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Synthesis and Properties of Supramolecular Ionic Networks

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A hallmark of supramolecular chemistry is the use of well-defined molecules or macromolecules and intermolecular forces to create larger, more complex chemical systems with new and unique properties.[1–4] This noncovalent synthetic strategy affords a variety of structures ranging from host−guest complexes and lipid organizations to linear metallopolymers through the use of, for example, hydrogen bonding, van der Waals forces, or metal−ligand bonds.[5–9] Of the various supramolecular assemblies known, networks are particularly interesting as their macroscopic properties can be significantly different than the properties of the individual building blocks.[3] The creation of a supramolecular network requires two different molecular structures whereby one structure possesses at least two and the other three or more complementary molecular recognition groups. Such a strategy has been applied to prepare supramolecular polymer networks using hydrogen and metal−ligand bonding.[10,11] Herein, we report the discovery of "supramolecular ionic networks" created using multicationic and multianionic molecules. These fluidic materials, held together through noncovalent electrostatic interactions, are easily prepared from a diverse set of readily available starting materials, facilitating the design of new ionic materials with a high level of molecular control.

As these materials are ionic networks that flow at ambient temperatures, we chose to compare their properties to ionic liquids. Ionic liquids are "salt-like" materials held together through electrostatic interactions that have melting points at relatively low temperatures (<100 °C). An example of a common ionic liquid is tetradecyl(trihexyl)phosphonium chloride which has a melting point below 20 °C.[12] Ionic liquids have found use in a wide range of applications, among them industrial solvents, separation media, fuel cells, protein crystallization matrices, liquid crystals, batteries, and thermal fluids.[13–16] Current ionic liquid compositions have both a charge and molar ratio of 1:1 (e.g., tetradecyl(trihexyl)phosphonium chloride) where a monocationic species is stochiometrically paired with a monoanionic species. Alteration of the molar ratio while maintaining the charge ratio of 1:1 by using multivalent cationic/anionic molecular pairs affords new ionically cross-linked supramolecular networks.

Specifically, we chose to prepare an ionic network using a phosphonium dication, P^{2+}, and a tetraanion, ethylenediaminetetraacetate ($EDTA^{4-}$). We selected a geminal dication since these symmetric compounds possess two positive charges and have recently been of interest for a variety of applications.[17] The specific chemical structures under investigation are shown in Figure 1. These structures enabled us to evaluate the effect of varying the mole and charge ratio for these ionic materials held together by Coulombic interactions. The dichloride salt of the dicationic phosphonium (P^{2+}:$2Cl^-$) was prepared by reacting 2 equiv of trihexylphosphine with 1 equiv of 1,10-dichlorodecane at 140 °C for 24 h. This ionic liquid readily flows and is a colorless liquid. The silver salts of dodecanedioic acid, DDA^{2-}, and ethylenediaminetetraacetic acid, $EDTA^{4-}$, were prepared as described in the Supporting Information. The ethyl ester analogue of ethylenediaminetetraacetic acid, EE, was prepared by esterification in methanol in the presence of *para*-toluene sulfonic acid. Addition of the silver salt of $EDTA^{4-}$ to the P^{2+}:$2Cl^-$ afforded ionic liquid $2P^{2+}$:$EDTA^{4-}$ and AgCl(s). A similar procedure was used to prepare the ionic liquids and networks described herein.

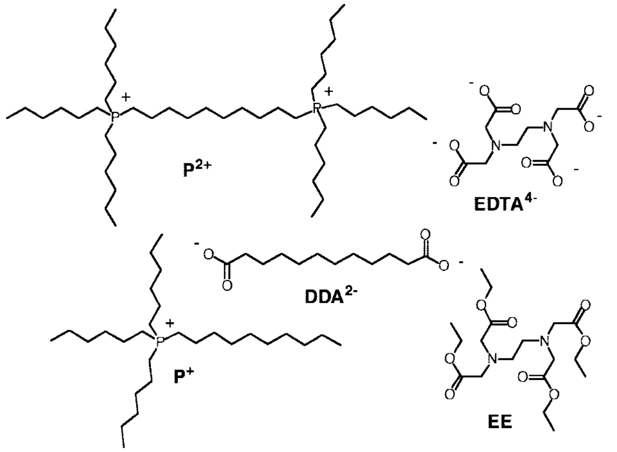

Figure 1. Chemical structures under investigation.

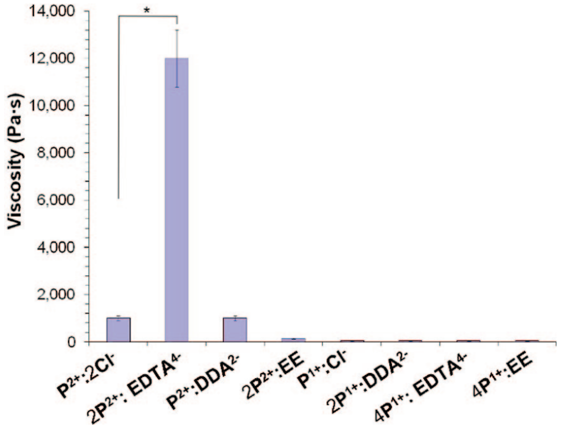

Figure 2. Viscosity data for the various ionic liquids and network ionic liquids at 25 °C ($N = 3$; mean ± SD; $*p < 0.001$).

The viscosities of the ionic liquids were measured using a AR 1000 controlled strain rheometer (TA Instruments). Ionic liquid P^{2+}:$2Cl^-$ possesses a viscosity of 1000 Pa•s. Substitution of the monoanion, Cl^-, for the tetraanion, $EDTA^{4-}$, while maintaining the charge ratio (1:1) with P^{2+}, affords a significant increase in the viscosity (Figure 2). The resulting ionic liquid $2P^{2+}$:$EDTA^{4-}$ has a viscosity of approximately 12 000 Pa•s. The viscosity is dependent on the charge ratio as evident by a significant decrease in the viscosity with ionic liquid P^{2+}:$EDTA^{4-}$ (see Supporting Information for graph). The enhanced viscosity is a consequence of the network formed between the dication and tetraanion. To confirm this ionic network formation, several control experiments were performed. First, an ionic liquid was prepared with the dianion, DDA^{2-}, and P^{2+} which cannot form a network due to the insufficient number of cooperative Coulombic

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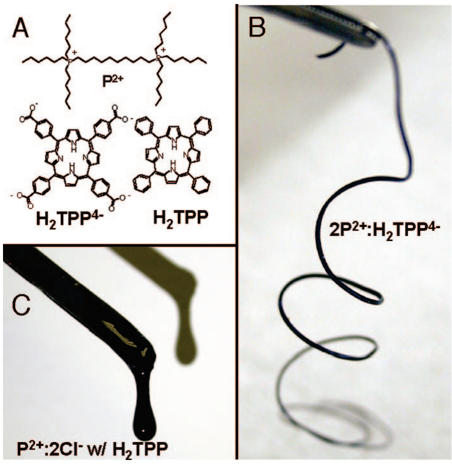

Figure 3. (A) Chemical structures of the geminal phosphonium dication and porphyrins under investigation. (B) Photograph of an ionic network fiber prepared from $2P^{2+}$:H_2TPP^{4-}. (C) Photograph of the P^{2+}:$2Cl^-$ with H_2TPP.

interactions. Ionic liquid P^{2+}:DDA^{2-}, like P^{2+}:$2Cl^-$, has a viscosity of ≈1000 Pa•s. Next the esterfied EDTA, EE, which cannot form ionic bonds, was mixed with P^{2+}:$2Cl^-$. The resulting mixture had a low viscosity, further confirming the importance of carboxylate residues in these networks. Moreover, substitution of the phosphonium dication, P^{2+}, with a phosphonium monocation, P^+, also gives low viscous fluids because a network cannot be formed. Ionic liquids P^+:Cl^-, $2P^+$:DDA^{2-}, $4P^+$:$EDTA^{4-}$, and P^+:EE possess viscosities less than 1000 Pa•s.

Importantly, the connectivity that is present in an ionic network enables the preparation of macroscopic materials with specific sizes and shapes. To illustrate this feature, we prepared ionic materials from geminal phosphonium dication, P^{2+}, with either *para*-tetracarboxy-5,10,15,20-tetraphenyl-21*H*,23*H*-porphine, H_2TPP^{4-}, or as a control, 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine, H_2TPP (Figure 3). The former is expected to form an ionic network as it possesses four carboxylate residues available for ionic bonding. Ionic liquid $2P^{2+}$:H_2TPP^{4-} has a viscosity of $\approx 10^6$ Pa•s at 25 °C. The storage and loss modulus were also determined and found to be $\approx 10^7$ and 10^6 Pa, respectively. The mixture of $2P^{2+}$ and H_2TPP^{4-} was heated to 160 °C, and a fiber was hand-pulled from the solution. The fiber was dark purple in color, flexible, moldable into a coil, and was approximately 1 mm in diameter and 10 cm in length (Figure 3B). Under the same conditions, if P^{2+} is mixed with H_2TPP, which lacks the anionic carboxylate groups for ionic bonding, a low viscous P^{2+}:$2Cl^-$ ionic liquid with dissolved H_2TPP is obtained (≈1000 Pa•s; $G' \approx 2500$ Pa, $G'' \approx 1500$ Pa; Figure 3C). A scanning electron micrograph of the $2P^{2+}$:H_2TPP^{4-} fiber is shown in Figure 4A,B. The fiber is relatively smooth with few defects, and the beginnings of a twist can be observed in the image. Fluorescence microscopy was performed to determine if the porphyrin continues to fluoresce when assembled as a fiber. A fluorescent micrograph at 40X magnification of the fiber is shown in Figure 4C under 514 nm illumination. The solid-state fluorescent spectrum possesses a λ_{max} at 645 nm, consistent with the reported literature value (Figure 4D).[18]

In summary, a geminal phosphonium dication has been synthesized and subsequently coordinated with mono-, di-, and tetraanions. When coordinated with a tetraanion, a new network ionic material is created. Specifically, the network ionic liquid prepared from the geminal phosphonium dication and ethylenediaminetetraacetate ($2P^{2+}$:$EDTA^{4-}$) possesses increased viscosity compared to conventional ionic liquids such as P^{2+}:$2Cl^-$ and P^+:Cl^- as a consequence of the cooperative Coulombic interactions. Incorporation of a porphyrin in the network ($2P^{2+}$:H_2TPP^{4-}) and the observation of fluorescence suggest that ionic networks containing specific functional building blocks continue to possess their original properties. For example, self-assembled solid-state-based porphyrin materials are of interest for many uses (e.g., sensors).[19,20] The strategy demonstrated using multicationic and multianionic molecules provides an opportunity to prepare new supramolecular ionic networks with properties not attainable with current ionic liquids. Moreover, the generality, ease of preparation, diversity of starting materials available, and straightforwardness of the approach will facilitate the design of new ionic materials for a range of applications.

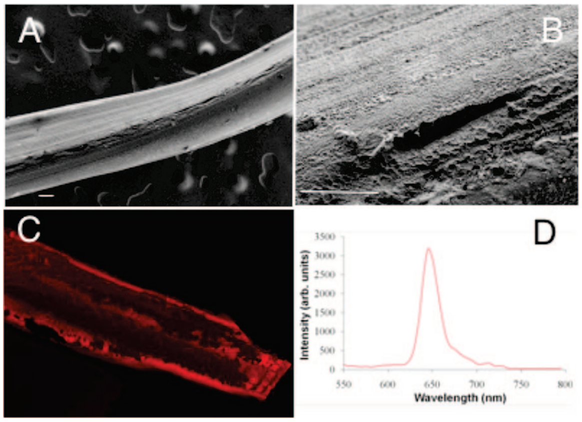

Figure 4. (A) Scanning electron micrograph of a fiber composed of $2P^{2+}$:H_2TPP^{4-} (bar = 100 μm). (B) Scanning electron micrograph of the fiber at higher magnification (bar = 50 μm). (C) Fluorescent micrograph of a fiber. (D) Solid-state fluorescence spectrum of a fiber.

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Supporting Information Available: Syntheses and rheological measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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