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Anion−Anion Assembly: A New Class of Anionic Supramolecular Polymer Containing 3,4-Dichloro-2,5-diamido-substituted Pyrrole Anion Dimers

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The use of anionic components to direct self-assembly is a relatively new area of supramolecular chemistry but one which is expanding the available noncovalent and coordinate bonding motifs for the construction of interlocked materials and new noncovalently linked molecular architectures.[1] Early examples include de Mendoza and co-workers' sulfate-directed double helix[2] and Lehn and co-workers' chloride-templated pentametallic circular helicate.[3] Stoddart and co-workers[4] and Beer and co-workers[5] have reported examples of anion-assisted formation of pseudorotaxanes using hexafluorophosphate and chloride, respectively, while Vögtle and co-workers[6] have used an anion-template approach to the synthesis of rotaxanes. Sessler and co-workers have shown that calixpyrroles and sapphyrins containing appended carboxylate groups form anionic dimers,[7] while in the inorganic arena, Mingos, Vilar, and co-workers[8] and McCleverty, Ward, and co-workers[9] have used anions to direct the formation of new inorganic complexes. In the solid state, Hosseini and co-workers have used amidinium−carboxylate interactions to assemble molecular rods, tapes, and sheets,[10] while Ward and co-workers have studied in detail the factors influencing guanidinium−sulfonate interactions.[11] We have recently reported the synthesis and anion-binding properties of 2,5-diamidopyrrole cleft species[12] and the dimerization of 3,4-dichloro-analogues which when deprotonated change conformation and form dimers via NH−N$^-$ hydrogen bonds (Figure 1).[13] Unlike the hydrogen-bonding arrays found in systems such as DNA, the two components in the pyrrole anion dimer are almost orthogonal, and this system could be regarded as an organic analogue of Cu(I) phenanthroline complexes used in the construction of various complex supramolecular architectures.[14] In this communication we report the first examples of new interlocked materials based upon this hydrogen-bonding motif consisting of supramolecular polymers consisting of purely anionic components.

Molecules **1** and **2** were synthesized in a stepwise procedure. 3,4-Dichloro-1*H*-pyrrole-2,5-dicarboxylic acid diethyl ester was synthesized by literature methods.[15] This material was reacted with 1 equiv of the aluminum amide formed by reacting 1 equiv of trimethylaluminum with aniline,[16] affording 3,4-dichloro-5-phenylcarbamoyl-1*H*-pyrrole-2-carboxylic acid ethyl ester in 13% yield. Subsequent saponification in an aqueous ethanolic solution of sodium hydroxide afforded the acid in 75% yield. This was then coupled with 0.5 equiv of either 1,3-phenylenediamine or 1,4-phenylenediamine using 1.05 equiv of PyBOP, HOBt (cat.), and triethylamine in dry DMF to afford the dimers **1** and **2** in 50 and 69% respective yields.

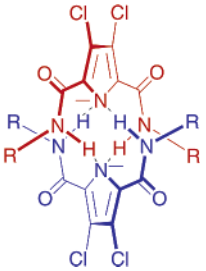
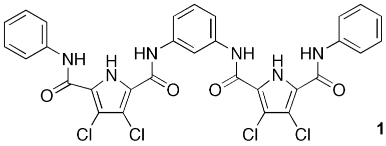


Figure 1. Hydrogen-bonding array between 2,5-diamidopyrrole anions.



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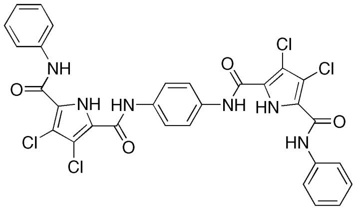

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Compounds **1** and **2** have limited solubility; however, it was possible to obtain ^{1}H NMR spectra of the materials in DMSO-d_6. Solubility was improved upon addition of tetrabutylammonium fluoride, allowing ^{13}C NMR and mass spectroscopic characterization studies to be completed.

Crystals of compounds **1** and **2** were obtained by slow evaporation of acetonitrile solutions of the amidopyrroles in the presence of excess tetrabutylammonium fluoride.[17] Both compounds crystallize as doubly deprotonated pyrrole anions (**1**-2H$^+$ or **2**-2H$^+$) forming interlocked chains of anions via NH−N$^-$ hydrogen bonds (Figures 2 and 3). In bis-tetrabutylammonium (**1**-2H$^+$), the anionic chains consist of a single crystallographically unique molecule with NH−N$^-$ interactions in the range 3.10(4)−3.239(13) Å and extend

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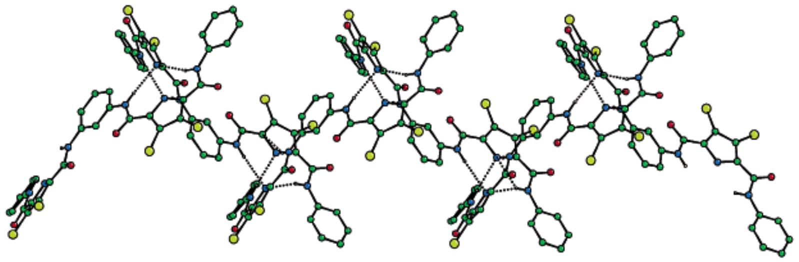

Figure 2. X-ray crystal structure of **1**-2H$^+$ (tetrabutylammonium countercations are omitted for clarity). Color key: carbon - green, chlorine - yellow, oxygen - red, nitrogen - blue, hydrogen - white.

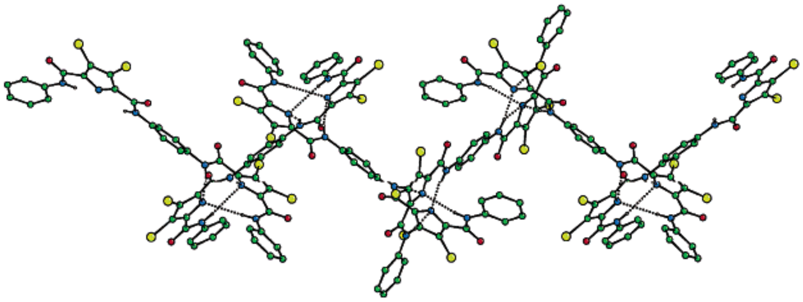

Figure 3. X-ray crystal structure of **2**-2H$^+$ (tetrabutylammonium countercations are omitted for clarity). Color key: carbon - green, chlorine - yellow, oxygen - red, nitrogen - blue, hydrogen - white.

along the *a* direction. In bis-tetrabutylammonium (**2**-2H$^+$) there are one and two half unique amidopyrrole anions in the unit cell. These anions form chains that repeat in a 1232123212... sequence extending in the $10\bar{1}$ direction.

The two half molecules are essentially planar, while the complete molecule, occurring at every other position in the chain, is twisted such that the angle between the least-squares planes of the pyrrole rings is 61.79(5)° and the NH−N interactions are in the range 3.112(9)−3.491(9) Å. In both cases the tetrabutylammonium countercations occupy the spaces between the chains.

These two structures demonstrate the generality of 2,5-diamidopyrrole anion dimer and its potential as a new motif for the construction of interlocked hydrogen-bonded molecular assemblies formed by orthogonal components. We are currently investigating the formation of other interlocked materials based upon this motif and also the role of the countercation in the assembly process. The results of these studies will be reported in due course.

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Supporting Information Available: CIF files for the two crystal structures together with characterization and preparation data for compounds **1** and **2** and space filling models of the polyanionic chains (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Cell dimensions and intensity data were recorded at 120 K, using a Bruker Nonius KappaCCD area detector diffractometer mounted at the window of a molybdenum rotating anode ($\lambda = 0.71073$) following standard procedures. Crystal data for **1**: Colorless block, $C_{62}H_{90}N_8O_4Cl_4$, $M_r = 1153.22$, $T = 120(2)$ K, orthorhombic, space group $P2_12_12_1$, $a = 13.3899(3)$ Å, $b = 16.3267(3)$ Å, $c = 28.0813(7)$ Å, $V = 6138.9(2)$ Å^3, $\rho_{calc} = 1.248$ g cm^{-3}, $\mu = 0.246$ mm^{-1}, $Z = 4$, reflections collected: 29984, independent reflections: 7462 ($R_{int} = 0.1000$), final R indices [$I > 2\sigma I$]: R1 = 0.1119, wR2 = 0.2814, R indices (all data): R1 = 0.1866, wR2 = 0.3306. Crystal data for **2**: Colorless block, $C_{124}H_{180}N_{16}O_8Cl_8$, $M_r = 2306.44$, T = 120(2) K, triclinic, space group P-1, $a = 16.472(5)$ Å, $b = 18.028(5)$ Å, $c = 24.398(5)$ Å, $\alpha = 69.036(5)°$, $\beta = 76.520(5)°$, $\gamma = 73.183(5)°$, $V = 6408.0(3)$ Å^3, $\rho_{calc} = 1.195$ g cm^{-3}, $\mu = 0.235$ mm^{-1}, $Z = 2$, reflections collected: 31321, independent reflections: 17550 ($R_{int} = 0.0616$), final R indices [$I > 2\sigma I$]: R1 = 0.1107, wR2 = 0.2954, R indices (all data): R1 = 0.2051. wR2 = 0.3389.

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