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# COMMUNICATION

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pyrene units triggered by release and binding of alkali metal ions<sup>†</sup>

contraction motions of a double-stranded helicate bearing terminal

Fluorescent molecular spring that visualizes the extension and

A novel double-stranded spiroborate helicate bearing terminal pyrene residues exhibited reversible fluorescence color changes (green and blue colors) due to the unique unidirectional springlike motions of the helicate triggered by catch and release of alkali metal ions.

The development of artificial helical molecules and polymers which undergo reversible musclelike extension and contraction (elastic) motions by responding to external stimuli has attracted continuous interest because of their possible application to molecular actuators, nanodevices and molecular nanomachines.<sup>1</sup> In contrast to biological helical systems, however, most of synthetic helical systems rarely exhibit a unidirectional twisting motion.<sup>2,3</sup>

We previously reported that an ortho-linked tetraphenol strand with a biphenylene unit in the middle formed a unique double-stranded helicate bridged by two spiroborates in which a Na<sup>+</sup> ion is encapsulated in the center of the helicate (rac- $\mathbf{DH1}_{\mathbf{BNaB}^{-}}$  Na<sup>+</sup>)<sup>4</sup> (Fig. 1a). This helicate displayed an intriguing Na<sup>+</sup> ion-triggered, reversible extension and contraction motion coupled with a unidirectional twisting motion (Fig. 1b) upon the release and binding of the Na<sup>+</sup> ion.<sup>4</sup> Detailed thermodynamic studies using its extended tetrabutylammonium (TBA) salts (rac-DH1<sub>BB</sub><sup>2-·</sup>(TBA<sup>+</sup>)<sub>2</sub>) revealed that the extended helicate also formed similar inclusion complexes with a series of monovalent cations and their binding constants  $(K_a)$ decreased with the increasing size of the cations (Fig. 1b).<sup>5</sup> The replacement of the central biphenylene units of the rac-DH1<sub>BNaB</sub>-·Na<sup>+</sup> with other functional units, such as the 4,4'linked 2,2'-bipyridine and its N,N'-dioxide residues<sup>6</sup> and the introduction of substituents at the *meta*-position of the terminal phenyl residues (*rac*-**DH2a**<sub>**BNaB**</sub><sup>-</sup>·**Na**<sup>+</sup> and *rac*-**DH2b**<sub>**BNaB**</sub><sup>-</sup>·**Na**<sup>+</sup>)<sup>7</sup> (Fig. 1a) maintained their double-stranded helicate structures, thus showing reversible ion-triggered springlike motions.<sup>8</sup>

On the other hand, pyrene and its derivatives have been extensively used as a powerful fluorescent probe for the sensing and detection of specific molecules, ions and biomolecules9 as well as for studying the structures of synthetic and biological macromolecules10 because of their characteristic excimer formations, thus displaying a green fluorescence, being different from the corresponding blue monomer's fluorescence.9,10 However, to the best of our knowledge, fluorescent color changes have never been utilized to visualize unidirectional springlike molecular motions of artificial helical systems. To this end, we have synthesized a novel spiroboratebased double-stranded racemo-helicate (rac-DH3<sub>BNaB</sub>- Na<sup>+</sup>) composed of ortho-biphenylene-linked tetraphenol strands (L3) bearing pyrene units at both terminals as a fluorophore and investigated its reversible fluorescent color change during the ion-triggered extension and contraction motions (Fig. 2).

The double-stranded spiroborate helicate bearing the pyrene units at both ends (rac-DH3<sub>BNaB</sub>-Na<sup>+</sup>) was first attempted to prepare in a similar manner for the synthesis of the analogous spiroborate helicates (rac-DH1<sub>BNaB</sub>- Na<sup>+</sup> and rac-DH2<sub>BNaB</sub>- $\cdot$ Na<sup>+</sup>) (Fig. 1a)<sup>4,6-8</sup> by the reaction of the pyrene-bound tetraphenol L3 with NaBH<sub>4</sub> (1 equiv) in 1,2dichloroethane/EtOH (6/1, v/v) at 80 °C for 18 h (Fig. 1c), resulting in the precipitate as the major product in 55% yield, which was composed of the spiroborate helicate as confirmed by the electron-spray ionization (ESI) mass spectrometry (Fig. S14a, ESI<sup>†</sup>). However, the X-ray crystallographic analysis of the single crystals of the helicate grown from its CH<sub>3</sub>CN solution in the presence of n-tetrabutylammonium bromide (TBA+·Br-) (10 equiv) revealed that the resulting doublestranded spiroborate helicate is not a racemo-helicate, but an extended *meso*-helicate (*meso*-**DH3**<sub>BB</sub><sup>2-</sup> (TBA<sup>+</sup>)<sub>2</sub>) with a plane of symmetry (Fig. 1c).<sup>11</sup> The two tetraphenol strands are bridged by two spiroborates in a parallel way with each other with a B-B distance  $(d_{B-B})$  of 12.8 Å, which is similar to those of the extended meso- (11.8 Å) and racemo- (13.0 Å) helicates

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: CCDC 1914679 (*meso*-**DH3**<sub>BB</sub><sup>2-</sup>·(TBA<sup>+</sup>)<sub>2</sub>). Experimental procedures, characterizations of ligand (**L3**) and helicates (*meso*-**DH3**<sub>BB</sub><sup>2-</sup>·(Na<sup>+</sup>)<sub>2</sub> and *rac*-**DH3**<sub>BNaB</sub><sup>-</sup>·Na<sup>+</sup>) and additional spectroscopic data. See DOI: 10.1039/XXXX

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**Fig. 1** (a) Chemical structures of double-stranded spiroborate helicates rac-**DH1**<sub>BNaB</sub>-·Na<sup>+</sup>, rac-**DH2a**<sub>BNaB</sub>-·Na<sup>+</sup> and rac-**DH2b**<sub>BNaB</sub>-·Na<sup>+</sup>. (b) Schematic illustration of the unidirectional springlike motion of the double-stranded spiroborate helicate rac-**DH1**<sub>BB</sub><sup>2-</sup>·(TBA<sup>+</sup>)<sub>2</sub> upon binding (or catch) and release of alkali metal (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup>) ions. TBA: tetrabutylammonium. (c) Synthesis of a double-stranded spiroborate *meso*-**DH3**<sub>BB</sub><sup>2-</sup>·(Na<sup>+</sup>)<sub>2</sub>. Capped-stick representation of the Xray crystal structure of *meso*-**DH3**<sub>BB</sub><sup>2-</sup>·(TBA<sup>+</sup>)<sub>2</sub> (side (left) and top (right) views). All the hydrogen atoms, solvent molecules and countercations are omitted for clarity. A photograph of *meso*-**DH3**<sub>BB</sub><sup>2-</sup>·(Na<sup>+</sup>)<sub>2</sub> in CH<sub>3</sub>CN under irradiation at 365 nm is also shown in (c). (d) Isomerization of *meso*-**DH3**<sub>BB</sub><sup>2-</sup>·(Na<sup>+</sup>)<sub>2</sub>.

#### of DH1<sub>BB</sub><sup>2-.4,5</sup>

The resulting *meso*-**DH3**<sub>**BB**</sub><sup>2-</sup>·(**N**a<sup>+</sup>)<sub>2</sub> was then quantitatively converted to the contracted *racemo*-helicate (*rac*-**DH3**<sub>**BNaB**</sub><sup>-</sup>·**N**a<sup>+</sup>) in 1,2-dichloroethane/CH<sub>3</sub>CN (6/1, v/v) at 60 °C for 48 h (Fig. 1d and Fig. S1, ESI<sup>+</sup>) based on a method for the *meso*-to*racemo* isomerization of the *meso*-**DH1**<sub>**BB**</sub><sup>2-</sup> helicate through water-mediated dynamic B–O bond cleavage/reformation of the spiroborate groups.<sup>5</sup> The formation of the intertwined doublestranded helical structure of *rac*-**DH3**<sub>**BNaB</sub><sup>-</sup>·<b>N**a<sup>+</sup>, in which a Na<sup>+</sup> ion was embraced within the helicate at the middle, was confirmed by ESI mass spectrometry (Fig. S14b, ESI<sup>+</sup>) and further supported by the interstrand ROE cross-peak (a··f) (Fig. S7, ESI<sup>+</sup>) and characteristic proton resonances of its <sup>1</sup>H NMR spectrum due to the contracted spiroborate-based helicate like the contracted *rac*-**DH1**<sub>**BNaB**</sub><sup>-</sup>·**N**a<sup>+</sup> (Fig. 3a(iii)); the aromatic proton signals of the terminal (a–c) and central (f–h) benzene</sub>



Fig. 2 Schematic representation of a reversible switching of the fluorescence emission induced by the extension and contraction motions of rac-DH3<sub>BNaB</sub>-·Na<sup>+</sup> upon the release and catch (or binding) of a Na<sup>+</sup> ion, respectively. The structures were obtained by DFT calculations (Fig. S3, ESI<sup>†</sup>).

rings significantly shifted upfield due to the ring current effects of the benzene rings of the other strand and those of the pyrene units, respectively. The calculated contracted structure of *rac*-**DH3**<sub>BNaB</sub>-·Na<sup>+</sup> by the density functional theory (DFT) supports this speculation (Fig. S3, ESI<sup>†</sup>). Further concrete evidence was obtained by a chiral HPLC analysis of *rac*-**DH3**<sub>BNaB</sub>-·Na<sup>+</sup> (CHIRALPAK IB, DAICEL), demonstrating complete separation into the enantiomers (Fig. S10, ESI<sup>†</sup>).

The ion-triggered extension and contraction motions of rac-**DH3**<sub>BNaB</sub><sup>-</sup> Na<sup>+</sup> were then investigated by <sup>1</sup>H NMR, absorption and fluorescent spectroscopy. Upon the addition of 2.5 equiv of cryptand[2.2.1] to a solution of the contracted rac-DH3<sub>BNaB</sub>-·Na<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (6/1, v/v),<sup>12,13</sup> which completely removed the weakly bound Na<sup>+</sup> ion within the contracted helicate at the middle, the <sup>1</sup>H NMR signals of the aromatic and <sup>t</sup>Bu protons remarkably shifted downfield (Fig. 3a(iv)), resulting from the formation of the extended helicate rac- $DH3_{BB}^{2-}(Na^{+} \subset [2.2.1])_{2}$ . Further addition of 2.5 equiv of  $NaN(SO_2CF_3)_2$  to the extended helicate quantitatively regenerated the original contracted helicate (rac-DH3<sub>BNaB</sub>- $\cdot$ Na<sup>+</sup>) as shown in the <sup>1</sup>H NMR spectral changes (Fig. 3a(v)). Since the extension is coupled with the twisting motion of the helicate in one direction, this (unidirectional) springlike motion could be reversibly repeated by the sequential addition of cryptand[2.2.1] and Na<sup>+</sup> ions as previously demonstrated for  $rac-DH1_{BNaB}^{-}$ ·Na<sup>+</sup> and  $rac-DH2_{BNaB}^{-}$ ·Na<sup>+</sup>.<sup>4,5,7</sup>

Of particular interest is that this ion-triggered springlike extension and contraction motions of rac-DH3<sub>BNaB</sub>-Na<sup>+</sup> are accompanied by a fluorescence color change due to a structural change in the terminal pyrene units between a free monomer and a stacked dimer, which are readily visible with the naked eye and can be quantified by fluorescence spectroscopy. The pyrene units of the contracted rac-DH3<sub>BNaB</sub>- Na<sup>+</sup> tilt away from each other (Fig. 2), thereby exhibiting the characteristic blue emission of the pyrene monomer at 440 nm in CH2Cl2/CH3CN (6/1, v/v) under irradiation at 365 nm (Fig. 3c(i)). The addition of 2.5 equiv of [2.2.1]cryptand resulted in the formation of the extended rac-DH3<sub>BNaB</sub>-Na<sup>+</sup>, in which the terminal pyrene residues in each strand are positioned in close spatial proximity (Fig. 2), thus showing the green excimer emission around 500 nm (Fig. 3c(ii)). Further addition of 2.6 equiv of NaN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> completely restored the fluorescence spectrum accompanied by

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**Fig. 3** (a) Partial <sup>1</sup>H NMR spectra (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>/CD<sub>3</sub>CN = 6/1 (v/v), 0.5 mM, 25 °C) of (i) **L3**, (ii) *meso*-**DH3**<sub>BB</sub><sup>2-</sup>·(Na<sup>+</sup>)<sub>2</sub>, (iii) *rac*-**DH3**<sub>BNaB</sub><sup>-</sup>·Na<sup>+</sup>, (iv) (iii) + [2.2.1] (2.5 equiv) and (v) (iv) + NaN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> (2.5 equiv). CD<sub>3</sub>CN was used as the solvent for *meso*-**DH3**<sub>BB</sub><sup>2-</sup>·(Na<sup>+</sup>)<sub>2</sub> (ii).<sup>12</sup> \* in (iii) denotes the <sup>7</sup>Bu and aromatic protons from *meso*-**DH3**<sub>BB</sub><sup>2-</sup>·(Na<sup>+</sup>)<sub>2</sub> (ca. 1 mol%). The peak assignments were done on the basis of gCOSY and ROESY spectra (Fig. S4 and S5, ESI<sup>†</sup>). Other sharp and broad peaks in (ii–iv) were assigned to the terminal pyrene protons. (b) Absorption and (c) fluorescence spectra (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN = 6/1 (v/v), 10 µM, ca. 25 °C) of (i) *rac*-**DH3**<sub>BNaB</sub><sup>-</sup>Na<sup>+</sup>, (ii) (i) + [2.2.1] (2.5 equiv) and (iii) (ii) + NaN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> (2.6 equiv). Excited wavelength: 365 nm. Photographs of (i) *rac*-**DH3**<sub>BNaB</sub><sup>-</sup>·Na<sup>+</sup> (10 µM), (ii) (i) + [2.2.1] (2.5 equiv) and (iii) (ii) + NaN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> (2.6 equiv). If the material start of the spectra start of the start of the spectra start of the spectra start of the spectra spectra (10 µM), (ii) (ii) + [2.2.1] (2.5 equiv) and (iii) (ii) + NaN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> (2.6 equiv). Excited wavelength: 365 nm are also shown in (c).

the fluorescence color change from green to blue (Fig. 3c(iii)), therefore, these changes could be reversibly repeated by the alternative addition of cryptand[2.2.1] and Na<sup>+</sup> ions. As a consequence, for the first time, we have achieved the fluorescent visualization of the molecular springlike motion triggered by the binding and release of Na<sup>+</sup> ions.

As expected from the crystal structure of meso-DH3<sub>BB</sub><sup>2-</sup> ·(TBA<sup>+</sup>)<sub>2</sub> (Fig. 1c), its <sup>1</sup>H NMR spectral pattern was similar to that of the extended *racemo*-helicate *rac*-DH3<sub>BB</sub><sup>2-</sup> ·(Na<sup>+</sup> $\subset$ [2.2.1])<sub>2</sub> (Fig. 3a(ii,iv)) and cross-peaks between the strands (j··g and j··h)<sup>5</sup> were observed in the 2D ROESY spectrum (Fig. S5, ESI<sup>+</sup>), indicating that the *meso*-DH3<sub>BB</sub><sup>2-</sup> ·(Na<sup>+</sup>)<sub>2</sub> maintained its *meso*-structure in solution as well as in the solid state. Because of the extended rigid *meso*-structure, *meso*-DH3<sub>BB</sub><sup>2-</sup>·(Na<sup>+</sup>)<sub>2</sub> cannot accommodate a Na<sup>+</sup> ion in the center. As a result, the springlike extension and contraction motions observed in *rac*-DH1<sub>BNaB</sub><sup>-</sup>·Na<sup>+</sup> did not proceed upon the Na<sup>+</sup> ion release by [2.2.1]cryptand and further binding of a Na<sup>+</sup> ion as supported by negligible changes in the <sup>1</sup>H NMR spectrum of *meso*-DH3<sub>BB</sub><sup>2-</sup>·(Na<sup>+</sup>)<sub>2</sub> after the addition of 3 equiv

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of [2.2.1]cryptand in CD<sub>3</sub>CN<sup>12</sup> (Fig. S8, ESI<sup>†</sup>)<sub>Vie</sub>The<sub>tid</sub> pytene units of *meso*-**DH3**<sub>BB</sub><sup>2-</sup>·(Na<sup>+</sup>)<sub>2</sub> are in close proximity, therefore, the helicate exhibited an intense interstrand excimer emission (green color) (Fig. 1c) around 500 nm in CD<sub>3</sub>CN, which also remained unchanged upon the addition of 3 equiv of [2.2.1]cryptand (Fig. S9, ESI<sup>†</sup>), indicating its structural feature which prevents the ion-triggered extension and contraction motions.

Recently, we have determined the  $K_a$  values of the extended  $rac-DH1_{BB}^{-}$  (TBA<sup>+</sup>)<sub>2</sub> for a series of alkali metal ions in CH<sub>3</sub>CN, which decreased in the following order:<sup>5</sup> Li<sup>+</sup>  $\ge$  Na<sup>+</sup> > $K^+ > Cs^+ > Rb^+$ . The extended *rac*-DH3<sub>BB</sub><sup>2-</sup>·(Na<sup>+</sup> $\subset$ [2.2.1])<sub>2</sub> was anticipated to have a similar trend in CH<sub>3</sub>CN, but in  $CH_2Cl_2/CH_3CN$  (6/1, v/v), the binding affinities toward alkali metals were significantly enhanced to form the contracted rac-**DH3**<sub>BMB</sub><sup>-.</sup>  $M^+$  ( $M^+ = Li^+$ ,  $Na^+$ ,  $K^+$  or  $Cs^+$ ).<sup>13,14</sup> If this is the case, the extended pyrene-bound helicate could be applied to the visual fluorogenic sensing of alkali metals,9a,16 since the contracted rac-DH3<sub>BMB</sub>- M<sup>+</sup> embracing the larger cations tended to adopt more elongated structures by an induced-fit mechanism.<sup>5</sup> The addition of 2.0 equiv of Li<sup>+</sup>, Na<sup>+</sup> or K<sup>+</sup> ions to a solution of the extended rac-DH3<sub>BB</sub><sup>2-</sup>·(Na<sup>+</sup> $\subset$ [2.2.1])<sub>2</sub> induced a drastic change in its fluorescence color from the green excimer emission to the blue monomer emission due to the contracted *rac*-**DH3**<sub>**BMB**<sup>-</sup>·**M**<sup>+</sup> (M<sup>+</sup> = Li<sup>+</sup>, Na<sup>+</sup> or K<sup>+</sup>) formation,</sub> whereas the excimer emission was predominant in the presence of 2.0 equiv of Cs<sup>+</sup> ions (Fig. 4). This is because the contracted helicate embracing the larger Cs<sup>+</sup> cation resulted in a more elongated structure being suitable for the excimer emission in part, indicating that the extended pyrene-bound helicate can be used as a fluorescent chemosensor for alkali metals based on the unique ion-triggered springlike motion.

In summary, we have successfully visualized a reversible springlike motion of a double-stranded helicate by introducing pyrene units at the terminal phenyl residues. The extension and contraction motions of the helicate are triggered by the release and binding of alkali metal ions, which eventually displays fluorescence color changes from green to blue emissions due to a pyrene excimer formation and its monomer, respectively. The fluorescent helicate can be resolved into optically-pure onehanded helicates (Fig. S10, ESI<sup>†</sup>), which will be further applied



**Fig. 4** Fluorescence spectra (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN = 6/1 (v/v), 10  $\mu$ M, ca. 25 °C) of *rac*-**DH3**<sub>BB</sub><sup>2-</sup>·(Na<sup>+</sup>⊂[2.2.1])<sub>2</sub> (10  $\mu$ M) in the presence of 2.0 equiv of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup> ions, respectively. Excited wavelength: 365 nm. Photographs of *rac*-**DH3**<sub>BB</sub><sup>2-</sup>·(Na<sup>+</sup>⊂[2.2.1])<sub>2</sub> (10  $\mu$ M) in the presence of 2.0 equiv of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup> ions, respectively, in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN under irradiation at 365 nm are also shown.

to the development of unique chirality-responsive molecular springs toward chiral guests, such as chiral organic ammoniums and  $\pi$ -electron-deficient aromatic molecules; the latter may be sandwiched between the pyrene units in a diastereoselective fashion, resulting in fluorescent color changes.<sup>17</sup> Research along this line is now in progress in our laboratory.

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### **Conflicts of interest**

There are no conflicts to declare.

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- 11 A similar meso-helicate (meso-DH1<sub>BB</sub><sup>2-</sup>·(Na<sup>+</sup>)<sub>2</sub>) has recently been found to form as a precipitate during the reaction of the corresponding tetraphenol strand with NaBH<sub>4</sub>.<sup>5</sup>
- 12 Acetonitrile was used as the solvent for the <sup>1</sup>H NMR, absorption and fluorescent measurements of *meso*-DH1<sub>BB</sub><sup>2-</sup>  $(Na^+)_2$  because the *meso*-to-*racemo* isomerization readily took place with the increasing amount of CH<sub>2</sub>Cl<sub>2</sub> in acetonitrile (Fig. S1a, ESI<sup>†</sup>).
- 13 The binding constant ( $K_a$ ) of the extended  $rac-DH3_{BB}^{2-}$  $(Na^+ \subset [2.2.1])_2$  to a Na<sup>+</sup> ion estimated in CD<sub>3</sub>CN by <sup>1</sup>H NMR titration  $(3.4 \times 10^3 \text{ M}^{-1})$  (Fig. S11, ESI†) was three orders of magnitude lower than that of the extended  $rac-DH1_{BB}^{2-}$  (2.68  $\times 10^{6}$  M<sup>-1</sup>),<sup>4</sup> probably because of the bulky pyrene units at both ends, while the  $K_a$  value increased to  $3.3 \times 10^6$  M<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (6/1, v/v) (Fig. S12, ESI<sup>†</sup>) which was estimated by fluorescence titrations. In addition, rac- $DH1_{BNaB}$  Na<sup>+</sup> almost retained its contracted form in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (6/1, v/v) at the concentration range between 10-3 and 10-6 M during dilution absorption and fluorescence experiments (Fig. S13a,b, ESI $\dagger$ ), indicating the  $K_a$  value was as high as ca.  $10^{6}$  M<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (6/1, v/v). Therefore, a CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (6/1, v/v) mixture was employed as the solvent throughout the course of the ion-triggered extension and contraction experiments.
- 14 The  $K_a$  value of the extended  $rac-DH3_{BB}^{2-}$  (Na<sup>+</sup> $\subset$ [2.2.1])<sub>2</sub> to a Cs<sup>+</sup> ion in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (6/1, v/v) roughly estimated by dilution experiments was ca. 10<sup>6</sup> M<sup>-1</sup> (Fig. S13c,d, ESI<sup>+</sup>), which is of the same order of magnitude as that to a Na<sup>+</sup> ion, probably due to the solvent effect of nonpolar CH<sub>2</sub>Cl<sub>2</sub>.<sup>15</sup>
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## Graphical abstract

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A unique springlike motion of a fluorescent pyrene-terminated double-stranded helicate is visualized by the catch and release of alkali metal ions.