Conformation and binding properties of polymethylene-linked bisviologens–2-naphthol complexes

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The effect of chain length on charge transfer (CT) complexation behavior between N',N''-poly(methylene)bis-(1-methyl-4,4'-bipyridinium) (VC_nV; bisviologen, $n = 3–8$) and 2-naphthol was studied by using NMR, UV and molecular modeling techniques. Complexation constants, determined by fitting both NMR and UV titration data, show that bisviologens were more effective in complex formation with 2-naphthol than N,N'-dimethyl-4,4'-bipyridinium (MV; methylviologen). For example, the complexation constant of VC_7V–2-naphthol obtained was more than 12 times as large as that of MV–2-naphthol. This implies formation of a sandwich-type complex for bisviologens, which is further supported by the increase of the CT band with added salts due to decreasing electrostatic repulsion. The complexation constants show significant dependence on the linkage chain length of bisviologen with an alternation phenomenon. The extent of complexation of VC_nV–2-naphthol was more pronounced for $n = 5$ and 7 than for $n = 4$, 6, and 8. The stabilization energies for sandwich-type complexes of VC_nV–2-naphthol obtained by molecular modeling showed the same trend. The even–odd alternate trend was explained by the backbone strain of folding that occurs in the formation of sandwich-type complexes, where VC_nV behaves like molecular tweezers.

Introduction

Charge transfer (CT) complexation has been an active area of research for a long time due to its importance in energetic processes including many biological and chemical reactions.[1] A critical aspect in determining the efficiency of electron transfer processes is the noncovalent donor (D)–acceptor (A) interaction, which correlates to the distance between and the relative orientation of the donor and acceptor.

Molecular tweezers[2] and molecular clips[3] that contain two aromatic chromophores connected by a spacer are suitable receptors for planar π-electron guests since they can hold the guest with two aromatic arms through a π–π interaction[4] resulting in sandwich-type complexes. Rigid spacers provide a pre-organized face-to-face geometry of the two aromatic chromophores, thereby giving stronger binding to guest molecules.[5] Flexible spacers,[6] on the other hand, can adapt to various types of guests and are essential components in an induced-fit mechanism[7] or in guest-induced allosterism.[8]

Bipyridinium units have been widely incorporated into many supramolecular systems due to their diverse chemical properties. For example, 4,4'-bipyridinium units were extensively used by Stoddart and co-workers to build rotaxanes[9] and catenanes[10]. Their role is mainly based on the electron-accepting and electrostatic properties resulting from positive charges on the nitrogen atoms. Many octahedral complexes use 2,2'-bipyridine as a bidendate ligand.[11] They also behave as good electron acceptors and show a variety of interesting photochemical and electrochemical properties.[12]

Recently, we reported a conformational study of naphthalene–viologen (1,1'-dialkyl-4,4'-bipyridinium salt) compounds linked by a flexible polymethylene chain, and the effect of the chain length on the conformation was examined in detail.[13] These molecules have the electron donor and acceptor groups inside the molecule. They form intramolecular as well as intermolecular CT complexes and show surprisingly rich dynamic and conformational features depending on the chain length. We also reported the linkage length dependence of intramolecular

photoinduced electron transfer reactions in aromatic donor–viologen acceptor dyads linked by polymethylene bridges, where the formation constants of the intramolecular CT complexes depend little on the length of the linkage.[14]

In this study, we explore the chain length dependence of sandwich-type charge transfer complex formation between bisviologen molecules with a polymethylene chain and 2-naphthol. N',N''-Polymethylenebis(1-methyl-4,4'-bipyridinium) (bisviologens, VC_nV: $n = 3–8$) salts are used as flexible tweezers for the electron donor, 2-naphthol. Intermolecular complexation constants and optimum chain length were determined from NMR and UV experiments. Molecular interpretations of chain length dependence are provided based on the molecular conformations obtained from molecular modeling. VC_nV and 2-naphthol represent the host and guest molecules used in this work.

VC_nV $n = 3 – 8$

2-Naphthol
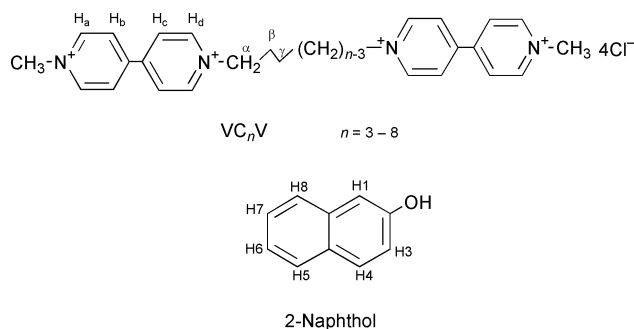
Experimental

Synthesis of bisviologens

N',N''-Polymethylenebis(1-methyl-4,4-bipyridinium) (VC_nV; $n = 3–8$) tetrachlorides were synthesized in a stepwise manner according to the following literature procedure.[15] To an acetonitrile solution of 4,4'-bipyridine, 0.25 equiv. of α,ω-

diiodoalkane (I(CH$_2$)$_n$I; n = 3–5) was added drop by drop over a period of 24 h while the temperature of the reaction mixture was maintained at 70 °C. For n = 6–8, DMF was used instead of acetonitrile. This yielded N',N''-polymethylenebis(4,4'-bipyridinium) diiodide. The yellow precipitate was purified through an ion exchange column (Sephadex CM C-25, ion exchange resin, Aldrich) and the counter ion was exchanged with PF$_6^-$. The product was subsequently treated with methyl iodide in DMF at 90 °C over 10 h to yield a red precipitate of salts. The counter ion was exchanged with PF$_6^-$ and then Cl$^-$ to give the N',N''-Polymethylenebis(1-methyl-4,4'-bipyridinium) tetrachlorides. ^{1}H NMR spectra of VC$_n$Vs were consistent with the structures and were shown to be free of impurity. The molar absorptivities of the compounds were in the range of 47000–51000 M^{-1} cm^{-1} at λ_{max} = 260 nm.

NMR and UV measurements

NMR spectra were obtained on a Bruker DPX-250 in D$_2$O solutions with TSSP (sodium 3-trimethylsilyl[2,2,3,3-^{2}H$_4$]-propionate) as the internal standard. UV spectra were recorded on a Hewlett-Packard 8452A spectrometer. The complexation constants were evaluated by probing the chemical shift variation in the NMR spectra and the charge-transfer band of the complexes (UV) employing a titration methodology [13,14,16] at 25 °C in D$_2$O or H$_2$O solutions. The concentration of the guest molecule was fixed at 2 mM for NMR measurements and at 1 mM for UV experiments. The concentration of the VC$_n$V host was at least 8 times that of 2-naphthol in both experiments. Unless otherwise specified, the ionic strength was kept at a constant value of 0.20 M using NaCl (NMR) and KCl (UV) salts to eliminate any variation in the ionic environment due to a change in the concentration of the charged host molecule.[13]

Calculations

Molecular modeling calculations were carried out using the CVFF force field provided in the Insight II/Discover modeling program package (Molecular Simulations Inc., 1995). A relative permittivity of 78 was used for calculations based in aqueous solution. The cut-off distances for the van der Waals and electrostatic interactions were set to 15 Å.

Results and discussion

Analysis of NMR and UV spectra

^{1}H NMR spectra of aromatic moieties for mixtures of VC$_n$V and 2-naphthol molecules are shown in Fig. 1, where peaks have been assigned with the aid of COSY and NOESY. For comparison, the ^{1}H NMR spectrum for a mixture of methylviologen (MV, N,N'-dimethyl-4,4'-bipyridinium) and 2-naphthol is also included in Fig. 1. Protons from the naphthalene ring show upfield shifts compared to free naphthol protons, which can be ascribed to the formation of charge transfer complexes between the aromatic donor (2-naphthol) and the viologen acceptor with a face-to-face arrangement.[17] However, the amount of shift in naphthol protons, $e.g.$, H$_1$ and H$_7$, is more pronounced for the mixtures containing bisviologens compared to that containing methylviologen, especially for n = 5 and 7. The same trend is observed in viologen protons especially for H$_c$ and H$_d$. As the geometry dependence of the complexation-induced chemical shifts for naphthalene–viologen complexes [13] is much less than the observed dependence of chemical shifts on the linkage length (n), the observations suggest stronger binding between bisviologens and 2-naphthol, presumably due to the formation of sandwich-type complexes.

UV difference spectra of donor–acceptor mixtures are shown in Fig. 2A, where the spectra were obtained using a divided cell with unmixed solutions as a blank. The appearance of a new broad band at >350 nm upon mixing is a characteristic
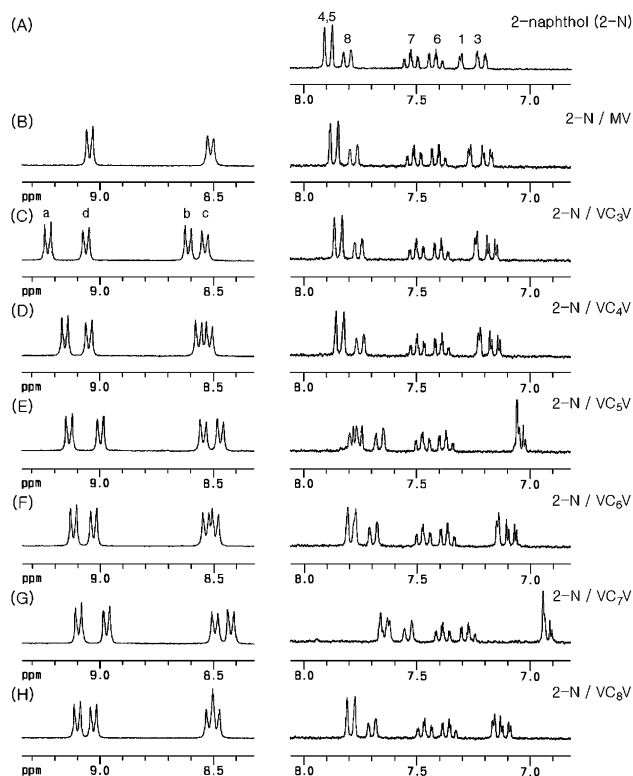

Fig. 1 Partial ^{1}H NMR spectra of ring protons in free 2-naphthol (2-N) (A), mixture of 2-N–MV (B) and mixture of 2-N–VC$_n$V (from C to H) with n = 3–8, respectively. Peak assignments of ring protons are shown in (A) for 2-naphthol and in (C) for bisviologen. The concentration of [2-N] = 2 mM, [MV] and [VC$_n$V] = 4.3 mM in D$_2$O at 25 °C. Ionic strength was adjusted to 0.20 M with NaCl.

feature of charge transfer complexation. The dependence of the magnitude of the charge transfer absorption on the linkage chain length is similar to that of the chemical shift of naphthyl protons. To check the possibility of the formation of sandwich-type complexes, NaCl was added to the VC$_5$V and 2-naphthol mixture. Absorbance of the VC$_5$V and 2-naphthol mixture increased by as much as 2.5 times as the salt concentration was increased up to 1.5 M (Fig. 2B), while that of the MV and 2-naphthol mixture increased by less than 40% in the presence of the same concentration of the salt (result not shown). This observation also supports the formation of a sandwich-type complex because the added salt is expected to stabilize this conformation by reducing the repulsion between the two positively charged viologens.

The complexation equilibria between bisviologens and 2-naphthol can be represented by Scheme 1. Bisviologens in an open conformation can certainly form a 2 : 1 complex with
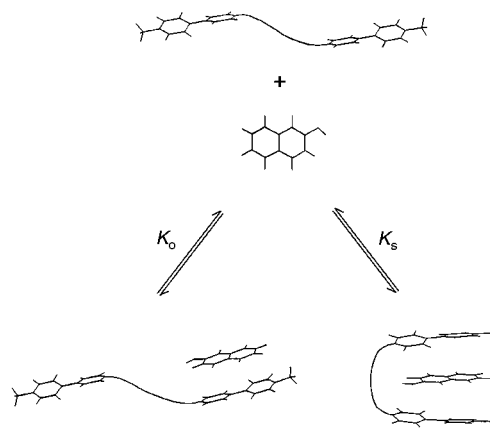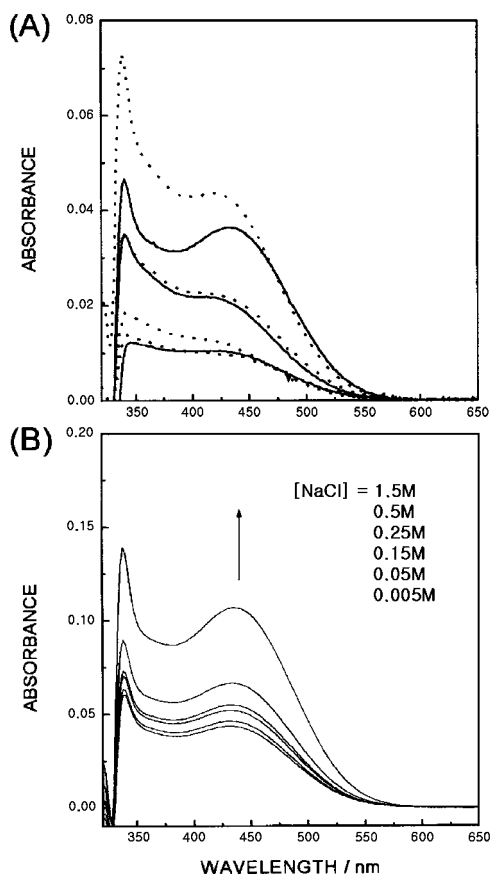

Scheme 1

Fig. 2 The difference absorption spectra of a mixture of 2-N–viologen obtained at 25 °C where spectra prior to mixing was used as a blank. Concentrations are [2-N] = 1.0 mM, [MV] = 1.9 mM and [VC$_n$V] = 0.9 mM; VC$_7$V, VC$_5$V, VC$_6$V, VC$_8$V, MV, VC$_4$V and VC$_3$V from top to bottom at 420 nm (A); effect of added NaCl on the spectra of 2-N–VC$_5$V. [2-N] = 1.0 mM and [VC$_5$V] = 1.5 mM (B) are used. The light path-length is 0.89 cm.

2-naphthol, but the population ratio of a 2 : 1 complex is expected to be negligible since the sandwich-type complex is more stable and 2-naphthol was the limiting species in complexation throughout the experiments.

Thermodynamic parameters of complexation

A titration method, where electron acceptors were progressively added at fixed donor concentration, was used to obtain thermodynamic parameters from NMR and UV spectral changes. Since the ratio of the two complexes is fixed (K_O/K_S, Scheme 1) as the acceptor molecule is added, it is not possible to separate the two equilibrium constants at a given temperature. Therefore, we obtain just the apparent equilibrium constant ($K = K_O + K_S$).

For a 1 : 1 complexation equilibrium between acceptor (A) and donor (D) to form complex (C), the observed chemical shift of the donor protons, δ_{obs}^D, can be written as eqn. (1),[18] where

$$\delta_{obs}^D = \frac{K([D]_t + [A]_t) + 1 - (\{K([D]_t + [A]_t) + 1\}^2 - 4K^2[D]_t[A]_t)^{1/2}}{2[D]_t K} \times$$
$$(\delta_{CIS}^D - \delta_{free}^D) + \delta_{free}^D \quad (1)$$

δ_{CIS}^D (complexation induced chemical shift) stands for the hypothetical chemical shift of the corresponding proton in the complex and the subscript t denotes total concentration. Nonlinear least-squares fitting of δ_{obs}^D as a function of $[A]_t/[D]_t$ gives two unknown parameters, K and δ_{CIS}^D. Four protons (H6, H7, H8, H1) in 2-naphthol were analyzed. Gibbs free

Table 1 Thermodynamic parameters for charge transfer complexation of 2-naphthol with VC$_n$V in D$_2$O solution[a]

	K/M^{-1}	$\Delta G°$/kJ mol^{-1}	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J mol^{-1} K^{-1}
MV	17	−6.98	−21.0	−47.0
$n = 3$	32	−8.54	−26.8	−61.3
$n = 4$	50	−9.71	−28.5	−63.0
$n = 5$	130	−12.0	−44.1	−107.8
$n = 6$	110	−11.6	−34.8	−78.0
$n = 7$	210	−13.2	−37.6	−81.8
$n = 8$	96	−11.3	−31.9	−69.3

[a] When repeated measurements were made, the K values were reproducible to within ±5%, which corresponds to an estimated error of 0.15 kJ mol^{-1} in $\Delta G°$.

energy of complexation is obtained from $\Delta G° = -RT\ln K$. Equilibrium constants were obtained at five different temperatures, and the standard enthalpies and entropies of complexation were obtained from the van't Hoff plot of ln K versus $1/T$. The resulting thermodynamic parameters are summarized in Table 1. Interestingly, the dependence of K values on the linkage length (n) of bisviologens shows an odd–even alternate trend. Bisviologens connected with odd numbers of polymethylene carbon form more stable complexes than those with even numbers of carbon.

Negative enthalpies of complexation indicate favorable van der Waals interactions for complex formation. Since the extent of stabilization would be relatively independent of chain length in the open conformation, the observed variation of $\Delta H°$ is mainly due to formation of a sandwich-type complex, which brings about a different amount of backbone strain depending on the chain length. van der Waals interactions including π–π and donor–acceptor interactions are expected to be approximately twice as strong in the sandwich conformation than in the open conformation, as manifested in the stabilization enthalpies for MV and VC$_5$V. It also suggests that VC$_5$V forms an almost strain-free sandwich-type complex.

The variation of $\Delta S°$ closely resembles that of $\Delta H°$. This implies that enthalpy–entropy compensation holds for this case. Formation of more stable complexes accompanies the loss of entropy. Therefore, it can be concluded that chain-length dependence of complexation is governed mainly by enthalpy change due to backbone strain in the sandwich-type complex.

UV spectra were analyzed in a similar fashion by using the Benesi–Hildebrand method[1] with a ratio of [VC$_n$V]/[2-naphthol] up to 16. Even though the general trend is essentially the same as shown in the NMR analyses, the actual numbers are different. For example, the equilibrium constants for VC$_4$V, VC$_5$V, VC$_6$V, VC$_7$V, and VC$_8$V at 20 °C were determined to be 61, 160, 130, 250, 120 dm^3 mol^{-1} from the NMR experiments, whereas UV experiments gave somewhat smaller values of 45, 130, 96, 170, 86 dm^3 mol^{-1}, respectively. This seems to be mainly due to the difference in the solvents; NMR experiments were carried out in D$_2$O solvent for field-frequency lock. Irwin *et al.* reported that the complexation constant between β-CD and chlorogenic acid was 17% smaller in H$_2$O than in D$_2$O.

Molecular modeling and conformations of complexes

Molecular modeling provides useful information on molecular structure, usually complementary to the experimental techniques. In an effort to see the origin of chain-length dependence of complexation constants, we conducted molecular modeling calculations using the CVFF force field provided in the InsightII/Discover modeling program package. Energy minimization from many initial conformations converged into two conformations, which represent the open and sandwich-type conformations: the open conformations appear as local minima. The optimized open and sandwich structures are shown in Figs. 3 and 4, respectively. Stabilization energies in

Table 2 Calculated energy (kJ mol^{-1}) of charge transfer complexation between 2-naphthol and VC$_n$V [a,b]

	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$
Interaction [a]						
ΔE_O	−77.03	−69.71	−70.04	−68.87	−68.91	−68.83
ΔE_S	−104.1	−110.3	−124.6	−119.2	−121.6	−114.3

[a] $\Delta E_{\text{O or S}} = E_{\text{O or S}} - (E_f \text{ of acceptor} + E_f \text{ of 2-naphthol})$. [b] ΔE_O with methylviologen (MV) is −64.89 kJ mol^{-1}.

forming two types of complexes (ΔE_O and ΔE_S) are shown in Table 2.

Bipyridinium and naphthol planes are parallel in most energy-minimized structures, which can be explained in terms of π–π interactions. Distances between donor and acceptor planes in sandwich-type complexes are about 3.8 Å and agree well with many experimental values.[20] A theoretical study by Hunter and Sanders predicted that a cofacial structure with offset is more stable than an exactly super-imposable structure.[21] It is also found that quinoid molecules prefer twisted face-to-face structures.[22] Optimized structures in Figs. 3 and 4 agree well with these observations.

Structures of the open conformers in Fig. 3 do not vary much according to the chain length except for VC$_3$V. 2-Naphthol is above one of the bipyridinium moieties for $n = 4$–8, but it is located between the two bipyridiniums in VC$_3$V. Except for VC$_3$V, stabilization energies of open conformations (ΔE_O) are virtually independent of the chain length (Table 2). This implies that the two viologen moieties are nearly independent in the formation of open chain 1 : 1 complexes. The shorter chain in VC$_3$V seems to allow 2-naphthol to have favorable van der Waals interactions with both bipyridiniums simultaneously, further stabilizing the complex, and giving lower ΔE_O values.

The sandwich-type conformers in Fig. 4 have structures more diverse in orientation as well as position of the donor molecule. For compounds with odd numbers of methylene carbons, the two bipyridiniums are superimposable and the naphthol ring plane is twisted-parallel with the bipyridinium moieties. It seems that the π–π interaction is maximized in this con-

figuration. We also observe that the naphthol ring is located near the outer pyridine ring for short chains and moves inside as the chain becomes longer. At the same time, the orientation of the naphthol ring becomes more parallel to the bipyridinium rings. This trend is more prominent for VC$_n$Vs, where $n = 4$, 6 and 8. These observations may be explained by combining steric effects and electrostatic interactions. The hydroxy group of 2-naphthol is pointing inside in all cases, which allows electrostatic attraction to the positively charged nitrogen atoms in the inner pyridine rings. This is supported experimentally by the fact that the naphthyl protons adjacent to the hydroxy group (H3 and H1) and the inner pyridyl protons (H$_c$ and H$_d$) show the most dramatic dependence on the chain length (see Fig. 1). However short chains do not allow enough room to accommodate the OH group, resulting in a twisted-parallel configuration. As the chain becomes longer, there is more space in the inner part to allow the 2-naphthol to move inside and to turn around to achieve the most favorable electrostatic interaction. The stabilization energies given in Table 2 for sandwich-type complexes (ΔE_S) also agree well with the alternating trend in equilibrium constants.

The hypothetical chemical shift of the completely complexed state, $\delta_{\text{CIS}}^{\text{D}}$, is also obtained by fitting of the NMR titration data (Table 3). Even though the details are somewhat obscure, the general trend agrees well with conclusions made from molecular modeling.

pH Dependence and complexation of 2-naptholate with VC$_5$V

The UV spectra of the VC$_5$V and 2-naphthol mixture change dramatically depending on pH as shown in Fig. 5 where $[VC_5V]_t = 16.3$ mM and $[2\text{-naphthol}]_t = 1.0$ mM. The absorption band near 550 nm, which was not observed at low pH, appears with increasing pH due to charge-transfer complexation between VC$_5$V and 2-naptholate. Complexation equilibria including acid–base chemistry is represented by Scheme 2.

K_1 and K_2 are the complexation constants of 2-naphthol and 2-naptholate with VC$_5$V, respectively. K_{a1} and K_{a2} are acid dis-
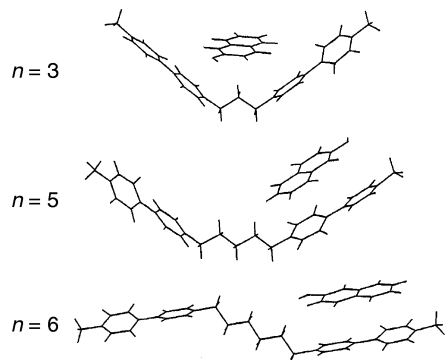

Fig. 3 Energy-minimized structures of open form charge transfer complexes of 2-naphthol–VC$_n$V depending on the chain length of VC$_n$V for $n = 3$, 5 and 6. The structures of VC$_4$V and VC$_8$V complexes were similar to that of VC$_6$V, and that of VC$_7$V was similar to that of VC$_5$V.

$$
\begin{array}{ccccc}
\text{2-naphthol} & + & VC_5V & \xrightleftharpoons{K_1} & \text{complex 1} \\
\Big\updownarrow {\scriptstyle -H^+, K_{a1}} & & & & \Big\updownarrow {\scriptstyle -H^+, K_{a2}} \\
\text{2-naptholate} & + & VC_5V & \xrightleftharpoons{K_2} & \text{complex 2}
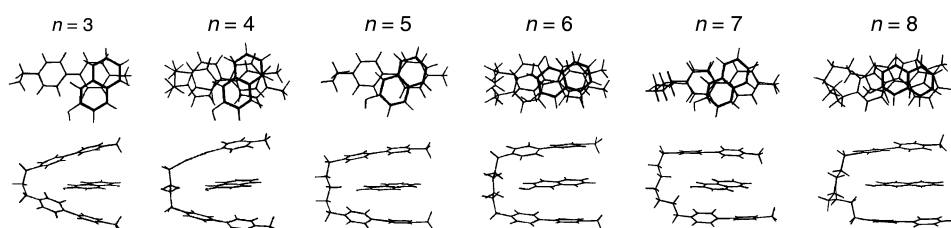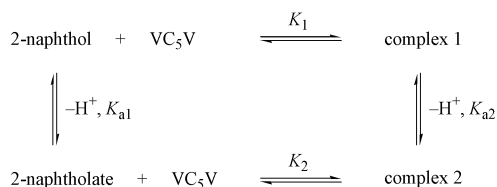\end{array}
$$

Scheme 2

Fig. 4 Optimized structures of sandwich-type charge transfer complexes of 2-naphthol–VC$_n$V depending on the chain length of VC$_n$V; top views (upper) and side views (lower).

Table 3 The calculated chemical shifts of protons in 2-naphthol in the completely complexed form with VC_nV

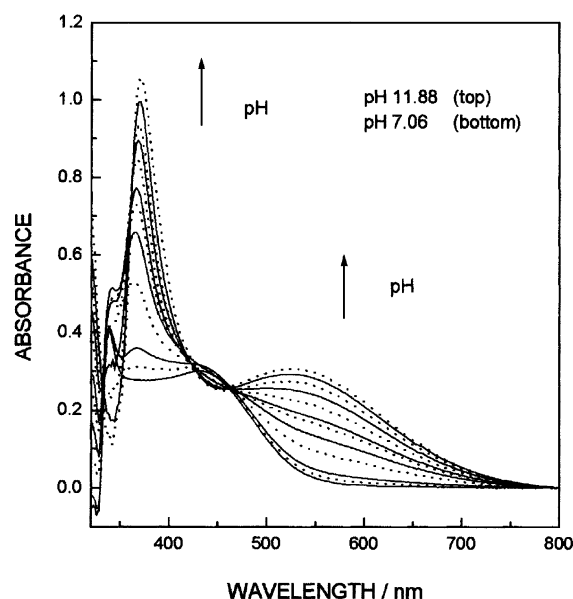| # of chain	Proton (ppm)					
	H	H8	H7	H6	H1	H3
Free 2-naphthol	7.89	7.81	7.53	7.42	7.31	7.22
3	7.48	7.37	7.28	7.19	6.70	6.79
4	7.56	7.45	7.34	7.23	6.79	6.84
5	7.47	7.34	7.35	7.26	6.49	6.71
6	7.54	7.41	7.34	7.24	6.72	6.76
7	7.40	7.28	7.24	7.13	6.59	6.62
8	7.51	7.39	7.29	7.18	6.76	6.80

Fig. 5 Variation of the absorption spectra of 2-naphthol–VC_5V with pH. [2-Naphthol] = 1.0 mM; [VC_5V] = 16.3 mM. pH values corresponding to absorbances at 550 nm are 7.1, 7.8, 8.2, 8.6, 9.0, 9.2, 9.3, 9.6, 9.9, 10.4, 10.9 and 11.9, respectively, from bottom to top.

sociation constants of 2-naphthol in the free and complexed states, respectively.

In a separate experiment with solutions of 2-naphthol in the absence of viologens, the absorption at around 350 nm increased with increasing pH as shown in Fig. 5. The pH dependences of the absorption at 360 nm for free 2-naphthol and at 580 nm for 2-naphthol in the presence of 16.3 mM of VC_5V were that of a typical titration curve (not shown). The pH at the mid-point of the absorption titration of 2-naphthol in the absence of viologen, which represents the pK_a of free 2-naphthol, was estimated to be 9.47. However, the same procedure for the complexed 2-naphthol yields only the apparent pK_a value (pK_{a2}') from the titration curve as the deprotonation reaction is coupled with two complexation reactions. We obtained a value of 9.08 for pK_{a2}'. The actual acidity constant for the complexed 2-naphthol may be obtained from the following analysis.

From Scheme 2, the concentration of complex 2 can be expressed by eqn. (2), where [2-naphthol]$_t$ = 1.0 mM. Using the

$$[\text{complex 2}] = \frac{[\text{2-naphthol}]_t}{1 + \dfrac{[H^+]}{K_{a2}} + \dfrac{1}{K_2[VC_5V]} + \dfrac{[H^+]}{K_1[VC_5V]K_{a2}}} \quad (2)$$

fact that [complex 2] at pH = pK_{a2}' is half of the concentration expected when all of 2-naphthol is present in the deprotonated form, its concentration can be written as eqn. (3).

$$[\text{complex 2}]_{pH = pK_{a2}'} = \frac{[\text{2-naphthol}]_t K_2[VC_5V]}{2(1 + K_2[VC_5V])} \quad (3)$$

Substituting eqn. (3) into eqn. (2), we obtain eqn. (4).

$$K_2[VC_5V] = \frac{2(1 + K_2[VC_5V])}{1 + \dfrac{10^{-pK_{a2}}}{K_{a2}} + \dfrac{1}{K_2[VC_5V]} + \dfrac{10^{-pK_{a2}'}}{K_1[VC_5V]K_{a2}}} \quad (4)$$

Furthermore, simple analysis of the equilibria in Scheme 2 gives $K_2/K_1 = K_{a2}/K_{a1}$.

Since VC_5V is in large excess over 2-naphthol, we can assume that the concentration of VC_5V is the same as the total concentration of VC_5V, 16.3 mM. Using pK_{a2}' = 9.08, K_1 = 130 dm³ mol⁻¹ and pK_{a1} = 9.47, [VC_5V] = 16.3 mM, the complexation constant (K_2) of naphtholate with VC_5V and the true acidity constant of the complexed 2-naphthol (pK_{a2}) are determined to be 410 dm³ mol⁻¹ and 8.97, respectively. This shows that 2-naphthol becomes a stronger acid in the complexed state, which can be rationalized in terms of the stabilization of the anion in the complex by favorable electrostatic interactions.

Conclusions

We have shown the dependence of the chain length on charge transfer complexation behavior between VC_nV (n = 3–8) and 2-naphthol. Complexation constants determined by fitting both NMR and UV titration data show that VC_nVs are as much as 12 times more effective in complex formation with 2-naphthol than MV, which implies the formation of sandwich-type complexes with VC_nV. Complexation constants obtained from NMR measurements at 25 °C are 17, 32, 50, 130, 110, 210 and 96 M⁻¹ for MV and n = 3–8 of VC_nV, respectively. Van't Hoff's analysis of temperature dependence shows that $\Delta H°$ values of VC_nV, for n = 6 and 8, are more negative than those of n = 3 and 4 by more than 3.4 kJ mol⁻¹ and more positive than those of n = 5 and 7 by more than 2.8 kJ mol⁻¹, with similar variation in $\Delta S°$. Such a chain-length dependence of complexation is interpreted by an enthalpy change due to backbone strain in a sandwich-type complex. The even–odd alternate trend was also observed in the stabilization energies for sandwich-type complexes of VC_nV–2-naphthol determined by molecular modeling calculations. The relative positions of the bipyridinium and naphthalene rings in energy-minimized structures support the most pronounced chemical shift of the protons adjacent to the hydroxy group of 2-naphthol depending on the chain length in VC_nV. A significant increase of CT absorbance in VC_5V–2-naphthol was observed with added salt compared with that in MV–2-naphthol probably by reducing electrostatic repulsion in the sandwich complex. The above results support unequivocally the belief that VC_nVs behave as effective molecular tweezers, especially when n = 7. The pK_a of 2-naphthol in the 2-naphthol–VC_5V complex is 8.97, which is 0.50 units lower than that of free 2-naphthol.

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