

New Hydrogen-Bonded Donor–Acceptor Pairs between Dipyritylacetylenes and 2,5-Dichloro-3,6-dihydroxy-1,4-benzoquinone

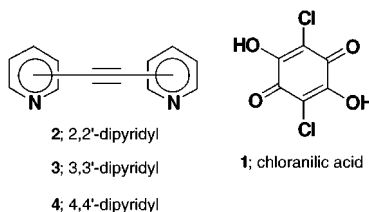
Md. Badruz Zaman,^{*†} Masaaki Tomura, and Yoshiro Yamashita^{*‡}

Research Center for Molecular Materials, Institute for Molecular Science,
Myodaiji, Okazaki 444-8585, Japan

zaman@ims.ac.jp

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ABSTRACT



The crystalline donor–acceptor hydrogen-bonding complexes between 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid) and dipyritylacetylenes (DPA) [2,2'-DPA, 3,3'-DPA, and 4,4'-DPA] were prepared, and crystal structures were revealed by X-ray analysis. The structures of the complexes are formed by intermolecular hydrogen-bonding interactions and demonstrate three supramolecular architectures based on a new common supramolecular synthon, which allows the formation of a different stacking arrangement and ionicity.

Certain functional groups, ions, and their intermolecular interactions display a supramolecular synthon,¹ which serves as the basis for the development of supramolecular chemistry² and, in the solid state, of crystal engineering.^{1,2b,3} The use of a similar supramolecular synthon with specific bonding features allows the control of molecular assembly. This can

[†] Permanent address: Department of Applied Chemistry and Chemical Technology, University of Dhaka, Dhaka 1000, Bangladesh.

[‡] yoshiro@ims.ac.jp

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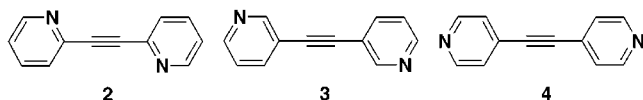
be employed to design materials with desired characteristics by incorporating specific properties. On the other hand, the proton transfer-mediated electron transfer in organic materials regulates the electronic properties of solids.⁴ Therefore, we have studied the noncovalent interactions along with intermolecular proton transfer with the aid of hydrogen bond interactions between donor (D) and acceptor (A) units.

Our recent findings that anilic acids, which are classical proton donors and electron acceptors, form complexes with π -donors and proton acceptors promoted our further investigation for the preparation of controlled organic donor–acceptor (DA) crystals.⁵ We have assumed that bipyridinium-type bridging ligands form molecular complexes with organic proton donors, which would be well-designed and strictly controlled aggregates and exhibit conceivable DA-type intermolecular interactions. Our aim is to synthesize new model complexes between dipyritylacetylenes as a set of

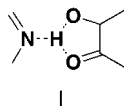
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proton acceptors and 2,5-dihalo-3,6-dihydroxy-1,4-benzoquinones and examine the structural control in crystal. We have chosen three isomeric molecules [2,2'-dipyridylacetylene (**2**), 3,3'-dipyridylacetylene (**3**), and 4,4'-dipyridylacetylene (**4**)] because they represent linear and rigid molecules with extended π -conjugation leading to reduced Coulombic repulsion and can be synthesized easily.⁶



Here, we report the creation of supramolecular complexes from complementary combinations of proton donor, chloranilic acid (**1**), and proton acceptors, **2–4**, via hydrogen-bonded interactions. The complexes were prepared by reacting dipyridylacetylenes with chloranilic acid.⁷ Single crystals were formed by the diffusion method, and the structures were obtained by X-ray crystal structure analyses.⁸ The stoichiometric ratios were confirmed by elemental analyses.⁹ These crystal structures are composed of a common supramolecular synthon (see structure **I**), formed by conceivable intermolecular O–H \cdots N, N⁺–H \cdots O, and N⁺–H \cdots O[–] hydrogen bonds.



These analyses reveal the unique structures of three different supramolecular assemblies having zigzag tapes,

(6) (a) For structure **2**, see: Teitei, T.; Collin, P. J.; Sasse, W. H. F. *Aust. J. Chem.* **1972**, *25*, 171. (b) For structure **3**, see: Teitei, T.; Wells, D.; Sasse, W. H. F. *Aust. J. Chem.* **1973**, *26*, 2129. (c) For structure **4**, see: Tanner, M.; Ludi, A. *Chimica* **1980**, *34*, 23.

(7) X-ray suitable single crystals were obtained by a diffusion method using 0.05 mmol of each component and 12–15 mL of solvents. Crystals **2**·**1**, **3**²⁺·**1**^{2–}·(H₂O)_{3,3}, and **4**⁺·**1**[–] were obtained from a mixture of methanol–acetone (1:1), both methanol and acetone, and acetone, respectively.

(8) (a) Crystal data for **2**·**1**: triclinic, space group $P\bar{1}$, $a = 3.8406(4)$, $b = 10.9748(14)$, and $c = 11.1523(11)$ Å, $\alpha = 59.665(9)^\circ$, $\beta = 84.586(9)^\circ$, $\gamma = 86.875(10)^\circ$, $V = 403.89(8)$ Å³, $Z = 1$. Of the 1898 reflections collected, 1643 were unique. Final $R_1 = 0.0673$ and $wR_2 = 0.1397$, GOF = 1.00 for 659 data with $I > 2\sigma(I)$. (b) Crystal data for **3**²⁺·**1**^{2–}·(H₂O)_{3,3}: triclinic, space group $P\bar{1}$, $a = 9.913(2)$, $b = 12.752(2)$, and $c = 3.8630(9)$ Å, $\alpha = 92.79(2)^\circ$, $\beta = 98.699(19)^\circ$, $\gamma = 84.595(19)^\circ$, $V = 480.32(18)$ Å³, $Z = 1$. Of the 2307 reflections collected, 2183 were unique. Final $R_1 = 0.048$ and $wR_2 = 0.118$, GOF = 0.94 for 1004 data with $I > 2\sigma(I)$. (c) Crystal data for **4**⁺·**1**[–]: monoclinic, space group $P2_1/n$, $a = 12.799(2)$, $b = 6.6870(13)$, and $c = 18.925(3)$ Å, $\beta = 93.641(10)^\circ$, $V = 1616.4(4)$ Å³, $Z = 4$. Of the 3384 reflections collected, 3285 were unique. Final $R_1 = 0.056$ and $wR_2 = 0.136$, GOF = 0.97 for 1631 data with $I > 2\sigma(I)$. (d) As a common feature, all non-hydrogen atoms were refined anisotropically and all hydrogen atoms were clearly localized in the Fourier maps and refined isotropically. Absorption correction was applied for **4**⁺·**1**[–] using empirical procedures based on azimuthal ψ scans of seven reflections. Structure solutions were accomplished with the aid of SHELXS-86 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467) and refinement was conducted using full-matrix least-squares on F^2 with SHELXL-93 (Sheldrick, G. M. SHELX93. *A Program for the Refinement of Crystal Structure*; Universität Göttingen, 1993) implemented on a Silicon Graphics computer.

(9) Anal. Calcd for **2**·**1** [C₁₈H₁₀N₂O₄Cl₂]: C, 55.55; H, 2.59; N, 7.20. Found: C, 55.34; H, 2.50; N, 7.07. Calcd for **3**²⁺·**1**^{2–}·(H₂O)_{3,3} [(C₁₈H₁₀N₂O₄·Cl₂)(H₂O)_{3,3}]: C, 48.19; H, 3.73; N, 6.24. Found: C, 48.12; H, 3.41; N, 6.28. Calcd for **4**⁺·**1**[–] [C₁₈H₁₀N₂O₄Cl₂]: C, 55.55; H, 2.59; N, 7.20. Found: C, 55.09; H, 3.18; N, 7.17.

square grids, and linear chains architectures. The space-filling views depicting the structures of **2**·**1**, **3**²⁺·**1**^{2–}·(H₂O)_{3,3}, and **4**⁺·**1**[–] are shown in Figures 1–3, respectively.

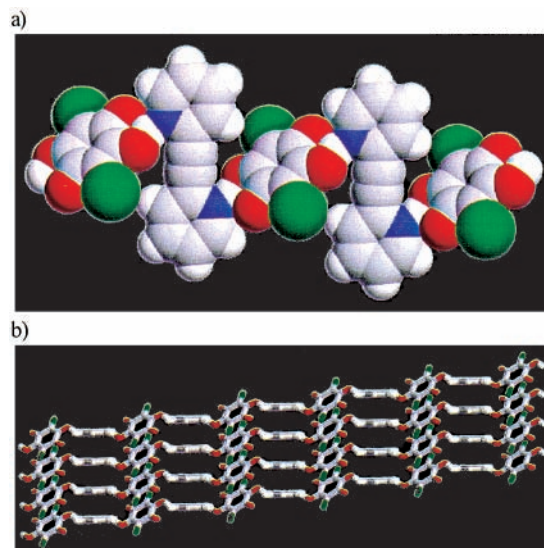


Figure 1. (a) Zigzag tapes of the **2**·**1** complex linked through O–H \cdots N hydrogen bonds (space-filling representation). (b) Sticks representation showing the segregated stacks arrangement as DD- and AA-type pairs.

In the crystalline architecture **2**·**1**,^{8a} the protons are localized on the oxygen atoms and a strong O–H \cdots N (1.47 Å) hydrogen bond is observed. The complex between **2** and **1** forms zigzag one-dimensional tapes (Figure 1a) through the O–H \cdots N hydrogen-bonded interactions and shows a segregated stacking assembly as DD- and AA-type pairs along the diagonal line of the ac plane (Figure 1b).

The bifurcated interionic N⁺–H \cdots O[–] (1.72 Å) and N⁺–H \cdots O (2.26 Å) hydrogen-bonded interactions dominate in the crystalline complex **3**²⁺·**1**^{2–}·(H₂O)_{3,3},^{8b} in which the N atoms at the 3 position form a zigzag tape structure, which

(10) The crystal structure of the complex between **4** and cyananilic acid^{5a} has been determined in the space group $P\bar{1}$, triclinic, $a = 8.910(7)$ Å, $b = 9.827(14)$ Å, $c = 5.323(6)$ Å, $\alpha = 102.71(14)^\circ$, $\beta = 104.88(9)^\circ$, $\gamma = 104.66(12)^\circ$, $V = 415.0(8)$ Å³, $Z = 1$; Zaman, M. B.; Tomura, M.; Yamashita, Y. Unpublished work.

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(12) Infrared spectroscopic analyses of the complexes **3**²⁺·**1**^{2–}·(H₂O)_{3,3} and **4**⁺·**1**[–] showed similar broad bands around 2100 and 2600 cm^{–1} and two intense bands around 3100 and 3050 cm^{–1}. This proves N⁺–H \cdots O[–] and N⁺–H \cdots O stretching vibration of the intermolecular hydrogen-bonded system. Apparently, such broad bands are not observed in complex **2**·**1**. A strong asymmetrical stretching band at 1650–1550 cm^{–1} and a weaker symmetrical stretching band near 1400 cm^{–1} support the deprotonation of anions.

(13) The calculations of the atomic charge (PM3) of each nitrogen atom (**2**, –0.0607; **3**, –0.0771; **4**, –0.0742) support the degree of protonation provided by X-ray analyses of the complexes.

is viewed as a square grid network along the *c* axis (Figure 2a). Within this network, cavities are formed, which are

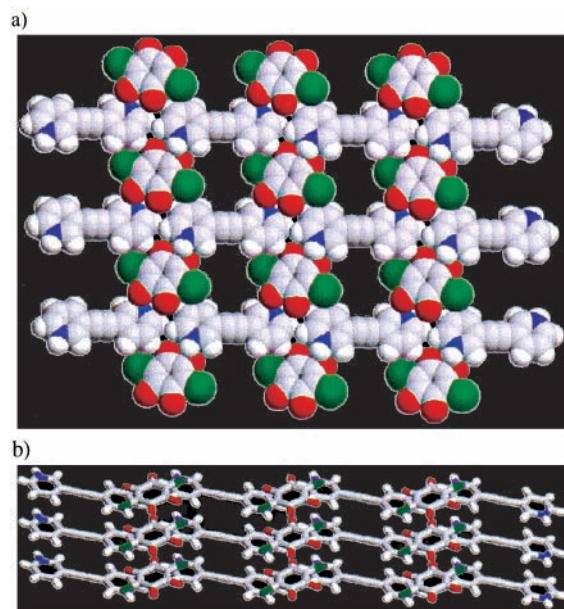


Figure 2. (a) Square grids of the $3^{2+}·1^{2-}·(H_2O)_{3.3}$ complex linked through $N^+–H···O$ and $N^+–H···O^-$ hydrogen bonds (space-filling representation). Water molecules are omitted for clarity. (b) Sticks representation showing the segregated stacks arrangement as DD- and AA-type pairs.

occupied by the water molecules. They are clearly visible and form apparent channels within the $3^{2+}·1^{2-}$ network. This structure also exhibits a one-dimensional segregated stacking arrangement along the *c* axis (Figure 2b). The distances between the planes of overlapping cations and anions are 3.45 and 3.37 Å, respectively, and the dihedral angle between the planes of the cation and anion is 17.4°.

In the crystalline architecture $4^+·1^-$,^{8c} one pyridine ring of **4** is protonated and combined with bifurcated $N^+–H···O^-$ (1.61 Å) and $N^+–H···O$ (2.33 Å) hydrogen-bond interactions, while the other pyridine ring is not protonated and combined with $O–H···N$ (1.65 Å) hydrogen-bonding interactions. Thus, infinite molecular chains (Figure 3a) are observed along the *c* axis (the average distance and angle between the least-squares planes of two parallel chains are 3.41 Å and 5.84°). Interestingly, the inversion center is not observed in the molecular component of this complex. Consequently, nonplanar pyridine rings are twisted along the conjugated acetylene with a dihedral angle of 74.6°. The dihedral angles between the protonated and nonprotonated pyridine rings and 1^- are 3.0° and 71.8°, respectively. This structure exhibits alternating DA-type overlapping pairs of

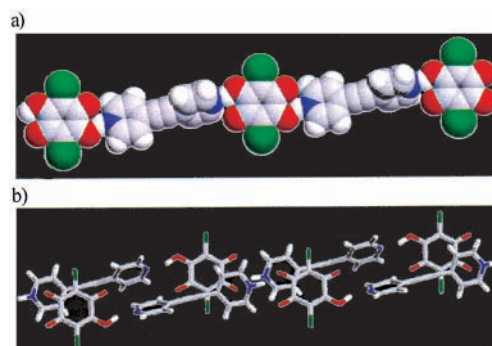


Figure 3. (a) Linear chains of the $4^+·1^-$ complex linked through $O–H···N$, $N^+–H···O$, and $N^+–H···O^-$ hydrogen bonds (space-filling representation). (b) Sticks representation showing the overlapped stacks arrangement as DA-type pairs.

the protonated pyridine ring and the anion molecule (Figure 3b). Furthermore, we have succeeded in changing the stacking pattern of such molecular chains as DD- and AA-type pairs using cyananilic acid (2,5-dicyano-3,6-dihydroxy-1,4-benzoquinone) as a stronger proton donor.¹⁰

In each case the $N···O$ (2.59–3.00 Å) distances are shorter than the mean distances observed for the hydrogen bonds between anilic acids and π -donors,^{5,11c} indicating the strength of the hydrogen bond interactions. The bond lengths and angles are also consistent with the molecular geometry of the chloranilic acid, hydrogen chloranilate, and chloranilate dianion.^{11,12}

The building blocks presented in this study afford unique hydrogen-bonded DA-type complexes in which D and A can be combined within robust hydrogen-bonded architectures. The positions of the N atoms in the dipyriddyacetylene molecules play an important role in the formation of different crystal architecture and determine the ionicity and stacking arrangement¹³ though the supramolecular synthon pattern **I** is unchanged. Therefore, the complexes between dipyriddy derivatives and anilic acids, with the capability for DA-type interactions through hydrogen bonding, are promising candidates for creating a variety of supramolecular architectures for self-assembly.

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Supporting Information Available: All X-ray crystallographic files, in CIF format, are available. This material is available free of charge via the Internet at <http://pubs.acs.org> OL991229Q