

In the Twilight Zone Between [2]Pseudorotaxanes and [2]Rotaxanes



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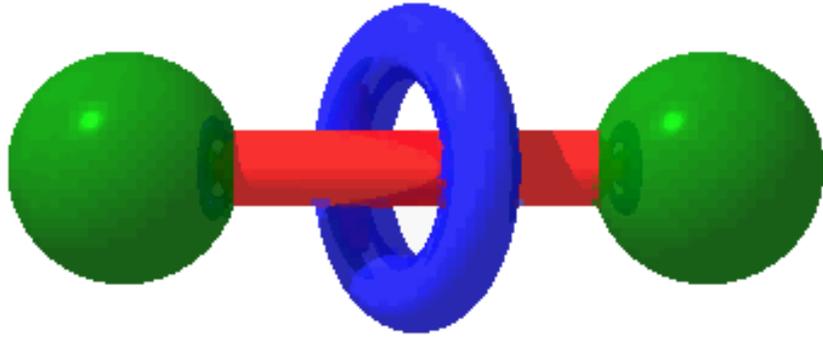
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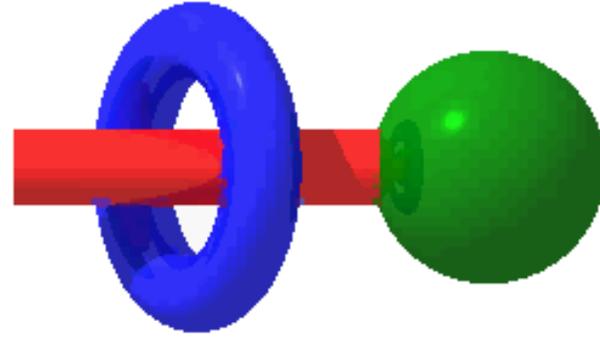
What is the Story About?

- A rare example of "piggy-back" supramolecular assistance leads to the formation in solution of two non-identical [2]pseudorotaxanes.
- One is on the brink of being a [2]rotaxane at room temperature.
- The other is in rapid equilibrium with a semi-dumbbell-shaped compound and the tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene).
- These two (supra)molecular entities, wherein the tetracationic cyclophane encircles two different recognition sites are in slow equilibrium with each other as a result of a "speed bump" in the form of a thiomethyl group being situated between the two recognition sites.
- The unique properties of these two entities allows the kinetics of the shuttling of cyclobis(paraquat-*p*-phenylene) between two recognition sites to be investigated at different temperatures.

Rotaxanes and Pseudorotaxanes

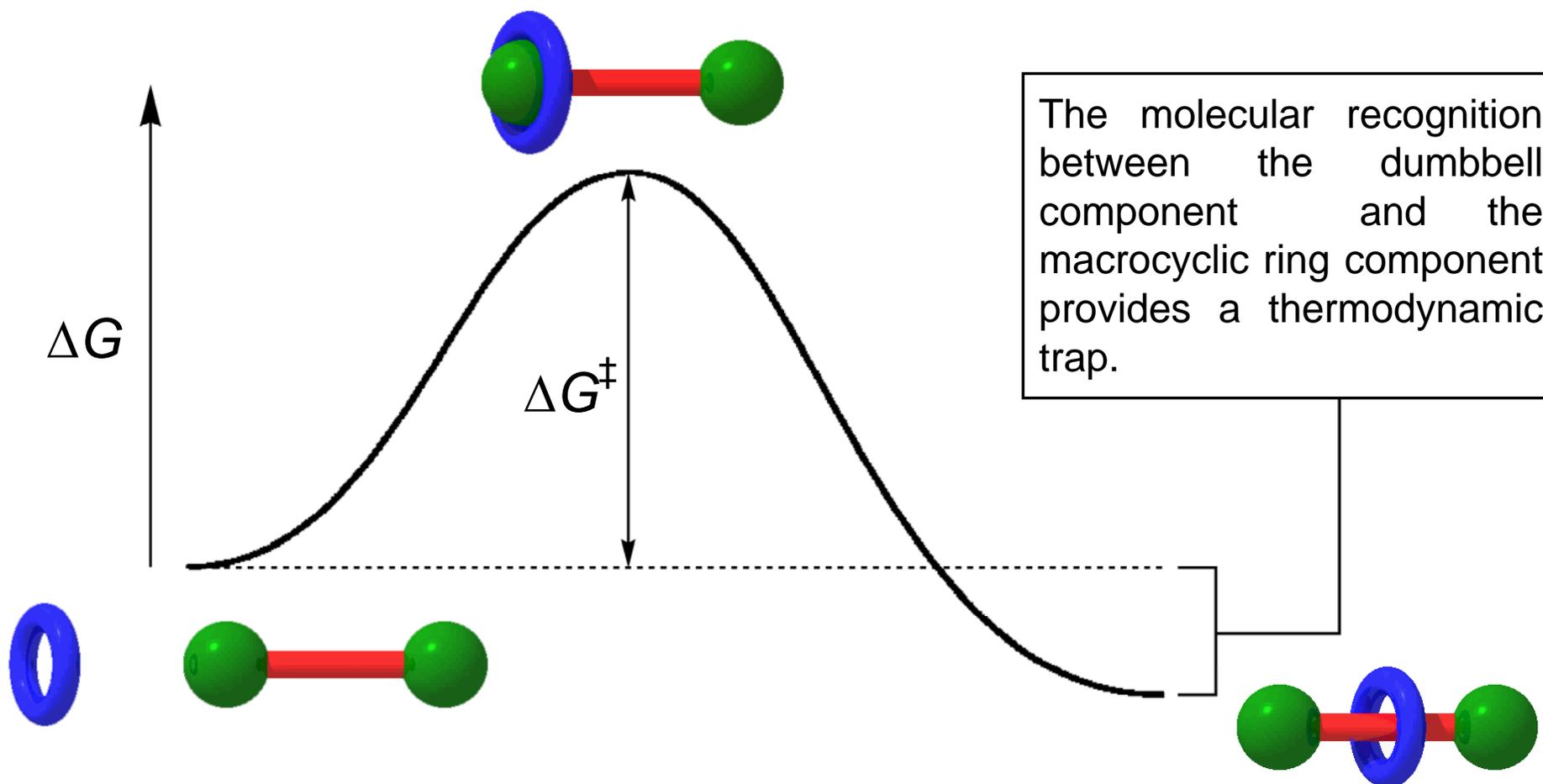


A [2]rotaxane is a molecule composed of a ring component and a dumbbell-shaped component. The ring component (blue) encircles the linear rodlike portion (red) of the dumbbell-shaped component and is trapped mechanically around it by two bulky stoppers (green). Thus, the two components cannot dissociate from one another, even although they are not linked covalently to each other.



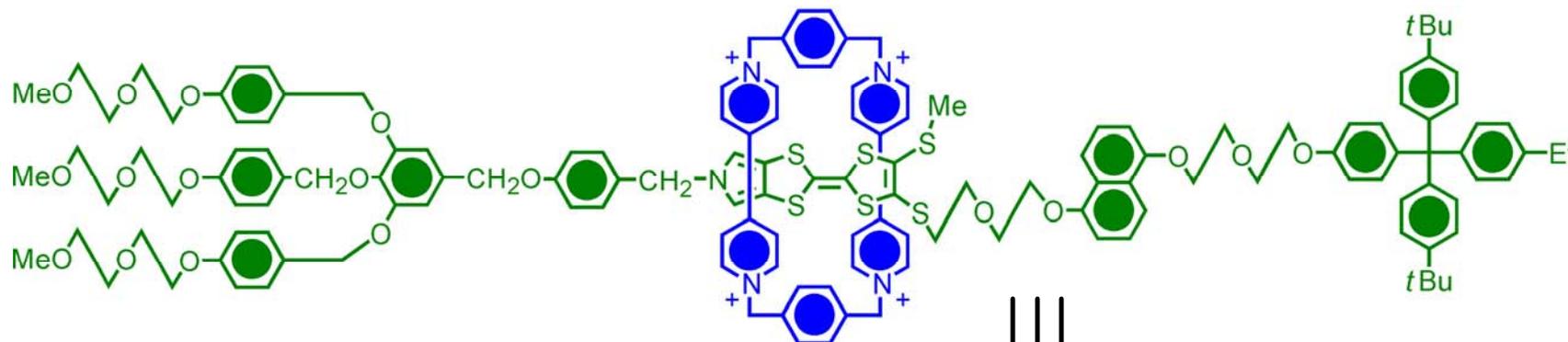
In a [2]pseudorotaxane, at least one of the stoppers on the dumbbell-shaped component is absent with the consequence that dissociation of the [2]pseudorotaxane into its components can occur, and the equilibrium between the species is controlled by the free energy of complexation, i.e., a [2]pseudorotaxane is a supramolecular species.

Slipping

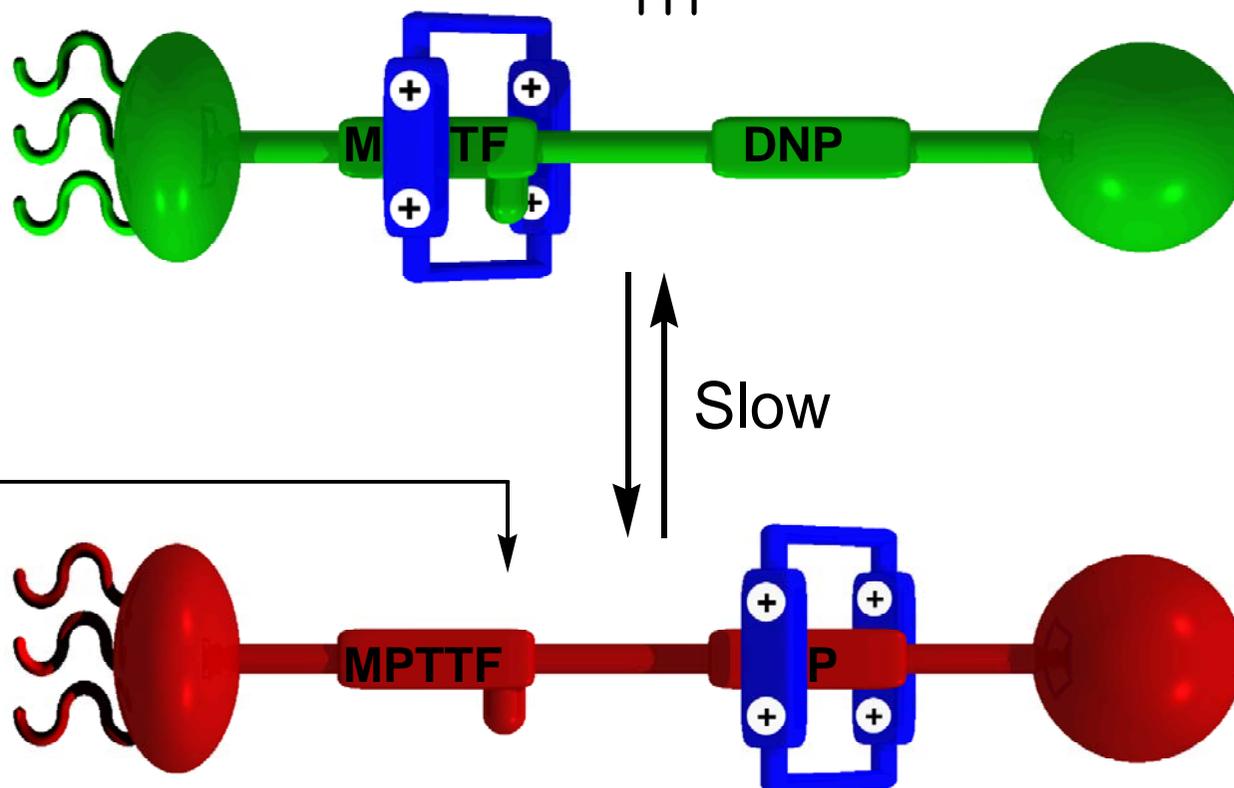


The change in energy associated with the slipping of a macrocycle over one of the stoppers of a dumbbell-shaped compound.

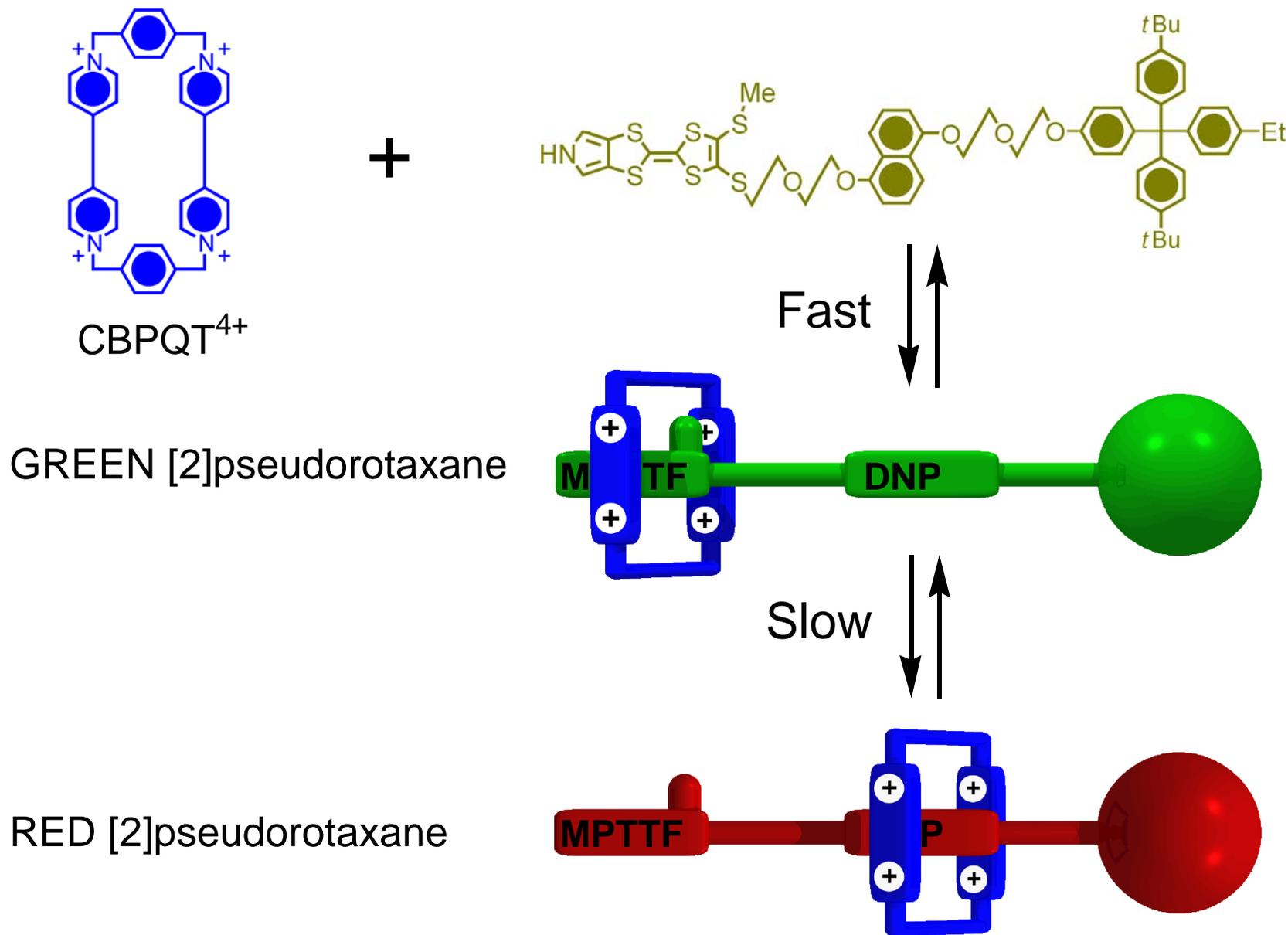
Hindered Interconversion in a "Slow" Amphiphilic Bistable [2]Rotaxane



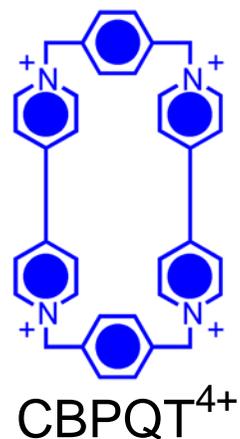
A "speed bump" in the form of an SMe group is situated between the monopyrrolotetrathiafulvalene (**MPTTF**) and the 1,5-dioxynaphthalene (**DNP**) recognition sites, which prevent a fast shuttling of the macrocyclic ring component, **cyclobis(paraquat-p-phenylene)**.



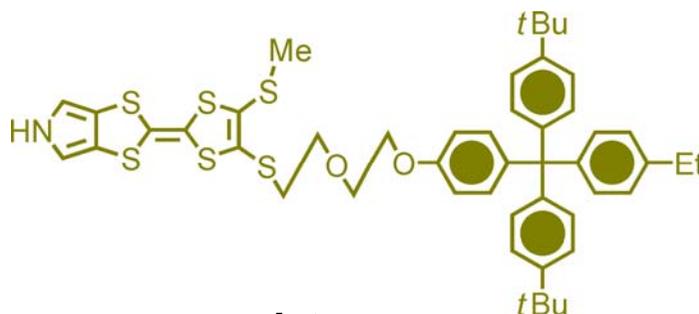
Self-Assembly of a Bistable [2]Pseudorotaxane and its Slow Interconversion



Investigation of the Complexation of a Model Compound by CBPQT⁴⁺

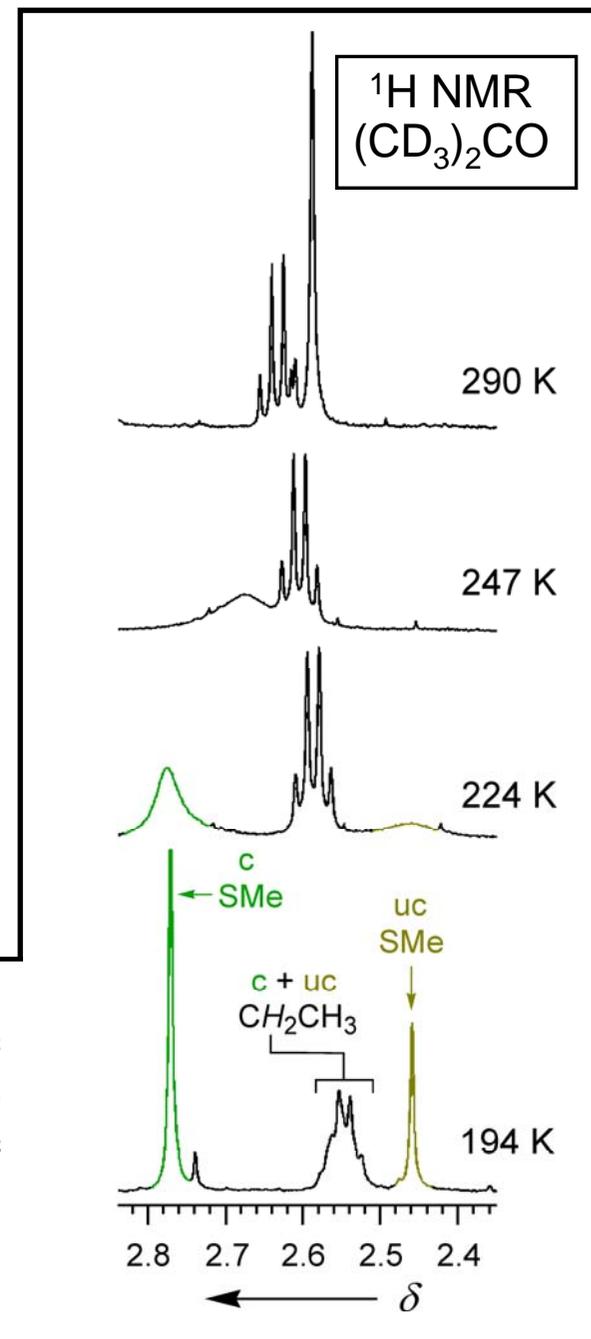
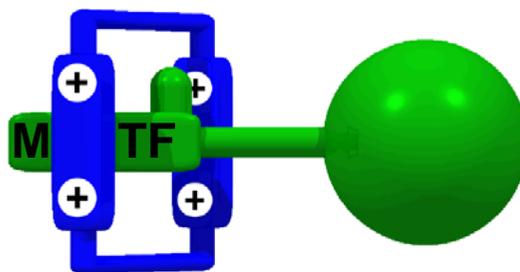


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$$\Delta G^\ddagger = 11.4 \text{ kcal mol}^{-1} \quad \rightleftharpoons \quad K_a = 1300 \text{ M}^{-1}$$

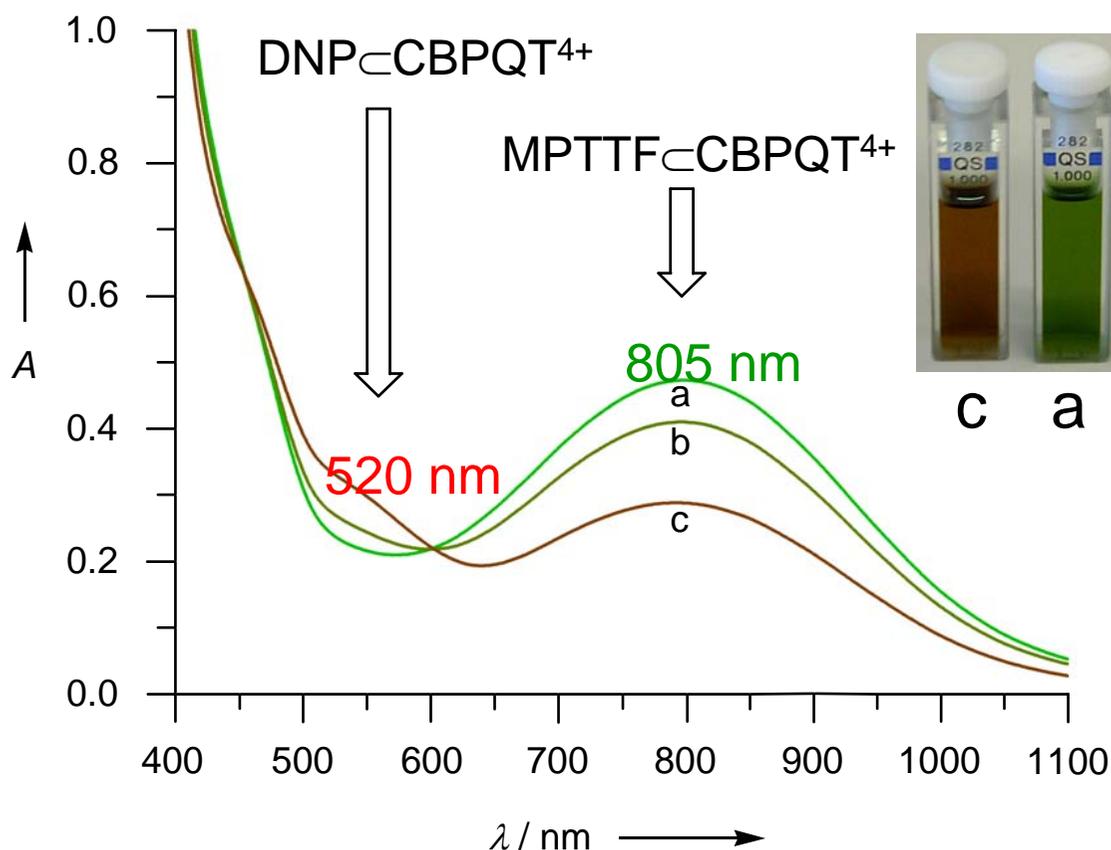
[2]Pseudorotaxane



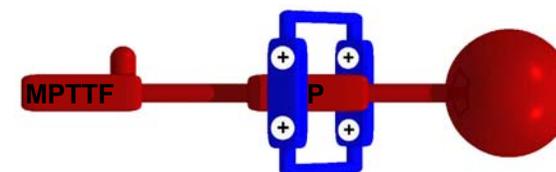
The activation barrier (ΔG^\ddagger) for the complexation/decomplexation process was determined at 247 K by studying a CD₃COCD₃ solution of the semi-dumbbell compound containing 0.70 equivalents of CBPQT⁴⁺ using variable temperature (VT) ¹H NMR spectroscopy. The rate of complexation/decomplexation for CBPQT⁴⁺ with the semi-dumbbell compound was determined by partial line shape analysis of the SMe signals for the **complexed** (c) and **uncomplexed** (uc) forms.

Preparation of the [2]Pseudorotaxanes

UV/Vis absorption spectra recorded in Me₂CO at 295 K on a 1:1 mixture of the yellow semi-dumbbell and the colorless CBPQT⁴⁺ (0.72 mM) immediately after their mixture (trace a), after 2.5 h (trace b), and after 48 h (trace c).

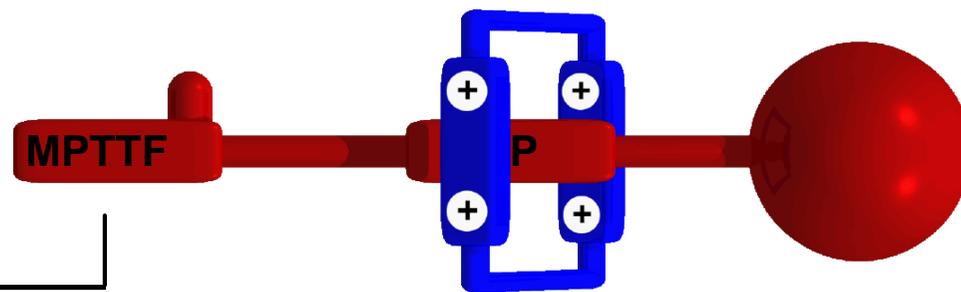
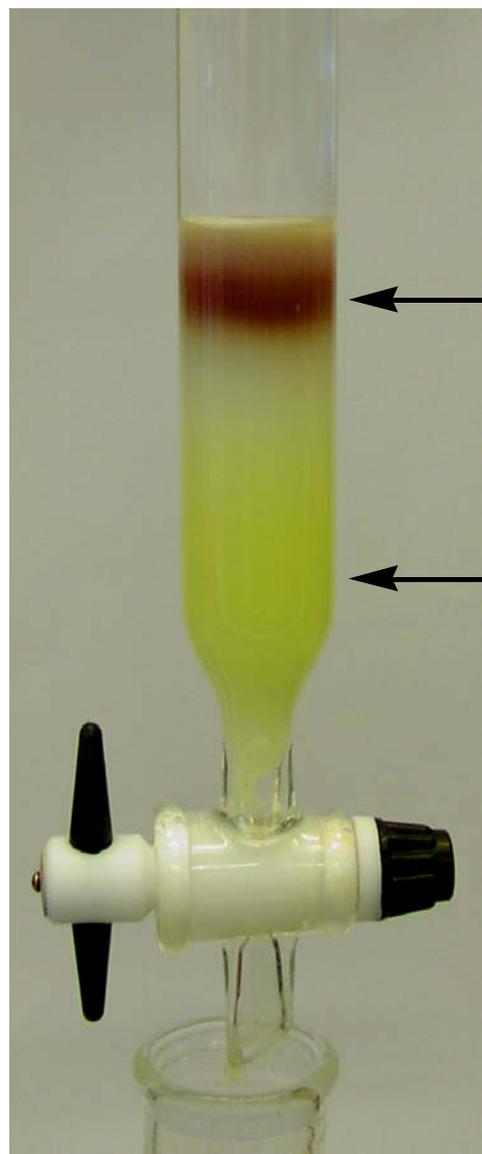


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Org. Lett. 2002, 4, 557–560

Isolation of the RED [2]Pseudorotaxane



[2]Pseudorotaxane



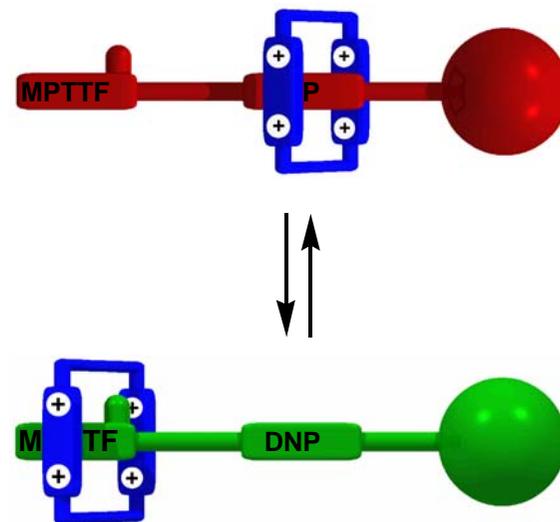
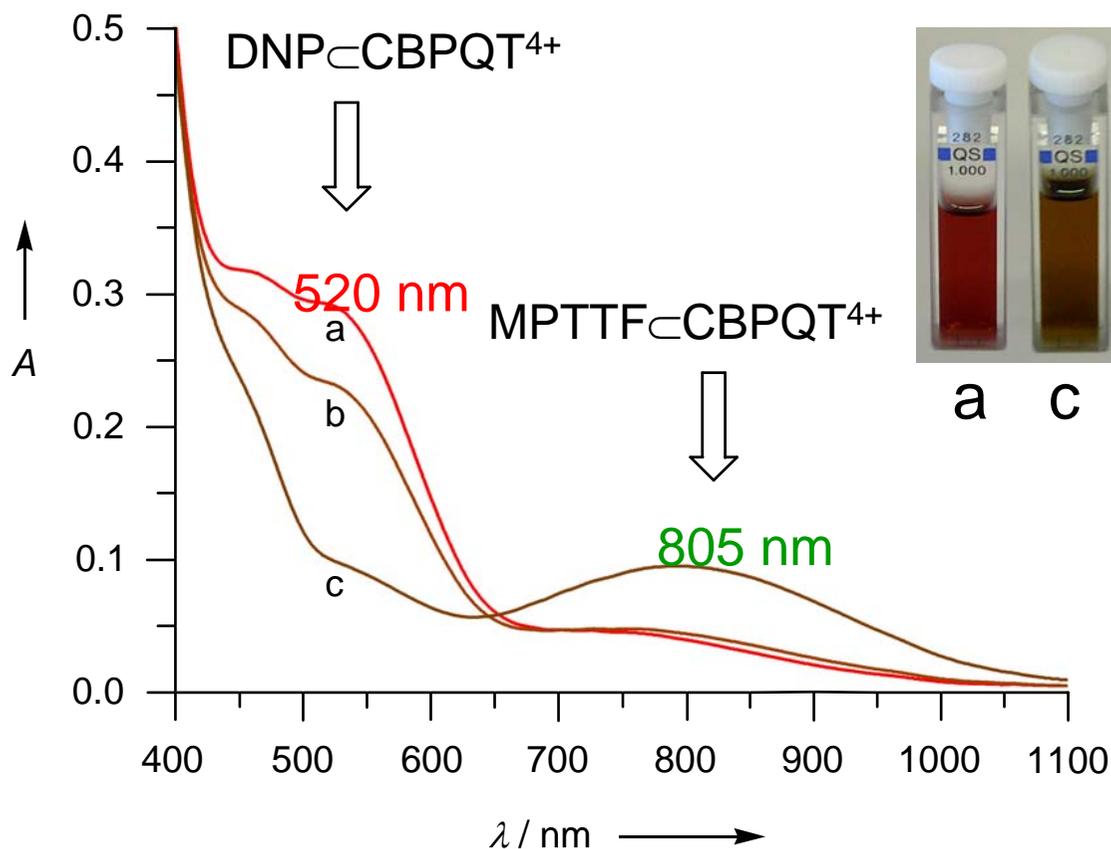
Semi-dumbbell

A column chromatogram showing the separation of the RED [2]pseudorotaxane from the yellow semi-dumbbell compound and CBPQT⁴⁺.

Conversion of RED into GREEN

UV/Vis absorption spectra recorded in Me₂CO at 296 K on the RED [2]pseudorotaxane (0.28 mM) immediately after its isolation (trace a), after 2.5 h (trace b), and after 48 h (trace c).

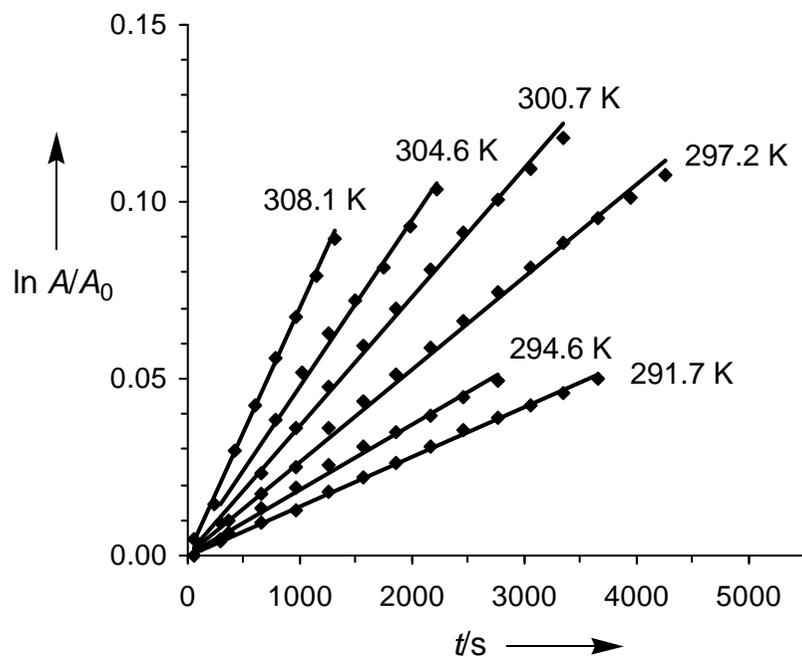
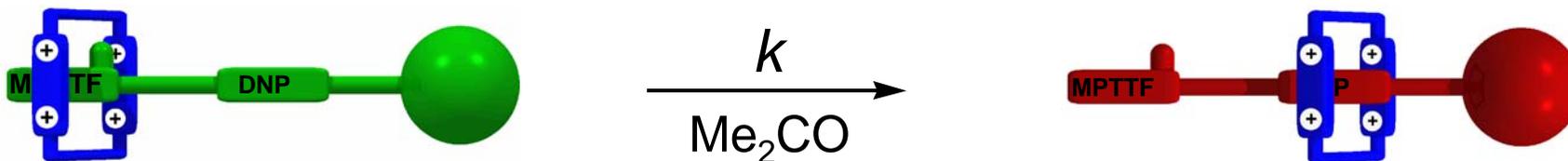
The red co-conformation was isolated in 20% yield and could be stored for more than two weeks in Me₂CO at -78°C.



The ¹H NMR spectra (273 K) recorded on an equilibrated Me₂CO (1.0 mM) solution, revealed that this solution contained 35% of the RED [2]pseudorotaxane.

Kinetic Investigations — GREEN to RED

The first-order kinetics for the process whereby CBPQT⁴⁺ moves from the MPTTF to the DNP recognition site were investigated by monitoring the increase in the CT band intensity resulting from the DNP moiety being located inside CBPQT⁴⁺.

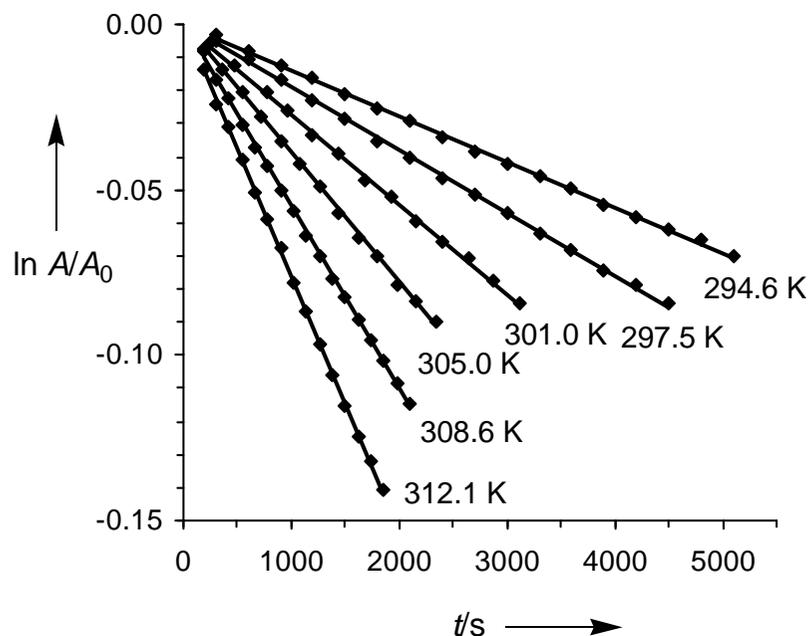
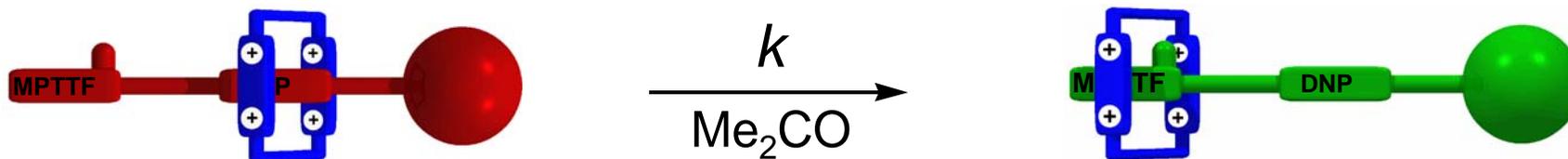


T / K	k / s^{-1}	$\Delta G^\ddagger / \text{kcal mol}^{-1}$
308.1	0.000069	23.9
304.6	0.000048	23.8
300.7	0.000036	23.7
297.2	0.000026	23.6
294.6	0.000019	23.6
291.7	0.000014	23.5

Linear plots of $\ln A/A_0$ against t for the slippage of CBPQT⁴⁺ over the SMe group in the direction from GREEN to RED in Me₂CO at different temperatures obtained by using the DNP/CBPQT⁴⁺ CT absorption band (520 nm) as probe. The values A and A_0 correspond to the absorbance (at 520 nm) at time t and A_0 to the initial absorbance (at 520 nm), respectively. The slope of each line give the rate constant (k), according to the relationship $\ln A/A_0 = k t$.

Kinetic Investigations — RED to GREEN

The first-order kinetics for the process whereby CBPQT⁴⁺ moves from the DNP to the MPTTF recognition site were investigated by monitoring the decrease in the CT band intensities resulting from the DNP moiety being located inside CBPQT⁴⁺.

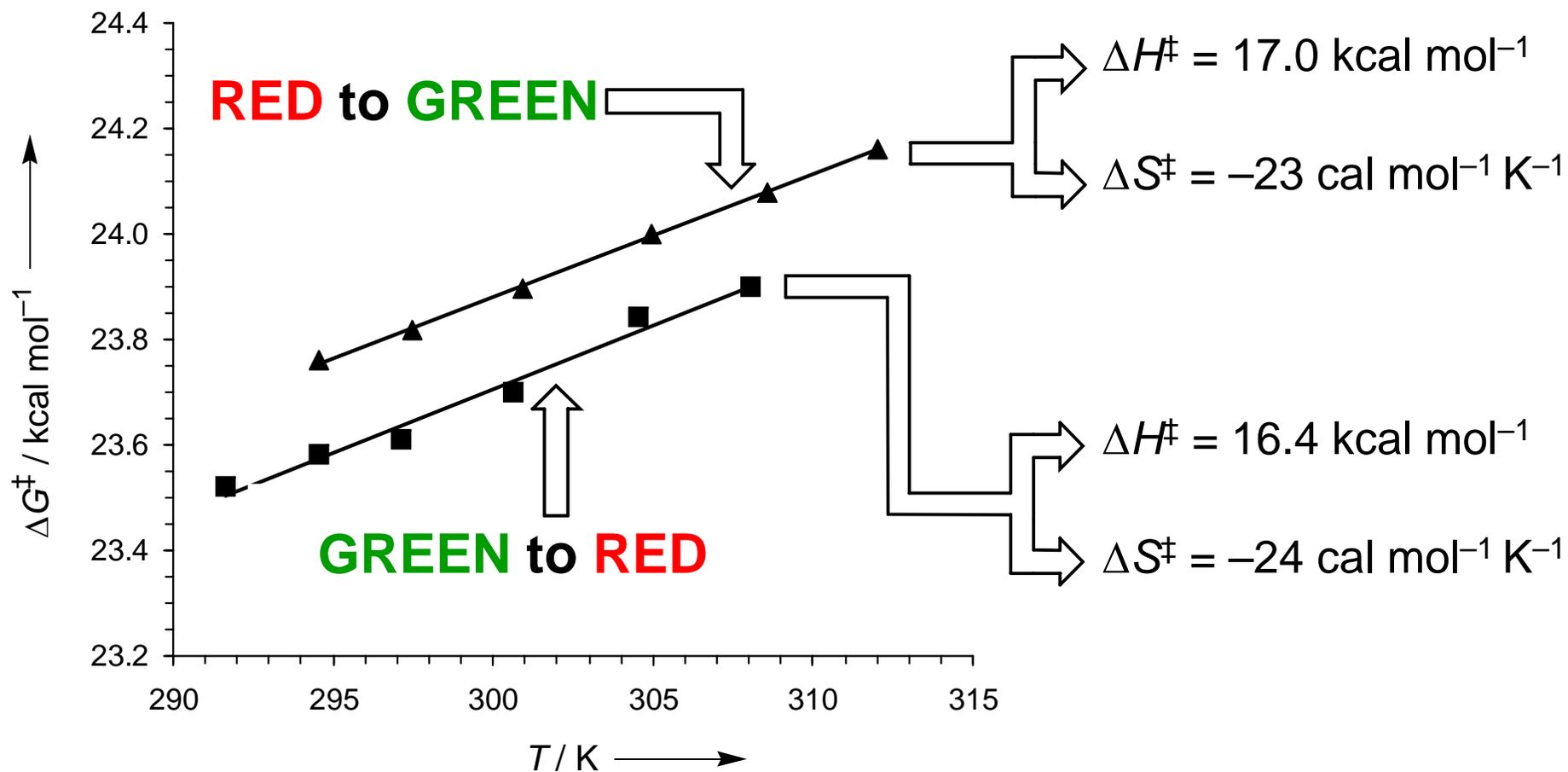


T / K	k / s^{-1}	$\Delta G^\ddagger / \text{kcal mol}^{-1}$
312.1	0.000076	24.2
308.6	0.000055	24.1
305.0	0.000039	24.0
301.0	0.000027	23.9
297.5	0.000019	23.8
294.6	0.000014	23.8

Linear plots of $\ln A/A_0$ against t for the slippage of CBPQT⁴⁺ over the SMe group in the direction from RED to GREEN in Me₂CO at different temperatures obtained by using the DNP/CBPQT⁴⁺ CT absorption band (520 nm) as probe. The values A and A_0 correspond to the absorbance (at 520 nm) at time t and A_0 to the initial absorbance (at 520 nm), respectively. The slope of each line give the rate constant (k) value, according to the relationship $\ln A/A_0 = -k t$.

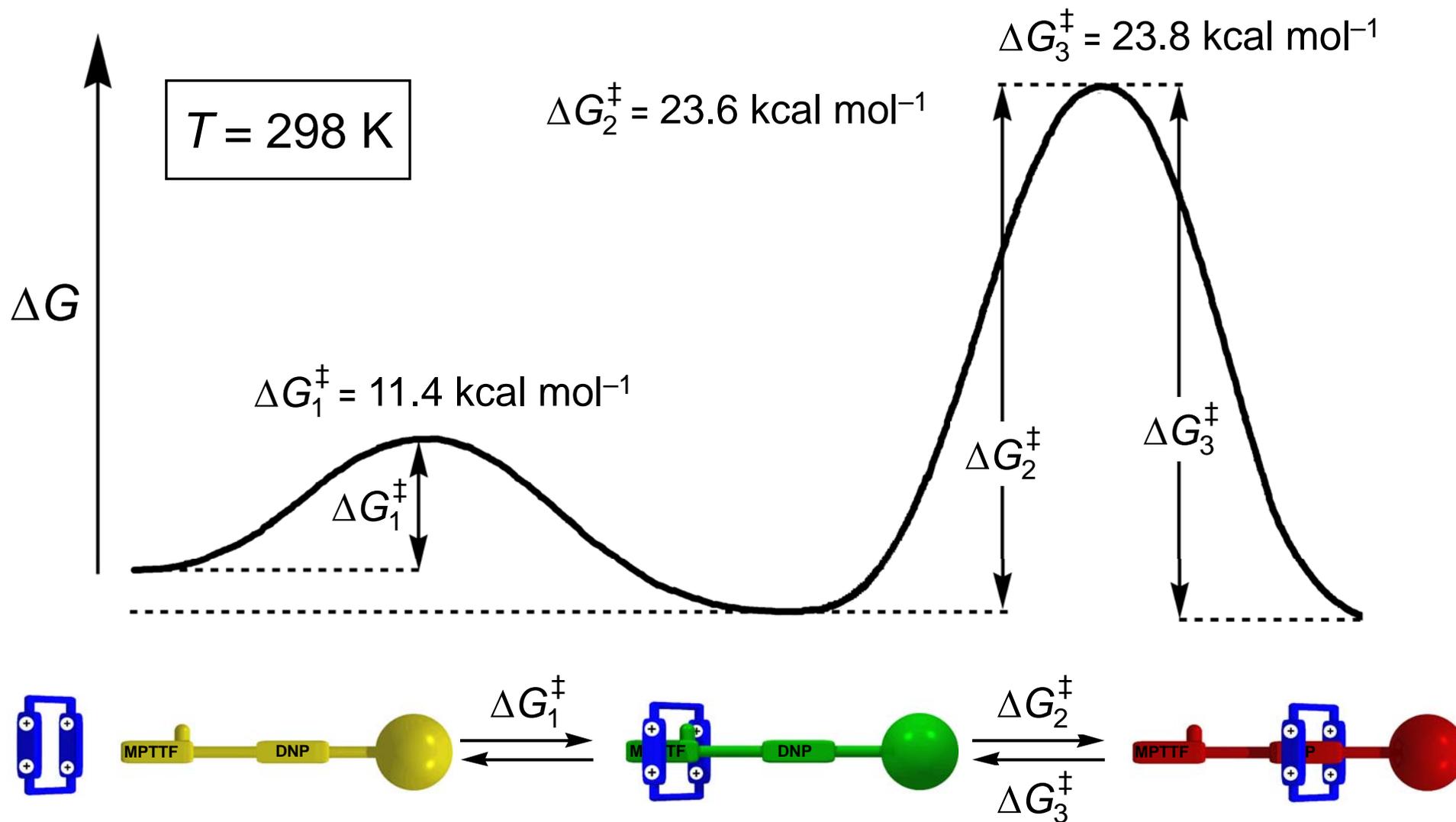
Determination of Thermodynamic Parameters

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$



Linear plots of ΔG^\ddagger against T for the slippage of CBPQT⁴⁺ over the SMe group in the direction from GREEN to RED in Me₂CO (■) and in the direction from RED to GREEN in Me₂CO (▲). The slope and intercept of each line of best fit give the values ΔS^\ddagger and ΔH^\ddagger , respectively, from the equation $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$.

Summary of Thermodynamic Parameters



Conclusions

- A bistable, supramolecular species, based on a CBPQT⁴⁺ ring component which threads onto a semi-dumbbell-shaped component containing two different recognition sites—a terminal MPTTF unit and an internal DNP moiety—initially in a fast step to form a kinetically labile [2]pseudorotaxane, which then progresses more slowly to form a second kinetically stable [2]pseudorotaxane, has been characterized.
- In these [2]pseudorotaxanes the CBPQT⁴⁺ ring encircles, respectively the MPTTF unit and the DNP moiety. A "speed bump" in the shape of an SMe group has made it possible to isolate the second of the two [2]pseudorotaxanes, suggesting that it has some [2]rotaxane character to it.
- Knowledge of the thermodynamic parameters associated with the shuttling processes between the MPTTF and DNP recognition sites at room temperature is of crucial importance in view of the use of these supramolecular entities in the fabrication of devices.