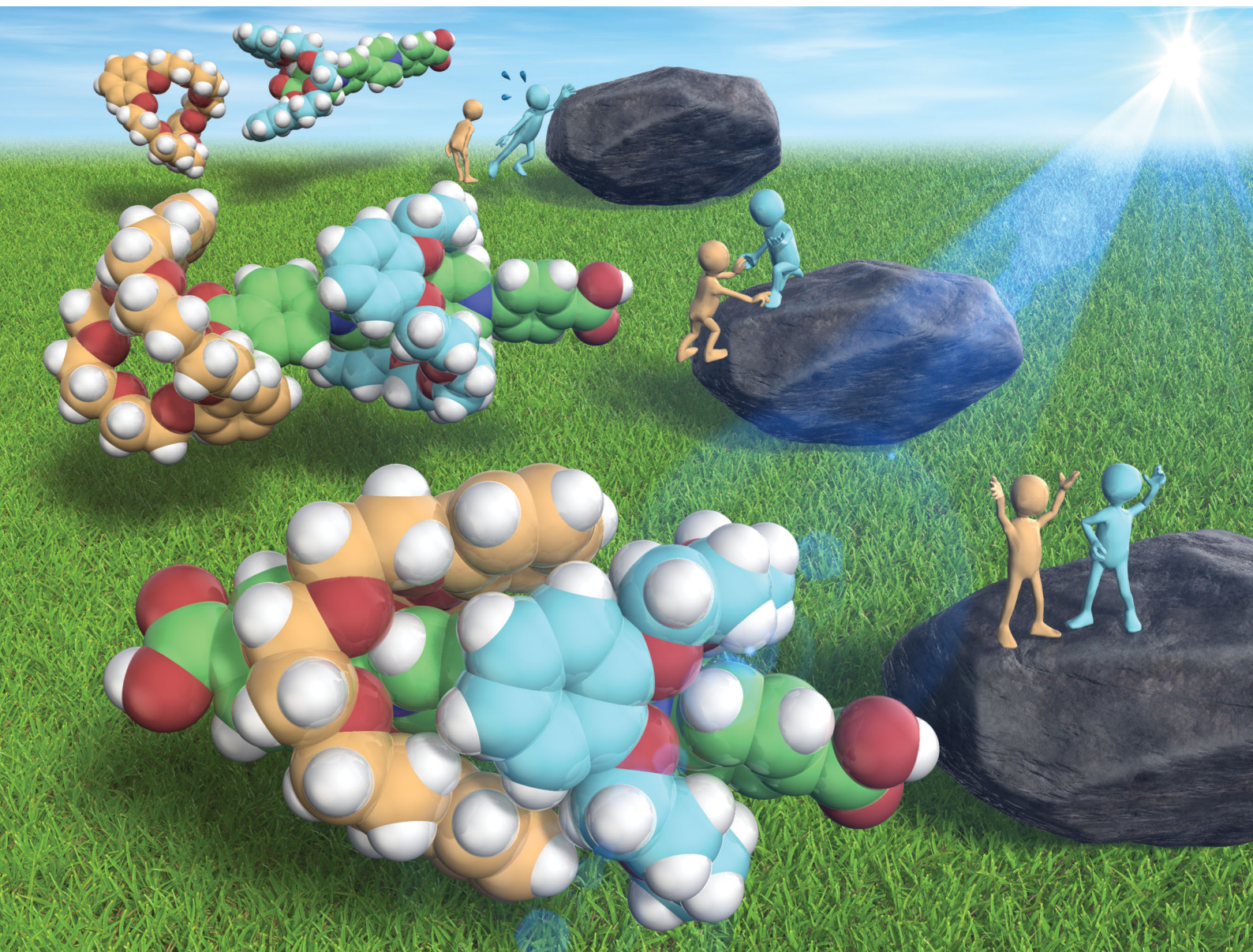


# ChemComm

Chemical Communications

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ISSN 1359-7345

**COMMUNICATION**

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 Cite this: *Chem. Commun.*, 2020, 56, 8735

 Received 30th April 2020,  
Accepted 9th June 2020

DOI: 10.1039/d0cc03131c

rsc.li/chemcomm

## Efficient formation of [3]pseudorotaxane based on cooperative complexation of dibenzo-24-crown-8 with diphenylviologen axle†

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**A novel cooperative [3]pseudorotaxane system consisting of dibenzo-24-crown-8 (DB24C8) and diphenylviologen axle has been developed. The two-step formation of the [3]pseudorotaxane occurred in a positive-cooperative manner. The corresponding [3]rotaxane was successfully obtained from just a stoichiometric mixture of each component by end-capping without dissociation.**

Among the various kinds of mechanically-interlocked molecules,<sup>1</sup> rotaxane derivatives have highly contributed to the development of new types of molecular machines, such as molecular shuttles,<sup>2</sup> a molecular elevator,<sup>3</sup> and a molecular muscle.<sup>4</sup> The dynamics of the [2]rotaxanes originates from rotating and shuttling motions *e.g.*, the change in the relative positions of the wheel and axle. Oligorotaxanes, such as [3]rotaxanes, which have an increased number of wheel components, can be good candidates to enable more complex motions, because they are expected to undergo a variety of movements such as the changes in the relative positions or orientations of the two or more wheel components.<sup>5</sup>

The general strategy to obtain [3]rotaxanes requires an axle molecule that has two station units so that each station unit can bind to one wheel component. In fact, [3]rotaxanes are easily available when the wheel-station interactions are strong enough, as seen in those based on metal-coordination.<sup>6</sup> If the interaction is not strong enough, however, the formation of [3]rotaxane becomes less efficient. The synthetic attempts often produce a mixture of [2]- and [3]rotaxanes unless a large excess amount of the wheel is used.<sup>7</sup> This is because the second wheel threading is less favourable than the first one due to a steric/electrostatic repulsion. This is interpreted as a negative-cooperative process,

but if the two-step complexation occurs in a positive-cooperative fashion,<sup>8</sup> [3]rotaxanes would be more efficiently synthesized, thus allowing us to use them as a convenient motif for dynamic functional molecules. Actually, positive cooperativity was observed for the formation of several [3]pseudorotaxanes or [3]rotaxanes containing a cryptand,<sup>9</sup> shape-persistent macrocycles, *etc.*<sup>10</sup> as the wheel units. Since crown ethers have been key players in rotaxane chemistry,<sup>1–3</sup> it is desirable to develop cooperative [3]pseudorotaxane systems based on crown ethers, which could be a versatile intermediate for the synthesis of [3]rotaxanes.

Recently, the crystal structure of a [3]pseudorotaxane, **MV**·(DB24C8)<sub>2</sub>, in which two crown ether wheels simultaneously interact with one dimethylviologen (**MV**) molecule, has been reported.<sup>11</sup> This was somewhat surprising because, previously, the **MV** motif had solely been used to obtain [2]pseudorotaxane structures, that is, only one wheel molecule interacts with the **MV** station of the rotaxane axle through  $\pi$ - $\pi$  and/or CT interactions between the electron-rich alkoxybenzene unit and the electron-deficient bipyridinium unit.<sup>2,3,12</sup> In this unique [3]pseudorotaxane **MV**·(DB24C8)<sub>2</sub>, however, the binding with the second wheel was reported to be weak so that only [2]pseudorotaxane was observable in solution. If the formation efficiency is improved, this [3]pseudorotaxane motif could be much more attractive not only for its unique structural feature but also for the redox behaviour of the viologen axles. In this study, we explored the [3]pseudorotaxane formation behaviour of the two **MV** analogues, **A1** and **A2**, having phenyl and benzyl groups, respectively, which could enhance the **MV**-crown ether interactions in solution (Fig. 1). We discovered that the combination of diphenylviologen **A1** and DB24C8 exhibits an unexpectedly highly positive cooperativity during the [3]pseudorotaxane formation. We successfully applied this positive-cooperative binding to the efficient synthesis of [3]rotaxane by end-capping of the carboxy groups at the two terminals of the axle molecule.

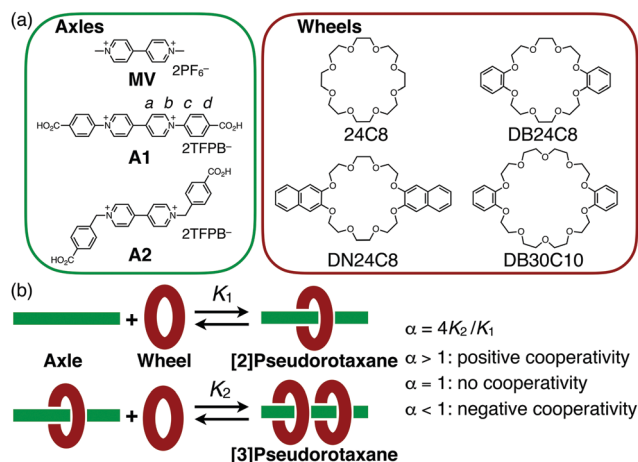
We used two kinds of viologen axles, diphenylviologen **A1** and dibenzylviologen **A2** as TFPB salts (TFPB<sup>−</sup> = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate),<sup>13</sup> which were prepared from the corresponding halide salts<sup>14,15</sup> (Fig. 1a). Two carboxy groups

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† Electronic supplementary information (ESI) available: Detailed synthetic procedures, crystallographic data, additional <sup>1</sup>H NMR spectra and ESI-TOF MS for the complexes. CCDC 1998063. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0cc03131c

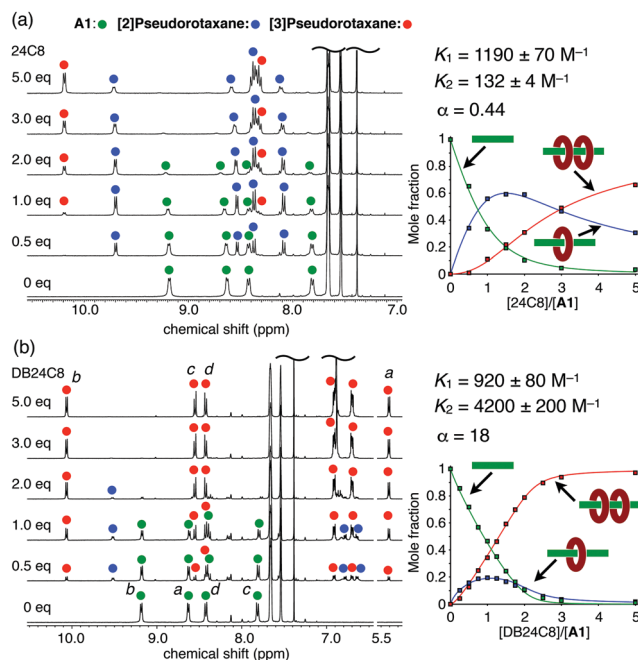


**Fig. 1** (a) Chemical structures of axle and wheel molecules used in this study (TFPB<sup>-</sup> = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate). (b) Equilibria for the formation of [3]pseudorotaxane and definition of the binding constants  $K_1$ ,  $K_2$  and the cooperativity factor  $\alpha$ .

are introduced at the two terminals as reaction sites for conversion to the corresponding [3]rotaxane by end-capping. As the wheel units, four kinds of crown ether derivatives, 24C8, DB24C8, DN24C8, and DB30C10, were used.

The pseudorotaxane formation behaviour of the viologen axle **A1** and 24C8 was investigated by <sup>1</sup>H NMR titration studies in CDCl<sub>3</sub>/CD<sub>3</sub>CN (4:1). The 1:1 complex, [2]pseudorotaxane **A1**·(24C8), was newly formed when 0.5 equiv. of 24C8 was added to the viologen axle **A1**, and the 1:2 complex, [3]pseudorotaxane **A1**·(24C8)<sub>2</sub>, was also observed upon further addition (1.0–5.0 equiv.) (Fig. 2a). The stepwise formation of **A1**·(24C8) and **A1**·(24C8)<sub>2</sub> was also confirmed by ESI-TOF mass spectrometry (Fig. S1, ESI<sup>†</sup>). The binding constants,  $K_1$  and  $K_2$ , for this two-step complexation (Fig. 1b) were determined by non-linear curve fitting of the changes in the mole fractions (Fig. 2a and Table 1). The negative cooperativity was clearly demonstrated ( $K_1 = 1190 \text{ M}^{-1}$ ,  $K_2 = 132 \text{ M}^{-1}$ , and  $\alpha = 4K_2/K_1 = 0.44$ ), which can be explained by steric/electrostatic repulsion between the first and second wheels.<sup>16</sup>

In contrast, a positive cooperativity was observed when DB24C8 was used instead of 24C8. Upon the addition of DB24C8 to **A1**, two sets of signals successively appeared in the <sup>1</sup>H NMR spectra as observed in the **A1**·24C8 system (Fig. 2b), indicating the formation of the [2]- and [3]pseudorotaxanes (**A1**·(DB24C8) and **A1**·(DB24C8)<sub>2</sub>). The significant upfield shift of the viologen signal H<sup>a</sup> upon the complexation (8.63 → 5.41 ppm) implied the strong shielding effect of the phenylene rings in DB24C8. In this case, 95% of **A1** was converted into the [3]pseudorotaxane, **A1**·(DB24C8)<sub>2</sub> when 3 equiv. of DB24C8 were added. This indicated that the DB24C8 more efficiently formed the [3]pseudorotaxane than 24C8, which was confirmed by the binding constants,  $K_1 = 920 \text{ M}^{-1}$  and  $K_2 = 4200 \text{ M}^{-1}$  (Fig. 2b and Table 1). To our surprise, this **A1**·DB24C8 system showed a highly positive cooperativity ( $\alpha = 18$ ), which is significantly greater than that of the **A1**·24C8 system ( $\alpha = 0.44$ ). A similar high cooperativity ( $K_1 = 900 \text{ M}^{-1}$ ,



**Fig. 2** <sup>1</sup>H NMR spectral changes of **A1** upon the addition of (a) 24C8 and (b) DB24C8 (400 MHz, 25 °C, CDCl<sub>3</sub>/CD<sub>3</sub>CN (4:1), [**A1**] = 5 mM). The plots of the mole fractions of the three components versus the equivalents of the wheel are also shown. See Fig. 1 for the signal assignments.

**Table 1** Binding constants for the complexation between the viologen axles and crown ethers

Axle	Crown ether	$K_1^a$	$K_2^a$	$\alpha$
<b>A1</b>	24C8	1190 ± 70	132 ± 4	0.44
<b>A1</b>	DB24C8	920 ± 80	4200 ± 200	18
<b>A1</b>	DN24C8	900 ± 500	4300 ± 1200	~20
<b>A1</b>	DB30C10	1190 ± 190	— <sup>b</sup>	~0
<b>A2</b>	DB24C8	36 ± 3	— <sup>b</sup>	~0
<b>A2</b>	DN24C8	71 ± 6	— <sup>b</sup>	~0

<sup>a</sup> The binding constants were determined by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub>/CD<sub>3</sub>CN (4:1) at 25 °C. <sup>b</sup> Negligibly small.

$K_2 = 4300 \text{ M}^{-1}$ , and  $\alpha \approx 20$ ) was observed for the combination of **A1** and DN24C8, which contains two naphthylene moieties (Fig. S5, ESI<sup>†</sup> and Table 1). Based on these results, we found that the introduction of aromatic rings into the 24C8 scaffold is essential to induce the positive cooperativity during the 1:2 complexation with **A1**.

In order to obtain further insight into the positive cooperativity, we investigated the complexation behaviour of **A1** with the DB30C10 wheel, a larger macrocycle having two phenylene moieties. Upon the addition of DB30C10, the H<sup>a</sup> signal in the viologen axle **A1** was gradually shifted upfield, indicating the formation of the pseudorotaxane complex (Fig. S6, ESI<sup>†</sup>). The chemical shift changes were nicely fitted to the 1:1 binding isotherm with  $K_1 = 1190 \text{ M}^{-1}$  (Table 1). Thus, in this case, [2]pseudorotaxane **A1**·(DB30C10) was mainly formed and the formation of the [3]pseudorotaxane **A1**·(DB30C10)<sub>2</sub> was negligible.<sup>17</sup>

We also investigated the complexation behaviour of the dibenzylviologen axle **A2** in a similar manner. When DB24C8 or DN24C8 was added to **A2**, a new set of signals appeared in the  $^1\text{H}$  NMR spectra (Fig. S7 and S8, ESI $^\dagger$ ). The quantitative analysis yielded smaller binding constants for the 1:1 complex,  $K_1 = 36$  and  $71 \text{ M}^{-1}$  for DB24C8 and DN24C8, respectively, without forming the 1:2 complex (Table 1). Thus, the 1:2 complexes (e.g., [3]pseudorotaxanes) were formed only when the combination of diphenylviologen **A1** and DB- or DN24C8 was used. This observation is consistent with previous reports describing that dialkyl- and dibenzylviologen axles form [2]pseudorotaxanes with DB24C8.<sup>11,12c</sup>

The formation of the [3]pseudorotaxane **A1**·(DB24C8)<sub>2</sub> was significantly influenced by the solvent. The [3]pseudorotaxane formation became less efficient in more polar media containing less  $\text{CDCl}_3$  (Fig. S9–S13, ESI $^\dagger$  and Table 2). Notably, however, higher cooperativity factors were observed in the polar solvents ( $\alpha = 63$  in  $\text{CD}_3\text{CN}$ ;  $\alpha = 41$  in  $\text{CD}_3\text{OD}$ ). Although the origin of the cooperativity is unclear at this point, the solvophobic effect or some other factors might contribute to the positive cooperativity.

Single crystals of [3]pseudorotaxane **A1**·(DB24C8)<sub>2</sub> were obtained by slow diffusion of pentane into a methanol/chloroform solution. As we expected, the **A1** axle was threaded into the two DB24C8 molecules in the crystal structure (Fig. 3). The two DB24C8 molecules were arranged in an interdigitated fashion so as to wrap the two pyridinium rings, but no  $\pi$ - $\pi$  stacking interaction was observed in the DB24C8–DB24C8 or DB24C8–**A1** combinations (Fig. 3a and b). A similar interdigitated arrangement was found in the crystal structure of **MV**·(DB24C8)<sub>2</sub>, although the formation of the [3]pseudorotaxane was negligible in solution probably due to the lack of phenyl groups in the viologen axle.<sup>11</sup> Each of the phenylpyridinium moieties was surrounded by eight oxygen atoms of the DB24C8 so that they can form eight intramolecular C–H···O hydrogen bonds ranging from 2.11 Å to 2.92 Å (Fig. 3c and Table S3, ESI $^\dagger$ ). This multiple hydrogen bonding, in which the phenyl C–H groups in **A1** also participate, might account for the enhanced interaction between the **A1** axle and the DB24C8 wheel. In addition, C–H··· $\pi$  interactions between the pyridinium C–H groups ( $\text{H}^a$  in Fig. 1a) in **A1** and the phenylene rings in DB24C8 were also observed (from 2.66 Å to 2.93 Å, Fig. 3b). This interdigitated structure of [3]pseudorotaxane in solution was supported by the NOE correlation between  $\text{H}^a$  viologen proton and phenylene protons of DB24C8 (Fig. S14, ESI $^\dagger$ ).

Table 2 Binding constants for the complexation between the viologen axle **A1** and DB24C8 in various kinds of solvents

Solvent	$K_1^a$	$K_2^a$	$\alpha$
$\text{CDCl}_3/\text{CD}_3\text{CN}$ (4:1)	$920 \pm 80$	$4200 \pm 200$	18
$\text{CD}_3\text{CN}$	$48 \pm 8$	$760 \pm 90$	63
$\text{CDCl}_3/\text{CD}_3\text{OD}$ (4:1)	$1500 \pm 200$	$4800 \pm 400$	13
$\text{CD}_3\text{OD}$	$201 \pm 13$	$2070 \pm 70$	41
$\text{CDCl}_3/\text{DMSO}-d_6$ (4:1)	$420 \pm 100$	$1500 \pm 200$	15
$\text{DMSO}-d_6$	— <sup>b</sup>	— <sup>b</sup>	— <sup>b</sup>

<sup>a</sup> The binding constants were obtained by  $^1\text{H}$  NMR spectroscopy at 25 °C. <sup>b</sup> Negligibly small.

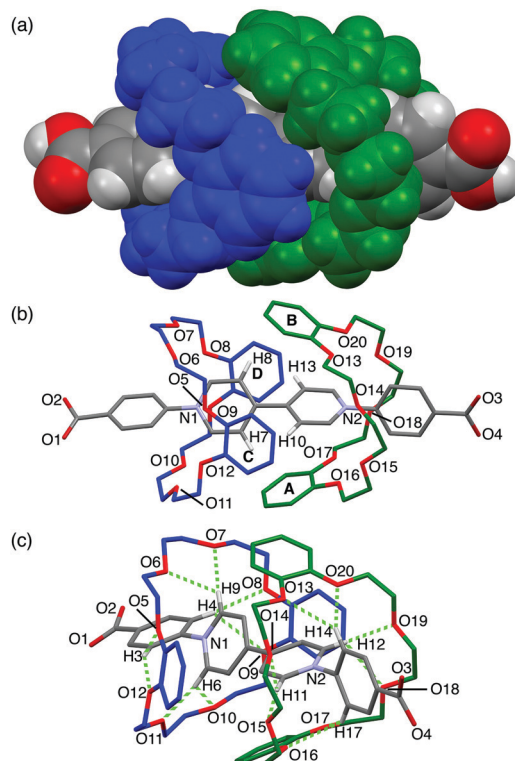


Fig. 3 Crystal structure of **A1**·(DB24C8)<sub>2</sub>. (a) Space-filling model, and (b and c) capped stick models. Hydrogen atoms (b and c), solvent molecules and TFPB anions are omitted for clarity. Hydrogen atoms participating in the C–H··· $\pi$  and C–H···O interactions are shown in (b) and (c), respectively (C–H··· $\pi$  distances, H7···PhA, 2.66 Å; H8···PhB, 2.93 Å; H10···PhC, 2.74 Å; H13···PhD, 2.83 Å). The green dotted lines indicate the C–H···O hydrogen bonds (for the C–H···O distances, see Table S3, ESI $^\dagger$ ).

Finally, we applied this positive-cooperative binding to the efficient synthesis of [3]rotaxane by end-capping of the carboxy groups in **A1** via amide formation (Fig. 4a).<sup>18</sup> We prepared a solution containing **A1** (20 mM) and DB24C8 (40 mM) in  $\text{CDCl}_3/\text{CD}_3\text{CN}$  (4:1), in which 89% of **A1** is converted to [3]pseudorotaxane **A1**·(DB24C8)<sub>2</sub> as estimated from the binding constants. The end-capping was achieved without dissociation of the wheel

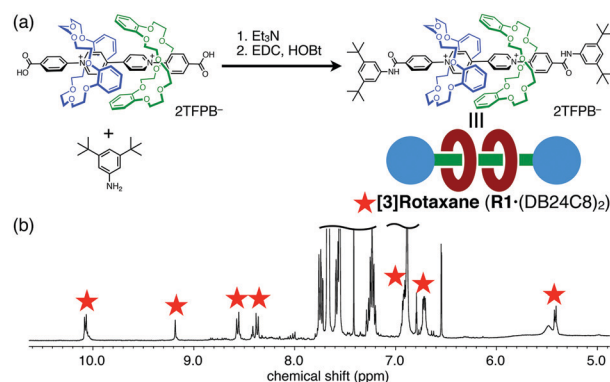


Fig. 4 (a) Reaction scheme of [3]rotaxane **R1**·(DB24C8)<sub>2</sub> formation by amide formation, and (b)  $^1\text{H}$  NMR spectrum of the reaction mixture (400 MHz,  $\text{CDCl}_3/\text{CD}_3\text{CN}$  (4:1)).

components by amide formation with 3,5-di-*tert*-butylaniline under the conditions using 1-hydroxybenzotriazole (HOBt) and 1-ethyl-3-(3-dimethylamino)propylcarbodiimide (EDC). The almost exclusive formation of [3]rotaxane **R1**·(DB24C8)<sub>2</sub> was confirmed by the <sup>1</sup>H NMR spectrum (Fig. 4b) and the ESI-TOF mass spectrum (*m/z* = 834.9 for [R1·(DB24C8)<sub>2</sub> – 2TFPB]<sup>2+</sup>, Fig. S15, ESI†). Notably, the signals for the [2]rotaxane **R1**·(DB24C8) were scarcely observed in the <sup>1</sup>H NMR spectrum even though only a stoichiometric amount of the DB24C8 wheel was used. Thus, the [3]rotaxane **R1**·(DB24C8)<sub>2</sub> was efficiently synthesized without consuming an excess amount of the wheel component based on the newly discovered [3]pseudorotaxane system exhibiting a positive-cooperative complexation behaviour.

In conclusion, we have demonstrated a new positive-cooperative [3]pseudorotaxane system consisting of DB24C8 and the diphenylviologen axle **A1**. The maximum cooperativity factor of 63 was achieved in the CD<sub>3</sub>CN solution. The X-ray crystallographic analysis revealed that both the multiple C–H···O and C–H···π interactions between the **A1** and DB24C8 components contributed to the stabilization of the [3]pseudorotaxane. With these results in hand, [3]rotaxane **R1**·(DB24C8)<sub>2</sub> was efficiently obtained *via* the amide formation from a 1:2 stoichiometric mixture of **A1** and DB24C8. We believe that these results open the way to the development of not only new [3]rotaxanes based on various kinds of DB24C8 derivatives, but also oligo- and polyrotaxanes that have more than two DB24C8 wheels for potential application to more complex molecular machines. The investigation of the electrochemical responses of the [3]rotaxane based on the redox active viologen unit is currently underway.

This work was supported by JSPS KAKENHI Grant Number JP20H04667, JP18H04511 (Soft Crystals), and JP16H06510 (Coordination Asymmetry), Inoue Science Research Award, the Asahi Glass Foundation, the Iwatani Naoji Foundation, and the World Premier International Research Center Initiative (WPI), MEXT, Japan.

## Conflicts of interest

There are no conflicts to declare.

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