Supporting Information for

Single-Color Pseudorotaxane-Based Temperature Sensing

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General

All commercially available reagents were used as received. Bis-*para*-phenylene-34-crown-10 (BPP34C10),¹ bis-1,5-naphtho-38-crown-10 (BN38C10),² N,N'-bis[3-(carboethoxy)propyl]-4,4'-bipyridinium bromide³ and tri(ethylene glycol) ditosylate⁴ were prepared according to reported procedures. Acetone was dried with CaSO₄, distilled under N₂ and stored over 4 Å molecular sieves. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. NMR and UV-Vis spectra were recorded on a Jeol JNM-ECP400 and Shimadzu UV 2101 PC spectrophotometer equipped with an Optistat DN cryostat, respectively. Electrochemical measurements were carried out using an electrochemical workstation Model 660B, CH instruments. Melting points were measured on a MEL-TEMP II (Laboratory Devices, USA) apparatus. X-Ray diffraction data, collected at room temperature (298 K) from a single crystal mounted atop a glass fiber with a Bruker SMART APEX II diffractometer using graphite-monochromated Mo-K α ($\lambda = 0.71073$ Å) radiation, were corrected for Lorentz and polarization effects. The structures were solved employing the SHELXTL-direct methods program and refined by full-matrix least-squares on F².⁵

Synthesis of bis-1,5-naphtho-32-crown-8 (BN32C8).

Step 1. 1,5-Bis[(*p*-toluenesulfonyl)-1,4,7,10-tetraoxadecyl]naphthalene. A solution of 1,5dihydroxynaphthalene (9.20 g, 58 mmol) and tri(ethylene glycol) ditosylate (132.06 g, 288 mmol) in dry acetone (1.5 L) was added to a refluxing suspension of K₂CO₃ (250 g, 1.8 mol) in dry acetone (1.5 L) over 2 h under N₂. Refluxing was continued for 6 days and then the mixture was cooled to room temperature, filtered, and evaporated to dryness under reduced pressure. The dark brown viscous liquid residue was column chromatographed over flash silica gel using a hexane/EtOAc gradient (6:1 to 1:2). The pure product (21.4 g) was obtained in 50 % yield. R_f = 0.44 (EtOAc:hexane -3:2); ¹H NMR (400 MHz, CDCl₃): 7.84 (d, 2H, J = 8.4 Hz), 7.78 (d, 4H, J = 8.4 Hz), 7.33 (t, 2H, J = 8.4 Hz), 7.30 (d, 4H, J = 8.4 Hz), 6.83 (d, 2H, J = 7.7 Hz), 4.27 (t, 4H, J = 4.4 Hz), 4.14 (t, 4H, J = 4.8 Hz), 3.95 (t, 4H, J= 4.4 Hz), 3.71 (m, 8H), 3.62 (t, 4H, J = 4.4 Hz), 2.39 (s, 6H) ppm.

Step 2. BN32C8. A solution of 1,5-dihydroxynaphthalene (4.67 g, 29.2 mmol) and 1,5-bis[(*p*-toluenesulfonyl)-1,4,7,10-tetraoxadecyl]naphthalene (21.4 g, 29.2 mmol) in dry acetone (1 L) was added to a refluxing suspension of K₂CO₃ (150 g, 1.08 mol) in dry acetone (3 L) over 3 h under N₂. The mixture was refluxed for 5 days under N₂ and then cooled to room temperature, filtered and evaporated to dryness under reduced pressure. The dark brown viscous liquid residue was column chromatographed over flash silica gel using EtOAc/hexane (1:1). Recrystallization from CHCl₃/Et₂O provided BN32C8 as a white crystalline powder (3.98 g, 25 %). R_f = 0.60 (EtOAc:hexane – 2:1). Melting point: 163-164 °C. For C₃₂H₃₆O₈, calculated/ found: C, 70.06/70.30; H, 6.61/6.86. ¹H NMR (400 MHz, CDCl₃): 7.64 (d, 4H, J = 8.4 Hz), 6.96 (t, 4H, J = 8.4 Hz), 6.53 (d, 4H, J = 7.3 Hz), 4.12 (t, 8H, J = 4.4 Hz), 3.92 (t, 8H, J = 4.4 Hz), 3.80 (s, 8H) ppm.

Synthesis of N,N'-bis[3-(carboethoxy)propyl]-4,4'-bipyridinium hexafluorophosphate (C4BP).

A solution of 2.32 g (4.23 mmol) N,N'-bis[3-(carboethoxy)propyl]-4,4'-bipyridinium bromide in 6.5 ml H₂O was treated with a solution of 2.79 g (17.1 mmol) NH₄PF₆ in 10 ml H₂O. The resulting white precipitate was filtered off, washed with 10 ml aqueous solution containing 2.79 g NH₄PF₆ and then with ice-cold water. Recrystallization from hot H₂O followed by washing with Et₂O and drying in vacuum provided 2.64 g (92 %) of pure C4BP. Melting point: 225-227 °C. ¹H NMR (400 MHz, DMSO-*d*₆): 9.37 (d, 4H, 6.6 Hz), 8.78 (d, 4H, 6.6 Hz), 4.71 (t, 4H, 7.1 Hz), 4.05 (q, 4H, 7.1 Hz), 2.46 (t, 4H, 7.5 Hz), 2.25 (m, 4H), 1.17 (t, 6H, 7.1 Hz) ppm.

Crystallographic data.

C4BP: $C_{22}H_{30}F_{12}N_2O_4P_2$, M = 676.42, T = 296(2) K, orthorhombic, space group Pbca, a = 12.7649(2), b = 14.3247(2), c = 15.5038(2) Å, V = 2834.92(7) Å³, D_c = 1.585 g/cm³, μ = 0.265 mm⁻¹, Z = 4, reflections collected = 45964, unique = 4333 (R_{int} = 0.0564), final R indices [I>2sigmaI]: R1 = 0.0871, wR2 = 0.2767, GoF = 1.742.

The structure of C4BP (Figure S1) shows that the dication lies about an inversion center, and that the two pyridine rings of the bipyridinium core are coplanar (crystallographically

imposed). The individual dication axle-molecules are spaced out by the PF_6^- counterions preventing any intermolecular aromatic interactions. The terminal –COOEt groups play an important role in crystal packing: the C=O oxygen atom forms a C–H…O hydrogen bond with an adjacent bipyridinium moiety (H…O distance: 2.25(1) Å, C…O distance: 3.17(1) Å), while the C–OEt oxygen atom participates in ion-dipole interaction with another bipyridinium moiety (O…N distance: 3.13(1) Å) (Figure S2).



Figure S1. Crystal structure of C4BP. Color code: O-red, N-blue, C-black, H-pink, P-purple, F-green.



Figure S2. Intermolecular interactions between the ester and 4,4'-bipyridinium groups of C4BP.

BN32C8: C₃₂H₃₆O₈, M = 548.61, T = 296(2) K, triclinic, space group P-1, a = 7.4523(3), b = 8.8380(3), c = 10.7212(5) Å, α = 84.569(2), β = 77.234(2), γ = 83.613(2)°, V = 682.61(5) Å³,

 $D_c = 1.335 \text{ g/cm}^3$, $\mu = 0.095 \text{ mm}^{-1}$, Z = 1, reflections collected = 9470, unique = 3269 (R_{int} = 0.0183), final R indices [I>2sigmaI]: R1 = 0.0429, wR2 = 0.1458, GoF = 1.153.

The two aromatic moieties of BN32C8, which lies about an inversion center (Figure S3), are stacked parallel to each other with one ring of a naphthalene unit over one ring of the other naphthalene unit (ring-center to ring-center distance: 3.65(1) Å). The other ring of each naphthalene unit (not participating in intramolecular π - π stacking) forms a C–H··· π contact with the ethyleneoxy arm of an adjacent crown ether molecule (H-centroid distance: 2.76(1) Å). There are no significant intermolecular aromatic interactions present within the lattice.



Figure S3. Crystal structure of BN32C8. Color code: O-red, C-black, H-pink.

¹H NMR data.

Samples for NMR were prepared as 1:1 acetone-d₆:CDCl₃ solutions. The 4.0 (±0.1) mM C4BP, BPP34C10 and C4BP/BPP34C10 solutions were prepared by dissolving 1.5 (±0.1) mg C4BP, 1.1 (±0.1) mg of BPP34C10, and 2.6 (±0.1) mg C4BP/BPP34C10 pseudorotaxane crystals, respectively, in 500 (±1) μ L of NMR solvent mixture. The 3.6 (±0.1) mM C4BP and BN38C10 solutions were prepared by dissolving 1.5 (±0.1) mg C4BP and 1.4 (±0.1) mg BN38C10, respectively, in 600 (±1) μ L NMR solvent mixture, while the 3.6 (±0.1) mM C4BP/BN38C8 pseudorotaxane solution was prepared by dissolving 1.5 (±0.1) mg C4BP and 1.4 (±0.1) mg C4BP/BN38C8 pseudorotaxane solution was prepared by dissolving 1.5 (±0.1) mg C4BP and 1.4 (±0.1) mg BN38C10 together in 600 (±1) μ L NMR solvent mixture. The 3.6 (±0.1) mM BN32C8 and C4BP/BN32C8 pseudorotaxane solutions were prepared similarly, using 1.2 (±0.1) mg BN32C8 instead of BN38C10.



Scheme 1. Proton assignment in the axle and wheel components



Figure S4. ¹H NMR spectra (ppm, 400 MHz, acetone- d_6 :CDCl₃ = 2:1, 4.0 mM, 25 °C) of C4BP (blue), BPP34C10 (red) and C4BP/BPP34C10 (green).

	Chemical shifts (δ , ppm) for free axle or wheel	Chemical shifts (δ, ppm) for pseudorotaxane	Δδ
C4BP proton			
a	9.38 (d, 4H, J=7.0 Hz)	9.26 (d, 4H, J=6.6 Hz)	0.12
b	8.77 (d, 4H, J=6.2 Hz)	8.50 (d, 4H, J=6.6 Hz)	0.27
с	4.98 (t, 4H, J=7.4 Hz)	4.95 (t, 4H, J=7.5 Hz)	0.03
d	4.06 (q, 4H, J=7.1 Hz)	4.10 (q, 4H, J =7.2 Hz)	- 0.04
e	2.52 (t, 4H, J=7.1 Hz)	2.56 (t, 4H, J=7.3 Hz)	- 0.04
f	2.44 (q, 4H, J=7.1 Hz)	2.47 (m, 4H)	- 0.03
g	1.18 (t, 6H, J=7.3 Hz)	1.20 (t, 6H, J=7.1 Hz)	- 0.02
BPP34C10 proton			
i	6.72 (s, 8H)	6.49 (s, 8H)	0.23
j 3.94 (m, 8H)		3.79 (m, 8H)	0.15
k	3.77 (m, 8H)	3.74 (m, 8H)	0.03
l+m	3.62 (m,16H)	3.73 (s, 16H)	- 0.09



Figure S5. ¹H NMR spectra (ppm, 400 MHz, acetone- d_6 :CDCl₃ = 2:1, 3.6 mM, 25 °C) of C4BP (blue), BN38C10 (red) and C4BP/BN38C10 (green).

	Chemical shifts (δ , ppm) for free axle or wheel	Chemical shifts (δ, ppm) for pseudorotaxane	Δδ
C4BP proton		-	
b	9.38 (d, 4H, J=7.0 Hz)	9.05 (d, 4H, J=6.2 Hz)	0.33
a	8.77 (d, 4H, J=6.2 Hz)	7.99 (s, 4H)	0.78
c	4.98 (t, 4H, J=7.4 Hz)	4.93 (t, 4H, J=7.4 Hz)	0.05
f	4.06 (q, 4H, J=7.1 Hz)	4.13 (q, 4H, J=7.2 Hz)	- 0.07
e	2.52 (t, 4H, J=7.1 Hz)	2.60 (t, 4H, J=7.3 Hz)	0.08
d	2.44 (q, 4H, J=7.1 Hz)	2.46 (m, 4H)	- 0.02
g	1.18 (t, 6H, J=7.3 Hz)	1.22 (t, 6H, J=7.1 Hz)	- 0.04
BN38C10 proton			
i	7.72 (d, 4H, J=8.4 Hz)	7.22 (d, 4H, J=8.4 Hz)	0.50
j	7.15 (t, 4H, J=8.1 Hz)	7.05 (t, 4H, J=8.1 Hz)	0.10
k	6.52 (d, 4H, J=7.7 Hz)	6.54 (d, 4H, J=7.7 Hz)	- 0.02
1	4.04 (t, 8H, J=4.6 Hz)	3.99 (d, 8H, J=4.4 Hz)	0.05
m	3.90 (t, 8H, J=4.4 Hz)	3.90 (d, 8H, J=4.0 Hz)	0.00
n + o	3.70 (m, 16H)	3.80 (s, 16H)	- 0.10



Figure S6. ¹H NMR spectra (ppm, 400 MHz, acetone- d_6 :CDCl₃ = 2:1, 3.6 mM, 25 °C) of C4BP (blue), BN32C8 (red) and C4BP/BN32C8 (green).

	Chemical shifts (δ, ppm) for free axle or wheel	Chemical shifts (δ, ppm) for pseudorotaxane	Δδ
C4BP proton			
b	9.38 (d, 4H, J=7.0 Hz)	9.13 (s, 4H)	0.25
a	8.77 (d, 4H, J=6.2 Hz)	8.16 (s, 4H)	0.61
с	4.98 (t, 4H, J=7.4 Hz)	4.90 (s, 4H)	0.08
f	4.06 (q, 4H, J=7.1 Hz)	4.12 (m, 4H)	- 0.06
e	2.52 (t, 4H, J=7.1 Hz)	2.56 (t, 4H, J=7.3 Hz)	0.04
d	2.44 (q, 4H, J=7.1 Hz)	2.48 (m, 4H)	- 0.04
g	1.18 (t, 6H, J=7.3 Hz)	1.21 (t, 6H, J=7.1 Hz)	- 0.03
BN32C8 proton			
i	7.55 (d, 4H, J=8.4 Hz)	7.30 (s, 4H)	0.25
j	6.93 (t, 4H, J=8.1 Hz)	6.94 (t, 4H, J=8.1 Hz)	0.01
k	6.59 (d, 4H, J=7.7 Hz)	6.60 (d, 4H, J=7.7 Hz)	- 0.01
1	4.12 (t, 8H, J=4.8 Hz)	4.12 (d, 8H, J=4.4 Hz)	0.00
m	3.88 (t, 8H, J=4.8 Hz)	3.95 (d, 8H, J=4.0 Hz)	-0.07
n	3.73 (s, 8H)	3.85 (s, 8H)	- 0.08

Pseudorotaxane stoichiometry, association contants and extinction coefficients

Job's plot method with varying mole fractions of axle and wheel was used to determine the stoichiometry of the complexes. The absorption maxima at 0.5 mole fractions indicate a 1:1 stoichiometry in all three pseudorotaxane solutions (Figure S7).

Standard solutions of 1.0 (\pm 0.1) mM C4BP, BPP34C10, BN38C10 and BN32C8 were prepared in 25.00 (\pm 0.03) mL volumetric flasks by dissolving 17.0 (\pm 0.1) mg, 13.4 (\pm 0.1) mg, 15.9 (\pm 0.1) mg, 13.7 (\pm 0.1) mg, respectively, in a 1:1 mixture of CH₃CN–CHCl₃. The solutions were mixed using a micropipette according to the table below to obtain the different molar ratios of axle/wheel in a final volume of 3.00 (\pm 0.01) mL.



Figure S7: Job's plot curves for C4BP/BN32C8 (A), C4BP/BN38C10 (B) and C4BP/BPP34C10 (C).

Sample	C4BP : wheel	Volume of	Volume of	Conc. of C4BP/ 10^{-4} H cl (10.1)	Conc. of wheel/ 10^{-4} H sl (10.1)
number	molar ratio	C4BP / mL	wheel / mL	$10^{-1} \text{molL}^{-1} (\pm 0.1)$	$10^{-1} \text{molL}^{-1} (\pm 0.1)$
1	10:0	3.00	0.00	10	0.0
2	9:1	2.70	0.30	9.0	1.0
3	8:2	2.40	0.60	8.0	2.0
4	7:3	2.10	0.90	7.0	3.0
5	6:4	1.80	1.20	6.0	4.0
6	5:5	1.50	1.50	5.0	5.0
7	4:6	1.20	1.80	4.0	6.0
8	3:7	0.90	2.10	3.0	7.0
9	2:8	0.60	2.40	2.0	8.0
10	1:9	0.30	2.70	1.0	9.0
11	0:10	0.00	3.00	0.0	10.0

Benesi-Hildebrand analysis was used to determine the equilibrium association constants of the 1:1 pseudorotaxanes. A standard solution of 1.0 (\pm 0.1) mM C4BP was prepared in 10.00 (\pm 0.02) mL volumetric flask by dissolving 6.8 mg (\pm 0.1) in a 1:1 CH₃CN–CHCl₃ mixture. Standard C4BP/wheel pseudorotaxane solutions were prepared to be 1.0 (\pm 0.1) mM in C4BP and 10.0 (\pm 0.1) mM in wheel by dissolving 13.4 (\pm 0.1) mg of BPP34C10, 15.9 (\pm 0.1) mg of BN38C10 and 13.7 (\pm 0.1) mg of BN32C8, respectively, in 2.50 (\pm 0.01) mL of standard C4BP solution. A volume of 2.00 (\pm 0.01) mL standard C4BP solution was transferred into a cuvette and titrated with a pseudorotaxane solution up to a wheel:axel ratio of 5:1.

The equilibrium for pseudorotaxane formation can be written as:

v

$$Axle + Wheel \xrightarrow{R_a} Rot \tag{1}$$

where *Rot* is the pseudorotaxane obtained and K_a is the equilibrium association constant. Then, K_a can be written as:

$$K_{a} = \frac{[Rot]}{[Axle][Wheel]}$$

$$K_{a} = \frac{C_{Rot}}{(C_{Axle}^{0} - C_{Rot})(C_{Wheel}^{0} - C_{Rot})}$$
(2)
(3)

where C_{Wheel}^{0} is the initial concentration of the wheel and C_{axle}^{0} is the initial concentration of

the axle molecule.

When $C_{Wheel}^{0} \gg C_{axle}^{0}$ and $C_{rot} = A/\varepsilon l$, then equation (3) can be rearranged as $\frac{C_{Wheel}^{0}}{A} = \frac{1}{K_a \varepsilon} \frac{1}{C_{axle}^{0}} + \frac{1}{\varepsilon}$ (4)

where ε is the extinction coefficient and A is the absorbance of the pseudorotaxane charge transfer complex.

The plot of $\frac{C_{Wheel}^0}{A}$ vs $\frac{1}{C_{axle}^0}$ gives a straight line with a slope of $\frac{1}{K_a\varepsilon}$ and an intercept of $\frac{1}{\varepsilon}$. Association constants and molar extinction coefficients for the different pseudorotaxanes were determined using equation (4) and the corresponding plots are given in Figure S8.



Figure S8: Benesi-Hildebrand plots for C4BP/BN32C8 (A), C4BP/BN38C10 (B) and C4BP/BPP34C10 (C).

Temperature-dependent absorption measurements - Thermodynamic parameters

Temperature-dependent optical absorption spectra for the pseudorotaxanes with wheels BN32C8 and BN38C10 are shown in Figure S9. 1.0 (± 0.1) mM C4BP/wheel solutions were prepared in 25.00 (± 0.03 mL) volumetric flasks by dissolving 16.9 (± 0.1) mg of C4BP together with 13.4 (± 0.1) mg of BPP34C10, 15.9 (± 0.1) mg of BN38C10 and 13.7 (± 0.1) mg of BN32C8, respectively, in a 2:1 mixture of acetone:CH₂Cl₂.



Figure S9: Temperature-dependent optical absorption spectra for 1.0 mM solutions of C4BP/BN32C8 (A) and C4BP/BN38C10 (B) in $(CH_3)_2CO/CH_2Cl_2$ (2:1).

Thermodynamic parameters are obtained by analysis of the temperature-dependent absorption spectra. The thermodynamics of pseudorotaxane formation can be given by conventional expressions:

$$\Delta G = \Delta H - T \Delta S \tag{5}$$

$$\Delta G = -RT ln K_a \tag{6}$$

where ΔG is the free energy change for pseudorotaxane formation, ΔH and ΔS are enthalpy and entropy of formation, respectively. *R* is the gas constant and *T* is the temperature in K.

With equimolar concentrations of Wheel and Axle and with 1:1 stoichiometry for the pseudorotaxane, K_a can be written as:

$$K_a = \frac{C_{Rot}}{(C_{Wheel}^0 - C_{Rot})^2} \tag{7}$$

and

$$K_a = \frac{A_{\ell el}}{(C_{Wheel}^0 - A_{\ell el})^2}$$
(8)

where A is the absorbance of the pseudorotaxane as a function of temperature and ε is the extinction coefficient of the pseudorotaxane obtained from Benesi-Hildebrand analysis. K_a values as a function of temperature are obtained from equation (8).

$$lnK_a = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{9}$$

 $\ln K_a$ is plotted as a function of 1/T which gives a slope of $-\Delta H/R$ and an intercept of $\Delta S/R$ (Figure S10). From these plots, enthalpy and entropy values are calculated and tabulated in Table 1.



Figure S10: Plot of ln(K_a) versus 1/T for the investigated pseudorotaxanes.

Temperature (K)	ϵ values (10 ² M ⁻¹ cm ⁻¹)		
(±0.1)	C4BP/BPP34C10	C4BP/BN38C10	C4BP/BN32C8
223	5.8 ± 0.6	7.7 ± 0.8	8.9 ± 0.9
233	5.4 ± 0.5	7.3 ± 0.7	8.1 ± 0.8
243	4.9 ± 0.5	6.8 ± 0.7	7.2 ± 0.7
253	4.3 ± 0.4	6.1 ± 0.6	6.2 ± 0.6
263	3.6 ± 0.4	5.1 ± 0.5	5.2 ± 0.5
273	2.9 ± 0.3	4.2 ± 0.4	4.2 ± 0.4
283	2.1 ± 0.2	3.3 ± 0.3	3.2 ± 0.3
293	1.4 ± 0.1	2.4 ± 0.2	2.3 ± 0.2
303	0.85 ± 0.09	1.7 ± 0.2	1.7 ± 0.2
313	0.47 ± 0.05	1.2 ± 0.1	1.2 ± 0.1
323	0.30 ± 0.03	0.81 ± 0.08	0.84 ± 0.08

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