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Centrosymmetric cyananilic acid: a molecule for functional solids

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Centrosymmetric cyananilic acid: a molecule for functional solids

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This article investigates the recent research on a series of anilic acid molecules. The crystallisation of molecules in high symmetry space groups is discussed and rationalised by the arrangement of charge-transfer complexes, which leads to the occurrence of repeated embrace motifs. Since 1997, cyananilic acid (2,5-dicyano-3,6-dihydroxy-1,4-benzoquinone) has been explored due to its valuable physico-chemical features. It is an organic acid that has Mott-insulator properties and organic ferroelectricity. Understanding these properties is an active area of supramolecular chemistry.

Keywords: anilic acid; crystal engineering; hydrogen bond; supramolecular synthons

Cyananilic acid (2,5-dicyano-3,6-dihydroxy-1,4-benzoquinone, **1**) (*1*) is categorised as an oxocarbon (*2*), having a six-membered ring, and possesses unique molecular features that control functionality of materials (*3–10*). In particular, the concept of the proton-transfer-mediated electron transfer reaction in organic materials is known to be regulated by the photonic and electronic properties of solids (*11*, *12*). An understanding of how protons and electrons interact through non-covalent molecular interactions such as charge-transfer (CT) interactions, coordination and hydrogen bonding (H-bonding) in organic and/or inorganic–organic molecules is fundamentally important in several areas of chemistry. These include: enzyme–substrate binding; signalling in biochemical molecules; rationalising proton–electron transfer in organic and biological molecules; switching mechanisms for synthetic molecular electronic devices; and developing single-molecule and single-electron devices.

Cyananilic acid, **1**, is a fascinating molecule among the series of anilic acids (3,6-dihydroxy-1,4-benzoquinone, **2**; 2,5-dibromo-3,6-dihydroxy-1,4-benzoquinone, **3**; 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone, **4**; 2,5-difluoro-3,6-dihydroxy-1,4-benzoquinone, **5**; 2,5-dinitro-3,6-dihydroxy-1,4-benzoquinone, **6**; etc.) and was not really used previous to 1997 (*3*), either as a building block in supramolecular chemistry (*7*, *8*) or as a chelating ligand in transition metal complexes (Figure 1). Only a few experimental and theoretical results were reported (*3–8*), although the elongated synthetic method of **1** was first reported in 1965 (*1*). Now, cyano-substituted anilic acid, **1**, is easily available in a reproducible manner from the centrosymmetric DDQ analogues and can be used for a variety of solid-state chemistries (*13*). This molecule has strong electron-accepting abilities, as well as has Brönsted-acid-bearing H-bonding and ionic interaction sites. Moreover, **1** is a flat molecule and may exist as a variety of species differing in the number of protons (0–4) and the charge (mainly $-2 \leq \delta \leq 0$) (*14*). In this article, we explore molecule **1** in highlighting a few molecular and supramolecular assemblies and their great prospects in technological applications from electronics to optics in the solid state (Scheme 1).

In view of its electron-accepting properties and molecular symmetry, **1** is of interest as an acceptor for organic conductors, molecule-based magnets, non-linear optics and as a building block for coordination monomers/polymer self-assemblies which under appropriate conditions form various mesophases. The first electrically conducting CT complex of the tetramethyltetrathiafulvalene (TMTTF) and mono-deprotonated **1** has shown semiconductive behaviour ($\sigma_{\mathrm{rt}} = 0.03\,\mathrm{S\,cm^{-1}}$ with an activation energy of 0.05 eV) (*3*). The magnetic spin

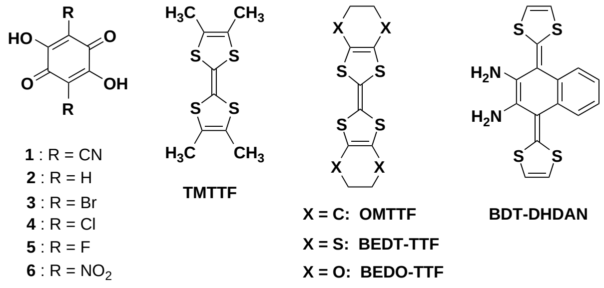

Figure 1. Chemical structures of compounds discussed in the text.

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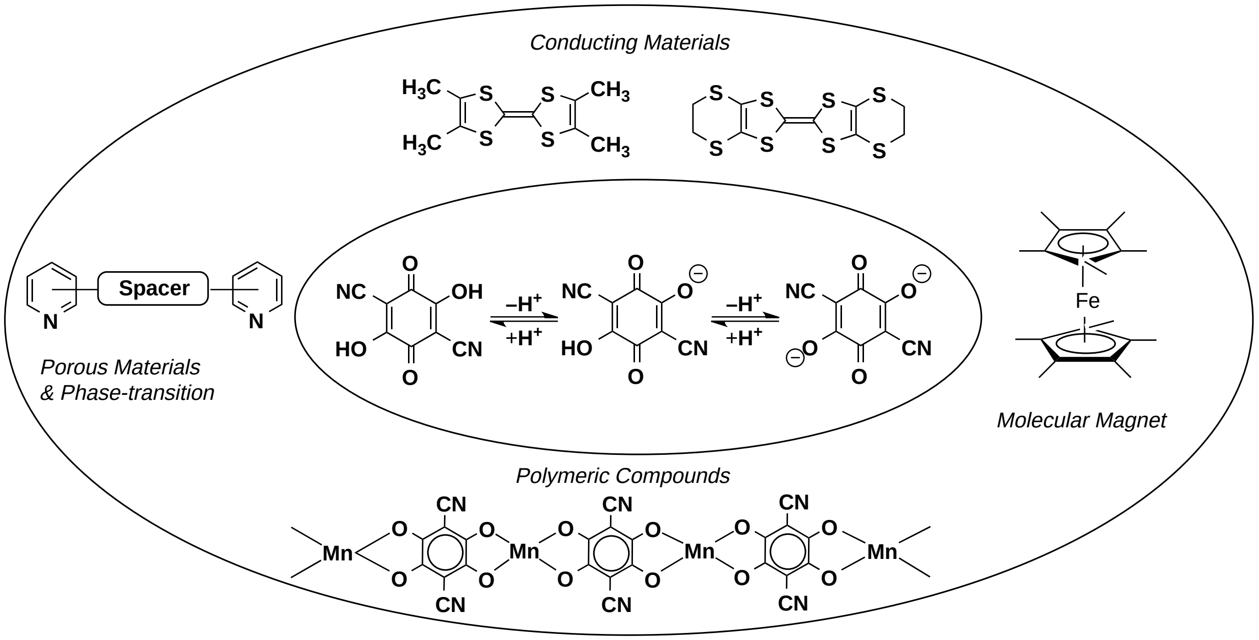
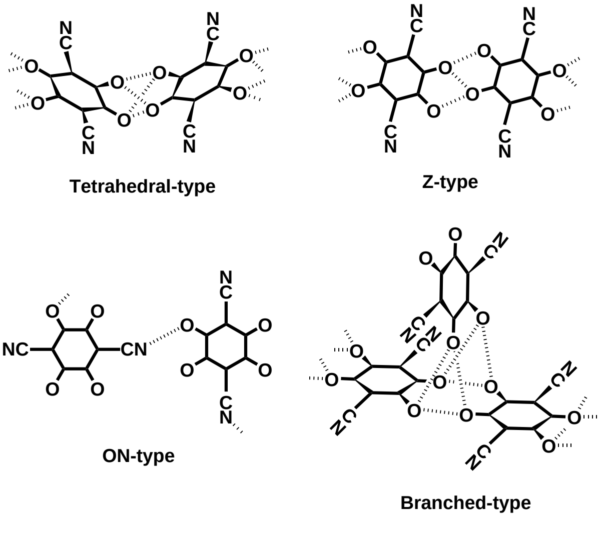


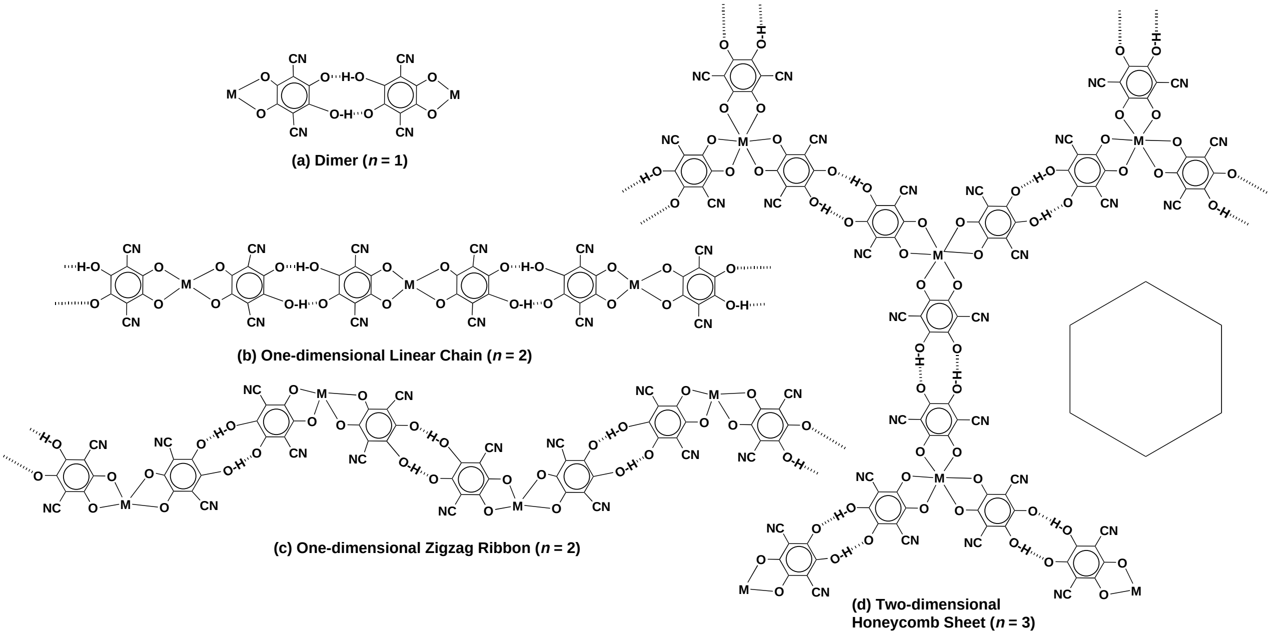
Scheme 1. Cyananilate anions: crystal engineering towards functionality.

susceptibility is described in terms of a one-dimensional (1D) antiferromagnet. The ionicity of the donor is established as +0.5. Then, several CT complexes were prepared from a variety of TTF derivatives and some of them were exploited for interesting physico-chemical properties (*3–6*). In the crystalline CT complex from octamethylenethiafulvalene (OMTTF) and **1** (*4*), a trimer of the donor molecules was found surrounded by an H-bonded network consisting of monoanion **1**. The average ionicity of each OMTTF molecule was established as +2/3. The bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) molecules form 1D columnar stacks composed of twisted dimers with a face-to-face overlap (α′-type stack), whereas the acid, **1**, forms ribbon-like aggregations by means of H-bonds (*6*). The ribbons form anionic layers that sandwich the BEDT-TTF layer. The crystal is semiconductive with a room temperature conductivity of 0.20–00.83 S cm^{-1} and an activation energy of 0.15 eV along the stacking direction, although a band calculation by the extended Hückel method suggested a metallic nature, indicating strong electron correlation in this system. The magnetic susceptibility was described by the 1D $S = 1/2$ antiferromagnetic Heisenberg chain model with $J/k_{\mathrm{B}} = -52 \pm 3$ K. The elemental, structural, electronic, magnetic and optical analyses indicated that **1** is deprotonated into a monoanion during crystal growth by the diffusion method to form a new Mott insulator α′-(BEDT-TTF)$_2$ **1**. The oxygen analogue of BEDT-TTF, bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF), also reacts with anilic acids, **2** and **4**, to form crystalline CT complexes (*15*). These complexes consist of 2D BEDO-TTF layers and 1D stacks of dianions. Interestingly, direct H-bonded donor···acceptor and acceptor···acceptor interactions are found in the complex between bis(dithiolylidene)dihydronaphthalenediamine (BDT-DHDAN) and **1**.



Scheme 2. Four types of supramolecular synthons in **1**. Dotted lines link the H-bonded atoms.

In organic–organometallic systems, the non-covalent intermolecular bonding capacity of organic molecules can be combined with the coordination geometry, variable ionic charges, oxidation and spin states typical of organometallic complexes. As an organic counterpart with organometallic $\mathrm{Fe(C_5Me_5)_2}$, anilic acids have been chosen to form characteristic intermolecular H-bonding



(a) Dimer ($n = 1$)

(b) One-dimensional Linear Chain ($n = 2$)

(c) One-dimensional Zigzag Ribbon ($n = 2$)

(d) Two-dimensional Honeycomb Sheet ($n = 3$)

Scheme 3. Schematic diagram of molecular building blocks including H-bonding and metal-coordination affinities.

interactions that might play an important role in transmitting the spin polarisation and CT along the supramolecular structure. The combination of $Fe(C_5Me_5)_2$ and **1**–**4** afforded unique crystalline architectures (*7*). These structural features are: (i) 1:1 complexes that contain monoanions of **1** and **3** and form ribbon-type structures through close CN···O and Br···O contacts, respectively. (ii) In 1:1:1(H_2O) complexes, dianions of **1** and **4** are linked with water molecules via O—H···O hydrogen bonds and form 1D tape architectures. (iii) The dianion of **1** in a 2:1 complex is stacked with a ···DDADDA··· type arrangement along the [−101] direction. To date, 27 crystalline compounds have been obtained from molecule **1** and the characterised intercomponent interactions are noted as novel supramolecular synthons (Scheme 2) (*5*) for crystal engineering.

The effective interplay between CT and H-bonding interactions on the molecular assemblies is currently appreciated as an important concept and method in the construction of new molecular materials and fine tuning of their physical properties, which was first observed in quinhydrone systems (*16*). We have recently dealt with the development of new organic proton–electron donor–acceptor interactions as supramolecular synthons for the preparation of ordered solid phases. Several proton acceptors, containing bipyridine as bidentate nitrogen ligands, have been investigated with proton-donors and/or electron-acceptors, **1**–**5**, to propagate oriented patterns in crystal engineering (*8*–*10*). These complex supramolecules have been evaluated via the control of stoichiometry, geometry and chemical modification of the molecules. The complexes have infinite 1D and 2D tape-like structures due to three intermolecular H-bonds ($N^+—H\cdots O^-$, $N^+—H\cdots O$ and $O—H\cdots N$) that lead to organic ferroelectrics (*17*), quite rarely encountered candidates for future organic electronic and optical devices.

Anilic acids are two enolone fragments linked with each other with a short O···O distance within the molecules (Scheme 2). These oxygen atoms can connect tightly with themselves and with the base molecules through a bifurcated O···H···N bonding system. A variety of supramolecular synthons (*8*) using the proton-donor (acid) and proton-acceptor (base) are constructed via intermolecular H-bonds. These H-bonded DA-type synthons are superior to those of the usual CT complexes, which turn into Mott insulators, and have advantageous physico-chemical features that show ferroelectricity and the corresponding applications. The crystalline arrangement of two molecular components, acid and base of the π-electron system, has greatly improved their performance such as permittivity and spontaneous polarisation compared with those of the conventional low-molecular-mass organic ferroelectrics (*18*).

Anilic acids can provide a variety of binding sites to metal cations and charged states and are considered a unique multifunctional ligand system. A large number of metal complexes based on **2**–**5** component molecules have been synthesised and their self-assembled frameworks are discussed via coordination, hydrogen, Coulombic linkage and electronic structures, which have also been accompanied by charged and spin states (*19*). A cyano-substituted anilic acid such as **1** has not been found in inorganic–organic coordination systems used for inorganic crystal engineering. This acid, **1**, has frontier orbitals with energies comparable to those of transition metal ions, together with redox-active π-electronic structures, affording rich coordination chemistry. In some molecular systems, it is possible to control molecular aggregation in the crystal by difunctional ligands that bond to metal with coordination–covalent interactions and to each other with H-bonding interactions. The bridging ligand **1** can be difunctionalised to form metal–chelate complexes as well as an intermolecular complementary H-bonding ligand with two sets of OH donors and O acceptors, as shown in Scheme 3(a). Design of such H-bondings and stable coordination bondings via altered metal coordination spheres can result in different types of self-organised superstructures (see Scheme 3) with infinite chains.

It thus seems reasonable to explore the capability of such a technique to evaluate the exchange coupling of transition metal ions through H-bonding and to search for magneto-structural correlations in progressing crystal engineering and in constructing the desired molecular-based materials.

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