Novel 3D Network: From the Reaction of Polyamine with Pyromellitic Dianhydride

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Under mild condition, the reaction of pyromellitic dianhydride with polyamine in methanol solution results in ammonium carboxylate salts rather than amide polymer. X-ray analysis indicates a manifestation of 3D network linked by $N-H^+\cdots O^-\cdots H-N^+$ hydrogen bonding for the three ammonium salts, in which the porous spaces are filled with water molecules.

INTRODUCTION

It is well documented that the organic or organic–inorganic self-assembly is the spontaneous association of molecular subunits into structurally well-defined aggregates which are organized by feeble interactions such as hydrogen bond, $\pi-\pi$ stacking, salt bridge and so on [1,2]. Such molecular solids often possess interesting properties: (1) optical behavior, electrical conductivity, and ferromagnetism; (2) potential ability for selective inclusion and transportation of ions and molecules and the catalysis for specific chemical reactions [3–6]. As for organic molecular aggregates, current efforts in assembling molecular solids mainly focus on 1D and 2D aggregates [7], while reports about the 3D networks of organic molecular aggregates are relatively fewer except for the diamonded networks [8]. In addition, the reported organic solids mostly from weak bonds are relatively unstable and most of

them will change their forms under fairly high temperature. Such disadvantage thus limits the further potential uses in practice. The carboxyl groups have been extensively applied in the molecular solid design [9], but the studies of their ammonium salts are relatively fewer [10]. It is predicated that the hydrogen bonds formed by carboxylate or water with ammonium will be much augmented by the electrostatic interactions in the ammonium salts, and then the stability of these organic salts will be enhanced as well. It is of much interest to investigate the delicate interactions of polyammonium benzenetetracarboxylate in the solid state so as to throw light on the design and synthesis of new self-assembling solids for functional materials, since the polyamine separated by flexible C–C bonds has more binding sites to form hydrogen bond. With this in mind, we investigate the reaction of pyromellitic dianhydride with polyamine in methanol solution under mild conditions and the results show that the carboxylate salts are preferably produced rather than amide polymer (Scheme 1). The X-ray analysis, IR and TG analysis have been performed in the investigation of
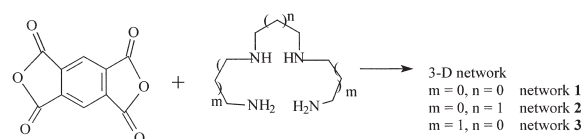
SCHEME 1 Schematic illustration of the formation of 3D networks.

the supramolecular structures self-assembled by carboxylate and ammonium. X-ray analysis indicates that the ammonium carboxylate salts recrystallized in water are of 3D networks connected by the hydrogen bonds of ammonium and carboxylate, and the stability of 3D networks is further enhanced by Coulombic forces and water molecules.

RESULTS AND DISCUSSION

Pyromellitic dianhydride is widely used in polymer and material science, and its derivatives have been extensively studied since the few past decades. When it reacts with polyamine at higher temperature, the main product is of amide polymer; while the ammonium salts predominate over others in the mild condition. Under room temperature, the reaction of pyromellitic dianhydride with polyamine in methanol solution leads to formation of ammonium salt as white powders. Single crystals are obtained from the slow evaporation of the respective ammonium salt in aqueous solution. X-ray analysis indicates a manifestation of network linked by $N-H^+ \cdots O^- \cdots H-N^+$ hydrogen bonding for the crystals **1−3**. Crystal structure analysis further indicates that the **1−3** are of 1:1 aggregates. In case of **2**, as shown in Fig. 2, the linear polyamine are tetra-protonated and each carboxylic acid is deprotonated, and thus the organic salts are neutral. The bond lengths of C−O are similar (1.24−1.26 Å), indicating the charge dispersing average along the O−C−O with the bond angles around 124°. As shown in Fig. 1, the four carboxylates are not in a
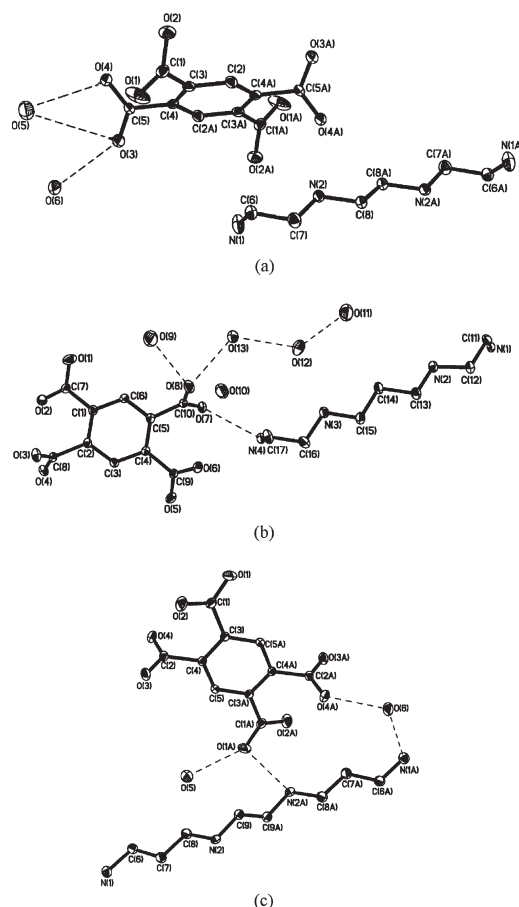

FIGURE 1   ORTEP drawings of the structural units for **1−3**. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms are omitted for clarity.

TABLE I   Selected bond distance (Å) and angles (°) for **1−3**

|			
*Data for **1***			
N(1)−C(6)	1.462(6)	N(2)−C(8)	1.481(5)
N(2)−C(7)	1.490(5)	C(1)−O(1)	1.225(5)
C(1)−O(2)	1.267(4)	C(5)−O(4)	1.245(4)
C(5)−O(3)	1.246(4)		
C(8)−N(2)−C(7)	112.0(3)	O(1)−C(1)−O(2)	123.7(4)
O(1)−C(1)−C(3)	120.2(4)	O(2)−C(1)−C(3)	116.1(4)
O(4)−C(5)−O(3)	124.2(4)	O(4)−C(5)−C(4)	119.1(3)
O(3)−C(5)−C(4)	116.7(3)	N(1)−C(6)−C(7)	113.0(4)
*Data for **2***			
C(5)−C(10)	1.5091(18)	C(7)−O(1)	1.243(2)
C(7)−O(2)	1.2456(19)	C(8)−O(3)	1.2441(19)
N(1)−C(11)	1.478(2)	N(2)−C(13)	1.490(2)
C(15)−N(3)	1.4841(19)	N(3)−C(16)	1.485(2)
O(1)−C(7)−O(2)	124.31(14)	O(2)−C(7)−C(1)	117.90(14)
O(3)−C(8)−O(4)	125.41(13)	O(8)−C(10)−O(7)	125.06(13)
C(13)−N(2)−C(12)	111.99(13)	C(15)−N(3)−C(16)	113.30(13)
*Data for **3***			
O(1)−C(1)	1.247(2)	O(2)−C(1)	1.241(2)
O(3)−C(2)	1.246(2)	O(4)−C(2)	1.2663(19)
C(8)−N(2)	1.496(2)	N(2)−C(9)	1.486(2)
O(2)−C(1)−O(1)	123.51(15)	O(2)−C(1)−C(3)	118.62(15)
O(3)−C(2)−O(4)	124.67(14)	N(2)−C(8)−C(7)	112.46(14)
C(9)−N(2)−C(8)	111.46(13)		

a)

b)

c)
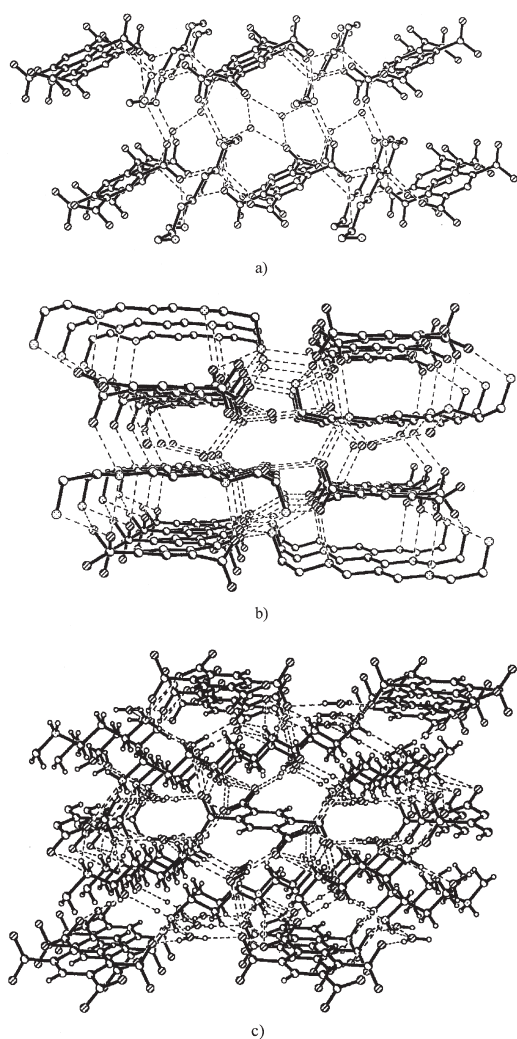
FIGURE 2 ORTEP views of the 3D hydrogen-bonded network present in crystals. In each view, hydrogen atoms are omitted for clearness and hydrogen bonds are represented by dashed line. (a) view from plane (100) of **1**; (b) view from plane (100) of **2**; (c) view from plane (100) of **3**.
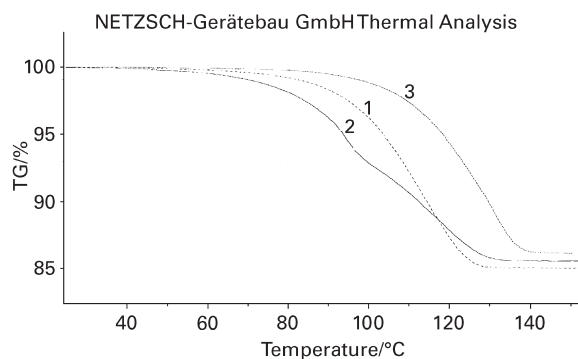

NETZSCH-Gerätebau GmbH Thermal Analysis

FIGURE 3 Overlay of TG traces of the title coordination polymer, for the sake of the clarity the DTG is deleted. The sample was heated at 20°C/min in a nitrogen atmosphere.

the flexible polyamine arrange in an interlaced sheet to give rise to a 3D architecture through the hydrogen bonding of $N–H^+ \cdots O^- \cdots H–N^+$ and $N–H^+ \cdots OCOO^-$. Just different to Zaworotko's report [11], there are no water-microchannels in such 3D networks. The water molecules, which are involved in the hydrogen bonding with ammonium and carboxylates, occupy the porous spaces and further strengthen the 3D network structure. Selected distance and angle data estimated from the X-ray crystallographic analyses are summarized in Table II (for the sake of clarity, only those of **2** are listed). In the supramolecular architecture, Coulombic forces between the oppositely charged ions, ammonium and carboxylate, and the included guest water molecules in the cavity further enhance the 3D stability. It is noteworthy to point out that the delicate structures of **2** differ from **1** and **3**, which have centric symmetry and therefore achrial. The self-assembled aggregate **2** is unique D_2 and is therefore chiral. This is a good example from achrial components to chiral products with losing symmetry by the organic synthesis design [12]. In view of these facts, we can study a series of polyamine and pick out the suitable chiral crystals with potential applications in non-linear optics.

The 3D crystals are stable in air and lose no moisture. But if allowed to immerse in methanol or ethanol under ambient conditions, the regular

plane, so that they can point out to three different directions. Furthermore, the protonated nitrogen atom in the flexible chain of polyamine is in tetrahedral environment and interacts with carboxylic acid through hydrogen bonds. In Fig. 2, it is observed that the rigid benzene carboxylic acid and

TABLE II Geometry of the selected hydrogen bonds in aggregates **2** (symmetry elements: (a) $x+1/2$, $-y+1/2$, $-z$; (b) $x+1$, y, z; (c) $x+1/2$, $-y+1/2$, $-z$; (d) $-x+1/2$, $-y+1$, $z-1/2$; (e) $x+1/2$, $-y+1/2$, $-z$; (f) x, y, $z-1$; (g) $x+1/2$, $-y+1/2$, $-z$; (h) $x-1/2$, $-y+1/2$, $-z$)

D–H$\cdots$A	r (D–H) (nm)	r(H$\cdots$A) (nm)	r(D$\cdots$A) (nm)	$\angle$(DH$\cdots$A) (°)
N1–H1A$\cdots$O2(a)	0.894	2.150	2.886	139.11
N1–H1B$\cdots$O4(b)	0.931	1.897	2.814	167.66
N1–H1C$\cdots$O2	0.992	1.881	2.857	167.27
N2–H2A$\cdots$O4(c)	0.860	1.877	2.683	155.49
N2–H2B$\cdots$O9	0.945	1.832	2.777	179.48
N3–H3B$\cdots$O3(d)	0.926	1.978	2.839	154.06
N3–H3C$\cdots$O5(e)	0.876	1.954	2.780	156.76
N4–H4A$\cdots$O7(f)	0.919	1.978	2.888	170.28
N4–H4B$\cdots$O5(g)	0.944	1.817	2.739	164.66
N4–H4C$\cdots$O7(h)	0.908	1.972	2.856	163.92

aggregates will lose crystallinity and turn into white powders with losing the included water molecules. Re-immersed in water, the powders will restore their beautiful crystallinity. The experiment implies that the included water plays an important role to sustain the regular structure of the self-assembly aggregates. To investigate the stability of the included water in such aggregates, TGA experiments were performed under N_2 atmosphere. The results show that at around 80°C, the crystals will lose water and turn into powders. At around 130°C, the pattern reaches platform (Fig. 3) and the weight loss is consistent with that of water filled in the porous space (**1**: 14.83, calcd 15.25; **2**: 14.40, calcd 14.85; **3**: 13.69, calcd 14.38). TGA indicates the white powders can be stable up to around 250°C, which are in the range of pure ammonium salts. It can be concluded that the hydrogen bonds formed by the included water with ammonium and carboxylate in the aggregates appear to be critically essential in stabilizing the regular structures of the open 3D polymeric networks.

In summary, the reaction of pyromellitic dianhydride with polyamine represents a new route to generate 3D network, which is connected by hydrogen bonding and coulombic forces. This type of 3D structure may shed highlight on the design and synthesis of the functional materials. Some important observations can be concluded. Firstly, the chain length of polyamine may be modified and further substituents (including chiral group) can be introduced. Secondly, chirality of the aggregate salts may be produced as suitable ammine is selected. If possible, a new series of NLO (non-linear optics) materials [13,14] might be produced.

EXPERIMENTAL SECTION

Materials

The chemicals and solvents used in the synthesis of products were of analytical reagent and were purified according to the literature methods [15].

Measurements

The Fourier-transform IR spectra were taken on a Nicolet 560 ESP spectrometer and elemental analyses were made on a Perkin–Elmer 240C analyzer. 200 MHZ ^{1}H NMR spectroscopic measurements were performed on a Bruker AM-200 NMR spectrometer, using TMS (SiMe$_4$) as an internal reference at 25°C. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed at a scan rate of 20°C/min using a Netzsch TG 209 analyzer under N_2 atmosphere.

General Procedures for Synthesis of 1−3

Pyromellitic dianhydride (5 mmol) was warmed to dissolve in 150 ml methanol and then cooled. A solution of the appropriate polyamine (5 mmol) in 30 ml methanol was added to such a stirred solution above at room temperature. The reaction mixture was stirred at room temperature for 5 h and filtered. The powder product was washed twice with methanol and then recrystallized with hot water to give colorless crystals. Yield: 50.5–78.2%.

The suitable single crystals for X-ray analysis were obtained under the slow evaporation of the respective aqueous solution.

1. ^{1}H NMR (D$_2$O, 200 MHz): $\delta = 7.57$ (s, 2H), 3.0–3.1 (m, 12H). IR (KBr pellet): 3421.2 (vs), 3020.6 (s), 2697.7 (b), 1655.9 (s), 1569.5 (vs), 1487.0 (s), 1408.4 (s), 1366.6 (s), 1318.1 (s), 865.7 (m), 814.9 (m) cm^{-1}.

2. ^{1}H NMR (D$_2$O, 200 MHz): $\delta = 7.50$ (s, 2H), 3.17 (m, 8H), 2.89 (m, 4H), 1.72 (s, 2H). IR (KBr pellet): 3536.1 (vs), 3415.7 (vs), 3028.3 (b), 2796.1 (b), 1636.4 (s), 1598.9 (vs), 1560.7 (vs), 1537.6 (s), 1486.7 (s), 1411.0 (s), 1371.3 (vs), 1320.7 (s), 862.8 (m), 814.0 (m) cm^{-1}.

3. ^{1}H NMR (D$_2$O, 200 MHz): $\delta = 7.64$ (s, 2H), 3.37 (m, 4H), 2.94–3.13 (m, 8H), 1.91–1.98 (s, 4H). IR (KBr pellet): 3512.6 (vs), 3353.5 (b), 3008.5 (b), 2804.1 (b), 1603.0 (s), 1559.5 (vs), 1481.0 (s), 1422.9 (s), 1367.2 (vs), 1323.2 (s), 864.9 (m), 810.6 (m), 810.6 (m) cm^{-1}.

X-ray Crystallography

Crystals of **1−3** suitable for single-crystal X-ray diffraction with suitable sizes were selected. Structural analyses for **1−3** was performed on a Siemens SMART CCD diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å). The structure was solved by direct methods using the SHELXTL-97 package [16]. The ORTEP structures and the selected bond distances and angles are shown in Fig. 1 and Table I, respectively.

1. Crystal data: C$_{16}$H$_{32}$N$_4$O$_{12}$, $M_r = 472.46$, triclinic, space group P-1. $a = 7.4765(13)$, $b = 7.6547(13)$, $c = 9.6846(16)$ Å, $\alpha = 76.213(3)$, $\beta = 85.473(4)$, $\gamma = 84.286(4)°$, $V = 527.26(15)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.488$ Mg/mm^{-3}, $F(000) = 252$, $T = 298(2)$ K, wavelength 0.71073 Å. A colorless plate with the dimension $0.05 \times 0.10 \times 0.20$ mm^3 was measured with a BRUKER SMART 1000. θ range for data collection 2.20–24.10°. A total of 1762 were measured, 1592 unique ($R_{int} = 0.0336$). Weighting scheme $w = 1/[S^2(F_O^2) + (0.0909P)^2 + 0.0000P]$, where $P = (F_O^2 + 2F_C^2)/3$. Goodness of fit on F^2 was 0.993. Final R indices [$I > 2\sigma(I)$] $R1 = 0.0621$, $wR2 = 0.1450$. Largest difference Fourier peak and hole 0.255 and -0.235 eÅ^{-3}.

2. Crystal data: C$_{17}$H$_{36}$N$_4$O$_{13}$, $M_r = 504.50$, orthorhombic, space group $P2_12_12_1$. $a = 7.7524(7)$,

$b = 14.8513(15)$, $c = 20.532(2)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, $V = 2363.9(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.418$ Mg/mm^{-3}, $F(000) = 1080$, $T = 293(2)$ K, wavelength 0.71073 Å. A colorless plate with the dimension $0.40 \times 0.35 \times 0.30$ mm^3 was measured with BRUKER SMART 1000. θ range for data collection 1.69–25.01°. A total of 9805 were measured, 4162 unique ($R_{int} = 0.0270$). Weighting scheme $w = 1/[S^2(F_O^2) + (0.0470P)^2 + 0.2988P]$, where $P = (F_O^2 + 2F_C^2)/3$. Goodness of fit on F^2 was 1.046. Final R indices $[I > 2\sigma(I)]$ $R1 = 0.0281$, $wR2 = 0.0749$. Largest difference Fourier peak and hole 0.185 and -0.134 eÅ^{-3}.

3. Crystal data: $C_{18}H_{36}N_4O_{12}$, $M_r = 500.51$, triclinic, space group P-1. $a = 7.1774(10)$, $b = 7.9927(10)$, $c = 11.4286(14)$ Å, $\alpha = 70.879(2)$, $\beta = 84.352(2)$, $\gamma = 68.202(2)°$, $V = 574.96(13)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.446$ Mg/mm^{-3}, $F(000) = 268$, $T = 293(2)$ K, wavelength 0.71073 Å. A colorless plate with the dimension $0.35 \times 0.30 \times 0.30$ mm^3 was measured with a BRUKER SMART 1000. θ range for data collection 1.89–25.02°. A total of 2417 were measured, 2023 unique ($R_{int} = 0.0144$). Weighting scheme $w = 1/[\sigma^2(F_O^2) + (0.0777P)^2 + 0.1852P]$, where $P = (F_O^2 + 2F_C^2)/3$. Goodness of fit on F^2 was 1.048. Final R indices $[I > 2\sigma(I)]$ $R1 = 0.0425$, $wR2 = 0.1202$. Largest difference Fourier peak and hole 0.265 and -0.238 eÅ^{-3}.

SUPPORTING INFORMATION AVAILABLE

Crystallographic files in CIF format are available free from the author.

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