Narcissistic Self-Sorting and Enhanced Luminescence via Catenation in Water

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Article

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Abstract

Narcissistic self-sorting, namely that components are able to distinguish “self” from “nonself” during self-assembly, 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 are thermodynamically more favored than their hetero counterparts, because the former containing two identical macrocyclic components are able to maximize the inter-component noncovalent forces. One of these catenanes contains four 4-phenylpyridinium units, which are often considered barely luminescent due to intramolecular rotations and vibrations that lead to nonradiative 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.

Introduction

Nature employs 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 reactivity¹ 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. Self-sorting², which could be expressed in the manner of either narcissistic³ or social⁴, is also accomplished. These events are conceptually more reminiscent of the biological systems. Here, 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 self-assembled products become less thermodynamically favored, probably due to disturbance of some inter-component noncovalent forces. As a consequence, the “wrong” subcomponents are repelled, enabling the self-assembled systems to distinguish “self” from “nonself”, 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 noncovalent forces⁷ are 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 on acylhydrazone condensation⁸ was developed by us⁹ and other groups.¹⁰ A variety of molecules with complex molecular architectures,

including rings,^{9c,10e} catenanes,^{9a,9e} cages^{9b} and knots^{10a,10b,10c,10f} are successfully obtained. Here, we employed 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 noncovalent forces between their building blocks are maximized, including hydrophobic effect, π - π interactions, hydrogen bonding, as well as CH- π interactions, as inferred from 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 precursor 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 4-phenylpyridinium 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 nonradiative 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 to that of the noninterlocked counterparts, by nearly six times. We thus envision that the catenation here provides us a novel approach for developing luminescent materials.

Results And Discussion

Two bisdialdehydes **1a**²⁺·2Cl⁻, **1b**²⁺·2Br⁻ were prepared via S_N2 reactions. Both of these two aldehydes are water soluble on account of their cationic nature. In **1a**²⁺·2Cl⁻, each of the formyl units and the corresponding pyridinium unit are bridged by a phenyl functional group (Figure 1). In **1b**²⁺·2Br⁻, the two formyl units are grafted directly onto the electron-withdrawing pyridinium units (Figure 1). These formyl units in **1b**²⁺ are more electrophilic than those in **1a**²⁺ and therefore, the former are 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 -OCH₂CH₂- units, respectively (Figure 1).

The attempts to form [2]catenanes were performed by combining each of these bisaldehydes, namely either **1a**²⁺·2Cl⁻ or **1b**²⁺·2Br⁻, and each of these three bishydrazides in D₂O in the presence of catalytic amount of DCl (Figure 1, Schemes S4-5). ¹H 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 (**1a**²⁺·**2a**)₂, (**1a**²⁺·**2b**)₂, (**1a**²⁺·**2c**)₂, (**1b**²⁺·**2b**)₂ and (**1b**²⁺·**2c**)₂ whose counterions are either Cl⁻ or Br⁻, were successfully self-assembled. However, the condensation of **1b**²⁺·2Br⁻ and **2a** produced a mixture of the macrocycle (**1b**²⁺·**2a**) and the [2]catenane (**1b**²⁺·**2a**)₂, as inferred from ¹H NMR spectra, mass spectra and the HPLC analytic results (Figures S23-26). The self-assembly yields in the corresponding NMR samples of (**1a**²⁺·**2a**)₂, (**1a**²⁺·**2b**)₂, (**1a**²⁺·**2c**)₂, (**1b**²⁺·**2b**)₂ and (**1b**²⁺·**2c**)₂, whose counterions are either Cl⁻ or Br⁻, 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 $(\mathbf{1a}^{2+}\cdot\mathbf{2c})_2$ and $(\mathbf{1b}^{2+}\cdot\mathbf{2c})_2$ 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 structures from crystallography, which will be discussed later. This hypothesis was also justified by competition experiments. Combining a 1:1:1 mixture of $\mathbf{1a}^{2+}\cdot 2\text{Cl}^-$, **2b** and **2c** in water selectively produced $(\mathbf{1a}^{2+}\cdot\mathbf{2c})_2$ as the predominant product, as indicated by the ^1H NMR spectrum (Figure S52), leaving **2b** unreacted in the solution. Only trace amount of $(\mathbf{1a}^{2+}\cdot\mathbf{2b})_2$ was observed in the mass spectrum (Figure S58). Such self-assembly preference did not occur when a 1:1:1 mixture of $\mathbf{1a}^{2+}\cdot 2\text{Cl}^-$, **2a** and **2b** was combined in water, which produced both $(\mathbf{1a}^{2+}\cdot\mathbf{2a})_2$ and $(\mathbf{1a}^{2+}\cdot\mathbf{2b})_2$, as well as their hybridized catenane $(\mathbf{1a}^{2+}\cdot\mathbf{2a})(\mathbf{1a}^{2+}\cdot\mathbf{2b})$ (Figures S62B and S64). We also compared the self-assembly preference between $\mathbf{1a}^{2+}$ and $\mathbf{1b}^{2+}$. Combining $\mathbf{1a}^{2+}\cdot 2\text{Cl}^-$, $\mathbf{1b}^{2+}\cdot 2\text{Br}^-$ and bishydrazide **2c** in a 1:1:1 ratio in water produced $(\mathbf{1a}^{2+}\cdot\mathbf{2c})_2$ as the major product, leaving most of $\mathbf{1b}^{2+}$ as a unreacted reactant (Figures S45B and S47). Changing **2c** to **2b** provided similar results (Figures S48B and S50). This observation is not surprising, because compared to $\mathbf{1b}^{2+}$, $\mathbf{1a}^{2+}$ has two more phenyl units that enhance 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 $(\mathbf{1a}^{2+}\cdot\mathbf{2a})_2\cdot 4\text{PF}_6^-$, $(\mathbf{1a}^{2+}\cdot\mathbf{2b})_2\cdot 4\text{PF}_6^-$, $(\mathbf{1a}^{2+}\cdot\mathbf{2c})_2\cdot 4\text{PF}_6^-$, $(\mathbf{1b}^{2+}\cdot\mathbf{2b})_2\cdot 4\text{PF}_6^-$ and $(\mathbf{1b}^{2+}\cdot\mathbf{2c})_2\cdot 4\text{PF}_6^-$, all of which were soluble in MeCN and full characterized by both ^1H 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 ^1H NMR spectra. For example, in the ^1H NMR spectrum of $(\mathbf{1a}^{2+}\cdot\mathbf{2c})_2\cdot 4\text{Cl}^-$ recorded in D_2O , the corresponding resonances split into two sets of peaks (Figure 2A), an observation indicating that within the catenane framework, the circumvolution occurs in a relatively slow rate on the ^1H 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 ^1H NMR spectrum of $(\mathbf{1a}^{2+}\cdot\mathbf{2c})_2\cdot 4\text{PF}_6^-$ (Figure 2B) recorded in CD_3CN at room temperature exhibits only one set of resonances, indicating the circumvolution motion becomes faster on the ^1H NMR timescale. By performing variable-temperature (VT) ^1H NMR spectroscopic experiments, the energy barrier (ΔG) of the circumvolution motion of $(\mathbf{1a}^{2+}\cdot\mathbf{2c})_2\cdot 4\text{PF}_6^-$ in CD_3CN was calculated to be $58.5\text{ kJ}\cdot\text{mol}^{-1}$ (Figure S83). Calculating the corresponding (ΔG) of $(\mathbf{1a}^{2+}\cdot\mathbf{2c})_2\cdot 4\text{Cl}^-$ in D_2O by using VT NMR experiments was unsuccessful, because of the relatively high frozen point of water.

Single crystals of [2]catenanes $(\mathbf{1a}^{2+}\cdot\mathbf{2c})_2\cdot 4\text{Cl}^-$, $(\mathbf{1b}^{2+}\cdot\mathbf{2b})_2\cdot 4\text{Cl}^-$ and $(\mathbf{1b}^{2+}\cdot\mathbf{2c})_2\cdot 4\text{Cl}^-$ (Figures 3, S88-90), were prepared by slow vapor diffusion of 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 π - π interactions with an adjacent phenyl unit in another ring, as inferred from their short interplane distances, i.e., around 3.4 Å (Figure 3). Close contacts also indicate the occurrence of CH...O hydrogen bonding and CH- π interactions (Figure 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 $\mathbf{1a}^{2+}\cdot\mathbf{2Cl}^-$, $\mathbf{1b}^{2+}\cdot\mathbf{2Br}^-$ and bishydrazide **2c** were combined in D₂O 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 $(\mathbf{1a}^{2+}\cdot\mathbf{2c})(\mathbf{1b}^{2+}\cdot\mathbf{2c})$, was not observed in either ¹H NMR (Figure S45C) or mass spectra (Figures 4 and S46). This observation is not surprising, because in such a putative heteroleptic [2]catenane $(\mathbf{1a}^{2+}\cdot\mathbf{2c})(\mathbf{1b}^{2+}\cdot\mathbf{2c})$, a larger ring namely $(\mathbf{1a}^{2+}\cdot\mathbf{2c})$ is mechanically interlocked by a smaller one namely $(\mathbf{1b}^{2+}\cdot\mathbf{2c})$. Because the larger ring could not be fully occupied by the smaller one, some of aforementioned intramolecular noncovalent forces were suppressed or weakened, and therefore the catenane becomes less thermodynamically favored compared to its homo counterparts. Similar narcissistic self-sorting behaviors also occurred by combining $\mathbf{1a}^{2+}\cdot\mathbf{2Cl}^-$, $\mathbf{1b}^{2+}\cdot\mathbf{2Br}^-$ and **2b** in a 1:1:2 ratio in water (Figures S48C and S49).

When we combined the bisaldehyde $\mathbf{1a}^{2+}\cdot\mathbf{2Cl}^-$ with two bishydrazides, namely **2b** and **2c**, in a 2:1:1 ratio in D₂O, 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 **2b** and **2c** subcomponents has 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 noncovalent 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 to the homo counterparts. The formation of heteroleptic [2]catenanes was also observed by combining the bisaldehyde $\mathbf{1a}^{2+}\cdot\mathbf{2Cl}^-$ with either **2a** and **2b** or **2a** and **2c**, as well as by combining the bisaldehyde $\mathbf{1b}^{2+}\cdot\mathbf{2Br}^-$ 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** (Figure 5), whose structure is sharply different from

those of **2a-2c**. The **2d** (Figure 5) contains a p-xylene bridge between the two acylhydrazide units. Our previous result demonstrated that condensing **2d** and **1a**²⁺ produced a [2]catenane (**1a**²⁺·**2d**)₂ in close to quantitative yield^{9e}. Heating a 1:1:2 mixture of **2c**, **2d** and **1a**²⁺·2Cl⁻ in D₂O produced two homo [2]catenane products, namely (**1a**²⁺·**2c**)₂ and (**1a**²⁺·**2d**)₂ (Figures 5 and S68-69). The hybridized [2]catenane containing two different macrocycles, namely (**1a**²⁺·**2c**)(**1a**²⁺·**2d**), was not observed in either ¹H NMR (Figure S68) or mass spectra (Figures 5 and S69). Again, narcissistic self-sorting here was driven by the intramolecular noncovalent forces that were maximized only in the homo [2]catenanes. Such forces might be disturbed in the putative hetero [2]catenane owing to its mismatched architectures of the two different rings.

4-Phenylpyridinium that has a π-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 nonradiative 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 goal was accomplished by using macrocycle to encircle 4-phenylpyridinium.^{11a} For example, when two 4-phenylpyridinium were concurrently encapsulated by cucurbit[8]uril, the phosphorescence emission was significantly enhanced.^{12c} In our homo [2]catenanes such as (**1a**²⁺·**2c**)₂, two of the four 4-phenylpyridinium units are encapsulated by another ring. We thus envision that catenation might also lead to luminescence enhancement. In order to justify such proposition, we recorded and compared the fluorescences of **1a**²⁺·2PF₆⁻, the [2]catenane (**1a**²⁺·**2c**)₂·4PF₆⁻, as well as a linear reference compound (**1a**²⁺·**2e**)·2PF₆⁻. (**1a**²⁺·**2e**)·2PF₆⁻ is a non-interlocked counterpart of the [2]catenane (**1a**²⁺·**2c**)₂·4PF₆⁻, because the attempts to synthesize a pure macrocycle (**1a**²⁺·**2c**) were unsuccessful. In fluorescence spectrum of **1a**²⁺·2PF₆⁻ (Figure 6, black trace), a broad band with maximal emission at 387 nm was observed. As a comparison, in the case of both (**1a**²⁺·**2c**)₂·4PF₆⁻ (Figure 6, blue trace) and (**1a**²⁺·**2e**)·2PF₆⁻ (Figure 6, red trace), the maximal emission underwent significant red shifts by nearly 110 nm. More remarkably, compared to **1a**²⁺·2PF₆⁻ and (**1a**²⁺·**2e**)·2PF₆⁻, the emission at the maximal wavelength of (**1a**²⁺·**2c**)₂·4PF₆⁻ was significantly enhanced. Accordingly, the absolute photoluminescence quantum yields (PLQY) of (**1a**²⁺·**2c**)₂·4PF₆⁻, **1a**²⁺·2PF₆⁻ and (**1a**²⁺·**2e**)·2PF₆⁻ were determined to be 0.82%, 0.15% and 0.14% in CH₃CN, respectively, thus showing a relatively higher emission efficiency of the catenane system relative to its noninterlocked 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 emission¹³ (AIE) systems. However, our approach represents one step of advance. First, different from AIE materials that often function in 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 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.

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, π - π interactions, CH- π 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, yielding the corresponding homo [2]catenanes selectively. Such narcissistic self-sorting results from the inherent tendency of a macrocycle to template another version of “itself”, in order to maximize the inter-component noncovalent 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 self-sorting accomplished in artificial systems in aqueous solution improves our fundamental understanding on how nature takes advantage of noncovalent interactions to achieve precise syntheses of molecular entities with complex three-dimensional structures when the subcomponents contain same or competitive ligating sites. That is, the target molecules are able to maximize the inter-component noncovalent driving forces.

Within the catenane framework, the intramolecular motions of the 4-phenylpyridinium units, such as rotation around the central C-C bond, are efficiently restricted. Such behaviour helps to suppress nonradiative annihilation of the luminophore, helping to enhance the fluorescence of the [2]catenanes. Different from the luminescence enhancement based on supramolecular manner which allows host-guest association/dissociation, the fluorescent molecules obtained via catenation are pure substances. We envision that the usage of such strategy could be expanded to a broader field of developing luminescent materials, which requires better repeatability and quantitative controllability.

Declarations

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Figures

Figure 1

Structural formulas of two dicationic bisaldehydes 1a2+, 1b2+ and three bishydrazides 2a, 2b and 2c. Upon combining one bisaldehyde and one bishydrazide in water, a set of [2]catenanes including (1a2+·2a)2, (1a2+·2b)2, (1a2+·2c)2, (1b2+·2a)2, (1b2+·2b)2 and (1b2+·2c)2 are self-assembled. Charges are balanced by Cl[−] or Br[−] counteranions, which are omitted here for the sake of clarity.

Figure 2

Partial ^1H NMR spectra (500 MHz, 298 K) of A) (1a2+·2c)2·4Cl[−] and B) (1a2+·2c)2·4PF6[−], which were recorded in D_2O and CD_3CN 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.

Figure 3

Solid-state structures of (1b2+·2b)₂ (top), (1b2+·2c)₂ (middle), and (1a2+·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.

Figure 4

Partial high resolution ESI-MS spectrum of a 1:1:2 mixture of 1a²⁺·2Cl⁻, 1b²⁺·2Br⁻ and 2c in water. The signals labeled in the spectrum correspond to molecular cations of the homo [2]catenanes namely (1b²⁺·2c)₂ and (1a²⁺·2c)₂ that contain four charges. Counterions are omitted in the figure for the sake of clarity.

Figure 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.

Figure 6

Fluorescence spectra of (1a²⁺·2c)₂·4PF₆⁻ (1 × 10⁻⁵ M, blue), 1a²⁺·2PF₆⁻ (2 × 10⁻⁵ M, black), and (1a²⁺·2e)·2PF₆⁻ (2 × 10⁻⁵ M, red) in CH₃CN, excited at 317 nm. In all the three compounds, the concentration of 4-Phenylpyridinium was kept constant, namely 4 × 10⁻⁵ M.

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