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Electrochemically Controllable Reversible Formation of Cucurbit[8]uril-Stabilized Charge-Transfer Complex on Surface

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The reversible formation of cucurbit[8]uril (CB[8])-stabilized charge-transfer (CT) complex on gold, which can be regulated by electrochemical stimuli, is reported. A viologen-based thread molecule with a thiol terminus was designed to synthesise a stable CB[8]-threaded [2]pseudorotaxane (5^{2+}). A mixed self-assembled monolayer (SAM) of 5^{2+} and 3-mercaptopropionic acid (3-MPA) on gold was prepared and characterised by reflectance FT-IR spectroscopy. The formation and disruption of a CT complex on surface was investigated by cyclic voltammetry with the SAM on gold as a working electrode in a supporting electrolyte solution containing 2,6-dihydroxynaphthalene (DHNp). The cathodic peak was shifted to a more negative potential ($\Delta E \sim 40$ mV) when compared with that measured without DHNp in the electrolyte, which confirmed the formation of a CT complex on gold upon immersion of the SAM of 5^{2+} on gold in the supporting electrolyte containing DHNp. When the viologen unit was reduced, the CT complex was destroyed and the electron-rich guest molecule was released. Upon reoxidation of the reduced viologen unit, however, the CT complex was slowly reformed.

Keywords: Charge-transfer complex; Cucurbituril; Cyclic voltammetry; Host–guest chemistry; Self-assembled monolayer

INTRODUCTION

Cucurbit[*n*]uril (CB[*n*], $n = 5–8, 10$) [1–5], a family of macrocycles comprising *n* glycoluril units, has been employed not only in molecular recognition but also in the construction of a wide variety of supramolecular assemblies including mechanically interlocked molecules [6] and molecular machines and switches [7,8]. In particular, CB[8] with a cavity comparable to that of γ-cyclodextrin can include two identical guest molecules to form a 1:2 complex [3], or two different guest molecules to form a 1:1:1 complex [9]. The formation of the ternary complex is driven by the markedly enhanced charge-transfer (CT) interaction between an electron-deficient and electron-rich guest pair inside the hydrophobic cavity of CB[8]. The discovery of the host-stabilised CT complex formation inside of CB[8] offered a new opportunity to construct novel supramolecular assemblies [10–12]. For the last several years, we and others reported a wide variety of supramolecular assemblies and their applications [13–20] including molecular necklaces [13], molecular loop locks [14], redox-controllable vesicles [15] and dendrimers [16,17], based on this chemistry. Recent developments in supramolecular chemistry include the applications of such supramolecular assembles to create molecular devices [21–26]. To realise such a goal, the immobilisation of supramolecular assembles on surface and coherent operation is important. We recently reported the self-assembled monolayer (SAM) of CB[6]-threaded [2]pseudorotaxane on a gold surface and its unprecedented ion-gating behaviour associated with threading and dethreading of CB[6] [27], which was controlled by the pH of the solution. In our continuing efforts to develop molecular machines on surface, we decided to investigate electrochemically controllable,

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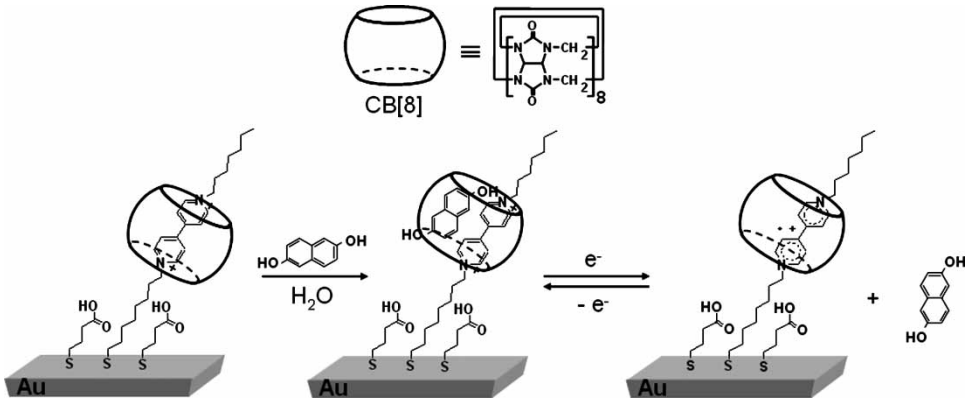


SCHEME 1 Schematic representation for the preparation of a CT complex on gold surface and its reversible formation and disruption by electrochemical stimuli.

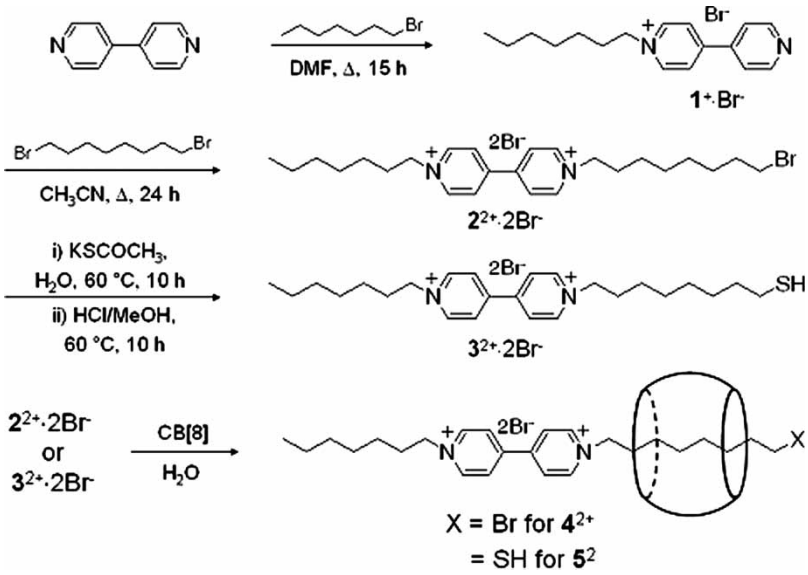
reversible, host-stabilised CT complex formation on surface. Here, we report the immobilisation of a CB[8]-threaded [2]pseudorotaxane, and reversible formation and disruption of CT complex on a gold electrode (Scheme 1) which is controlled by applied potentials.

RESULTS AND DISCUSSION

Synthesis of CB[8]-threaded Viologen-based [2]pseudorotaxane and Corresponding CT Complex With Dihydroxynaphthalene

To synthesise a stable CB[8]-threaded [2]pseudorotaxane to be anchored on gold the viologen-based thread $\mathbf{3}^{2+}$ was designed and synthesised (Scheme 2). CB[8] and methyl viologen ($\mathbf{MV}^{2+}$) are known to readily form a thermodynamically stable 1:1 host–guest complex [9,28], which is however in fast dynamic equilibrium with the individual components in solution. When immobilised on a surface, the dynamic nature of the host–guest complex may lead to dethreading of the ring component, CB[8]. Therefore, we decided to introduce a long alkyl chain at both the sides of a viologen unit to prevent the dethreading of CB[8] from the corresponding [2]pseudorotaxane on surface upon washing with or soaking in solution. A heptyl group at one end and a bromooctyl group at the other end of the viologen unit were introduced sequentially to produce $\mathbf{2}^{2+}$. The terminal bromo group of $\mathbf{2}^{2+}$ was then converted to a thiol group to yield $\mathbf{3}^{2+}$. Bulky stoppers such as benzyl or naphthyl groups were excluded because they may reduce the solubility of the complex in aqueous solution and hinder the complexation with CB[8].

The formation of [2]pseudorotaxanes $\mathbf{4}^{2+}$ and $\mathbf{5}^{2+}$ was achieved by adding 1 equiv of CB[8] to an aqueous solution of $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$, respectively and stirring the mixture (Scheme 2). [2]Pseudorotaxane $\mathbf{4}^{2+}$ has been fully characterised by NMR,



SCHEME 2 Synthetic scheme for $\mathbf{3}^{2+}$ and [2]pseudorotaxanes $\mathbf{4}^{2+}$ and $\mathbf{5}^{2+}$.

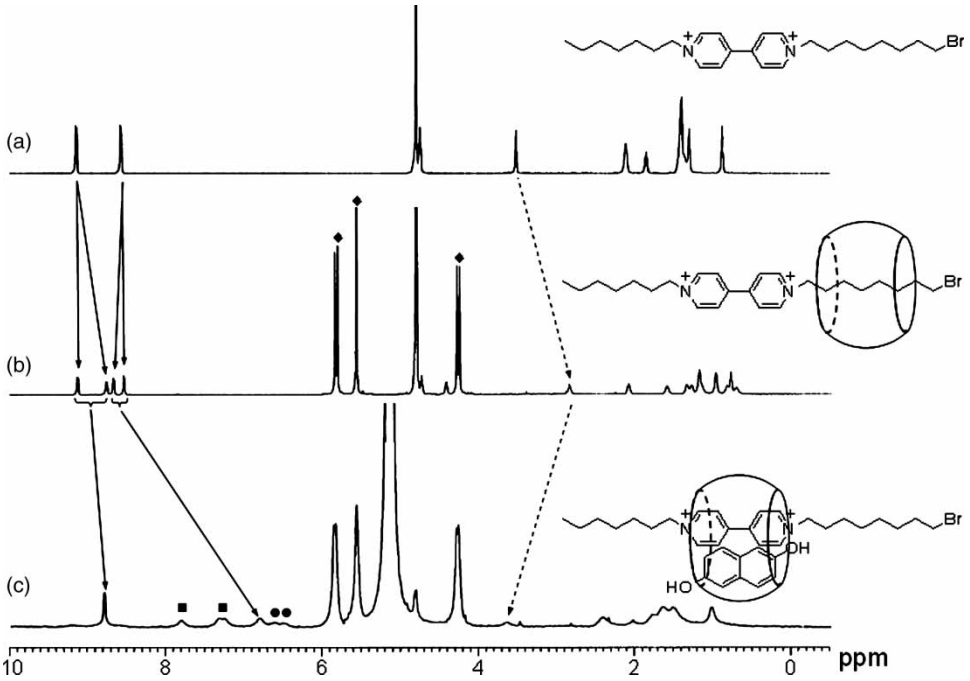


FIGURE 1 Comparison of ^{1}H NMR spectra in D_2O of (a) $\mathbf{2}^{2+}$, (b) $\mathbf{4}^{2+}$ and (c) $\mathbf{5}^{2+}$ in the presence of slightly excess **DHNp**. The changes in the signals of the pyridinium and methylene protons right next to Br are indicated by the solid and dashed arrows, respectively. Signals for CB[8] (◆) in (b) and free (■) and complexed (●) **DHNp** in (c) are also shown. The NMR spectrum of (c) was taken at 5°C.

MALDI-TOF mass spectroscopy and elemental analysis. The ^{1}H NMR spectrum of $\mathbf{4}^{2+}$ (Fig. 1), the peak assignment of which was aided by 2D NMR techniques (COSY and ROESY), confirmed the formation of a 1:1 complex between CB[8] and $\mathbf{2}^{2+}$ (see also Fig. S1). The signal for the bromooctyl protons of $\mathbf{4}^{2+}$ shifted up-field relative to those of $\mathbf{2}^{2+}$ while those for the viologen and heptyl protons showed little shift (Fig. 1(b)), which indicated that CB[8] is located on the bromooctyl chain in $\mathbf{4}^{2+}$. Similarly, the formation of [2]pseudorotaxane $\mathbf{5}^{2+}$ was confirmed by NMR and MALDI-TOF mass spectroscopy, but isolation of pure product $\mathbf{5}^{2+}$ was hampered by the rapid oxidation of its thiol group to disulphide. Therefore, we freshly prepared $\mathbf{5}^{2+}$ by mixing $\mathbf{3}^{2+}$ and CB[8] in a 1:1 ratio and immediately used it for the formation of SAM of $\mathbf{5}^{2+}$ without further purification or isolation.

When 1 equiv of 2,6-dihydroxynaphthalene (**DHNp**) was added to a solution of $\mathbf{4}^{2+}$ in H_2O, the colour of the solution turned from colourless to violet with a characteristic CT band at around 551 nm in UV–visible spectrum (Fig. 2), which indicated the formation of a CT complex. The formation of the CT complex was confirmed by NMR spectroscopy (Fig. 1(c)). When slightly excess **DHNp** was added to the $\mathbf{4}^{2+}$ solution, the signals for the viologen and **DHNp** protons were up-field-shifted with respect to those of $\mathbf{4}^{2+}$ and free **DHNp**, respectively, while those for the bromooctyl protons (in particular, those for the methylene protons right next to Br) more or less returned to their original positions found in $\mathbf{2}^{2+}$ (compare the spectra in Fig. 1), which indicated that the CB[8] ring now moves to the viologen unit which forms a CT complex with **DHNp** inside the CB[8] cavity. The broad NMR signals (Fig. 1(c)) taken at 5°C indicated the dynamic nature of the CT complex even at a low temperature; the CB[8] ring may move back and forth along the thread rapidly. A similar CT complex was formed when **DHNp** was added to $\mathbf{5}^{2+}$ as judged by UV–visible and NMR spectroscopy. However, similar to $\mathbf{5}^{2+}$ itself, the characterisation

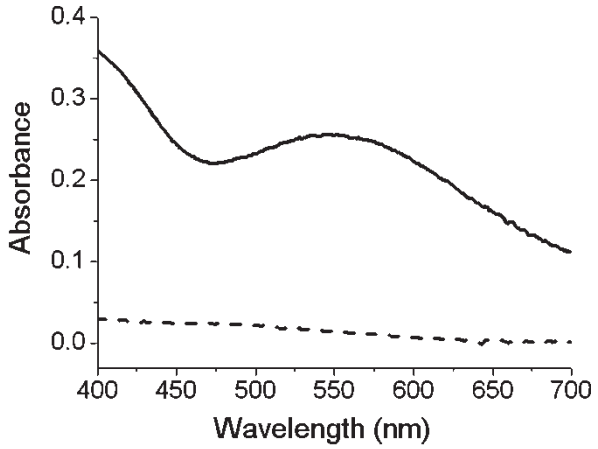


FIGURE 2 Absorption spectra of a 1:1 mixture of $\mathbf{2}^{2+}$ and **DHNp** (dashed line) and a CT complex formed from $\mathbf{2}^{2+}$, **DHNp** and CB[8] (1:1:1) (solid line) in H_2O (2 mM in both cases).

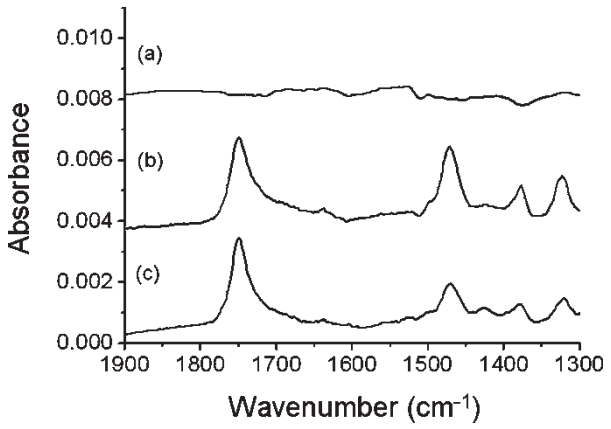


FIGURE 3 The reflectance FT-IR spectra of 3-**MPA** mixed SAM of (a) $\mathbf{3}^{2+}$, (b) $\mathbf{5}^{2+}$ and (c) CT complex on a gold surface.

of the CT complex of $\mathbf{5}^{2+}$ was hampered by the rapid oxidation of its thiol group to disulphide.

Formation of Self-assembled Monolayer of [2]pseudorotaxane $\mathbf{5}^{2+}$ on Gold

A mixed SAM of $\mathbf{5}^{2+}$ and 3-mercaptopropionic acid (**3-MPA**) was prepared by immersing a gold substrate in a freshly prepared aqueous solution of $\mathbf{5}^{2+}$ (0.1 mM) and 6 equiv **3-MPA** for 1 week under nitrogen atmosphere. The latter was used to prevent the anchored $\mathbf{5}^{2+}$ from being damaged by reductive desorption during electrochemical studies. The reflectance FT-IR spectrum of the $\mathbf{5}^{2+}$ SAM on gold (Fig. 3(b)) showed two strong peaks at 1750 and 1472 cm^{-1} corresponding to CO and CN stretching vibrations, respectively, of CB[8]. On the other hand, the IR spectrum of mixed SAM of $\mathbf{3}^{2+}$ and 3-**MPA** showed no noticeable peaks (Fig. 3(a)). No significant dethreading of CB[8] from the $\mathbf{5}^{2+}$ SAM was observed even after repeated washing with water as judged by IR spectroscopy.[1] The CT complex SAM was prepared by immersion of the $\mathbf{5}^{2+}$ SAM in **DHNp** (1 mM) solution for 2 h. However, attempts to characterise the resulting CT complex on gold by IR spectroscopy failed as the IR spectrum of the CT complex on gold was essentially the same as that of the $\mathbf{5}^{2+}$ SAM (Fig. 3(c)), which was presumably due to the low signal intensity of **DHNp**.

The mixed SAM of $\mathbf{5}^{2+}$ on gold was characterised by cyclic voltammetry using it as a working electrode. Because the SAM on gold was damaged at highly negative potentials, only the first redox wave of the SAM was examined. As shown in Fig. 4(a) (dashed line), the voltammetric response of the SAM in pure 0.1 M $NaNO_3$ solution exhibited a pair of cathodic and anodic waves (-0.860 and -0.784 V, respectively) characteristic of the reversible one-electron reduction of a viologen group immobilised on an electrode (see also Fig. S2). From the linear relationship between the scan rate and peak current (Fig. S2, inset), the surface coverage of $\mathbf{5}^{2+}$ was calculated to be 5.2×10^{-11} mol/cm^2, which reasonably matched well with the estimated value based on the ideal packing of CB[8] on a flat surface (3.5×10^{-11} mol/cm^2).

The formation of the CT complex on gold was also investigated by cyclic voltammetry. Fig. 4(a) (solid line) shows a typical cyclic voltammogram of the SAM of $\mathbf{5}^{2+}$ obtained with a supporting electrolyte (0.1 M $NaNO_3$) containing **DHNp** (6 mM). A cathodic peak was observed at -0.900 V and an anodic peak at -0.786 V. The former was shifted to a more negative potential ($\Delta E \sim 40$ mV) when compared with that measured without **DHNp** in the electrolyte, which is consistent with the formation of the CT complex on gold upon immersion of the SAM of $\mathbf{5}^{2+}$ on gold in the supporting electrolyte containing **DHNp** as a similar negative shift in the first reduction potential of viologen has been observed in CB[8]-stabilised CT complexes of viologen with **DHNp**. On the other hand, the anodic peak was not affected by the presence of **DHNp**, which indicated that once the viologen unit was reduced by one-electron, the CT complex was destroyed and **DHNp** was released from the cavity. This conjecture is also supported by the fact that immediately following, the second scan showed a voltammogram essentially the same as that obtained in the absence of **DHNp**. Reformation of the CT complex was investigated by successive cyclic voltammetric scans with different time intervals. The cathodic peak potential was slowly recovered over a period of 30 min as shown in Fig. 4(b) (and inset) indicating that the CT complex was slowly reformed during this period of time. The slow recovery of the cathodic peak potential is understandable as it would take some time for the released **DHNp** to return to the electrode surface by diffusion and react with $\mathbf{5}^{2+}$ to reform the CT complex on the surface. Once again, almost no change in the anodic peak potential was observed, which is due to the disruption of the CT complex upon reduction of the viologen unit of the CT complex.

In summary, we prepared a CB[8]-threaded, viologen-based [2]pseudorotaxane SAM on a gold surface and investigated the reversible formation of the CT complex with **DHNp** on surface by cyclic voltammetry. When the viologen unit was reduced, the CT complex was destroyed and the electron-rich guest molecule was released. However, upon

[1]However, when we used a 'thread molecule' with a methyl group instead of a heptyl group at the terminal, significant dethreading of CB[8] from the corresponding [2]pseudorotaxane SAM was observed upon washing with water. Apparently, the introduction of a long alkyl chain at the terminal effectively prevents dethreading of CB[8] from the SAM.

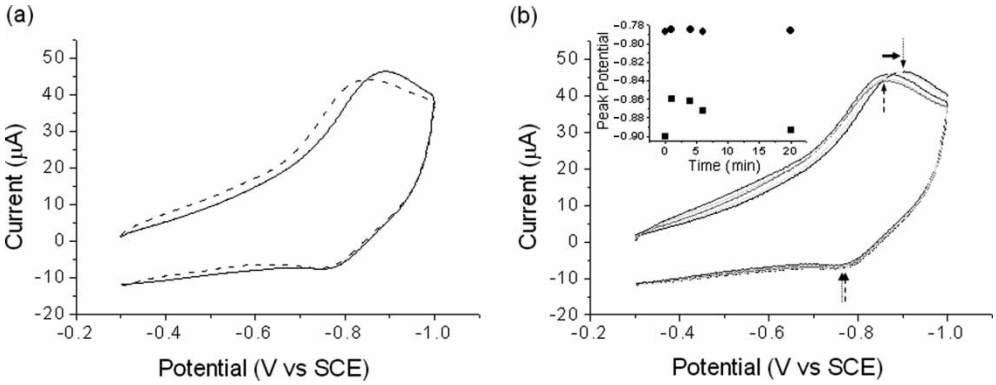


FIGURE 4 (a) Voltammetric response of the mixed SAM of $\mathbf{5}^{2+}$ and 3-**MPA** on gold electrode with (solid line) and without (dashed line) **DHNp** in supporting electrolyte (0.1 M $NaNO_3$). Scan rate = 0.6 V s^{-1}. (b) Successive cyclic voltammetric scans with different time intervals. For comparison, the cathodic and anodic peaks of the first and second scans are indicated by dashed and dotted arrows, respectively. The cathodic peak potential was slowly recovered as indicated by a thick arrow. Almost no change in the anodic peak potential was observed. Inset: time-dependent cathodic (■) and anodic (●) peak potential changes. Supporting electrolyte: 0.1 M $NaNO_3$ with 6 mM **DHNp**; scan rate = 0.6 V s^{-1}.

reoxidation of the reduced viologen unit, the CT complex was slowly reformed. The reversible formation of the CT complex on a surface regulated by a redox process may provide a new platform for the construction of redox-controllable CB[*n*]-based supramolecular assembles on surface.

EXPERIMENTAL

General

All the reagents and solvents employed were commercially available and used as supplied without further purification. Water purified using a Millipore purification train was used for all electrolyte and monolayer preparations. All the NMR data were recorded on a Bruker DRX500 spectrometer. The UV–visible absorption spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. Reflectance FT-IR measurements were performed using a Perkin–Elmer Spectrum GX FT-IR spectrophotometer equipped with a Harrick Scientific Segull variable angle reflectance accessory and a liquid N_2-cooled MCT detector. All spectra were obtained at 4 cm^{-1} resolution using a *p*-polarised light with an incident angle of 83°C.

Synthesis and Characterisation

N-(n-Heptyl)-4-(4′-pyridyl)pyridinium Bromide, $\mathbf{1}^{+}\cdot Br^{-}$

To a solution of 4,4′-bipyridine (3.84 g, 21.4 mmol) dissolved in DMF (50 ml) was added 1-bromoheptane (4.0 g, 26 mmol). The mixture was refluxed for 15 h. After cooling to room temperature, the solvent was removed by evaporation and the residue was dissolved in toluene (50 ml). The mixture of $\mathbf{1}^{+}$ and diquaternised product was separated as a precipitate. The precipitate was dissolved in hot acetonitrile and the diquaternised product was removed by filtration and the filtrate evaporated to give a brown-coloured product (5.43 g, 76%). ^{1}H NMR (500 MHz, D_2O) $\delta = 0.87$ (t, $J = 6.7$ Hz, 3H), 1.21–1.43 (m, 8H), 2.08 (t, $J = 7.2$ Hz, 2H), 4.69 (t, $J = 7.3$ Hz, 2H), 7.94 (d, $J = 4.7$ Hz, 2H), 8.43 (d, $J = 6.7$ Hz, 2H), 8.81 (d, $J = 4.8$ Hz, 2H), 8.98 (d, $J = 6.7$ Hz, 2H); ^{13}C NMR (125 MHz, D_2O) $\delta = 13.8$, 22.3, 25.6, 28.2, 31.0, 31.2, 62.1, 122.9, 126.3, 142.7, 145.2, 150.5, 153.7. FAB-MS; m/z 255.2 $[M]^+$. Elemental analysis (%) calcd for $C_{17}H_{23}N_2Br$: C 60.90, H 6.91, N 8.36; found: C 60.72, H 6.83, N 8.24.

N-(n-Heptyl)-N′-(8-bromooctyl)-4,4′-pyridinium Dibromide, $\mathbf{2}^{2+}\cdot 2Br^{-}$

To a solution of compound $\mathbf{1}^{+}\cdot Br^{-}$ (0.94 g, 2.6 mmol) dissolved in acetonitrile (50 ml) was added dibromooctane (2.1 g, 7.8 mmol). The mixture was refluxed for 24 h. After cooling the solution, the resulting precipitate was filtered out and washed with acetonitrile and diethylether, and dried to give a yellow-coloured product (1.0 g, 65%). ^{1}H NMR (500 MHz, D_2O) $\delta = 0.87$ (t, $J = 6.7$ Hz, 3H), 1.26–1.47 (m, 16H), 1.85 (q, $J = 6.8$ Hz, 2H), 2.11 (m, 4H), 3.52 (t, $J = 6.7$ Hz, 2H), 4.74 (t, $J = 5.4$ Hz, 4H), 8.56 (d, $J = 5.4$ Hz, 4H), 9.14 (d, $J = 4.2$ Hz, 4H); ^{13}C NMR (125 MHz, D_2O) $\delta = 13.7$, 22.2, 25.4, 25.5, 27.4, 27.8, 28.1, 30.8, 30.9, 31.0, 31.1, 32.3, 35.7, 62.6, 127.3, 145.8, 150.4. FAB-MS; m/z 446.2 $[M]^+$. Elemental analysis (%) calcd for $C_{25}H_{39}N_2Br_3$: C 49.44, H 6.47, N 4.61; found: C 49.54, H 6.45, N 4.64.

N-(n-Heptyl)-N′-(8-mercaptoctyl)-4,4′-pyridinium Dibromide, $\mathbf{3}^{2+}\cdot 2Br^{-}$

To a solution of compound $\mathbf{2}^{2+}\cdot 2Br^{-}$ (0.30 g, 0.47 mmol) dissolved in water (50 ml) was added

potassium thiosulphate (80 mg, 0.7 mmol). The mixture was stirred at 60°C for 10 h under N_2 atmosphere. After cooling, the solvent was removed by evaporation and MeOH (100 ml) was added to the resulting solid. After filtration, to the filtrate was added 5% HCl (10 ml) and stirred at 60°C for 10 h under N_2 atmosphere. After cooling the solution, NH_4PF_6 (0.15 g, 1.0 mmol) dissolved in water (10 ml) was added dropwise to the solution. The white precipitate was filtered out and dried *in vacuo*. To the resulting PF_6 salt dissolved in acetone (20 ml) was added tetrabutylammonium bromide (0.32 g, 1.0 mmol). The resulting precipitate was filtered and dried *in vacuo* to give a yellow-coloured solid (0.18 g, 68%). ^{1}H NMR (500 MHz, D_2O) $\delta = 0.87$ (t, $J = 6.8$ Hz, 3H), 1.23–1.47 (m, 16H), 1.58 (q, $J = 7.2$ Hz, 2H), 2.10 (m, 4H), 2.54 (t, $J = 6.9$ Hz, 2H), 4.74 (t, $J = 6.0$ Hz, 4H), 8.57 (d, $J = 6.0$ Hz, 4H), 9.13 (d, $J = 5.7$ Hz, 4H); ^{13}C NMR (125 MHz, D_2O) $\delta = 13.7$, 22.2, 24.2, 25.4, 25.6, 27.6, 28.1, 28.2, 28.4, 30.9, 31.0, 31.2, 33.2, 62.7, 127.4, 145.9, 150.4. FAB-MS; m/z 400.3 $[M]^+$. Elemental analysis (%) calcd for $C_{25}H_{40}N_2SBr_2{\cdot}H_2O$: C 51.91, H 7.32, N 4.84, S 5.54; found: C 52.12, H 7.12, N 4.65, S 5.51.

[2]Pseudorotaxane, $4^{2+}{\cdot}2Br^-$

To a solution of $\mathbf{2}^{2+}{\cdot}2Br^-$ (6.1 mg, 10 μmol) in water (2.0 ml) was added CB[8]·$H_2SO_4{\cdot}16H_2O$ (19 mg, 11 μmol) and the resulting mixture was sonicated with occasional heating until all the solid materials were dissolved. Undissolved solid was filtered off and the filtrate was slowly evaporated under a reduced pressure to yield the product as a bromide salt (21 mg, 91%). ^{1}H NMR (500 MHz, D_2O) $\delta = 0.71$ (br, 2H), 0.78 (s, 3H), 0.83 (br, 2H), 0.98 (s, 4H), 1.19 (s, 6H), 1.29 (s, 2H), 1.34 (d, $J = 7.0$ Hz, 2H), 1.60 (br, 2H), 2.08 (t, $J = 6.7$ Hz, 2H), 2.85 (s, 2H), 4.25 (d, $J = 15.3$ Hz, 16H), 4.42 (s, 2H), 4.73 (t, $J = 6.9$ Hz, 2H), 5.57 (s, 16H), 5.81 (d, $J = 15.2$ Hz, 16H), 8.53 (d, $J = 6.2$ Hz, 2H), 8.66 (d, $J = 6.0$ Hz, 2H), 8.75 (d, $J = 5.1$ Hz, 2H), 9.11 (d, $J = 6.4$ Hz, 2H). MALDI-MS: m/z 1774.2 $[M]^+$. Elemental analysis (%) calcd for ($\mathbf{2}^{2+}{\cdot}2Br^-$·CB[8]·$H_2SO_4{\cdot}19H_2O$) $C_{73}H_{127}N_{34}O_{39}SBr_3$: C 36.89, H 5.39, N 20.04, S 1.35; found: C 37.01, H 5.62, N 20.16, S 1.25.

[2]Pseudorotaxane, $5^{2+}{\cdot}2Br^-$

To a solution of $\mathbf{3}^{2+}{\cdot}2Br^-{\cdot}H_2O$ (5.8 mg, 10 μmol) in degassed water (2.0 ml) was added CB[8]·$H_2SO_4{\cdot}16H_2O$ (19 mg, 11 μmol) and the resulting mixture was sonicated with occasional heating until all the solid materials were dissolved. Undissolved solid was filtered off, and the filtrate was used for the next experiments including characterisation by MALDI-TOF mass spectrometry without further purification or isolation of the product. MALDI-MS: m/z 1728.5 $[M]^+$.

Preparation of Gold Substrates

Evaporated gold substrates (Silicon (100) wafer, 2 nm Ti, 250 nm Au) were purchased from Metallhandel Schroer (Lienen, Germany). Gold substrates with a size of about 10 × 25 mm were used without annealing. Before preparing SAM, the substrates were rinsed with ethanol and immersed into freshly prepared 'piranha' solution ($3H_2SO_4$:$1H_2O_2$, *caution*: this mixture reacts violently with organic materials; hence should not be stored in closed containers) for 1 min. The substrates were rinsed thoroughly with water followed by ethanol and dried under a stream of N_2 gas.

Preparation of [2]pseudorotaxane 5^{2+} on Gold Substrates

To a solution of $\mathbf{3}^{2+}{\cdot}2Br^-{\cdot}H_2O$ (5.8 mg, 10 μmol) in degassed water (10 ml) was added CB[8]·$H_2SO_4{\cdot}16H_2O$ (19 mg, 11 μmol) and the resulting mixture was sonicated with occasional heating until all the solid materials were dissolved to generate $\mathbf{5}^{2+}{\cdot}2Br^-$. Undissolved solid was filtered off, and 6 equiv of 3-mercaptopropionic acid (0.64 mg) was added to the solution. The SAM of pseudorotaxane $\mathbf{5}^{2+}$ on gold surface was prepared by immersing a gold substrate to this solution for 1 week under inert atmosphere. The substrate was then washed copiously with water and dried with a gentle flow of N_2 gas.

Preparation Of 3^{2+} on Gold Substrates

To a solution of $\mathbf{3}^{2+}{\cdot}2Br^-{\cdot}H_2O$ (5.8 mg, 10 μmol) in degassed water (10 ml) was added 6 equiv of 3-**MPA** (0.64 mg). The SAM of $\mathbf{3}^{2+}$ on gold surface was prepared by immersing a gold substrate into this solution for 1 week under inert atmosphere. The substrate was then washed copiously with water and dried with a gentle flow of N_2 gas.

Preparation of CT Complex on [2]pseudorotaxane SAM for IR Experiments

To a solution of **DHNp** (1 mM) in degassed water (10 ml) was immersed [2]pseudorotaxane SAM of $\mathbf{5}^{2+}$ on gold, which had been prepared as described above, for 2 h. The substrate was then washed with water and dried with a gentle flow of N_2 gas.

Electrochemical Experiments

The electrochemical experiments were performed with a Princeton Applied Research Model 273 multipurpose instrument interfaced to a personal

computer. The mixed SAM of $\mathbf{5}^{2+}$ on gold surface as a working electrode, a Pt counter electrode and a saturated calomel electrode as a reference electrode separated with a fine glass frit were utilised in a single-compartment cell. A home-made Teflon cell was cleaned in piranha solution for 1 h prior to use and then thoroughly rinsed with water. All solutions were deoxygenated by purging with argon gas and maintained under an inert atmosphere during the electrochemical experiments. For CT complex experiments, **DHNp** solution (6 mM) in 0.1 M $NaNO_3$ was used as a supporting electrolyte.

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