# Single-color pseudorotaxane-based temperature sensing†

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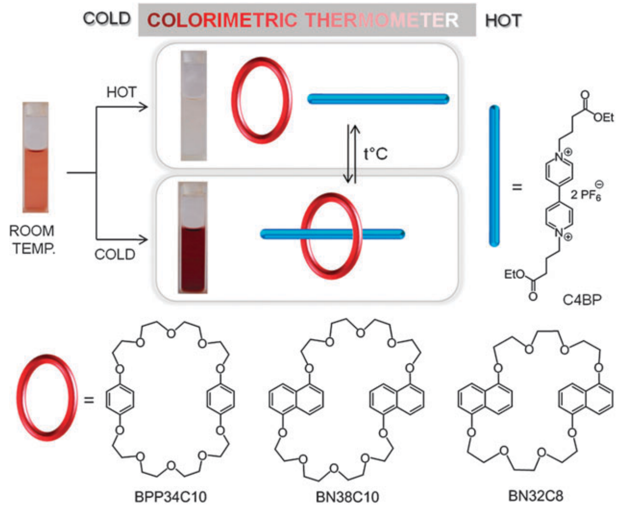
**Colored pseudorotaxane solutions can be used to assess temperature changes over large temperature windows. The color intensity of our novel pseudorotaxane systems decreases gradually from −50 to +50 °C with no shift in absorption maximum, making these and similar pseudorotaxanes attractive candidates for single-wavelength colorimetric temperature sensors.**

Pseudorotaxanes are supramolecules comprised of an axle-like molecule threaded through a wheel-like molecule, where the two components are held together by intermolecular forces such as ion–dipole interactions, hydrogen bonding, π–π stacking, electrostatic interactions or coordination bonds. Attachment of bulky groups (stoppers) to the two ends of the axle component results in a rotaxane, in which the wheel component is mechanically locked onto the axle component.[1] One of the most interesting features of such molecular architectures is the possibility of switching the position of the wheel along the axle in a controlled and reversible fashion, triggered by external stimuli such as chemical (pH change, metal ion, *etc.*), electrochemical or light input. The resulting "molecular machines" can potentially be used in a variety of molecular-level applications, including mechanical (shuttles, nanovalves, elevators, muscles, *etc.*) and electronic devices (information storage, components for molecular electronics such as switches and single-molecule transistors, *etc.*).[2] Herein we show that a colored pseudorotaxane solution has a hitherto unexplored potential: temperature sensing at a single wavelength over a temperature window of 100 °C. Although the influence of temperature on the color intensity of some pseudorotaxane systems has occasionally been noticed,[3,4] to our knowledge this is the first reported systematic study of the temperature/optical absorption relationship in these systems.

The axle-component of the pseudorotaxanes used in this work consists of *N*,*N*′-bis[3-(carboethoxy)propyl]-4,4′-bipyridinium hexafluorophosphate (C4BP), while the wheel-component is an aromatic crown ether: bis-*para*-phenylene-34-crown-10 (BPP34C10), bis-1,5-naphtho-38-crown-10 (BN38C10) or bis-1,5-naphtho-32-crown-8 (BN32C8) (Scheme 1). The driving force for pseudorotaxane assembly using the above mentioned components is the combined effect of π–π stacking and ion–dipole interactions between the electron-deficient bipyridinium dication (axle) and the electron-rich crown-ether (wheel). The resulting charge-transfer imparts an orange/red color to the pseudorotaxane system and serves as a visual indicator for the self-assembly process. C4BP is prepared from the corresponding bromide salt[4] by anion exchange in $H_2O$ using a saturated aqueous solution of $NH_4PF_6$. Single-crystals were obtained from 1 : 1 $CH_3CN/CHCl_3$ solutions by $Et_2O$ or $^iPr_2O$ vapour diffusion.† BN32C8 is a novel crown ether reported here for the first time, while BPP34C10[5] and BN38C10[6] are prepared according to previously published procedures. BN32C8 is prepared in two steps similarly to BN38C10,[6] from 1,5-dihydroxynaphthalene and tri(ethylene glycol) ditosylate in 13% overall yield. Single-crystals were grown from $CHCl_3$ by $Et_2O$ or $^iPr_2O$ vapour diffusion.†



**Scheme 1** Temperature-dependent pseudorotaxane formation equilibrium.

Pseudorotaxane solutions are prepared by mixing the axle- and wheel-components in various solvents/solvent mixtures, depending on the solubility of the individual components. C4BP is soluble in acetone and acetonitrile, while the wheel molecules are soluble in chloroform and dichloromethane. BPP34C10 is also soluble in acetone and methanol. Both the axle- and wheel-components are colorless; upon mixing at room temperature, a dark orange (with BPP34C10) or red (with BN38C10 or BN32C8) color appears. A charge transfer band centred at 448, 490 and 501 nm, respectively, is observed in the UV-Vis spectra of the resulting solutions in $(CH_3)_2CO/CH_2Cl_2$ (2 : 1), indicating pseudorotaxane formation. $^1H$ NMR spectroscopy in $(CD_3)_2CO/CDCl_3$ (2 : 1) solutions also confirms complex formation, as indicated by significant shifts of proton signals relative to the individual components.† The most affected peaks are those of the moieties involved in charge transfer: the bipyridinium protons of the axle (up to 0.78 ppm shift) and aromatic protons of the

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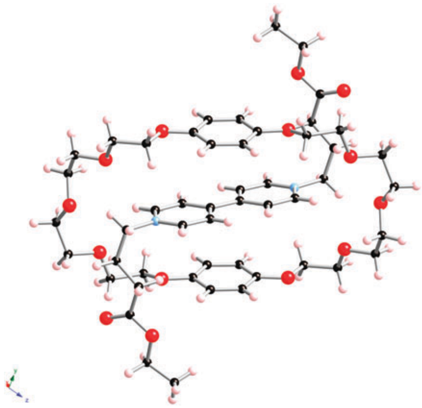

**Fig. 1** Crystal structure of C4BP/BPP34C10 (two $PF_6^-$ counterions are omitted for clarity), color code: O—red, N—blue, C—black, H—pink.

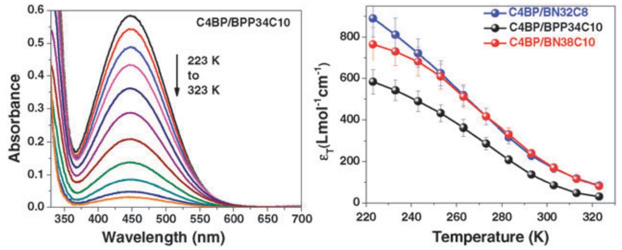

**Fig. 2** (a) Optical absorption spectra of 1.0 mM C4BP/BPP34C10 pseudorotaxane (1 : 1) in $(CH_3)_2CO/CH_2Cl_2$ (2 : 1) as a function of temperature (±0.1 K); (b) plot of extinction coefficients as a function of temperature for the different pseudorotaxanes investigated.

wheel (up to 0.50 ppm shift). Similar results have been observed in related systems.[4,7] Addition of excess axle or wheel component to a 1 : 1 pseudorotaxane solution leads only to slight changes in chemical shifts but not to the appearance of new peaks, indicating a fast exchange equilibrium between individual components and the corresponding pseudorotaxane at room temperature.

Dark orange crystals of C4BP/BPP34C10 pseudorotaxane, suitable for X-ray diffraction, were obtained in 90% yield from 1 : 1 $(CH_3)_2CO/CH_3OH$ or $(CH_3)_2CO/CHCl_3$ solutions by layering with $^{i}Pr_2O$ at −20 °C.‡ The crystal lattice contains one [2]pseudorotaxane (wheel and axle lie about a common inversion center) and two $PF_6^-$ counterions per unit (Fig. 1). The absence of interstitial solvent molecules accounts for the stability of the crystals in air at room temperature. Within the pseudorotaxane units, the two phenylene rings of the crown-ether are symmetrically located above and below the centre of the bipyridinium core, with a 3.55(1) Å separation between the centres of the donor and acceptor units (similar to previously characterized related systems).[8] Pseudorotaxane units within the crystal lattice interact weakly with each other through π–π stacks between adjacent crown-ether phenylene groups (center-to-center distance: 5.24(1) Å).

During previous work on pseudomorphism and crystal growth of similar pseudorotaxane systems at different temperatures, we observed a variation of color intensity with temperature: the absorption more than doubled on cooling a solution from room temperature to −40 °C.[4] To better understand the temperature dependence of absorption and to describe the thermodynamics of pseudorotaxane formation in solution, optical absorption measurements were carried out on three systems using C4BP as the axle and three different wheels, BPP34C10, DN38C10 and DN32C8. Fig. 2a shows the optical absorption spectra of C4BP/BPP34C10 at different temperatures from −50 °C to +50 °C (similar results were obtained with BN38C10 and BN32C8).† Since the individual axle and wheel components do not absorb in the visible region, the absorptions of the three different pseudorotaxane solutions centred at 448, 490 and 501 nm, respectively, are attributed to charge transfer complexation as a result of the interaction between the electron donor benzene or naphthalene units of the crown ether wheel and the electron acceptor bipyridinium dication axle. Similarly colored charge transfer complexes formed by the bipyridinium moiety with various electron donor systems are well documented in the literature.[4,9] The continuous and reversible change in absorption with temperature observed in the present systems is indicative of an equilibrium between the colored pseudorotaxane and the colorless axle- and wheel-components in solution over a 100 °C window. Interestingly, the color of C4BP/BPP34C10 pseudorotaxane crystals is lost abruptly at 107–109 °C before melting at 191–193 °C. The pseudorotaxane solutions studied here are stable over time and the absorption values are reproducible. These results suggest that the present pseudorotaxane systems could be used to measure temperature. Fig. 2b shows the plot of extinction coefficients of the three systems studied as a function of temperature. The obtained calibration curves can be employed as scales for colorimetric thermometers. Most known colorimetric thermometers contain thermochromic pigments based on liquid crystals. The color change in liquid crystals,[10] as in most inorganic[11] and organic[12] thermochromic compounds, occurs at specific temperatures over a very narrow range. Only a few examples of *individual* chemical systems are known today where the color change spans a large temperature range.[13] In these systems, the temperature dependent color change often involves a shift in the absorption maximum. For application purposes, such as in microfluidic devices[14] and other complex systems where conventional thermometers are inappropriate, it would be advantageous to have a colorimetric thermometer that can be read at a single wavelength.

While in the solid state the 1 : 1 axle/wheel ratio is clearly indicated by the crystal structure of C4BP/BPP34C10, the stoichiometry of pseudorotaxane formation in solution was investigated by optical absorption measurements using Job's plot. The absorption maximum at 0.5 mole fractions for all three systems investigated confirms a 1 : 1 complexation.† Benesi–Hildebrand analysis[15] of concentration-dependent absorption measurements provides the corresponding association constants and extinction coefficients (Table 1). The larger association constants in the case of BN38C10 and BN32C8 suggest stronger interactions of the C4BP axle with naphthalene- than benzene-based wheels. Thermodynamic parameters (free energy change, enthalpy and entropy) were determined from the results of temperature-dependent UV-Vis measurements (Table 1) and found to be consistent with

**Table 1** Thermodynamic parameters for the formation of the three pseudorotaxanes studied in 1.0 mM $(CH_3)_2CO/CH_2Cl_2$ (2 : 1) solutions (* 294 K, ** 298 K)

| Wheel component | $K_a$* ($10^2$ $M^{-1}$) | $\varepsilon$ ($10^3$ $M^{-1}$ $cm^{-1}$) | $\Delta H$/kcal $mol^{-1}$ | $\Delta S$/cal $mol^{-1}$ $K^{-1}$ | $\Delta G$**/kcal $mol^{-1}$ |
|---|---|---|---|---|---|
| BPP34C10 | 1.0 (±0.2) | 0.63 (±0.08) | −11 (±0.2) | −26 (±1) | −3.2 (±0.1) |
| BN38C10 | 2.4 (±0.3) | 1.0 (±0.1) | −8.1 (±0.2) | −16 (±1) | −3.4 (±0.1) |
| BN32C8 | 1.7 (±0.3) | 1.3 (±0.1) | −7.1 (±0.2) | −13 (±1) | −3.2 (±0.1) |

literature reports on similar systems.[8,16]† Pseudorotaxane formation from its components in the present systems is barrierless and is driven by entropy, with higher temperatures favoring dissociation. It is important to note that a temperature-dependent color intensity change would not be observable in the case of related rotaxanes, where dissociation of the wheel from the axle is prevented by the bulky stoppers.

Preliminary electrochemical studies show a correlation between the reduction/oxidation potential of the axle and wheel, respectively, and the absorption spectrum of the corresponding pseudorotaxane. Square-wave voltammograms (Fig. 3) show two reversible reduction peaks (−0.76 V and −1.20 V) for C4BP and two partially reversible oxidation peaks (0.84 V and 0.96 V) for BPP34C10. As expected, in the case of the corresponding pseudorotaxane these peaks shift to slightly more negative/more positive potentials, respectively, due to the charge transfer. The higher oxidation potential of BPP34C10 (0.84 V) than BN38C10 (0.70 V) and BN32C8 (0.63 V) is in accord with the higher energy charge transfer absorption band of C4BP/BPP34C10 (448 nm) than C4BP/BN38C10 (490 nm) and C4BP/BN32C8 (501 nm).

In summary, we have prepared and characterized three new orange/red pseudorotaxane systems using a new 4,4′-bipyridinium-based axle and three aromatic crown ether wheels (including the novel bis-1,5-naphtho-32-crown-8). We suggest that the temperature-dependent absorption intensity of these and other known and yet to be prepared colored charge-transfer based pseudorotaxane solutions, which are expected to display similar behavior, could potentially be exploited in single-color temperature sensors over large temperature windows.

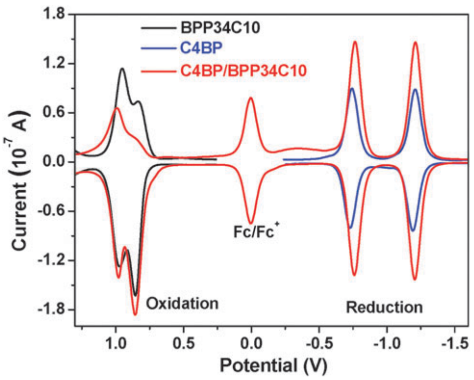

**Fig. 3** Square-wave voltammogram of 1.0 mM BPP34C10, C4BP, and the corresponding 1 : 1 pseudorotaxane in $CH_3CN : CH_2Cl_2$ (1 : 2) with 0.1 M $Bu_4NPF_6$ *versus* ferrocene/ferrocenium.

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## Notes and references

‡ Crystal data: C4BP/BPP34C10: $C_{50}H_{70}F_{12}N_2O_{14}P_2$, $M$ = 1213.02, $T$ = 100(2) K, triclinic, space group $P\bar{1}$, $a$ = 10.5908(2), $b$ = 11.5200(3), $c$ = 13.0613(5) Å, $\alpha$ = 102.140(2)°, $\beta$ = 101.609(2)°, $\gamma$ = 109.620(1)°, $V$ = 1402.07(7) Å$^3$, $D_c$ = 1.437 g $cm^{-3}$, $\mu$ = 0.182 $mm^{-1}$, $Z$ = 1, reflections collected = 78 662, unique = 8541 ($R_{int}$ = 0.0354), final $R$ indices [$I > 2\sigma I$]: $R_1$ = 0.0435, w$R_2$ = 0.1537, GoF = 1.271.

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