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(54) Title: DENSELY CHARGED CATENANES

(57) Abstract: Cationic radial catenane comprising a central cationic ring and two or more radial cationic rings mechanically interlocked central cationic ring and methods for making the same are disclosed herein.



WO 2019/195754 A1

DENSELY CHARGED CATENANES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims benefit of priority to U.S. Provisional Application No. 62/691,923,
5 filed June 29, 2018, and U.S. Provisional Application No. 62/653,301, filed April 5, 2018, the
contents of each are hereby incorporated by reference in their entireties.

BACKGROUND

The advent of supramolecular chemistry has paved the way for the template-directed
syntheses of mechanically interlocked molecules (MIMs) whose unique structural features raise
10 the prospect of their potential use in areas as diverse as molecular electronics and artificial
molecular machines. Notwithstanding the many synthetic protocols for producing MIMs,
mechanically interlocked structures containing multiple components, which intrinsically repel
each other, remain undocumented for the most part.

BRIEF SUMMARY OF THE INVENTION

15 Disclosed herein are densely-charged radial catenanes and methods of making the same.
The catenane comprising a central cationic ring and two or more radial cationic rings mechanically
interlocked with the central cationic ring. The central cationic ring comprises two or more viologen
subunits and two reactive linkers, and the catenane comprises an equal number of radial cationic
rings as viologen subunits. Suitably, the central cationic ring may comprise two, three, or four
20 viologen subunits.

Suitably the catenanes are cationic catenanes or radical/cationic catenanes. Moreover, the
catenanes disclosed herein demonstrate reversible molecular switching and changing the redox
state of the catenanes results in reversible switching of the molecular topologies. In some
embodiments, the catenanes may reversibly switch between a 12+ cationic oxidation state and a
25 6(•+) radical/cationic oxidation state, a 18+ cationic oxidation state and a 9(•+) radical/cationic
oxidation state, and a 24+ cationic oxidation state and a 12(•+) radical/cationic oxidation state.

Compositions, including crystalline compositions, and devices comprising the catenanes
are also described herein.

Another aspect of the method comprises methods for making the catenanes described
30 herein. The method comprises providing a pseudorotaxane. The pseudorotaxane comprises a

threading component having a first terminal moiety, a second terminal moiety, and two or more radical/cation viologen subunits between the first terminal moiety and the second terminal moiety. Suitably, the threading component comprises two, three, or four viologen subunits. The pseudorotaxane also comprises two or more diradical/dicationic rings threaded by the threading
5 component. The number of diradical/dicationic rings threaded by the threading component is equal to the number viologen subunits of the threading component. The method further comprises contacting the first terminal moiety with the second terminal moiety to form a central cationic ring that mechanically interlocks the two or more diradical/dicationic rings, thereby forming the catenane. The method may optionally comprise preparing the pseudorotaxane from one or more
10 pseudorotaxanes and/or oxidizing the catenane.

These and other features, objects and advantages of the present invention will become better understood from the description that follows. In the description, reference is made to the accompanying drawings, which form a part hereof and in which there is shown by way of illustration, not limitation, embodiments of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Non-limiting embodiments of the present invention will be described by way of example with reference to the accompanying figures, which are schematic and are not intended to be drawn to scale. In the figures, each identical or nearly identical component illustrated is typically represented by a single numeral. For purposes of clarity, not every component is labeled in every
20 figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention.

FIGURES 1A-1D. ^1H NMR Spectra (600 MHz, CD_3CN) of $[\mathbf{3}]\text{C}^{12+}$ and its tetracationic non-interlocked macrocycles. (FIG 1A) $[\mathbf{3}]\text{C}\cdot 12\text{PF}_6$ recorded at 343 K showing much better resolved signals of the two CBPQT^{4+} rings compared to those recorded at RT (FIG 1D), an
25 indication of their fast pirouetting at this elevated temperature. (FIG 1B) $\text{CBPQT}\cdot 4\text{PF}_6$ recorded at 343 K. (FIG 1C) $\text{TB}\cdot 4\text{PF}_6$ recorded at 343 K. (FIG 1D) $[\mathbf{3}]\text{C}\cdot 12\text{PF}_6$ recorded at 298 K showing that the two chemically equivalent cyclobis(paraquat-*p*-phenylene) (CBPQT^{4+}) rings are pirouetting slowly on the ^1H NMR timescale. The resonance for H_p indicated with an asterisk (*) is very broad and could hardly be observed when plotted on the same intensity scale as the other
30 signals. The peak assignments correspond to the protons labeled in FIG 5A.

FIGURES 2A-2F. Solid-state structures of $[3]C^{12+}$ deduced from single-crystal X-ray crystallography. Two CBPQT $^{4+}$ rings are mechanically interlocked with a central TB $^{4+}$ ring. (Figs. 2A-2C) Ball-and-stick representations – (FIG 2A) viewed from above the plane containing the TB $^{4+}$ ring, (FIG 2B) viewed from above the plane containing the two CBPQT $^{4+}$ rings, and (FIG 2C) viewed along the axis connecting the centroids of three rings. Space-filling representations – (FIG 2D) viewed from above the plane containing the TB $^{4+}$ ring, (FIG 2E) viewed from above the plane containing the two CBPQT $^{4+}$ rings, and (FIG 2F) viewed along the axis connecting the centroids of three rings, showing the compactness and rigidity along the centroids of the three interlocked rings. Hydrogen atoms, PF $_6^-$ counter ions, and solvent molecules have been omitted for sake of clarity.

FIGURES 2G-2J. Space-filling representations of the structure of $[3]C \cdot 12PF_6$ from several views with hydrogen atoms, PF $_6^-$ counter ions, and solvent molecules omitted for the sake of clarity. FIG 2G shows a first space-filling representation. FIG 2H shows a space-filling representation from a second view of the representation of FIG 2G. FIG 2I shows a space-filling representation from a third view of the representation of FIG 2G. FIG 2J shows a space-filling representation from a fourth view of the representation of FIG 2G.

FIGURES 3A-3B. Reversible switching between $[3]C^{12+}$ and $[3]C^{6(++)}$. (FIG 3A) Cyclic voltammogram of $[3]C \cdot 12PF_6$ recorded in a MeCN solution containing 0.1 M TBAPF $_6$ as supporting electrolyte. Scan rate, 100 mV s $^{-1}$. (FIG 4B) UV-vis-NIR Spectra of $[3]C^{12+}$ (transparent sample) and $[3]C^{6(++)}$ (colored sample), along with the photographs of the two solutions.

FIGURES 3C-3D. UV-Vis-NIR spectra during reversible switching between the fully oxidized $[3]C^{12+}$ and the reduced-state $[3]C^{6(++)}$ catenanes using chemical stimuli. UV-Vis-NIR spectra of the two [3]catenane $[3]C^{12+}$ and $[3]C^{6(++)}$ states. (FIG 3C) Absorption intensities of $[3]C^{12+}$ (lower points) and $[3]C^{6(++)}$ (upper points) at 1162 nm wavelength showing the reversible switching between the two states during each cycle. (FIG 3D) Absorption intensity of $[3]C^{12+}$ (upper points) and $[3]C^{6(++)}$ (lower points) at 272 nm recorded during each cycle.

FIGURES 4AI-4AII. Mass spectrum of the hexaradical / hexacationic [3]catenane $[3]C^{6(++)}$. (FIG 4AI) ESI-TOF Mass spectrum of $[3]C^{6(++)}$ (PF $_6$ salt) recorded under N $_2$. FIG 4AII shows the expanded spectrum of the 3+ peak, both calculated (top) and observed (bottom).

FIGURES 4B-4D. Ball-and-stick representations of the solid-state structures of **[3]C6^(•+)**(FIG 4B) viewed from above the plane containing the TB⁴⁺ ring, (FIG 4C) viewed from above the plane containing the two CBPQT⁴⁺ rings, and (FIG 4D) viewed along the axis connecting the centroids of three rings.

FIGURE 4E shows a comparison of the solid-state superstructures of **[3]C6^(•+)** (left) and **[3]C12⁺** (right) depicted with combinations of ball-and-stick and space-filling representations.

FIGURE 4F. Space-filling representations of the supramolecular arrangements of **[3]C6^(•+)** revealing the molecular packing into 2D layers as a result of both radical-radical interactions between BIPY^(•+) units and the π - π interactions of the phenylene units in the CBPQT^{2(•+)} rings. Hydrogen atoms, PF₆⁻ counter ions, and solvent molecules have been omitted for sake of clarity.

FIGURES 4G-4J. Space filling representations of the structure of the solid state structure of **[3]C•6PF₆**. FIG 4G shows a first space-filling representation. FIG 4H shows a space-filling representation from a second view of the representation of FIG 4G. FIG 4I shows a space-filling representation from a third view of the representation of FIG 4G. FIG 4J shows a space-filling representation from a fourth view of the representation of FIG 4G.

FIGURES 5A-5B. Chemical formulae of **[3]C12⁺** (FIG 5A) and **r[5]C24⁺** (FIG 5B) showing proton assignments.

FIGURES 6AI-6AII. Structural characterization of **r[5]C24⁺**. (FIG 6AI) ¹H NMR Spectrum (500 MHz, CD₃CN) of **r[5]C•24PF₆** recorded at 298 K. The spectrum has been abridged in the region of the residual solvent and water resonances, while all signals for **r[5]C24⁺** are displayed with peak assignments corresponding to the protons labelled in Figure 5B. FIG 6AII shows the HR-ESI-TOF mass spectrum of **r[5]C24⁺** (PF₆ salt) with signals corresponding to the loss from three to five PF₆⁻ counter ions. Calculated peaks m/z = 2092.9542 [$M - 3PF_6$]³⁺; 1533.2693 [$M - 4PF_6$]⁴⁺; 1197.6225 [$M - 5PF_6$]⁵⁺.

FIGURES 6B-6D. Solid-state structures of **r[5]C24⁺** deduced from single-crystal X-ray crystallography. (FIG 6B) View from above the plane containing the BTB⁸⁺ ring. The CBPQT⁴⁺ rings are represented in the space-filling fashion. (FIG 6C) A first side-on view. (FIG 6D) A second side-on view. Hydrogen atoms in FIGS 6C and 6D, PF₆⁻ counter ions, and solvent molecules have been omitted for the sake of clarity.

FIGURES 6E-6F. Representations of the structure of **r[5]C•24PF₆**. Solid-state structures of **r[5]C24⁺** including a view from above the plane containing the BTB⁸⁺ central ring (FIG 6E) and

side-on view (FIG 6F). Hydrogen atoms, PF_6^- counter ions, and solvent molecules omitted for the sake of clarity.

FIGURES 7A-7B. Redox switching behavior of $\mathbf{r}[5]\mathbf{C}^{24+}$. (FIG 7A) UV-vis-NIR Spectrum along with the photograph of the solutions of the dodecacationic/dodecaradical radial [5]catenane $\mathbf{r}[5]\mathbf{C}^{12(\bullet+)}$ and the tetracosacationic $\mathbf{r}[5]\mathbf{C}^{24+}$ obtained by reducing $\mathbf{r}[5]\mathbf{C}^{24+}$ with Zn dust in MeCN. (FIG 7B) Cyclic voltammogram of $\mathbf{r}[5]\mathbf{C}\cdot 24\text{PF}_6$ recorded in a DMF solution containing 0.1 M TBAPF_6 as supporting electrolyte. Scan rate, 100 mV s^{-1} .

FIGURES 7C-7D. Cyclic voltammograms of $\mathbf{r}[5]\mathbf{C}\cdot 24\text{PF}_6$ in the -0.6 to $+0.9 \text{ V}$ potential window. (FIG 7C) CV scans starting with a positive sweep. As there is little to no current found at potential ca. $+478 \text{ mV}$ in the first scan, the detected current at this potential region in the second and third scans is, therefore, attributed to the oxidation of the generated reduced species, i.e., $\mathbf{r}[5]\mathbf{C}^{12(\bullet+)}$. (FIG 7D) CV scans starting with a negative sweep showing no change in peak currents for the first three scans.

FIGURES 8A-8B. Analytical RP-HPLC trace of $\text{TB}\cdot 4\text{PF}_6$ (FIG 8A) and $[3]\mathbf{C}\cdot 12\text{PF}_6$ (FIG 8B). The photodiode array was set to detect absorbance at 300 nm .

DETAILED DESCRIPTION

Disclosed herein are densely-charged radial catenanes and methods of making the same. The densely-charged radial catenanes may be a [3]catenane, [4]catenane, or a [5]catenane. The present invention demonstrates a rational strategy, using radical-radical interaction and tandem Click chemistry, to synthesize mechanically interlocked molecules, i.e., radial catenanes, consisting all electrostatically repulsive components. Moreover the catenanes disclosed herein demonstrate reversible molecular switching and changing the redox state of the catenanes results in reversible switching of the molecular topologies.

The presented materials are suited for use in applications that require either (i) densely charged or high-energy-density organic redox materials or (ii) effective switching between different states of a molecule and therefore the material properties, which has been utilized in many electronic devices such as switches, transistors, memory devices and electrochromic devices. Suitably, compositions comprising the catenanes described herein may have a charge density of $5.0+ \text{ charge / nm}^3$ or greater, including $6.0+ \text{ charge / nm}^3$ or greater or $7.0+ \text{ charge / nm}^3$ or greater. The archetypical molecular structure and switching in our invention could hold great promise for

the fabrication of next generation organic electronic devices and/or nonaqueous redox-flow batteries.

As demonstrated in the Examples that follow, the radial catenanes may have a high cationic charge density such as a 12+ or a 24+ charge. One exemplary embodiment includes a dodecacationic [3]catenane, comprising three mechanically interlocked positively charged rings despite their mutual Coulombic repulsion. The constitution and topology of this [3]catenane were confirmed by NMR spectroscopy, mass spectrometry, and X-ray crystallography on a single crystal. The solid-state structure shows that two mechanical bonds result in the nano-confinement of 12 positive charges within a volume of less than 1.65 nm³, corresponding to 7.3+charges / nm³. Another exemplary embodiment includes a radial [5]catenane, comprising four mechanically interlocked rings around a fifth ring and can bears up to 24 positive charges in its co-constitution. The solid-state structure of this organic tetracosacation, determined by X-ray crystallography, reveals a molecular length of 3.7 nm and a charge density of 6.0+charge / nm³. The template-directed strategy for constructing MIMs, consisting of multiply charged interlocked rings, represents a departure in the chemistry of these compounds that is tantamount to producing a blueprint to explore a novel class of organic molecules which boast large numbers and high densities of like charges.

Definitions

As used herein, an asterisk “*” or a plus sign “+” may be used to designate the point of attachment for any radical group or substituent group.

The term “alkyl” as contemplated herein includes a straight-chain or branched alkyl radical in all of its isomeric forms. The number of atoms in the alkyl group can be specified using C_n-C_m nomenclature where n is an integer specifying the lowest number of carbon atoms, m is an integer specifying the greatest number of carbon atoms, and the group may comprise any number of carbon atoms inclusive of n and m. In some embodiments, the alkyl is a C₁-C₁₂ alkyl, a C₁-C₆ alkyl, or a C₁-C₃ alkyl.

The term “alkylene” refers to a diradical of an alkyl group. An exemplary alkylene group is —(CH₂)_n— where n is an integer greater than or equal to 1. In some embodiments, n is equal to any of 1-12, 1-6, or 1-3.

The term “alkenyl” as used herein refers to an unsaturated straight or branched hydrocarbon having at least one carbon-carbon double bond. The number of atoms in the alkenyl group can be

specified using C_n-C_m nomenclature where n is an integer specifying the lowest number of carbon atoms, m is an integer specifying the greatest number of carbon atoms, and the group may comprise any number of carbon atoms inclusive of n and m. In some embodiments, the alkenyl is a C₁-C₁₂ alkenyl, a C₁-C₆ alkenyl, or a C₁-C₃ alkenyl.

5 The term “alkynyl” as used herein refers to an unsaturated straight or branched hydrocarbon having at least one carbon-carbon triple bond. The number of atoms in the alkynyl group can be specified using C_n-C_m nomenclature where n is an integer specifying the lowest number of carbon atoms, m is an integer specifying the greatest number of carbon atoms, and the group may comprise any number of carbon atoms inclusive of n and m. In some embodiments, the
10 alkynyl is a C₁-C₁₂ alkynyl, a C₁-C₆ alkynyl, or a C₁-C₃ alkynyl.

 The term “aryl” as used herein refers to a carbocyclic aromatic group. Representative aryl groups include phenyl and the like. Unless specified otherwise, the aromatic ring may be substituted, for example, an alkyl. In certain other embodiments, the aromatic ring is not substituted, i.e., it is unsubstituted. The number of atoms in the aryl group can be specified using
15 C_n-C_m nomenclature where n is an integer specifying the lowest number of carbon atoms, m is an integer specifying the greatest number of carbon atoms, and the group may comprise any number of carbon atoms inclusive of n and m. In some embodiments, the aryl is a C₅-C₁₀ alkenyl or a C₆-C₁₀ aryl.

 The term “azide moiety” as used herein refers to a radical comprising —N₃.

20 As described herein, “catenane” means a mechanically-interlocked molecular architecture consisting of two or more interlocked macrocyclic components. Once the catenane is formed, the interlocked macrocyclic components cannot be separated without breaking a covalent bond of at least one macrocyclic component. Catenanes may be prefixed with an integer to indicate the number of mechanically-interlocked macrocyclic components, e.g., [2]catenane or [2]C indicates
25 a catenane comprises two interlocked macrocyclic components, [3]catenane or [3]C indicates a catenane comprises three interlocked macrocyclic components, [4]catenane or [4]C indicates a catenane comprises four interlocked macrocyclic components, and [5]catenane or [5]C indicates a catenane comprises five interlocked macrocyclic components. A radial catenane comprises a central ring and three or more radial rings each mechanically interlocked with the central ring.

30 The terms “heterocyclyl” and “heterocyclic group” are art-recognized and refer to saturated, partially unsaturated, or aromatic 3- to 10-membered ring structures, alternatively 3-to

7-membered rings, whose ring structures include one to four heteroatoms, such as nitrogen, oxygen, and sulfur. The number of ring atoms in the heterocyclyl group can be specified using C_n-C_m nomenclature where n is an integer specifying the lowest number of atoms in the ring, m is an integer specifying the greatest number of atoms in the ring, and the group may comprise any number of atoms inclusive of n and m . Exemplary heterocyclic groups include triazole groups and alkyl triazole groups.

As described herein, "macrocyclic component" means a molecule that has at least one ring (cycle) large enough to allow it to be threaded onto a linear sub-chain of another molecule. Macrocyclic components include cyclobis(paraquat-*p*-phenylene) (CBPQT). Depending on context, the macrocyclic component may be used interchangeably with "ring".

"Pseudorotaxane" means a molecular assembly comprising at least one molecule with a linear section threaded through at least one macrocyclic component of another or the same molecule in which the threading component has an end small enough to permit threading or dethreading of the macrocyclic component. Pseudorotaxanes may be prefixed with an integer to indicate the number of threading components and macrocyclic components, e.g., [2]pseudorotaxane indicates a pseudorotaxane comprising a molecular with at least one linear section onto which one macrocyclic component is threaded and [3]pseudorotaxane indicates a pseudorotaxane comprising a molecular with at least one linear section onto which two macrocyclic components is threaded.

"Reactive linker" means a linker formed from a reaction between moieties that allows for a continuous bridge of atom between viologen subunits. Reactive linkers may be used to extend threading components or close macrocyclic components. Suitably the reaction resulting in the formation of a reactive linker is a click chemistry, e.g., alkyne-azide reaction resulting in a triazole reactive linker, or other suitable reaction.

"Threading component" means a molecule with at least one linear section onto which at least one macrocyclic component is threaded.

"Viologen subunit" (V) means a subunit that is derivative of 4,4'-bipyridine ($C_{10}H_8N_2$). Viologens include 4,4'-bipyridinium (BIPY) subunits. Viologen subunits may be in a dicationic oxidation state (i.e., V^{2+}) or a radical/cationic oxidation state (i.e., V^{+}).

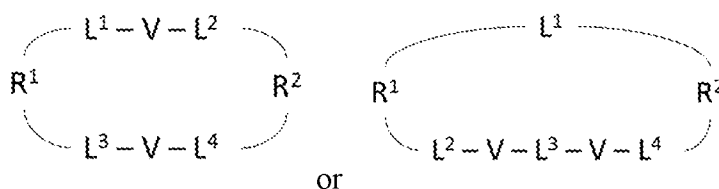
Densely charged radial catenanes

One aspect of the invention is directed to densely charged catenanes. The catenanes have a positive charge distributed between mechanically interlocked rings. Catenanes comprise a central cationic ring and two or more radial cationic rings mechanically interlocked with the central cationic ring. Each of the rings is a macrocyclic component that is threaded by a sub-chain of another ring. The central cationic rings comprises two or more viologen subunits (V) and two reactive linkers. Suitably, the central cationic ring may comprise two, three, or four V. V may comprise 4,4'-bipyridinium (BIPY) subunits.

V may reversibly switch between a dicationic oxidation state (V^{2+}) or a radical/cationic oxidation state ($V^{•+}$). In certain embodiments each V is in a dicationic state. In other embodiments, each V is in a radical/cationic oxidation state. In yet other embodiments, the V of the central cationic ring may be in any combination of the dicationic state and the radical/cationic oxidation state. For example when the central cationic ring comprises two V, one V may be in the dicationic state and the other V may be in the radical/cationic state. Similarly when the cationic rings comprises three V, one V may be in the dicationic state and the other two V may be in the radical/cationic state or one V may be in the radical/cationic state and the other V may be in the dicationic state.

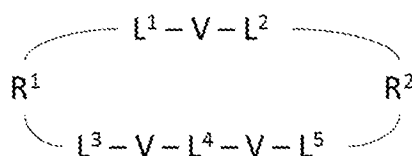
The catenane comprises an equal number of radial cationic rings as V of the central cationic ring. For example, when the central cationic ring comprises two, three, or four V, the catenane comprises two, three, and four radial cationic rings, respectively. Suitably, the radial cationic rings may reversibly switch between oxidation states. In some embodiments, each of the radial cationic rings are in the same oxidation state. In other embodiments, the radial cationic rings are in different oxidation states. Suitably the radial cationic rings comprises cyclobis(paraquat-p-phenylene) (CBPQT) which may reversibly switch between the tetracationic oxidation state ($CBPQT^{4+}$) and the diradical/dicationic state ($CBPQT^{2(•+)}$). In certain embodiments each CBPQT is in a tetracationic state. In other embodiments, each CBPQT is in a diradical/dicationic oxidation state. In yet other embodiments, the CBPQT of the central cationic ring may be in any combination of the tetracationic state and the diradical/dicationic oxidation states.

In some embodiments, the central cationic ring comprises two V. Suitably, the central cationic ring may comprise



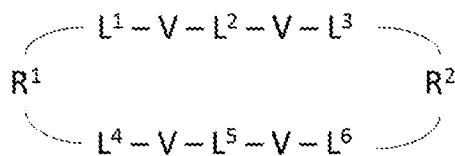
In some embodiments, each V may be in a dicationic oxidation state, resulting in a positive charge of 4+ on the central cationic ring. When each V is in a dicationic oxidation state, the two radial rings may be in a tetracationic oxidation state. In such cases, the catenane is a dodecacationic catenane (**[3]C¹²⁺**). In other embodiments, each V may be in a radical/cationic oxidation state, resulting in a positive charge of 2+. When each V is in a radical/cationic oxidation state, each radial rings may be in a diradical/dicationic oxidation state. In such cases, the radial catenane is a dodecacationic radial catenane (**[3]C⁶⁽⁺⁺⁾**).

In some embodiments, the central cationic ring comprises three V. Suitably, the central cationic ring may comprise



In some embodiments, each V may be in a dicationic oxidation state, resulting in a positive charge of 6+ on the central cationic ring. When each V is in a dicationic oxidation state, the two radial rings may be in a tetracationic oxidation state. In such cases, the radial catenane is a octodecacationic radial catenane (**(r[4]C¹⁸⁺)**). In other embodiments, each V may be in a radical/cationic oxidation state, resulting in a positive charge of 2+. When each V is in a radical/cationic oxidation state, each radial rings may be in a diradical/dicationic oxidation state. In such cases, the radial catenane is a nonacationic radial catenane (**(r[4]C⁹⁽⁺⁺⁾)**).

In some embodiments, the central cationic ring comprises four V. Suitably, the central cationic ring may comprise



In some embodiments, each V may be in a dicationic oxidation state, resulting in a positive charge of 8+ on the central cationic ring. When each V is in a dicationic oxidation state, the two radial rings may be in a tetracationic oxidation state. In such cases, the radial catenane is a tetracosacationic radial catenane ($r[5]C^{24+}$). In other embodiments, each V may be in a radical/cationic oxidation state, resulting in a positive charge of 2+. When each V is in a radical/cationic oxidation state, each radial rings may be in a diradical/dicationic oxidation state. In such cases, the radial catenane is a dodecacationic radial catenane ($r[5]C^{12+}$).

V is a viologen subunit. R^1 and R^2 are reactive linkers. Each L is a linker bridging adjacent V, either alone or in combination with another L and/or a reactive linker.

Suitably the reactive linkers R^1 and R^2 may be formed from a click chemistry reaction. Click chemistry encompasses a group of linking reactions that are simple to perform, have high yields, require no or minimal purification, and are versatile in joining diverse structures without the prerequisite of protection steps. Suitably the click chemistry is a cycloaddition, nucleophilic ring-opening, non-aldol carbonyl chemistry, or a carbon multiple bond reaction. In some embodiments, R^1 and R^2 are formed from the same click chemistry reaction. In other embodiments, R^1 and R^2 are formed from different click chemistry reactions. Suitably, R^1 and/or R^2 is formed from a cycloaddition reaction such as an alkyne-azide reaction forming a triazole.

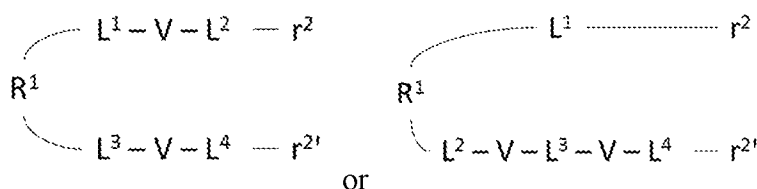
Suitably each L is independently selected from an alkyl, an alkenyl, an aryl, an alkylaryl, a triazole, or an alkyltriazole. A linker L may bridge adjacent V, either alone or in combination with another L and/or a reactive linker. In some embodiments, the bridge comprises a continuous bridge of 8, 9, 10, 11, or 12 atoms between V.

Methods of making densely charged radial catenanes

Methods for making the catenanes described above are also provided. The method for forming the catenane comprises contacting terminal moieties of a pseudorotaxane to form a central cationic ring that mechanically interlocks radial cationic rings. The pseudorotaxane comprises a threading component having a first terminal moiety, a second terminal moiety, and two or more radical/cation viologen subunits between the first terminal moiety and the second terminal moiety and two or more diradical/dicationic rings threaded by the threading component. The pseudorotaxane may comprise an equal number of diradical/dicationic rings as viologen subunits. Suitably, the threading component may comprises two, three, or four viologen subunits.

Suitably V is in a radical/cationic oxidation state (V^{*+}). Although V may be in a dicationic state, when V is in the radical/cationic oxidation state the viologen subunit may form stabilizing radical-radical interactions with radial rings that also have unpaired electrons that are threaded by the threading component. Suitably the radial cationic rings comprises cyclobis(paraquat-p-phenylene) (CBPQT) in the diradical/dicationic state ($CBPQT^{2(•+)}$). In certain embodiments each CBPQT is in a tetracationic state. In other embodiments, each CBPQT is in a diradical/dicationic oxidation state. In yet other embodiments, the CBPQT of the central cationic ring may be in any combination of the tetracationic state and the diradical/dicationic oxidation states.

In some embodiments, the threading component comprises two V. The threading component of the pseudorotaxane may comprise



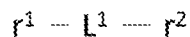
Suitably, each V may be in a radical/cationic oxidation state, resulting in a positive charge of 2+ as well as two unpaired electrons, which may interact with radial cationic rings that also have unpaired electrons to stabilize the pseudorotaxane.

The first of these threading components may be formed by contacting threading components

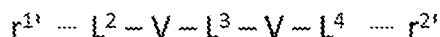


Suitably, each V may be in a radical/cationic oxidation state, resulting in a positive charge of 1+ as well as one unpaired electrons. Suitably each of these threading components form a pseudorotaxane that threads a radial ring. These threading components may interact with a radial cationic ring having unpaired electrons to stabilize the pseudorotaxane.

The second of these threading components may be formed by contacting

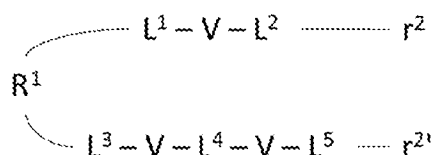


and threading component



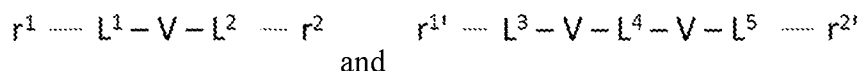
Suitably, each V may be in a radical/cationic oxidation state, resulting in a positive charge of 2+ as well as two unpaired electrons on the threading component. Suitably the threading component forms a pseudorotaxane that threads two radial rings. These threading component may interact with the radial cationic rings having unpaired electrons to stabilize the pseudorotaxane.

5 In some embodiments, the threading component comprises three V. Suitably, the threading component of the pseudorotaxane comprises



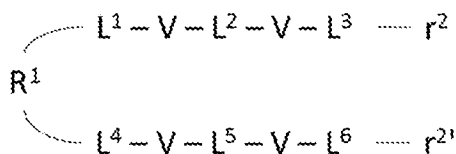
Suitably, each V may be in a radical/cationic oxidation state, resulting in a positive charge of 3+ as well as three unpaired electrons, which may interact with radial cationic rings that also have
10 unpaired electrons to stabilize the pseudorotaxane.

The threading components may be formed by contacting threading components



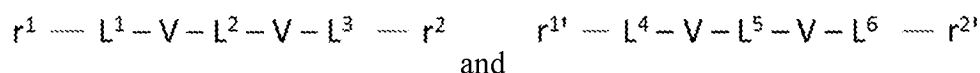
Suitably, each V may be in a radical/cationic oxidation state, resulting in a positive charge of 1+ as well as one unpaired electron, one of the threading components and a positive charge of 2+ as
15 well as two unpaired electrons on the other threading component. Suitably each of these threading components may form a pseudorotaxanes that threads one or two radial rings, respectively. These threading components may interact with radial cationic rings associated therewith that also have unpaired electrons to stabilize the pseudorotaxanes.

In some embodiments, the threading component comprises four V. The threading
20 component of the pseudorotaxane may comprise



Suitably, each V may be in a radical/cationic oxidation state, resulting in a positive charge of 4+ as well as four unpaired electrons, which may interact with radial cationic rings that also have unpaired electrons to stabilize the pseudorotaxane.

The threading components may be formed by contacting threading components



Suitably, each V may be in a radical/cationic oxidation state, resulting in a positive charge of 2+ as well as two unpaired electrons on each threading component. Suitably each of these threading component may form a pseudorotaxane that threads two radial rings. These threading components may interact with radial cationic rings associated therewith that also has unpaired electrons to stabilize the pseudorotaxane reactants.

Terminal moieties r^2 and $r^{2'}$ may suitably be selected to react and form the reactive linker R^2 and r^1 and $r^{1'}$ may suitably be selected to react and form the reactive linker R^1 . Suitably r^2 and $r^{2'}$ and r^1 and $r^{1'}$ may be selected from moieties capable of performing a click chemistry reaction. In some embodiments, r^2 and $r^{2'}$ and r^1 and $r^{1'}$ are selected to perform a cycloaddition reaction such as an alkyne-azide reaction forming a triazole.

Suitably, the catenanes may be reversibly oxidized with a suitably selected oxidant or reductant. For example, a radial catenane in a reduced state may be oxidized by an oxidant such as NOPF_6 or a radial catenane in an oxidized state may be reduced by a reductant such as Zn dust.

Dodecacationic and hexaradical/hexacationic radial [3]catenanes

One aspect of the invention is directed to dodecacationic and hexaradical/hexacationic [3]catenanes. As will be shown in the Examples below, the dodecacationic and hexaradical/hexacationic [3]catenanes may be reversibly interconverted between the different oxidation states as well as molecular topologies.

The dodecacationic [3]catenane ($r[3]C^{12+}$) comprises a central tetracationic ring mechanically interlocked with a second tetracationic ring and a third tetracationic ring. An exemplary $[3]C^{12+}$ is provided in FIG 5A.

The hexaradical/hexacationic [3]catenane ($r[3]C^{6(\bullet+)}$) comprises a central diradical/dicationic ring mechanically interlocked with a second diradical/dicationic ring and a third diradical/dicationic ring.

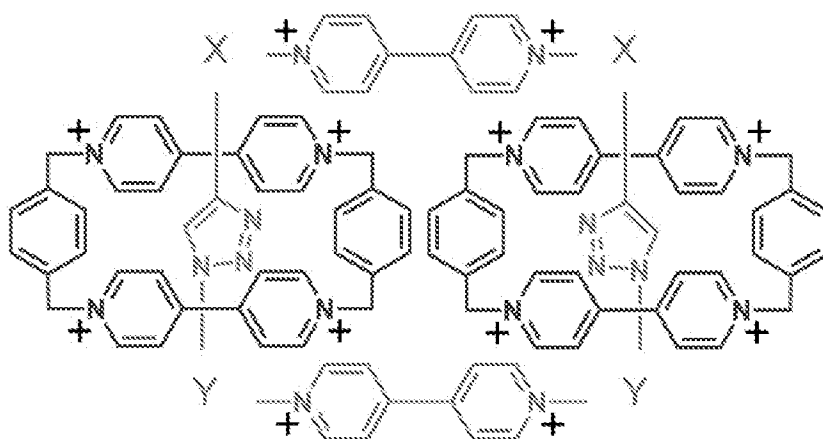
Linker R^1 , linker R^2 , or both linker R^1 and linker R^2 may comprise a triazole group formed from a click reaction between an azide and alkyne moiety. Both or at least one of the linkers R^1 and

R^2 may allow the opposing viologen subunits to be separated by a distance of about 9.5 Å and restrict the separation from 8.0 to 12.0 Å or anything in between, including from about 9.0 Å to about 11.0 Å. In order to allow for these separations, the linkers may comprise a continuous bridge of about 7 to about 16 atoms or anything in between, including from about 8 to about 12 atoms.

5 For the purposes of counting, if the continuous bridge of atoms bifurcates, e.g., at a triazole group, one counts the atoms along the bridge formed by the fewest number of atoms.

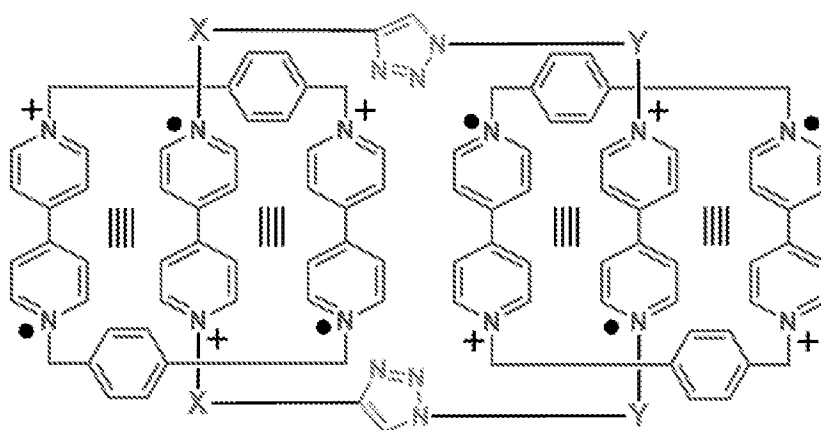
The second tetracationic ring and the third tetracationic ring may be any tetracationic macrocyclic component. In some embodiments, the second or third ring comprises cyclobis(paraquat-p-phenylene) tetracation ($CBPQT^{4+}$).

10 In some embodiments, the $[3]C^{12+}$ comprises the catenane of Formula Ia



(Formula Ia).

or the hexaradical/hexacationic $[3]C^{6(\bullet+)}$ comprises the catenane of Formula IIa



(Formula IIa).

X and Y together with the triazole group form the linkers R^1 and R^2 . X may comprise diradicals
15 of alkyl groups, alkenyl groups, aryl groups, alkylaryl groups, triazole groups, or alkyltriazole

groups. Y may comprise diradicals of alkyl groups, alkenyl groups, aryl groups, alkylaryl groups, triazole groups, or alkyltriazole groups.

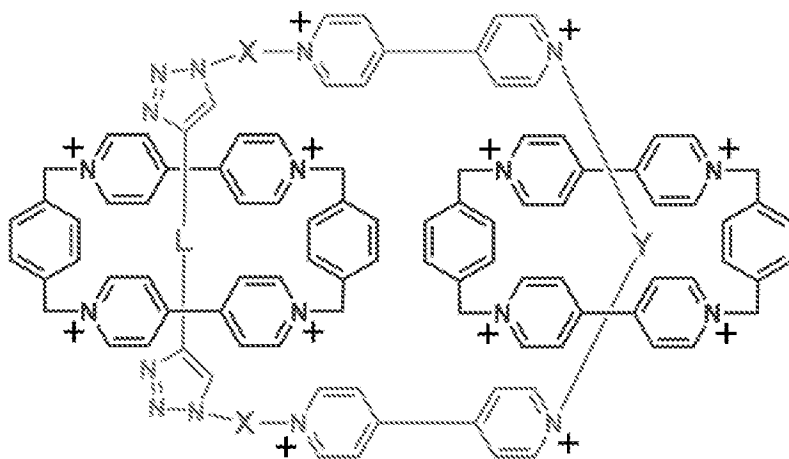
The length of the X-triazole-Y linker may be any suitable length. In some cases, the X-triazole-Y linker of Formula Ib or Formula IIa comprises a continuous bridge of 8, 9, 10, 11, or 12 atoms. In some embodiments, X comprises $-(CH_2)_{n_x}-$ where n_x is 0, 1, 2, 3, 4, 5, or 6, $-(CH_2)_{m_x}(C_2N_3H)(CH_2)_{m_x}'-$ where $m_x + m_x'$ is 0, 1, or 2, or $-(CH_2)_{l_x}(C_6H_4)(CH_2)_{l_x}'-$ where $l_x + l_x'$ is 0, 1, or 2. In some embodiments, Y comprises $-(CH_2)_{n_y}-$ where n_y is 0, 1, 2, 3, 4, 5, or 6, $-(CH_2)_{m_y}(C_2N_3H)(CH_2)_{m_y}'-$ where $m_y + m_y'$ is 0, 1, or 2, or $-(CH_2)_{l_y}(C_6H_4)(CH_2)_{l_y}'-$ where $l_y + l_y'$ is 0, 1, or 2. In some embodiments, X comprises $-(CH_2)_{n_x}-$ where n_x is 0, 1, 2, 3, 4, 5, or 6, $-(CH_2)_{m_x}(C_2N_3H)(CH_2)_{m_x}'-$ where $m_x + m_x'$ is 0, 1, or 2, or $-(CH_2)_{l_x}(C_6H_4)(CH_2)_{l_x}'-$ where $l_x + l_x'$ is 0, 1, or 2 and Y comprises $-(CH_2)_{n_y}-$ where n_y is 0, 1, 2, 3, 4, 5, or 6, $-(CH_2)_{m_y}(C_2N_3H)(CH_2)_{m_y}'-$ where $m_y + m_y'$ is 0, 1, or 2, or $-(CH_2)_{l_y}(C_6H_4)(CH_2)_{l_y}'-$ where $l_y + l_y'$ is 0, 1, or 2.

In some embodiments, X and Y both comprise alkyl groups. In certain embodiments, X comprises $-(CH_2)_{n_x}-$, Y comprises $-(CH_2)_{n_y}-$, and $n_x + n_y = 6$, including an embodiment where $n_x = 4$ and $n_y = 2$, $n_x = 3$ and $n_y = 3$, or $n_x = 2$ and $n_y = 4$.

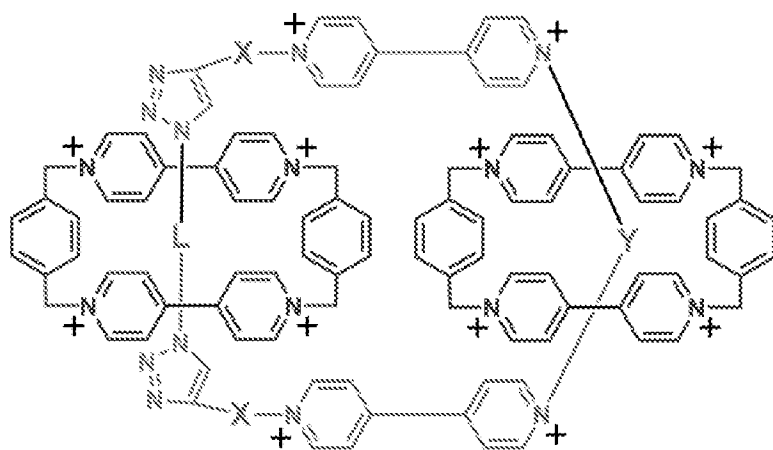
In some embodiments, X comprises an alkyl group and Y comprises an aryl or alkylaryl group. In certain embodiments, X comprises $-(CH_2)_{n_x}-$, Y comprises $-(CH_2)_{l_y}(C_6H_4)(CH_2)_{l_y}'-$, and $n_x + l_y + l_y' = 3$, including an embodiment where $n_x = 2$ and $l_y + l_y' = 1$.

In some embodiments, X comprises a triazole or alkyltriazole group and Y comprises an alkyl. In certain embodiments, wherein X comprises $-(CH_2)_{m_x}(C_2N_3H)(CH_2)_{m_x}'-$, Y comprises $-(CH_2)_{n_y}-$, and $m_x + m_x' + n_y = 4$, including an embodiment where $m_x + m_x' = 2$ and $n_y = 2$.

In some embodiments, the $[3]C^{12+}$ comprises the catenane of Formula Ib or Formula Ic

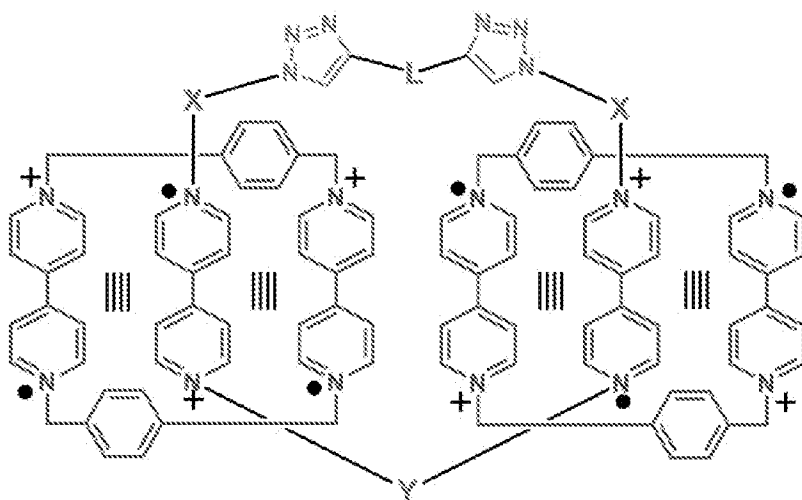


(Formula Ib) or

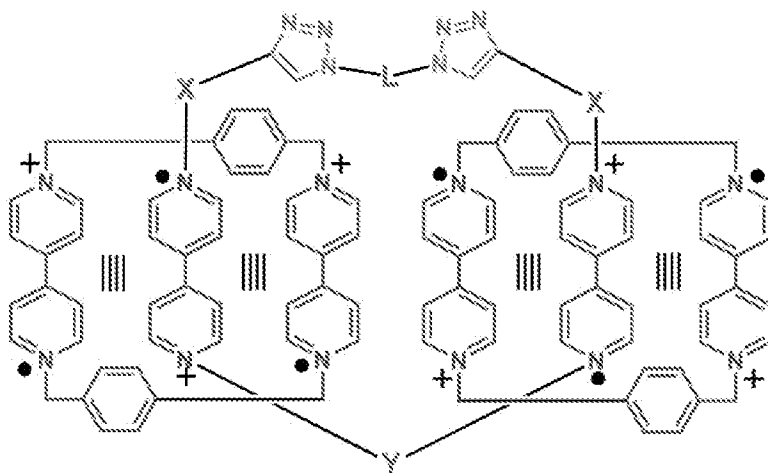


(Formula Ic)

or the hexaradical/hexacationic [3]catenane (**[3]C^{6(•+)}**) comprises the catenane of Formula IIb or IIc



(Formula IIb) or



(Formula IIc).

X may comprise an alkyl, an alkenyl, an aryl, an alkylaryl, a triazole, or an alkyltriazole and Y may comprise an alkyl, an alkenyl, an aryl, an alkylaryl, a triazole, or an alkyltriazole.

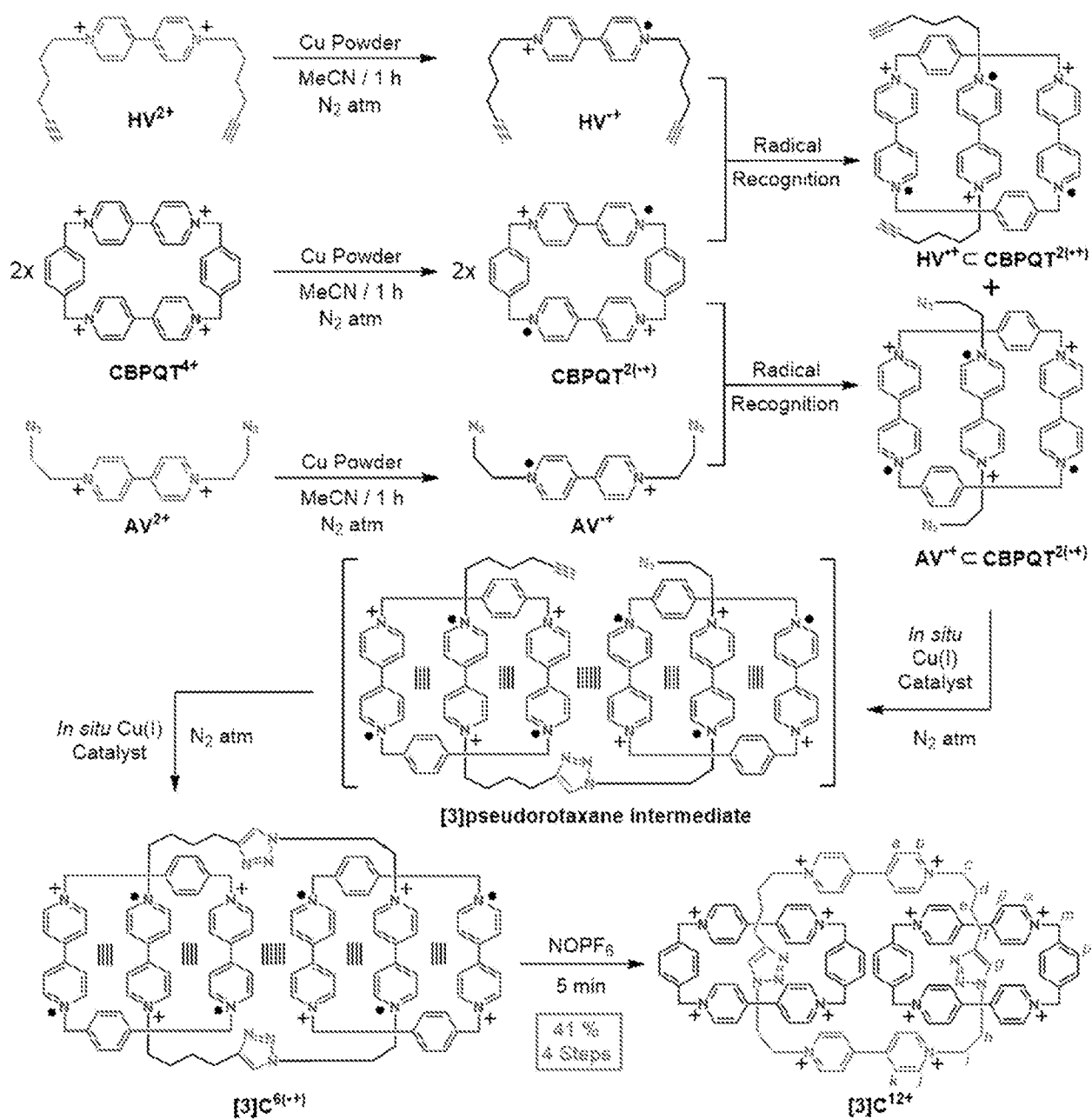
The X-triazole-L-triazole-X linker and the Y linker may be any suitable length. In some embodiments, X-triazole-L-triazole-X linker of Formulas Ib, Ic, IIb or IIc may comprise a continuous bridge of 8, 9, 10, 11, or 12 atoms. In some embodiment, Y linker of Formulas Ib, Ic, IIb or IIc may comprise a continuous bridge of 8, 9, 10, 11, or 12 atoms. In certain embodiment, X-triazole-L-triazole-X linker and the Y linker of Formulas Ib, Ic, IIb or IIc may comprise a continuous bridge of 8, 9, 10, 11, or 12 atoms. In some embodiments, X may comprise $-(CH_2)_{n_x}-$ where n_x is 0, 1, 2, 3, or 4. In some embodiments, Y may comprise $-(CH_2)_{n_l}-$ where n_l is 0, 1, 2, 3, or 4. In some embodiments, Y may comprise $-(CH_2)_{n_y}-$ where n_y is 8, 9, 10, 11, or 12. In certain embodiments, X may comprise $-(CH_2)_{n_x}-$ where n_x is 0, 1, 2, 3, or 4, L may comprise $-(CH_2)_{n_l}-$ where n_l is 0, 1, 2, 3, or 4, and, Y may comprise $-(CH_2)_{n_y}-$ where n_y is 8, 9, 10, 11, or 12. In particular embodiments, $n_x = 1$ or 2, $n_l = 1$ or 2, and $n_y = 9$ or 11.

Crystalline compositions may be prepared from the [3]catenanes described herein. The crystalline composition may comprise any of the [3]catenanes described above. In some embodiments, the composition further comprises a counter anion, e.g., PF_6^- as used in the Examples that follow. The counter anion may be provided to balance the charge of the [3]catenane, including having a molar ration of counter anion to [3]catenane from about 12:1 to 6:1 or anything in between.

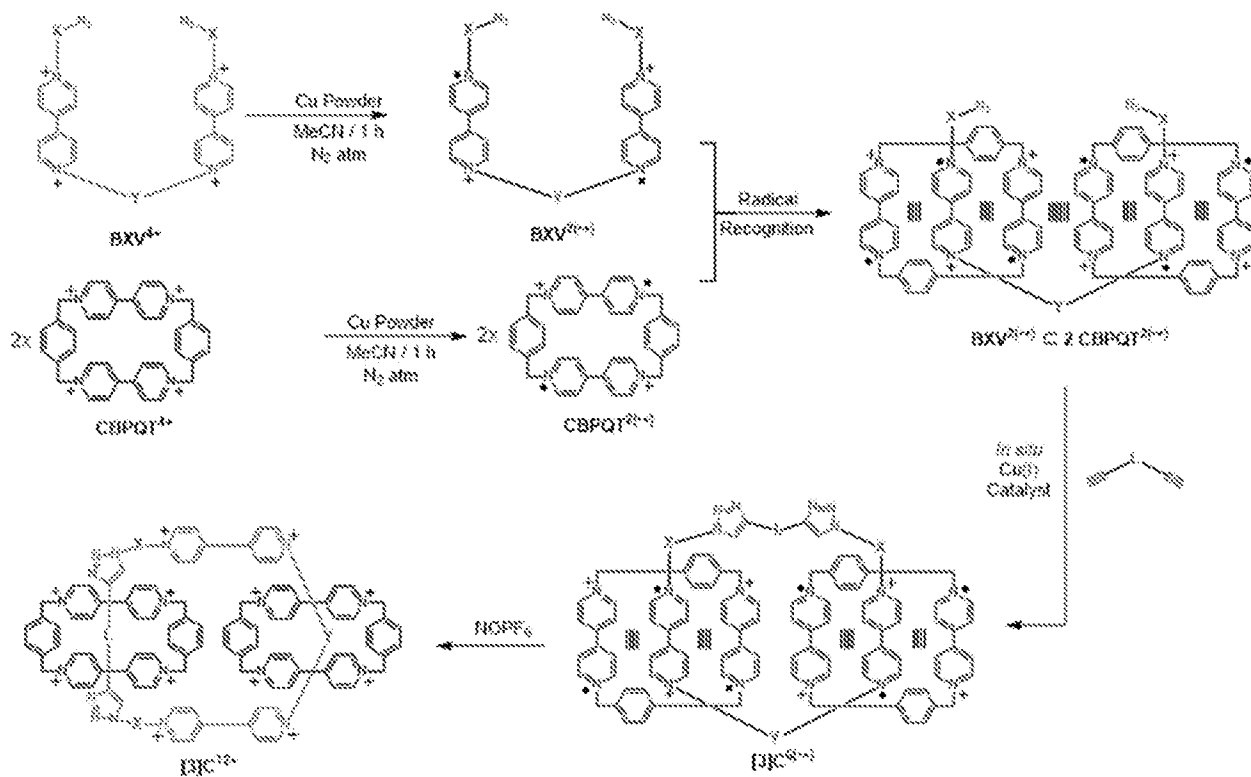
Synthesis of [3]Catenane

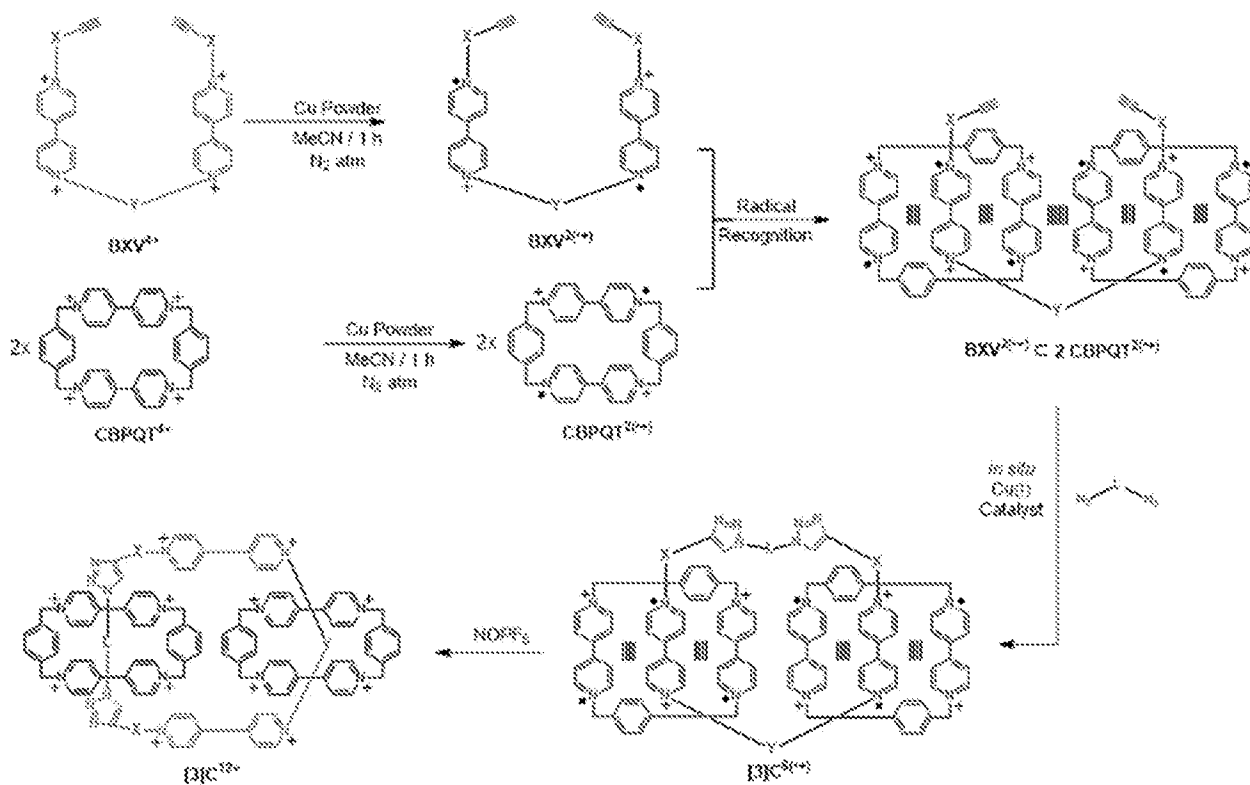
Another aspect of the invention is methods of preparing [3]catenanes. Exemplary methods for preparing [3]catenanes are provided in Schemes 1-3. The method comprises ring-closing a [3]pseudorotaxane to prepare the [3]catenane. The [3]pseudorotaxane comprises a threading component threading two diradical/dicationic rings, and the threading component comprises two viologen subunits between terminal moieties that each comprise a click-functionalized moiety. The method also comprises contacting a click-functionalized terminal moiety with a corresponding click-functionalized moiety to form a central diradical/dicationic ring mechanically interlocking the two diradical/dicationic rings. The two diradical/dicationic rings may each comprise cyclobis(paraquat-p-phenylene) bisradical dication (CBPQT^{2(•+)}).

Scheme 1. Preparation of [3]C¹²⁺ and [3]C^{6(•+)} via ring-closing of a [3]pseudorotaxane prepared from two [2]pseudorotaxanes



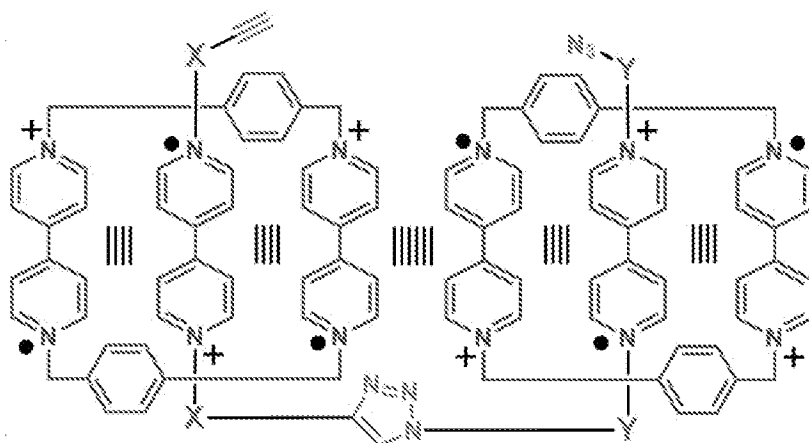
Scheme 2. Preparation of [3]C¹²⁺ and [3]C⁶⁽⁺⁾ via ring-closing of a [3]pseudorotaxane



Scheme 3. Preparation of [3]C¹²⁺ and [3]C⁶⁽⁺⁾ via ring-closing of a [3]pseudorotaxane

- 5 The click-functionalized moiety may be any click-functionalized moiety. In some embodiments, the [3]pseudorotaxane comprises one azide terminal moiety or two azide terminal moieties. In some embodiments, the [3]pseudorotaxane comprises one alkynyl terminal moiety or two alkynyl terminal moieties. In yet another embodiment, the [3]pseudorotaxane comprises one alkynyl terminal moiety and one azide terminal moiety. Ring-closing via a click reaction results in
- 10 the macrocyclic component of Formula II as described above.

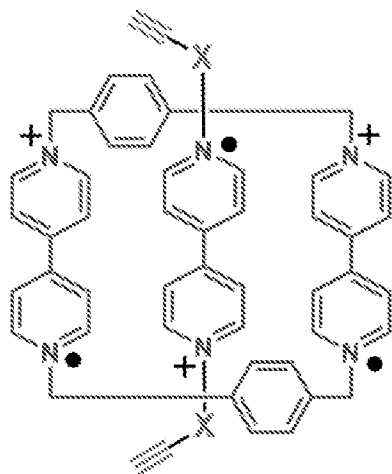
As shown in Scheme 1, a [3]catenane may be formed by ring-closing the [3]pseudo rotaxane



(Formula IIIa).

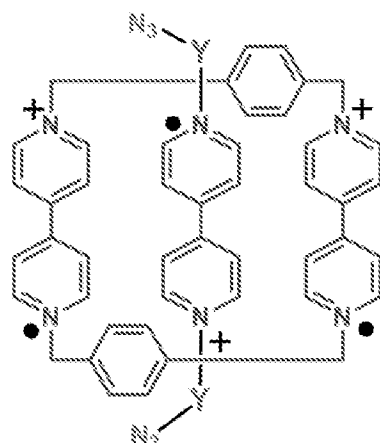
When the azide terminal moiety is contacted with the alkynyl terminal moiety, the central diradical/dicationic ring is formed mechanically interlocking the CBPQT²⁽⁺⁺⁾ rings to form the [3]catenane of Formula IIa. The [3]catenane of Formula IIa may be oxidized to form the [3]catenane of Formula Ia.

The [3]pseudorotaxane may be prepared from reaction of a first [2]pseudorotaxane and a second [2]pseudorotaxane. One of the [2]pseudorotaxanes may comprise a pseudorotaxane of Formula IVa



(Formula IVa).

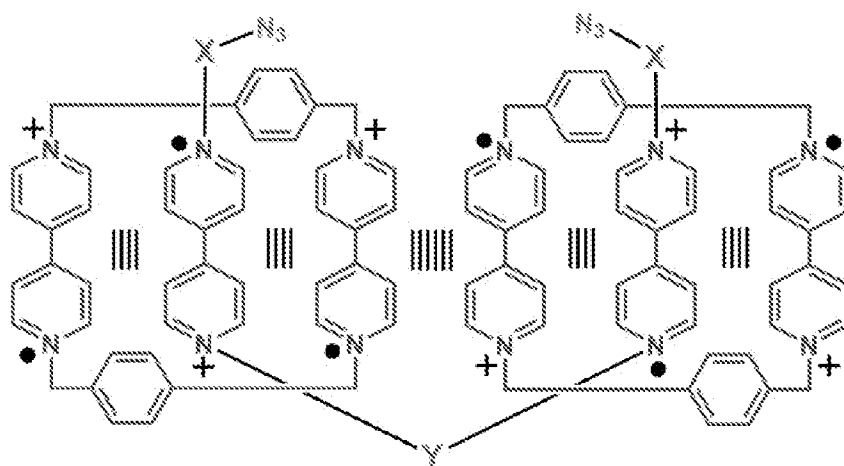
The other [2]pseudorotaxane comprises a pseudorotaxane of Formula IVb



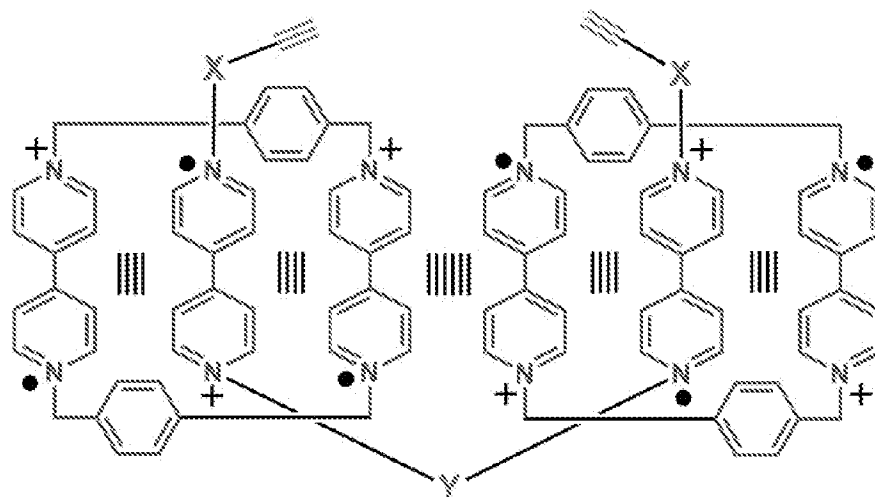
(Formula IVb).

When the azide terminal moiety of a [2]pseudorotaxane reacts with the alkynyl terminal moiety of the other [2]pseudorotaxane, the [3]pseudorotaxane of Formula IIIa is formed.

Alternative methods of preparing the [3]catenane is shown in Schemes 2-3. In this embodiment, the [3]pseudorotaxane comprises terminal moieties each comprising the same click-
 5 functionalized moiety. The [3]pseudorotaxane may comprise a compound of Formula IIIb or a compound of Formula IIIc

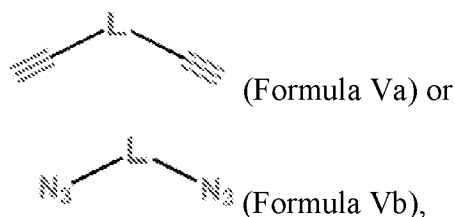


(Formula IIIb)



(Formula IIIc).

Ring-closing may be accomplished by reacting the [3]pseudorotaxane of Formula IIIb and Formula IIIc with compounds of Formula Va



respectively. Ring-closing forms the central diradical/dicationic ring to mechanically interlocking the $\text{CBPQT}^{2(\bullet+)}$ rings to form the [3]catenane of Formula IIb and IIc. The [3]catenane of Formulas IIb or IIc may be oxidized to form the [3]catenane of Formulas Ib or Ic, respectively.

An exemplary [3]catenane may be prepared from the synthetic scheme shown in Scheme 1 and as demonstrated in the Examples. Two trisradical [2]pseudorotaxanes – one azide-functionalized and the other alkyne-functionalized – were synthesized by treating two independent solutions of (i) bis(2-azidoethyl)viologen (AV^{2+}) and CBPQT^{4+} and (ii) bis(6-hexynyl)viologen (HV^{2+}) and CBPQT^{4+} with Cu powder under an inert atmosphere in a N_2 -filled glovebox. The complexation between the viologens and their respective $\text{CBPQT}^{2(\bullet+)}$ bisradical dication is driven by radical-radical recognition to form $[\text{AV}^{(\bullet+)}\text{cCBPQT}^{2(\bullet+)}]$ and $[\text{HV}^{(\bullet+)}\text{cCBPQT}^{2(\bullet+)}]$ inclusion complexes, which were allowed to coalesce over a period of an hour before the two dark-purple solutions were mixed together. Tandem copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reactions then occurred between the two bis(azide)-functionalized and bis(alkyne)-functionalized axles of the two [2]pseudorotaxanes with the lingering copper(I) catalytic species *in situ* generated from the previous reduction step. The first of the two Click reactions brings together the two

[2]pseudorotaxanes to produce a [3]pseudorotaxane intermediate, while the second CuAAC is the ring-closing step, driven by the face-to-face radical interactions between two bipyridinium radical cations of the CBPQT²⁽⁺⁾ subunits of the [3]pseudorotaxanes. This inter-ring recognition, coupled with the high dilution conditions (1.25 mM), resulted in the formation of a more complex mechanically interlocked species, i.e., a [3]catenane, in a hexaradical / hexacationic state. The fully oxidized [3]catenane **[3]C¹²⁺** was obtained either by reacting the reduced-state [3]catenane with nitrosonium hexafluorophosphate (NOPF₆), which oxidized all three rings within seconds, or by exposing the dark purple intermediate in air overnight. The formation of all the radical intermediates (Scheme 1) was monitored by mass spectrometry, UV-vis-NIR spectroscopy, and single-crystal X-ray diffraction when possible. Upon purification by reverse-phase flash chromatography (C₁₈: water/acetonitrile, 0.1% TFA - trifluoroacetic acid) and counterion exchange (NH₄PF₆ / H₂O) to give **[3]C•12PF₆** which was obtained in 41% yield overall. The identity and purity of the [3]catenane were confirmed by high-resolution electrospray mass spectrometry (HR-ESI-MS) and analytical high performance liquid chromatography (HPLC, FIG 8B), respectively.

The ¹H and ¹³C (data not shown) nuclear magnetic resonance (NMR) spectra of **[3]C•12PF₆**, recorded in CD₃CN at 298 K (FIG 1D), support the proposed structure of **[3]C¹²⁺** in solution with all the ¹H and ¹³C assignments being confirmed by two-dimensional NMR measurements (data not shown). The ¹H NMR spectrum (FIG 1D) of **[3]C•12PF₆** reveals that the two equivalent CBPQT⁴⁺ rings are located on the 1-(1-(ethylene)-1*H*-1,2,3-triazole-4-yl)butylene linkers in the central TB⁴⁺ ring and undergo slow pirouetting motions at room temperature as indicated by the broadening of all the ¹H CBPQT⁴⁺ resonances. The ¹H NMR spectrum (FIG 1A) of **[3]C•12PF₆**, recorded at 343 K, reveals that these resonances for the two CBPQT⁴⁺ ring protons become much better resolved as a result of fast exchange (i) associated with the facile pirouetting of the CBPQT⁴⁺ rings around the linkers and (ii) supplemented, most likely, by rapid rotation along the axes of the bipyridinium and phenylene units within the CBPQT⁴⁺ rings.

The characteristics of the mechanically interlocked structure of **[3]C•12PF₆** emerge clearly when comparing its ¹H NMR spectrum (FIG 1A) with those (FIG 1B-C) of its non-interlocked macrocyclic counterparts—**CBPQT•4PF₆** (FIG 1C) and **TB•4PF₆** (FIG 1B), which is synthesized from **AV•2PF₆** and **HV•2PF₆** using traditional CuAAC conditions. There are significant upfield shifts in the resonances associated with the methylene protons of the triazole linkers in **[3]C¹²⁺**

compared to those in **TB**⁴⁺. For example, the chemical shifts for protons H_d, H_e, and H_f change from 2.76, 2.06 and 1.63 ppm in the free macrocycle (**TB**⁴⁺) to 1.30, -0.36 and -0.46 ppm, respectively, in the interlocked [3]catenane **[3]C**¹²⁺. This evidence supports strongly the significant change in the local electronic environment induced by the constrained CBPQT⁴⁺ cations within the [3]catenane.

Unambiguous evidence for the constitution of the [3]catenane is achieved from X-ray crystallographic analysis of single crystals obtained by slow diffusion of diisopropyl ether into an MeCN solution of **[3]C**•12PF₆. The solid-state structure (FIG 2A-2J) confirms the topology and 12 positive charges (by counting the anions) associated with the dodecacationic [3]catenane where the two CBPQT⁴⁺ rings are mechanically interlocked to a central **TB**⁴⁺ macrocycle. The three tetracationic rings align themselves in a collinear fashion in which their centroids lie almost in a straight line. The compactness of the **[3]C**¹²⁺ dodecacation is illustrated in FIG 2D-2J by space-filling representations, where it becomes apparent that there is little or no free space between the two CBPQT⁴⁺ rings with a 3.2 Å plane-to-plane separation between their closest phenylene units. This separation is considerably shorter than the range (3.3 – 4.0 Å) of distances associated with typical π - π interactions. As a result of the compact mechanically interlocked structure, the six bipyridinium (**BIPY**²⁺) units in **[3]C**¹²⁺ exhibit much smaller torsional angles (mean angle = 17°) than those found for **BIPY** units in isolated **CBPQT**⁴⁺ (40°) and/or **TB**⁴⁺ (73°) free macrocycles.

The six bipyridinium units in the [3]catenane offer a possibility of the dodecacation taking up a total of 12 electrons in a system with potentially 13 redox states. Cyclic voltammetry of **[3]C**¹²⁺ revealed (FIG 3A), however, that the two most prevalent redox states characterized by widely separated potential windows are the dodecacationic **[3]C**¹²⁺ form and the hexaradical / hexacationic **[3]C**^{6(•+)} form. These two states can be interconverted reversibly by means of both electrochemical (FIG 3A) and chemical (FIG 3B-3D) stimuli. Treatment (298 K / 20 min) of **[3]C**•12PF₆ in MeCN with Zn dust resulted in a characteristic color change from colorless to dark purple, indicating the formation of **[3]C**^{6(•+)}. This color change was corroborated by air-free ESI-MS experiments (FIG 4AI-4AII) in which prominent peaks, corresponding to **[3]C**•6PF₆ – nPF₆]ⁿ⁺ (n = 3 – 5), were observed. The reverse process (**[3]C**^{6(•+)} to **[3]C**¹²⁺) occurs within seconds on treating the hexaradical hexacation **[3]C**^{6(•+)} with NOPF₆. Reversible switching can be repeated by up to five times as confirmed (FIG 3B-3D) by UV-vis-NIR spectroscopy.

X-Ray diffraction analysis (FIG 4B-4J) of a single crystal, grown by vapor diffusion of diisopropyl ether into an MeCN solution of $[3]C \cdot 6PF_6$ in an N_2 -filled glovebox, confirms the constitution of $[3]C^{6(++)}$, but reveals a marked difference in topology from that of its oxidized $[3]C^{12+}$ form. The two $CBPQT^{2(++)}$ rings display a change in their relative geometries when compared with their fully oxidized states in the $[3]C^{12+}$ form, i.e., moving from the triazole linkers to encircling the $BIPY^{(++)}$ unit of the $TB^{2(++)}$ ring. This change results in an intramolecular π - π interaction across the six adjacent viologen radical cations with an average plane-to-plane distance of 3.24 Å. All the $BIPY^{(++)}$ units become flattened in comparison to their corresponding $BIPY^{2+}$ units in $[3]C^{12+}$. The mean torsional angle in the $BIPY^{(++)}$, which is 3.6° , further corroborates the presence of radical cationic states for these $BIPY^{(++)}$ units. The changes in the relative dispositions of the three rings in $[3]C^{12+}$ and $[3]C^{6(++)}$ —wherein electron sharing and delocalization among the $BIPY^{n/(2-n)+}$ ($n = 0$ or 1) units are only present in $[3]C^{6(++)}$ —may explain the smaller number of observed redox states found in this [3]catenane, compared to the previously reported homo[2]catenane, wherein the two $CBPQT^{n/(4-n)+}$ ($n = 0 - 2$) rings are rigid and retain the same relative dispositions, irrespective of the different redox states. At the supramolecular level, the hexaradical/hexacations $[3]C^{6(++)}$ assemble (FIG 4F) into 2D layers wherein the $CBPQT^{2(++)}$ rings are located in a single plane within each layer driven by the intermolecular interactions between both BIPY-to-BIPY and phenylene-to-phenylene pairs.

Tetracosacationic and dodecaradical/dedecacationic radial [5]catenanes

Tetracosacationic and dodecaradical/dedecacationic r[5]catenanes may be prepared from the reaction of [3]pseudorotaxanes as described above. As will be shown in the Examples below, the tetracosacationic and dodecaradical/dedecacationic r[5]catenanes may be reversibly interconverted between the different oxidation states as well as molecular topologies.

The tetracosacationic r[5]catenane comprises a central octacationic ring mechanically interlocked with a second tetracationic ring, a third tetracationic ring, a fourth tetracationic ring, and a fifth tetracationic ring. An exemplary $r[5]C^{24+}$ is provided in FIG 5B.

The dodecaradical/dedecacationic r[5]catenane comprises a central tetradical/tetracationic ring mechanically interlocked with a second diradical/dicationic ring, a third diradical/dicationic ring, a fourth diradical/dicationic ring, and a fifth diradical/dicationic ring.

Each of the linkers R^1 and R^2 may comprise a triazole group prepared from azide-alkyne click reactions between the terminal moieties of the [3]pseudorotaxanes. Each of the linkers L^1 and L^2 may be independently selected from an alkyl, an alkenyl, an aryl, an alkylaryl, a triazole, or an alkyltriazole. Suitable linkers for each of R^1 , R^2 , L^1 , and L^2 are described above and those of skill in the art may make particular selections based upon the teachings herein.

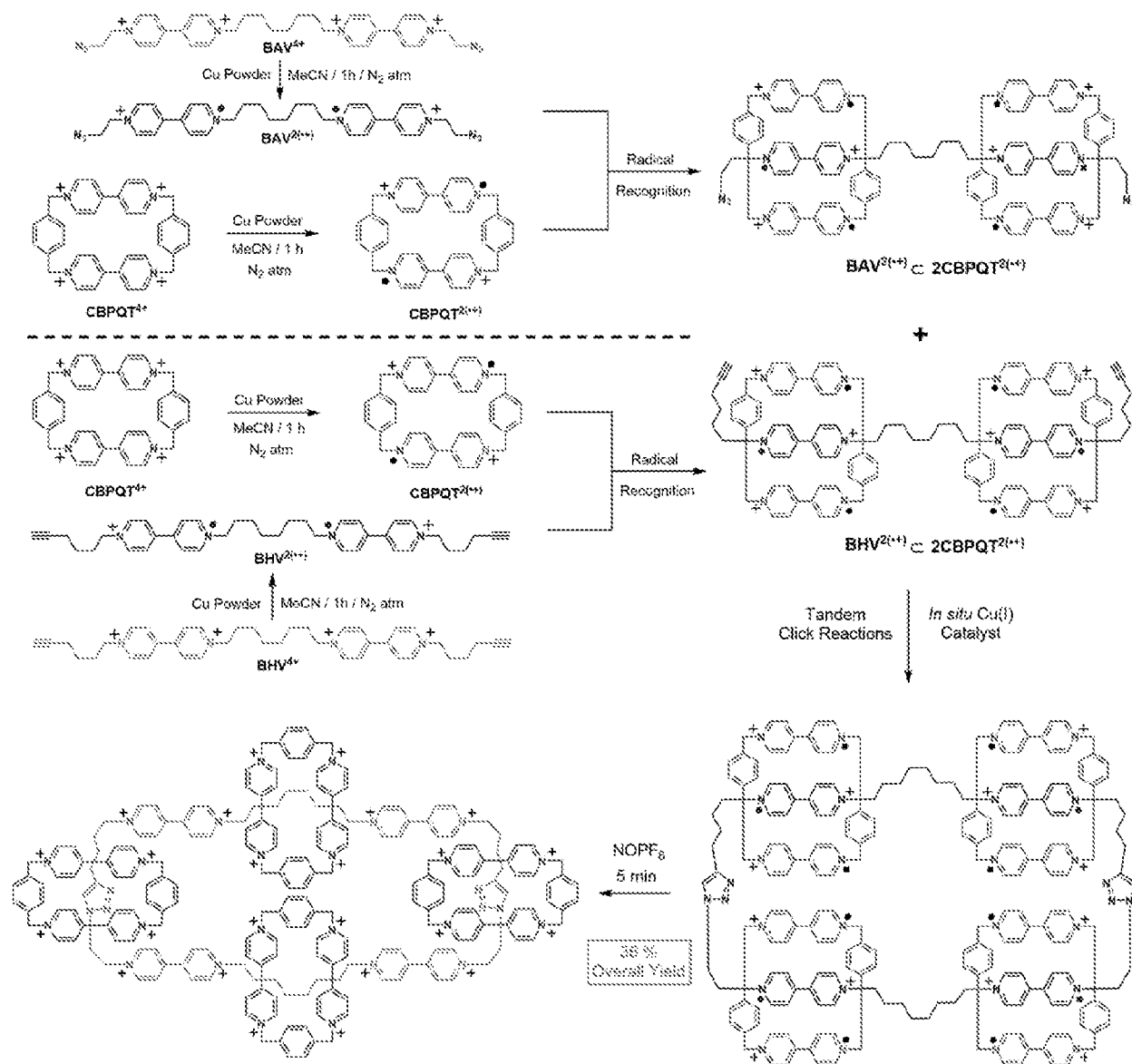
The tetracation ring may comprise cyclobis(paraquat-p-phenylene) tetracation ($CBPQT^{4+}$). The diradical/dication ring may comprise cyclobis(paraquat-p-phenylene) diradical/dication ($CBPQT^{2(\bullet+)}$).

Reversible switching between the fully oxidized tetracosacationic $[24^+]$ and the half-way-reduced dodecaradical/dodecacationic $[12(\bullet+)]$ states was also promoted in the case of the radial [5]catenane by both chemical and electrochemical means. Upon the reduction of $r[5]C^{24+}$ with Zn dust, the formation of the $r[5]C^{12(\bullet+)}$ species can be monitored (FIG 7A) by UV-Vis spectroscopy with a characteristic absorption band at 1116 nm. The identity of this dodecaradical/dodecacationic radial [5]catenane, which could be facilely converted back to $r[5]C^{24+}$ by an oxidation with NOPF₆, was confirmed by the air-free ESI-MS, wherein prominent peaks were observed at $m/z = 1512.8240$ and 1098.3773 , corresponding to the $[M - nPF_6]^{n+}$ peaks with $n = 3$ and 4 , respectively. Electrochemical studies on $r[5]C \cdot 24PF_6$ lend (FIG 7B) the reversible inter-conversion between the two dodecaradical/dodecacationic and tetracosacationic states, in which CV scans can be repeated several times without any changes (FIG 7C-7D) of the peak currents.

Synthesis of [5]Catenane

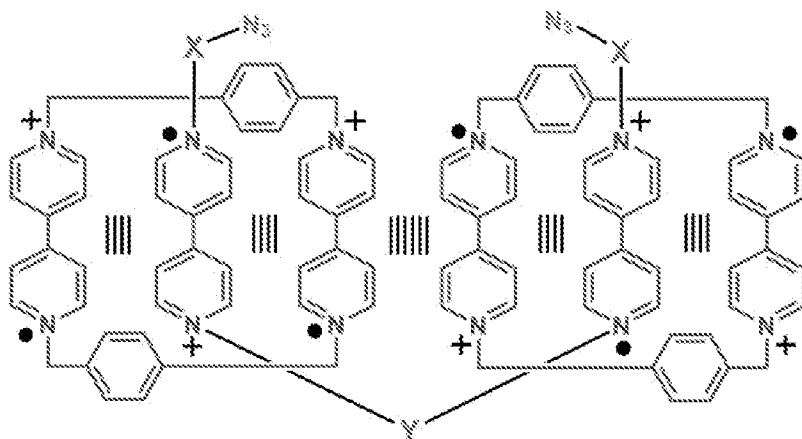
Another aspect of the invention is methods of preparing [5]catenanes. Exemplary methods for preparing [5]catenanes are provided in Scheme 4. The method comprises reacting two [3]pseudorotaxanes to prepare the [5]catenane. The [3]pseudorotaxane comprises a threading component threading two diradical/dicationic rings, and the threading component comprises two viologen subunits between terminal moieties that each comprise a click-functionalized moiety. The method also comprises contacting a click-functionalized terminal moiety with a corresponding click-functionalized moiety to form a central diradical/dicationic ring mechanically interlocking the two diradical/dicationic rings. The two diradical/dicationic rings may each comprise cyclobis(paraquat-p-phenylene) bisradical dication ($CBPQT^{2(\bullet+)}$).

Scheme 4. Preparation of $r[5]C^{24+}$ and $r[5]C^{12(++)}$ via ring-closing of a [5]pseudorotaxane prepared from two [3]pseudorotaxanes



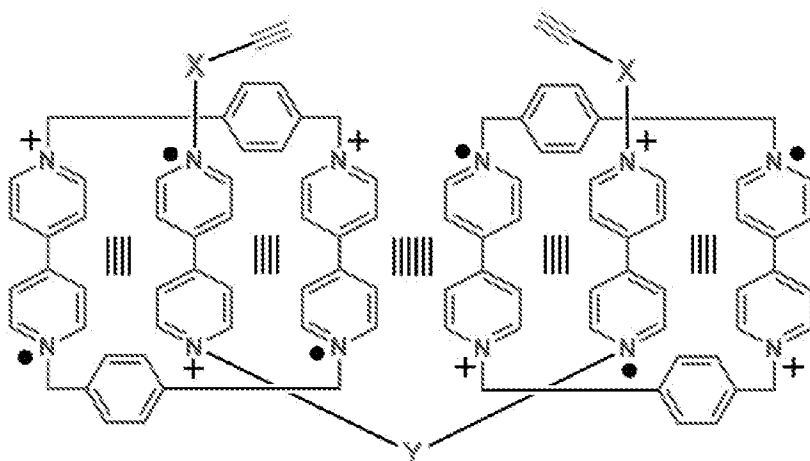
The click-functionalized moiety may be any click-functionalized moiety. In some embodiments, the [3]pseudorotaxane comprises two azide terminal moiety or two alkynyl terminal moieties. Ring-closing via a click reaction results in the macrocyclic component of Formula V as described above.

In particular embodiments, [3]pseudorotaxanes comprising a compound of Formula IIIb



(Formula IIIb)

and the second [3]pseudorotaxane comprises a pseudorotaxane of Formula IIIc



(Formula IIIc).

X of either of the [3]pseudorotaxanes may comprises an alkyl, alkenyl, aryl, alkylaryl, triazole, or
 5 alkyltriazole as described above. Y of either of the [3]pseudorotaxanes may comprise an alkyl, alkenyl, aryl, alkylaryl, triazole, or alkyltriazole. Suitably linkers are described above.

Employing the radical-templated synthetic strategy that was used to make **[3]C¹²⁺**, we have been able to synthesize (FIG 5) a radial [5]catenane **r[5]C²⁴⁺** – which can also be named a [5]molecular necklace – bearing up to 24 positive charges within its co-constitution. Two bis-
 10 viologen axles, **BAV⁴⁺** and **BHV⁴⁺**, with octamethylene spacers between the two viologen units were used to drive the formation of two pseudo[3]rotaxanes with bisradical dicationic **CBPQT^{2(•+)}** rings under reducing conditions. The tandem click reactions between these two pseudo[3]rotaxanes, catalyzed by the *in situ* generated Cu(I) species, followed by oxidation with NOPF₆, gave **r[5]C²⁴⁺** in 36% overall yield. The use of Cu⁰ powder as both a reducing agent and
 15 a catalytic precursor for the click reactions together with the triazole-based ETB linkers to facilitate

the cyclization of the central ring, has been shown, yet again, to be an effective way for the production of highly charged MIMs.

The mechanically interlocked nature of the radial [5]catenane **r[5]C²⁴⁺** was established by NMR spectroscopy. The ¹H NMR spectrum (FIG 6AI) of **r[5]C•24PF₆**, recorded in CD₃CN at 298 K, reveals significant upfield chemical shifts for methylene protons associated with the octamethylene chains and the triazole-based ETB linkers. In particular, the dramatic shielding of protons H_a ($\delta = -2.37$ ppm) and H_w ($\delta = -2.41$ ppm) on the two octamethylene chains indicates their encirclement by two CBPQT⁴⁺ rings. The resonances ($\delta = \text{ca. } -0.58$ and -0.15 ppm) associated with protons H_i and H_k, respectively, suggest that the other two CBPQT⁴⁺ rings reside on the triazole-based ETB linkers as in the case of **[3]C¹²⁺**. The ¹H NMR spectrum of the radial [5]catenane supports the averaged C_{2v} symmetry of this molecule as demonstrated by (i) a small chemical shift difference (H_{p1} and H_{p3}; $\Delta\delta = 0.1$ ppm, FIG 6AI) for the resonances associated with the phenylene protons in the two CBPQT⁴⁺ rings encircling the octamethylene chains and (ii) a single set of proton resonances for the two CBPQT⁴⁺ rings encircling the triazole-based ETB linkers. HR-ESI-MS supports the structural assignment of **r[5]C²⁴⁺** as its PF₆[−] salt, in which *m/z* fragments, corresponding to the $[M - n\text{PF}_6]^n+$ species for *n* = 3, 4, and 5, are observed (FIG 6AII) for the radial [5]catenane along with the loss of three to five PF₆[−] counter ions, respectively. The 3D geometry of **r[5]C²⁴⁺** was determined unequivocally by X-ray diffraction analysis on single crystals grown by slow diffusion of diisopropyl ether into a MeCN solution of **r[5]C•24PF₆**. FIG 6B-D illustrate the solid-state structure of **r[5]C²⁴⁺**, demonstrating clearly the mechanically interlocked nature of the tetracosacationic radial [5]catenane and further supporting the structural assignments from the NMR spectroscopic investigations, as well as the relative location of the four CBPQT⁴⁺ rings within the co-constitution of this MIM. The tetracosacation **r[5]C²⁴⁺** with a molecular formula of $[\text{C}_{218}\text{H}_{216}\text{N}_{30}]^{24+}$ exhibits a length of 3.7 nm in one dimension and occupies a volume ca. 4.0 nm³, corresponding to 6.0+charges / nm³.

Summary

We demonstrate the synthesis and characterization of densely charged catenanes. We synthesized by radical templation a dodecacationic [3]catenane, which consists of three mechanically interlocked 4+ charged rings despite their mutual Coulombic repulsion. This highly (12+) charged [3]catenane has the ability to accept up to 12 electrons and occupies a volume of less than 1.65 nm³, corresponding to 7.3 +charges / nm³ which, to the best of our knowledge, is

the highest charge density ever observed in a polycationic organic mechanically interlocked molecule. Moreover, this catenane can be switched either electrochemically or chemically between two stable states, i.e., its dodecationic and hexaradical / hexacationic forms. It turned out to be possible to grow good quality single crystals of these two different redox states, which were shown
5 by X-ray diffraction to exist in two distinct geometries in the solid states. These geometries are the result of circumrotation of the two outer cyclophanes from encircling the triazole linkers to encircling the BIPY⁽⁺⁺⁾ units, following their reduction from CBPQT⁴⁺ to CBPQT²⁽⁺⁺⁾. The molecular switch is reversible in its operation and can be switched in solution as monitored by UV-vis-NIR spectroscopy. We envision that such redox switching, accompanied by relative
10 geometrical changes, could be harnessed in the development of new stimuli-responsive macromolecular architectures and could be of potential use in molecular electronics which require bistable switching of electron conductance.

The possibility of expanding the radical templation strategy has been realized with the construction of a more complex MIM, namely, a tetracosacationic radial [5]catenane that bears up
15 to 24 positive charges in its co-constitution. With a length of up to 3.7 nm, this redox-active tetracosacation has a capability of storing as many as 24 electrons per molecule. Overall, our synthetic approach lays the foundation for exploring highly and densely charged organic materials which could find applications in energy storage technologies where novel oligomeric organic redox-active molecules capable of storing and transferring multiple electrons are highly desired.
20 In particular, these MIMs are potentially well-suited to be incorporated into redox flow batteries utilizing oligomeric organic redox-active materials in size exclusion strategies to overcome membrane cross-contamination and, therefore, improve cell performance.

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EXAMPLES

General Methods

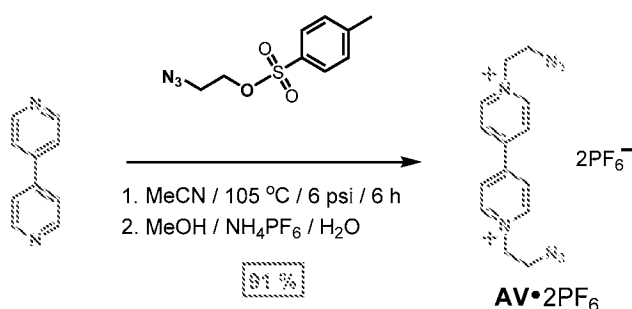
All chemicals and reagents were purchased from commercial suppliers (Aldrich or Fisher) and used without further purification. 2-Azidoethyl 4-methylbenzenesulfonate was prepared according to literature procedures.¹ Thin layer chromatography (TLC) was carried out on silica gel 60 F254 (E. Merck). Analytical high performance chromatography (HPLC) was performed on

reverse phase HPLC (RP-HPLC) instruments, using C18 columns and a binary solvent system (MeCN and H₂O with 0.1% CF₃CO₂H). Column chromatography was carried out on silica gel 60F (Merck 9385, 0.040–0.063 mm). UV/Vis/NIR Absorption spectra were recorded using a UV-3600 Shimadzu spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded at 298 K on a Bruker Advance 500 and 600 spectrometers, with working frequencies of 500 and 600 MHz for ¹H, and 125 and 150 MHz for ¹³C, respectively. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents (CD₃CN: δ 1.94 ppm; CDCl₃: δ 7.26 ppm). High-resolution mass spectra were measured on an Agilent 6210 Time of Flight (TOF) LC-MS, using an ESI source, coupled with Agilent 1100 HPLC stack, using direct infusion (0.6 mL/min). Cyclic voltammetry (CV) experiments were carried out at room temperature in Ar-purged solutions of MeCN with a Gamry multipurpose instrument (Reference 600) interfaced to a PC. All CV experiments were performed using a platinum working electrode (0.0314 cm²). The electrode surface was polished routinely with 0.05 μm alumina-methanol slurry on a felt surface immediately before use. The counter electrode was a Pt coil and the reference electrode was an Ag/AgCl electrode. The concentration of the sample and supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAPF₆), were 1.0 mM and 0.1 M, respectively. The CV cell was dried in an oven immediately before use, and Ar was flushed continually through the cell as it was cooled down to room temperature to avoid condensation of water.

Synthetic Protocols

a) AV•2PF₆.

Scheme 5. Preparation of AV

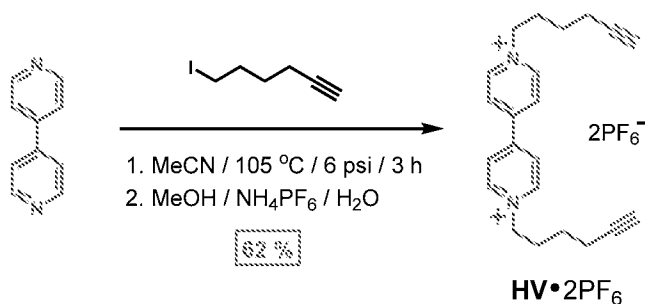


As depicted in Scheme 5, a mixture of 4,4'-bipyridine (450 mg, 2.9 mmol) and 2-azidoethyl 4-methylbenzenesulfonate¹ (2.0 g, 8.7 mmol) in dry MeCN (20 mL) was heated at 105 °C / 6 psi under N₂ for 3 h. The reaction mixture was cooled to room temperature followed by the addition

of an excess tetraethylammonium bromide. The resulting precipitate was filtered and washed thoroughly with MeCN. The solid was dissolved in H₂O (100 mL), followed by the addition of excess of NH₄PF₆, resulting in the precipitation of an off-white solid which was collected by centrifugation, washed with H₂O several times and dried *in vacuo* to yield **AV•2PF₆** as a white solid (1.57 g) in 91% yield. ¹H NMR (500 MHz, CD₃CN, 298 K) δ = 8.92 (d, *J* = 6.4 Hz, 4H), 8.42 (d, *J* = 6.4 Hz, 4H), 4.74 (t, *J* = 5.3 Hz, 4H), 4.01 (4.74 (t, *J* = 5.3 Hz, 4H). ¹³C NMR (125 MHz, CD₃CN, 298 K) δ = 151.4, 147.1, 128.1, 61.6, 51.2. ESI-HRMS calcd for [M – PF₆]⁺ *m/z* = 441.1134, found 441.1141.

b) HV•2PF₆.

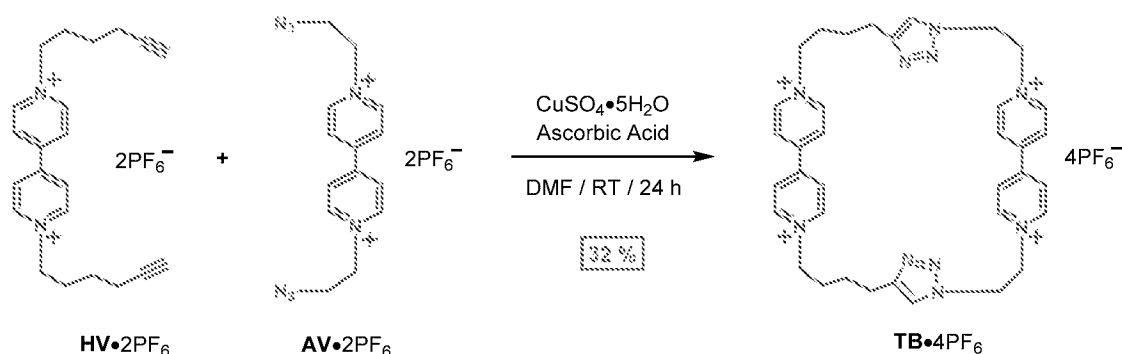
Scheme 6. Preparation of HV



As depicted in Scheme 6, a mixture of 4,4'-bipyridine (1.0 g, 6.4 mmol) and 6-iodo-1-hexyne (4.6 g, 22 mmol) in dry MeCN (30 mL) was heated at 105 °C / 6 psi under N₂ for 3 h. The reaction mixture was cooled to room temperature and the resulting reddish precipitate was filtered and washed thoroughly with MeCN. The solid was dissolved in H₂O (100 mL), followed by the addition of excess of NH₄PF₆, resulting in the precipitation of an off-white solid which was collected by centrifugation, washed with H₂O (3 × 20 mL), MeOH (1 × 20 mL) and dried *in vacuo* to yield **HV•2PF₆** as a light brown solid (2.4 g) in 62% yield. ¹H NMR (500 MHz, CD₃CN, 298 K) δ = 8.90 (d, *J* = 6.4 Hz, 4H), 8.39 (d, *J* = 6.4 Hz, 4H), 4.65 (t, *J* = 7.5 Hz, 4H), 2.28 (dt, *J* = 2.6 Hz, *J* = 7.0 Hz, 4H), 2.23 (t, *J* = 2.6 Hz, 2H), 2.13 (p, *J* = 7.6 Hz, 4H), 1.60 (p, *J* = 7.4 Hz, 4H). ¹³C NMR (125 MHz, CD₃CN, 298 K) δ = 150.9, 146.5, 128.2, 84.2, 70.5, 62.5, 31.0, 25.5, 18.2. ESI-HRMS calcd for [M – PF₆]⁺ *m/z* = 463.1732, found 463.1740.

c) TB•4PF₆.

Scheme 7. Preparation of AV



As depicted in Scheme 7, a solution of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (10 mg, 0.04 mmol) in DMF (15 mL) was added to a solution of **HV•2PF₆** (98 mg, 0.16 mmol) and **AV•2PF₆** (95 mg, 0.16 mmol) in DMF (50 mL). After stirring for 30 min under a N_2 atmosphere, an excess of ascorbic acid (80 mg) was added. The reaction mixture was then stirred for 1 day at room temperature. Solvent was removed by rotary evaporation and the residue was redissolved in MeCN, followed by vacuum filtration. The filtrate was concentrated to ca. 5 mL and an excess of NH_4PF_6 (aq) solution was added. The resulting white precipitate was filtered and purified by RP-HPLC (H_2O –MeCN, 0.1% TFA, 0–100% MeCN in 60 min). A counter anion exchange from TFA salt to PF_6^- salt using NH_4PF_6 resulted in a white precipitate which was collected by centrifugation and washed several times with H_2O to afford **TB•4PF₆** as a white solid (62 mg, 32 %). ^1H NMR (500 MHz, CD_3CN , 298 K) δ = 8.86 (d, J = 6.8 Hz, 4H), 8.71 (d, J = 6.8 Hz, 4H), 8.35 (d, J = 6.8 Hz, 4H), 8.29 (d, J = 6.8 Hz, 4H), 7.83 (s, 2H), 5.18 (m, 4H), 5.01 (m, 4H), 4.70 (t, J = 6.5 Hz, 4H), 2.76 (t, J = 6.5 Hz, 4H), 2.06 (p, J = 6.9 Hz, 4H), 1.63 (p, J = 7.7 Hz, 4H). ^{13}C NMR (125 MHz, CD_3CN , 298 K) δ = 151.2, 151.0, 147.0, 146.9, 146.3, 128.1, 128.1, 125.6, 62.7, 61.1, 51.5, 30.6, 25.0, 24.3. Low-resolution ESI-MS calcd m/z = 1049.2 [$M - \text{PF}_6$] $^+$, found 1049.1; m/z = 452.1 [$M - 2\text{PF}_6$] $^{2+}$, found 452.2; m/z = 253.1 [$M - 3\text{PF}_6$] $^{3+}$, found 253.1. High-resolution ESI-MS calcd for [$M - \text{PF}_6$] $^+$ m/z = 1049.2514 and [$M - 2\text{PF}_6$] $^{2+}$ m/z = 452.1433, found 1049.2517 and 452.1433, respectively.

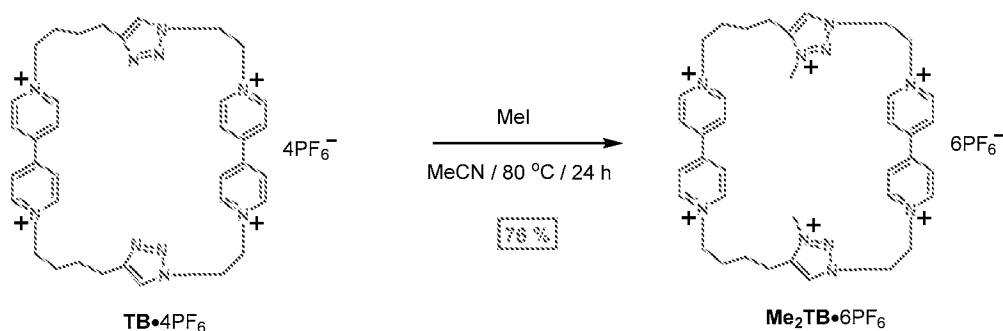
d) [3]C•12PF₆.

As depicted in Scheme 1, an excess of Cu powder was added to a solution of **AV•2PF₆** (29 mg, 0.05 mmol) and **CBPQT•4PF₆** (55 mg, 0.05 mmol) dissolved in dry MeCN (20 mL) in an N_2 -filled glovebox. In a separate flask, **HV•2PF₆** (30 mg, 0.05 mmol) and **CBPQT•4PF₆** (55 mg, 0.05 mmol) were dissolved in dry MeCN (20 mL) and subjected to an excess amount of Cu powder. The two solutions were stirred at room temperature for 1 h before being mixed together quickly in another reaction flask. The reaction mixture was stirred at room temperature in the inert

environment of a N₂-filled glovebox for 4 days. The resulting dark purple mixture was filtered inside the glovebox and NOPF₆ was added in small aliquots to the filtrate until the dark purple solution turned clear. The resulting solution was taken out of the glovebox and solvent was removed by rotary evaporation. The residue was purified using reversed-phase flash chromatography (C₁₈: water/MeCN 0.1% TFA 0-100%), followed by anion exchange from TFA⁻ to PF₆⁻ by treating the aqueous fractions with an excess amount of NH₄PF₆, resulting in a white precipitate which was collected by centrifugation and washed with H₂O several times before being dried *in vacuo* to yield an off-white solid (69 mg, 41 %). ¹H NMR (500 MHz, CD₃CN, 298 K) δ = 9.61 (d, *J* = 6.7 Hz, 4H), 9.43 (d, *J* = 6.7 Hz, 4H), 9.38 (d, *J* = 6.7 Hz, 4H), 9.36 (d, *J* = 6.7 Hz, 4H), 8.95–8.45 (s, br, 16H), 8.15–7.95 (s, br, 16H), 6.60 (s, br, 16H), 5.93 (s, 2H), 5.48 (s, br, 16H), 5.46 (m, 4H), 4.99 (m, 4H), 4.74 (t, *J* = 6.1 Hz, 4H), 1.30 (p, *J* = 6.8 Hz, 4H), –0.36 (t, *J* = 6.2 Hz, 4H), –0.46 (p, *J* = 7.6 Hz, 4H). ¹³C NMR (125 MHz, CD₃CN, 298 K) δ = 149.5, 149.0 (br), 148.6, 147.5, 147.4, 146.1 (br), 142.9, 135.9 (br), 130.9 (br), 128.9 (br, 2C), 127.5 (br), 123.4, 65.0 (br), 64.1, 62.1, 48.6, 30.3, 23.4, 23.3. Low-resolution ESI-MS calcd *m/z* = 986.8 [*M* – 3PF₆]³⁺, found 986.6, *m/z* = 703.9 [*M* – 4PF₆]⁴⁺, found 703.8, *m/z* = 534.1 [*M* – 5PF₆]⁵⁺, found 534.1, *m/z* = 420.9 [*M* – 6PF₆]⁶⁺, found 420.9. High-resolution ESI-MS calcd for [*M* – 2PF₆]²⁺ *m/z* = 1552.7641 and [*M* – 3PF₆]³⁺ *m/z* = 986.8540, found 1552.7628 and 986.8540, respectively.

e) Me₂TB•6PF₆.

Scheme 8. Preparation of ME₂TB

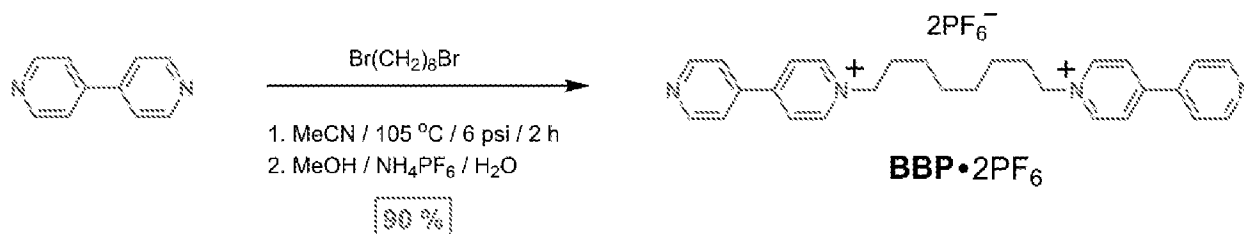


As depicted in Scheme 8, an excess of methyl iodide (0.1 mL) was added to a solution of TB•4PF₆ (8.0 mg, 6.7 μ mol) in MeCN (1.0 mL) and the reaction mixture was heated to 80 °C and stirred for 1 day. After cooling to room temperature, the solution was concentrated to ca. 0.2 mL and an excess of NH₄PF₆ (aq) solution was added. The resulting white precipitate was collected by centrifugation, washed several times with H₂O, and dried *in vacuo*. Recrystallization of the

crude mixture (~90% pure by NMR) by slow diffusion of $^i\text{Pr}_2\text{O}$ vapor into its solution in MeCN yielded **Me₂TB•6PF₆** as an off-white solid (7.8 mg, 76 %). ^1H NMR (500 MHz, CD₃CN, 298 K) δ = 8.86 – 8.81 (two overlapping doublets, J = 8.7 Hz each, 4H each), 8.32 (two overlapping doublets, J = 8.7 Hz each, 4H each), 8.10 (s, 2H), 7.83 (s, 2H), 5.30 (m, 4H), 5.15 (m, 4H), 4.69 (t, J = 6.5 Hz, 4H), 4.02 (s, 6H), 2.82 (t, J = 6.5 Hz, 4H), 2.10 (p, J = 6.9 Hz, 4H), 1.59 (p, J = 7.7 Hz, 4H). ^{13}C NMR (125 MHz, CD₃CN, 298 K) δ = 151.7, 150.9, 147.2, 146.5, 145.5, 130.1, 128.5, 128.2, 62.6, 59.3, 53.7, 38.7, 30.3, 23.5, 23.2. ESI-MS calcd m/z = 612.13 [$M - 2\text{PF}_6$]²⁺, found 612.10; m/z = 359.77 [$M - 3\text{PF}_6$]³⁺, found 359.71.

f) BBP•2PF₆.

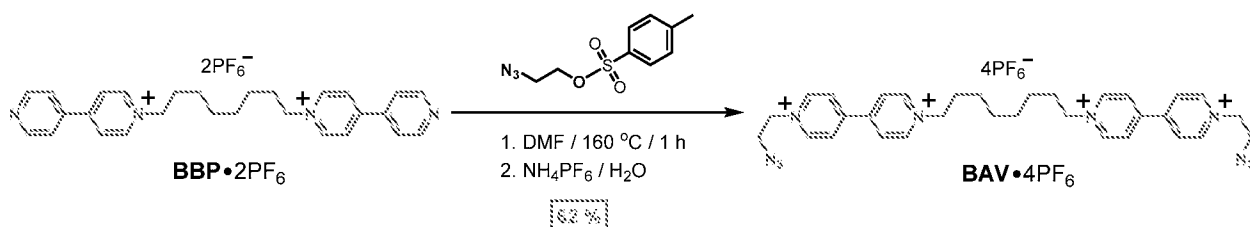
Scheme 9. Preparation of BBP



As depicted in Scheme 9, 4,4'-Bipyridine (5.0 g, 32 mmol) was dissolved in MeCN (50 mL) and heated under reflux. A solution of 1,8-dibromooctane (1.75 g, 6.4 mmol) in MeCN (20 mL) was added to the above solution during 30 min using a syringe pump. The reaction mixture was then heated at 105 °C / 6 psi under N₂ for 2 h before cooled to room temperature. The resulting precipitate was collected by vacuum filtration and washed thoroughly with MeCN. The solid was dissolved in H₂O (50 mL), followed by the addition of excess of NH₄PF₆, resulting in the precipitation of a white solid, which was collected by centrifugation, washed with H₂O several times and dried *in vacuo* to yield **BBP•2PF₆** as a white solid (4.6 g) in 90% yield. ^1H NMR (500 MHz, CD₃CN, 298 K) δ = 8.84 (d, J = 6.4 Hz, 4H), 8.76 (d, J = 6.4 Hz, 4H), 8.31 (d, J = 6.4 Hz, 4H), 7.79 (d, J = 6.4 Hz, 4H), 4.54 (t, J = 7.5 Hz, 4H), 1.99 (m, 4H), 1.37 (m, 8H). ^{13}C NMR (125 MHz, CD₃CN, 298 K) δ = 154.9, 152.0, 145.8, 142.2, 126.9, 122.7, 62.4, 31.7, 29.2, 26.3. ESI-HRMS calcd for [$M - \text{PF}_6$]⁺ m/z = 569.2263, found 569.2270.

g) BAV•4PF₆.

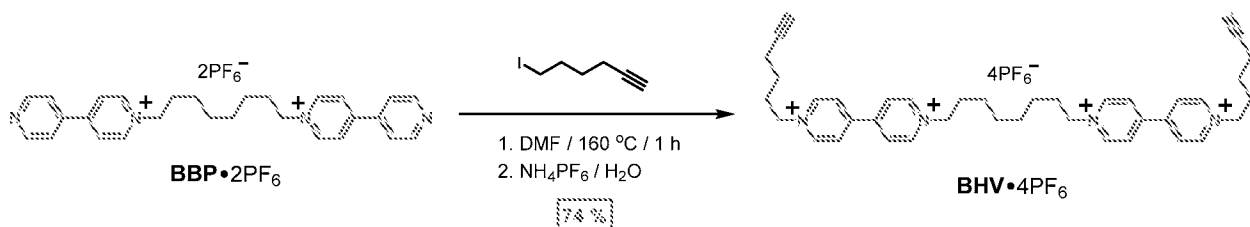
Scheme 10. Preparation of BAV



As depicted in Scheme 10, a mixture of **BBP•2PF₆** (130 mg, 0.18 mmol) and 2-azidoethyl 4-methylbenzenesulfonate¹ (200 mg, 0.83 mmol) in dry DMF (1.0 mL) was heated at 160 °C under N₂ for 1 h. The reaction mixture was cooled to room temperature, followed by the addition of an excess of a saturated solution of tetraethylammonium bromide in MeCN. The resulting precipitate was filtered off and washed thoroughly with MeCN. The solid was dissolved in H₂O (15 mL), followed by the addition of excess of NH₄PF₆, resulting in the precipitation of an off-white solid which was collected by centrifugation, washed with H₂O several times and dried *in vacuo* to yield **BAV•4PF₆** as an off-white solid (129 mg) in 62% yield. ¹H NMR (500 MHz, CD₃CN, 298 K) δ = 8.90 (m, 8H), 8.40 (m, 8H), 4.74 (t, *J* = 5.4 Hz, 4H), 4.61 (t, *J* = 7.5 Hz, 4H), 4.01 (t, *J* = 5.4 Hz, 4H), 2.02 (m, 4H), 1.40 (m, 8H). ¹³C NMR (125 MHz, CD₃CN, 298 K) δ = 151.5, 150.8, 147.1, 146.5, 128.2, 128.1, 63.1, 61.6, 51.2, 31.9, 29.3, 26.5, 23.1. ESI-HRMS calcd for [*M* – PF₆]⁺ *m/z* = 999.2356, found 999.2384.

h) BHV•4PF₆.

Scheme 11. Preparation of BHV



As depicted in Scheme 11, a mixture of **BBP•2PF₆** (150 mg, 0.21 mmol) and 6-iodo-1-hexyne (200 mg, 0.96 mmol) in dry DMF (1.0 mL) was heated at 160 °C under N₂ for 1 h. The reaction mixture was cooled to room temperature and suspended in MeCN (10 mL), followed by the addition of an excess of a saturated solution of tetraethylammonium bromide in MeCN. The resulting precipitate was filtered and washed thoroughly with MeCN. The solid was dissolved in H₂O (15 mL), followed by the addition of excess of NH₄PF₆, resulting in the precipitation of an off-white solid which was collected by centrifugation, washed with H₂O several times and dried

in vacuo to yield **BHV•4PF₆** as an off-white solid (180 mg) in 74% yield. ¹H NMR (500 MHz, CD₃CN, 298 K) δ = 8.90 (m, 8H), 8.38 (m, 8H), 4.65 (t, J = 7.6 Hz, 4H), 4.61 (t, J = 7.6 Hz, 4H), 2.29 (dt, J = 2.6 Hz, J = 7.0 Hz, 4H), 2.23 (t, J = 2.6 Hz, 2H), 2.13 (p, J = 7.6 Hz, 4H), 2.02 (m, 4H), 1.60 (p, J = 7.4 Hz, 4H), 1.40 (m, 8H). ¹³C NMR (125 MHz, CD₃CN, 298 K) δ = 151.0, 150.9, 146.5, 128.3, 128.2, 84.3, 70.6, 63.1, 62.6, 31.9, 31.1, 29.3, 26.5, 25.6, 18.3. ESI-HRMS calcd for $[M - \text{PF}_6]^+$ m/z = 1021.2955, found 1021.3019.

i) r[5]C•24PF₆.

As depicted in Scheme 4, an excess of Cu powder was added to a solution of **BAV•4PF₆** (7 mg, 6.1 nmol) and **CBPQT•4PF₆** (27 mg, 24.5 nmol) dissolved in dry MeCN (6 mL) in an N₂-filled glovebox. In a separate flask, **BHV•4PF₆** (7.1 mg, 6.1 nmol) and **CBPQT•4PF₆** (27 mg, 24.5 nmol) were dissolved in dry MeCN (6 mL) and subjected to an excess of Cu powder. The two solutions were stirred at room temperature for 2 h before being mixed together quickly in another reaction flask. The reaction mixture was stirred at room temperature in the inert environment of a N₂-filled glovebox for 4 days. The resulting dark purple mixture was filtered inside the glovebox and NOPF₆ was added in small aliquots to the filtrate until the dark purple solution turned clear. The resulting solution was taken out of the glovebox and solvent was removed by rotary evaporation. The residue was purified using reverse-phase flash chromatography (C₁₈: water/MeCN 0.1% TFA 0-100%), followed by anion exchange from TFA⁻ to PF₆⁻ by treating the aqueous fractions with an excess of NH₄PF₆, resulting in a white precipitate which was collected by centrifugation and washed with H₂O several times before being dried *in vacuo* to yield an off-white solid (14.8 mg, 36 %). ¹H NMR (500 MHz, CD₃CN, 298 K) δ = 9.28 (d, J = 6.8 Hz, 4H), 9.13–9.05 (br, 22H), 8.96 (d, br, 8H), 8.88 (br, 2H), 8.82 (br, 4H), 8.77 (d, J = 6.3 Hz, 2H), 8.46 (d, J = 6.7 Hz, 8H), 7.98 (d, J = 6.7 Hz, 8H), 7.66 (s, 16H), 7.48 (s, 8H), 7.47 (s, 8H), 5.81 (s, 8H), 5.79 (s, 8H), 5.78 (s, 16H), 5.37 (s, 2H), 5.21 (t, J = 6.5 Hz, 4H), 4.68 (t, J = 6.5 Hz, 4H), 4.60–4.51 (m, br, 6H), 1.43 (p, J = 7.7 Hz, 4H), 0.85 (p, J = 7.7 Hz, 4H), 0.79 (p, J = 7.7 Hz, 4H), –0.15 (p, J = 7.7 Hz, 4H), (–0.49) – (–0.63) (m, br, 8H), –2.37 (m, br, 4H), –2.41 (m, br, 4H). ¹³C NMR (125 MHz, CD₃CN, 298 K) δ = 152.2, 151.5, 151.1, 151.1, 149.2 (x2), 148.7, 147.5, 146.8, 146.5, 146.4, 146.3, 143.7, 137.1, 137.0 (x2), 131.4, 131.2, 128.8, 128.5, 127.9, 127.2, 122.2, 68.7, 65.9, 65.7, 62.1 (x2), 62.0, 60.0, 49.6, 32.0, 31.6, 31.4, 28.8 (x2), 26.6, 26.5, 24.1, 23.6. High-resolution ESI-MS calcd m/z = 2092.6833 $[M - 3\text{PF}_6]^3+$, found 2092.6853, m/z = 1533.2713 $[M - 4\text{PF}_6]^4+$, found 1533.2693, m/z = 1197.6241 $[M - 5\text{PF}_6]^5+$, found 1197.6225.

Analytical HPLC Analysis

HPLC was performed as described in the methods. The HPLC traces of the compounds **TB**•4PF₆ and **[3]C**•12PF₆ are shown in FIG 8A and FIG 8B, respectively.

Crystallographic Characterization

In a typical data collection, a suitable crystal was selected and mounted in inert oil and transferred to the cold gas stream of a Bruker Kappa APEX CCD area detector diffractometer. The crystal was kept at 100.0 K during data collection. Using Olex2,² the structure was solved with the XT³ structure solution program employing Dual Space and refined with the XL⁴ refinement package using least squares minimization. The coordinates of the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the calculation isotropically but not refined. The crystallographic information, structural parameters, and additional refinement details for **TB**•4PF₆, **[AVC**BPQT]**•3PF**₆, **[3]C**•12PF₆, **[3]C**•6PF₆, and **r[5]C**•24PF₆ are given below.

a) **TB**•4PF₆

Method. Single crystals of **TB**•4PF₆ were grown by slow diffusion of *i*Pr₂O vapor into a solution of **TB**•4PF₆ in MeCN over the course of three days.

Crystal Parameters. C₃₆H₄₂F₂₄N₁₀P₄. Clear block (0.255 × 0.117 × 0.090 mm). Monoclinic, *C* 2/*m*, *a* = 12.5832(9), *b* = 26.390(2), *c* = 17.5713(13) Å, α = 90, β = 96.326(4), γ = 90°, *V* = 5799.4(7) Å³, *Z* = 4, *T* = 100(2) K, ρ_{calc} = 1.534 g cm⁻³, μ = 0.292 mm⁻¹. Of a total of 38804 reflections which were collected, 5302 were unique (*R*_{int} = 0.0618). Final *R*₁ (*F*² > 2σ*F*²) = 0.0657 and *wR*₂ = 0.2047 (all data). CCDC deposition number 1828432.

Refinement Details. The two bipyridinium units within one **TB**⁴⁺ macrocycle were found to be crystallography equivalent while there is disorder found for the two 1-(1-(ethylene)-1*H*-1,2,3-triazole-4-yl)butylene linkers, which have been modeled over two sites with a 50% occupancy for each site. The solvent-masking procedure, as implemented in Olex2, was used to remove the electronic contributions of heavily disordered solvent molecules from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported here in the formula. Total solvent accessible volume / cell = 206.1 Å³ [3.6%]. Three of the four PF₆⁻ anions were modeled over two positions and their anisotropic displacement parameters were refined using SIMU and DELU restraints.⁵

b) [AV $\subset$ CBPQT]•3PF₆

Method. Single crystals of the trisradical tricationic complex [AV $\subset$ CBPQT]•3PF₆ – a [2]pseudorotaxane – were grown in a glovebox under positive N₂ by treating a solution of 1:1 HV•2PF₆/ CBPQT•4PF₆ in MeCN with Cu powder for 1 h, followed by filtration of the resulted purple solution through a 0.2- μ m filter into a culture tube. Thereafter, slow diffusion of *i*Pr₂O vapor into the MeCN solution was allowed to happen over the course of 2 days under nitrogen atmosphere. A rod-like crystal was picked out, quickly mounted using paratone oil (Infineum V8512) on a microloop and flash frozen under a continuous cold stream of nitrogen gas.

Crystal Parameters. C₅₄H₅₄F₁₈N₁₄P₃. Dark block (0.203 $\times$ 0.114 $\times$ 0.084 mm). Triclinic, $P\bar{1}$, $a = 9.7754(13)$, $b = 11.0040(14)$, $c = 14.024(2)$ Å, $\alpha = 73.827(3)$, $\beta = 76.518(3)$, $\gamma = 80.565(3)^\circ$, $V = 1401.0(3)$ Å³, $Z = 1$, $T = 100(2)$ K, $\rho_{\text{calc}} = 1.581$ g cm⁻³, $\mu = 0.220$ mm⁻¹. Of a total of 17383 reflections which were collected, 4757 were unique ($R_{\text{int}} = 0.0286$). Final R_1 ($F^2 > 2\sigma F^2$) = 0.0343 and $wR_2 = 0.0839$ (all data). No disorder was observed in the sample; no restraints were used in the refinement.

c) [3]C•12PF₆

Method. Single crystals of [3]C•12PF₆ were grown by slow diffusion of *i*Pr₂O vapor into a solution of [3]C•12PF₆ in MeCN under ambient conditions at room temperature over the course of four days.

Crystal Parameters. C₁₁₂H₁₁₂F₇₂N₂₀P₁₂. Colorless block (0.117 $\times$ 0.083 $\times$ 0.074 mm). Triclinic, $P\bar{1}$, $a = 13.0318(3)$, $b = 17.5225(5)$, $c = 20.1997(6)$ Å, $\alpha = 64.483(2)$, $\beta = 89.085(2)$, $\gamma = 72.334(2)$, $V = 3930.9(2)$ Å³, $Z = 1$, $T = 100(2)$ K, $\rho_{\text{calc}} = 1.469$ g cm⁻³, $\mu = 0.264$ mm⁻¹. Of a total of 44829 reflections which were collected, 13817 were unique ($R_{\text{int}} = 0.0471$). Final R_1 ($F^2 > 2\sigma F^2$) = 0.1232 and $wR_2 = 0.3963$ (all data). CCDC deposition number 1828429.

Refinement Details. The two CBPQT⁴⁺ macrocycles as well as the two bipyridinium units of the central macrocycle (TB⁴⁺) in [3]C¹²⁺ were found to be crystallography equivalent with an inversion center at the centroid of the TB⁴⁺ ring. As such, the 1-(1-(ethylene)-1*H*-1,2,3-triazole-4-yl)butylene linkers of the TB⁴⁺ macrocycle were found to be disordered and were modeled over two positions with half-occupancy. The solvent-masking procedure, as implemented in Olex2, was used to remove the electronic contributions of heavily disordered solvent molecules from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported here in the formula. Total solvent accessible volume / cell = 109.2 Å³ [2.8%]. Three

of the six PF_6^- anions in the asymmetric unit were modeled over two positions and their anisotropic displacement parameters were refined using SIMU and DELU restraints.⁵ Stick representations of the solid-state structure of **[3]C•12PF₆** are shown in FIG 2A-2C and space-filling representations of the superstructure are shown in FIG 2D-2J. As the result of being interlocked in a [3]catenane, the two crystallography equivalent **CBPQT⁴⁺** macrocycles exhibit much smaller torsional angles (mean angle = 17.1°) of the bipyridinium units compared to either those found in the non-interlocked **CBPQT⁴⁺** structure (torsional angle = 39.8°)⁶ or the **BIPY^{•+}** units within the non-interlocked **TB⁴⁺** (torsional angle = 72.8°).

d) **[3]C•6PF₆**

Method. The hexaradical hexacationic **[3]C^{6(•+)}** [3]catenane was obtained by treating a solution of its oxidized form **[3]C•12PF₆** in MeCN with Zn dust for 20 minutes in a glovebox under positive N_2 . The purple solution was filtered through a 0.2- μm filter into a culture tube to remove the excess of zinc dust and single crystals of **[3]C•6PF₆** were grown by slow diffusion of $i\text{Pr}_2\text{O}$ vapor into the MeCN solution over the course of 1 week under a nitrogen atmosphere at room temperature. A plate-shape crystal was picked out, quickly mounted using paratone oil (Infineum V8512) on a microloop and flash frozen under a continuous cold stream of nitrogen gas.

Crystal Parameters. $\text{C}_{108}\text{H}_{80}\text{F}_{36}\text{N}_{18}\text{P}_6$. Dark purple plate ($0.116 \times 0.098 \times 0.057$ mm). Triclinic, $P\bar{1}$, $a = 13.7572(11)$, $b = 19.6568(17)$, $c = 24.923(2)$ Å, $\alpha = 112.045(7)$, $\beta = 103.053(7)$, $\gamma = 91.634(7)$, $V = 6037.5(9)$ Å³, $Z = 2$, $T = 100(2)$ K, $\rho_{\text{calc}} = 1.375$ g cm⁻³, $\mu = 1.792$ mm⁻¹. Of a total of 31109 reflections which were collected, 9216 were unique ($R_{\text{int}} = 0.0528$). Final R_1 ($F^2 > 2\sigma F^2$) = 0.1326 and $wR_2 = 0.4126$ (all data). CCDC deposition number 1828430.

Refinement Details. The two 1-(1-(ethylene)-1*H*-1,2,3-triazole-4-yl)butylene linkers of the **TB^{2(•+)}** macrocycle within the structure of **[3]C^{6(•+)}** were found to be disordered and were modeled over two positions with half-occupancy. The solvent-masking procedure, as implemented in Olex2, was used to remove the electronic contributions of heavily disordered solvent molecules from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported here in the formula. Total solvent accessible volume / cell = 61.88 Å³ [1.0%]. Three of the six PF_6^- anions were modeled over two positions and their anisotropic displacement parameters were refined using SIMU and DELU restraints.⁵

On account of the poor diffraction power of the crystal (resolution of 1.11 Å) and the disorders of both the 1-(1-(ethylene)-1*H*-1,2,3-triazole-4-yl)butylene linkers and three of the PF_6^-

anions, the CheckCif gives 3 A and 8 B alerts. All A alerts result from the poor scattering of the crystal while the B alerts are due to the disorders of the structure components. Stick representations of the X-ray crystal structure of **[3]C•6PF₆** are shown in FIG 4B-4D and space-filling representations of the superstructure are shown in FIG 4F-4J.

5 **e) **r**[5]C•24PF₆**

Method. Single crystals of **r**[5]C•24PF₆ were grown by slow diffusion of *i*Pr₂O vapor into a solution of **r**[5]C•24PF₆ in MeCN under ambient conditions at room temperature over the course of a week.

Crystal Parameters. C₂₄₈H₂₆₄F₁₃₂N₄₆P₂₂. Colorless block (0.444 × 0.179 × 0.173 mm).
10 Triclinic, $P\bar{1}$, $a = 12.349(14)$, $b = 27.43(3)$, $c = 28.24(3)$, $\alpha = 117.225(18)$, $\beta = 92.74(2)$, $\gamma = 100.084(19)^\circ$, $V = 8285(17) \text{ \AA}^3$, $Z = 1$, $T = 100.0 \text{ K}$, $\mu(\text{MoK}\alpha) = 0.238 \text{ mm}^{-1}$, $\rho_{\text{calc}} = 1.419 \text{ g/cm}^3$, 72212 reflections measured ($1.64^\circ \leq 2\theta \leq 45.44^\circ$), 21338 unique ($R_{\text{int}} = 0.0781$, $R_{\text{sigma}} = 0.0890$) which were used in all calculations. The final R_1 was 0.1371 ($I > 2\sigma(I)$) and wR_2 was 0.4050 (all data). CCDC deposition number 1844970.

15 *Refinement Details.* Two sets of CBPQT⁴⁺ rings, as well as the bipyridinium units of the central ring (BTB⁸⁺), in **r**[5]C²⁴⁺ were found to be crystallography equivalent with an inversion center at the centroid of the BTB⁸⁺ ring. The 1-(1-(ethylene)-1*H*-1,2,3-triazole-4-yl)butylene linkers of the BTB⁸⁺ ring were found to be disordered and were modeled over two positions with half-occupancy. The solvent-masking procedure, as implemented in Olex2,² was used to remove
20 the electronic contributions of one PF₆[−] counterion and solvent molecules, which were found to be heavily disordered and could not be refined satisfactorily, from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported here in the formula. Total solvent accessible volume / cell = 364.85 Å³ [4.4%]. Three of the 12 PF₆[−] counterions in the asymmetric unit were modeled over two positions and their anisotropic displacement
25 parameters were refined using SIMU and DELU restraints.⁵ Solid-state structures of **r**[5]C²⁴⁺ are shown in FIG 6A-6C and space-filling representations of the superstructure of **r**[5]C•24PF₆ are shown in FIG 6D-6E.

UV-Vis-NIR Absorption Spectroscopy

UV-Vis-NIR spectroscopy was performed as described in the methods. UV-Vis-NIR
30 spectra of all radical intermediates during the synthesis of dodecacationic [3]catenane, **[3]C¹²⁺** (Scheme 1) were obtained (data not shown). The radical species **AV^(•+)**, **HV^(•+)**, and **CBPQT^{2(•+)}**

were obtained by treating their oxidized forms (HV^{2+} , AV^{2+} , and CBPQT^{4+} , respectively) either with copper powder for 1 h or with activated zinc dust for 20 min under inert atmosphere. The two [2]pseudorotaxanes $[\text{AV}\subset\text{CBPQT}]^{3(++)}$ and $[\text{HV}\subset\text{CBPQT}]^{3(++)}$ were prepared either by mixing their two corresponding radical cations ($\text{AV}^{(++)} + \text{CBPQT}^{2(++)}$ and $\text{HV}^{(++)} + \text{CBPQT}^{2(++)}$, respectively) in 1 : 1 ratio or by treating the corresponding oxidized components with copper powder/zinc dust under inert atmosphere. $[\text{3}]\text{C}^{6(++)}$ was obtained by treating the purified $[\text{3}]\text{C}^{12+}$ with copper powder for an hour or with zinc dust for 20 min under inert atmosphere. The concentration of all solutions used in these UV-Vis-NIR measurements is 0.05 mM in MeCN. The reduction was carried out inside a N_2 -filled glove box while the UV-Vis-NIR measurements were performed outside the glovebox using an airtight cuvette.

UV-Vis-NIR spectra were obtained during reversible switching between the fully oxidized $[\text{3}]\text{C}^{12+}$ and the reduced-state $[\text{3}]\text{C}^{6(++)}$ [3]catenanes using chemical stimuli. UV-Vis-NIR Spectra of the two [3]catenane $[\text{3}]\text{C}^{12+}$ and $[\text{3}]\text{C}^{6(++)}$ states are shown in FIG 3B-3D. The switching between the two states was repeated five times starting with $[\text{3}]\text{C}^{12+}$. In one cycle, a spectrum of the $[\text{3}]\text{C}\cdot 12\text{PF}_6$ solution (1.5 mL / 0.03 mM in MeCN) was recorded before being treated with zinc dust for 20 min, filtered through a 0.2- μm filter and subjected to the UV-vis-NIR measurement for the resulting reduced [3]catenane. The re-oxidization of the $[\text{3}]\text{C}^{6(++)}$ back to $[\text{3}]\text{C}^{12+}$ was achieved by using NOPF_6 (which takes place in less than 3 s) to complete one cycle. Absorption intensities of $[\text{3}]\text{C}^{12+}$ (blue) and $[\text{3}]\text{C}^{6(++)}$ (purple) at 1162 nm wavelength showing the reversible switching between the two states during each cycle are shown in FIG 3C, and absorption intensity of $[\text{3}]\text{C}^{12+}$ (blue) and $[\text{3}]\text{C}^{6(++)}$ (purple) at 272 nm recorded during each cycle are shown in FIG 3D.

UV-Vis-NIR spectra were also obtained of radical intermediates form in the synthesis of $\text{r}[\text{5}]\text{C}^{24+}$, (data not shown), and of $\text{r}[\text{5}]\text{C}^{12(++)}$ and $\text{r}[\text{5}]\text{C}^{24+}$ generated by the reduction of $\text{r}[\text{5}]\text{C}\cdot 24\text{PF}_6$ with Zn dust, followed by a re-oxidation of the reduced state $\text{r}[\text{5}]\text{C}^{12(++)}$ by NOPF_6 , respectively, shown in FIG 7A.

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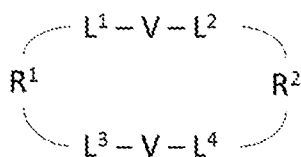
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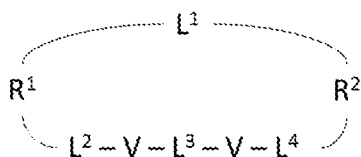
CLAIMS

We claim:

1. A cationic catenane comprising a central cationic ring and two or more radial cationic rings mechanically interlocked with the central cationic ring, wherein the central cationic ring comprises two or more viologen subunits and two reactive linkers and wherein the catenane comprises an equal number of radial cationic rings as viologen subunits.
2. The catenane of claim 1, wherein each of the radial cationic rings comprise cyclobis(paraquat-p-phenylene) (CBPQT).
3. The catenane of claim 1, wherein the central cationic ring comprises two, three, or four viologen subunits.
4. The catenane of claim 3, wherein the central cationic ring comprises two viologen subunits.
5. The catenane of claim 4, wherein the central cationic ring comprises

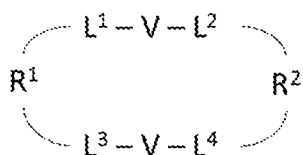


wherein V is a viologen subunit, R¹ and R² are reactive linkers formed by a click reaction, and L¹, L², L³, and L⁴ are independently selected from an alkyl, an alkenyl, an aryl, an alkylaryl, a triazole, or an alkyltriazole or



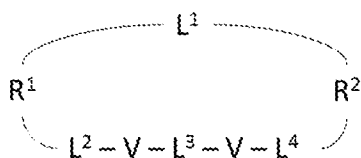
wherein V is a viologen subunit, R¹ and R² are reactive linkers formed by a click reaction, and L¹, L², L³, and L⁴ are independently selected from an alkyl, an alkenyl, an aryl, an alkylaryl, a triazole, or an alkyltriazole.

6. The catenane of claim 5, wherein the central cationic ring comprises



and wherein either or both of $\text{L}^1\text{-R}^1\text{-L}^3$ and $\text{L}^2\text{-R}^2\text{-L}^4$ comprise a continuous bridge of 8, 9, 10, 11, or 12 atoms between viologen subunits.

7. The catenane of claim 5, wherein the central cationic ring comprises



and wherein either or both of $\text{L}^2\text{-R}^1\text{-L}^1\text{-R}^2\text{-L}^4$ and L^3 each independently comprise a continuous bridge of 8, 9, 10, 11, or 12 atoms between viologen subunits.

8. The catenane of any one of claims 5-7, wherein (i) each of the viologen subunits are in a dicationic oxidation state, (ii) each of the viologen subunits are in a radical-cationic oxidation state, or (iii) viologen subunits are in a combination of the dicationic oxidation state and the radical-cationic oxidation state.

9. The catenane of claim 8, wherein each of the viologen subunits are in the dicationic oxidation state.

10. The catenane of claim 9, wherein the catenane is a dodecacationic catenane ($\text{r}[3]\text{C}^{12+}$).

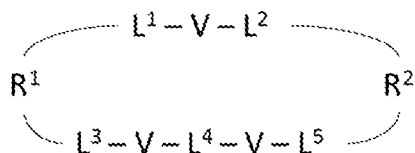
11. The catenane of any of claims 4-10, wherein each of the radial cationic rings comprise cyclobis(paraquat-p-phenylene) tetracation (CBPQT^{4+}).

12. The catenane of claim 8, wherein each of the viologen subunits are in the radical-cationic oxidation state.

13. The catenane of claim 9, wherein the catenane is a hexaradical/hexacationic catenane ($\text{r}[3]\text{C}^{6(•+)}$).

14. The catenane of any of claims 4-8 or 12-13, wherein each of the radial cationic rings comprise cyclobis(paraquat-p-phenylene) bisradical dication ($\text{CBPQT}^{2(•+)}$).

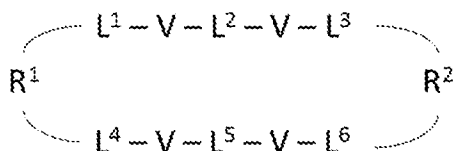
15. The catenane of claim 8, wherein the viologen subunits are in the combination of the dicationic oxidation state and the radical-cationic oxidation state.
16. The catenane of claim 3, wherein the central cationic ring comprises three viologen subunits.
- 5 17. The catenane of claim 4, wherein the central cationic ring comprises



wherein V is a viologen subunit, R^1 and R^2 are reactive linkers formed by a click reaction, and L^1 , L^2 , L^3 , L^4 , and L^5 are independently selected from an alkyl, an alkenyl, an aryl, an alkylaryl, a triazole, or an alkyltriazole.

- 10 18. The catenane of claim 17, wherein any or all of L^1 - R^1 - L^3 , L^4 , and L^2 - R^2 - L^5 comprise a continuous bridge of 8, 9, 10, 11, or 12 atoms between viologen subunits.
19. The catenane of any one of claims 16-18, wherein (i) each of the viologen subunits are in a dicationic oxidation state, (ii) each of the viologen subunits are in a radical-cationic oxidation state, or (iii) viologen subunits are in a combination of the dicationic oxidation state and the radical-cationic oxidation state.
- 15 20. The catenane of claim 19, wherein each of the viologen subunits are in the dicationic oxidation state.
21. The catenane of claim 20, wherein the catenane is an octodecacationic catenane ($\text{r}[4]\text{C}^{18+}$).
22. The catenane of any one of claims 16-21, wherein each of the radial cationic rings comprise cyclobis(paraquat-p-phenylene) tetracation (CBPQT^{4+}).
- 20 23. The catenane of claim 19, wherein each of the viologen subunits are in the radical-cationic oxidation state.
24. The catenane of claim 23, wherein the catenane is a nonaradical/nonacationic catenane ($\text{r}[4]\text{C}^{9(\bullet+)}$).

25. The catenane of any one of claims 16-19 or 23-24, wherein each of the radial cationic rings comprise cyclobis(paraquat-p-phenylene) bisradical dication (CBPQT²⁽⁺⁺⁾).
26. The catenane of claim 3, wherein the central cationic ring comprises four viologen subunits.
- 5 27. The catenane of claim 26, wherein the central cationic ring comprises



wherein V is a viologen subunit, R¹ and R² are reactive linkers formed by a click reaction, and L¹, L², L³, L⁴, L⁵, and L⁶ are independently selected from an alkyl, an alkenyl, an aryl, an alkylaryl, a triazole, or an alkyltriazole.

- 10 28. The catenane of claim 17, wherein any or all of L¹-R¹-L³, L², L⁵, and L³-R²-L⁶ each independently comprise a continuous bridge of 8, 9, 10, 11, or 12 atoms between viologen subunits.
29. The catenane of any one of claims 26-28, wherein (i) each of the viologen subunits are in a dicationic oxidation state, (ii) each of the viologen subunits are in a radical-cationic oxidation state, or (iii) viologen subunits are in a combination of the dicationic oxidation state and the radical-cationic oxidation state.
- 15 30. The catenane of claim 29, wherein each of the viologen subunits are in the dicationic oxidation state.
31. The catenane of claim 30, wherein the catenane is a tetracosacationic catenane (r[5]C²⁴⁺).
- 20 32. The catenane of any one of claims 26-31, wherein each of the radial cationic rings comprise cyclobis(paraquat-p-phenylene) tetracation (CBPQT⁴⁺).
33. The catenane of claim 19, wherein each of the viologen subunits are in the radical-cationic oxidation state.
34. The catenane of claim 23, wherein the catenane is a dodecaaradical/dodecacationic catenane (r[5]C¹²⁽⁺⁺⁾).
- 25

35. The catenane of any one of claims 16-19 or 23-24, wherein each of the radial cationic rings comprise cyclobis(paraquat-p-phenylene) bisradical dication (CBPQT²⁽⁺⁺⁾).
36. A composition comprising the catenane of claim 1.
37. The composition of claim 36 further comprising a counterion.
- 5 38. The composition of claim 37, wherein the composition has a molar ratio of the counterion to the catenane is greater than or equal to 6:1.
39. The composition of claim 37, wherein the composition has a molar ratio of the counterion to the catenane is greater than or equal to 12:1.
40. The composition of claim 38 or 39, wherein the molar ratio is 6:1, 9:1, 12:1, 18:1, or 24:1.
- 10 41. The composition of any one of claims 36-40, wherein the catenane is the catenane of any one of claims 2-35.
42. A crystalline composition comprising the catenane of claim 1.
43. The crystalline composition of claim 42, wherein the catenane further comprises a counterion.
- 15 44. The crystalline composition of claim 42 or 43, wherein the crystalline composition catenane comprises the catenane of any one of claims 2-35 or the composition of any one of claims 37-41.
45. A device comprising the catenane of any one of claim 1.
46. The device of claim 42, wherein the device is a switch, transistor, memory device,
20 electrochromic device, or redox-flow battery.
47. The device of claim 45 or 46, wherein the device comprises the catenane of any one of claims 2-35, the composition of any one of claims 36-41, or the crystalline composition of any one of claims 42-44.
48. A method of forming a cationic catenane, the method comprising:
25 providing a pseudorotaxane, the pseudorotaxane comprising:

a threading component having a first terminal moiety, a second terminal moiety, and two or more radical/cation viologen subunits between the first terminal moiety and the second terminal moiety and

two or more diradical/dicationic rings threaded by the threading component,

5 wherein the pseudorotaxane comprises an equal number of diradical/dicationic rings as viologen subunits; and

contacting the first terminal moiety with the second terminal moiety to form a central cationic ring that mechanically interlocks the two or more diradical/dicationic rings, thereby forming the catenane.

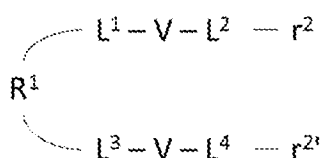
10 49. The method of claim 48, wherein each of the radial cationic rings comprise cyclobis(paraquat-p-phenylene) bisradical dication (CBPQT^{2(•+)}).

50. The method of claim 48 or 49 further comprising oxidizing the catenane.

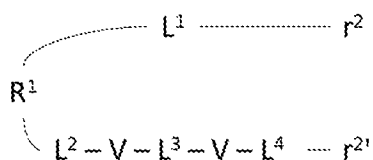
51. The method of claim 48, wherein the threading component comprises two, three, or four viologen subunits.

15 52. The method of claim 51, wherein the threading component comprises two viologen subunits.

53. The method of claim 52, wherein the threading component comprises

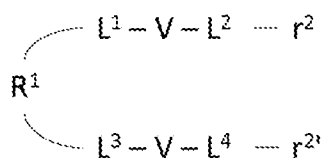


20 wherein V is a viologen subunit, R¹ is a reactive linker formed by a click reaction, r² is the first terminal moiety comprising a click-functionalized moiety, r^{2'} is the second terminal moiety comprising a corresponding click-functionalized moiety to the first terminal moiety, and L¹, L², L³, and L⁴ are independently selected from an alkyl, an alkenyl, an aryl, an alkylaryl, a triazole, or an alkyltriazole or



wherein V is a viologen subunit, R¹ is a reactive linker formed by a click reaction, r² is the first terminal moiety comprising a click-functionalized moiety, r^{2'} is the second terminal moiety comprising a corresponding click-functionalized moiety to the first terminal moiety, and L¹, L², L³, and L⁴ are independently selected from an alkyl, an alkenyl, an aryl, an alkylaryl, a triazole, or an alkyltriazole or

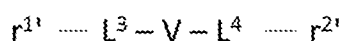
54. The method of claim 53, wherein the threading component comprises



55. The method of claim 54, wherein the threading component is prepared by contacting

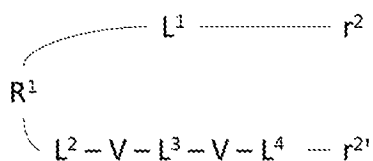


and

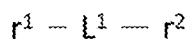


wherein r¹ is a terminal moiety comprising a click-functionalized moiety and r^{1'} is a corresponding click-functionalized moiety to r¹.

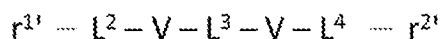
56. The method of claim 53, wherein the threading component comprises



57. The method of claim 54, wherein the threading component is prepared by contacting



and



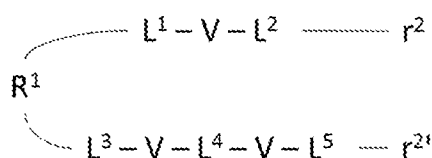
wherein r^1 is a terminal moiety comprising a click-functionalized moiety and $r^{1'}$ is a corresponding click-functionalized moiety to r^1 .

58. The method of any one of claims 52-57, wherein each of the radial cationic rings comprise cyclobis(paraquat-p-phenylene) bisradical dication (CBPQT^{2(•+)}).

59. The method of any one of claims 52-58 further comprising oxidizing the catenane.

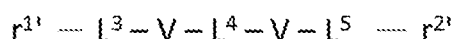
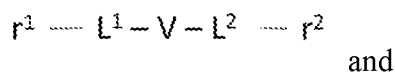
60. The method of claim 51, wherein the threading component comprises three viologen subunits.

61. The method of claim 60, wherein the threading component comprises



wherein V is a viologen subunit, R^1 is a reactive linker formed by a click reaction, r^2 is the first terminal moiety comprising a click-functionalized moiety, $r^{2'}$ is the second terminal moiety comprising a corresponding click-functionalized moiety to the first terminal moiety, and L^1 , L^2 , L^3 , L^4 , and L^5 are independently selected from an alkyl, an alkenyl, an aryl, an alkylaryl, a triazole, or an alkyltriazole.

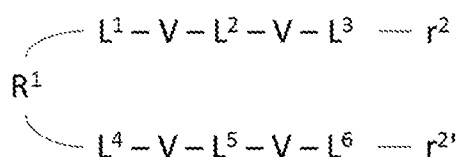
62. The method of claim 61, wherein the threading component is prepared by contacting



wherein r^1 is a terminal moiety comprising a click-functionalized moiety and $r^{1'}$ is a corresponding click-functionalized moiety to r^1 .

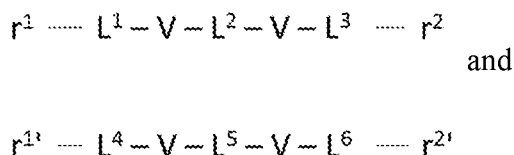
63. The method of any one of claims 60-62, wherein each of the radial cationic rings comprise cyclobis(paraquat-p-phenylene) bisradical dication (CBPQT^{2(•+)}).

64. The method of any one of claims 60-63 further comprising oxidizing the catenane.
65. The method of claim 51, wherein the threading component comprises four viologen subunits.
66. The method of claim 65, wherein the threading component comprises



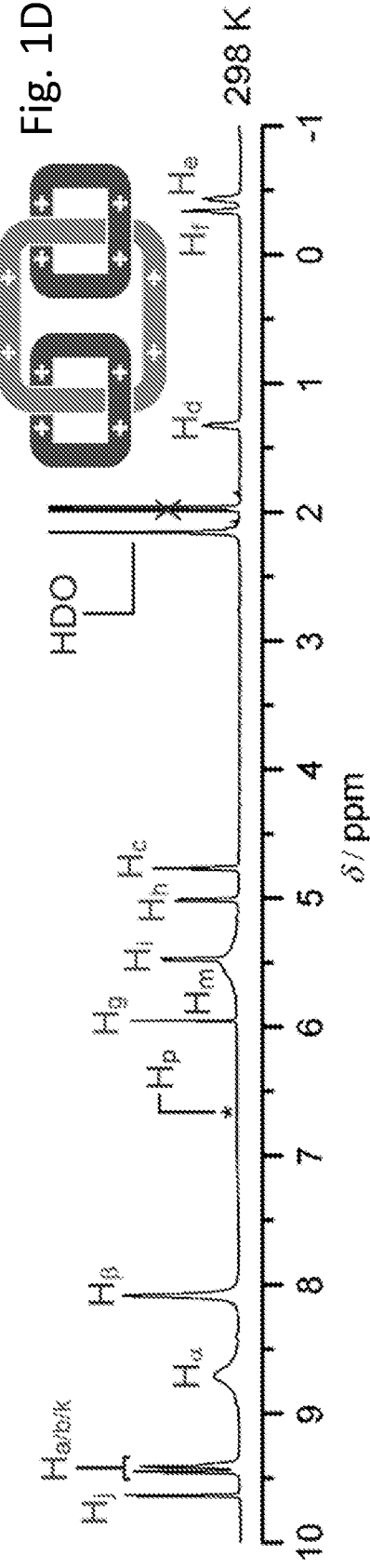
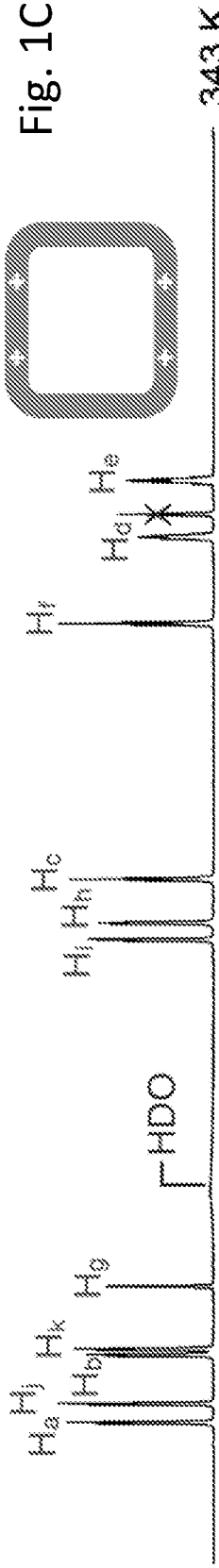
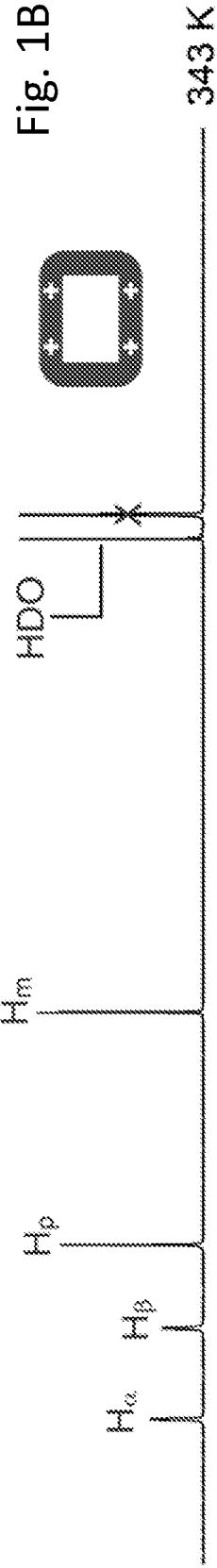
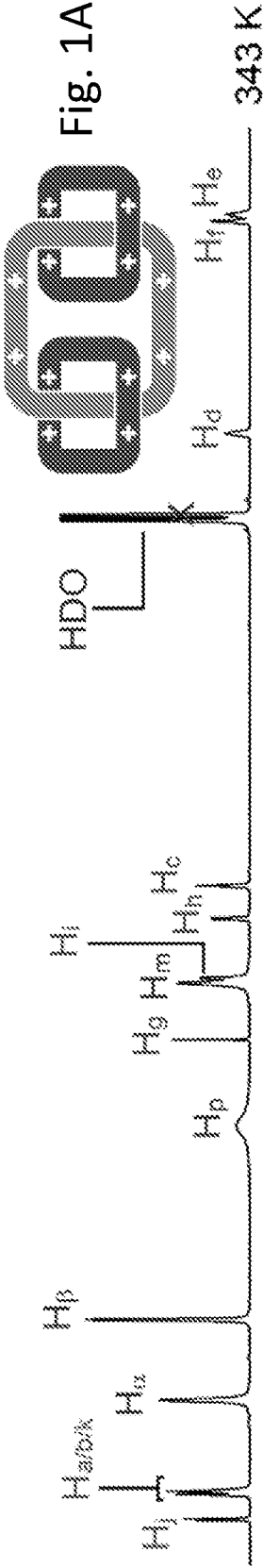
wherein V is a viologen subunit, R¹ is a reactive linker formed by a click reaction, r² is the first terminal moiety comprising a click-functionalized moiety, r^{2'} is the second terminal moiety comprising a corresponding click-functionalized moiety to the first terminal moiety, and L¹, L², L³, L⁴, L⁵, and L⁶ are independently selected from an alkyl, an alkenyl, an aryl, an alkylaryl, a triazole, or an alkyltriazole.

67. The method of claim 66, wherein the threading component is prepared by contacting



wherein r¹ is a terminal moiety comprising a click-functionalized moiety and r^{1'} is a corresponding click-functionalized moiety to r¹.

68. The method of any one of claims 65-67, wherein each of the radial cationic rings comprise cyclobis(paraquat-p-phenylene) bisradical dication (CBPQT²⁽⁺⁺⁾).
69. The method of any one of claims 65-68 further comprising oxidizing the catenane.



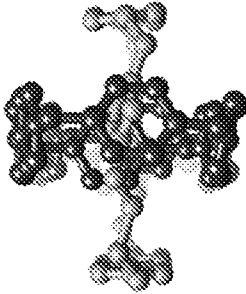


Fig. 2C

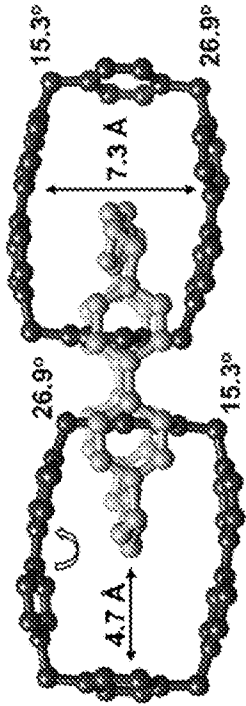


Fig. 2B

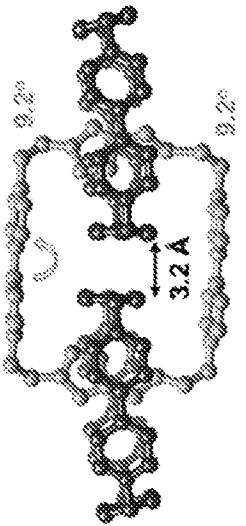


Fig. 2A

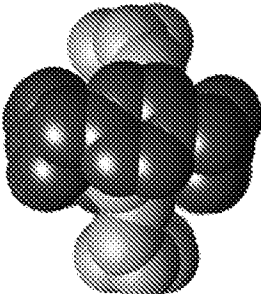


Fig. 2F

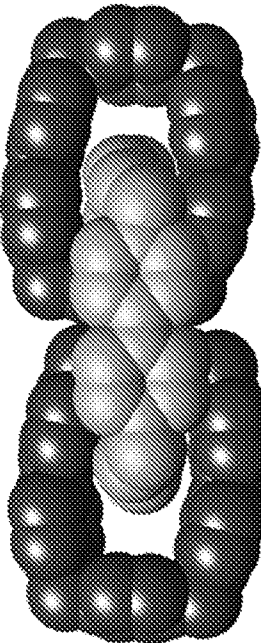


Fig. 2E

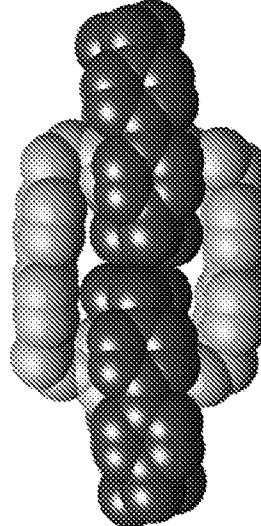


Fig. 2D

Fig. 2G

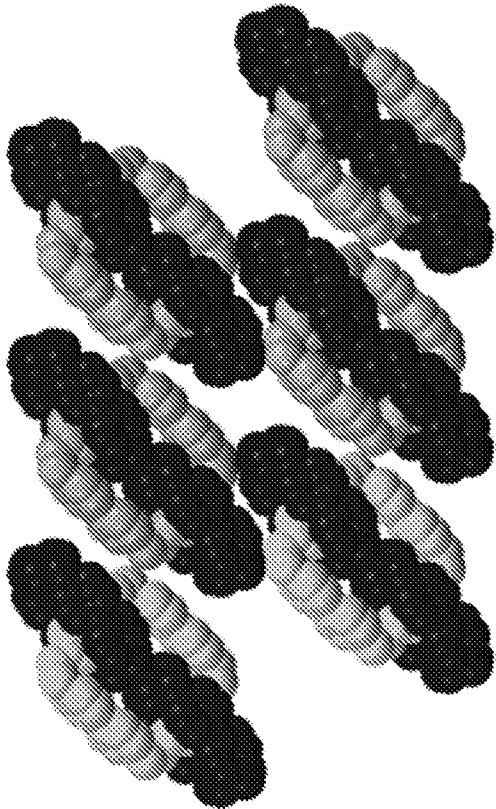


Fig. 2I

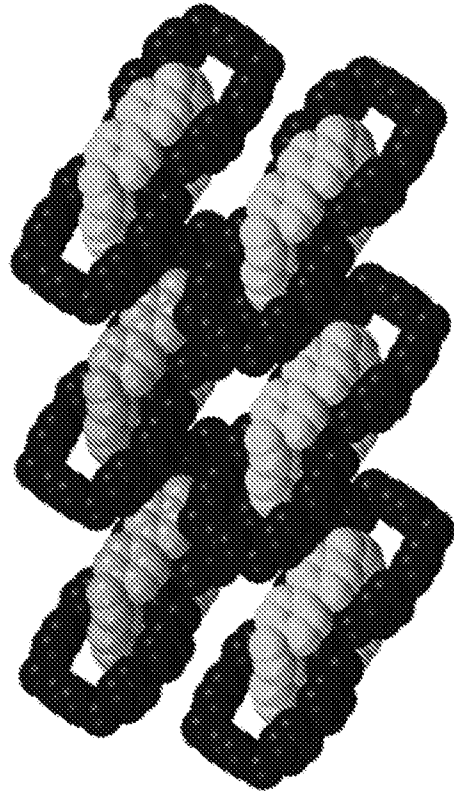


Fig. 2H

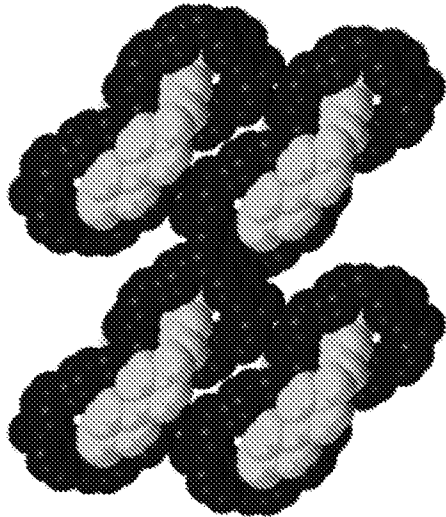


Fig. 2J

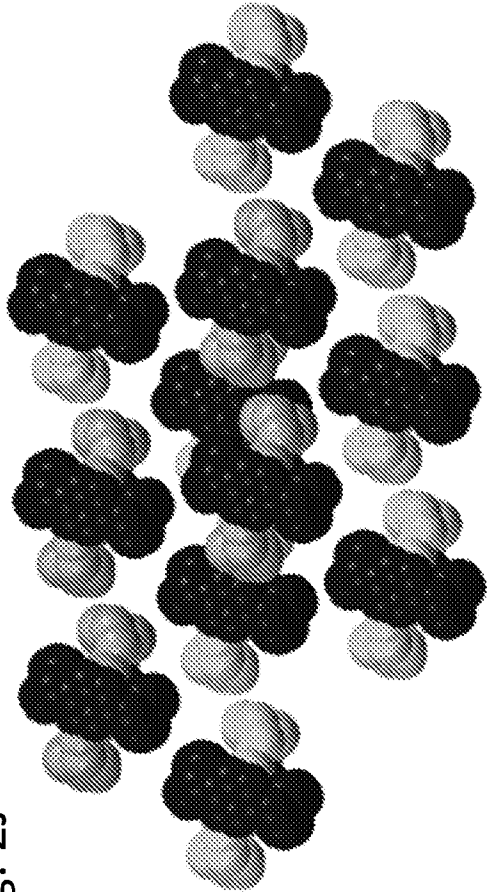


Fig. 3A

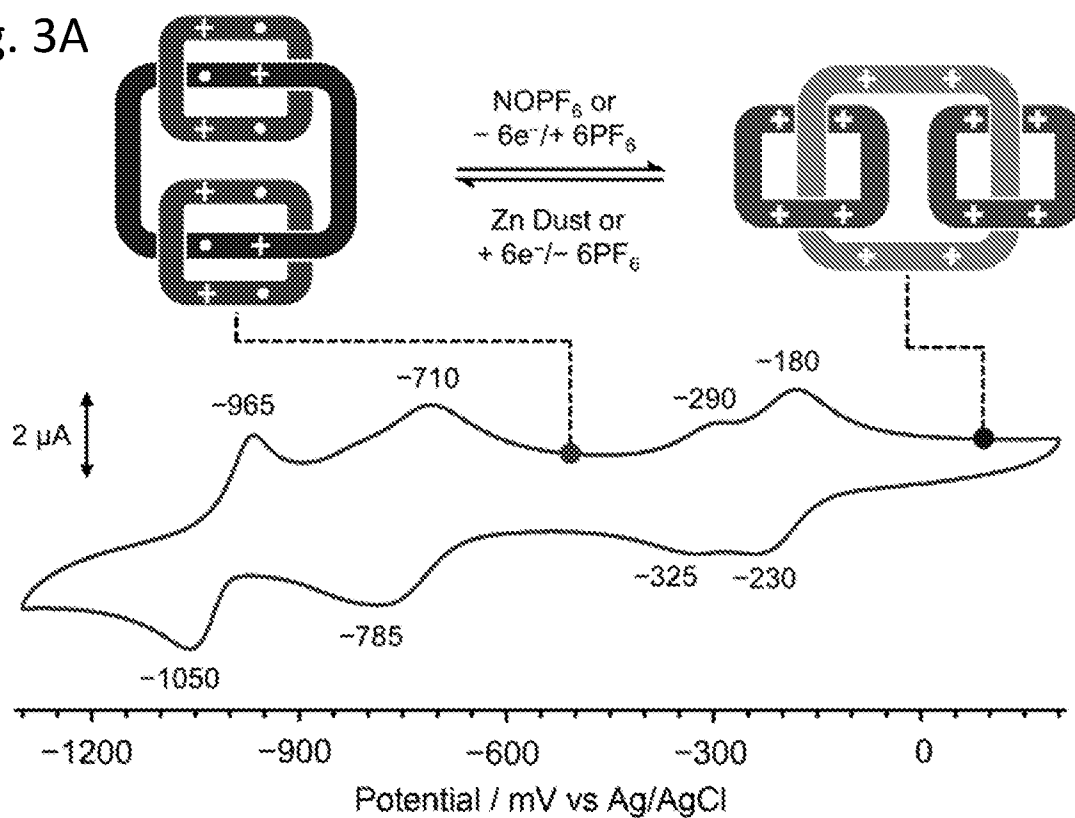


Fig. 3B

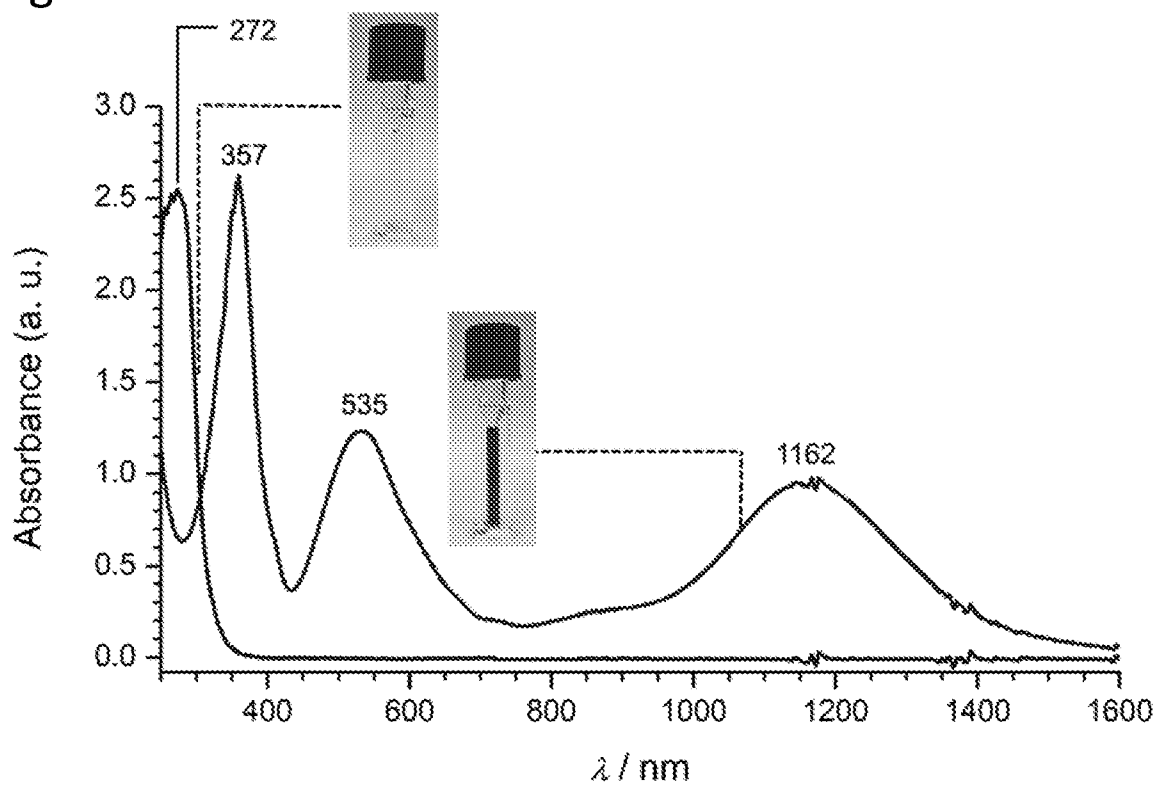


Fig. 3C

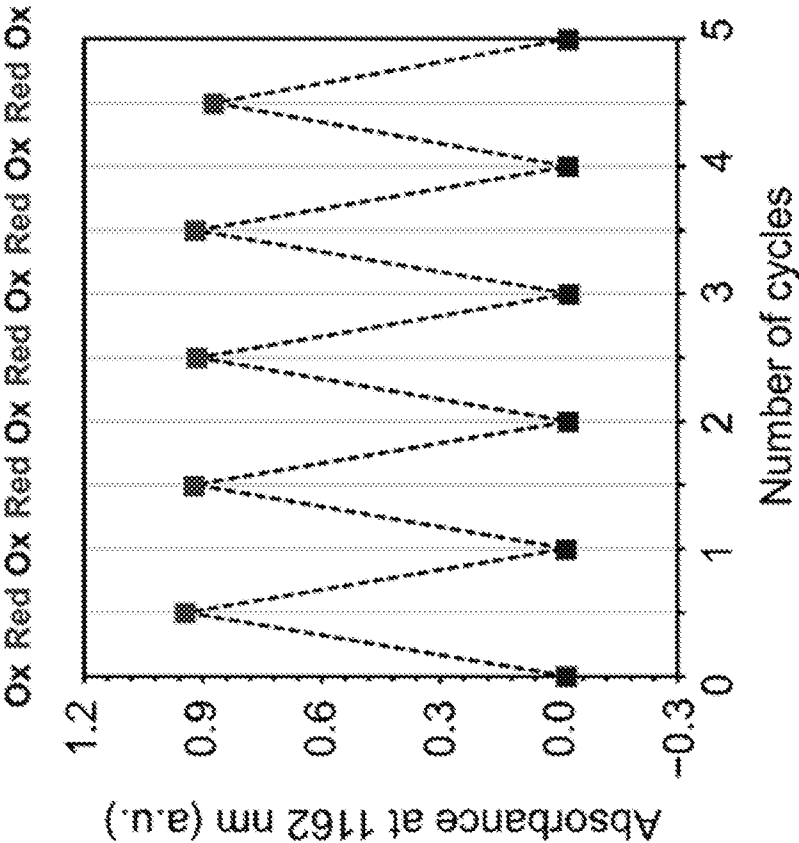


Fig. 3D

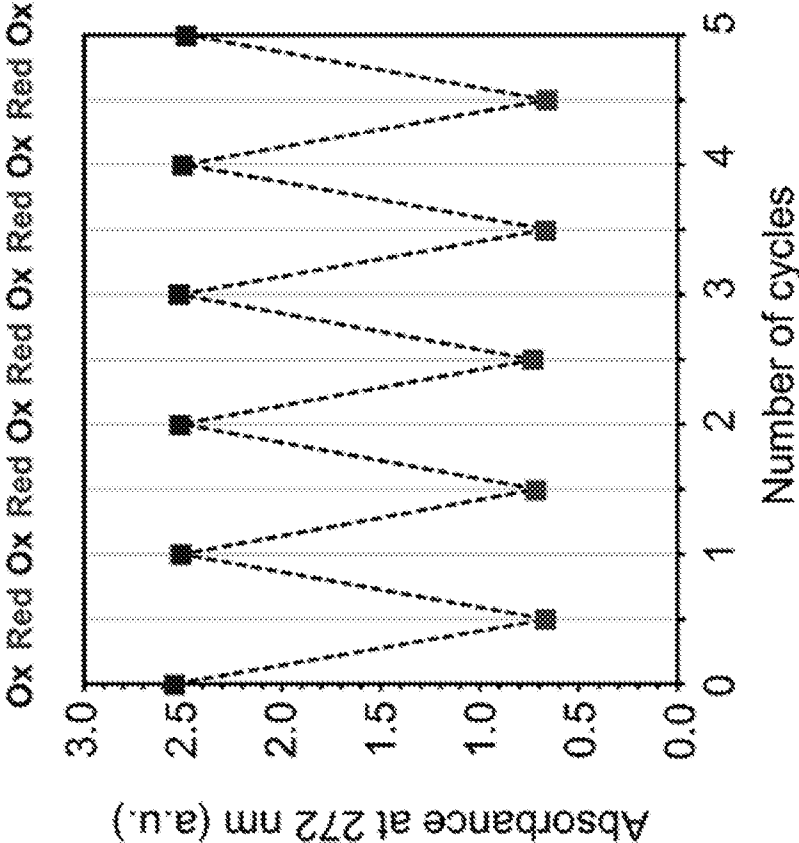
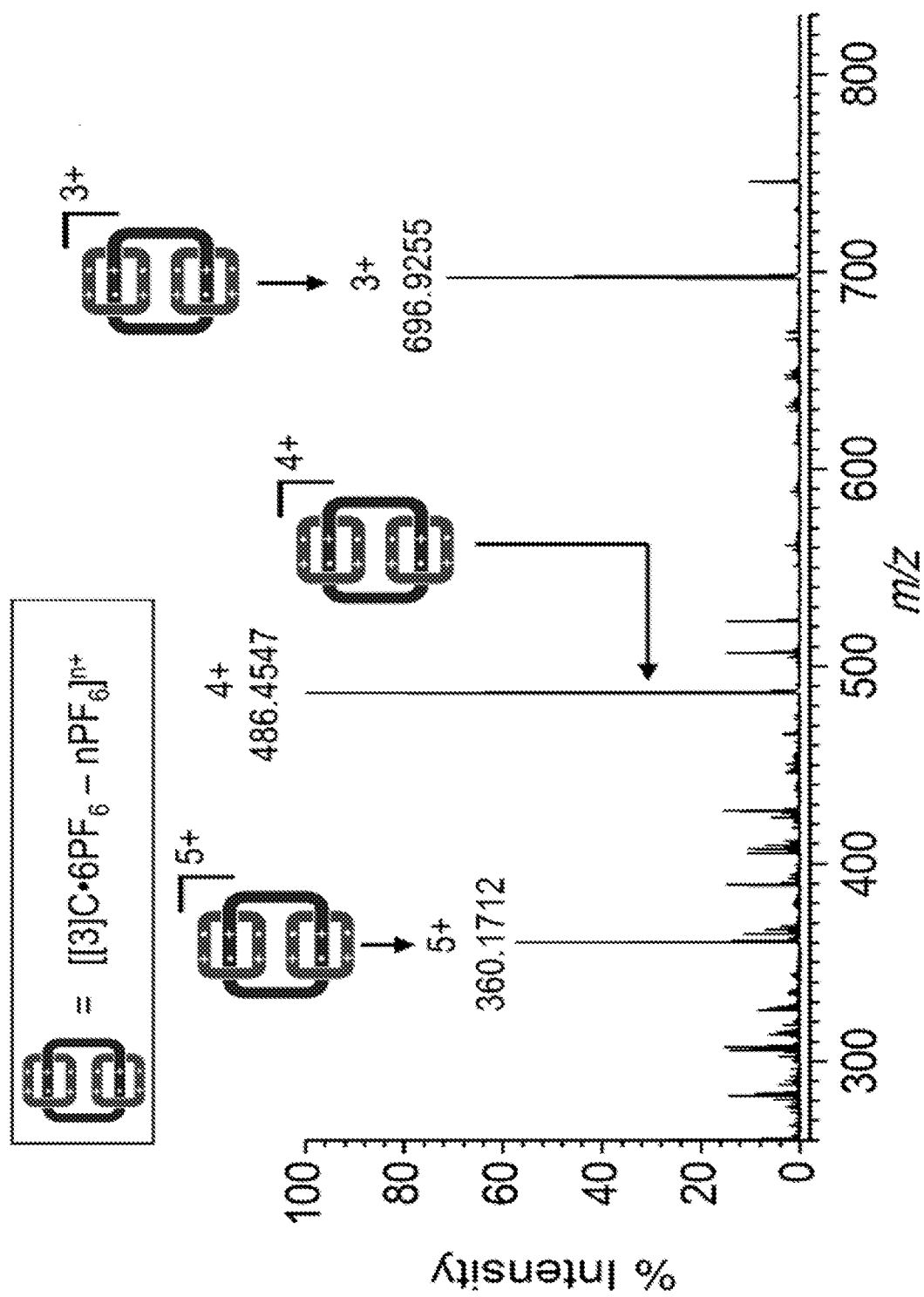


Fig. 4AI



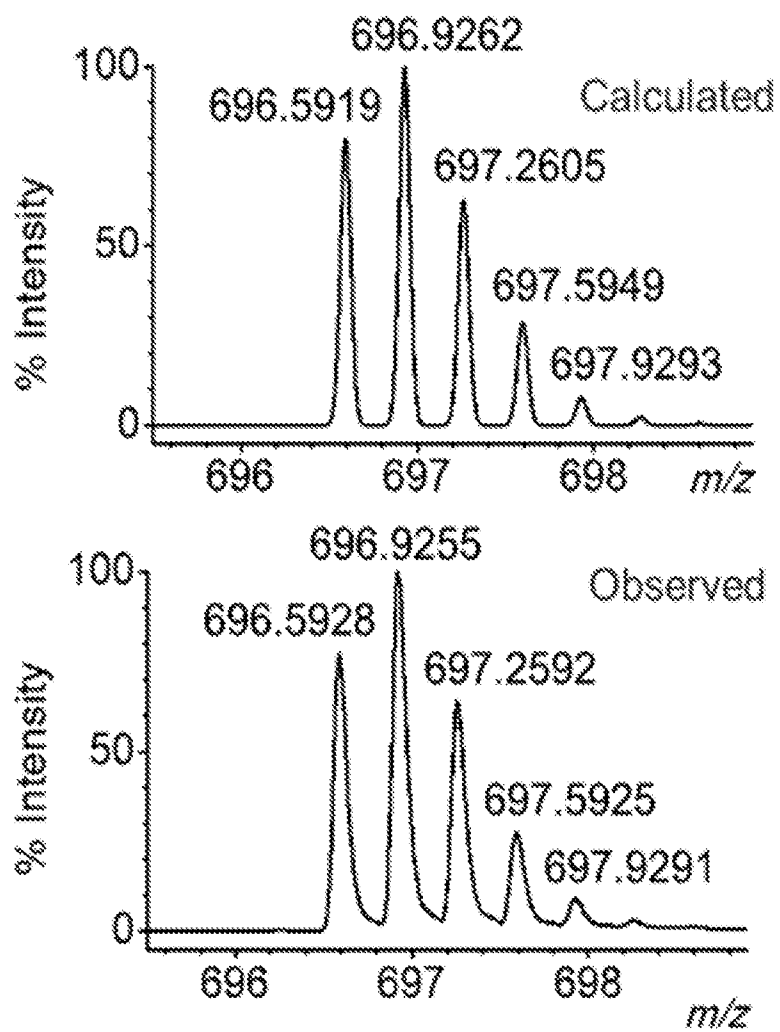


Fig. 4All

Fig. 4B

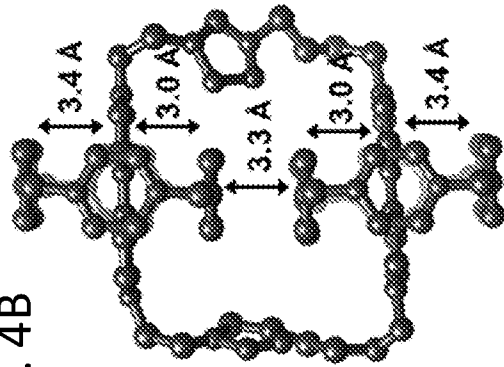


Fig. 4C

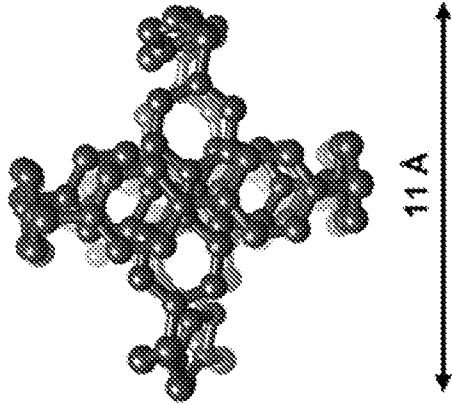


Fig. 4D

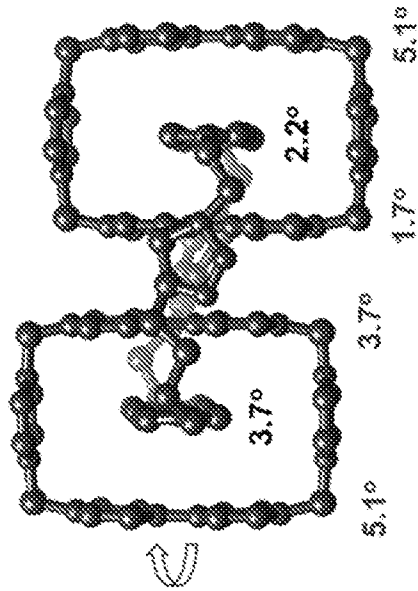


Fig. 4E

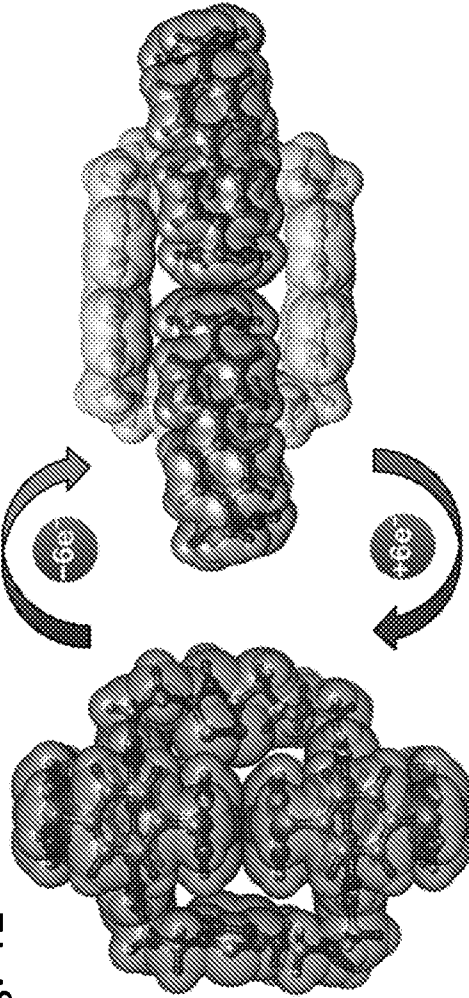


Fig. 4F

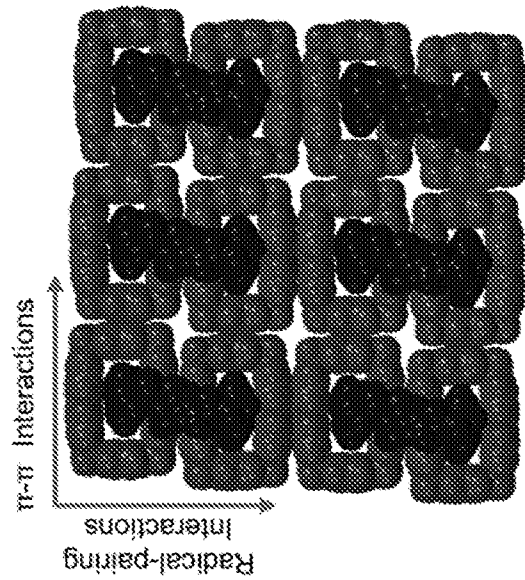


Fig. 4G

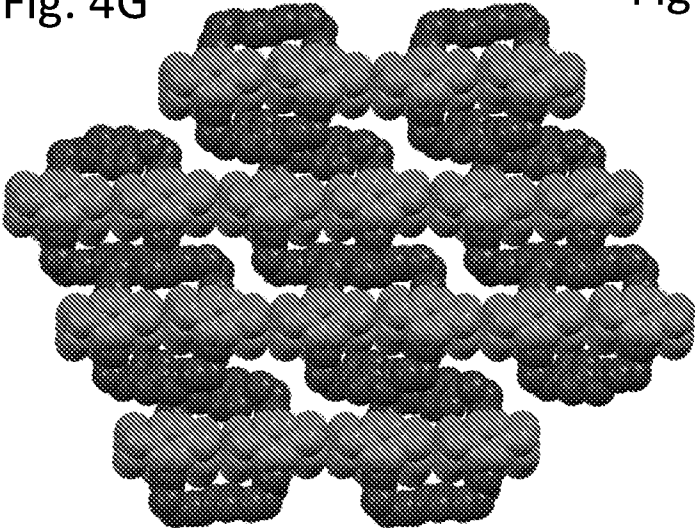


Fig. 4I

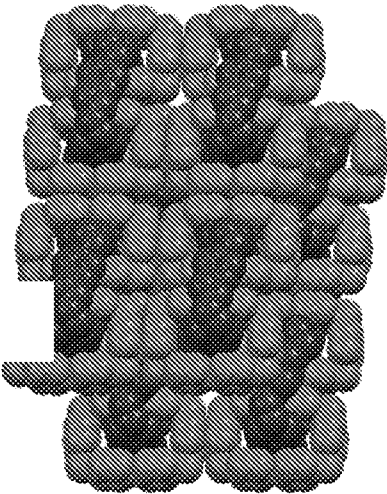


Fig. 4H

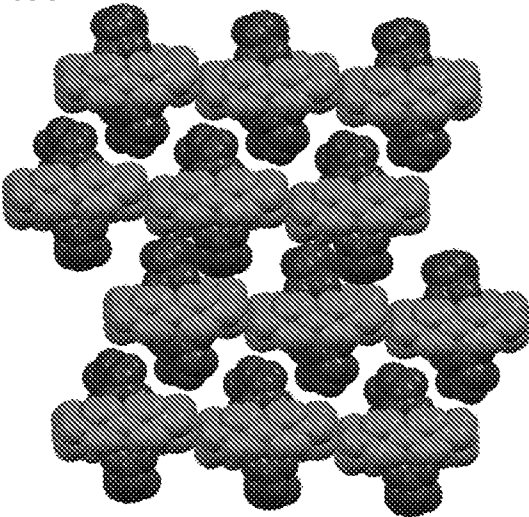


Fig. 4J

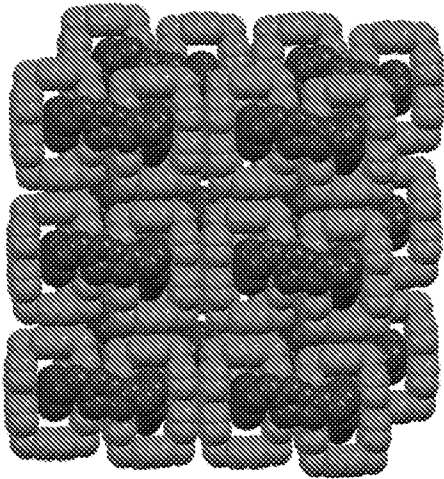


FIG. 5A

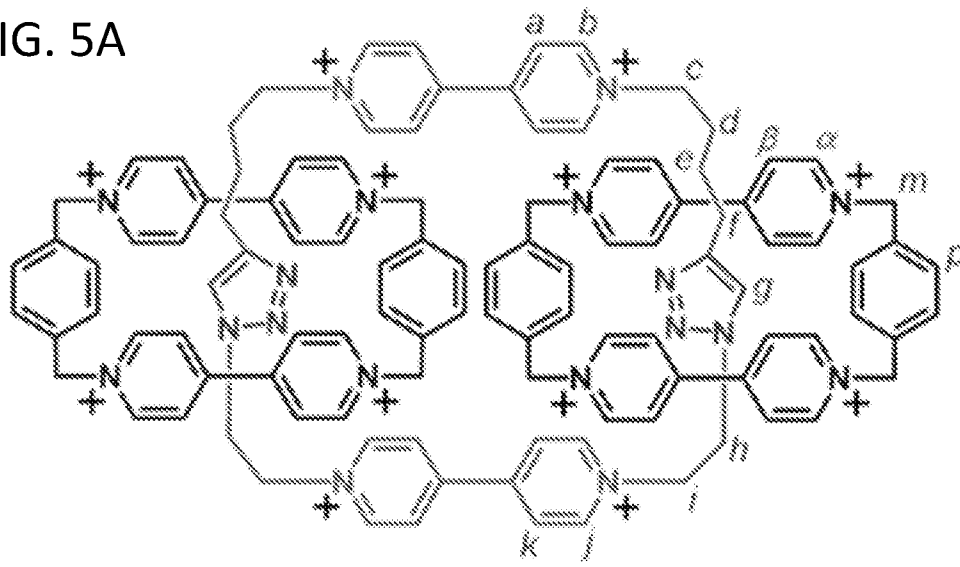


FIG. 5B

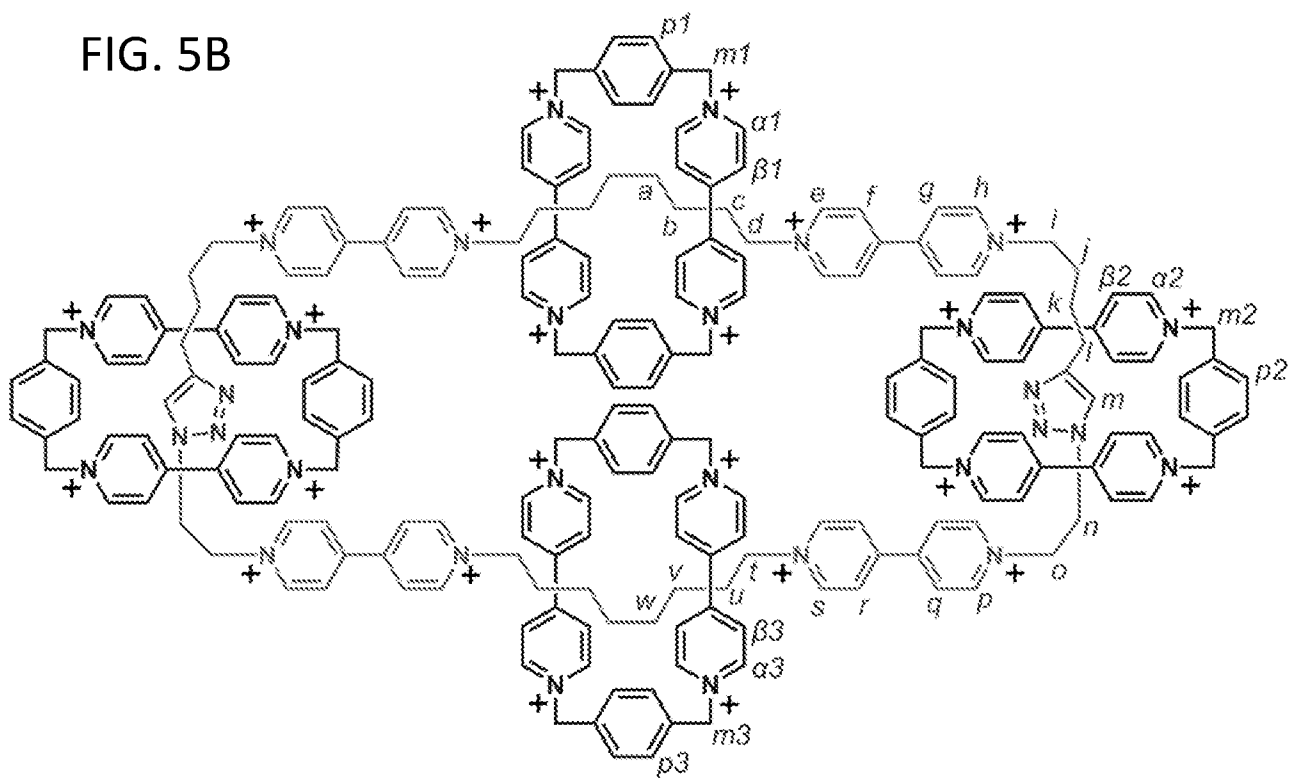


FIG. 6AI

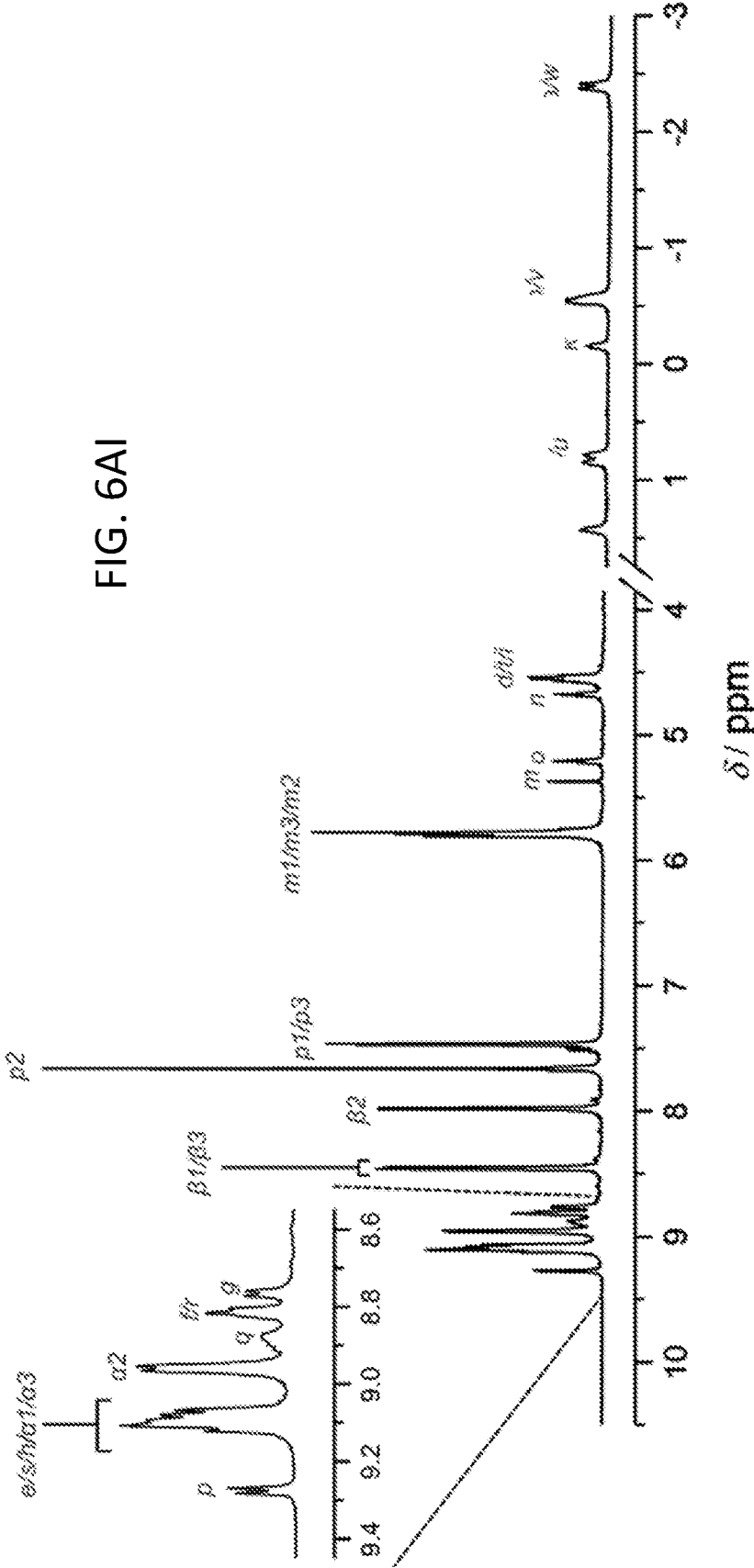
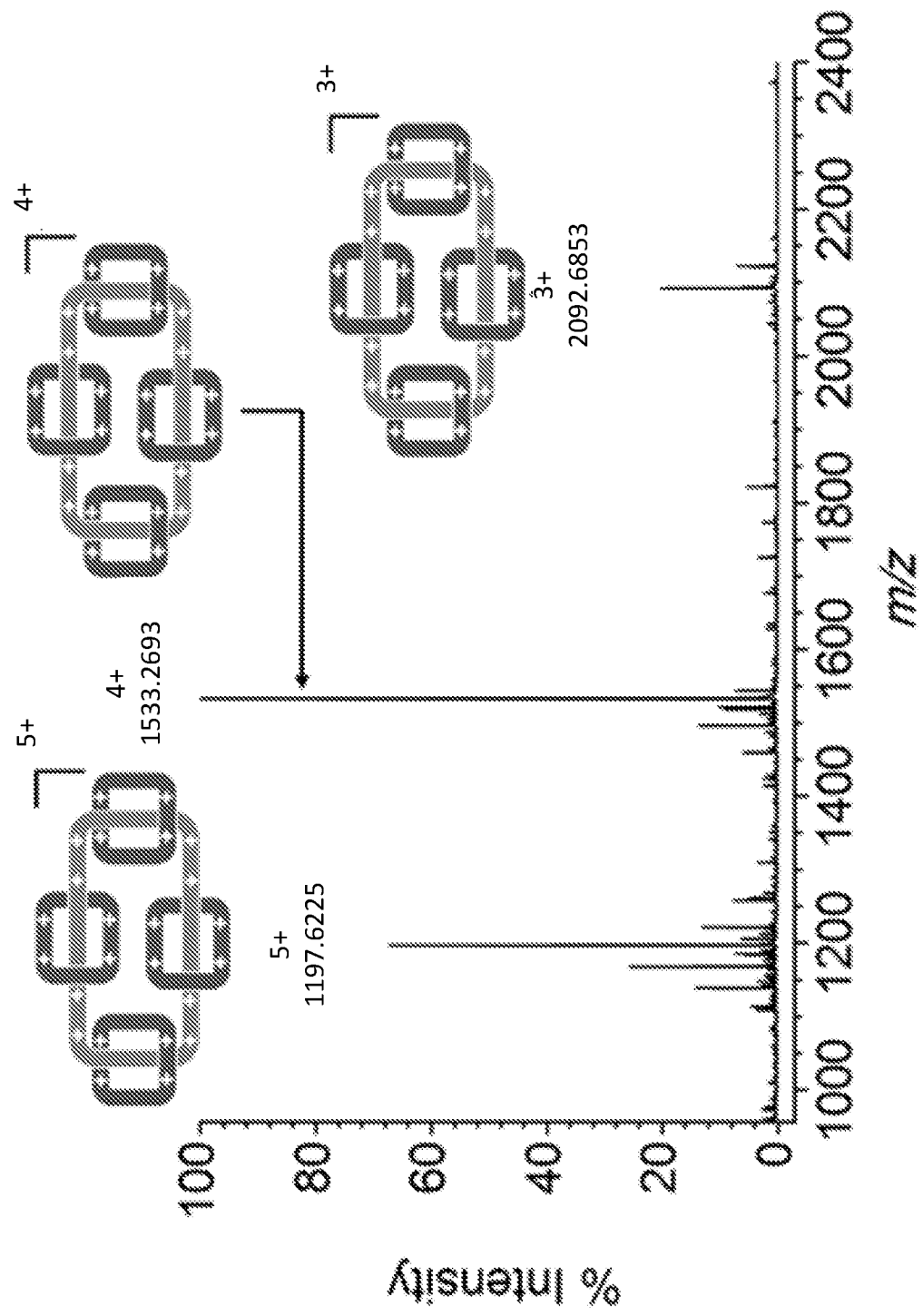


FIG. 6AII



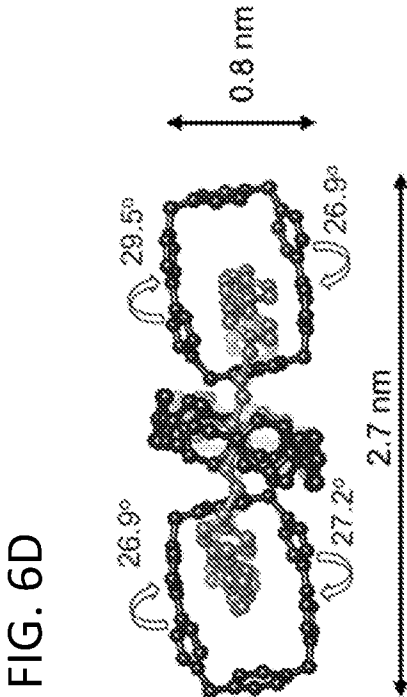
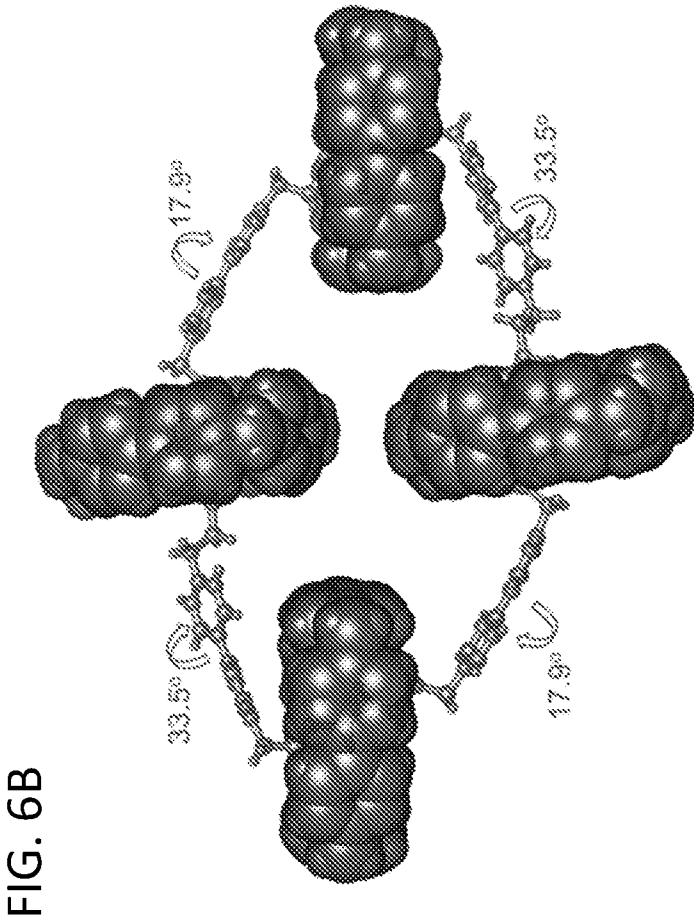
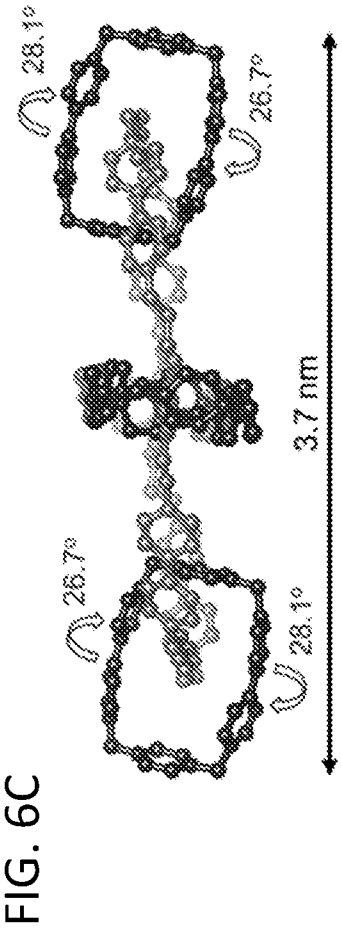


Fig. 6E

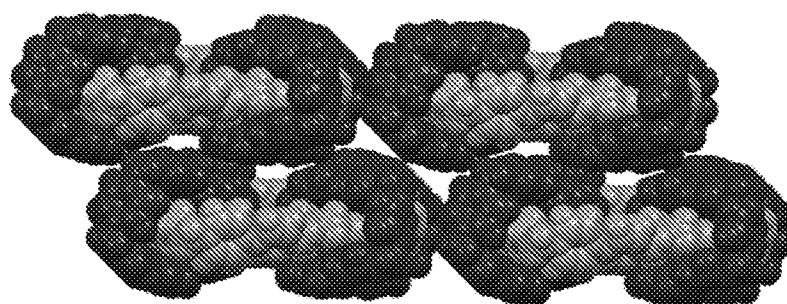
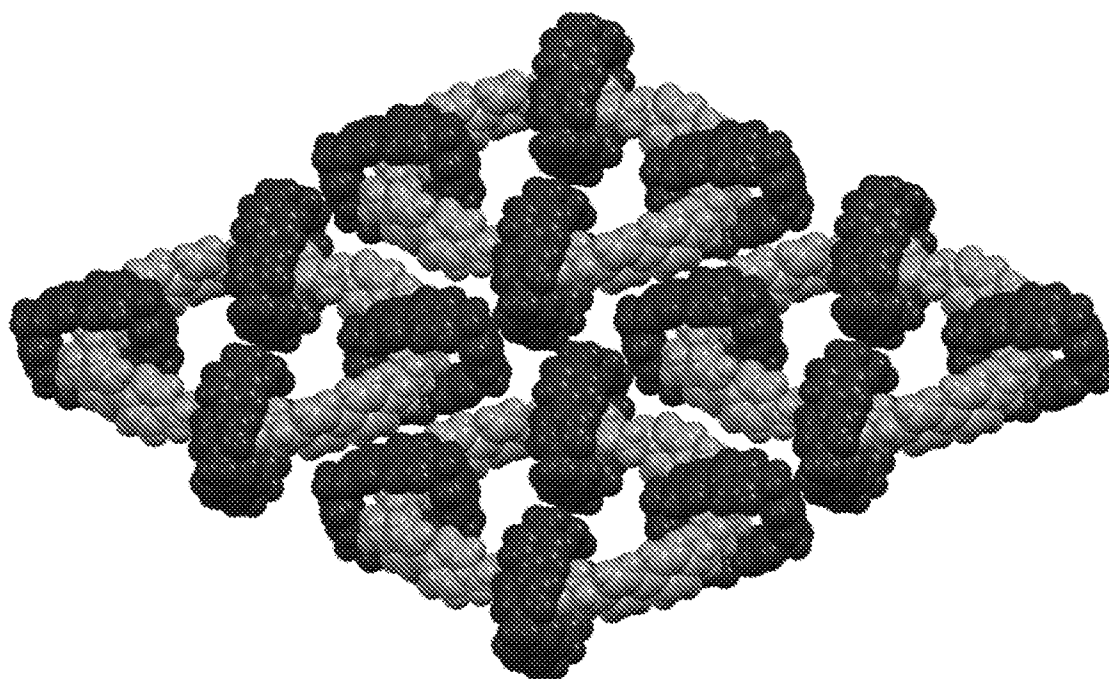


Fig. 6F

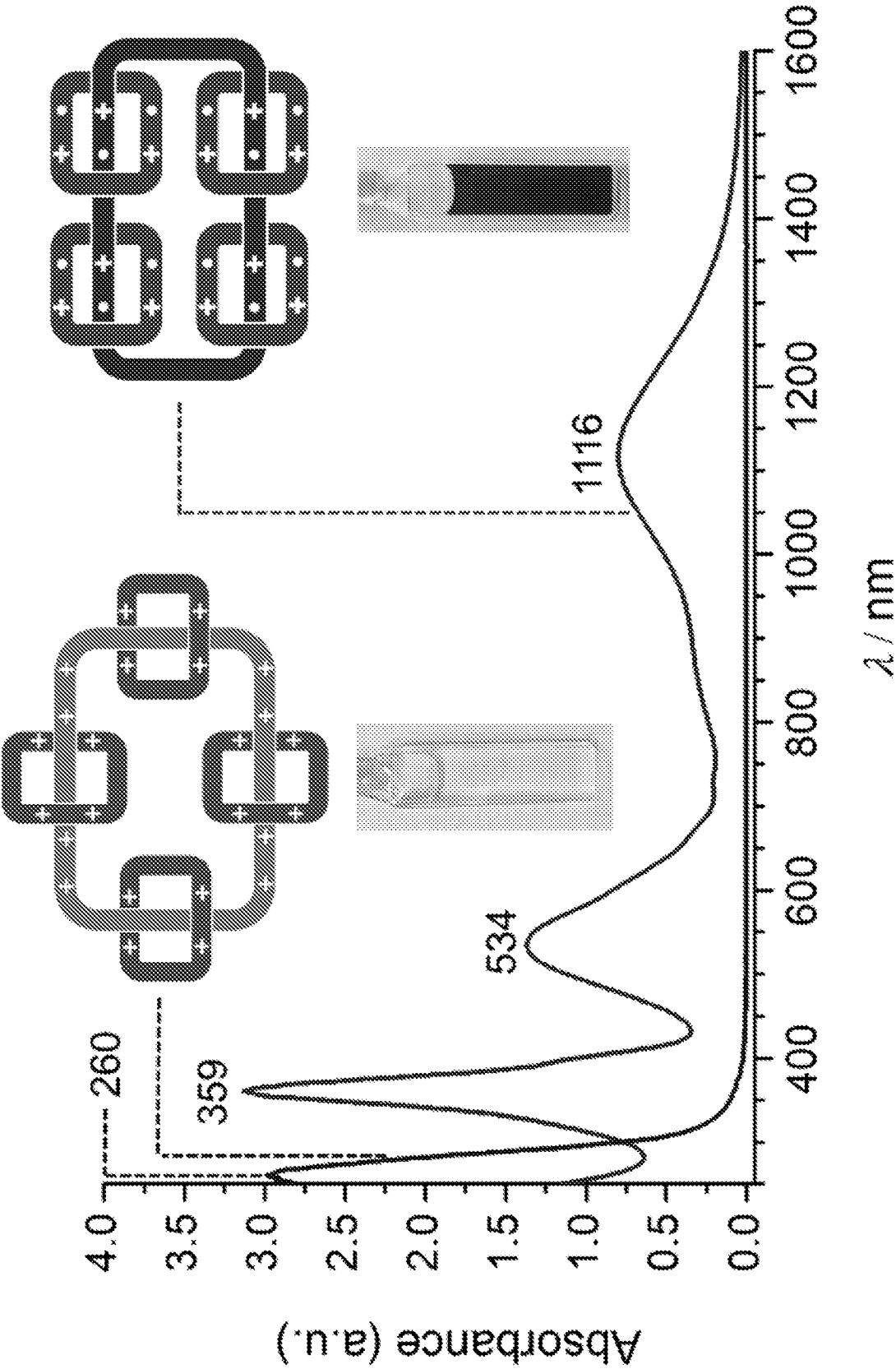


Fig. 7A

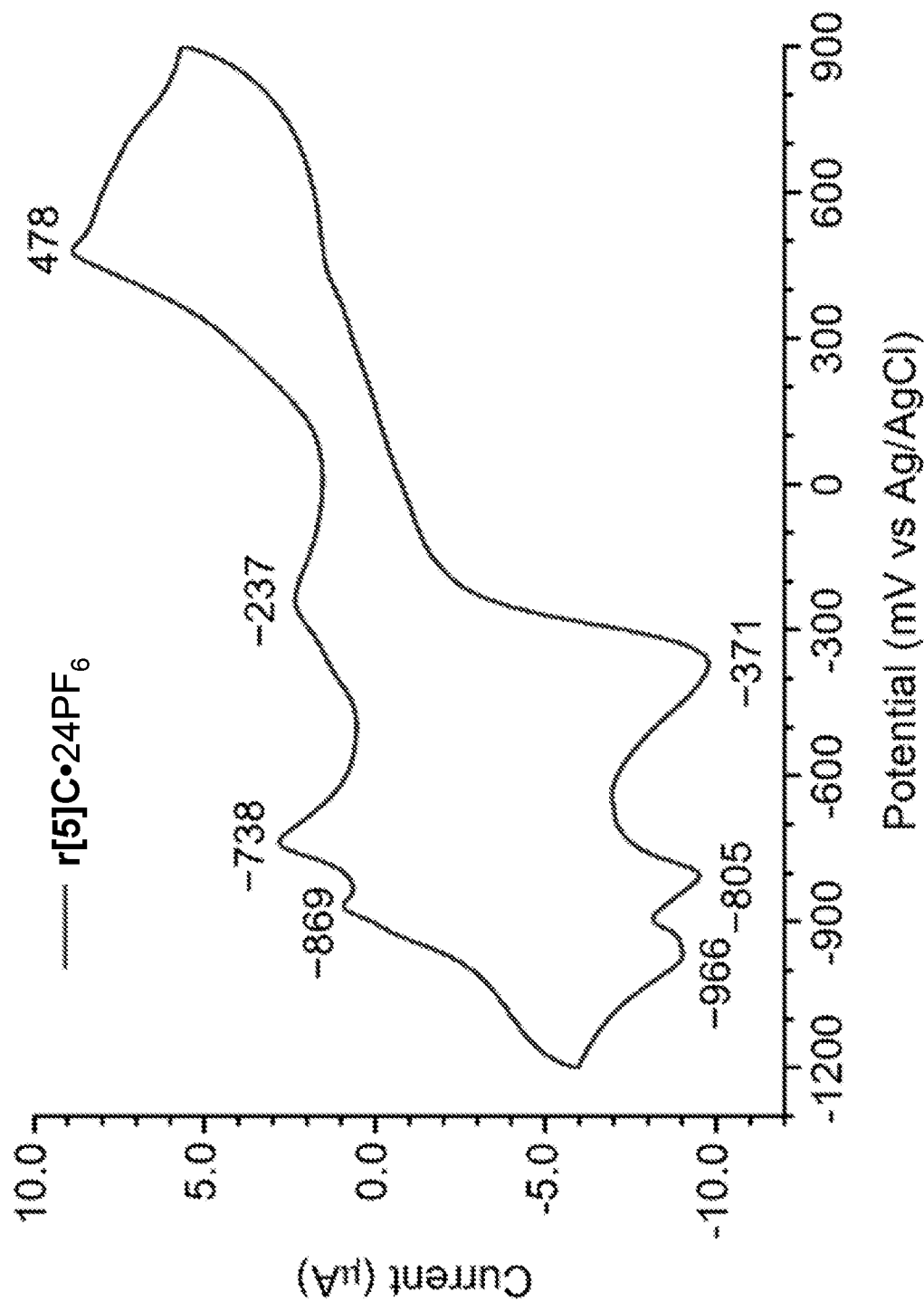


FIG. 7B

Fig. 7C

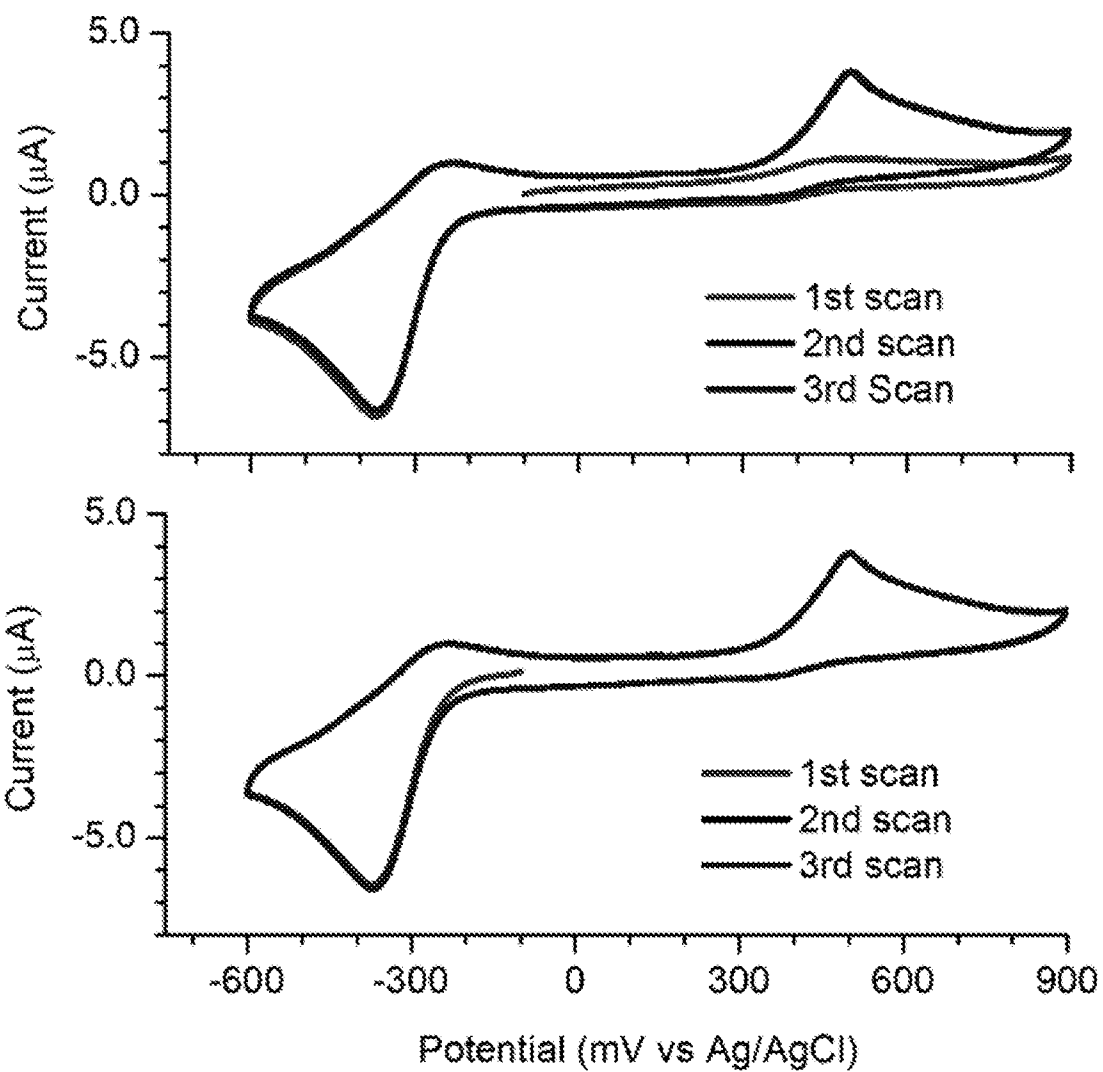


Fig. 7D

Fig. 8A

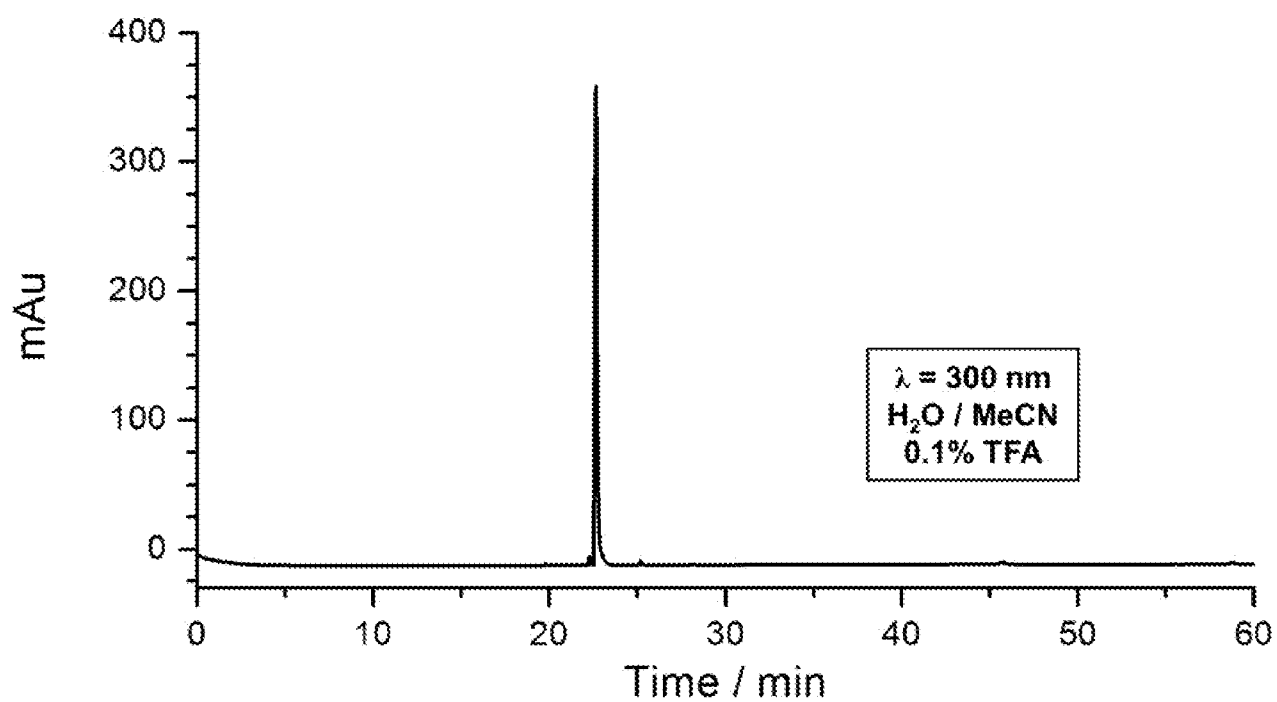
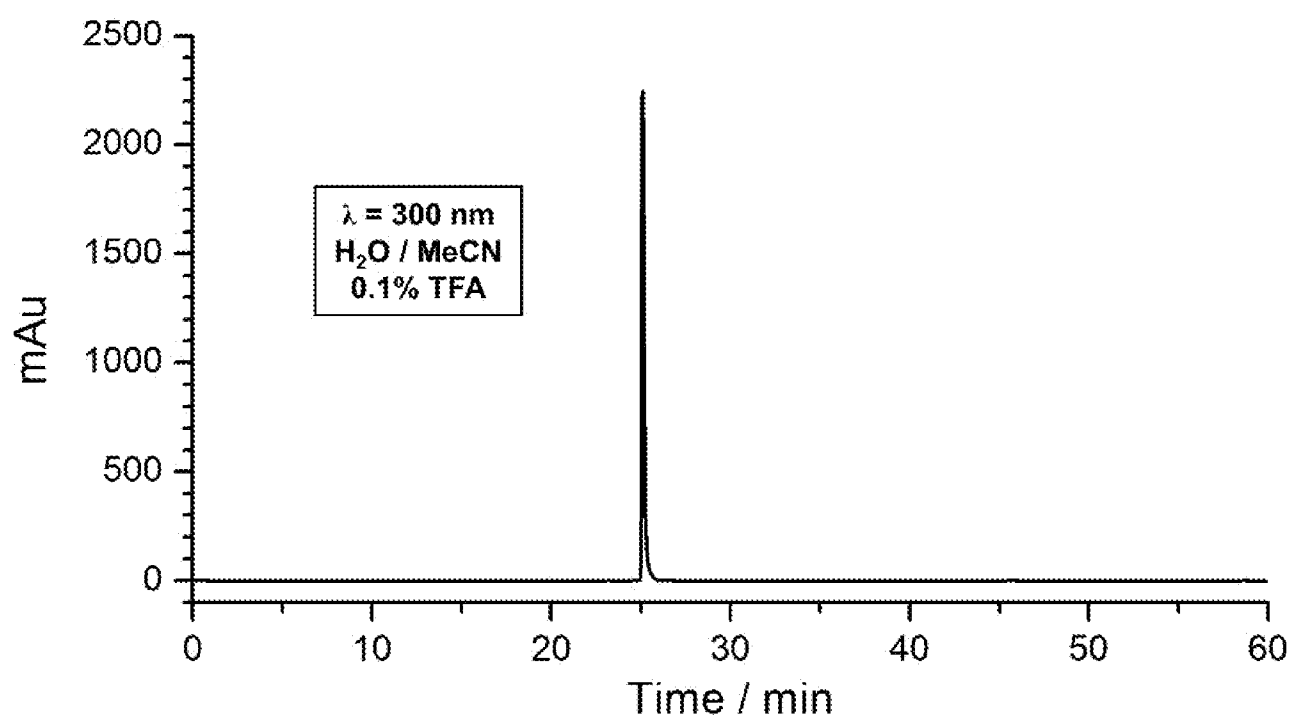


Fig. 8B



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/26095

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C07D 323/00; C07D 405/12; C07D 498/06 (2019.01)

CPC - C07C 275/28; C07D 249/16; C07D 267/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Amabilino et al. 'Olympiadane', Angewandte Chemie International Edition, 06 June 1994 (06.06.1994), Vol.33, pages1286-1290; p1287	1-10, 12-13, 15-21, 23-24, 26-31, 33-34, 36-40, 42-43, 45-46
A	Gibbs-Hall et al. 'Catenation through a Combination of Radical Templation and Ring-Closing Metathesis', Journal of the American Chemical Society, 14 December 2015 (14.12.2014), Vol.137, pages15640-15643; p15640	1-10, 12-13, 15-21, 23-24, 26-31, 33-34, 36-40, 42-43, 45-46
A	Au-Yeung et al. 'Strategies To Assemble Catenanes with Multiple Interlocked Macrocycles', Inorganic Chemistry, 11 December 2017 (11.12.2017), Vol.57, pages3475-3485; p3480	1-10, 12-13, 15-21, 23-24, 26-31, 33-34, 36-40, 42-43, 45-46
A	US 2014/0350242 A1 (National Taiwan University) 27 November 2014 (27.11.2014); entire document	1-10, 12-13, 15-21, 23-24, 26-31, 33-34, 36-40, 42-43, 45-46
A, P	Nguyen et al. 'Densely Charged Dodecacationic [3]- and Tetracosacationic Radial [5]Catenans', Chem, 09 August 2018 (09.08.2018), Vol.4, pages2329-2344; entire document	1-10, 12-13, 15-21, 23-24, 26-31, 33-34, 36-40, 42-43, 45-46



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

03 June 2019

Date of mailing of the international search report

05 AUG 2019

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/26095

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 11, 14, 22, 25, 32, 35, 41, 44, 47, 59, 64, and 69
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Supplemental Box

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: 1-10, 12-13, 15-21, 23-24, 26-31, 33-34, 36-40, 42-43, and 45-46

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/26095

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I: Claims 1-10, 12-13, 15-21, 23-24, 26-31, 33-34, 36-40, 42-43, and 45-46 drawn to a cationic catenane comprising a central cationic ring and two or more radial cationic rings mechanically interlocked with the central cationic ring, wherein the central cationic ring comprises two or more viologen subunits and two reactive linkers and wherein the catenane comprises an equal number of radial cationic rings as viologen subunits

Group II: Claims 48-58, 60-63, and 65-68 drawn to a method of forming a cationic catenane, the method comprising: providing a pseudorotaxane, the pseudorotaxane comprising: a threading component having a first terminal moiety, a second terminal moiety, and two or more radical/cation viologen subunits between the first terminal moiety and the second terminal moiety and two or more diradical/dicationic rings threaded by the threading component, wherein the pseudorotaxane comprises an equal number of diradical/dicationic rings as viologen subunits; and contacting the first terminal moiety with the second terminal moiety to form a central cationic ring that mechanically interlocks the two or more diradical/dicationic rings, thereby forming the catenane

The inventions listed as Groups I-II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features

Group II requires a method of forming a cationic catenane, the method comprising: providing a pseudorotaxane, the pseudorotaxane comprising: a threading component having a first terminal moiety, a second terminal moiety, and two or more radical/cation viologen subunits between the first terminal moiety and the second terminal moiety and two or more diradical/dicationic rings threaded by the threading component, wherein the pseudorotaxane comprises an equal number of diradical/dicationic rings as viologen subunits; and contacting the first terminal moiety with the second terminal moiety to form a central cationic ring that mechanically interlocks the two or more diradical/dicationic rings, thereby forming the catenane, not required by Group I

Shared Common Features

Groups I-II share technical feature of a cationic catenane comprising two or more radial cationic rings as viologen subunits.

However, these shared technical feature does not represent a contribution over prior art, because the shared technical feature as being anticipated by the journal article entitled 'Catenation through a Combination of Radical Templation and Ring-Closing Metathesis' by Gibbs-Hall et al. (hereinafter 'Gibbs-Hall'). Gibbs-Hall discloses a cationic catenane (p15640, Scheme 1. "Synthesis of the Hexacationic [2]Catenane 4.6PF6") comprising two or more radial cationic rings as viologen subunits (Abstract "Synthesis of an electrochemically addressable [2]catenane has been achieved following formation by templation of a [2]pseudorotaxane employing radically enhanced molecular recognition between the bisradical dication obtained on reduction of the tetracationic cyclophane, cyclobis(paraquat-p-phenylene), and the radical cation generated on reduction of a viologen disubstituted with p-xylylene units, both carrying tetraethylene glycol chains terminated by allyl groups", p15640, Scheme 1. "Final Product").

As the technical features were known in the art at the time of the invention, this cannot be considered a special technical feature that would otherwise unify the groups. Groups I-II therefore lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature.

Note Re: Item 4: claims 11, 14, 22, 25, 32, 35, 41, 44, 47, 59, 64, and 69 are determined unsearchable because they are not drafted in accordance with the second and third sentences of Rule 6.4(a).