the blue color characteristic of reduced viologen appeared. NH_4PF_6 was added to the solution to exchange the counter anions. The resulting solid was filtered, washed with water, THF and dried under vacuum. Yield : 59 %, (4.25g, 7.56mmol).

^{1}H NMR of **NHV^{2+}**(300MHz, 0.2M NaCl-D_2O) δ (ppm) 9.05 (d, J=6.6Hz, 4H, α of viologen), 8.47 (d, J=6.6Hz, 4H, β of viologen), 4.71 (t, 4H, CH_2), 2.88 (t, 4H, CH_2), 2.29(m, 6H, CH_3), MS (FAB): 272 ($M^{+\cdot}$)

Synthesis of NHDBV•$(PF_6)_2$

A mixture of aminopropyl-viologen hydrochloride (185mmg, 0.444mmol) and 2,4,6-collidine (0.74mL) in water (2mL) was stirred at room temperature. A solution of 2,4-dinitro fluorobenzene in CH_3CN (2mL) was added to the first solution. The reaction was stirred for 20 h at room temperature. The resulting solid was filtered, washed with water, THF, ether and dried under vacuum. Yield : 81 %, (243mg, 0.36mmol). Counter ion exchange of the product was accomplished by treatment with excess NH_4PF_6.

^{1}H NMR of **NHDBV^{2+}** (DMSO-d_6, 500MHz) δ (ppm) 9.37 (d, J=6.5Hz, 4H, α of viologen), 8.85 (t, 2H, Ar), 8.84 (s, 2H, NH), 8.73 (d, J=6.5Hz, 4H, β of viologen), 8.28 (dd, 2H, Ar), 7.27 (d, J=10, 2H, Ar), 4.76 (t, 4H, CH_2), 3.67(m, 4H, CH_2), 2.36(m, 4H, CH_2)
^{13}C NMR (DMSO-d_6, 500MHz) δ (ppm) 148.47, 147.86, 147.73, 145.99, 134.98, 130.14, 129.87, 126.30, 123.49, 115.22, 58.972, 29.36.
MS (FAB): 605 $(M+H-2PF_6)^+$, 750 $(M-PF_6)^+$