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COMMUNICATION

Coordination Polymers of Organic Polymers via Photopolymerization in Single Crystals: Two-dimensional Hydrogen Bonding Layers with Amazing Shock Absorbing Nature

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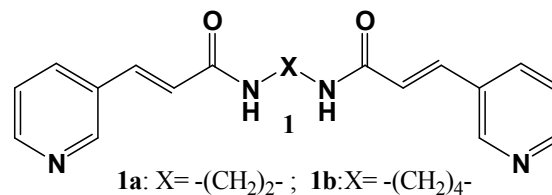
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Crystalline coordination polymers of organic polymers (CPOPs) were synthesized via photopolymerization of Ag(I) coordination polymers of dienes which have a self-templating nature due to the formation of N-H...O hydrogen bonded layers. The shock absorbing nature of the H-bonded layer facilitated the SCSC [2+2] transformation upon irradiation to produce CPOPs.

Coordination polymers (CPs) are of current interest due to their intriguing structures, multifunctional aspects and their dynamic aspects.¹⁻³ Several thousands of CPs reported to date by linking transition metals with small organic molecules. However, CPs using an organic polymer (OP) as a linker between the metal atoms had not been reported to date given the lower solubility of organic polymers and difficulty in obtaining single crystals of such complexes. Here, we demonstrate very rare examples of CPs of OPs. In the literature, there are some examples in which the solid state photo-dimerization was used as a tool for increase in the dimensionality of the network as the molecules belong to the neighbouring networks dimerize via [2+2] reaction in SCSC fashion.⁴ However, such reactions to date were not used for polymerization of the organic ligands containing olefin moieties that are already serving as the backbone of CPs. Recently we have reported that **1b** upon photo-irradiation polymerizes to produce 1D-covalent polymers in SCSC fashion.⁵ In those studies, it was found that the formation of N-H...O hydrogen bonding layer is an essential requirement for such polymerization reactions. The hydrogen bonding layer found to retain before and after the reaction by changing the angles between the hydrogen bonded amide groups which was attributed as shock absorbing nature of the layer. Therefore, it occurred to us that the synthesis of CPs of derivatives of **1** containing such hydrogen bonding layer provides an excellent opportunity of producing unprecedented

crystalline CPs of organic polymers (CPOP), the first reports, via single-crystal-to-single-crystal.⁶



Scheme 1.

The molecule **1a** was found to be photostable in its crystal structure as it forms a β -sheet network which places the double bonds at unreactive distances. Single crystals of CPs of **1a** & **1b** with Ag(I) are prepared in anticipation of hydrogen bonding layer which can polymerize the molecules of **1**.⁷ The single crystals of complex **2**, [Ag(**1a**)(ClO₄)]_n, were obtained by the reaction of **1a** with AgClO₄ in EtOH and drop of NH₄OH. The single crystal analysis reveals that the **2** contains a one-dimensional zig-zag chains of Ag.**1a** which are cross-linked by disordered perchlorate ions. The asymmetric unit is constituted by half unit each of Ag(I), **1a** and ClO₄ ions. The Ag(I) exhibits a square planar geometry with the coordination of two pyridyl N-atoms and two O-atoms of perchlorate ions. The cross-linking of 1D chains of Ag.**1a** takes place such that the linked Ag(I) atoms (inter-chain) are separated by perchlorate ions by 5.634 Å (Fig. 1). The Ag.**1a** chains are further interlinked by N-H...O hydrogen bonding layers between the molecules of **1a**. Such hydrogen bonding layer was described by us earlier as self-templating polymerization layer, which allows facile transformation to polymerization in single crystal to crystal manner due to the shock absorbing nature of hydrogen bonds.⁷ The double bonds in **2** were found to be placed in reactive orientations as required (3.714 Å and

C=C...C=C torsion angle 0°). Accordingly, the single crystals of **2** were irradiated in sunlight to obtain single crystals of **2'**.

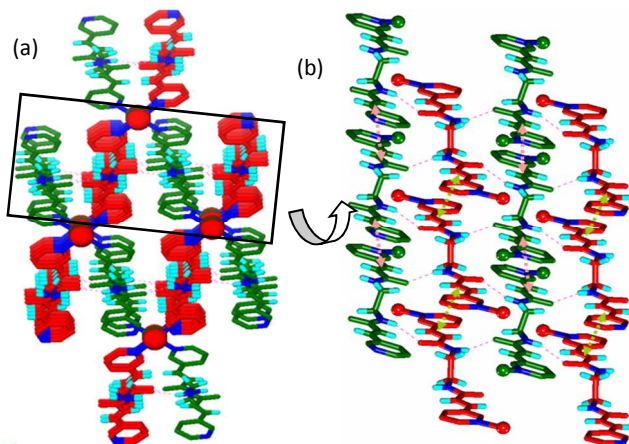


Fig. 1 Illustrations for the crystal structures of **2**: (a) cross packing of 1D-chains (green and red) via N-H...O hydrogen bonding; (b) 2D-hydrogen bonding network that serves as self-template for polymerization, notice double-headed arrows showing the reactive sites.

The crystal structure analysis of **2'** reveals that the polymerization occurred to yield crystals of CP of an organic polymer (CPOP) with significant changes in the crystal structure (Fig. 2). Although the space group remains same, the contents in the asymmetric unit of **2'** were increased to three times (unit cell volume 1974 versus 5783 Å³) with overall compression due to polymerization by 2.5 % of crystal volume.

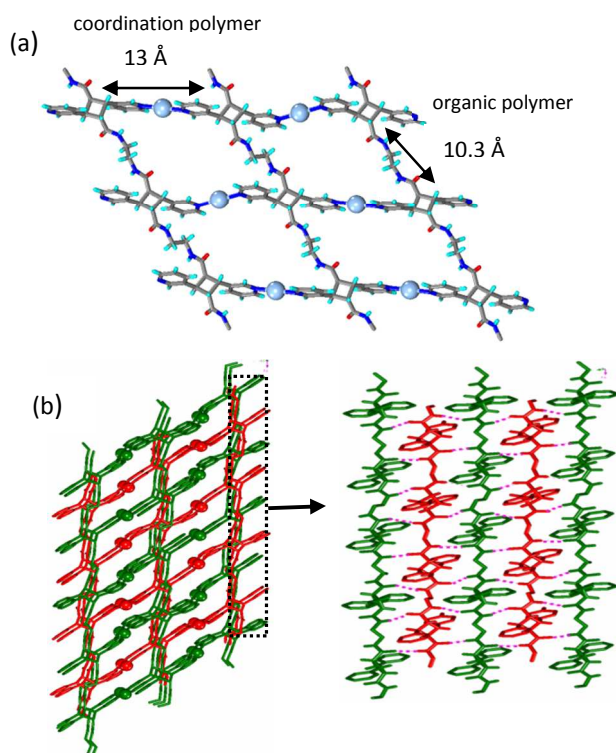


Fig. 2 Illustrations for the crystal structure of **2'**: (a) inclined interpenetrated 3D-network, (b) top view of 2D-layers of hydrogen bonding.

Interestingly, the hydrogen bonding layer remains intact during the entire course of reaction with albeit minor differences in the form of interplanar angles between the H-bonded amide planes (5° in **2** and 0° & 17° in **2'**) and changes in torsions of N-C-C-N (180° in **2** and 180° & 173° in **2'**). Significant differences in ClO₄ ions between **2** and **2'** were observed: in **2**, disordered ClO₄ ion is coordinated to Ag(I) with a distance as short as 2.497 Å, whereas in **2'** they are ordered and coordinated with a longer distances of 2.797, 2.979 and 3.007 Å and the cross-linked Ag atoms exhibit the Ag...Ag distance of 4.851 and 5.505 Å (5.634 Å in **2**).

The polymerization occurred between the CP chains but within the hydrogen bonding layers. As a result, 1D-CPs are converted in to 2D-CPs (Fig. 2a). The layers contain rectangular grids of dimension 10.3 × 13 Å in which two of the edges are formed by organic polymers and two of the edges are formed by coordination polymer. Two of such layers are interpenetrated (inclined mode) *via* amide-to-amide hydrogen bonds to result in overall 3D-network (Fig. 2b). It was also found that the organic polymer can be isolated from CPOP by acid-base work up. The ¹H NMR of separated material in D₂O with a drop of HCl reveals the presence of cyclobutane protons at δ = 4.40 and 3.92 ppm and absence of olefinic protons indicating the quantitative conversion to a polymer (Fig. 3).

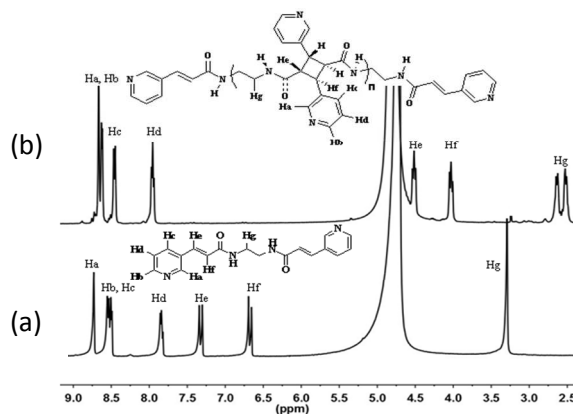


Fig. 3 ¹H NMR spectra in D₂O+HCl: (a) for **1a**, notice the doublets at 7.32 & 6.67 ppm for olefin protons of **1a**; (b) for the isolated polymer of **1a**, notice the absence of doublets and the presence of signals for cyclobutane protons at 4.40 & 3.92 ppm.

Further, the longer ligand containing butyl spacer was also found to form crystals of iso-structural complex **3**, [Ag(**1b**)(ClO₄)]_n, when reacted with AgClO₄ in above mentioned manner. The irradiation of these crystals resulted in the single crystals of complex **3'**. The crystal structure analysis reveals that the contents of asymmetric unit of **3'** are four times to those of **3** (unit cell volume 2212 versus 4352 Å³) due to the doubling of the cell and change of space group (C2/c to C2) with overall compression of 1.6% of crystal volume. The cross-linked Ag(I) atoms exhibit Ag...Ag distances of 6.380 Å (Ag-O 2.776 Å) in **3** and 6.188 and 6.625 Å in **3'** (Ag-O 3.167 Å, 3.073 Å, 2.985 Å). The CPOP layer contains square grids of dimension 12.75 and 12.95 Å which are doubly interpenetrated

via 2D-hydrogen bonding layer to result in three-dimensional structure (Figure S21, see in the Supporting Information). We note here that the hydrogen bonding parameters remain almost similar in both the structures but several adjustments in the layers were observed in terms of interplanar angles between the amide planes (16° in **3** and 17° and 8° in **3'**) and alkyl chain geometries (180° in **3** and 179° , 74° in **3'**). In case of **2** & **2'**, the H-bonded amide planes are parallel to each other before reaction whereas they become angular after reaction. In case of **3** & **3'**, the H-bonded amide groups are in plane before reaction which becomes separated into two parallel planes after reaction.

To see the influence of anion, the reactions of **1a** & **1b** with AgNO_3 were conducted in MeOH-DCM with a drop of NH_4OH to produce single crystals of **4**, $[\text{Ag}(\mathbf{1a})(\text{NO}_3)]_n$ and **5**, $[\text{Ag}(\mathbf{1b})(\text{NO}_3)]_n$ respectively. The crystal structures of **4** (Triclinic, P-1) and **5** (Monoclinic, C_2/c) found to contain similar one-dimensional chains which are observed in **2** and **3**. The one-dimensional chains are interlinked by the similar 2D-hydrogen bonding layers which facilitate polymerization. In case of **4**, the asymmetric unit is constituted by two Ag(I) ions, one and two half units of **1a** and two nitrate ions which are disordered. The Ag(I) ion exhibits linear coordination geometry and connected to two 3-pyridyl units. The zig-zag chains pack in crisscrossed manner such that the molecules of **1a** from adjacent networks are linked through N-H...O hydrogen bonds to form an anticipated layer. Accordingly, the irradiation of **4** leads to the formation of single crystals of **4'**.

The crystal structure analysis of **4'** reveals significant changes in crystallographic symmetries. Although the space group remains same, in contrast to the above two examples, the contents in **4'** are reduced to half (unit cell volume 1874 versus 917 \AA^3) indicating overall compression of 2%. Interestingly, the hydrogen bonding layer remains intact during the entire course of reaction with albeit minor differences. In case of **5**, the quality of crystals as formed are very poor and small in size, the butyl groups and nitrate ions are found to be in severe disorder, therefore the crystal structure after irradiation could not be determined. However, quantitative conversion of the **1b** units to organic polymer was observed using ^1H NMR spectroscopy. We note here both nitrate and perchlorate are neither interfering in the hydrogen bonding nor strongly coordinated to Ag(I) ions, therefore in all four cases, studied here, the formation of 2D-hydrogen bonding layer which is required for polymerization is facilitated. Further, the complexes **2-5** can also be produced by mechano-chemical dry grinding process of the corresponding components, the similarities between grounded materials and conventionally produced materials were identified by comparing their XRPD patterns. The irradiation of these materials found to produce **2'-5'** in quantitative yield which is evidenced by ^1H NMR and XRPD patterns.

To determine the molecular weight of these polymers (**2'-5'**), the MALDI-TOF mass spectra was recorded using 2,5 dihydroxy benzoic acid (DBH) as a matrix and sodium tri-fluoro acetate as cationizing agent. In all the cases, the molecular weight corresponding to 7-mer was observed.

In summary, four examples of crystalline material of coordination polymer of organic polymer was produced by [2+2] reaction of diene in SCSC manner. The 2D-hydrogen bonding layer of the ligands in the crystal structure of CPs helps in self templating the reaction and also the layer adjusts itself according to the demands of structural transformation in the crystal. This reaction serves as a means of producing crystalline CPs of OPs otherwise impossible to produce. The fragment **1** as such is amenable to functionalizations and modifications which provide an opportunity for the creation of several such CPOPs by extending the similar strategy.

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Notes and references

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Electronic Supplementary Information (ESI) available: Experimental details and characterization of the compounds by ^1H -NMR spectra, FTIR spectra, PXRD patterns, MALDI-TOF mass spectroscopy, Thermal analysis and Crystallographic data and refinement details.

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