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# Narcissistic self-sorting and enhanced luminescence via catenation in water

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# ABSTRACT

Narcissistic self-sorting, namely that components are able to distinguish 'self' from 'non-self' during selfassembly, was accomplished via catenation by condensing multiple hydrazides and an aldehyde, or a hydrazide and multiple aldehydes in water. The underneath mechanism of this behavior relies on the corresponding homo [2]catenanes which are thermodynamically more favored than their hetero counterparts because the former containing two identical macrocyclic components are able to maximize the inter-component non-covalent forces. One of these catenanes contains four 4-phenylpyridinium units, which are often considered barely luminescent because of intramolecular rotations and vibrations that lead to non-radiative annihilation of their excited states. These intramolecular motions, however, are restricted upon integrating 4-phenylpyridiniums within the catenane architecture. As a consequence, compared to its non-interlocked counterparts, this catenane exhibits enhanced fluorescence, which represents a novel conceptual model for developing luminescent materials.

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# 1. Introduction

Nature uses self-assembly to obtain many functional molecular architectures, such as DNA double strands and the protein shells of viruses, by gathering many subcomponents together, without the need of performing compound purification or reacting group protection/deprotection. Even though these subcomponents often contain many competitive ligating sites or interacting units such as base pairs, they are still able to undergo selective ligation in a noninterference manner to produce the target products. Chemists have attempted to mimic these biological behaviors of precise syntheses in artificial systems. Orthogonal reactivity [1] was taken advantage of for this purpose, namely that two or more non-interacting reactions are used in ligation for synthesizing complex molecules. Each of these reactions does not interfere with each other. Selfsorting [2], which could be expressed in the manner of either dynamic reactions are used, allowing the systems to perform error checking and search for their thermodynamic minima [5,8]. The target molecules are sophisticatedly designed to represent the most thermodynamically favored products. When a 'wrong' subcomponent takes the place of a 'right' one in self-assembly, the selfassembled products become less thermodynamically favored, probably because of disturbance of some inter-component noncovalent forces. As a consequence, the 'wrong' subcomponents are repelled, enabling the self-assembled systems to distinguish 'self' from 'non-self', even though both ligands might have the same or competitive ligating groups. While most of the artificial self-sorting systems reported in the literature rely on metal-ligand coordination systems [6], using dynamic bonds or non-covalent forces [7] is less extensively studied. In addition, given that Nature chooses water as the life medium, approaches to accomplish self-sorting in aqueous media must be developed, which helps to fully unravel the underneath mechanisms of the biological events. Recently, a water-compatible dynamic covalent approach based

narcissistic [3] or social [4], is also accomplished. These events are conceptually more reminiscent of the biological systems. Here,

Recently, a water-compatible dynamic covalent approach based on acylhydrazone condensation [8] was developed by us [9] and other groups [10]. A variety of molecules with complex molecular







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architectures, including rings [9c,10e], catenanes [9a,9e], cages [9b], and knots [10a,10b,10c,10f] were successfully obtained. Here, we used this dynamic approach to self-assemble a series of catenanes in relatively high yields, each of which is composed of two identical macrocycles. Within each framework of these homo [2]catenanes, the intramolecular non-covalent forces between their building blocks are maximized, including hydrophobic effect,  $\pi$ - $\pi$  interactions, hydrogen bonding, as well as  $CH-\pi$  interactions, as inferred from the crystallographic analysis. Such driving forces allow some of these [2]catenanes to be self-assembled in close to quantitative yields. Narcissistic self-sorting behaviors were clearly observed during self-assembly. That is, combining two different formyl precursors and one acylhydrazide, or one formyl precursor and two acylhydrazides in water only yielded the homo [2]catenanes composed of two identical macrocyclic components selectively, without forming their hybridized catenanes containing two different rings.

One of these homo [2]catenanes contains four luminescent 4phenylpyridinium groups. In the literature [11a], it is reported that the luminescence of 4-phenylpyridinium is relatively weak because the central C–C single bond allows the occurrence of intramolecular rotations and vibrations that lead to non-radiative annihilation of its excited states. Within the framework of this [2] catenane, these intramolecular motions are efficiently restricted. As a consequence, the luminophore in the catenane exhibits enhanced luminescence compared with that of the non-interlocked counterparts, by nearly six times. We thus envision that the catenation here provides us with a novel approach for developing luminescent materials.

#### 2. Results and discussion

Two bisdialdehydes  $1a^{2+} \cdot 2Cl^-$ ,  $1b^{2+} \cdot 2Br^-$  were prepared via  $S_N^2$  reactions. Both of these two aldehydes are water-soluble on account of their cationic nature. In  $1a^{2+} \cdot 2Cl^-$ , each of the formyl units and the corresponding pyridinium units is bridged by a phenyl functional group (Fig. 1). In  $1b^{2+} \cdot 2Br^-$ , the two formyl units are grafted directly onto the electron-withdrawing pyridinium units (Fig. 1). These formyl units in  $1b^{2+}$  are more electrophilic than those in  $1a^{2+}$ , and therefore, the former is fully hydrolyzed in water. A set of bishydrazide linkers, namely 2a, 2b, and 2c, were prepared (Schemes S1-3), each of which bears a glycol chain containing two, three, and four  $-OCH_2CH_2-$  units, respectively (Fig. 1).

The attempts to form [2]catenanes were performed by combining each of these bisaldehydes, namely either **1a**<sup>2+</sup> 2Cl<sup>-</sup> or  $1b^{2+} \cdot 2Br^{-}$ , and each of these three bishydrazides in D<sub>2</sub>O in the presence of the catalytic amount of DCl (Fig. 1, Schemes S4-5). <sup>1</sup>H NMR spectroscopy (see the SI) indicated that after heating the corresponding 1:1 mixtures at 60 °C for no less than 8 h, five [2] catenanes, including  $(\mathbf{1a}^{2+}\cdot\mathbf{2a})_2$ ,  $(\mathbf{1a}^{2+}\cdot\mathbf{2b})_2$ ,  $(\mathbf{1a}^{2+}\cdot\mathbf{2c})_2$ ,  $(\mathbf{1b}^{2+}\cdot\mathbf{2b})_2$ , and  $(\mathbf{1b}^{2+}\cdot\mathbf{2c})_2$  whose counterions are either Cl<sup>-</sup> or Br<sup>-</sup>, were successfully self-assembled. However, the condensation of  $1b^{2+} \cdot 2Br^{-}$  and **2a** produced a mixture of the macrocycle ( $1b^{2+} \cdot 2a$ ) and the [2]catenane  $(\mathbf{1b}^{2+}\cdot\mathbf{2a})_2$ , as inferred from <sup>1</sup>H NMR spectra, mass spectra, and the HPLC analytic results (Figures S23-26). The self-assembly yields in the corresponding NMR samples of  $(1a^{2+}\cdot 2a)_2$ ,  $(1a^{2+}\cdot 2b)_2$ ,  $(1b^{2+}\cdot 2b)_2$ , and  $(1b^{2+}\cdot 2c)_2$ ,  $(1b^{2+}\cdot 2b)_2$ , and  $(1b^{2+}\cdot 2c)_2$ ,  $(1b^{2+}\cdot 2b)_2$ , (1bwhose counterions are either Cl<sup>-</sup> or Br<sup>-</sup>, were measured to be 78%, 73%, 94%, 61%, and 94% (Figures S73-77). It seems that 2c represents the best bishydrazide linker favoring catenation among these three bishydrazides, i.e. the yields of both  $(1a^{2+} \cdot 2c)_2$  and  $(1b^{2+} \cdot 2c)_2$  are significantly higher than those containing either 2a or 2b. This is probably because 2c is long enough to avoid ring strain when it forms macrocycles with each of the two bisaldehyde subcomponents. In fact, this is indeed the case in the solid-state



**Fig. 1.** Structural formulas of two dicationic bisaldehydes  $1a^{2+}$ ,  $1b^{2+}$ , and three bishydrazides **2a**, **2b**, and **2c**. Upon combining one bisaldehyde and one bishydrazide in water, a set of [2]catenanes including  $(1a^{2+}\cdot 2a)_2$ ,  $(1a^{2+}\cdot 2b)_2$ ,  $(1a^{2+}\cdot 2c)_2$ ,  $(1b^{2+}\cdot 2b)_2$ , and  $(1b^{2+}\cdot 2c)_2$  are self-assembled. Charges are balanced by Cl<sup>-</sup> or Br<sup>-</sup> counteranions, which are omitted here for the sake of clarity.

structures from crystallography, which will be discussed later. This hypothesis was also justified by competition experiments. Combining a 1:1:1 mixture of  $1a^{2+}$  2Cl<sup>-</sup>, 2b, and 2c in water selectively produced  $(1a^{2+} 2c)_2$  as the predominant product, as indicated by the <sup>1</sup>H NMR spectrum (Figure S52), leaving **2b** unreacted in the solution. Only a trace amount of  $(1a^{2+}.2b)_2$  was observed in the mass spectrum (Figure S58). Such self-assembly preference did not occur when a 1:1:1 mixture of  $1a^{2+} 2Cl^{-}$ , 2a, and **2b** was combined in water, which produced both  $(1a^{2+} \cdot 2a)_2$ and  $(1a^{2+}\cdot 2b)_2$ , as well as their hybridized catenane  $(1a^{2+}\cdot 2a)$  $(1a^{2+}\cdot 2b)$  (Figures S62B and S64). We also compared the self-assembly preference between  $1a^{2+}$  and  $1b^{2+}$ . Combining  $1a^{2+} \cdot 2Cl^{-}, 1b^{2+} \cdot 2Br^{-}$ , and bishydrazide 2c in a 1:1:1 ratio in water produced  $(1a^{2+} \cdot 2c)_2$  as the major product, leaving most of  $1b^{2+}$  as an unreacted reactant (Figures S45B and S47). Changing 2c to 2b provided similar results (Figures S48B and S50). This observation is not surprising because compared with  $1b^{2+}$ ,  $1a^{2+}$  has two more phenyl units that enhance the hydrophobic effect and thus favor

catenation. The [2]catenanes were isolated from the corresponding self-assembly solutions by performing counterion exchange, yielding the corresponding solid-state samples, including  $(1a^{2+} \cdot 2a)_2 \cdot 4PF_{6}^-$ ,  $(1a^{2+} \cdot 2b)_2 \cdot 4PF_{6}^-$ ,  $(1a^{2+} \cdot 2c)_2 \cdot 4PF_{6}^-$ , all of which were soluble in MeCN and fully characterized by both <sup>1</sup>H NMR spectroscopy and mass spectrometry (see the SI).

Within the framework of each [2]catenane, the two macrocyclic components undergo circumvolution motion with respect to each other. The rates of this motion vary in different solvents, as inferred from the corresponding <sup>1</sup>H NMR spectra. For example, in the <sup>1</sup>H NMR spectrum of  $(1a^{2+} \cdot 2c)_2 \cdot 4Cl^-$  recorded in D<sub>2</sub>O, the corresponding resonances split into two sets of peaks (Fig. 2A), an observation indicating that within the catenane framework, the circumvolution occurs in a relatively slow rate on the <sup>1</sup>H NMR timescale. As a consequence, each of the ring components becomes chemically asymmetrical, i.e. the building block in each macrocyclic component that is encircled within another ring is chemically inequivalent relative to the one outside. In contrast, the <sup>1</sup>H NMR spectrum of  $(1a^{2+} \cdot 2c)_2 \cdot 4PF_6^-$  (Fig. 2B) recorded in CD<sub>3</sub>CN at room temperature exhibits only one set of resonances, indicating the circumvolution motion becomes faster on the <sup>1</sup>H NMR timescale. By performing variable-temperature <sup>1</sup>H NMR spectroscopic experiments, the energy barrier ( $\Delta G$ ) of the circumvolution motion of  $(1a^{2+} \cdot 2c)_2 \cdot 4PF_6^-$  in CD<sub>3</sub>CN was calculated to be 58.5 kJ· mol<sup>-1</sup> (Figure S83). Calculating the corresponding ( $\Delta G$ ) of ( $1a^{2+} \cdot 2c$ )<sub>2</sub> · 4Cl<sup>-</sup> in D<sub>2</sub>O by using variable-temperature NMR experiments was unsuccessful because of the relatively high frozen point of water.

Single crystals of [2]catenanes  $(\mathbf{1a}^{2+}\cdot\mathbf{2c})_2\cdot4\text{Cl}^-$ ,  $(\mathbf{1b}^{2+}\cdot\mathbf{2b})_2\cdot4\text{Cl}^-$ , and  $(\mathbf{1b}^{2+}\cdot\mathbf{2c})_2\cdot4\text{Cl}^-$  (Fig. 3, S88-90) were prepared by slow vapor diffusion of tetrahydrofuran (THF) into their corresponding aqueous solutions, which provided unambiguous evidence to convince their mechanically interlocked architectures.

In each of these [2]catenanes, the cavity of each of the two mutually mechanically interlocked rings is almost fully occupied by another ring, leading to a variety of inter-component close contacts. For example, the framework of  $(\mathbf{1a}^{2+}\cdot\mathbf{2c})_2$  exhibits a tightly packed sandwich-shaped architecture. Each of the pyridinium building blocks in one ring undergoes  $\pi$ - $\pi$  interactions with an adjacent phenyl unit in another ring, as inferred from their short interplane distances, i.e. around 3.4 Å (Fig. 3). Close contacts also indicate the occurrence of CH···O hydrogen bonding and CH- $\pi$  interactions (Fig. 3). In the framework of  $(\mathbf{1b}^{2+}\cdot\mathbf{2b})_2$ , ring strain is observed in each of the two macrocycles, i.e. some of its aromatic building blocks become bent to some extent. Such ring strain does not occur in either  $(\mathbf{1a}^{2+}\cdot\mathbf{2c})_2$  or  $(\mathbf{1b}^{2+}\cdot\mathbf{2c})_2$ , an observation consistent with the aforementioned results that the formation of the catenanes containing **2c** residues is more favored and higher-yielding than the [2]catenane counterparts containing either 2a or 2b.

The ability of these homo [2]catenanes to maximize the intercomponent covalent interactions encourages us to envision that self-sorting might occur via catenation. When the two bisaldehydes  $1a^{2+} \cdot 2Cl^{-}, 1b^{2+} \cdot 2Br^{-}$ , and bishydrazide **2c** were combined in D<sub>2</sub>O in a 1:1:2 ratio, heating the mixture solution produced two homo [2] catenane products, namely  $(\mathbf{1a}^{2+}\cdot\mathbf{2c})_2$  and  $(\mathbf{1b}^{2+}\cdot\mathbf{2c})_2$ , almost exclusively. The hybridized [2]catenane containing two different macrocycles, namely  $(1a^{2+} \cdot 2c)$   $(1b^{2+} \cdot 2c)$ , was not observed in either <sup>1</sup>H NMR (Figure S45C) or mass spectra (Fig. 4 and S46). This observation is not surprising because in such a putative heteroleptic [2]catenane  $(1a^{2+} \cdot 2c)$   $(1b^{2+} \cdot 2c)$ , a larger ring namely  $(1a^{2+} \cdot 2c)$  is mechanically interlocked by a smaller one namely  $(1b^{2+} 2c)$ . Because the larger ring could not be fully occupied by the smaller one, some of the aforementioned intramolecular noncovalent forces were suppressed or weakened, and therefore, the catenane becomes less thermodynamically favored compared with its homo counterparts. Similar narcissistic self-sorting behaviors



**Fig. 2.** Partial <sup>1</sup>H NMR spectra (500 MHz, 298 K) of A) ( $\mathbf{1a}^{2+} \cdot \mathbf{2c}_{)_2} \cdot 4CI^-$  and B) ( $\mathbf{1a}^{2+} \cdot \mathbf{2c}_{)_2} \cdot 4PF_{\overline{6}}$ , which were recorded in D<sub>2</sub>O and CD<sub>3</sub>CN, respectively. The assignment of each resonance was made by the corresponding two-dimensional NMR spectra shown in the SI. Counterions are omitted in the figure for the sake of clarity.



**Fig. 3.** Solid-state structures of  $(\mathbf{1b}^{2+}\cdot\mathbf{2b})_2$  (top),  $((\mathbf{1b}^{2+}\cdot\mathbf{2c})_2$  (middle), and  $(\mathbf{1a}^{2+}\cdot\mathbf{2c})_2$  (bottom), obtained from single-crystal X-ray diffraction analysis. Oxygen atoms, red; nitrogen, blue; carbon, gray; hydrogen, white. Counteranions and solvent molecules are omitted for clarity. Some of the close contacts were labeled with dash lines, indicating the occurrence of intramolecular interactions.

also occurred by combining **1a**<sup>2+</sup>·2Cl<sup>-</sup>, **1b**<sup>2+</sup>·2Br<sup>-</sup>, and **2b** in a 1:1:2 ratio in water (Figures S48C and S49).

When we combined the bisaldehyde  $\mathbf{1a}^{2+} \cdot 2CI^{-}$  with two bishydrazides, namely  $\mathbf{2b}$  and  $\mathbf{2c}$ , in a 2:1:1 ratio in D<sub>2</sub>O, three different [2]catenanes, namely  $(\mathbf{1a}^{2+} \cdot \mathbf{2b})_2$ ,  $(\mathbf{1a}^{2+} \cdot \mathbf{2c})_2$  and their hybridized form  $(\mathbf{1a}^{2+} \cdot \mathbf{2b})$   $(\mathbf{1a}^{2+} \cdot \mathbf{2c})$  were observed in mass spectra (Figure S53). This observation can be explained by the fact that the difference in structures of the flexible bishydrazides  $\mathbf{2b}$  and  $\mathbf{2c}$  subcomponents has a very subtle impact on the intramolecular forces within the catenanes. Or expressed in another way, the geometries and sizes of the macrocyclic components, namely  $(\mathbf{1a}^{2+} \cdot \mathbf{2b})$  and  $(\mathbf{1a}^{2+} \cdot \mathbf{2c})$ , whose rigid parts are almost identical, are structurally similar. The intramolecular non-covalent forces within the framework of the hetero [2]catenane  $(\mathbf{1a}^{2+} \cdot \mathbf{2b})$   $(\mathbf{1a}^{2+} \cdot \mathbf{2c})$  are barely disturbed compared with the homo counterparts. The formation of heteroleptic [2]catenanes was also observed by combining the bisaldehyde  $\mathbf{1a}^{2+} \cdot \mathbf{2c}$ 

and **2c**, as well as by combining the bisaldehyde **1b**<sup>2+</sup>·2Br<sup>-</sup> with **2b** and **2c** (Figures S59-67).

The observation that **2b** and **2c** with analogous structures failed to undergo narcissistic self-sorting encouraged us to introduce a bishydrazide, namely **2d** (Fig. 5), whose structure is sharply different from those of **2a-2c**. The **2d** (Fig. 5) contains a p-xylene bridge between the two acylhydrazide units. Our previous result demonstrated that condensing **2d** and **1a**<sup>2+</sup> produced a [2]catenane (**1a**<sup>2+</sup>·**2d**)<sub>2</sub> in close to quantitative yield [9e]. Heating a 1:1:2 mixture of **2c**, **2d**, and **1a**<sup>2+</sup>·**2c**l<sup>-</sup> in D<sub>2</sub>O produced two homo [2]catenane products, namely (**1a**<sup>2+</sup>·**2c**)<sub>2</sub> and (**1a**<sup>2+</sup>·**2d**)<sub>2</sub> (Fig. 5 and S68-69). The hybridized [2]catenane containing two different macrocycles, namely (**1a**<sup>2+</sup>·**2c**) (**1a**<sup>2+</sup>·**2d**), was not observed in either <sup>1</sup>H NMR (Figure S68) or mass spectra (Fig. 5 and S69). Again, narcissistic self-sorting here was driven by the intramolecular non-covalent forces that were maximized only in the homo [2]catenane owing to its mismatched architectures of the two different rings.

4-Phenylpyridinium that has a  $\pi$ -conjugated molecular skeleton is reported luminescent [11]. However, the central C–C single bond allows the occurrence of intramolecular rotations and vibrations, which often leads to luminescence quenching via non-radiative annihilation of the excited states of this luminophore. The implication is that the luminescence of 4-phenylpyridinium could be enhanced by prohibiting or restricting these intramolecular motions. Indeed, such a goal was accomplished by using macrocycle to encircle 4-phenylpyridinium [11a]. For example, when two 4phenylpyridinium were concurrently encapsulated by cucurbit [8] uril, the phosphorescence emission was significantly enhanced [12c]. In our homo [2] catananes, such as  $(\mathbf{1a}^{2+}\cdot\mathbf{2c})_2$ , two of the four 4phenylpyridinium units are encapsulated by another ring. We thus envision that catenation might also lead to luminescence enhancement. To justify such proposition, we recorded and compared the fluorescences of  $1a^{2+} \cdot 2PF_6^-$ , the [2] catenane  $(1a^{2+} \cdot 2c)_2 \cdot 4PF_6^-$ , as well



**Fig. 4.** Partial high-resolution electrospray mass spectrometry (ESI-MS) spectrum of a 1:1:2 mixture of  $1a^{2+}.2CI^-$ ,  $1b^{2+}.2BI^-$ , and **2c** in water. The signals labeled in the spectrum correspond to molecular cations of the homo [2]catenanes, namely  $(1b^{2+}.2c)_2$  and  $(1a^{2+}.2c)_2$  that contain four charges. Counterions are omitted in the figure for the sake of clarity.



**Fig. 5.** Partial high-resolution ESI-MS spectrum of a 2:1:1 mixture of  $1a^{2+} \cdot 2Cl^-$ , **2c**, and **2d** in water. The signals labeled in the spectrum correspond to molecular cations of the homo [2]catenanes, namely  $(1a^{2+} \cdot 2c)_2$  and  $(1a^{2+} \cdot 2d)_2$  that contain four charges. Counterions are omitted in the figure for the sake of clarity.

as a linear reference compound  $(1a^{2+} \cdot 2e) \cdot 2PF_6^-$ .  $(1a^{2+} \cdot 2e) \cdot 2PF_6^-$  is a non-interlocked counterpart of the [2]catenane  $(1a^{2+} \cdot 2c)_2 \cdot 4PF_6^$ because the attempts to synthesize a pure macrocycle  $(1a^{2+}.2c)$ were unsuccessful. In the fluorescence spectrum of  $1a^{2+} \cdot 2PF_6^-$ (Fig. 6B, black trace), broadband with maximal emission at 387 nm was observed. As a comparison, in the case of both  $(1a^{2+} \cdot 2c)_2 \cdot 4PF_6^-$ (Fig. 6B, blue trace) and  $(1a^{2+} \cdot 2e) \cdot 2PF_6^-$  (Fig. 6B, red trace), the maximal emission underwent significant redshifts by nearly 110 nm. More remarkably, compared to  $1a^{2+} \cdot 2PF_6^-$  and  $(1a^{2+} \cdot 2e) \cdot 2PF_6^-$ , the emission at the maximal wavelength of  $(1a^{2+} \cdot 2c)_2 \cdot 4PF_6^-$  was significantly enhanced. Accordingly, the absolute photoluminescence quantum yields (PLQY) of  $(1a^{2+} \cdot 2c)_2 \cdot 4PF_6, 1a^{2+} \cdot 2PF_6, 1a^{2+}$ and  $(\mathbf{1a}^{2+} \cdot \mathbf{2e}) \cdot 2PF_6^-$  were determined to be 0.82%, 0.15%, and 0.14% in CH<sub>3</sub>CN, respectively, thus showing a relatively higher emission efficiency of the catenane system relative to its non-interlocked counterparts. Such observation confirms our hypothesis that the [2] catenane framework is able to restrict the intramolecular motions of 4-phenylpyridinium. This mechanically interlocked architecture is thus believed to represent a novel conceptual model in attaining highly emissive nano-constructs.

The mechanism of the luminescence enhancement via catenation is essentially not different from the host-guest recognition systems [12], as well as the aggregation-induced emission [13] systems. However, our approach represents one step of advance. First, different from aggregation-induced emission materials that often function in the solid state, the luminescence enhanced via catenation occurs in a homogeneous solution, where the catenane molecules are homogeneously dispersed. Second, the supramolecular complexes are essentially a library of the mixture, i.e. the ratio of complexes, and the dissociated components might differ by modulating the conditions, such as concentrations, temperature, as well as solvent. As a comparison, the luminescent molecules obtained via catenation are essentially pure substances. This feature, at least to some extent, would help to develop luminescent materials with better quantitative controllability and stability.

#### 3. Conclusion

In summary, a series of homo [2]catenanes were self-assembled in water via hydrazone condensation. Some of their yields are remarkably high, on account of a variety of intramolecular noncovalent interactions, including hydrophobic effect,  $\pi$ - $\pi$  interactions, CH- $\pi$  interactions, as well as hydrogen bonding. When two competitive bisaldehydes, namely  $1a^{2+}$  and  $1b^{2+}$ , were combined with a bishydrazide, or two competitive bishydrazides, namely 2c and 2d, with sharply different structures were combined with a bisaldehyde, narcissistic self-sorting occurred, vielding the corresponding homo [2]catenanes selectively. Such narcissistic self-sorting results from the inherent tendency of a macrocycle to template another version of 'itself' to maximize the intercomponent non-covalent forces that might be disturbed in the putative hetero [2] catenanes. In contrast, combining  $1a^{2+}$  with two structurally analogous hydrazides, namely 2b and 2c in aqueous media, yielded both homo- and hetero- [2]catenanes. Such selfsorting accomplished in artificial systems in aqueous solution improves our fundamental understanding on how nature takes advantage of non-covalent interactions to achieve precise syntheses of molecular entities with complex three-dimensional structures when the subcomponents contain the same or competitive ligating sites. That is, the target molecules are able to maximize the inter-component non-covalent driving forces.

Within the catenane framework, the intramolecular motions of the 4-phenylpyridinium units, such as rotation around the central



Fig. 6. (A) UV–Vis absorption spectra and (B) fluorescence spectra ( $\lambda_{ex} = 317 \text{ nm}$ ) of  $(\mathbf{1a}^{2+} \cdot 2\mathbf{c})_2 \cdot 4PF_6^-$  (1 × 10<sup>-5</sup> M, blue),  $\mathbf{1a}^{2+} \cdot 2PF_6^-$  (2 × 10<sup>-5</sup> M, black), and  $(\mathbf{1a}^{2+} \cdot 2\mathbf{e}) \cdot 2PF_6^-$  (2 × 10<sup>-5</sup> M, red) in CH<sub>3</sub>CN. In all the three samples, the concentrations of 4-phenylpyridinium were kept constant, namely 4 × 10<sup>-5</sup> M.

C-C bond, are efficiently restricted. Such behavior helps to suppress non-radiative annihilation of the luminophore and helps to enhance the fluorescence of the [2]catenanes. Different from the luminescence enhancement based on a supramolecular manner, which allows host-guest association/dissociation, the fluorescent molecules obtained via catenantion are pure substances. We envision that the usage of such a strategy could be expanded to a broader field of developing luminescent materials, which requires better repeatability and quantitative controllability.

### Credit author statement

Conceptualization: Hao Li, Qiong Chen. Data curation: Qiong Chen, Ye Lei. Formal analysis: Qiong Chen, Hao Li. Funding acquisition: Hao Li, Yu Liu, Investigation: Olong Chen, Ye Lei, Hongve Wang, Wenwen Xu, Methodology: Oiong Chen, Guangcheng Wu, Tianvu Jiao, Yuanijang Pan, Project administration: Qiong Chen. Resources: Hao Li, Yu Liu, Ying-Ming Zhang, Qisheng Zhang. Software: Qiong Chen, Guangcheng Wu, Tianyu Jiao. Supervision: Qiong Chen, Hao Li. Validation: Qiong Chen, Ye Lei. Visualization: Qiong Chen, Hao Li. Roles/Writing – original draft: Oiong Chen. Writing – review & editing: Hao Li

## **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mtchem.2021.100679.

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