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Orientational Isomers of Cyclodextrin Semirotaxanes and Rotaxanes With Organic and Transition Metal Complex Stoppers

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The novel asymmetric dicationic ligands $[Quin(CH_2)_{10}tbp]^{2+}$, $[Quin(CH_2)_{10}bpy]^{2+}$, and $[Lut(CH_2)_{10}bpy]^{2+}$ ($Quin^+$ = quinuclidinium, Lut = 3,5-lutidinium, tbp^+ = 4-*tert*-butylpyridinium, and bpy^+ = 4,4′-bipyidinium) form [2]semirotaxanes with α- and β-cyclodextrins in aqueous solution, with the cyclodextrin passage possible only over the 4-*tert*-pyridinium or bipyridinium end groups to yield two orientational isomers. The kinetics of the formation and dissociation of the kinetically and thermodynamically preferred orientational isomers of the $[Quin(CH_2)_{10}tbp]^{2+}$[2]semirotaxane with α-CD have been investigated by ^1H NMR spectroscopy. Complexation of the free nitrogen on the 4,4′-bipyridinium end groups of the $[R(CH_2)_{10}bpy]^{2+}$ ligands by the aquapentacyanoferrate(II) ion results in the formation of the corresponding [2]rotaxanes.

Keywords: Cyclodextrin; Rotaxanes; Self-assembly; Kinetics; Pentacyanoferrate(II); Orientational isomers

INTRODUCTION

Rotaxanes [1,2] are complexes in which a cyclic bead is threaded by a linear chain stoppered by bulky end groups which prevent the dissociation of the complex into its cyclic and linear component. If the two end groups are not sufficiently bulky to prevent dissociation, a pseudorotaxane is formed, while with only one bulky end group the complex may be termed a semirotaxane. One commonly employed family of cyclic hosts molecules in the assembly of rotaxanes is the cyclodextrins (CD) [3–5], composed of α-(1 → 4)-linked D-(+)-glucopyranose units, of which six (α-CD), seven (β-CD), and eight (γ-CD) units are the most common. The stopper end groups used in cyclodextrin rotaxanes have been either organic compounds and/or transition metal complexes [6–9]. We have used the pentacyanoferrate(II) ion to coordinate to aromatic nitrogen atoms at the ends of the linear chains such as $[R(CH_2)_nR']^{2+}$ (R,R′ = 4,4′-bipyridine (bpy) [10–12], pyrazine [12], and 4-cyanopyridine [13], $n = 8$–12) or pyrXpyr (X=—N=N— [14], —CH=CH— [14], and —CH=N—$(CH_2)_n$—N=CH— [15], $n = 2$, 4, and 6) to assembly cyclodextrin [2]rotaxanes. Other metal centers, such as $[Ru(NH_3)_5]^{2+}$[16], $[Ru(bpy)_2]^{2+}$[17], Co(III) amines [18] and cob(III)alamins [19], and ferrocenes [20,21] have also been employed in the syntheses of cyclodextrin rotaxanes and polyrotaxanes. Bulky organic groups, such as 3,5-lutidinium (Lut^+) and quinuclidinium ($Quin^+$) for example [22,23], also provide a steric barrier preventing the threading or dethreading of α-CD over them. Other cationic end groups, such as $N(CH_3)_3^+$[24], $P(CH_3)_3^+$[24], and 4-*tert*-butylpyridinium (tbp^+) [25] allow for slow threading of α-CD, by a slippage mechanism [26–29], with the rate constants for the threading and the dethreading processes depending on the steric bulk of the end groups.

Recently, we reported that orientational isomers of α-CD [2]semirotaxanes are formed when asymmetric dicationic threads such as $[Quin(CH_2)_{10}R]^{2+}$ and $[Lut(CH_2)_{10}R]^{2+}$, where $R^+ = N(CH_3)_3^+$ and $N(CH_3)_2CH_2CH_3^+$, are employed [22]. Subsequently, Harada and coworkers have described similar behavior with the $[Lut(CH_2)_{10}Mepy]^+$ ($Mepy^+$ = 2-methylpyridinium) thread, with the kinetics controlling the orientation of threading at lower temperatures and the thermodynamics controlling the equilibrium at higher temperatures [23]. Isnin

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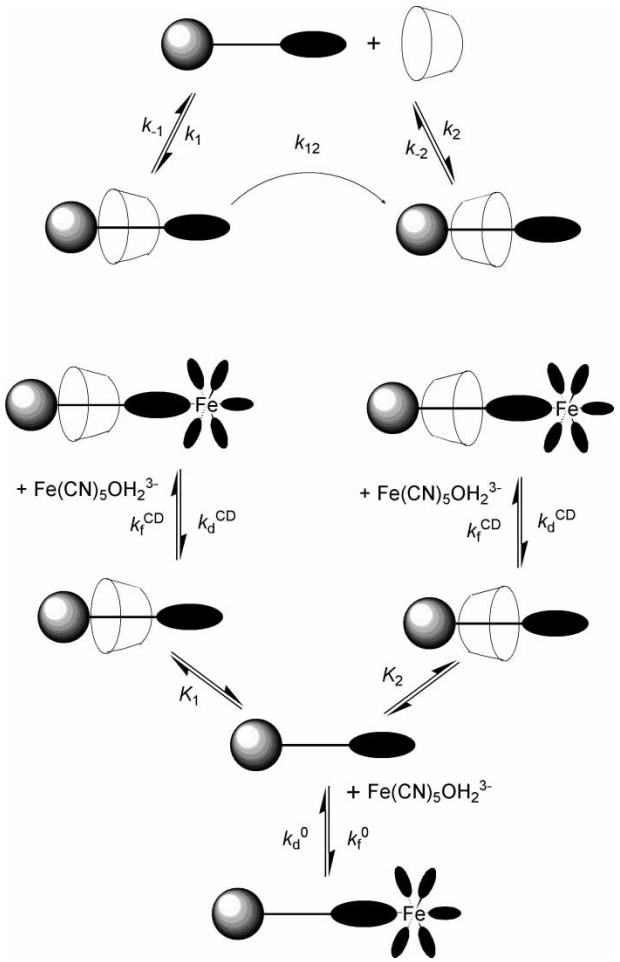
and Kaifer have reported the synthesis of orientational isomers of asymmetric zwitterionic [2]rotaxanes of α-CD, in which one stopper is an organic species (napthalenesulfonate), while the other is a transition metal complex (a substituted ferrocene) [20,21]. Park and Song have prepared the two orientational isomers of a α-CD [2]rotaxane with carbazole and bulky viologen stoppers [30]. The assemblies of α-CD [2]- and [3]rotaxanes with asymmetric threads that exhibit only one orientational isomer have also been prepared, by the research groups of Anderson [31–33], Tian [34,35] and Park [36,37]. Park has recently re-evaluated the rate and equilibrium constants for the formations and dissociations of CD inclusion complexes to incorporate bidirectional inclusion pathways involving orientational isomers [38].

In this paper, we describe the kinetics and mechanisms of the self-assemblies of [2]semirotaxanes of α- and β-CD using $[Quin(CH_2)_{10}tbp]I_2$, $[Quin(CH_2)_{10}bpy]Br_2$ and $[Lut(CH_2)_{10}bpy]Br_2$ where tbp^+ = 4-*tert*-butylpyridinium, bpy^+ is 4,4′-bipyridinium, $Quin^+$ is quinuclidinium, and Lut^+ is 3,5-lutidinium, and subsequently the corresponding [2]rotaxanes by coordinating the free pyridine nitrogen of the $[R(CH_2)_{10}bpy]^{2+}$ ligands with the pentacyanoferrate(II) ion (Scheme 1). The rate and equilibrium constants obtained from UV-visible and ^1H NMR kinetic studies are compared with our previous studies on [2]pseudorotaxanes and [2]rotaxanes with symmetric threads, such as $[tbp(CH_2)_{10}tbp]^{2+}$[25] and $[bpy(CH_2)_{10}bpy]^{2+}$[10,11] and [2]semirotaxanes and [2]rotaxanes with asymmetric threads containing the $Quin^+$ and Lut^+ stopper groups [22].



SCHEME 1 Formations of the cyclodextrin [2]semirotaxanes (top) and [2]rotaxanes (bottom).

RESULTS AND DISCUSSION

[2]Semirotaxanes

The additions of α-cyclodextrin (α-CD) to aqueous solutions of $[Quin(CH_2)_{10}tbp]^{2+}$(**1**), $[Quin(CH_2)_{10}bpy]^{2+}$(**2**), and $[Lut(CH_2)_{10}bpy]^{2+}$(**3**) ligands result in the formation of [2]semirotaxane complexes. As a result of the asymmetries in both the guest and host molecules of the semirotaxane, two orientational isomers are generated in solution. In the ^1H NMR spectra of the semirotaxanes, each proton resonance in the free guest molecule becomes a pair of resonances upon inclusion in the α-CD cavity. The chemical shifts of the guest protons in the free guest and the two orientational isomers (referred to as the kinetically and thermodynamically favored isomers; see below for explanation) of the semirotaxanes are given in Fig. 1. For the $[R\{(CH_2)_{10}\alpha\text{-CD}\}R']^{2+}$ semirotaxanes, the proportions of the two orientational isomers (kinetic:thermodynamic) could be determined from the relative integrations of the included guest proton resonances, with the [2]semirotaxanes exhibiting a modest preference for one isomer over the other: 30:70 for (**1**), 42:58 for (**2**), and 41:59 for (**3**).

In our previous report on the [2]semirotaxanes of α-CD with $[Quin(CH_2)_{10}R]^{2+}$ and $[Lut(CH_2)_{10}R]^{2+}$, where $R^+ = N(CH_3)_3^+$ and $N(CH_3)_2CH_2CH_3^+$[22], it was determined from ROESY ^1H NMR spectrum (using correlations between the CD internal H3 and H5 protons and the Hβ and Hγ protons of the threads) of $[Quin(CH_2)_{10}N(CH_3)_2CH_2CH_3\alpha\text{-CD}]^{2+}$ (the only complex which could be successfully purified from the excess α-CD) that the α-CD was oriented with its narrower and wider ends towards the $Quin^+$ end group in the thermodynamic and kinetic isomers, respectively. Unfortunately, it was not possible to purify the [2]semirotaxanes in this study sufficiently to unambiguously assign the orientations of the kinetic and thermodynamic isomers from their ROESY ^1H NMR spectra. The electrospray mass spectra of the [2]semirotaxanes (assembled in solutions of 1 mM guest and 10 mM host) are consistent with the formation of the $\{R(CH_2)_{10}R'CD\}^{2+}$ species (m/z = 679.4 (α-CD) for (**1**); 698.9 (α-CD) and 771.0 (β-CD) for (**2**); 1166.3 (α-CD) and 768.9 (β-CD) for (**3**). The stability constants for the [2]semirotaxanes

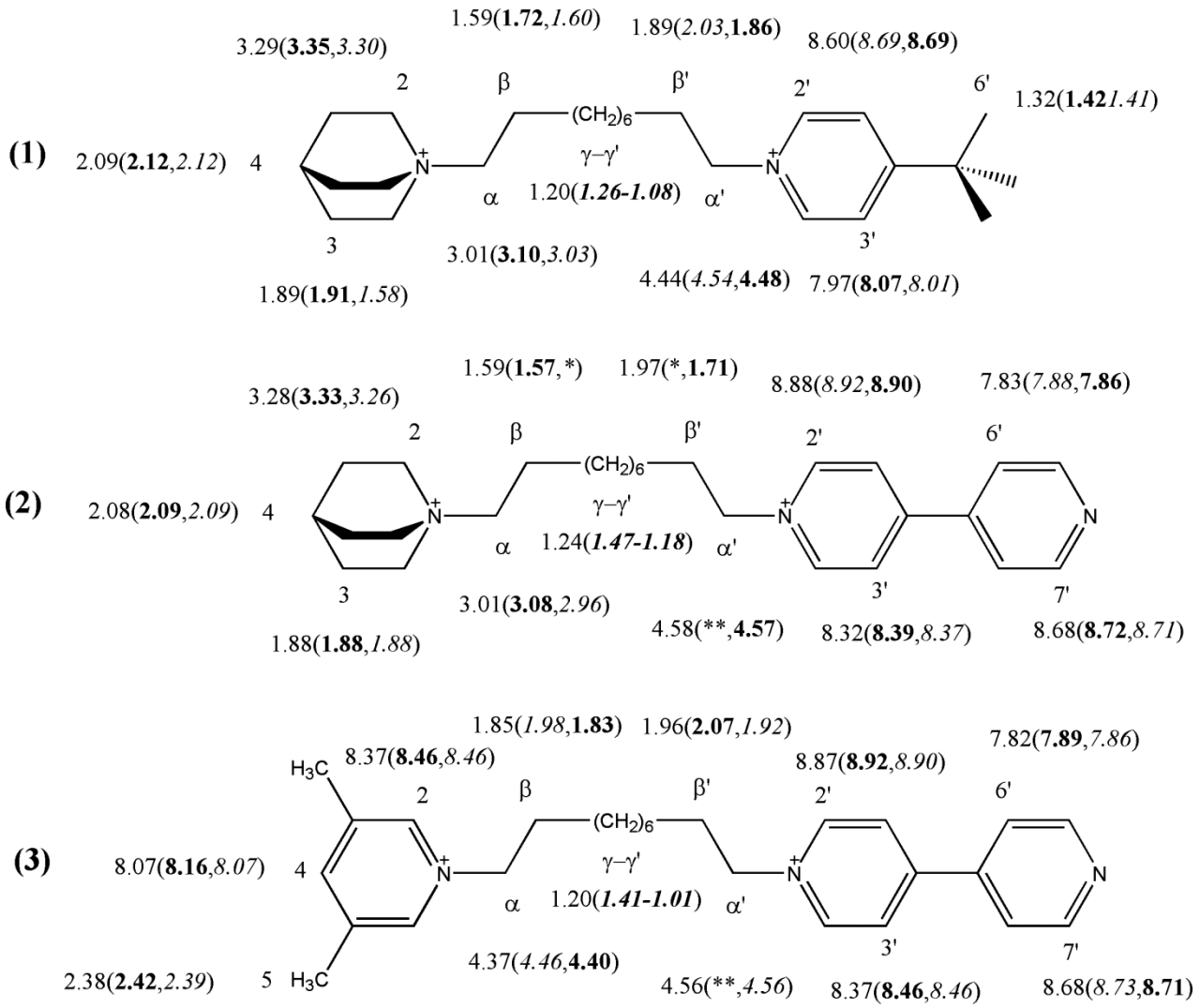


FIGURE 1 The proton resonances of the guests (1) $[Quin(CH_2)_{10}tbp]^{2+}$, (2) $[Quin(CH_2)_{10}bpy]^{2+}$, and (3) $[Lut(CH_2)_{10}bpy]^{2+}$ before and after inclusion in α-CD. The chemical shifts listed before the brackets are the proton resonances prior to inclusion. The chemical shifts for the kinetically preferred isomer are given in italics in the brackets, while the chemical shifts for the thermodynamically preferred isomer are given in bold in the brackets. The peaks obscured by other guest peaks and by HOD are indicated by * and **, respectively.

formed from the $[R(CH_2)_2bpy]^{2+}$ ligands and α- and β-cyclodextrin, K_L, were determined using ^1H NMR titrations. With the α-CD titrations, increasing the concentration of the host resulted in the formation of new peaks of the [2]semirotaxane at the expense of the peaks for the free ligand, indicating that the [2]semirotaxanes form and dissociate slowly on the NMR timescale. Stability constants of $K_L^{\alpha\text{-CD}} = 2000 \pm 200\,M^{-1}$ and $3000 \pm 300\,M^{-1}$ were determined for the [2]semirotaxanes where R = $Quin^+$ and R = Lut^+, respectively, at 25°C. The values of $K_L^{\alpha\text{-CD}}$ for these ligands are similar to the range of values measured for other $\{R(CH_2)_{10}R\alpha\text{-CD}\}^{2+}$ pseudorotaxanes [10–13,24,25,39–42] and semirotaxanes [22,43].

In the cases of the $[R(CH_2)_2bpy]^{2+}$ ligands, peaks associated with $\{R(CH_2)_2bpy2CD\}^{2+}$ species are also observed in the electrospray mass spectra (m/z = 679.4 (α-CD) for (**1**); 1176.0 (α-CD) and 1337.9 (β-CD) for (**2**); 1174.2 (α-CD) and 1336.0 (β-CD) for (**3**)), suggesting that a second host molecule is associated with the 4,4′-bipyridinium end group. At higher concentrations of α-CD, the proton resonances of the 4,4′-bipyridinium end group on the $[Quin(CH_2)_{10}bpy]^{2+}$ ligand exhibited shifts in their proton resonances, also consistent with the binding of a second α-CD host molecule to this end of the ligand. Fits of the observed changes in the H7′ chemical shift against [α-CD] yielded a stability constant for the binding of a second α-CD of $K_L^{2CD} = 3 \pm 2\,M^{-1}$. With β-CD, the [2]semirotaxanes form and dissociate rapidly on the NMR timescale, resulting simply in complexation induced shifts (CIS) in the proton resonances. The stability constants for the β-CD [2]semirotaxanes were determined from ^1H NMR chemical shift titrations (monitoring the Hβ protons) to be $203 \pm 20\,M^{-1}$ and $400 \pm 90\,M^{-1}$ for R = $Quin^+$ and R = Lut^+, respectively.

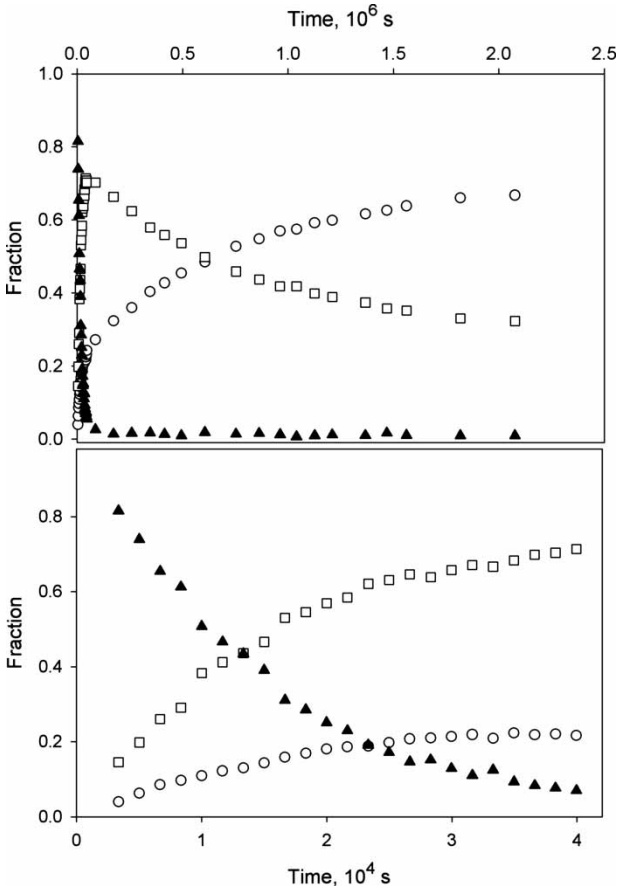


FIGURE 2 Plots of the fractions of the reactant [Quin(CH2)10tbp]2 + (▲) and the kinetically preferred (□) and thermodynamically preferred (○) orientation isomers of the $[Quin\{(CH_2)_{10}\ \alpha\text{-CD}\}tbp]^{2+}$[2]semirotaxane products. The upper plot shows the overall reaction time course, while the lower plot displays the initial 40,000 seconds of reaction.

Kinetics of the Formation and Dissociation of the [2]Semirotaxanes

While the addition of α-cyclodextrin to aqueous solutions of the $[Quin(CH_2)_{10}bpy]^{2+}$ and $[Lut(CH_2)_{10}bpy]^{2+}$ ligands result in the rapid formation of [2]semirotaxanes by the threading of the α-CD over the 4,4′-bipyridinium end group, the formation of the [2]semirotaxane with the $[Quin(CH_2)_{10}tbp]^{2+}$ thread is much slower as a result of the bulkier 4-*tert*-pyridinium end group, as we have shown with the symmetrical $[tbp(CH_2)_{10}tbp]^{2+}$ thread [25]. The 4-*tert*-butylpyridinium end group can pass through either the wider or narrower end of the cyclodextrin, generating the two orientation isomers. The kinetics of the formation and dissociation of the $[Quin\{(CH_2)_{10}\alpha\text{-CD}\}tbp]^{2+}$ species were measured using ^{1}H NMR spectroscopy at 25°C (Fig. 2). The reaction proceeds in two steps, with an initial formation of a distribution of the two isomers after about 12 hours, followed by a second step leading to a final equilibrium mixture of the orientational isomers after several weeks. The kinetic data were fit to double exponential curves [22] with the faster portion corresponding to k_1 or k_2 for the two orientational isomers (Fig. 2).

The rate constants for the formation of both semirotaxane isomers were found to be dependent on the concentration of α-CD, with slight curvature at higher [α-CD], as shown in Fig. 3. The curvature is consistent with the formation of a weak inclusion complex between the 4-*tert*-butylpyridinium group and α-CD, as was observed for the formation of the pseudorotaxane with the $[tbp(CH_2)_{10}tbp]^{2+}$ thread

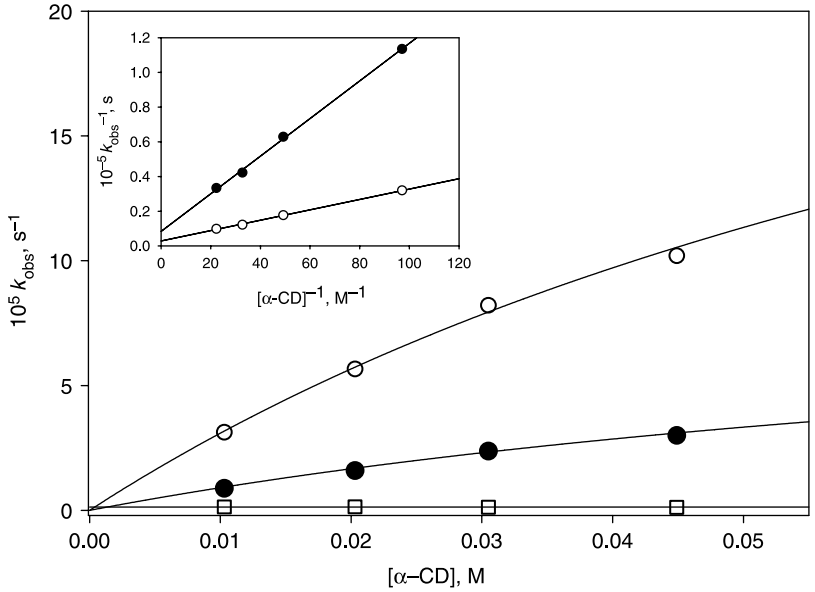


FIGURE 3 Plots of observed rate constants for the formation of the $[Quin\{CH_2)_{10}\cdot\alpha\text{-CD}\}tbp]^{2+}$ [2]semirotaxanes at 25 °C in D_2O: (○) kinetically preferred isomer, (•) thermodynamically preferred isomer, and (□) rate of conversion between the kinetically and thermodynamically preferred isomers. The inset is a double reciprocal plot of k_{obs}^{-1} against $[\alpha\text{-CD}]^{-1}$ for the formation reactions.

($K_{CD} = 18 \pm 3\,M^{-1}$[25]). This initial α-CD inclusion of the 4-*tert*-butylpyridinium groups is also supported by the small downfield shifts observed in the proton resonances of this end group (+0.08 ppm for the methyl protons, +0.06 ppm for H2, and +0.02 ppm for H3) upon the initial addition of α-CD. The observed first-order rate constants may be expressed as in Eq. (1) [25].

$$k_{obs} = \frac{k_n K_{CD}[\alpha - CD]}{1 + K_{CD}[\alpha - CD]} \quad (1)$$

A double reciprocal plot of k_{obs}^{-1} against $[\alpha\text{-CD}]^{-1}$ (inset in Fig. 3) gives limiting values (at high [α-CD]) of $k_1 = (3.6 \pm 0.3) \times 10^{-4}\,s^{-1}$ and $k_2 = (1.2 \pm 0.1) \times 10^{-4}\,s^{-1}$ from the reciprocals of the intercepts and $K_{CD} = 8.5 \pm 1.5\,M^{-1}$ from an average of the ratios of the intercepts to the slopes. This value of K_{CD} is approximately half the value determined for the $[tbp(CH_2)_{10}tbp]^{2+}$ thread as it has only one 4-*tert*-butylpyridinium end unit to potentially bind to. The second-order rate constant for the formations of the [2]semirotaxanes, k_1 (for the kinetically preferred isomer) and k_2 (for the thermodynamically preferred isomer), are given by the product of the limiting first-order rate constant and K_{CD}, with $k_1 = (3.0 \pm 0.5) \times 10^{-3}\,M^{-1}\,s^{-1}$ and $k_2 = (1.0 \pm 0.2) \times 10^{-3}\,M^{-1}\,s^{-1}$. The overall formation rate constant, $k_f = k_1 + k_2$, is $(4.0 \pm 0.7) \times 10^{-3}\,M^{-1}\,s^{-1}$, which is approximately half of the value determined for the $[tbp(CH_2)_{10}tbp]^{2+}$ thread ($(7.6 \pm 1.8) \times 10^{-3}\,M^{-1}\,s^{-1}$ [25]), as would be expected. The rate constant for the conversion between the kinetic and the thermodynamic isomers, determined from a first-order fit of the data for the slower second portion of the reaction in Fig. 2 (upper plot), is independent of the [α-CD] (Fig. 3), with $k_{12} = (1.3 \pm 0.2) \times 10^{-6}\,s^{-1}$ at 25°C.

The rate constants for the dissociation of the thread from $[Quin\{(CH_2)_{10}\alpha\text{-CD}\}tbp]^{2+}$ were determined by adding a large excess of $[bpy(CH_2)_{12}bpy]^{2+}$, a competing thread ($K^{\alpha\text{-CD}} = 3.7 \times 10^3\,M^{-1}$ [11]), to a solution of the [2]semirotaxane at 25°C. The simultaneous dissociation reactions of the two orientational isomers were monitored by ^1H NMR spectroscopy with values of $k_{-1} = (8.3 \pm 0.8) \times 10^{-6}\,s^{-1}$ and $k_{-2} = (0.56 \pm 0.03) \times 10^{-6}\,s^{-1}$ determined for the kinetically preferred and thermodynamically preferred isomers, respectively. From the formation and dissociation rate constants, the stability constants ($K_n = k_n/k_{-n}$) for the two orientational isomers are $K_1 = 360 \pm 40\,M^{-1}$ and $K_2 = 1800 \pm 200\,M^{-1}$. The relative stability constants for the two orientational isomers is clearly governed by the differences in the dissociation rate constants, an observation made previously with CD rotaxanes containing other asymmetric guest molecules [22,38].

Ligand Substitution Kinetics

The ligand substitution reactions of the aquapentacyanoferrate(II) ion ($Fe(CN)_5OH_2^{3-}$) with the $[R(CH_2)_{10}bpy]^{2+}$ ligands result in the formation of $[Fe(CN)_5(bpy(CH_2)_{10}R)]^-$ complexes, which exhibit an intense metal-to-ligand charge transfer (MLCT) band in their visible spectra. The kinetics of the metal complex formations were investigated at 25.0°C using stopped-flow techniques, monitoring the increase in the absorption of the MLCT band. The second-order rate constants were calculated from the linear dependences of the observed pseudo-first-order rate constants on the concentrations of the ligands (in excess). With no cyclodextrin present, the rate constants were determined to be $2620 \pm 300\,M^{-1}\,s^{-1}$ and $2440 \pm 200\,M^{-1}\,s^{-1}$, respectively for $R = Quin^+$ and $R = Lut^+$. The formation rate constant for the related ligand $[bpy(CH_2)_{10}bpy]^{2+}$ was previously determined to be $7300 \pm 220\,M^{-1}\,s^{-1}$ [11], consistent with the $[R(CH_2)_{10}bpy]^{2+}$ ligands having only one 4,4′-bipyridinium group available for coordination, while the $[bpy(CH_2)_{10}bpy]^{2+}$ ligand has two potential coordination sites.

In the presence of α- and β-cyclodextrins, the ligand substitution rate constants decrease, as shown in Figs. 4 and 5. The inclusion of the decamethylene chain of the $[Quin(CH_2)_{10}bpy]^{2+}$ ligand in one α-CD cavity causes the rate constant for the formation reaction to drop to $1650 \pm 160\,M^{-1}\,s^{-1}$ (Fig. 4), approximately half that of the free ligand. This drop is of similar magnitude to those measured for other $[R(CH_2)_{10}R]^{2+}$ ligands, where R = 4,4′-bipyridinium [11], pyrazinium [12], and 3- and 4-cyanopyridinium [13]. Similar behaviour is observed with β-CD, lowering the rate constant to $1100 \pm 160\,M^{-1}\,s^{-1}$ (Fig. 5). The rate constant for the formation reaction drops to zero

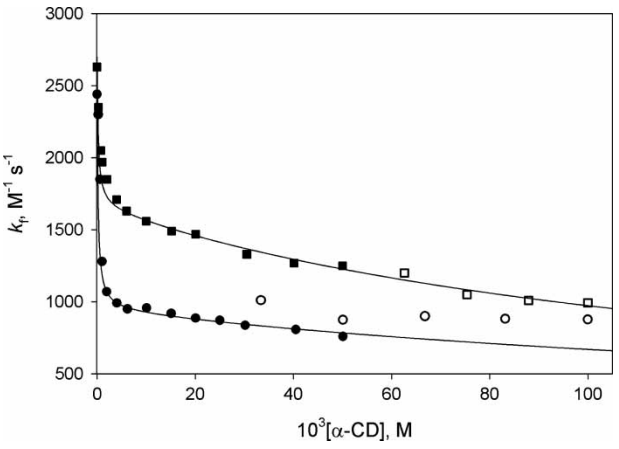


FIGURE 4 Plots of *kf* against [α-CD] for the ligand substitution reaction of the pentacyanoferrate(II) ion with $[Quin(CH_2)_{10}bpy]^{2+}$ (squares) and $[Lut(CH_2)_{10}bpy]^{2+}$ (circles) at 25.0°C ($I = 0.10$ M (NaCl). The filled symbols represent reactions in which the α-CD was in the ligand solution prior to mixing, whereas the unfilled symbols represent reactions in which the α-CD was in both the ligand and metal complex solutions prior to mixing.

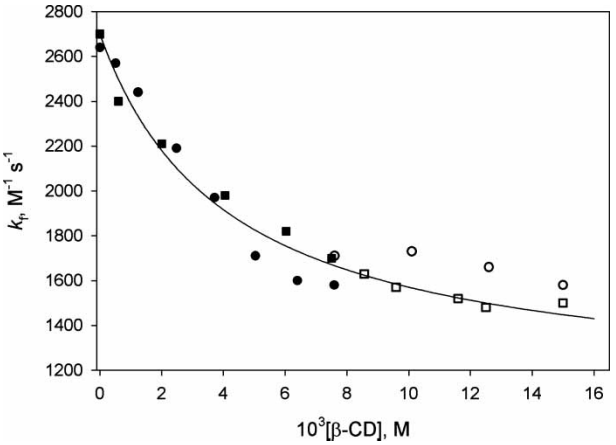


FIGURE 5 Plots of *k*f against [β-CD] for the ligand substitution reaction of the pentacyanoferrate(II) ion with $[Quin(CH_2)_{10}bpy]^{2+}$ (squares) and $[Lut(CH_2)_{10}bpy]^{2+}$ (circles) at 25.0°C ($I = 0.10$ M(NaCl). The filled symbols represent reactions in which the β-CD was in the ligand solution prior to mixing, whereas the unfilled symbols represent reactions in which the β-CD was in both the ligand and metal complex solutions prior to mixing.

TABLE I Kinetics and thermodynamic parameters associated with the formation (k_f) and dissociation (k_d) of $[Fe(CN)_5(R(CH_2)_{10}R')]^-$ complexes at 25.0°C ($I = 0.10$ M (NaCl)

Parameter	$[Quin(CH_2)_{10}bpy]^{2+}$	$[Lut(CH_2)_{10}bpy]^{2+}$
k_f^0, M^{-1} s^{-1}	2620 ± 300	2440 ± 200
$k_f^{\alpha-CD}$, M^{-1} s^{-1}	1650 ± 160	925 ± 90
$k_f^{\beta-CD}$, M^{-1} s^{-1}	1100 ± 100	
$K_L^{\alpha-CD}$, M^{-1}	4640 ± 400 (7 ± 4)†	4810 ± 400 (4 ± 2)†
$K_L^{\beta-CD}$, M^{-1}	240 ± 20	
10^3 k_d^0, s^{-1}	2.23 ± 0.13	2.12 ± 0.05
10^3 $k_d^{\alpha-CD}$, s^{-1}	1.28 ± 0.02	1.28 ± 0.02
10^3 $k_d^{\beta-CD}$, s^{-1}	1.33 ± 0.02	1.30 ± 0.02
$K_{ML}^{\alpha-CD}$, M^{-1}	2260 ± 400	2180 ± 400
$K_{ML}^{\beta-CD}$, M^{-1}	236 ± 20	192 ± 20

† Values in parentheses refer to the stability constant for the binding a second CD molecule.

when $[\{Quin(CH_2)_{10}bpy{\cdot}\alpha\text{-CD}\}]^{2+}$ is included by a second α-CD. This is consistent with the second α-CD including the 4,4′-bipyridinium end group and thus preventing its reaction with the $[Fe(CN)_5OH_2]^{3-}$ ion. The specific rate constants and [2]semirotaxane stability constants derived from these kinetics studies are summarized in Table I.

The formation reaction of the $[Lut(CH_2)_{10}bpy]^{2+}$ ligand with the $[Fe(CN)_5OH_2]^{3-}$ ion is also inhibited by α-CD (Fig. 4) and β-CD. However, unlike $[Quin(CH_2)_{10}bpy]^{2+}$, the extent of this inhibition is dependant on how the CD hosts were partitioned between the solutions containing the ligand and the metal ion before mixing. Behavior similar to this was observed for the formation kinetics of the $[bpy(CH_2)_{10}bpy]^{2+}$ ligand in the presence of α-CD [11]. In that case the dependence was attributed to the cyclodextrin moiety competing with the metal ion for the free ligand. The rate constant for the inclusion of the ligand in α-CD was of similar magnitude to the formation rate constant for the substitution reaction. It may be that a similar process is occurring in this case. However it is unclear if this is the case, why the formation kinetics of the $[Quin(CH_2)_{10}bpy]^{2+}$ does not show the same behavior.

The behavior of the ligand substitution reactions with the dicationic ligands in the presence of α-CD is consistent with the reaction occurring through a dissociative ion-pair (D_{IP}) mechanism [44–49]. The rate determining step of the formation reaction is the dissociation of the aqua ligand (k_{-s}) from the $[Fe(CN)_5OH_2]^{3-}$ ion, after the formation of an ion-pair complex (K_{os}) between the anionic metal complex and the cationic entering ligand. The steric bulk of α-CD results in only a small proportion of these ion-pair complexes undergoing ligand substitution to form the final product. With the α-CD host binding to the decamethylene chain, the end methylene groups will lie outside the α-CD cavity. However, the positively charged nitrogens of the end groups will be in close proximity to the edge of the cavity. This may result in the α-CD partially insulating any approaching $[Fe(CN)_5OH_2]^{3-}$ ion from the full charge on the quaternary nitrogen. Consequently, inclusion in α-CD would result in a reduced outer-sphere ion-pair stability constant, K_{os}, which would lead to a reduction in k_f, since $k_f = k_{-s}K_{os}$. In addition, when the ligand is not included in α-CD, the polymethylene chain would tend to be coiled up on itself causing the 4,4′-bipyridinium and $Quin^+$ or Lut^+ groups to be closer together. The closer proximity of these end groups would present a higher localized positive charge to the incoming $[Fe(CN)_5OH_2]^{3-}$ ion than would be true with the semirotaxane. In the semirotaxane, the 4,4′-bipyridinium group would be further apart from the $Quin^+$ or Lut^+, leading to a lower localized positive charge being felt by the incoming $[Fe(CN)_5OH_2]^{3-}$ ion.

The presence of cyclodextrin in solution also causes the rate constants for the dissociation of the $[Fe(CN)_5(bpy(CH_2)_{10}R)]^-$ complexes, measured in the presence of an excess of DMSO (which traps the $[Fe(CN)_5]^{3-}$ intermediate [46]), to decrease. With no CD present, the k_d^0 values (Table I) are similar to those measured for the $[Fe(CN)_5(bpy(CH_2)_{10}bpy)]^-$ complex ($2.6 \times 10^{-3}\,s^{-1}$) [11]. Inclusion of either of the coordinated $bpy(CH_2)_{10}R^{2+}$ ligands in α- or β-CD results in a decrease in their dissociation rate constants to approximately $1.3 \times 10^{-3}\,s^{-1}$, again similar to the value of k_d^{CD} of $1.5 \times 10^{-3}\,s^{-1}$ reported for $[Fe(CN)_5(bpy(CH_2)_{10}bpy)]^-$ [11]. The decrease in the rate constants generally observed for pentacyanoferrate(II)-coordinated aromatic N-heterocycles upon inclusion in CD has been attributed to a strengthening of the Fe-N bond through enhanced π-backbonding. The concept of strengthening the Mdπ-Lpπ* interaction by the differential solvation of

the metal ion (in water) and the ligand (in the less polar CD cavity) is supported by observed the bathochromic shifts in the metal-to-ligand charge transfer bands [11–14,44,45] upon CD inclusion.

[2]Rotaxane Self-assembly Reactions

The self-assemblies of the [2]rotaxanes, $[Fe(CN)_5\{bpy(CH_2)_{10}R{\cdot}\alpha\text{-CD}\}]^-$, from the reaction of $[Fe(CN)_5(bpy(CH_2)_{10}R)]^-$ (R = $Quin^+$ or Lut^+) complexes with α-cyclodextrin (Fig. 1) were monitored by ^1H NMR spectroscopy. The [2]rotaxanes synthesized through this slower self-assembly process displayed the same preferences of orientational isomers at equilibrium that were observed for the [2]rotaxanes prepared more rapidly by adding the $[Fe(CN)_5OH_2]^{3-}$ ion to the corresponding [2]semirotaxanes (Fig. 6). It was observed that the thermodynamically preferred isomers form over time from an initial kinetically preferred orientation. It is likely that a similar process would occur for the [2]semirotaxanes. As a result of the rapid threading of α-CD over the bipyridinium end group, however, these processes are much too rapid to be observed by the ^1H NMR method. By forming the [2]rotaxanes by the slower mechanism it is possible, therefore, to observe this process. Unfortunately, due to the tendency of the $[(R(CH_2)_{10}bpy)Fe(CN)_5]^-$ species to decompose over long periods of time, it was impractical to determine the kinetics of isomer (kinetic to thermodynamic) conversion process. The self-assembly studies, therefore, examined the overall rate constant of formation and not those of the individual isomers. The overall rate constants measured for the self-assembly reactions of both ligands were found to independent of the concentration of α-CD over the range of $(0.5–1.7)\times10^{-2}$ M, with a value of $k = (1.9 \pm 0.4)\times10^{-3}\,s^{-1}$ for $[Quin(CH_2)_{10}bpy]^{2+}$ and $(1.7 \pm 0.3)\times10^{-3}\,s^{-1}$ for $[Lut(CH_2)_{10}bpy]^{2+}$, in reasonably good agreement with the rate constants of $(2.1–2.2)\times10^{-3}\,s^{-1}$ for the dissociation of the $[Fe(CN)_5(R(CH_2)_{10}bpy)]^-$ complexes (Table I).

CONCLUSIONS

In conclusion, the additions of α- or β-cyclodextrins to aqueous solutions of the dicationic asymmetric threads, $[Quin(CH_2)_{10}tbp]^{2+}$, $[Quin(CH_2)_{10}bpy]^{2+}$, and $[Lut(CH_2)_{10}bpy]^{2+}$, result in the formation of [2]semirotaxanes, with kinetically and thermodynamically preferred orientation isomers being observed. The resulting $\{R(CH_2)_{10}bpyCD\}^{2+}$ [2]semirotaxanes may be used to generate the corresponding [2]rotaxanes by the coordination of the pentacyanoferrate(II) ion to the free 4,4′-bipyridinium nitrogen donor atom.

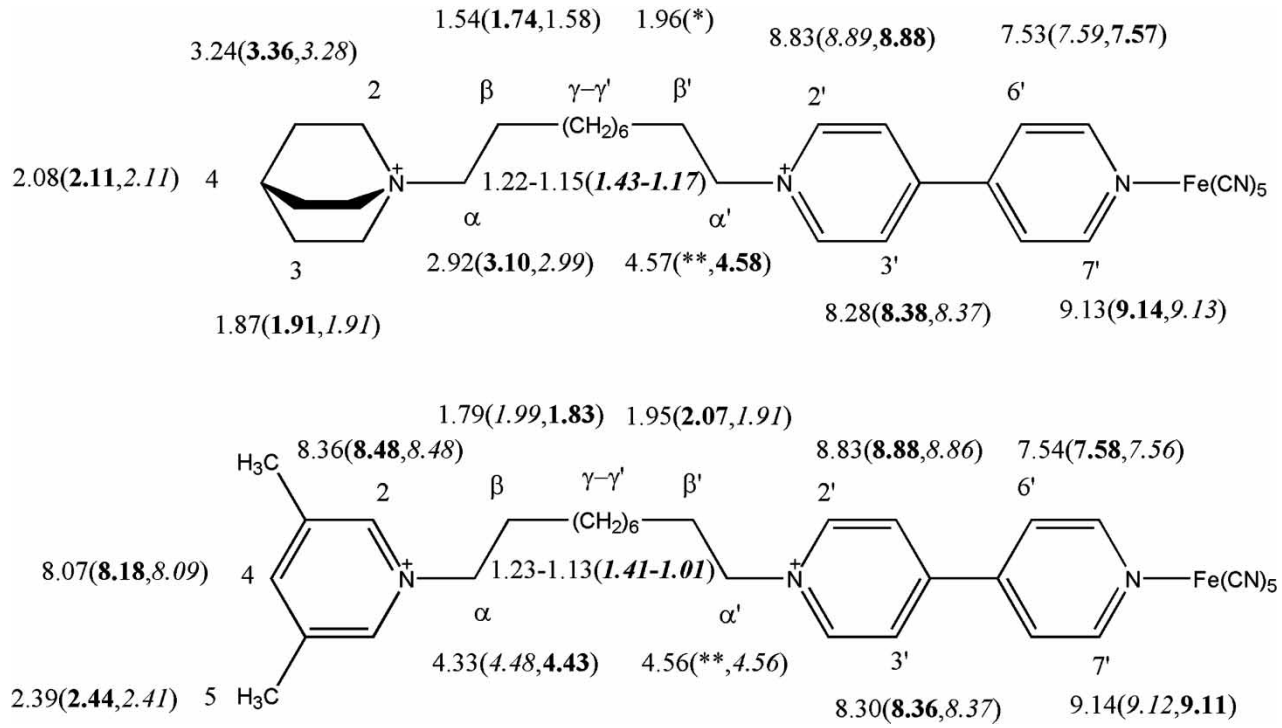


FIGURE 6 The proton resonances of the $[Quin(CH_2)_{10}bpy]Fe(CN)_5]^-$ and $[(Lut(CH_2)_{10}bpy)Fe(CN)_5]^-$ complexes before and after inclusion in α-CD. The chemical shifts listed before the brackets are for the proton resonances prior to inclusion. The chemical shifts for the kinetically preferred isomer are given in italics in the brackets, while the chemical shifts for the thermodynamically preferred isomer are given in bold in the brackets. The peaks obscured by other guest peaks and by HOD are indicated by * and **, respectively.

EXPERIMENTAL

Materials

The 4-*tert*-butylpyridine, 3,5-lutidine, quinuclidine hydrochloride, 1,10-dibromodecane, and 4,4′-bipyridine (Aldrich) were used as received. The α-cyclodextrin (Aldrich) was dried under vacuum at 80°C for at least 12 hours prior to use. The sodium aminepentacyanoferrate(II) hydrate, $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ was prepare by reducing sodium nitroprusside (Fisher) with concentrated ammonia [50]. The crude product was then dissolved in a minimum of ammonia and recrystallized at 0°C. The product was collected, washed with cold methanol and dried *in vacuo*. The $[Fe(CN)_5OH_2]^{3-}$ ion was prepared by aquation of the ammine salt and its concentration determined spectrophotometrically at $\lambda_{max} = 444\,nm$ ($\varepsilon = 660\,M^{-1}\,cm^{-1}$) [51]. The compound $[Quin(CH_2)_{10}Br]Br$ was prepared as described previously [25].

[Quin(CH₂)₁₀tbp]Br₂

A solution of $[Quin(CH_2)_{10}Br]Br$ (2.4 mmol) in 10 mL of DMF was added dropwise to a solution of 4-*tert*-butylpyridine (6.8 mmol) in 5 mL of DMF and then stirred at 50°C for 5 days. The solution was cooled and added to 100 mL of diethyl ether. The resulting oil was dissolved in a minimum of ethanol and then added to 100 mL of diethyl ether producing another oil. The oil was dissolved in ethanol with a ten-fold excess of NaBr after standing for 12 hr the ethanol solution was evaporated *in vacuo* and the resulting solid was extracted with chloroform. The volume was then reduced *in vacuo* to approximately 15 mL and added to 100 mL of diethyl ether resulting in an orange oil, which was washed with a 1:1 toluene/-diethyl ether mixture with vigorous scraping until the oil solidified. The very hygroscopic solid was washed with diethyl ether and dried *in vacuo*. Anal. Calcd. for $C_{26}H_{46}N_2Br_2\cdot 2H_2O$: C, 53.61; H, 8.65; N, 4.81, Found: C, 54.15; H, 8.41, N, 4.81. The compound was very hygroscopic and became an oil on exposure to the atmosphere. For kinetic experiments, it was converted to the more stable iodide salt.

[Quin(CH₂)₁₀tbp]I₂

The $[Quin(CH_2)_{10}tbp]Br_2$ product was dissolved in ethanol with a ten-fold excess of NaI. after standing for 12 hours the ethanol solution was evaporated *in vacuo* and the resulting solid was extracted with chloroform. The chloroform was then reduced *in vacuo* to approximately 15 mL and added to an excess of diethyl ether (100 mL), causing an orange oil to form from solution. The oil was washed with a 1:1 toluene:diethyl ether mixture with vigorous scraping until the oil solidified. This precipitate was washed with diethyl ether and dried *in vacuo*. Yield 28%. M.p. 54–56°C (decomposed). ^{1}H NMR (D_2O) δ 8.60 (d, 2H, H2′, $J_{2',3'} = 6.9\,Hz$), 7.97 (d, 2H, H3′), 4.44 (t, 2H, Hα′, $J_{\alpha',\beta'} = 7.2\,Hz$), 3.29 (m, 6H, H2), 3.01 (m, 2H, Hα), 2.09 (m, 1H, H4), 1.89 (m, 8H, H2 and Hβ′), 1.59 (m, 2H, Hβ), 1.32 (s, 9H, H6′), 1.20 (m, 12H, Hγ—Hγ′) ppm. ^{13}C NMR (D_2O) δ 171.7 (C4′), 143.6 (C2′), 125.6 (C3′), 64.66(Cα), 61.16 (Cα′), 54.87 (C2), 36.22 (C5′), 30.63 (Cβ′), 29.43 (C6′), 28.54 (Cε and Cε′), 28.35 (Cδ), 28.25 (Cδ′), 25.96 (Cγ), 25.44 (Cγ′), 23.69 (C3), 21.72 (Cβ), 19.34 (C4) ppm.

[Quin(CH₂)₁₀bpy]Br₂

A solution of $[Quin(CH_2)_{10}Br]Br$ (2.5 mmol) in 20 mL of ethanol was added dropwise to a 50°C solution of 4,4′-bipyridine (12.6 mmol) in 15 mL of DMF with stirring. The reaction was then maintained at 50°C with stirring for 48 hours. The solution was then allowed to cool and added to approximately 100 mL of a 1:1 toluene/diethyl ether mixture, causing an orange oil to separate from the solution. This oil was collected and dissolved in a minimum of ethanol, after which diethyl ether was added to initiate the precipitation of a brown solid. The recrystallization step was repeated an additional two times and the final product was washed with diethyl ether and dried *in vacuo*. Yield 43%. M.p. 126–128°C. Anal. Calcd. For $C_{27}H_{41}N_3Br_2\cdot 1.5\,H_2O$: C, 54.55; H, 7.46; N, 7.07. Found: C, 54.93; H, 7.44; N, 6.97. ^{1}H NMR (D_2O): δ 8.88 (d, 2H, H2′, $J_{2',3'} = 5.6\,Hz$), 8.68 (d, 2H, H7′, $J_{6',7'} = 4.4\,Hz$), 8.32 (d, 2H, H3′), 7.83 (d, 2H, H6′), 4.58 (t, 2H, Hα′, $J_{\alpha',\beta'} = 7.2\,Hz$), 3.28 (m, 6H, H2), 2.98 (m, 2H, Hα), 2.08 (m, 1H, H4), 1.97 (m, 2H, Hβ′), 1.88 (m, 6H, H3), 1.59 (m, 2H, Hβ), 1.23 (m, 12H, Hγ—Hγ′) ppm. ^{13}C NMR (D_2O): d 153.9 (C4′), 150.3 (C7′), 145.1 (C2′), 142.9 (C5′), 126.3 (C3′), 122.8 (C6′), 64.65 (Cα), 54.84 (C2), 30.76 (Cβ′), 28.56 (Cε and Cδ′), 28.37 (Cδ), 28.28 (Cδ′), 25.98 (Cγ), 23.68 (C3), 21.70 (Cβ), 19.38 (C4) ppm.

[bpy(CH₂)₁₀Br]Br

4,4′-Bipyridine (13 mmol) and 1,10-dibromodecane (26 mmol) were mixed together in 20 mL of toluene and 5 mL of DMF. The reaction solution was left for approximately one week, over which time a white precipitate formed. After a week, 100 mL of diethyl ether was added to the solution to precipitate any additional dissolved product. The precipitate was then collected, washed with diethyl ether and extracted with acetone to separate the desired $[bpy(CH_2)_{10}Br]Br$ product (soluble in acetone) from the undesired $[bpy(CH_2)_{10}bpy]Br_2$ (insoluble in acetone). This acetone solution was filtered to remove the undesired product and reduced *in vacuo* to produce the crude product. The product was then dissolved in ethanol and recrystallized through the addition of excess diethyl ether.

Yield 20%. M.p. 123–124°C (dec.). Anal. Calcd. For $C_{20}H_{28}N_2Br_2$: C, 52.65; H, 6.19; N, 6.14. Found: C, 52.20; H, 5.82, N, 5.98. ^{1}H NMR (D_2O): d 8.86 (d, 2H, H2′), 8.67 (d, 2H, H7′, $J_{6',7'} = 4.8$ Hz, $J_{6,7'} = 1.8$ Hz), 8.31 (d, 2H, H3′, $J_{2',3'} = 6.9$ Hz), 7.81 (d, 2H, H6′), 4.55 (t, 2H, Hα, $J_{\alpha,\beta} = 7.2$ Hz), 3.36 (t, 2H, Hα′, $J_{\alpha',\beta'} = 6.8$ Hz), 1.95 (m, 2H, Hβ), 1.70 (m, 2H, Hβ′), 1.20 (m, 12H, Hγ—Hγ′).

[Lut(CH₂)₁₀bpy]Br₂

A solution of [bpy$(CH_2)_{10}$Br]Br (0.3 mmol) in 10 mL of DMF was added dropwise to a stirred solution at 50°C of 3,5-lutidine (3.0 mmol) in 5 mL of DMF. The reaction was maintained at 50°C and stirred for 48 hours. The solution was then allowed to cool and added to approximately 100 mL of diethyl ether and cooled at ice bath temperatures to induce precipitations. The pale brown precipitate was removed by vacuum filtration and then extracted with acetone to remove any starting materials remaining. The precipitate was then filtered from the acetone solution, washed with diethyl ether and dried *in vacuo*. Yield 48%. M.p. 66–68°C. Anal. Calcd. For $C_{27}H_{37}N_3Br_2{\cdot}3H_2O$: C, 52.52; H, 7.02; N, 6.81. Found: C, 52.03; H, 6.62; N, 6.68. ^{1}H NMR (D_2O): 8.87 (d, 2H, H2′, $J_{2',3'} = 6.8$ Hz), 8.68 (d, 2H, H7′, $J_{6',7'} = 6.0$ Hz), 8.37 (s, 2H, H2), 8.32 (d, 2H, H3′), 8.07 (s, 1H, H4), 7.82 (d, 2H, H6′), 4.56 (t, 2H, Hα′, $J_{\alpha',\beta'} = 7.2$ Hz), 4.37 (t, 2H, Hα, $J_{\alpha,\beta} = 7.2$ Hz), 2.38 (s, 6H, H5), 1.96 (m, 2H, Hβ′), 1.85 (m, 2H, Hβ), 1.20 (m, 12H, Hγ—Hγ′) ppm. ^{13}C NMR (D_2O): d 154.0 (C4′), 150.2 (C7′), 146.7 (C4?), 145.0 (C2′), 143.0 (C5′), 141.1 (C2), 139.2 (C3), 126.3 (C3′), 122.8 (C6′), 61.97 (Cα′), 61.74 (Ca), 30.71 (Cβ and Cβ′), 28.54 (Cε and Cε′), 28.26 (Cδ and Cδ′), 25.45 (Cγ and Cγ′), 17.69 (H5) ppm.

Methods

The 1D ^{1}H and ^{13}C and 2D COSY and ROESY NMR spectra and the kinetics of the self-assembly of the [2]rotaxanes, were recorded on Bruker AM-400 and AV-400 spectrometers in D_2O using the residual HOD as the reference signal. Electrospray mass spectrometry measurements were obtained on a VG Quattro quadrupole mass spectrometer with an atmospheric pressure electrospray ionization source and a mass range for single charged ions of 4000. Samples were prepared as solutions in distilled water containing the guest (2.5×10^{-3} M) and the appropriate amount of the cyclodextrin (α-CD = 0.025 M, [β-CD] = 0.015 M). Elemental analyses were performed by the Canadian Microanalytical Services Ltd., Delta, BC.

The kinetics of the formation of the α-CD semirotaxanes of [Quin$(CH_2)_{10}$tbp]$^{2+}$ were followed by ^{1}H NMR spectroscopy. In a typical experiment, 0.600 mL of a solution of the guest (2.0×10^{-3} M) and 0.10 M NaCl was added to a weighed quantity of α-CD (5–100 mg). An NMR tube containing the mixed solution was maintained at 25°C in a thermostatted water bath and ^{1}H NMR spectra were recorded at timed intervals for at least four half-lives, and then after 10–15 half-lives to establish the extent of semirotaxane formation at equilibrium. The rate constants (k_1, k_2, and k_{12}) were calculated using the procedure described previously [22,25]. The kinetics of the reactions of the $[Fe(CN)_5OH_2]^{3-}$ ion with the dicationic ligands (k_f) were performed on an applied Photophysics SX-17MV stopped-flow spectrophotometer. The UV-visible spectra and the slow dissociation kinetics (k_d) were measured using Hewlett-Packard 8452 diode-array and OLIS-modified Cary 17 UV-visible spectrometers. The temperatures of the reaction solutions were maintained at 25.0 ± 0.1°C using circulating water baths. The ionic strength was maintained at 0.10 M using NaCl. Pseudo-first-order conditions of excess ligand ($[R(CH_2)_{10}bpy]^{2+}$ ($0.7–1.0 \times 10^{-3}$ M) or DMSO (0.11 M)) over the concentration of $[Fe(CN)_5OH_2]^{3-}$ ($\sim 5 \times 10^{-5}$ M) or $[Fe(CN)_5(bpy(CH_2)_{10}R]$ ($\sim 2 \times 10^{-4}$ M) were employed and plots of $\ln(A_t - A_\infty)$ or $\ln(A_\infty - A_t)$ against time were linear for at least 3 half-lives.

The inclusion stability constants were determined from ^{1}H NMR and visible kinetic experiments by applying non-linear least-squares and simplex optimization programs to equations for 1:1 and 1:2 guest-host models as described previously [45].

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