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(54) Title: TRÖGER'S BASE-LINKED POLY (CROWN ETHERS)S

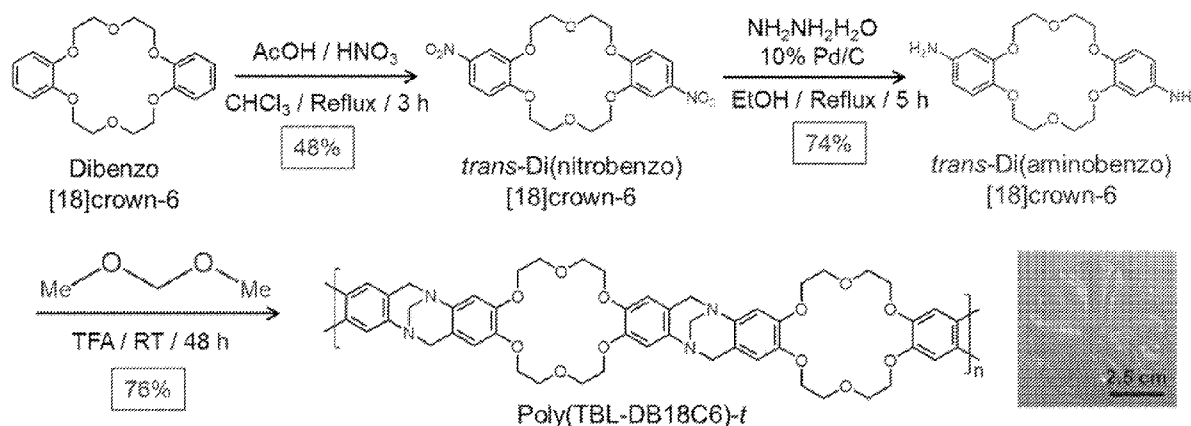


Fig. 1

(57) **Abstract:** Described herein are double-strand chain compositions suitable for use in the preparation of proton conductive membranes. The double-strand chains comprise a plurality of constitutional units joined to each other through two atoms on one side of the constitutional unit and two atoms on the other side of the constitutional unit. Constitutional units comprise a dibenzo-crown ether macrocycle fused with a bicyclic aliphatic linker. Polymers, membranes, and fuel cells comprising the double-strand chain are also described herein.



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TRÖGER'S BASE-LINKED POLY(CROWN ETHER)S

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims benefit of priority to U.S. Provisional Application No. 62/580,860, filed 2 November 2017, the content of which is incorporated herein by reference in its entirety.

FIELD OF INVENTION

The technology generally relates to compositions comprising poly(crown ethers)s. More particularly, the technology relates to double-strand chain, polymer, and membrane compositions comprising a plurality of constitutional units comprising a dibenzo-crown ether macrocycle fused with a bicyclic aliphatic linker.

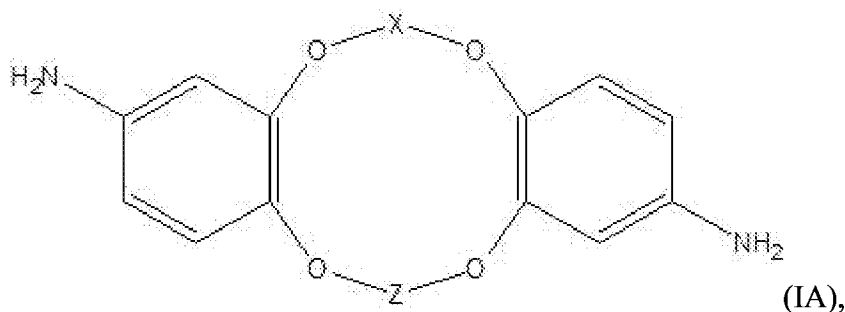
BACKGROUND

Since the invention of the first proton exchange membrane fuel cells (PEMFCs) in the mid-1960s, researchers have been devoting effort towards developing a significant component of PEMFCs, i.e., proton exchange membranes (PEMs). Nonetheless, there are few noteworthy PEMs, e.g., perfluorosulfonic acid ionomers (Nafion), sulfonated and phosphonic-based polyaromatics (polyphenylsulfone, poly(ether ether ketone), polyimides, polystyrene), polyphosphazenes, polybenzimidazoles, and their derivatives. As a result, there exists a need for new PEM materials.

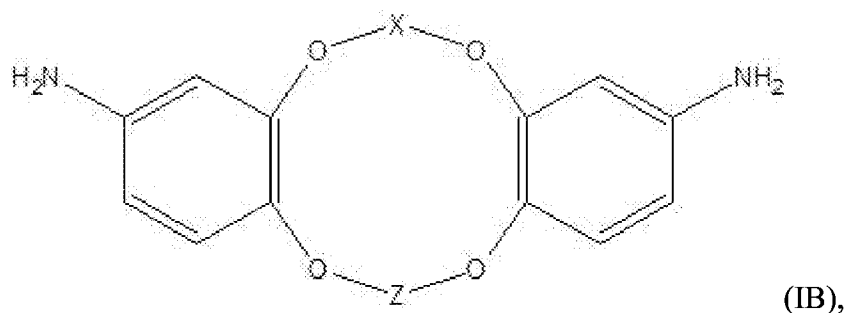
BRIEF SUMMARY OF THE INVENTION

Described herein are double-strand chain compositions suitable for use in the preparation of proton conductive membranes. The double-strand chains comprise a plurality of constitutional units joined to each other through two atoms on one side of the constitutional unit and two atoms on the other side of the constitutional unit. Constitutional units comprise a dibenzo-crown ether macrocycle fused with a bicyclic aliphatic linker. The aliphatic linker may comprise a diazocine linker having two bridgehead nitrogen atoms, suitably a [b,f][1,5]diazocine linker bridged by a methylene. The dibenzo-crown ether macrocycle may comprise a dibenzo[n]crown-m macrocycle and $m = 4, 5, 6, 7, \text{ or } 8$ and $n = 3m$. In certain embodiments, $m = 6$.

The double-strand chain compositions may be prepared from the cyclopolymerization of a plurality of di(aminobenzo)crown ethers. Suitably, the di(aminobenzo)crown ethers may be selected from the group consisting of Formula IA



5 Formula IB



and any combination thereof. X and Z may be selected from the group consisting of alkyl and ether. In some embodiments, X and Y are independently selected from $\text{—CH}_2\text{CH}_2\text{—}$, $\text{—CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{—}$, or $\text{—CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{—}$.

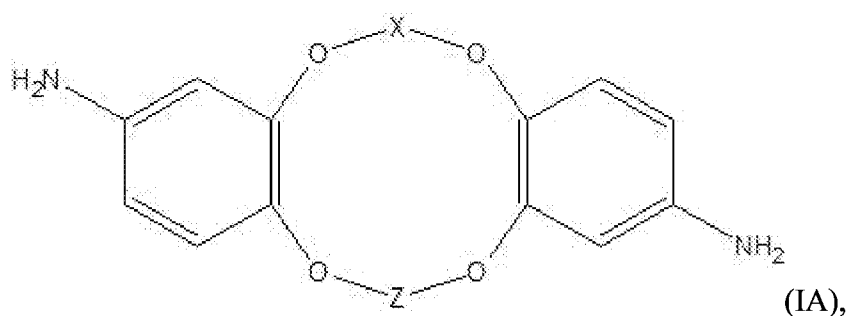
10 Polymers are also provided for. The polymer may comprise any of the double-strand chains described herein. Suitably, the polymer has a weight-average molecular weight (M_w) of at least 100,000 Da; the polymer is thermally stable in an inert atmosphere up to a temperature of at least 200°C; the polymer is at least partially soluble in a halogenated alkane solvent; the polymer has a water uptake capacity of at least 10 wt% at 90% relative humidity; the polymer is
15 capable of forming films; or any combination thereof.

Membranes are also provided for. The membrane may comprise any of the double-strand chains or polymers described herein. Suitably, the membrane is proton conductive; capable of binding ions or small molecules; is capable of separating gases; is capable of treating water; or any combination thereof. In some embodiments, the membrane is a proton exchange membrane.

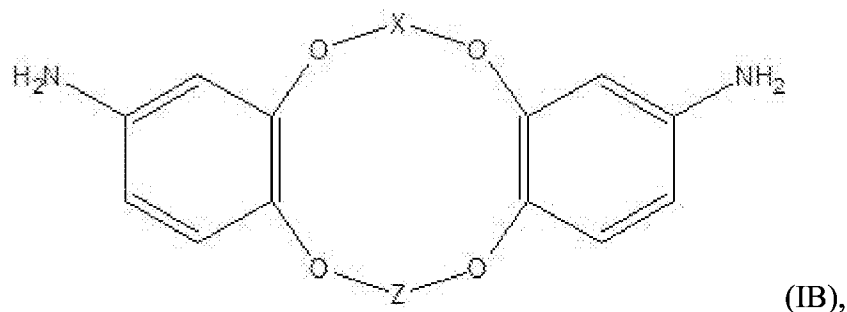
20 The membrane may have a proton conductivity of at least $1.0 \times 10^{-8} \text{ S cm}^{-1}$.

Proton exchange membrane fuel cells are also provided for. The proton exchange membrane fuel cells may comprise any of the membranes described herein.

Methods of preparing the proton conductive membranes are also provided for. The method comprises providing any of the double-strand chains described herein or a polymer comprising any of the double-strand chains described herein and forming a membrane. The method may further comprise absorbing water onto the membrane. The double strand chain may be prepared from cyclopolymerization of a plurality of di(aminobenzo)crown ethers. Suitably, the di(aminobenzo)crown ethers may be selected from the group consisting of Formula IA



10 Formula IB



and any combination thereof. X and Z may be selected from the group consisting of alkyl and ether. In some embodiments, X and Y are independently selected from $\text{—CH}_2\text{CH}_2\text{—}$, $\text{—CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{—}$, or $\text{—CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{—}$. In some embodiments, the membrane is formed by solution casting.

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

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.

Figure 1A illustrates the Synthesis of *trans*-Di(nitrobenzo)[18]crown-6, *trans*-Di(aminobenzo)[18]crown-6, and Poly(TBL-DB18C6)-*t*. A film (inset) was obtained by the slow evaporation of a solution of poly(TBL-DB18C6)-*t* (200 mg) in CHCl₃ (10 mL) from a Petri dish at room temperature overnight, followed by drying at 80°C for 5 h. The dried film in the Petri dish was soaked in de-ionized water for 1 h and peeled off to obtain a free-standing membrane.

Figure 2A depicts an annotated ¹H NMR Spectrum (500 MHz, CDCl₃ / (CD₃)₂SO, 298K) of *trans*-Di(nitrobenzo) [18]crown-6, *trans*-Di(aminobenzo)[18]crown-6, and Poly(TBL-DB18C6)-*t*. *trans*-Di(nitrobenzo)[18]crown-6: δ = 7.89 (dd, J = 9.0, 2.6 Hz, 2H), 7.73 (d, J = 2.6 Hz, 2H), 7.16 (d, J = 9.1 Hz, 2H), 4.22 (m, 8H), 3.90 – 3.83 (m, 8H). *trans*-Di(aminobenzo)[18]crown-6: δ = 6.62 (d, J = 8.4 Hz, 2H), 6.23 (d, J = 2.3 Hz, 2H), 6.05 (dd, J = 8.4, 2.3 Hz, 2H), 4.63 (s, 4H), 4.04 – 3.87 (m, 8H), 3.86 – 3.71 (m, 8H). Poly(TBL-DB18C6)-*t*: δ = 6.62, 6.35, 4.55, 4.23, 4.16 – 3.78.

Figure 2B depicts an annotated ¹H NMR spectrum (500 MHz, (CD₃)₂SO, 298 K) of *cis*-di(nitrobenzo) [18]crown-6.

Figure 2C depicts an annotated ¹H NMR spectrum (500 MHz, (CD₃)₂SO, 298 K) of *cis*-di(aminobenzo) [18]crown-6.

Figure 2D depicts an annotated ¹H NMR spectrum (500 MHz, CDCl₃, 298 K) of poly(TBL-DB18C6)-*c*.

Figure 2E depicts an annotated ¹³C NMR spectrum (125 MHz, (CD₃)₂SO, 298 K) of *trans*-di(nitrobenzo) [18]crown-6.

Figure 2F depicts an annotated ¹³C NMR spectrum (125 MHz, (CD₃)₂SO, 298 K) of *cis*-di(nitrobenzo) [18]crown-6.

Figure 2G depicts an annotated ¹³C NMR spectrum (125 MHz, (CD₃)₂SO, 298 K) of *trans*-di(aminobenzo)[18]crown-6.

Figure 2H depicts an annotated ¹³C NMR spectrum (125 MHz, (CD₃)₂SO, 298 K) of *cis*-di(aminobenzo) [18]crown-6.

Figure 2I depicts an annotated ¹³C NMR spectrum (125 MHz, CDCl₃, 298 K) of poly(TBL-DB18C6)-*t*.

Figure 2J depicts an annotated ^{13}C NMR spectrum (125 MHz, CDCl_3 , 298 K) of poly(TBL-DB18C6)-*c*.

Figure 3 depicts a FTIR spectra of *cis*-di(nitrobenzo)[18]crown-6, *trans*-di(nitrobenzo)[18]crown-6, *cis*-di(aminobenzo)[18]crown-6, *trans*-di(aminobenzo)[18]crown-6, poly(TBL-DB18C6)-*t*, and poly(TBL-DB18C6)-*c*. FTIR (ATR, 4000–400 cm^{-1} , RT): N–H (3480–3250 cm^{-1}), C–H (2660–2828 cm^{-1}), Ph–O–C (1230 cm^{-1}), C–O–C (1125 cm^{-1}), N–O (1340 cm^{-1}), and C–N (1360, 1090 cm^{-1}).

Figure 4 depicts thermogravimetric analyses (TGA) of poly(TBL-DB18C6)-*t* and poly(TBL-DB18C6)-*c* in an N_2 atmosphere ranging from 25–800°C at a heating rate of 10 °C min^{-1} . TGAs confirm the thermal stability of these polymers up to 300°C.

Figure 5 depicts powder Xray diffraction profiles for poly(TBLDB18C6)t and poly(TBLDB18C6)c. The lack of ordered structure is clearly identified from the PXRD patterns of the Tröger's base linked polymers.

Figure 6 depicts Gel Permeation Chromatography (GPC) traces for poly(TBL-DB18C6)-*t* and poly(TBL-DB18C6)-*c*. Weight average molecular weights were determined from a calibration against polystyrene standards. $M_w = 633,000$ and 530,000 Dalton for poly(TBL-DB18C6)-*t* and poly(TBL-DB18C6)-*c*, respectively. Dilute solutions of polymers in CHCl_3 were used for the GPC analyses.

Figure 7A-7B depicts water adsorption-desorption isotherms of (Fig. 7A) poly(TBL-DB18C6)-*t* and (Fig. 7B) poly(TBL-DB18C6)-*c* at 25°C, showing H_2O vapor uptake capacities (%wt) with respect to relative humidity.

Figures 8A-8G depicts Proton Conductivity Measurements. Fig. 8A illustrates the behavior of palladium hydride (PdH_x) protode behavior. PdH contacts split into Pd , H^+ , and e^- under an applied voltage. Protons are injected into the polymer and electrons travel through the external circuit. Fig. 8B illustrates the geometry of a transmission line measurement (TLM). Bulk and contact resistances can be separated by changing the distance between the source and the drain (L_{SD}). Fig. 8C illustrates the calculated conductivity from transient current responses to a 1 V potential applied to poly(TBL-DB[18]C-6)-*t* under 50, 75 and 90% relative humidities with 5% H_2 gas. The data curves appear in the following order from top to bottom on the left side of the graph: 90% RH with 5% H_2 , 90% RH, 75% RH, then 50% RH. Fig. 8D illustrates the calculated conductivity from transient current responses to a 1 V potential displaying a kinetic

isotope effect. Deuterium conductivity is half as much as proton conductivity. The data curves appear in the following order from top to bottom on the left side of the graph: 90% RH with 5% H₂, then 90% RH with 5% D₂. Fig. 8E illustrates resistance (R_L) against L_{SD} plot for poly(TBL-DB18C6)-*t* and the calculated conductivity — from the slope obtained from a linear fit of resistance — yields a value of $1.4 \times 10^{-4} \text{ mS cm}^{-1}$. Fig. 8F illustrates the calculated conductivity from transient current responses to a 1 V potential applied to poly(TBL-DB[18]C) under 50, 75 and 90% relative humidities with 5% H₂ gas. The data curves appear in the following order from top to bottom on the left side of the graph: 90% RH with 5% H₂, 90% RH, 75% RH, then 50% RH. Fig. 8G illustrates resistance (R_L) against L_{SD} plot for poly(TBL-DB18C6)-*c* and the calculated conductivity — from the slope obtained from a linear fit of resistance — yields a value of $1.1 \times 10^{-4} \text{ mS cm}^{-1}$.

Figures 9A-9C depicts representative AFM Images of (Fig. 9A) an uncoated transmission line device channel and poly(TBL-DB18C6)-*t* (Fig. 9B) and coated poly(TBL-DB18C6)-*c* (Fig. 9C) channel under ambient condition. The uncoated and poly(TBL-DB18C6)-*t* coated device has an RMS roughness of 0.262 and 0.242 nm, respectively. The low RMS roughness for poly(TBL-DB18C6)-*t* and poly(TBL-DB18C6)-*c* coated channel corresponds to a uniform coating of a channel device.

Figures 10A-10B depicts conductivity measurement in devices with 50 μm gaps and 1V applied bias for (Fig. 10A) trans-di(aminobenzo)[18]crown-6 and (Fig. 10B) cis-di(aminobenzo)[18]crown-6. High current with Au electrodes and the relatively small difference in current between Au and Pd contacts indicate that electronic conduction is present in the monomers. In Fig. 10A, the data curves appear in the following order from top to bottom on the left side of the graph: 90% RH + H₂ (Pd), 90% RH + H₂ (Au), then 90% RH. In Fig. 10B, the data curves appear in the following order from top to bottom on the left side of the graph: 90% RH + H₂ (Au), 90% RH + H₂ (Pd), then 90% RH.

Figures 11A-11C illustrates modeling Studies Conducted on Representative Short Polymer Chains of Poly(TBL-DB18C6)-*t*. Fig. 11A shows a potential energy surface of the double layer in stacked and displaced forms, computed at B97D3/6-31G(d) level with the geometry of each layer kept fixed during the scan. Figs. 11B and 11C illustrate optimized structures of double layer DB18C6 with (Fig. 11B) one H₂O molecule and (Fig. 11C) two H₂O molecules between the layers forming H⁺-conduction pathways through the formation of

hydrogen-bonds between H₂O molecules and oxygen atoms in the crown ether cavities. Geometries were optimized at B3LYP/6-31G(d,p) level with layers kept fixed at a distance of 5.2 Å in the stacked form.

Figures 12A-12B illustrates structures from DFT optimization of the (Fig. 12A) stacked and (Fig. 12B) displaced forms of the double layer at a 5.2 Å inter-layer distance (as measured between atom centers).

Figures 13 shows potential energy surfaces of the double layer in stacked and displaced forms of representative units of poly(TBL-DB18C6)-t and poly(TBL-DB18C6)-c, computed at B97D3/6-31G(d) level with the geometry of each layer kept fixed during the scan. The data curves appear in the following order from top to bottom on the left side of the graph: Displaced *Cis*, Displaced *Trans*, Stacked *Trans*, then Stacked *Cis*.

DETAILED DESCRIPTION OF THE INVENTION

Disclosed herein are double-strand chains and polymers comprising crown ether moieties. These polymers are robust, processable, hydrophilic, and have a high molecular weight. These hydrophilic polymers retain H₂O and facilitate proton conduction in humid environments. As a result, these polymers are a new class of proton exchange membranes (PEMs), expanding the ever-growing need to identify new materials for proton exchange membrane fuel cells (PEMFCs) in order to enhance proton conductivity. The sub-nanometer-sized crown cavities and the membrane-forming ability of the polymers will also allow for a number of different applications, including, but not limited to, ion binding, small molecule binding, gas separation, and/or water treatment.

PEMFCs are one of the best alternatives to the combustion of fossil fuels as a result of their efficiency in transforming chemical into electrical energy by means of a clean and carbon-free route. The redox reaction of hydrogen (H₂) and oxygen (O₂) generates water (H₂O), heat and electricity in PEMFCs. In the fuel cell, the oxidized protons from the anode are transported through the electrolytic membrane to the cathode where they react with reduced oxygen.

PEMs are key components of PEMFCs. The PEMs act as an electrolyte to facilitate ionic pathways for the protons from the anode. Currently, available PEM materials include perfluorosulfonic acid ionomers sulfonated and phosphonic-based polyaromatics (polyphenylsulfone, poly(ether ether ketone), polyimides, polystyrene), polyphosphazenes, polybenzimidazoles, and their derivatives. The state-of-the-art material for PEMs is Nafion since

it displays proton conductivity of 10^{-1} S cm⁻¹ under conditions of 100% relative humidity at room temperature. The limited number of alternative PEMs has led to researchers modifying the existing families of polymeric materials. The double-strand chains and polymers disclosed herein, however, provide an entirely new class of materials that can be prepared into PEMs for PEMFCs.

PEMs have to fulfill three major requirements in order to be considered for applications in PEMFCs: they include (i) the presence of proton-conducting functionalities, (ii) the ability to form free-standing films to support the conductivity, and (iii) the need for robust, thermal and aqueous acid stabilities. We address these requirements with the Tröger's base-linked double-strand chains and polymers obtained by *in situ* polymerization of amino-functionalized crown macrocycles, which are described herein.

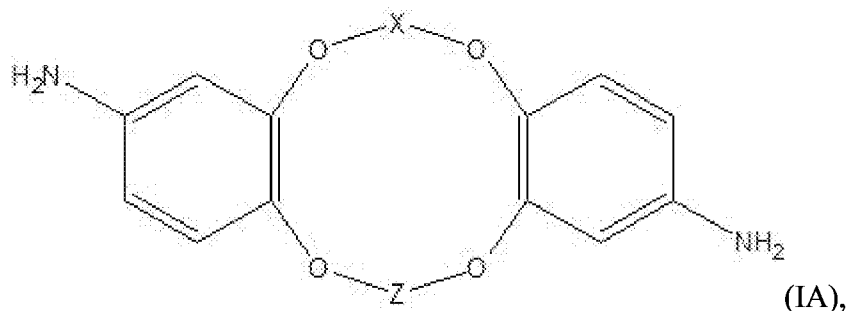
The double-strand chains and polymers described herein may be prepared from dibenzo-crown macrocycles. A "crown" is a molecular entity comprising a monocyclic ligand assembly that contains three or more binding sites held together by covalent bonds and capable of binding a guest in a central (or nearly central) position. The adducts formed are sometimes known as "coronates". Crown macrocycles may be described as "[n]crown-m macrocycles" or "nCm", where m is a number of repeating units and n is the total number of atoms forming the macrocycle. Suitably m is equal to 4, 5, 6, 7, or 8, but larger macrocycles may also be prepared. Because crowns are typically formed from repeating units, n is usually an integer multiple of m. Suitably, n is equal to 3 m.

Members of this group include macrocyclic polyethers (also known as "crown ethers"). Crown ethers comprise m repeating units of $\text{-CR}_2\text{CR}_2\text{O-}$ forming the macrocycle. An exemplary crown ether is [18]crown-6 (18C6), comprising 6 repeating units of $\text{-CR}_2\text{CR}_2\text{O-}$ and forming the macrocycle having 18 total atoms and 6 oxygen atoms. The radical R is often hydrogen, but need not be. Suitably one or more of the repeating units of the crown ether may be optionally substituted or fused with another ring structure.

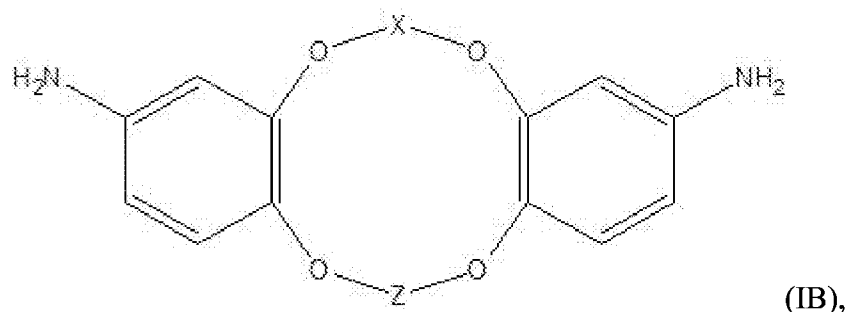
The Tröger's base-linked chains or polymers may be synthesized by polymerization of di(aminobenzo)-crowns. As shown in the Examples that follow, dibenzo-crowns or DBnCm are capable of reacting to form di(nitrobenzo)-crowns and further di(aminobenzo)-crowns. For example, DB18C6 may be reacted with nitric acid to form two constitutional isomers, namely

trans- and *cis*-di(nitrobenzo)[18]crown-6. Further, these isomers may be reduced affording *trans*- and *cis*-di(aminobenzo)[18]crown-6, respectively.

Exemplary di(aminobenzo)-crowns suitable for use with the present invention include a compound of Formula IA



which is referred to as “*trans*-di(aminobenzo)-crown”, or a compound of Formula IIB



which is referred to as “*cis*-di(aminobenzo)-crown”, and combinations thereof. Other di(aminobenzo)-crown ethers may also be used to prepare the compositions of the present invention, including di(aminobenzo)-crowns having amino groups on any of the aryl carbons that are not fused with the crown moiety, substituted-aryl di(aminobenzo)-crowns, and/or crown-substituted di(aminobenzo)-crowns. Substituents on the aryl moiety of the substituted-aryl di(aminobenzo)-crowns may include electron-donating or –withdrawing substituents. Suitably, electron-donating substituents may include halo, alkyl, haloalkyl, alkoxy, amino, sulfanyl, or alkoxy carbonyl.

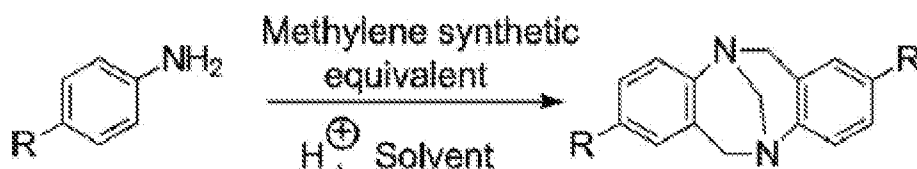
In some embodiments, the crown is a crown ether. Suitable moieties X and Z for crown ethers include alkyl and/or ether moieties. The term “alkyl”, when used in reference to the crown, may be used synonymously with alkylene and includes a substituted or unsubstituted C₂ – C₆ alkyl diradical in all of its isomeric forms, including a C₂ – C₄ alkyl diradical, or C₂ alkyl diradical such as a substituted or unsubstituted ethylene. The term “ether”, when used in

reference to the crown, includes two or more C₂ – C₆ alkyl diradicals covalently linked by oxygen atoms, including two or more C₂ – C₄ alkyl diradicals covalently linked by oxygen atoms or two or more C₂ alkyl diradicals, such as a substituted or unsubstituted ethylenes, covalently linked by oxygen atoms.

In some embodiments, X may be —CH₂CH₂—, —CH₂CH₂OCH₂CH₂—, or —CH₂CH₂OCH₂CH₂OCH₂CH₂—. In certain embodiments, X is —CH₂CH₂OCH₂CH₂—. In some embodiments, Z is selected from —CH₂CH₂—, —CH₂CH₂OCH₂CH₂—, or —CH₂CH₂OCH₂CH₂OCH₂CH₂—. In certain embodiments, Z is —CH₂CH₂OCH₂CH₂—. In some embodiments, X and Z are the same.

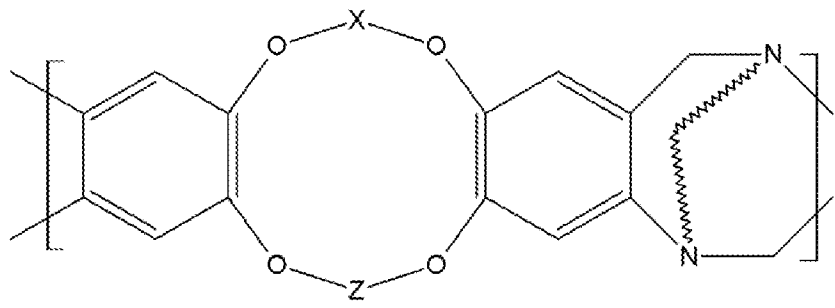
In certain embodiments, X is —CH₂CH₂— and Z is —CH₂CH₂—, resulting in a 12-crown-4 (12C4) crown ether moiety. In some embodiments, X is —CH₂CH₂— and Z is —CH₂CH₂OCH₂CH₂—, resulting in a 15-crown-5 (15C5) crown ether moiety. In some embodiments, X is —CH₂CH₂— and Z is —CH₂CH₂OCH₂CH₂OCH₂CH₂—, resulting in an 18-crown-6 (18C6) crown ether moiety. In some embodiments, X is —CH₂CH₂OCH₂CH₂— and Z is —CH₂CH₂—, resulting in a 15-crown-5 (15C5) crown ether moiety. In some embodiments, X is —CH₂CH₂OCH₂CH₂— and Z is —CH₂CH₂OCH₂CH₂—, resulting in an 18-crown-6 (18C6) crown ether moiety. In some embodiments, X is —CH₂CH₂OCH₂CH₂— and Z is —CH₂CH₂OCH₂CH₂OCH₂CH₂—, resulting in a 21-crown-7 (21C7) crown ether moiety. In some embodiments, X is —CH₂CH₂OCH₂CH₂OCH₂CH₂— and Z is —CH₂CH₂—, resulting in an 18-crown-6 (18C6) crown ether moiety. In some embodiments, X is —CH₂CH₂OCH₂CH₂OCH₂CH₂— and Z is —CH₂CH₂OCH₂CH₂—, resulting in a 21-crown-7 (21C7) crown ether moiety. In some embodiments, X is —CH₂CH₂OCH₂CH₂OCH₂CH₂— and Z is —CH₂CH₂OCH₂CH₂OCH₂CH₂—, resulting in a 24-crown-8 (24C8) crown ether moiety.

Tröger's Base (TB) condensation results in the formation of a bicyclic aliphatic linker via cyclopolymerization. TB condensation is illustrated in the following example: *p*-toluidine reacts in the presence of a synthetic equivalent of methylene under acidic conditions to form a diazocine linker having two bridgehead nitrogen atoms.

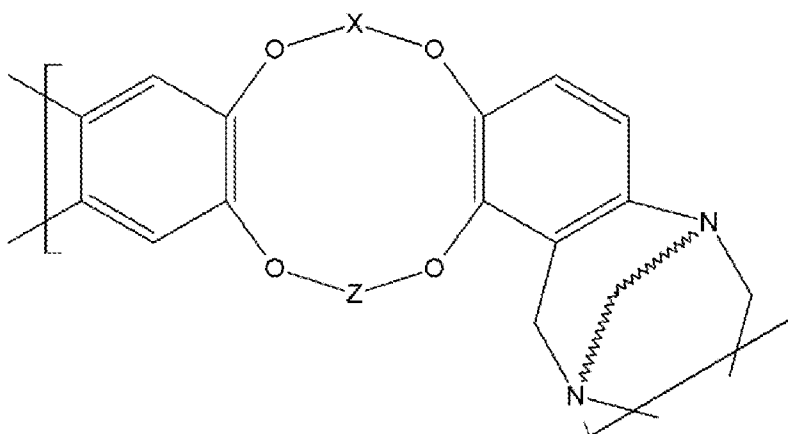


The synthetic equivalent of methylene may be any suitable reactant, including, without limitation, formaldehyde or a precursor, such as methylal, paraformaldehyde, or hexamethylenetetramine. The acidic conditions are typically aqueous or alcoholic HCl solutions, acetic acid, trifluoroacetic acid (TFA), or methanesulfonic acid. The resulting linker comprises
5 [b,f][1,5]diazocine bridged by a methylene that is fused with an aryl ring of the dibenzo-crown.

Because each of the aryl moieties of the di(aminobenzo)-crowns possess a reactive amine group, double-strand chains may be prepared from constitutional units comprising the dibenzo-crown macrocycles fused with bicyclic aliphatic linkers. The chains produced via cyclopolymerization lack an ordered structure. This is a result of the fact that the chains may be
10 comprised of a multiplicity of different stereoisomers and/or structural isomers of the constitutional unit. For an example of stereoisomerism, the relative configurations, syn and anti, defined by the bridging methylene groups of the bicyclic aliphatic linker may be arranged randomly along the chain. For an example of structural isomerism, either of the carbon-carbon bonds adjacent to the TB reactive amine may be fused to the aliphatic linker resulting in linear
15 constitutional units and non-linear constitutional units. "Linear constitutional units" comprise a carbon-carbon bond fusing the dibenzo-crown and bicyclic aliphatic linker at carbon positions 4 and 5 of the aryl ring, e.g.,



as shown in Scheme 3. "Non-linear constitutional units" comprise a carbon-carbon bond fusing
20 the dibenzo-crown and bicyclic aliphatic linker at carbon positions 3 and 4 of the aryl ring, e.g.,



Polymers may be prepared from any of the double-strand chains described herein. Polymers of the present invention have a number of advantages advantageous such as being robust, processable, hydrophilic, and have a high molecular weight. In some embodiments, the polymers have a weight-average molecular weight (M_w) of at least 100,000 Da. Suitably the M_w is at least 200,000 Da, 300,000 Da, 400,000 Da, 500,000 Da, or 600,000 Da. In some embodiments, the polymers are thermally stable in an inert atmosphere up to a temperature of at least 200°C. Suitably, the polymers are thermally stable in an inert atmosphere up to a temperature of at least 225°C, 250°C, 275°C, 300°C, 325°C, or 350°C. In some embodiments, the polymers are at least partially soluble in a halogenated alkane solvent. Suitable halogenated alkane solvents include, without limitation, haloforms such as chloroform. In some embodiments, the polymers have a water uptake capacity of at least 10 wt% at 90% relative humidity. Suitably, the polymers have a water uptake capacity of at least 15 wt% or 20 wt% at 90% relative humidity. In some embodiments, the polymers are capable of forming films or membranes. In certain embodiments, the polymers possess at least two of the properties described above. In particular embodiments, the polymers possess all of the properties described above.

Membranes may be prepared from the polymers and double strand chains described herein. Membranes of the present invention have a number of advantageous properties, including, without limitation, capable of being proton conductive, capable of binding ions or small molecules, capable of separating gases, or capable of sequestering pollutants from water for treatment. In certain embodiments, the membranes possess at least two of the properties described above. In particular embodiments, the membranes possess all of the properties described above.

Membranes prepared from the polymer and double strand chain composition of the present invention include proton exchange membranes. "Proton exchange membranes" or "PEMs" are semipermeable membrane capable of conducting protons while acting as an electrical insulator and reactant barrier. Suitably the membranes described herein have a proton conductivity of at least $1.0 \times 10^{-8} \text{ S cm}^{-1}$, $1.1 \times 10^{-8} \text{ S cm}^{-1}$, $1.2 \times 10^{-8} \text{ S cm}^{-1}$, $1.3 \times 10^{-8} \text{ S cm}^{-1}$, $1.4 \times 10^{-8} \text{ S cm}^{-1}$, $1.5 \times 10^{-8} \text{ S cm}^{-1}$, $1.6 \times 10^{-8} \text{ S cm}^{-1}$, $1.7 \times 10^{-8} \text{ S cm}^{-1}$, $1.8 \times 10^{-8} \text{ S cm}^{-1}$, $1.9 \times 10^{-8} \text{ S cm}^{-1}$, $1.0 \times 10^{-7} \text{ S cm}^{-1}$, $1.1 \times 10^{-7} \text{ S cm}^{-1}$, $1.2 \times 10^{-7} \text{ S cm}^{-1}$, $1.3 \times 10^{-7} \text{ S cm}^{-1}$, or $1.4 \times 10^{-7} \text{ S cm}^{-1}$.

PEMs may be used in the construction of proton exchange membrane fuel cells. "Proton exchange membrane fuel cells" or "PEMFCs" are a type of fuel cell comprising PEMs that transforms chemical energy liberated during the electrochemical reaction of hydrogen and oxygen to electrical energy. PEMFCs comprise membrane electron assemblies. "membrane electron assemblies" or "MEAs" comprises an assembled stack of a PEM between two electrodes where the PEM allows for the migration of protons from one electrode to the other while also electrically and chemically insulating the electrodes and associated reactions from each other. Typically the reaction at the anode is $\text{H}_2 \rightarrow 2 \text{H}^+ + 2 \text{e}^-$ and the reaction of the cathode is $\frac{1}{2} \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2\text{O}$, resulting in a net reaction of $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$. PEMs should minimize gas crossover, *i.e.*, minimize the passage of H_2 and O_2 gas from one side of the cell to the other as well as being robust enough to resist the reducing environment of the cathode and the oxidizing environment of the anode.

Membranes suitable for use with PEMFCs may be prepared from the compositions and polymers described herein. The method for preparing the membrane comprises providing a composition or polymer described herein and forming the membrane. The membrane may be formed by any suitable process, including solution casting as described in the Examples that follow. The method may additionally comprise absorbing water onto the membrane. Suitably at least 10 wt%, 15 wt%, or 20 wt% of water is absorbed onto the membrane.

Definitions

The term "alkyl" as contemplated herein includes a straight-chain or branched alkyl radical in all of its isomeric forms, such as a straight or branched group of 1-12, 1-10, or 1-6 carbon atoms, referred to herein as $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_1\text{-C}_{10}$ -alkyl, and $\text{C}_1\text{-C}_6$ -alkyl, respectively.

The term “alkylene” refers to a diradical of an alkyl group. An exemplary alkylene group is $-\text{CH}_2\text{CH}_2-$.

The term “haloalkyl” refers to an alkyl group that is substituted with at least one halogen. For example, $-\text{CH}_2\text{F}$, $-\text{CHF}_2$, $-\text{CF}_3$, $-\text{CH}_2\text{CF}_3$, $-\text{CF}_2\text{CF}_3$, and the like.

5 The terms “alkoxyl” or “alkoxy” are art-recognized and refer to an alkyl group, as defined above, having an oxygen radical attached thereto. Representative alkoxyl groups include methoxy, ethoxy, tert-butoxy and the like.

10 An “ether” is two hydrocarbons covalently linked by an oxygen. Accordingly, the substituent of an alkyl that renders that alkyl an ether is or resembles an alkoxyl, such as may be represented by one of $-\text{O-alkyl}$, $-\text{O-alkenyl}$, $-\text{O-alkynyl}$, and the like. “Ether” as used herein may also include three or more $\text{C}_2 - \text{C}_6$ alkyl diradicals covalently linked by oxygens, including three or more $\text{C}_2 - \text{C}_4$ alkyl diradicals covalently linked by an oxygen or three or more C_2 alkyl diradicals, such as a substituted or unsubstituted ethylenes, covalently linked by an oxygen., e.g., diethers.

15 The terms “amine” and “amino” are art-recognized and refer to both unsubstituted and substituted amines, wherein substituents may include, for example, alkyl, cycloalkyl, heterocyclyl, alkenyl, and aryl.

20 The term “aryl” is art-recognized and refers to a carbocyclic aromatic group. Representative aryl groups include phenyl, naphthyl, anthracenyl, and the like. The term “aryl” includes polycyclic ring systems having two or more carbocyclic rings in which two or more carbons are common to two adjoining rings (the rings are “fused rings”) wherein at least one of the rings is aromatic and, e.g., the other ring(s) may be cycloalkyls, cycloalkenyls, cycloalkynyls, and/or aryls. Unless specified otherwise, the aromatic ring may be substituted at one or more ring positions with, for example, halogen, azide, alkyl, aralkyl, alkenyl, alkynyl, cycloalkyl, hydroxyl, 25 alkoxyl, amino, nitro, sulfhydryl, imino, amido, carboxylic acid, $-\text{C}(\text{O})\text{alkyl}$, $-\text{CO}_2\text{alkyl}$, carbonyl, carboxyl, alkylthio, sulfonyl, sulfonamido, sulfonamide, ketone, aldehyde, ester, heterocyclyl, aryl or heteroaryl moieties, $-\text{CF}_3$, $-\text{CN}$, or the like. In certain embodiments, the aromatic ring is substituted at one or more ring positions with halogen, alkyl, hydroxyl, or alkoxyl. In certain other embodiments, the aromatic ring is not substituted, i.e., it is 30 unsubstituted. In certain embodiments, the aryl group is a 6-10 membered ring structure.

The compounds of the disclosure may contain one or more chiral centers and/or double bonds and, therefore, exist as stereoisomers, such as geometric isomers, enantiomers or diastereomers. The term “stereoisomers” when used herein consist of all geometric isomers, enantiomers or diastereomers. These compounds may be designated by the symbols “R” or “S,” depending on the configuration of substituents around the stereogenic carbon atom. The present invention encompasses various stereoisomers of these compounds and mixtures thereof. Stereoisomers include enantiomers and diastereomers. Mixtures of enantiomers or diastereomers may be designated “(±)” in nomenclature, but the skilled artisan will recognize that a structure may denote a chiral center implicitly. It is understood that graphical depictions of chemical structures, e.g., generic chemical structures, encompass all stereoisomeric forms of the specified compounds unless indicated otherwise. Compositions comprising substantially purified stereoisomers, epimers, or enantiomers, or analogs or derivatives thereof are contemplated herein (e.g., a composition comprising at least about 90%, 95%, or 99% pure stereoisomer, epimer, or enantiomer.)

“Chain” means a whole or part of a macromolecule, an oligomer molecule, or a block, comprising a linear or branched sequence of constitutional units between two boundary constitutional units, each of which may be either an end-group, a branch point, or an otherwise-designated characteristic feature of the macromolecule. “Constitutional unit” means an atom or group of atoms (with pendant atoms or groups, if any) comprising a part of the essential structure of a macromolecule, an oligomer, a block, or a chain.

“Double-strand chain” means a chain consisting of an uninterrupted sequence of rings with adjacent rings having one atom in common (spiro chain) or two or more atoms in common (ladder chain). “Double-strand macromolecule” means a macromolecule consisting of an uninterrupted sequence of rings with adjacent rings having one atom in common (spiro macromolecule) or two or more atoms in common (ladder macromolecule). “Double-strand polymer” means a polymer, the macromolecules of which are double-strand macromolecules.

“Macromolecule” or “polymer molecule” means a molecule of high relative molecular mass, the structure of which essentially comprises multiple repetitions of units derived, actually or conceptually, from molecules of low relative molecular mass. “Polymer” means a substance composed of macromolecules.

“Oligomer molecule” means a molecule of intermediate relative molecular mass, the structure of which essentially comprises a small plurality of units derived, actually or conceptually, from molecules of lower relative molecular mass. “Oligomer” means a substance composed of oligomer molecules.

5 “Block” means a portion of a macromolecule, comprising many constitutional units, that has at least one constitutional or configurational feature which is not present in the adjacent portions.

“Monomer molecule” means a molecule which can undergo polymerization, thereby contributing constitutional units to the essential structure of a macromolecule. “Monomeric unit”
10 means the largest constitutional unit contributed by a single monomer molecule to the structure of a macromolecule or oligomer molecule. “Monomer” means a substance composed of monomer molecules.

“Polymerization” means a process of converting a monomer or a mixture of monomers into a polymer. “Cyclopolymerization” means polymerization in which the number of structures
15 in the constitutional units of the resulting macromolecule, oligomer, block, or chain is larger than in the monomer molecules.

Miscellaneous

Unless otherwise specified or indicated by context, the terms “a”, “an”, and “the” mean “one or more.” For example, “a molecule” should be interpreted to mean “one or more
20 molecules.”

As used herein, “about”, “approximately,” “substantially,” and “significantly” will be understood by persons of ordinary skill in the art and will vary to some extent on the context in which they are used. If there are uses of the term which are not clear to persons of ordinary skill in the art given the context in which it is used, “about” and “approximately” will mean plus or
25 minus $\leq 10\%$ of the particular term and “substantially” and “significantly” will mean plus or minus $>10\%$ of the particular term.

As used herein, the terms “include” and “including” have the same meaning as the terms “comprise” and “comprising.” The terms “comprise” and “comprising” should be interpreted as being “open” transitional terms that permit the inclusion of additional components further to
30 those components recited in the claims. The terms “consist” and “consisting of” should be interpreted as being “closed” transitional terms that do not permit the inclusion of additional

components other than the components recited in the claims. The term “consisting essentially of” should be interpreted to be partially closed and allowing the inclusion only of additional components that do not fundamentally alter the nature of the claimed subject matter.

All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

Preferred aspects of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred aspects may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect a person having ordinary skill in the art to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

The following examples are meant only to be illustrative and are not meant as limitations on the scope of the invention or of the appended claims.

EXAMPLES

We demonstrate proton conductivity in Tröger’s base-linked polymers through hydrogen-bonded networks formed from adsorbed water molecules on the oxygen atoms of DB18C6 under humid conditions. Tröger’s base-linked polymers — poly(TBL–DB18C6)-*t* and poly(TBL–DB18C6)-*c* — synthesized by the *in situ* alkylation and cyclization of either *trans*- or *cis*-di(aminobenzo) [18]crown-6 at room temperature have been isolated as high molecular weight polymers. The macromolecular structures of the isomeric poly(TBL–DB18C6)s have been

established by spectroscopic techniques and size-exclusion chromatography. The excellent solubility of these polymers in chloroform allows the formation of free-standing membranes which are thermally stable and also show stability under aqueous conditions. The hydrophilic nature of the DB18C6 building blocks in the polymer facilitates retention of the water as confirmed by water-vapor adsorption isotherms which show a 23 wt% water uptake. The adsorbed water is retained even after reducing the relative humidity to 25 %. The proton conductivity of poly(TBL-DB18C6)-*t* and poly(TBL-DB18C6)-*c* is found to be 1.4×10^{-4} and 1.1×10^{-4} mS cm⁻¹, respectively, in a humid environment. The proton conductivity arises from the hydrogen bonding and the associated proton hopping mechanism, as supported by a modeling study. In addition to proton conductivity, the Tröger's base-linked polymers reported here promise a wide range of applications utilizing sub-nanometer-sized cavities of the crown ethers and/or the robust film-forming ability.

Treatment of DB18C6 by reacting with a mixture of acetic acid and nitric acid results in the formation of two constitutional isomers, namely *trans*- and *cis*-di(nitrobenzo)[18]crown-6. Reduction of these isomers in the presence of NH₂NH₂·H₂O and 10% Pd/C affords *trans*- or *cis*-di(aminobenzo)[18]crown-6. The Tröger's base-linked polymers, poly(TBL-DB18C6)s, were synthesized by a polymerization of *trans*- or *cis*-di(aminobenzo) [18]crown-6 with dimethoxymethane in trifluoroacetic acid in an N₂ atmosphere at room temperature. *In situ* formation of formaldehyde from dimethoxymethane enables the alkylation³⁴ and subsequent cyclization of the amino groups to form ladder-type Tröger's base-linked polymers. Viscous liquids which are obtained after 2 days were poured into aqueous NH₄OH solutions, resulting in formation of precipitates of the two polymers, poly(TBL-DB18C6)-*t* and poly(TBL-DB18C6)-*c* from *trans*-di(aminobenzo)[18]crown-6 and *cis*-di(aminobenzo)[18]crown-6, respectively. We believe that the relative configurations — *syn* and *anti* — defined by the bridging methylene groups in TB are arranged randomly along the polymer backbones.

The fact that poly(TBL-DB18C6)s have good solubilities in CHCl₃ may be attributed³³ to their contorted and stereochemically ill-defined macromolecular structures. A film has been obtained from slow evaporation of a solution of poly(TBL-DB18C6)-*t* (200 mg) in CHCl₃ (10 mL) as depicted in the inset in Figure 1. Slow evaporation of a solution of poly(TBL-DB18C6)-*c* leads to a similar outcome. Both poly(TBL-DB18C6)s exhibit excellent chemical robustness as indicated by their stabilities in aqueous acidic and basic solutions. The monomers and Tröger's

base-linked polymers were characterized by Fourier transform infrared (FTIR) spectroscopy, ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, gel permeation chromatography (GPC), thermogravimetric analysis (TGA), water-vapor adsorption, and atomic force microscopy (AFM).

5 **FTIR and NMR Spectroscopy:** FTIR Spectra (Figure 3) were collected in attenuated total reflection mode. The N–O stretching bands at 1340 cm^{-1} of *trans*- and *cis*-di(nitrobenzo)[18]crown-6 disappear upon the reduction to give, respectively, *trans*- and *cis*-di(aminobenzo)[18]crown-6, characterized by the emergence of N–H stretching bands associated with the amino groups in the range of $3480\text{--}3250\text{ cm}^{-1}$. The formation of the Tröger's base-linked polymers — namely, poly(TBL–DB18C6)-*t* and poly(TBL–DB18C6)-*c* from *trans*- and *cis*-di(aminobenzo)[18]crown-6, respectively — were supported by the presence of C–N stretching bands at 1360 and 1090 cm^{-1} . Furthermore, the characteristic bands in the range of $2963\text{--}2828\text{ cm}^{-1}$, and those centered on 1230 and 1125 cm^{-1} , corresponding to C–H stretches and Ar–O–C and C–O–C asymmetric stretches, respectively, proved the integration of DB18C6 into the Tröger's base-linked polymers.

The formation of the monomers and the Tröger's base-linked polymers were confirmed by recording ^1H and ^{13}C NMR spectra (Figures 2A–2J) in $(\text{CD}_3)_2\text{SO}$ or CDCl_3 at room temperature. *trans*- and *cis*-Di(nitrobenzo)[18]crown-6 displays the characteristic resonances for the aromatic protons in the downfield region ($7.89\text{--}7.16\text{ ppm}$) and for the *O*-methylene protons in the crown ether in the upfield region ($4.22\text{--}3.83\text{ ppm}$) of ^1H NMR spectrum (Figure 2A). The resonances of the aromatic protons are shifted upfield ($6.62\text{--}6.05\text{ ppm}$) in the case of *trans*- and *cis*-di(aminobenzo) [18]crown-6 upon reduction of *trans*- and *cis*-di(nitrobenzo)[18]crown-6, respectively. The signal at $\delta\ 4.63\text{ ppm}$ is assigned to the amino protons, while the *O*-methylene protons give rise to resonances in the upfield region at $\delta\ 4.06\text{--}3.71\text{ ppm}$. The formation of poly(TBL–DB18C6)-*t* and poly(TBL–DB18C6)-*c* were also confirmed by the presence of signals for aromatic and *N*-methylene protons in the TB repeating units and *O*-methylene protons in the ranges $6.64\text{--}6.35$, $4.55\text{--}4.23$ and $4.16\text{--}3.78\text{ ppm}$, respectively. The ^{13}C NMR spectra (Figures 2E–2J) reveal signals for *trans*- and *cis*-di(nitrobenzo)[18]crown-6 at $\delta = 153.7$, 147.6 , 140.2 , 117.5 , 111.2 , 106.5 and 68.4 , which can be assigned to aromatic, *N*-methylene and *O*-methylene carbons. *trans*- and *cis*-Di(aminobenzo)[18]crown-6 give rise to resonances at $\delta = 149.2$, 143.4 , 139.1 , 115.6 , 105.3 , 100.7 and $71.5\text{--}65.8$ that are shifted upfield on reduction. A

step-growth polymerization of *trans*- or *cis*-di(aminobenzo)[18]crown-6 leads to the new resonances at $\delta = 110.1$ and 58.1 ppm in poly(TBL-DB18C6)-*t* and poly(TBL-DB18C6)-*c*, which can be assigned to the *N*-methylene TB repeating units.

Thermal Stability, Average Molecular Weight, and Water-Vapor Adsorption

5 **Analyses:** TGA Profiles (Figure 3) for poly(TBL-DB18C6)-*t* and poly(TBL-DB18C6)-*c* in the range of 25–800°C in an N₂ atmosphere indicate that both polymers undergo almost identical degradation processes. Poly(TBL-DB18C6)-*t* and poly(TBL-DB18C6)-*c* were thermally stable up to 360°C in an inert atmosphere. The initial weight losses, observed for both polymers, can be associated with trapped solvents. Powder X-ray diffraction profiles (Figure 5) for poly(TBL-DB18C6)-*t* and poly(TBL-DB18C6)-*c* were collected to confirm the formation of crystalline or amorphous structures. The lack of ordered structure is clearly identified from the patterns of the TB-linked polymers. The good solubilities of poly(TBL-DB18C6)-*t* and poly(TBL-DB18C6)-*c* in CHCl₃ made it possible to determine their weight-average molecular weights (M_w) by GPC analyses (Figure 6). Calibration of the GPC column using polystyrene standards indicated that 10 the polymerization yields Tröger's base-linked polymers with $M_w = 633,000$ and 530,000 Daltons for poly(TBL-DB18C6)-*t* and poly(TBL-DB18C6)-*c*, respectively. It is worth mentioning that the high M_w values, along with good thermal stabilities and excellent solubilities of the Tröger's base-linked polymers made it possible to form robust films using the solvent-casting method. The film-forming property is one of the significant parameters for any materials 15 to be considered for PEMs in fuel cell membrane electrode assemblies, fabricated for proton conduction with long-range order.

Proton conduction in PEMs can occur by one of two mechanisms^{38–41} — either a vehicle mechanism (migrating protons) or a Grotthuss mechanism (hopping of protons associated with hydrogen bonds) — depending on the functional groups present in the materials. Here, we fused 25 a hydrophilic building block, DB18C6, into ladder-type polymers connected by TB linkages. Water-vapor adsorption studies were conducted in order to verify the H₂O uptake efficiencies of the Tröger's base-linked polymers. Water adsorption-desorption isotherms (Figures 7A-7B) for poly(TBL-DB18C6)-*t* and poly(TBL-DB18C6)-*c* show water-vapor uptake capacities with respect to a relative humidity (RH). Both polymers demonstrate water-uptake capacities of 23 30 wt% at 90% RH. Remarkably, they show significant hysteresis and retain water molecules, even

after reducing the RH to 25% and confirming the water retention characteristic of poly(TBL–DB18C6)-*t* and poly(TBL–DB18C6)-*c*.

Proton Conductivity (σ): We performed proton conductivity measurements on poly(TBL–DB18C6)-*t* and poly(TBL–DB18C6)-*c*. with a standard two-terminal (Figure 8A) and
 5 a transmission line (TLM) geometry-based devices (Figure 8B) according to a procedure reported^{42,43} in the literature. In brief, a solution of poly(TBL–DB18C6)-*t* or poly(TBL–DB18C6)-*c* in CHCl₃ (20 mg mL⁻¹) was spin-coated onto devices at 500 rpm for 5 s prior to drying at 80 °C for 2 h. Poly(TBL–DB18C6)-*t* or poly(TBL–DB18C6)-*c* forms a continuous film on a SiO₂ surface between two Pd contacts (source, S and drain, D) as visualized (Figures 9A–
 10 9C) by AFM imaging. With a source-drain potential difference, V_{SD} , the PdH_x source and drain inject and drain protons (H⁺) into and from the poly(TBL–DB18C6) channel, effectively serving as protodes (Figure 3A). For each proton injected into poly(TBL–DB18C6) or, an electron is collected by the leads, which complete the circuit and results in a current measured at the drain (I_D). Bulk and contact resistances (Figure 3B) are separated using a TLM geometry in which the
 15 source-drain length (L_{SD}) ranges from 5 to 200 μ m.⁴²

We performed DC measurements of electrical conductivity (Figure 8C), calculated from I_D, as a function of time (t) at room temperature in N₂ and H₂ atmospheres with controlled RH at an applied V_{SD} of 1V. At 50 and 75% RH, poly(TBL–DB18C6)-*t* shows almost no electrical conductivity in an N₂ atmosphere with Pd contacts that are electronically conducting but are not
 20 proton conductive. This result indicates that the poly(TBL–DB18C6)-*t* channel is not conductive towards electrons, which are the only species able to contribute to electrical conductivity at low RHs since the movement of ions and protons require a highly hydrated material.

At 90% RH, ionically conductive materials are generally hydrated enough to support conduction. We do not observe a significant increase in conductivity when the RH is increased to
 25 90% using electronically conducting Pd contacts in an N₂ atmosphere. A sharp increase in electrical conductivity related to the conduction of protons, however, was observed when the atmosphere was switched to a gas mixture (95% N₂ + 5% H₂) by forming proton conducting PdH_x contacts. The fact that conductivity arises from protons, rather than from other ions, was confirmed (Figure 8D) with the kinetic isotope effect (KIE).^{30,42} Measurements were conducted
 30 by hydrating poly(TBL–DB18C6)-*t* with deuterated water (D₂O) and exposing Pd to deuterium (D₂) instead of hydrogen. Although deuterium ions (D⁺) have the same transport mechanism as

protons in a hydrated poly(TBL-DB18C6)-*t*, the mobility of D⁺ ions is lower than that of protons, leading to a decrease in conductivity. This decrease in D⁺ ion conductivity, in keeping with the KIE, is a characteristic signature for conductivity based primarily on protons.⁴² The TLM geometry allows for the separation of bulk and contact resistances since the bulk resistance of the channel scales linearly with L_{SD}, while the resistances at the source-polymer and drain-polymer channel remain constant.⁴² A plot of R_L, the channel resistance normalized as a function of different channel widths of the devices, L_{SD} leads to a linear fit (Figure 8E), the slope of which is proportional to the channel resistivity. We calculated the bulk proton conductivity of poly(TBL-DB18C6)-*t* to be 1.4×10^{-4} mS cm⁻¹, which is consistent with the data from the two-terminal geometry. Poly(TBL-DB18C6)-*c* shows (Figures 8F-8G) proton conductivity of 1.1×10^{-4} mS cm⁻¹. A relatively low proton conductivity is expected in an unmodified poly(TBL-DB18C6)-*t* without acid functionalities and a comparably low number of charge carriers.

We have also carried out conductivity studies (Figures 10A-10B) of monomers and trans- and cis-di(aminobenzo)[18]crown-6. Both monomers demonstrated higher the number of electronic conductivities, which clearly suggest the higher number of electrons passing through the monomers. The two isomers trans- and cis-di(aminobenzo)[18]crown-6 show a high electronic conductivity likely because of π -stacking in the monomers. Although this property may be of interest, low electronic conductivity with proton conductivity is necessary for PEM applications. It is noteworthy to mention that there are no reports on proton conductivity studies on crown ether based polymers; therefore, we compared (Table 1) TB-linked polymers with metallo-supramolecular materials and related polymers. TB-linked polymers showed proton conductivity in addition to film-forming ability.

Table 1. Comparison of proton conductivity and film-forming ability of Tröger's base-linked polymers with supramolecular polymers.

Materials	Proton Conductivity (S cm ⁻¹)	Free-standing film formation ability	Reference
Poly(TBL-DB18C6)- <i>t</i>	1.4×10^{-7}	Yes	This work
Poly(TBL-DB18C6)- <i>c</i>	1.1×10^{-7}	Yes	This work
Pt(II)-based metallo-	1.5×10^{-5}	No	ACS Appl. Mater.

supramolecular polymer			Inter. 2017, 9 (15), 13406–13414
Mo(VI)-based metallo- supramolecular polymer	8.5×10^{-5}	No	Chem. Commun. 2015, 51, 11012– 11014
Benzotriazole-based comb polymers	6×10^{-6}	No	Nat. Chem. 2010, 2, 503–508
LiCl@RT-COF-1	6.45×10^{-3}	No	J. Am. Chem. Soc. 2017, 139(29), 10079–10086
Im@Td-PNDI	9.04×10^{-5}	Yes	J. Am. Chem. Soc. 2015, 137, 913–918
[Zn(HPO ₄)- (H ₂ PO ₄)](ImH ₂) ₂ coordination polymer	2.6×10^{-4}	No	J. Am. Chem. Soc. 2012, 134, 7612–7615
CB[6]•H ₂ SO ₄	1.3×10^{-3}	No	Angew. Chem. Int. Ed. 2011, 50, 7870– 7873

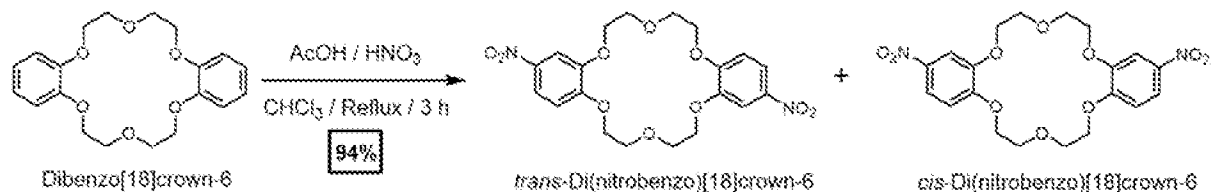
Proton conductivity in hygroscopic PEMs is understood to arise through the organization of H₂O molecules and acidic functions into hydrogen-bonded networks that facilitate the rapid tunneling-like transport of protons, known as proton wires and employing the Grotthuss mechanism.^{6,8,30} We believe the adsorbed H₂O molecules and oxygen atoms in the DB18C6 cavities in poly(TBL–DB18C6) can support the formation of these hydrogen-bonded networks under high RH and so enhance proton transport. A plausible proton conduction mechanism has been proposed as a result of modeling studies (Figures 11A, 12A-12B), carried out on a representative short chain of poly(TBL–DB18C6)-*t*. The structure of the repeating units of poly(TBL–DB18C6)-*t* was optimized using density functional theory (DFT) calculations. The

optimized structure (Figures 11A, 12A-12B) results in a zig-zag pattern on account of the rigidity of the Tröger's base links. The formation of hydrogen-bonded networks — studied experimentally and computationally — in DB18C6 under hygroscopic conditions has been well-established. While keeping the geometry of every single layer rigid, the potential energy surface, as a function of inter-layer distance, was calculated for a double layer system (Figure 11A) using a dispersion-corrected DFT method. The stacked form is observed to be more favorable energetically than the displaced form, with an optimal inter-layer distance of 5.2 Å in which the benzo rings of the crown ethers are located in ideal π - π stacking geometries. In the case of poly(TBL-DB18C6)-c where *cis*-di(benzoamino)[18]crown-6 was used as a monomer, we observed a similar potential energy surface (Figure 13), that is, the stacked form is observed to be more favorable energetically than a displaced form. We have demonstrated plausible pathways for proton conduction in the stacked form of the repeating units by inserting H₂O molecules between the layers to represent the hygroscopic environment (Figures 11B-11C). We were able to obtain optimized structures with one or two H₂O molecules forming hydrogen bonds with the oxygen atoms in the crown ether cavity and bridging adjacent layers to form proton conduction pathways with long-range order. We postulate — based on the observed proton conductivity and the modeling studies — that the proton conduction mechanism in poly(TBL-DB18C6)-*t* under humid conditions results from protons hopping through H₂O molecules and [18]crown-6 cavities, i.e., by a Grotthuss mechanism.

Conclusions: We have demonstrated how to integrate hydrophilic crown ethers into ladder-type polymer backbones and evaluated their proton conduction performance in humid environments. High molecular weight, robust, processable Tröger's base-linked polymers have been prepared by one-pot polymerizations of both constitutional isomers of di(aminobenzo)[18]crown-8 in the presence of a Lewis acid which acts as both a catalyst and a solvent. The characterization of the precursors — *trans*- or *cis*-di(nitrobenzo)[18]crown-8 and *trans*- or *cis*-di(aminobenzo) [18]crown-8 — as well as the Tröger's base-linked polymers was carried out by FTIR, ¹H and ¹³C NMR spectroscopy, and GPC analyses. Free-standing membranes obtained by solution casting of the Tröger's base-linked polymers, synthesized from both constitutional isomers, exhibit excellent thermal and water stabilities as a result of their high molecular mass. These Tröger's base-linked polymers have been shown to retain 23 wt% of water molecules at 25% RH. The adsorbed water molecules form hydrogen-bonded networks,

which sustain long-range proton conductivity throughout the polymers. The proton conductivity of poly(TBL-DB18C6)-*t* and poly(TBL-DB18C6)-*c*, measured on a device with two terminal geometries in the presence of 5% of hydrogen, reveals a value of $1.4 \times 10^{-4} \text{ mS cm}^{-1}$ and $1.4 \times 10^{-1} \text{ mS cm}^{-1}$, respectively, in humid conditions at room temperature. Examination of a kinetic isotope effect — transport of D^+ ions — confirms that proton conductivity originates from the transport of protons rather than by ionic conduction in the polymers. Structural analyses, using DFT calculations, suggest that the short polymer chains of poly(TBL-DB18C6)-*t*, arranged in a stacked form with an inter-layer distance suitable for H_2O molecules to form hydrogen-bonded networks, enable hopping of protons through these networks which are sustained by the oxygen atoms in the crown ether cavities. The addition of this new polymer to already existing proton exchange membranes for application in PEMFCs will make it possible for scientists and engineers to improve proton conductivities. In addition, the presence of crown ethers with a range of different cavity sizes in the Tröger's base-linked polymers could lead to membrane-based small molecule separations.

Synthesis Schemes

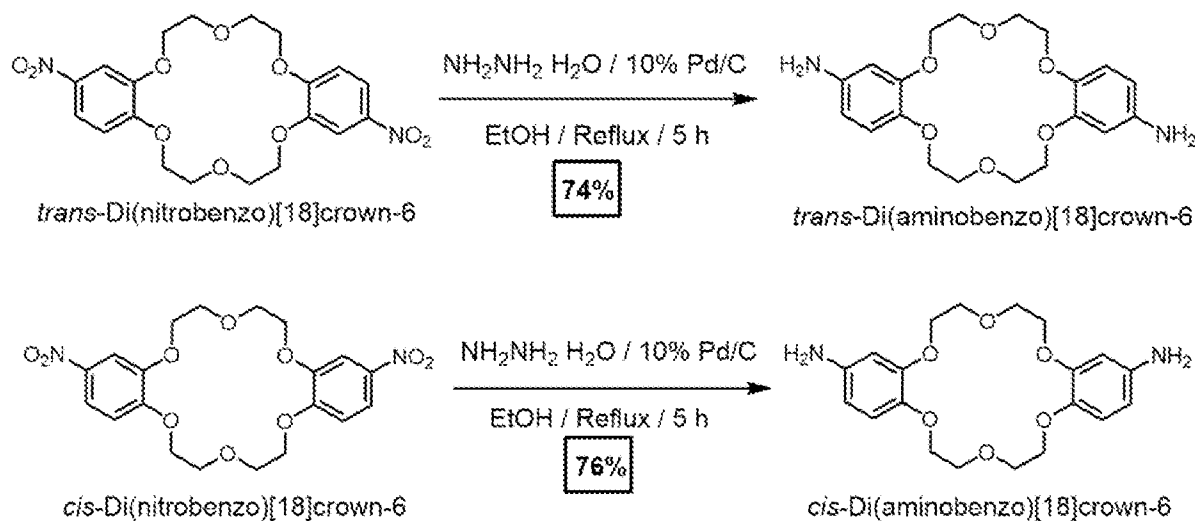


Scheme 1. Synthesis of dinitro-derivatives of dibenzo[18]crown-6.

***trans* and *cis*-Di(nitrobenzo)[18]crown-6.** The compounds — *trans*-di(nitrobenzo)[18]crown-6 and *cis*-di(nitrobenzo)[18]crown-6 — were prepared according to procedures already reported^{3–5} in the literature. Dibenzo[18]crown-6 (10.38 g) was dissolved in CHCl_3 (208 mL). Acetic acid (156 mL) was added to the solution over 10 min and it was stirred at room temperature for 5 min. A solution of HNO_3 (7.2 mL) in acetic acid (20.8 mL) was added dropwise over 20 min and the solution was stirred for 1 h. The reaction mixture was heated under reflux for 3 h and cooled to room temperature. The precipitate which formed was filtered off, washed with CHCl_3 (2 x 25 mL), and the filtrate transferred to a conical flask. The residual acetic acid in the precipitate was washed using H_2O (3 x 25 mL) before drying it at 70°C under

vacuum for 24 h. The *trans*-di(nitrobenzo)[18]crown-6 was obtained as a pale yellow compound. The filtrate, which was left at room temperature for 48 h, resulted in the formation of a pale yellow crystalline compound, which was filtered, washed with CHCl₃ (2 x 25 mL) and H₂O (3 x 25 mL) to remove the residual acetic acid. The *cis*-di(nitrobenzo)[18]crown-6 was dried at 80°C under vacuum for 24 h. Total recovery of the dinitro derivatives — *trans*-di(nitrobenzo)[18]crown-6 (46%, 4.7 g) and *cis*-di(nitrobenzo)[18]crown-6 (48 %, 5 g) — was 94% (9.7 g).

***trans*-Di(nitrobenzo)[18]crown-6:** ¹H NMR (500 MHz, CD₃SOCD₃) δ = 7.89 (dd, *J* = 9.0, 2.6 Hz, 2H), 7.73 (d, *J* = 2.6 Hz, 2H), 7.16 (d, *J* = 9.1 Hz, 2H), 4.22 (m, 8H), 3.90 – 3.83 (m, 8H). ¹³C NMR (125 MHz, CD₃SOCD₃) δ = 153.7, 147.6, 140.2, 117.5, 111.2, 106.5, 68.4. ***cis*-Di(nitrobenzo)[18]crown-6:** ¹H NMR (500 MHz, CD₃SOCD₃) δ = 7.89 (dd, *J* = 9.0, 2.6 Hz, 2H), 7.73 (d, *J* = 2.6 Hz, 2H), 7.16 (d, *J* = 9.0 Hz, 2H), 4.22 (m, 8H), 3.86 (m, 8H). ¹³C NMR (125 MHz, CD₃SOCD₃) δ = 153.7, 147.6, 140.5, 117.5, 111.2, 106.5, 68.2.



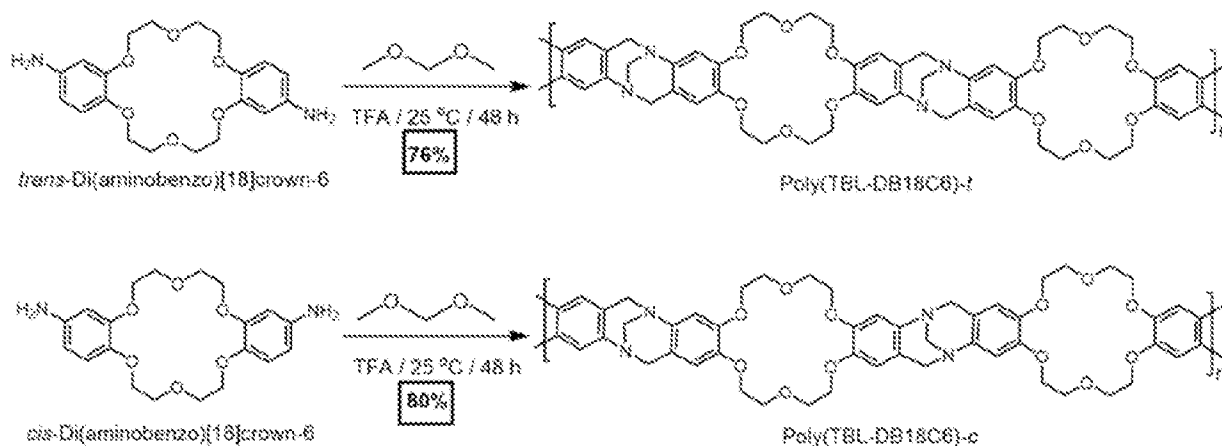
Scheme 2. Synthesis of diamino-derivatives of dibenzo[18]crown-6.

***trans and cis*-Di(aminobenzo)[18]crown-6.** The diamino derivative was prepared by the catalytic hydrogenation of the dinitro compound. *trans*-Di(nitrobenzo)[18]crown-6 (5 g) and 10% Pd/C (500 mg) were added in EtOH (170 mL). The reaction mixtures were stirred under N₂ atmosphere and heated under reflux as NH₂NH₂·H₂O (35 mL) was added over 20 min. The reaction was allowed to continue at 90°C for 5 h to ensure complete removal of ammonia under

an N₂ atmosphere. The hot reaction mixture was filtered in order avoid immediate crystallization of a product. The white crystalline compound — *trans*-di(aminobenzo)[18]crown-6 — was washed using EtOH (3 x 5 mL) before drying it at 80°C for 24 h under vacuum, resulted (3.7 g) in 74% yield. The similar procedure was also employed for the synthesis of *trans*-di(aminobenzo)[18]crown-6, in which *cis*-di(nitrobenzo)[18]crown-6 (2.75 g), 10% Pd/C (280 mg), EtOH (100 mL), and NH₂NH₂·H₂O (20 mL) were used. The *trans*-di(aminobenzo)[18]crown-6 was obtained (2.1 g) as a white crystalline material in 76% yield.

***trans*-Di(aminobenzo)[18]crown-6:** ¹H NMR (500 MHz, CD₃SOCD₃) δ = 6.62 (d, *J* = 8.4 Hz, 2H), 6.23 (d, *J* = 2.3 Hz, 2H), 6.05 (dd, *J* = 8.4, 2.3 Hz, 2H), 4.63 (s, 4H), 4.04 – 3.87 (m, 8H), 3.86 – 3.71 (m, 8H). ¹³C NMR (125 MHz, CD₃SOCD₃) δ = 149.2, 143.5, 139.1, 115.7, 105.3, 100.7, 71.5–65.8.

***cis*-Di(aminobenzo)[18]crown-6:** ¹H NMR (500 MHz, CD₃SOCD₃) δ = 6.62 (d, *J* = 8.4 Hz, 2H), 6.24 (d, *J* = 2.5 Hz, 2H), 6.05 (dd, *J* = 8.4, 2.4 Hz, 2H), 4.63 (s, 4H), 4.06 – 3.87 (m, 8H), 3.86 – 3.71 (m, 8H). ¹³C NMR (125 MHz, CD₃SOCD₃) δ = 149.2, 143.5, 139.1, 115.7, 105.3, 100.7, 71.5–65.8.



Scheme 3. Synthesis of Tröger's base linked poly(dibenzo[18]crown-6)s, Poly(TBL-DB18C6)-*t* and Poly(TBL-DB18C6)-*c* from *trans* and *cis*-di(aminobenzo)[18]crown-6, respectively.

Poly(dibenzo[18]crown-6)s. In a two-neck flask placed in an ice bath, *trans*-di(aminobenzo)[18] crown-6 (1.2 g, 3.07 mmol) was added into dimethoxymethane (1.36 mL, 15.4 mmol) under an N₂ atmosphere. Trifluoroacetic acid (12 mL) was added dropwise over 15

min with vigorously stirring for 30 min at 0°C. Subsequently, the solution was allowed to reach room temperature and stirred for 48 h. A viscous liquid obtained was added into aqueous NH₄OH solution with stirring and it was allowed to stir for an additional 1 h, resulting in fibrous materials. The polymers were filtered off, soaked in H₂O (3 x 100 mL), washed with MeOH, THF, and Me₂CO (3 x 25 mL), and dried at 80°C under vacuum for overnight to yield 1.27 g of poly(TBL-DB18C6)-*t*. The poly(TBL-DB18C6)-*c* was synthesized in accordance with above protocol, using *cis*-di(aminobenzo)[18]crown-6 (1.2 g, 3.07 mmol) as a monomer, resulting in 1.32 g of poly(TBL-DB18C6)-*c*. **Poly(TBL-DB18C6)-*t***: ¹H NMR (500 MHz, CDCl₃) δ = 6.62, 6.35, 4.55, 4.23, 4.16 – 3.78. ¹³C NMR (125 MHz, CDCl₃) δ = 148.3, 146.0, 141.2, 119.6, 111.6, 110.1, 71.0–68.1, 58.1. **Poly(TBL-DB18C6)-*c***: ¹H NMR (500 MHz, CDCl₃) δ = 6.64, 6.35, 4.55, 4.24, 4.16 – 3.80. ¹³C NMR (125 MHz, CDCl₃) δ = 148.3, 146.1, 141.1, 119.6, 111.5, 110.2, 70.5–68.5, 58.1.

Materials and Methods.

All chemicals and reagents were purchased from commercial suppliers (Sigma-Aldrich, TCI America or Fisher) and used without further purification.

Spectroscopy. Fourier transform infrared (FTIR) spectra were recorded in attenuated total reflection (ATR) mode within the range 400–4000 cm⁻¹ using a Bruker Tensor 37 FTIR (MiD IR/ATR) spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 600, with working frequencies of 500 MHz (¹H NMR) and 125 MHz (¹³C NMR). Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents ((CD₃)₂SO: δ 2.5 ppm; CDCl₃: δ 7.26 ppm).

Thermal Stability. Thermogravimetric analysis (TGA) was conducted on polymers using a Mettler Toledo TGA/SDTA851e thermal analyzer. Polymers (3–5 mg) were loaded in an alumina pan and heated up to 800°C at a rate of 10°C min under the flow of N₂ gas (50 mL min⁻¹). The instrument was purged with N₂ gas for 1 h prior to examining samples and empty reference pan.

Average Molecular Weight. The average molecular weight of the polymers was determined by Gel Permeation Chromatography (GPC). The analyses were carried out using a Wyatt technology GPC system which includes two PolyPore 300 x 7.5 mm columns (Varian p/n 5M-POLY-008-112) and detectors — MALS (18 Angles Dawn Heleos II), Viscometer (ViscoStar-II), and differential refractive index (OptiLab T-rex). Average molecular weights

were determined from a calibration against polystyrene standards. Dilute solutions of polymers in CHCl_3 was used for the GPC analyses.

Water Vapor Adsorption. A Hiden isochema intelligent gravimetric analyzer (IGA-200) was used to characterize the dynamic vapor sorption (DVS). The temperature of the sample and target vapor were controlled by two water baths equipped with an IGA-200. Data from both isotherms were collected using IGASwin software (v.1.06) which applies the buoyancy effect correction via a linear driving force model to every data point — i.e, each adsorbed mass recorded at a given vapor composition was determined by the difference between the mass gain at that point and that recorded with dry N_2 — at 25°C . Vapor composition was modulated by mixing dry N_2 and the N_2 gas stream saturated with H_2O vapor; N_2 carrier gas was bubbled through an H_2O reservoir at 25°C till saturation. The combined flow rate at any given concentration or relative pressure was $100 \text{ cm}^3 \text{ min}^{-1}$. The time for each point of adsorption/desorption varies in accordance with reaching either an equilibrium or the time limit of 2 h.

Device Construction. Devices consisted of 100 nm Pd contacts with a 5 nm Cr adhesion layer deposited on Si wafers with a 100 nm SiO_2 layer. Contact widths of either 600 or 200 μm , and distances between source and drain contacts (L_{SD}) of 5, 10, 20, 50, 100, and 200 μm were defined. Polymers were dissolved in CHCl_3 (20 mg mL^{-1}) and spun onto devices at 500 rpm for 5 s prior to drying at 80°C for 2 h.

Electrical Measurements. Electronic recordings were carried out on an Agilent 4155C semiconductor parameter analyzer. Measurements were performed on a Signatone probe station fitted with a custom atmospheric isolation chamber using Dakota Instruments mass flow controllers.

Relative Humidity and Gas Composition. Measurements in the chamber were carried out in an N_2 atmosphere which was varied between 50, 75, and 90% relative humidity. Proton current measurements were performed at 90% relative humidity with H_2O and a mixture (95% N_2 + 5% H_2) of gases. Kinetic isotope effects were measured at 90% relative humidity with D_2O and a mixture (95% N_2 + 5% D_2) of gases. All samples were incubated for a minimum of 1 h after switching to new atmospheric conditions.

Atomic Force Microscopy. Film thickness and morphology were recorded with an Asylum MFP-3D Infinity AFM operating in AC Tapping Mode. Thickness measurements were

carried out by removing a section of the film with a probe tip and looking at the height difference between the film top and exposed SiO₂. Morphology images of the channel were carried out between TLM contacts. All AFM measurements on the device were performed after electrical measurements at room temperature.

5 **Simulation.** The computational studies on dibenzo[18]crown-6 in hygroscopic environment have been well-established. First, a single layer model was constructed by linking three units of dibenzo[18]crown-6 with two Tröger's base linkages. The geometry was then optimized using the B3LYP density functional with a 6-31G(d) basis set. Then, the potential energy surface as a function of inter-layer distance was calculated for the double layer system
10 with the geometry of two fixed single layers using the B97D3 density functional which provides a reasonable description of the dispersion interactions at an affordable computational cost with a 6-31G(d) basis set. Finally, possible the proton conducting network models were constructed by inserting 1 or 2 H₂O molecules between two layers of dibenzo[18]crown-6. The geometry was optimized with the two layers fixed at 5.2 Å distance (only H₂O molecules were allowed to
15 move) using B3LYP/6-31G(d,p), in which the enlarged basis set with diffuse functions and additional polarization functions on hydrogen was used to describe hydrogen-bonds. All calculations were performed using the Gaussian 09 (rev.D.01) software.²

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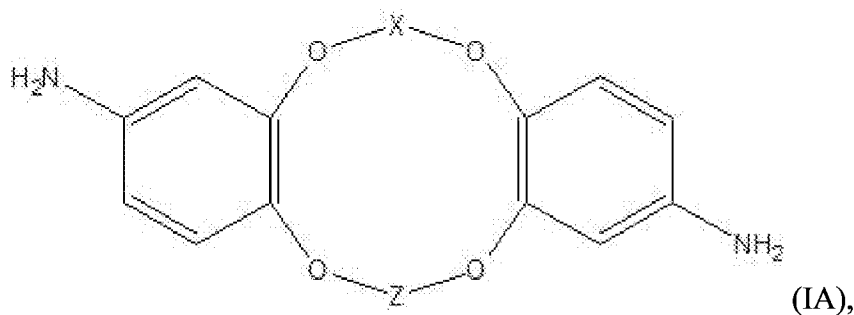
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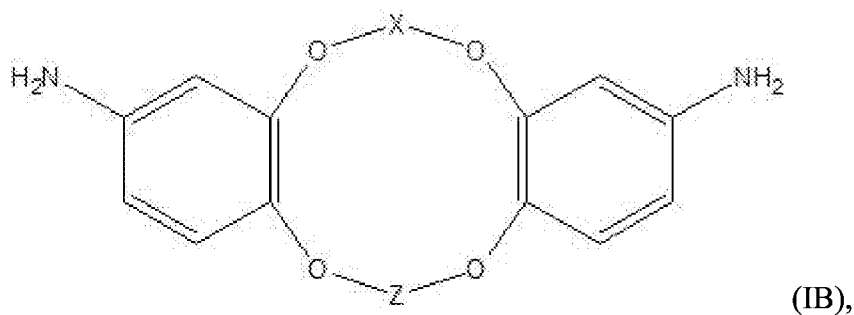
CLAIMS

We claim:

1. A composition comprising a double-strand chain, the double-strand chain comprising a plurality of constitutional units joined to each other through two atoms on one side of the constitutional unit and two atoms on the other side of the constitutional unit,
 5 wherein each of the plurality of constitutional units comprise a dibenzo-crown ether macrocycle fused with a bicyclic aliphatic linker.
2. The composition of claim 1, wherein the bicyclic aliphatic linker comprises a diazocine linker having two bridgehead nitrogen atoms.
- 10 3. The composition of claims 2, wherein the diazocine linker comprises a [b,f][1,5]diazocine linker bridged by a methylene.
4. The composition of any one of claims 1-3, wherein the dibenzo-crown ether macrocycle comprises a dibenzo[n]crown-m macrocycle and $m = 4, 5, 6, 7$, or 8 and $n = 3m$.
5. The composition of claim 4, wherein $m = 6$.
- 15 6. The composition of any one of claims 1-5, wherein the chain is prepared from the cyclopolymerization of a plurality of di(aminobenzo)crown ethers.
7. The composition of claim 6, wherein the di(aminobenzo)crown ethers are selected from the group consisting of Formula IA



20 Formula IB



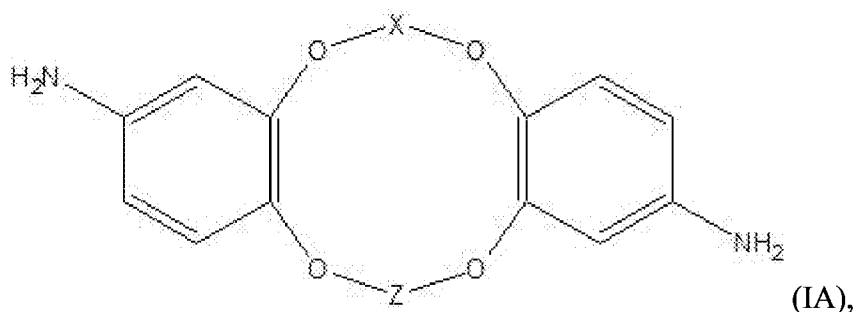
and any combination thereof,

wherein X and Z are selected from the group consisting of alkyl and ether.

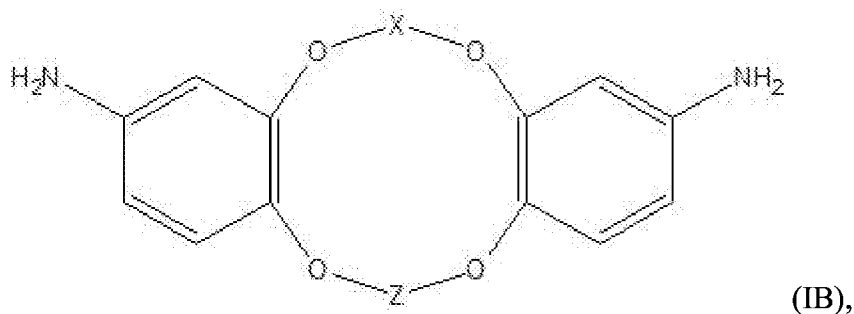
8. The composition of claim 7, wherein X and Y are independently selected from —
5 CH₂CH₂—, —CH₂CH₂OCH₂CH₂—, or —CH₂CH₂OCH₂CH₂OCH₂CH₂—.
9. The composition of claim 8, wherein X and/or Y comprises —CH₂CH₂OCH₂CH₂—.
10. A polymer comprising the composition of claim 1.
11. The polymer of claim 10, wherein—
the polymer has a weight-average molecular weight (M_w) of at least 100,000 Da;
10 the polymer is thermally stable in an inert atmosphere up to a temperature of at least 200°C;
the polymer is at least partially soluble in a halogenated alkane solvent;
the polymer has a water uptake capacity of at least 10 wt% at 90% relative humidity;
the polymer is capable of forming films; or
15 any combination thereof.
12. The polymer of claim 11, wherein the polymer has a weight-average molecular weight (M_w) of at least 100,000 Da.
13. The polymer of claim 11, the polymer is thermally stable in an inert atmosphere up to a temperature of at least 200°C.
- 20 14. The polymer of claim 11, the polymer is at least partially soluble in a halogenated alkane solvent.

15. The polymer of claim 11, the polymer has a water uptake capacity of at least 10 wt% at 90% relative humidity.
16. The polymer of claim 11, the polymer is capable of forming films.
17. The polymer of claim 10 or 16, wherein the polymer comprises the composition of any one of claims 2-9.
18. A membrane comprising the composition of claim 1.
19. The membrane of claim 18, wherein—
the membrane is proton conductive;
the membrane is capable of binding ions or small molecules;
the membrane is capable of separating gases;
the membrane is capable of treating water; or
any combination thereof.
20. The membrane of claim 19, wherein the membrane is proton conductive.
21. The membrane of claim 20, wherein the membrane is a proton exchange membrane.
22. The membrane of any one of claims 18-21, wherein the membrane has a proton conductivity of at least $1.0 \times 10^{-8} \text{ S cm}^{-1}$.
21. The membrane of claim 19, wherein the membrane is capable of binding ions or small molecules.
22. The membrane of claim 19, wherein the membrane is capable of separating gases.
23. The membrane of claim 19, wherein the membrane is capable of treating water.
24. The membrane of any one of claims 18-23, wherein the membrane comprises the double-strand chain of any one of claims 2-9 or the polymer of any one of claims 10-17.
25. A proton exchange membrane fuel cell comprising the membrane of claim 18.
26. The fuel cell of claim 25, wherein the membrane is a proton exchange membrane.
27. The fuel cell of claim 25 or 26, wherein the membrane has a proton conductivity of at least $1.0 \times 10^{-8} \text{ S cm}^{-1}$.

28. The fuel cell of any one of claims 25-27, wherein the membrane comprises the double-strand chain of any one of claims 2-9 or the polymer of any one of claims 10-17.
29. A method for preparing a proton conductive membrane, the method comprising providing the composition of claim 1 and forming the membrane.
30. The method of claim 29 further comprising absorbing water onto the membrane.
31. The method of claim 29 or 30, wherein then the double strand chain is prepared from the cyclopolymerization of a plurality of di(aminobenzo)crown ethers.
32. The method of claim 31, wherein the di(aminobenzo)crown ethers are selected from the group consisting of Formula IA



Formula IB



and any combination thereof,

wherein X and Z are selected from the group consisting of alkyl and ether.

33. The method of claim 32, wherein X and Y are independently selected from $\text{—CH}_2\text{CH}_2\text{—}$, $\text{—CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{—}$, or $\text{—CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{—}$.
34. The method of claim 33, wherein X and/or Y comprises $\text{—CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{—}$.

35. The method of any one of claims 29-34, wherein the membrane is formed by solution casting the composition.
36. The method of any one of claims 29-35, wherein the membrane comprises the double-strand chain of any one of claims 2-9 or the polymer of any one of claims 10-17.

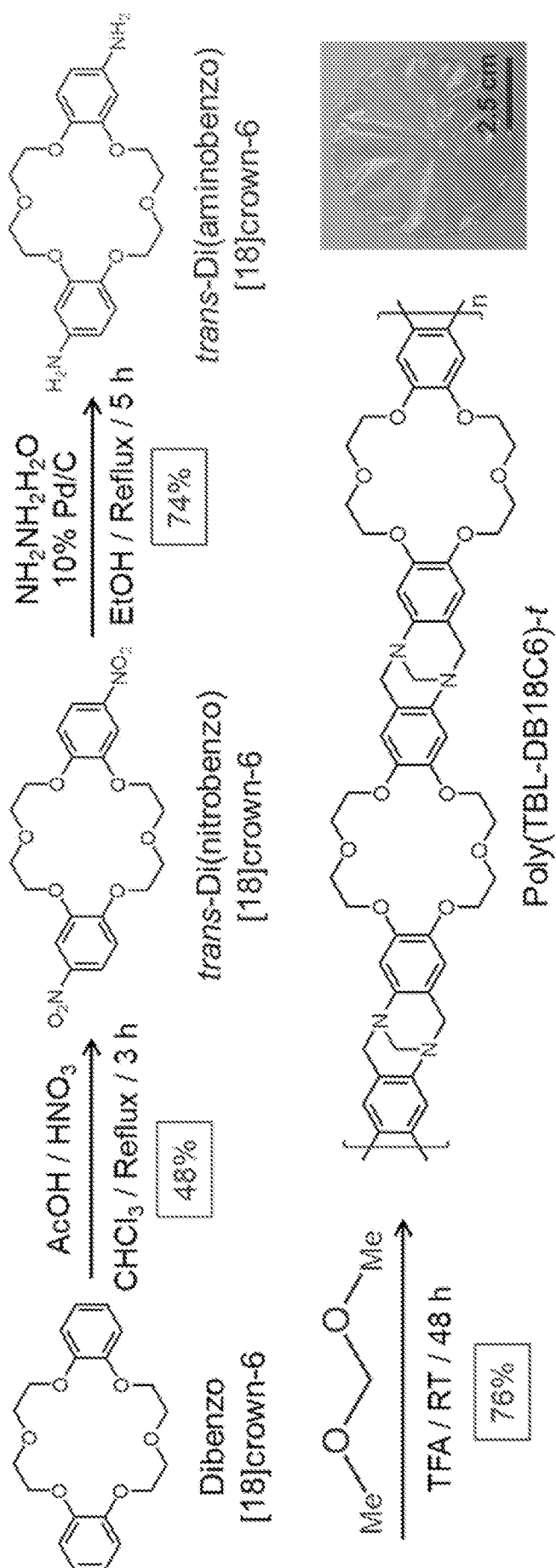


Fig. 1

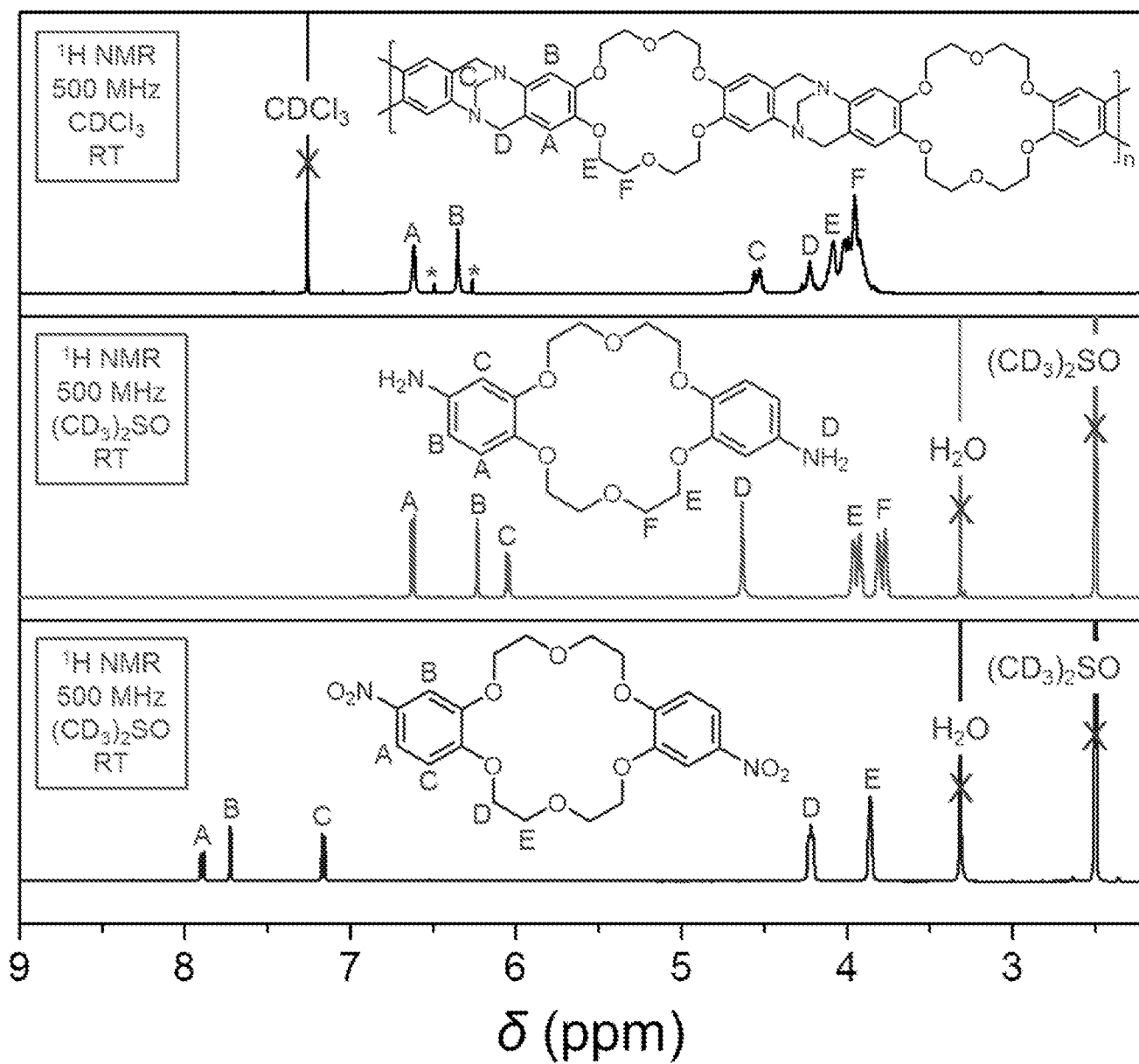


Fig. 2A

Fig. 2B

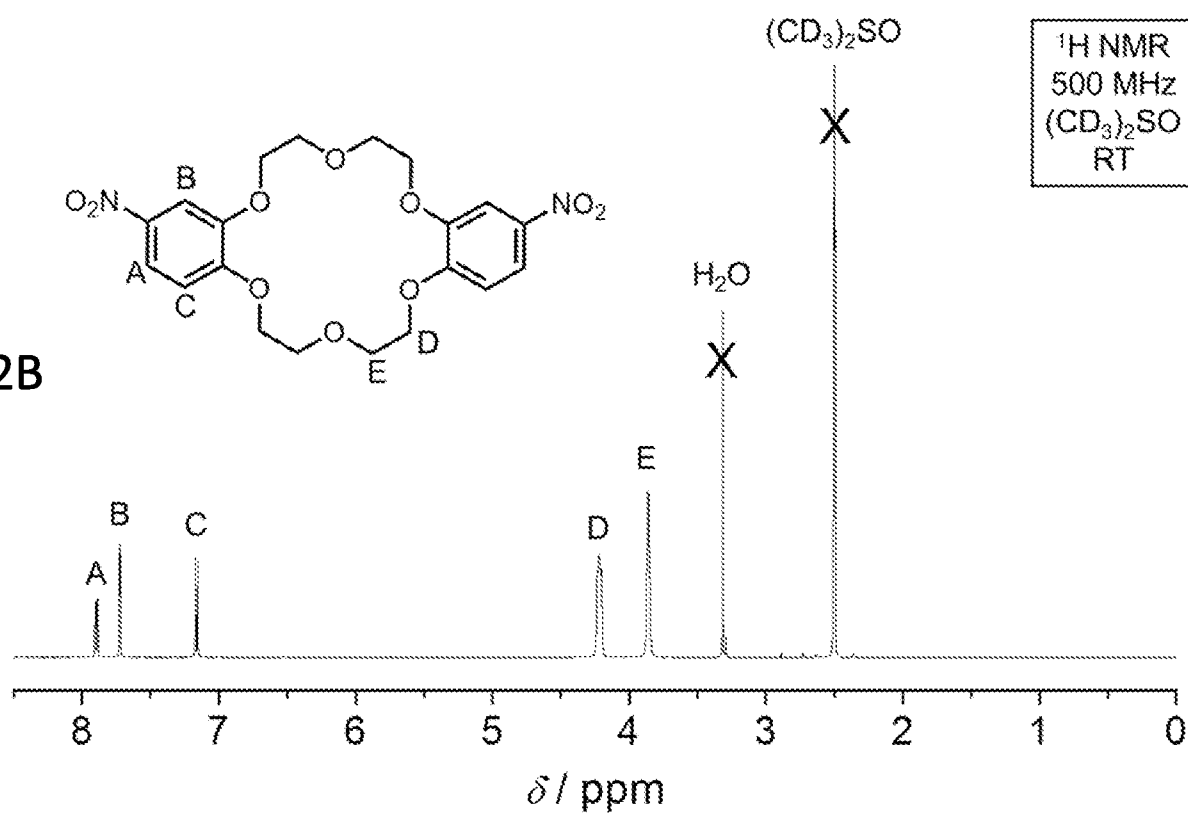


Fig. 2C

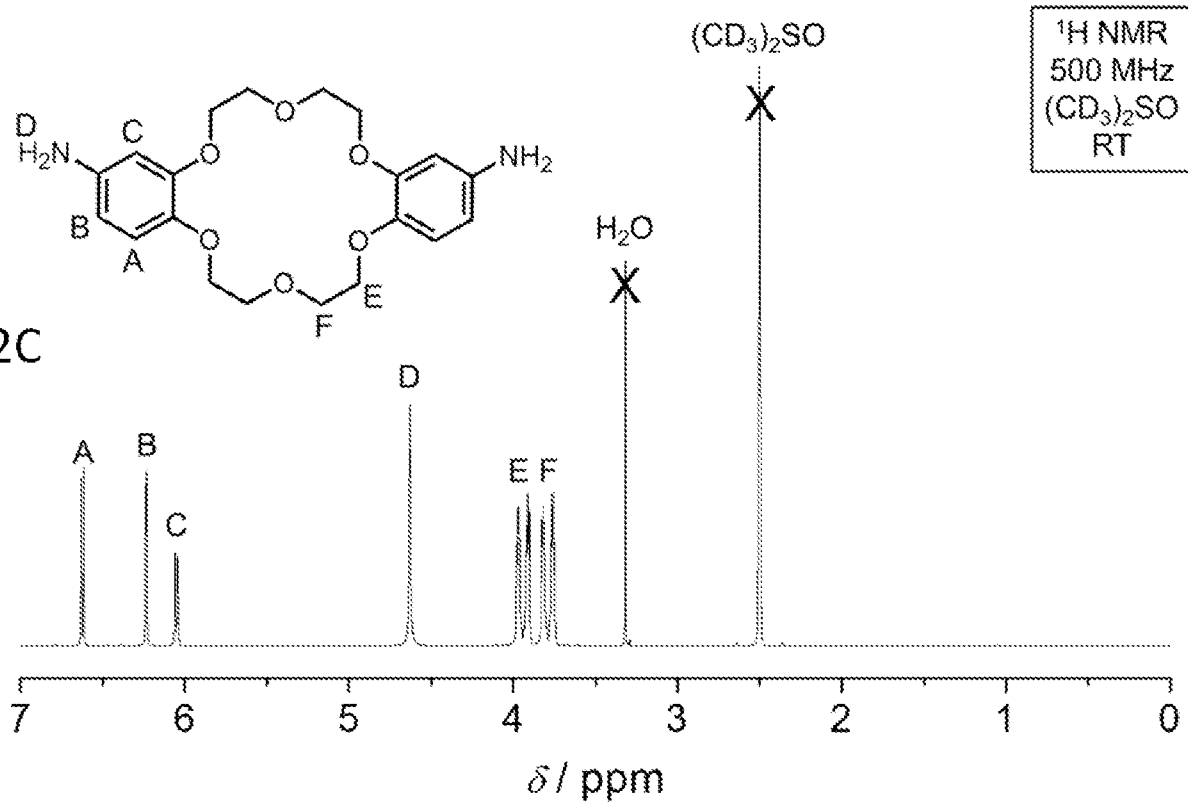


Fig. 2D

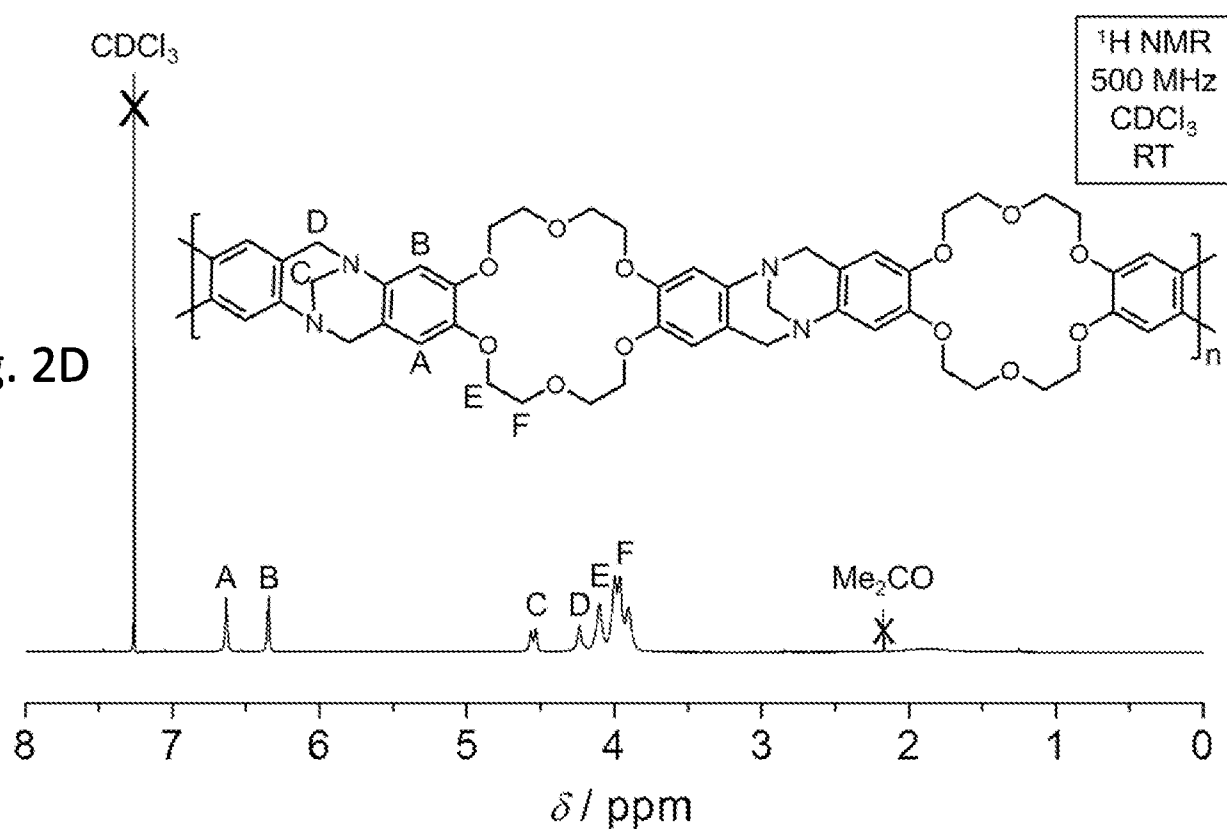


Fig. 2E

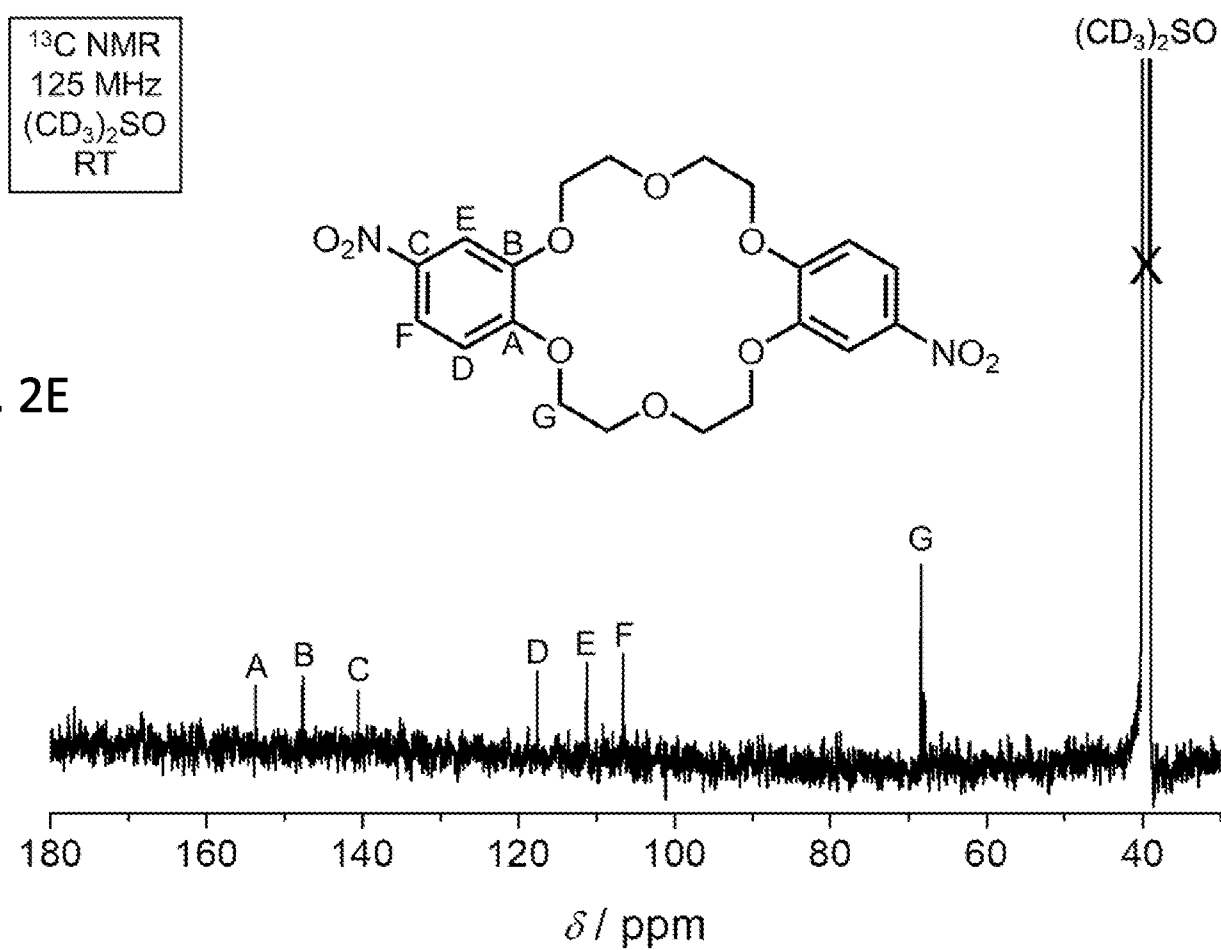


Fig. 2F

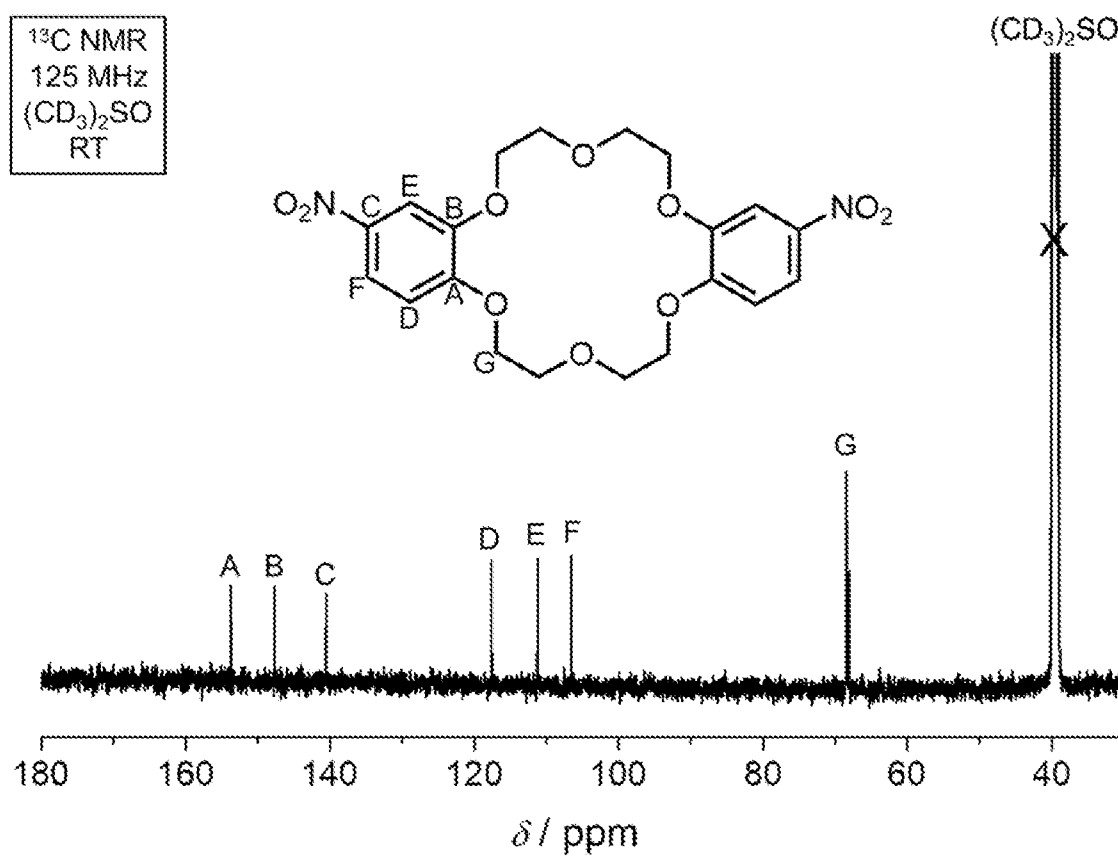
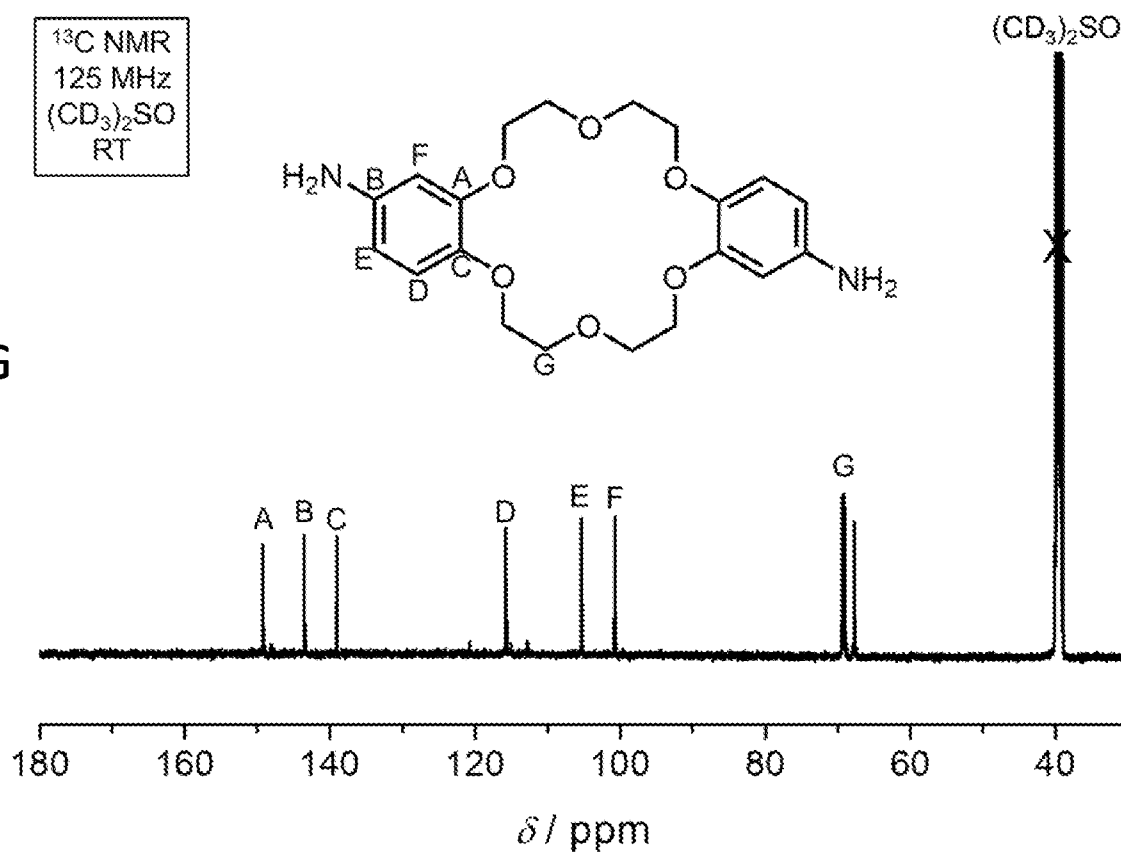


Fig. 2G



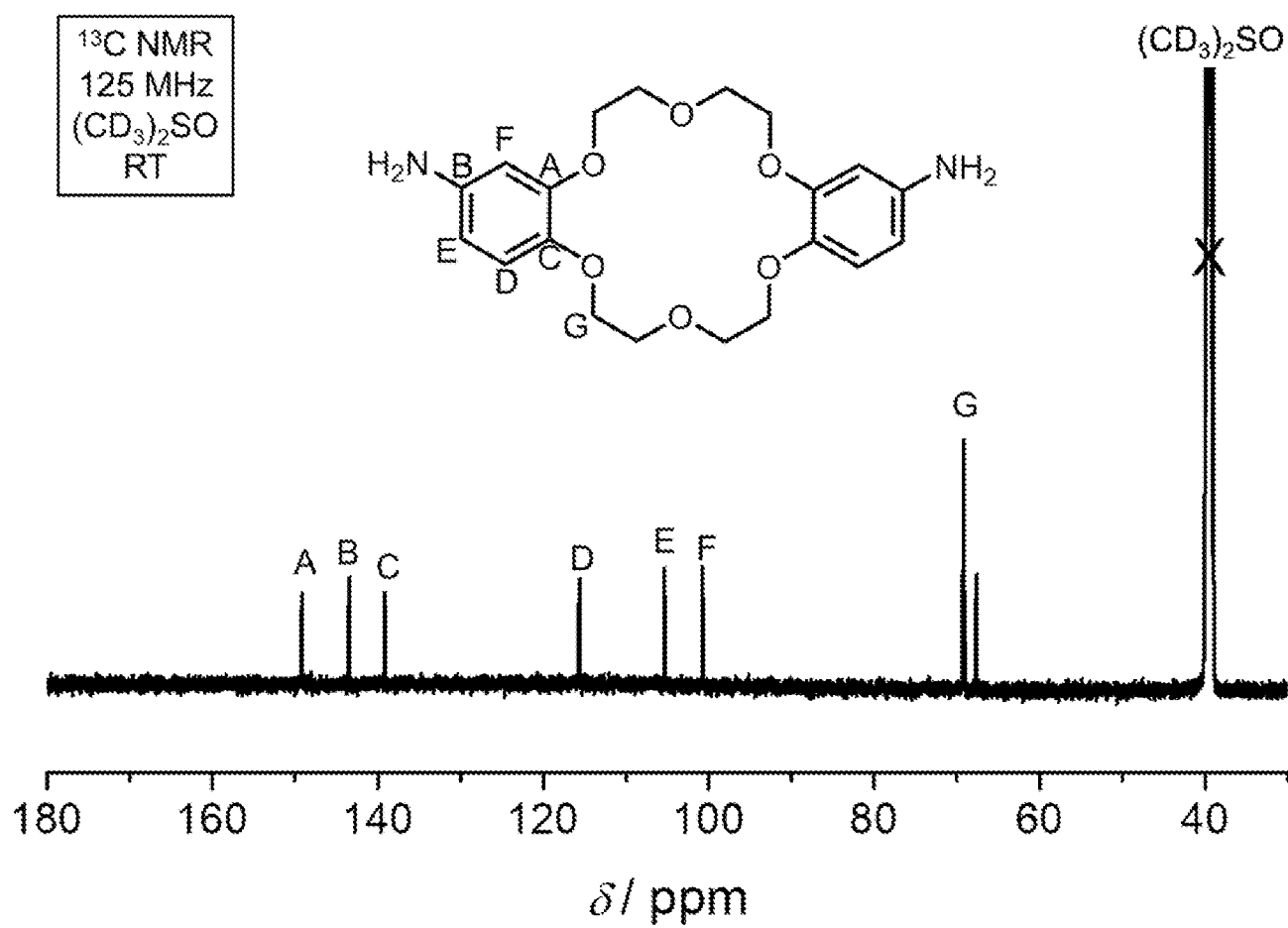


Fig. 2H

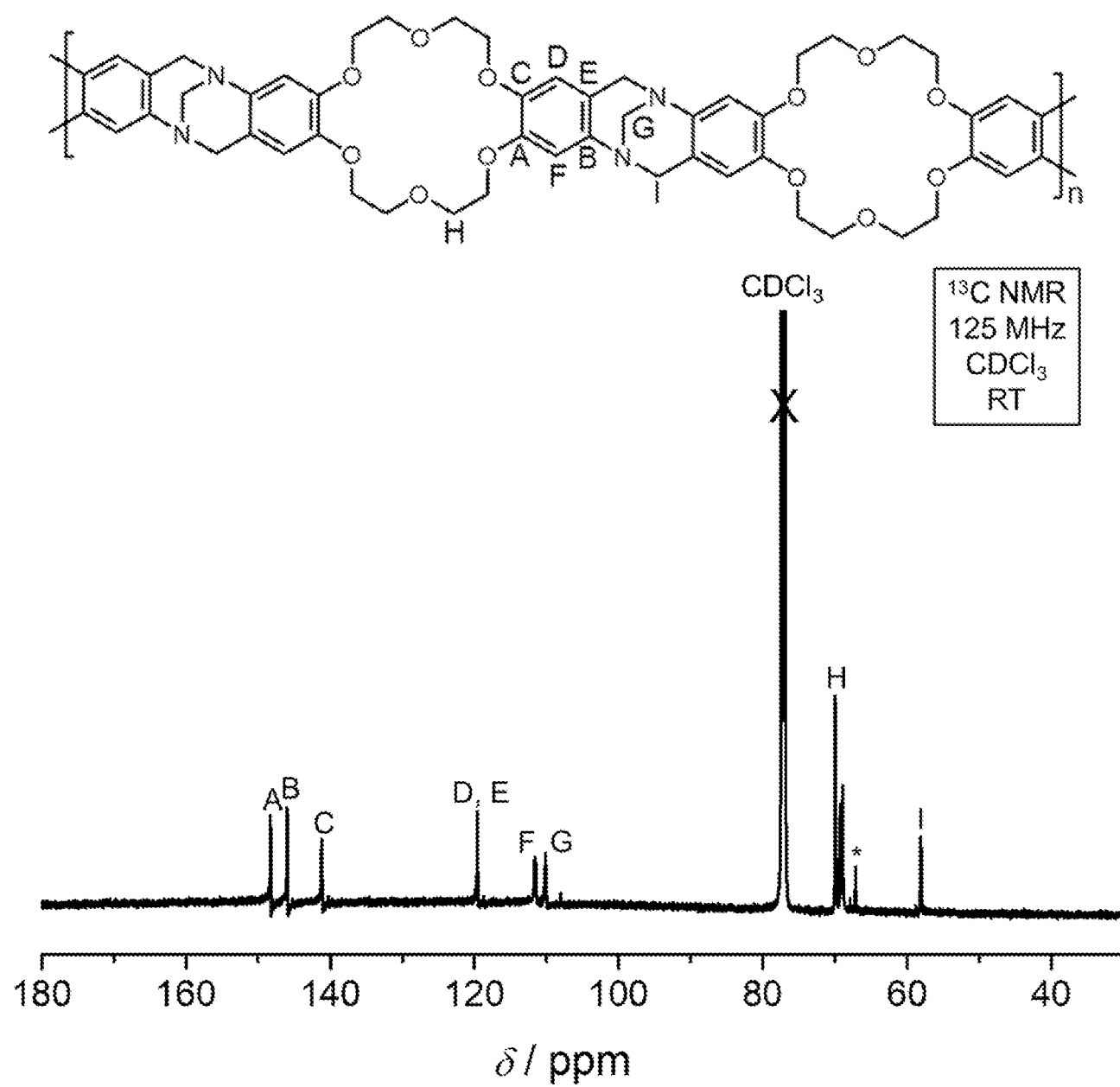


Fig. 2I

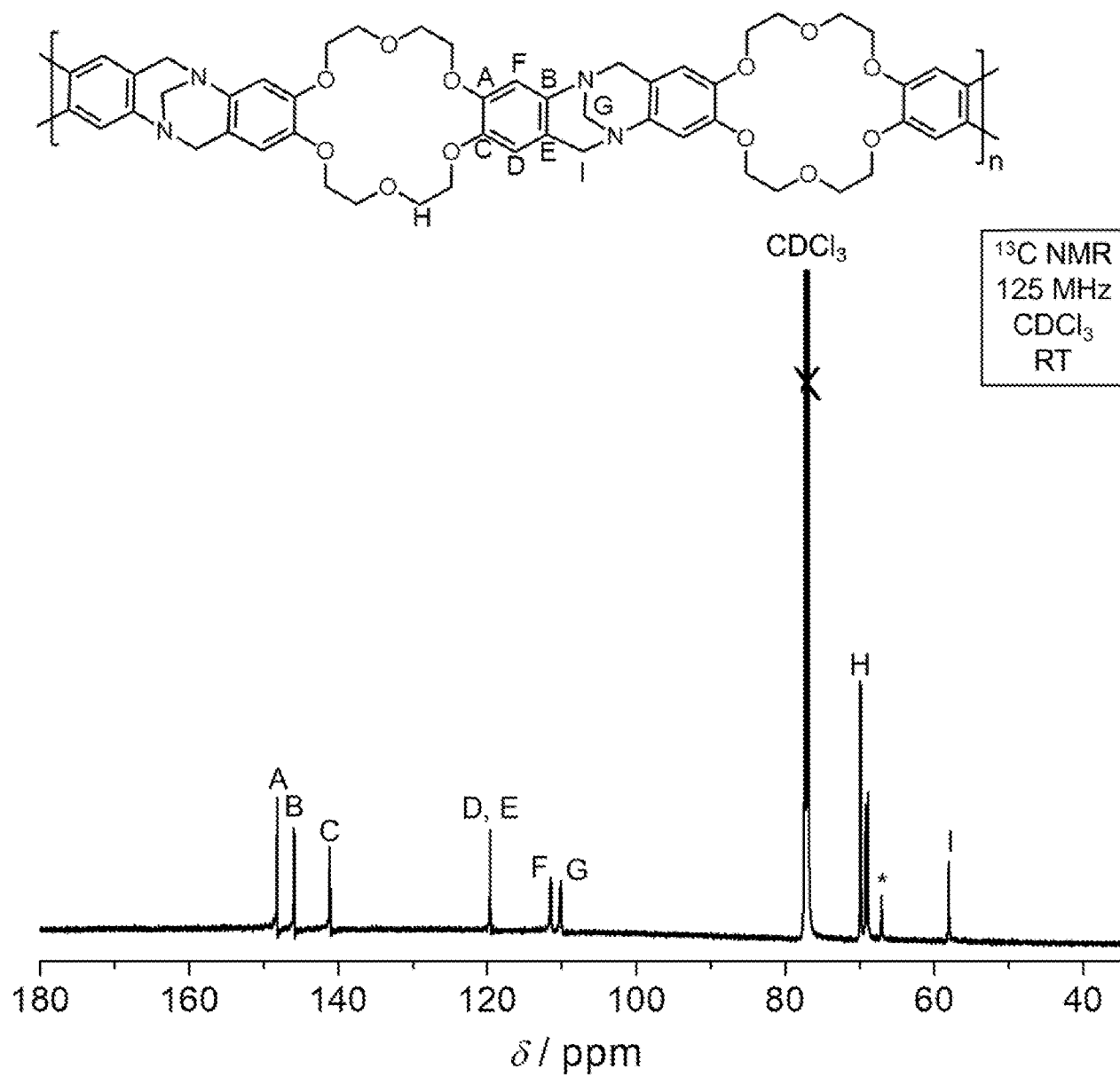


Fig. 2J

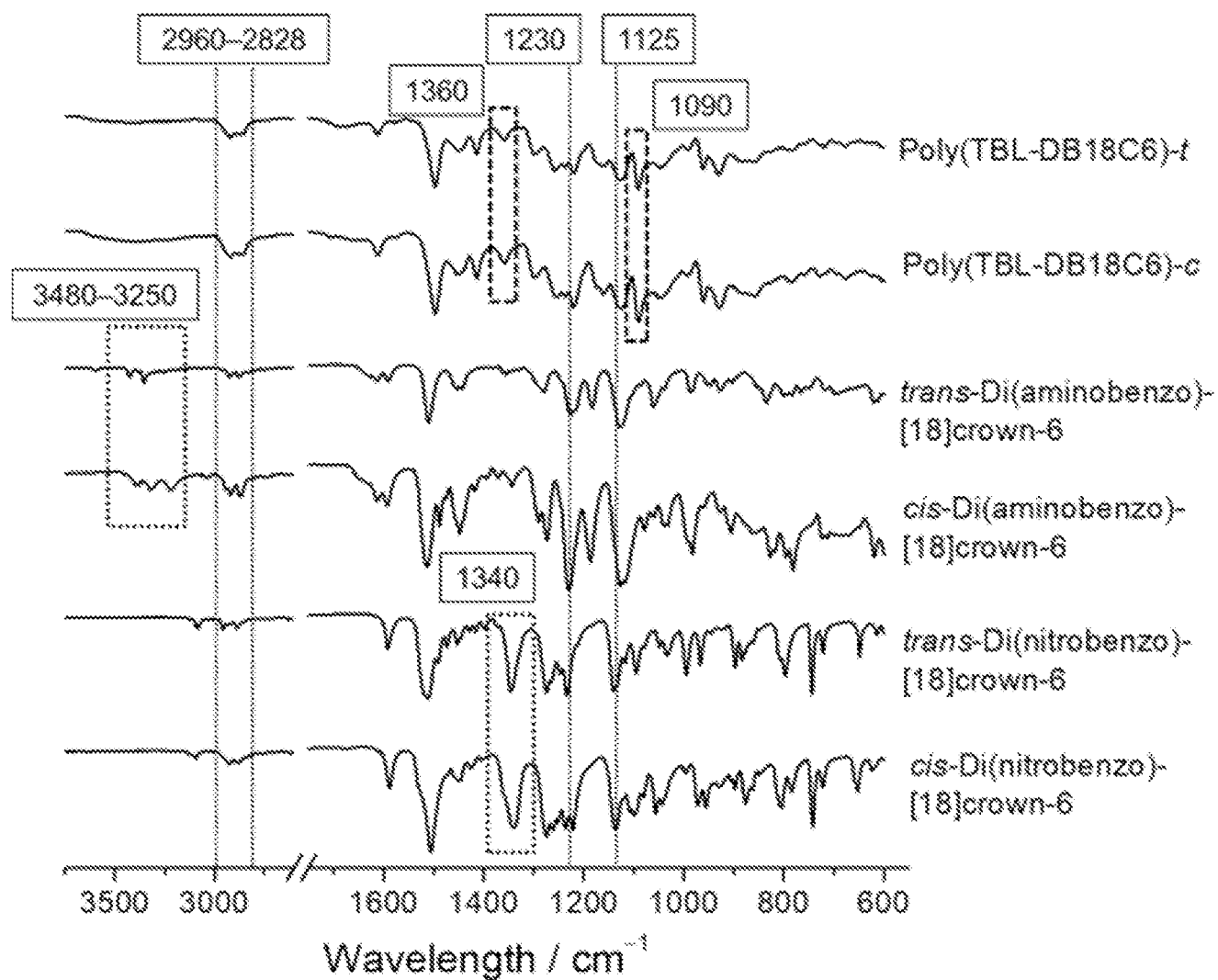


Fig. 3

Fig. 4

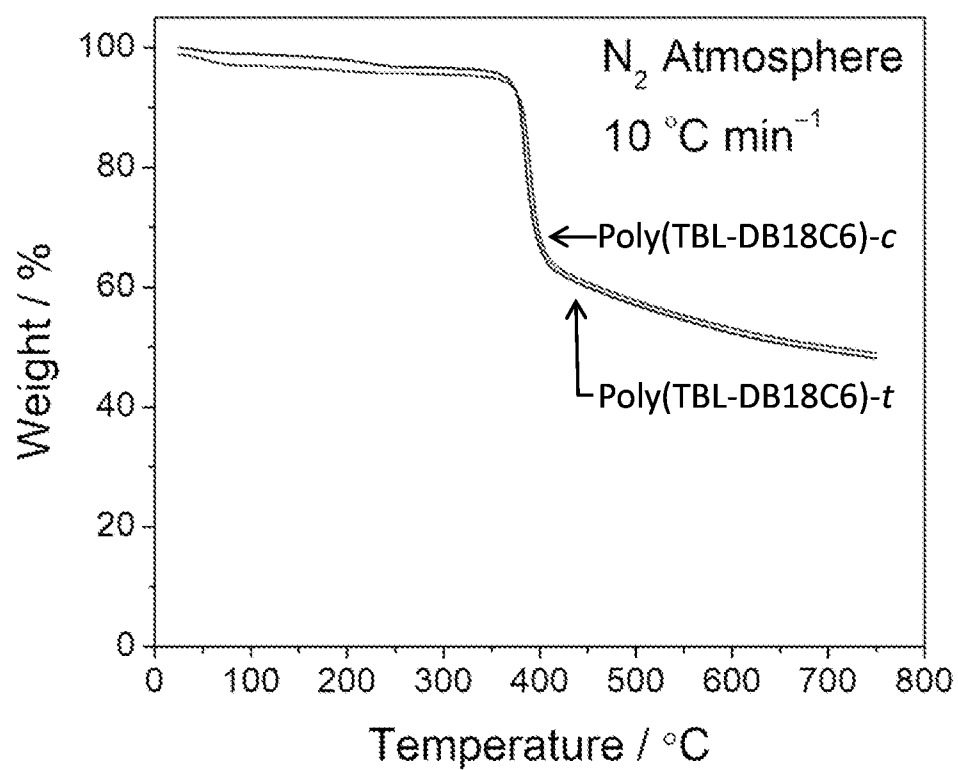
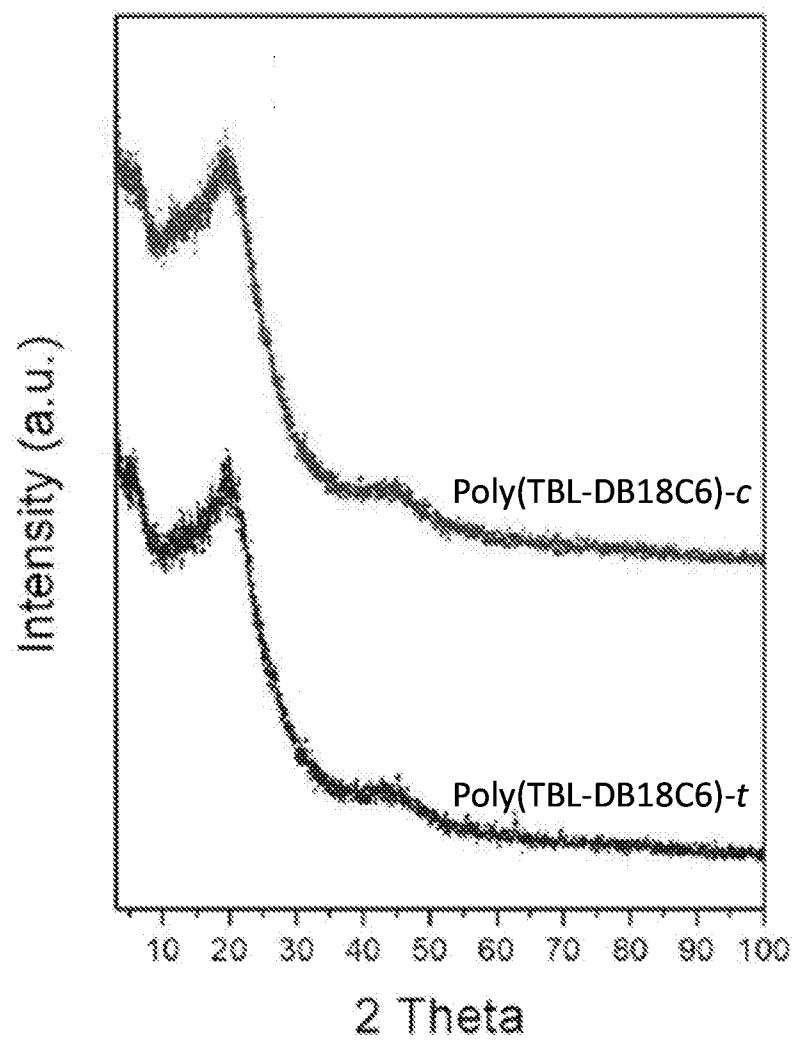


Fig. 5



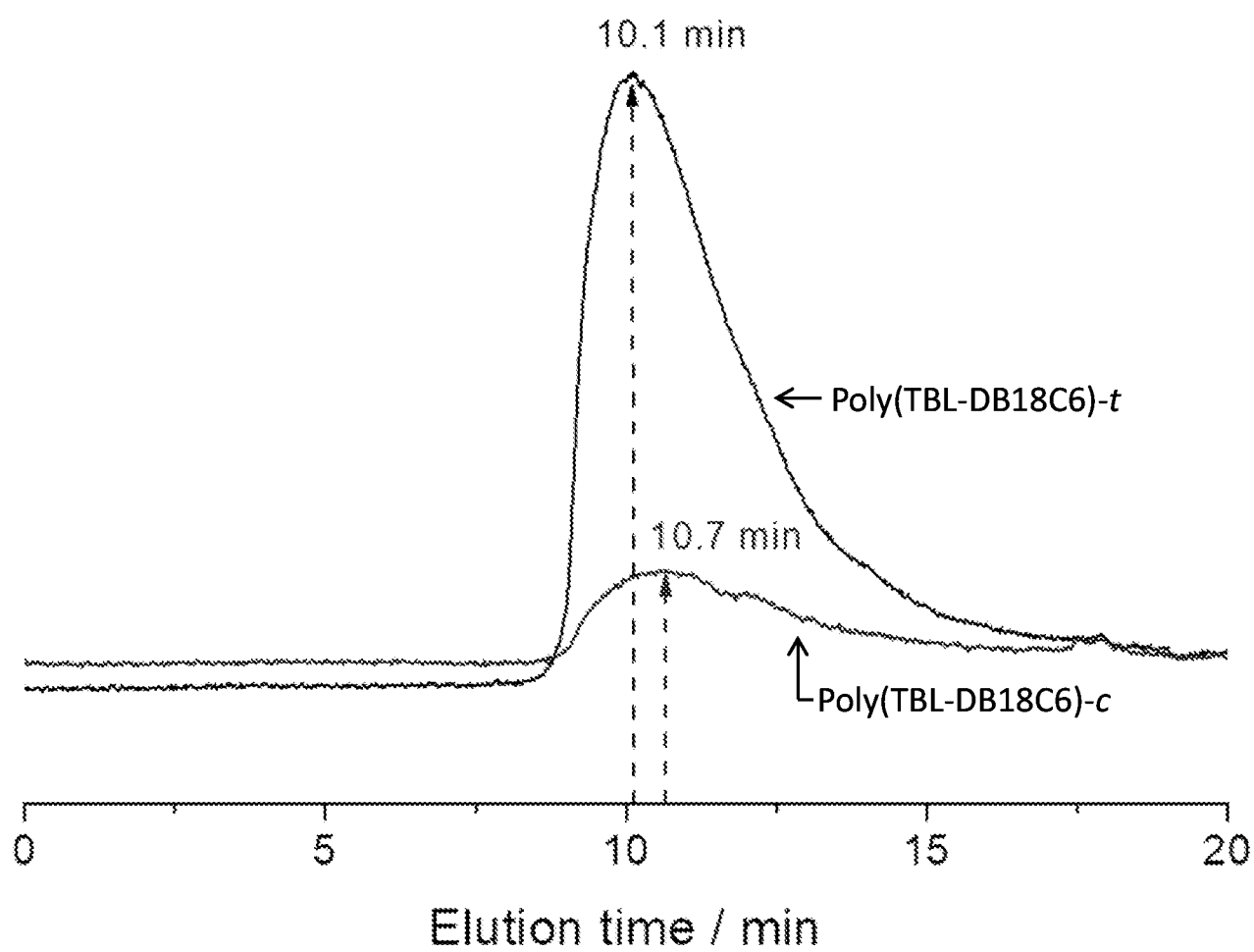


Fig. 6

Fig. 7A

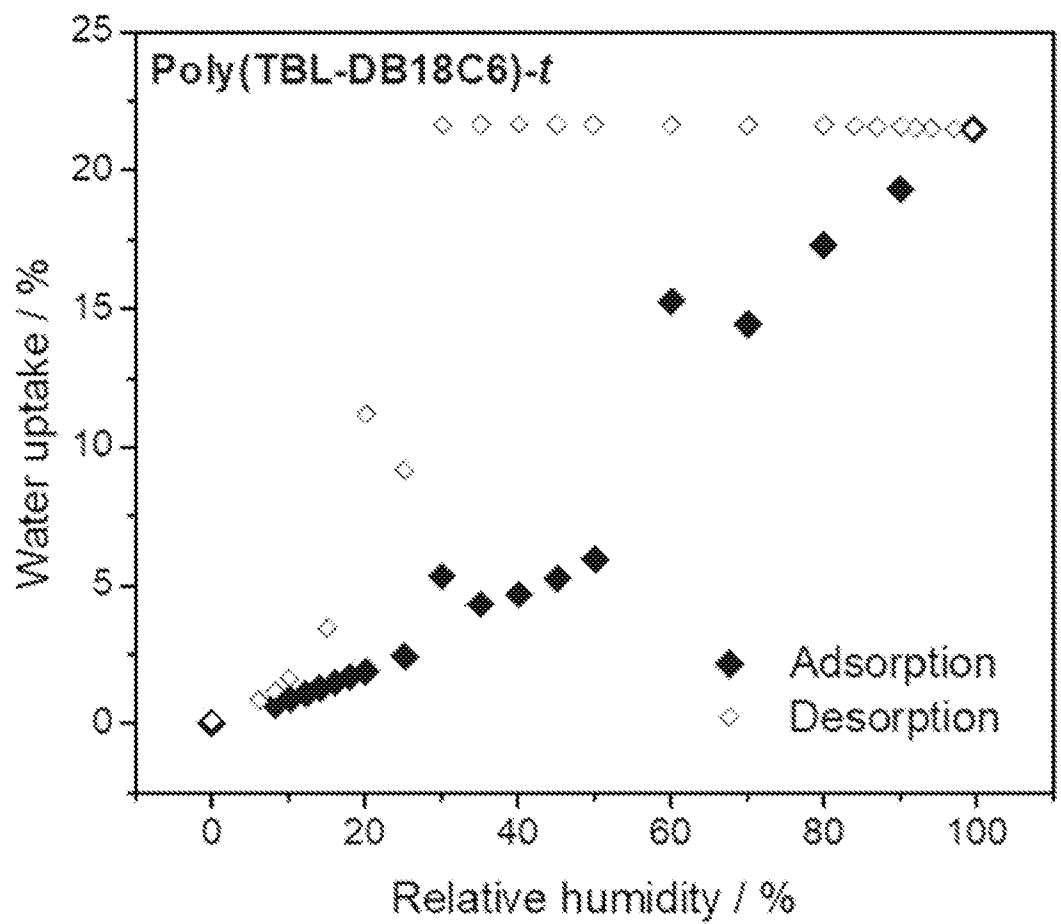


Fig. 7B

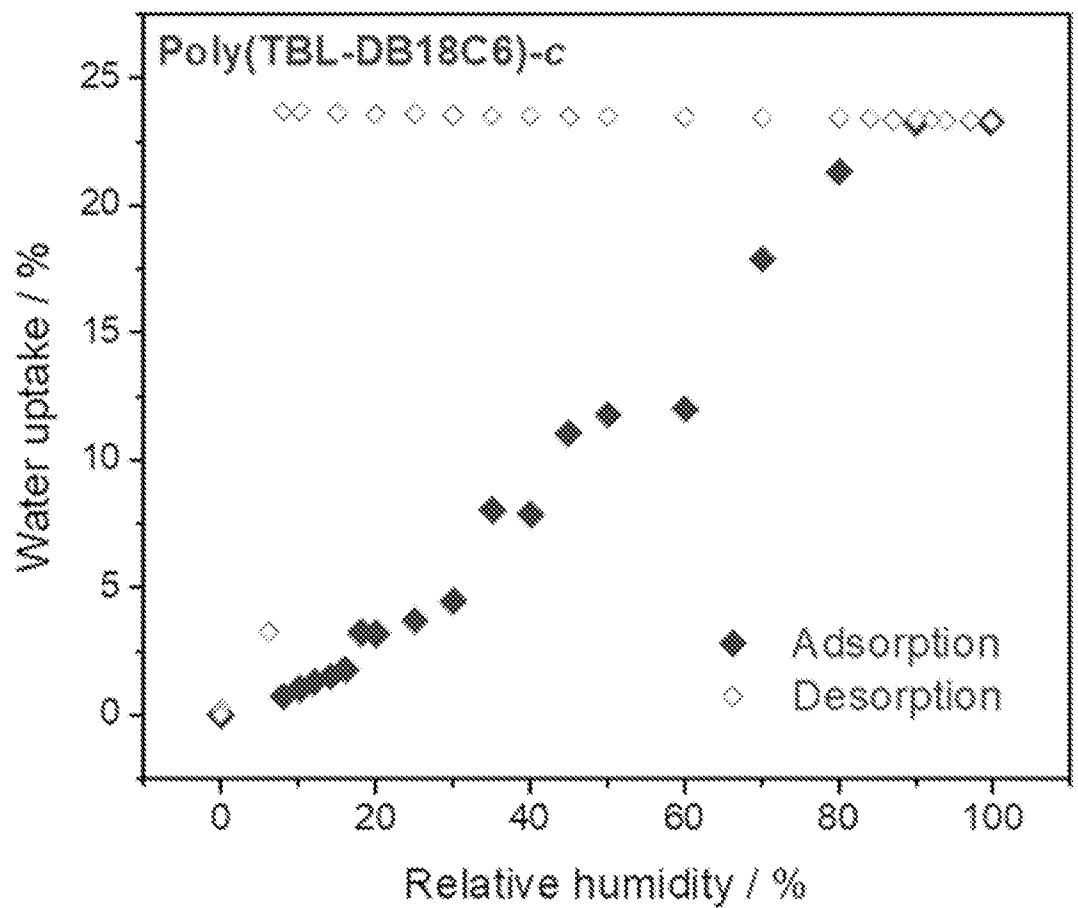


Fig. 8A

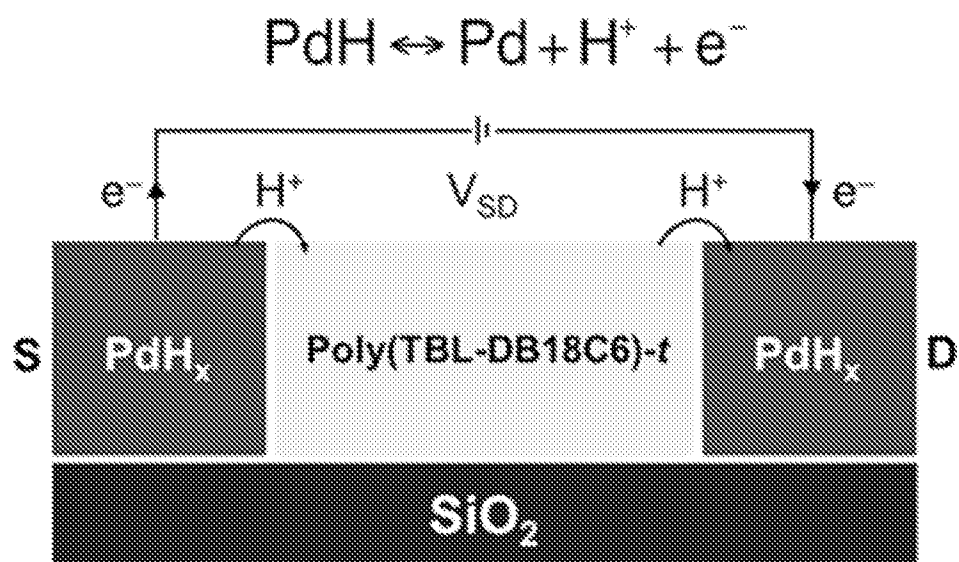


Fig. 8B

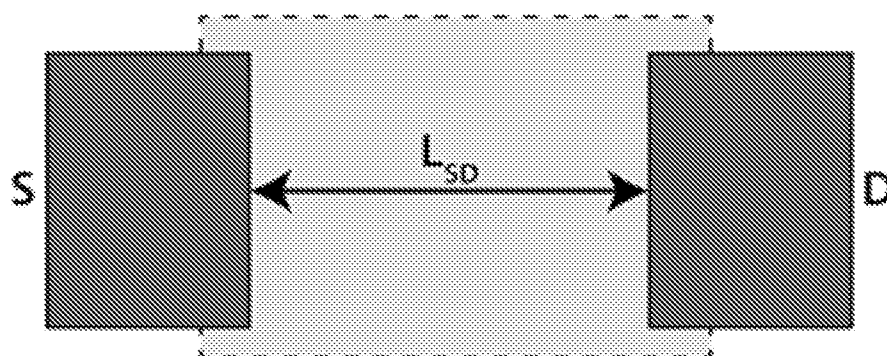


Fig. 8C

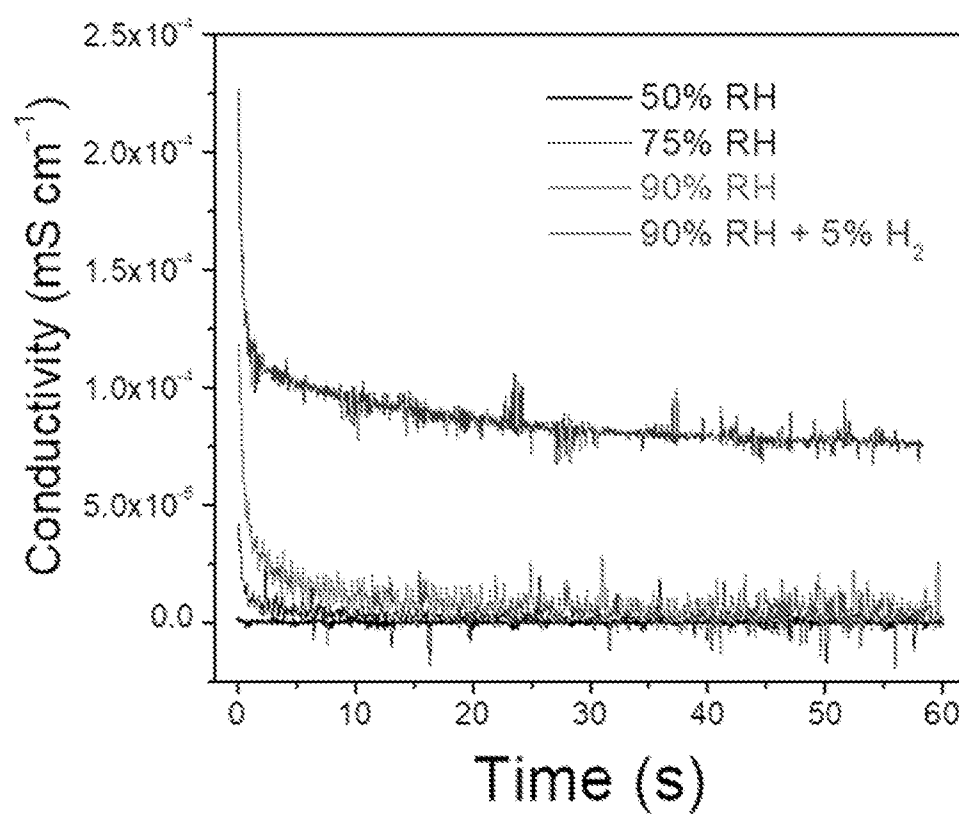


Fig. 8D

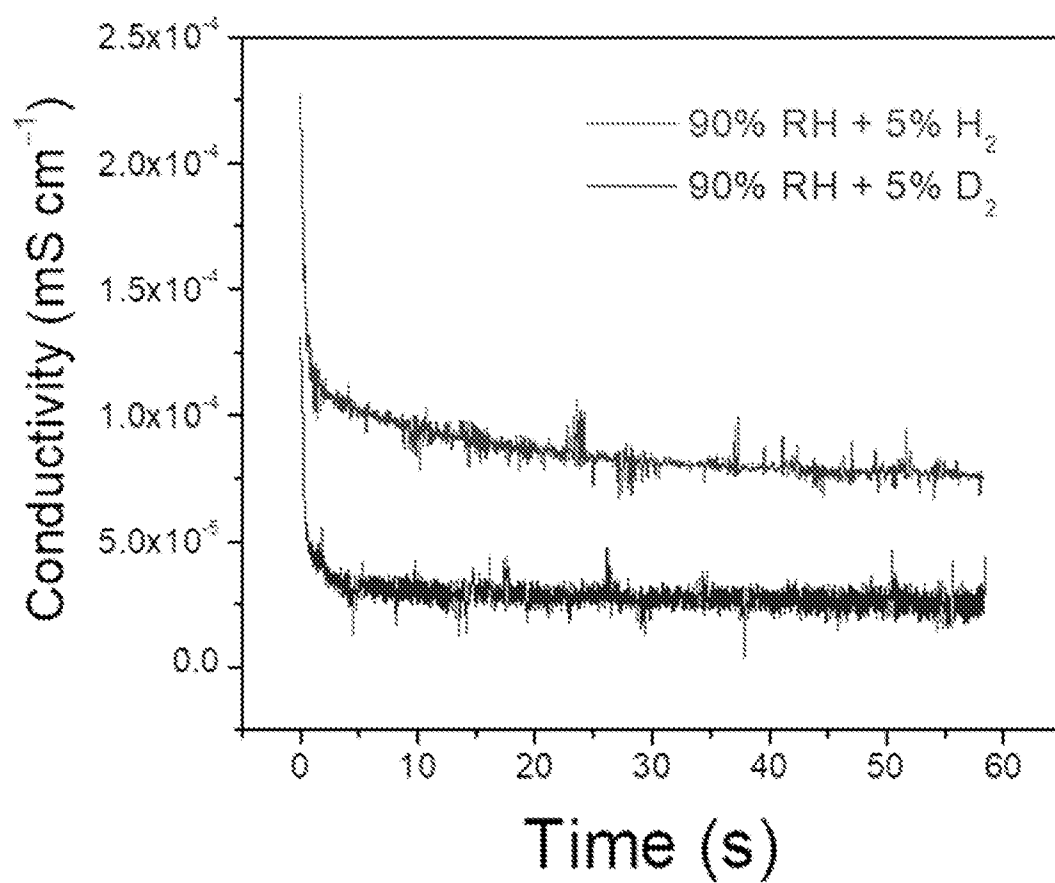


Fig. 8E

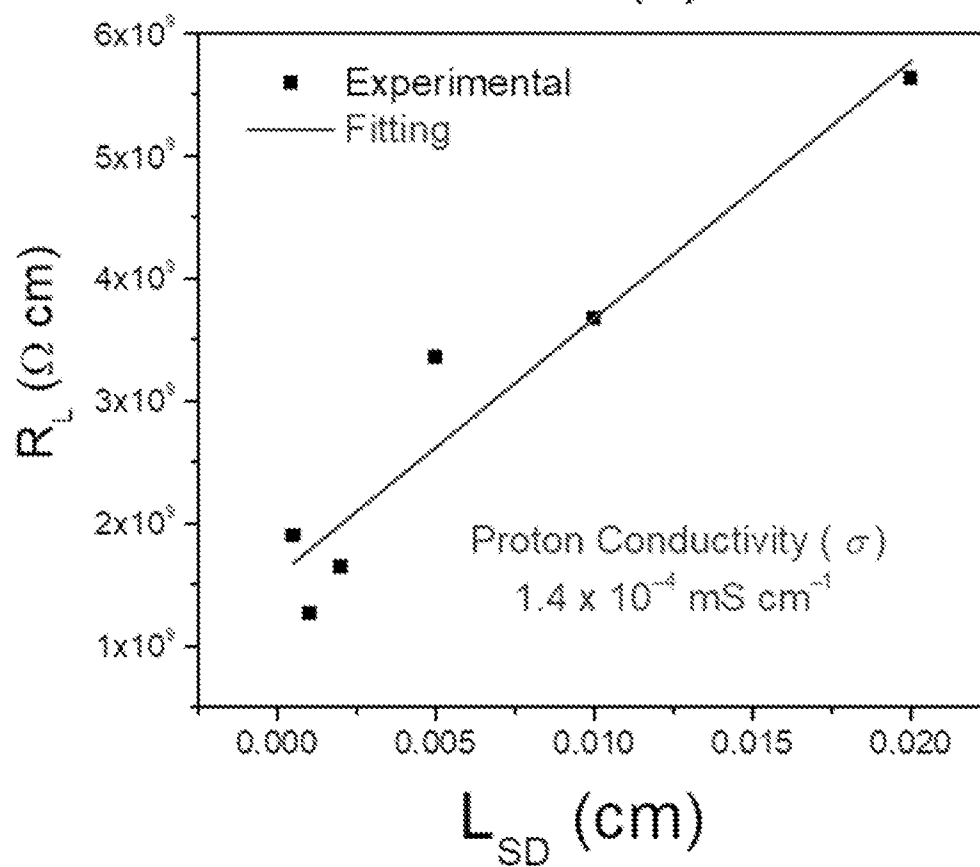


Fig. 8F

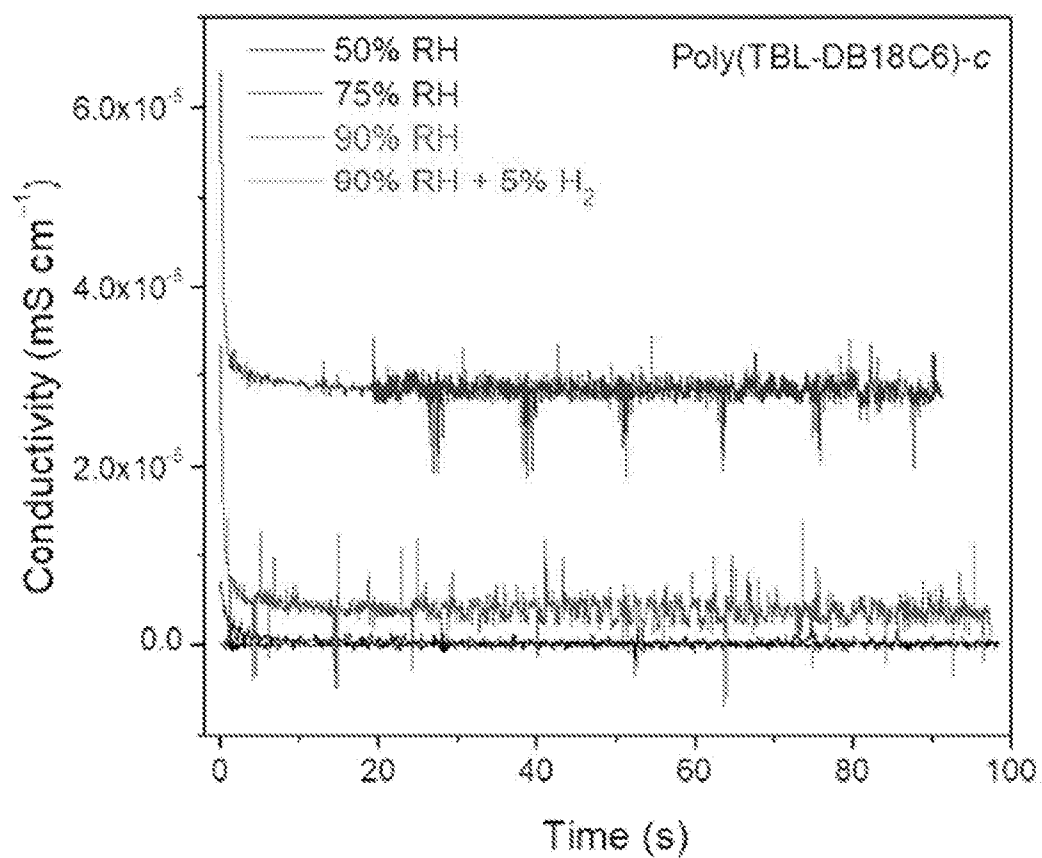


Fig. 8G

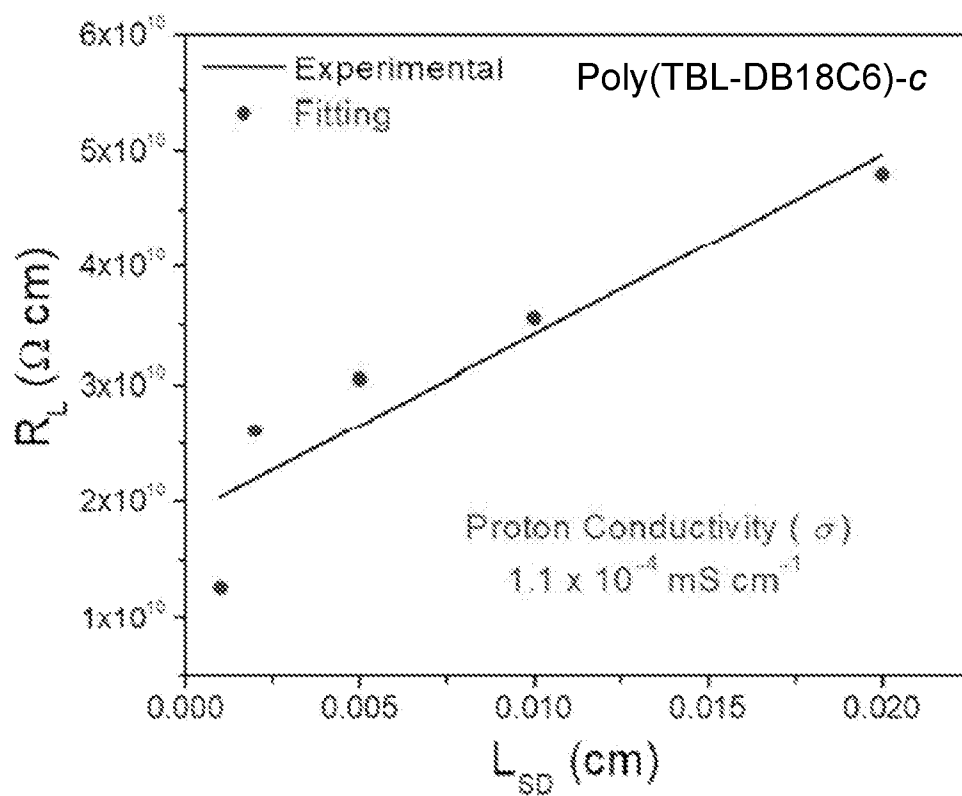


Fig. 9A

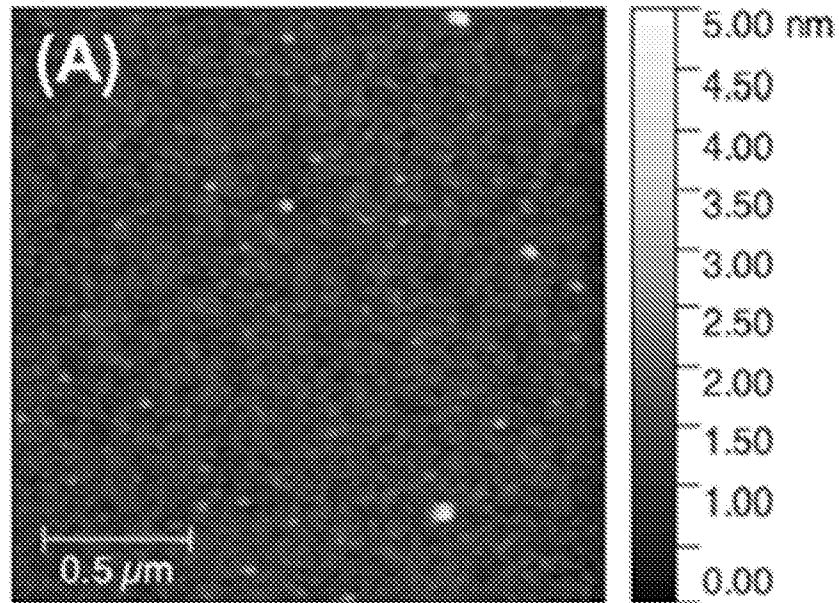


Fig. 9B

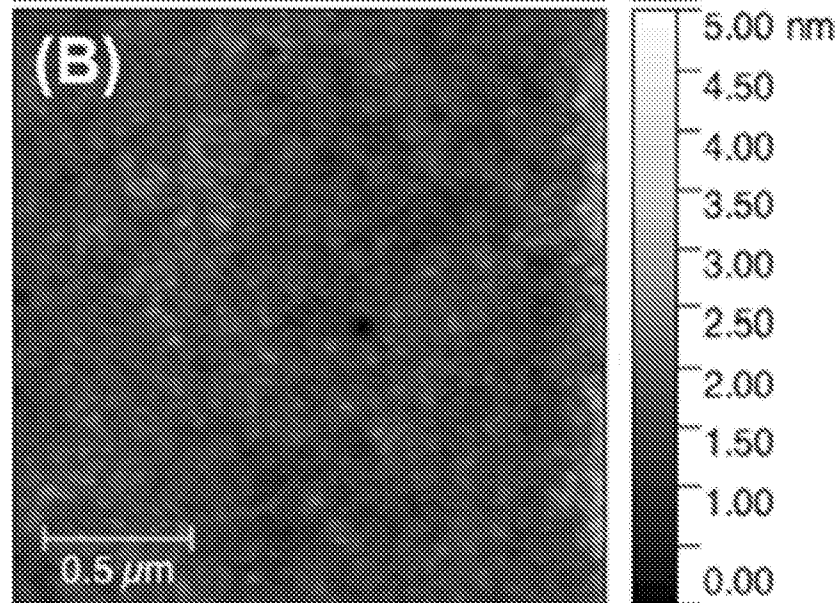


Fig. 9C

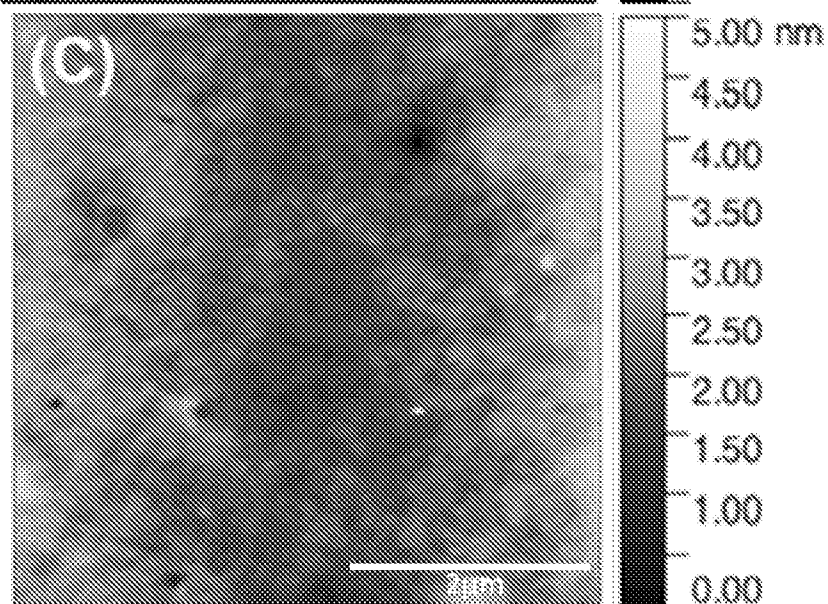


Fig. 10A

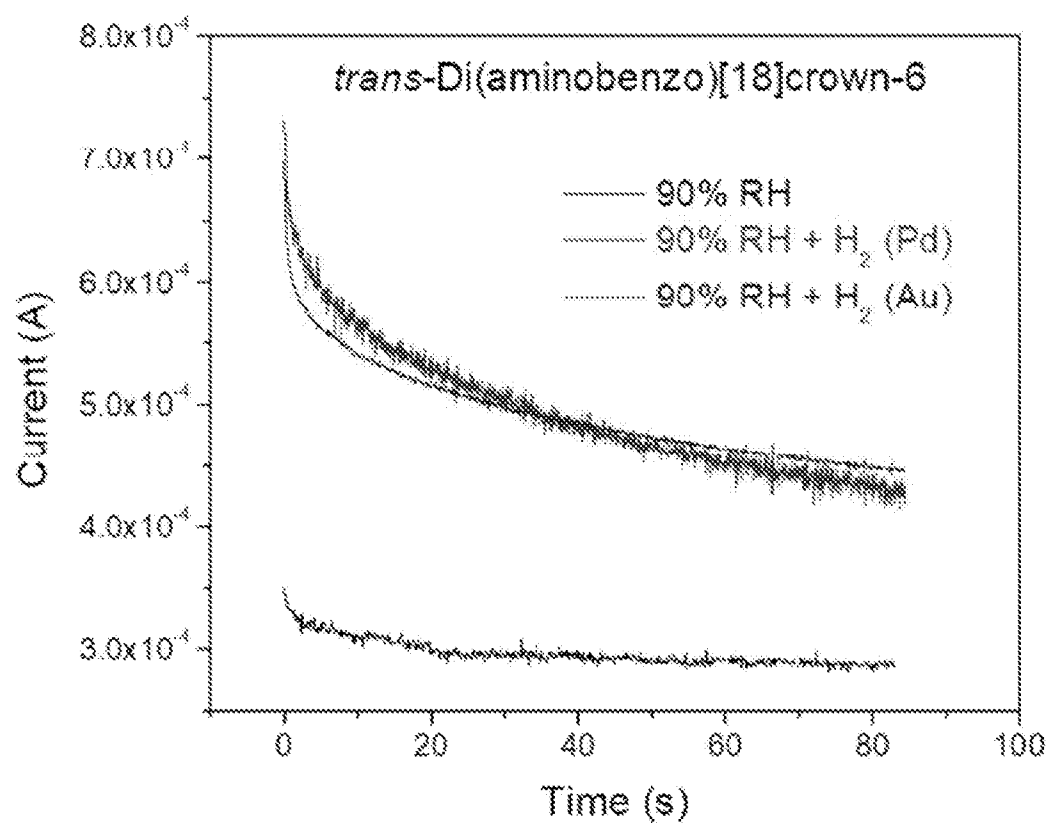


Fig. 10B

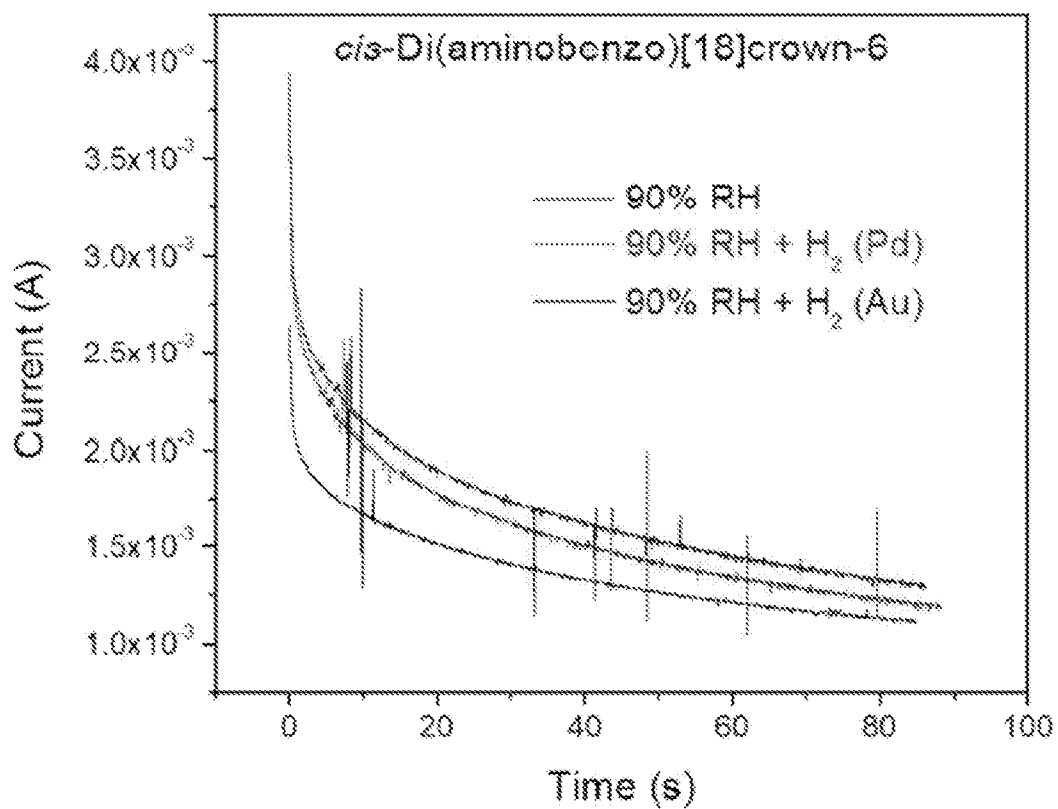


Fig. 11A

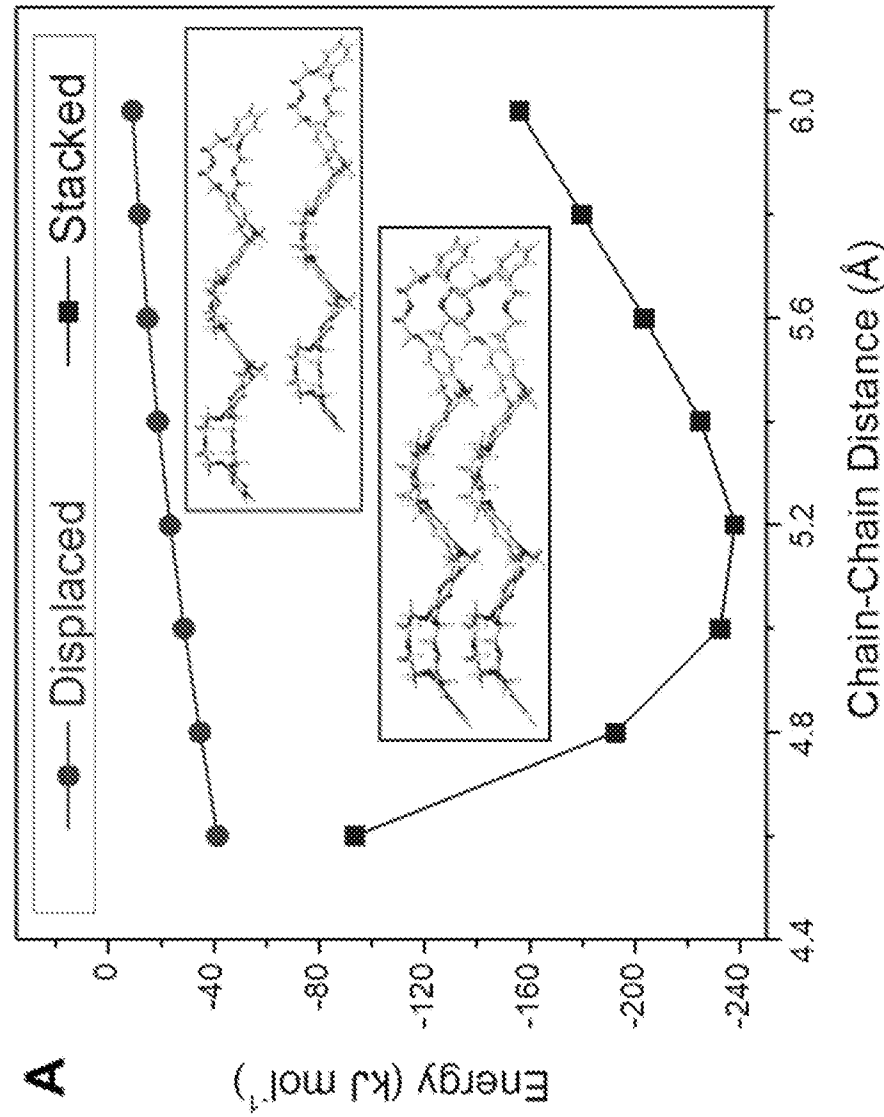


Fig. 11B

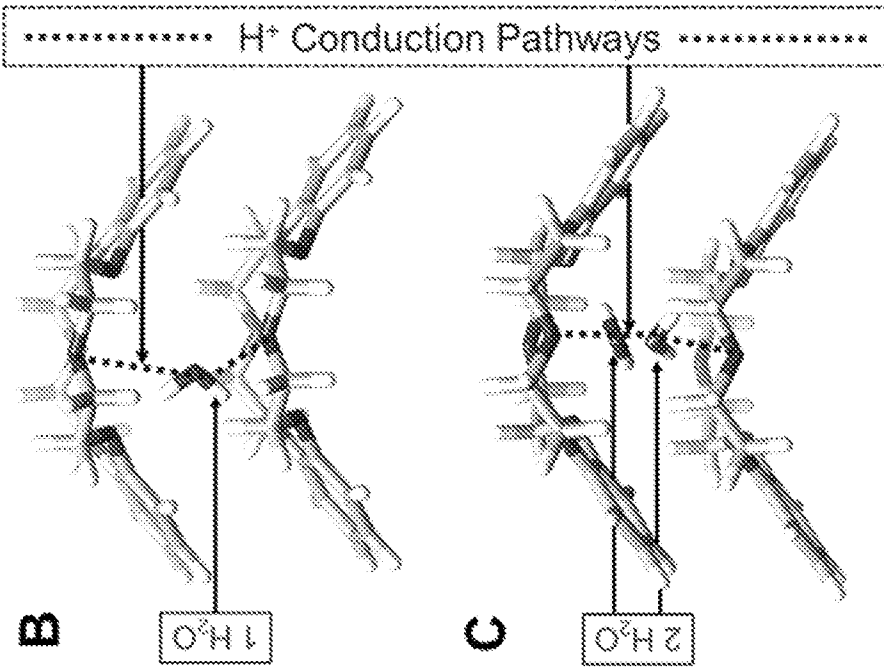


Fig. 11C

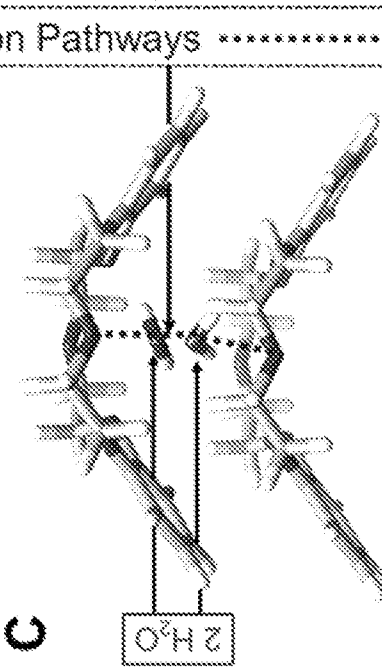


Fig. 12A

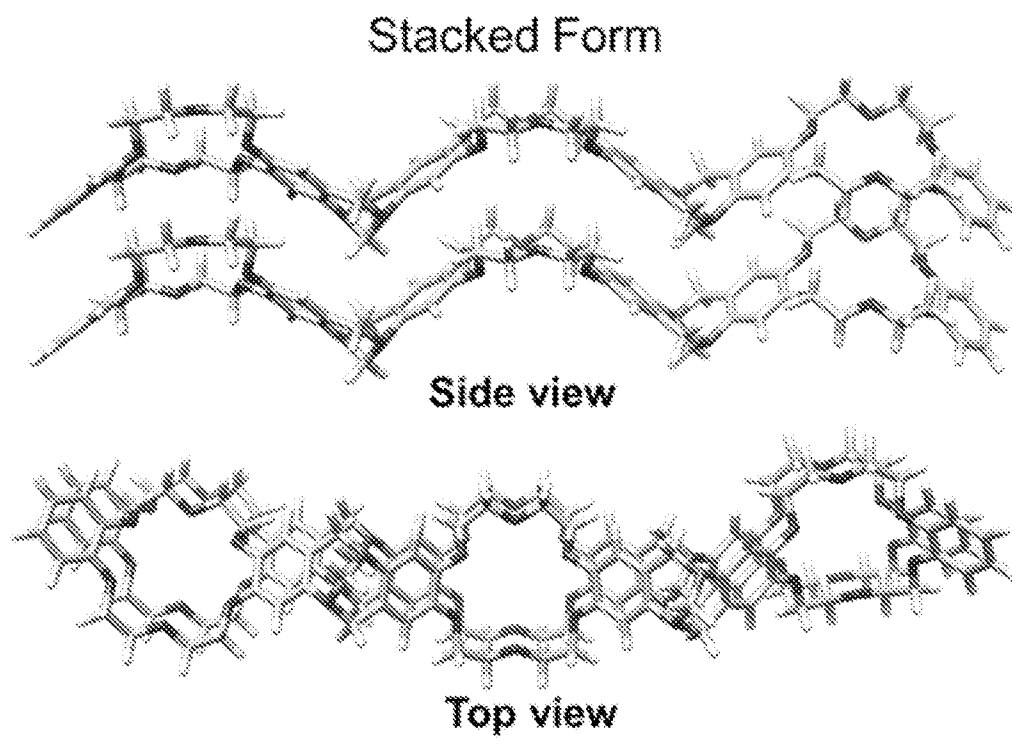
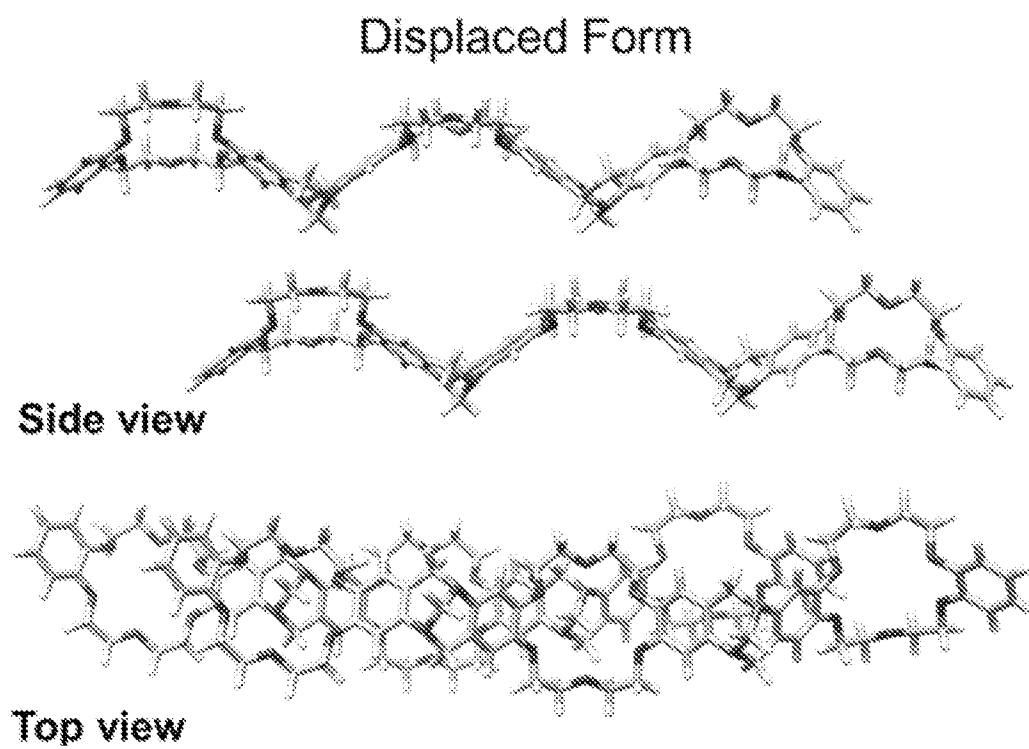


Fig. 12B



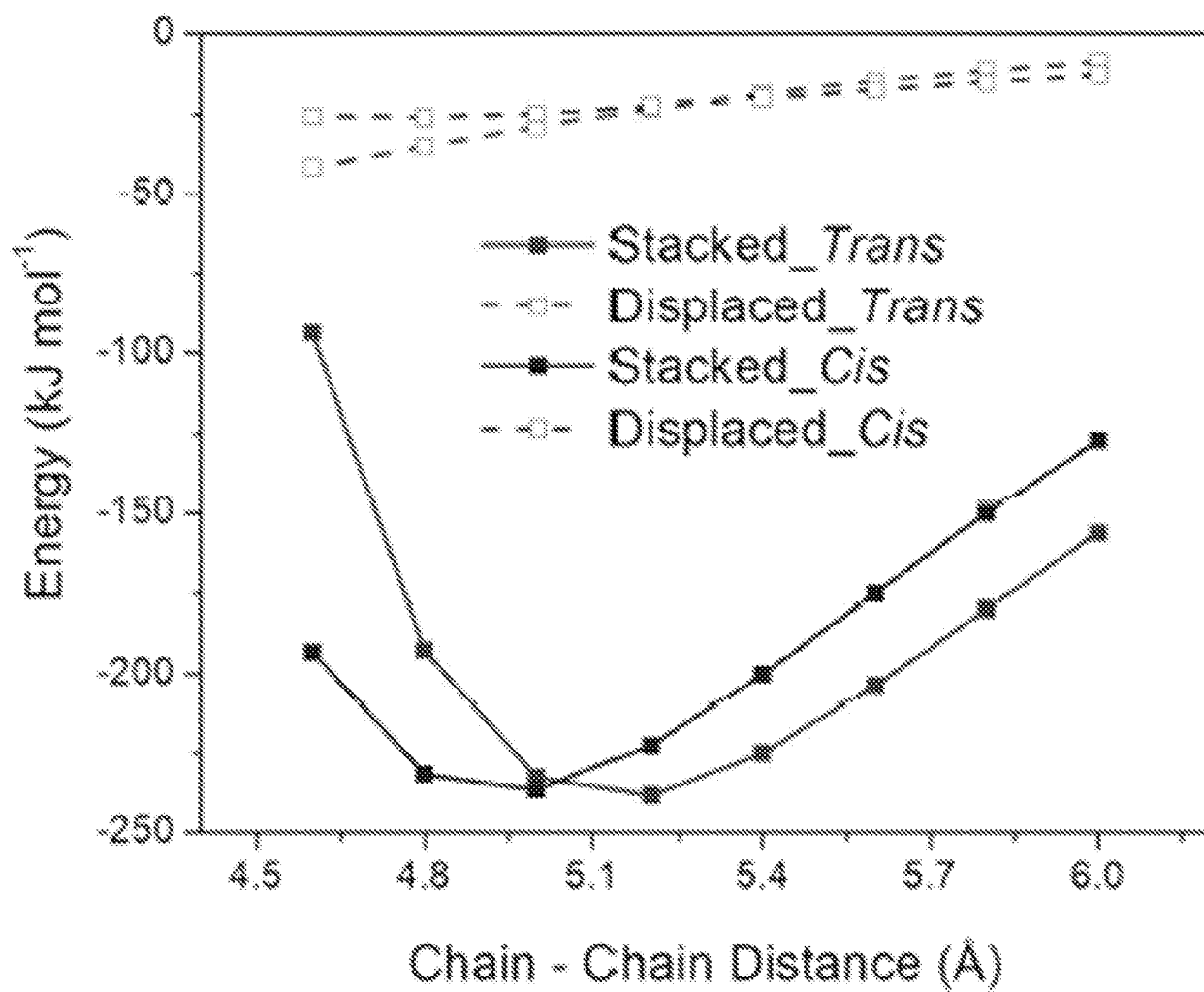


Fig. 13

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 18/59046

A. CLASSIFICATION OF SUBJECT MATTER
 IPC(8) - C08F 8/00, C08G 65/48, C08G 75/20 (2019.01)
 CPC - B01D 59/22, B01J 20/265, C07D 323/00

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	Hsueh et al. 'Highly Selective Na ⁺ -Templated Formation of [2]Pseudorotaxanes Exhibiting Significant Optical Outputs', <i>Angewandte Chemie International Edition</i> , 02 March 2007 (02.03.2007), Vol.46, pages2013-2017; p2013	1-5, 10-16, 18-23, 25-27, 29-34
A	Jiang et al. 'A Double Plug-Socket System Capable of Molecular Keypad Locks through Controllable Photooxidation', <i>Chemistry - A European Journal</i> , 23 September 2009 (23.09.2009), Vol.15, pages9938-9945; p9939	1-5, 10-16, 18-23, 25-27, 29-34
A	Wiktorowicz et al. 'Multi-stimuli responsive poly(azodibenzo-18-crown-6-ether)s', <i>Polymer Chemistry</i> , 16 April 2014 (16.04.2014), pages1-9; p2	1-5, 10-16, 18-23, 25-27, 29-34
A	US 2005/0065304 A1 (Asakawa et al.) 24 March 2005 (24.03.2005); entire document	1-5, 10-16, 18-23, 25-27, 29-34
P/X	Patel et al. 'Proton Conduction in Troger's Base-Linked Poly(crown ether)s', <i>ACS Applied Materials & Interfaces</i> , 05 June 2018 (05.06.2018), Vol.10, pages25303-25310; entire document	1-5, 10-16, 18-23, 25-27, 29-34

☐ 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 January 2019

Date of mailing of the international search report

22 JAN 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 18/59046

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.: 6-9, 17, 24, 28, 35-36
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:

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.:

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.