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Coordination polymers of organic polymers synthesized *via* photopolymerization of single crystals: two-dimensional hydrogen bonding layers with amazing shock absorbing nature†

Mousumi Garai and Kumar Biradha*

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 dynamic aspects.¹⁻³ Several thousands of CPs have been reported to date by linking transition metals with small organic molecules. However, CPs formed using an organic polymer (OP) as a linker between the metal atoms have 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 where the solid state photo-dimerization was used as a tool for increasing the dimensionality of the network, as the molecules belonging to the neighbouring networks dimerize via [2+2] reaction in a SCSC fashion.⁴ However, such reactions to date have not been used for polymerization of the organic ligands containing olefin moieties that serve as the backbone of CPs. Recently we have reported that 1b upon photo-irradiation polymerizes to produce 1D-covalent polymers in a SCSC fashion.⁵ In those studies, it was found that the formation of the N-H···O hydrogen bonding layer is an essential requirement for such polymerization reactions. The hydrogen bonding layer was retained before and after the reaction by changing the angles between the hydrogen bonded amide groups which was attributed to the shock absorbing nature of the layer. Therefore, we thought that the synthesis of CPs of derivatives of 1 containing such hydrogen



bonding layers provides an excellent opportunity for producing unprecedented crystalline CPs of organic polymers (CPOPs), the first reports, *via* single-crystal-to-single-crystal transformation (Scheme 1).⁶

Molecule 1a was found to be photostable in its crystalline state as it forms a β -sheet network, which places the double bonds at unreactive distances. Single crystals of CPs of 1a and 1b with Ag(1) are prepared in anticipation of the hydrogen bonding layer which can polymerize the molecules of 1.7 The single crystals of complex 2, $[Ag(1a)(ClO_4)]_n$, were obtained by the reaction of 1a with AgClO₄ in EtOH and a drop of NH4OH. The single crystal analysis reveals that 2 contains one-dimensional zig-zag chains of Ag-1a which are crosslinked by disordered perchlorate ions. The asymmetric unit is constituted by half unit each of Ag(1), 1a and ClO_4 ions. The Ag(1)exhibits a square planar geometry with the coordination of two pyridyl N-atoms and two O-atoms of perchlorate ions. The crosslinking of 1D chains of Ag 1a takes place such that the linked Ag(1) 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 a hydrogen bonding layer was described by us earlier as a selftemplating polymerization layer, which allows facile transformation to polymerization in a 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 \cdots C=C torsion angle 0°). Accordingly, the single crystals of 2 were irradiated with sunlight to obtain single crystals of 2'.

The crystal structure analysis of 2' reveals that the polymerization occurred to yield crystals of a CP of an organic polymer (CPOP) with

Department of Chemistry, Indian Institute of Technology, Kharagpur-721302, India. E-mail: kbiradha@chem.iitkgp.ernet.in; Tel: +91-3222-283346

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



Fig. 2 Illustration of the crystal structure of **2**': (a) two-dimensional layer of CPOP; (b) the double interpenetration of 2D-networks in inclined mode (left), hydrogen bonding between the interpenetrated networks (right).

significant changes in the crystal structure (Fig. 2). Although the space group remains the same, the content of the asymmetric unit of 2' was increased three times (unit cell volume 1974 *versus* 5783 Å³) with an overall compression due to polymerization by 2.5% of crystal volume.

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° and 17° in 2') and changes in torsion angles

of N–C–C–N (180° in 2 and 180° and 173° in 2′). Significant differences in ClO_4 ions between 2 and 2′ were observed: in 2, disordered ClO_4 ions are coordinated to Ag(i) with a distance as short as 2.497 Å, whereas in 2′ they are ordered and coordinated with longer distances of 2.797, 2.979 and 3.007 Å and the cross-linked Ag atoms exhibit the Ag···Ag distances 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 into 2D-CPs (Fig. 2a). The layers contain rectangular grids of dimensions 10.3×13 Å in which two of the edges are formed by organic polymers and two of the edges are formed by coordination polymers. Two of such layers are interpenetrated (inclined mode) *via* amide-to-amide hydrogen bonds to result in an overall 3D-network (Fig. 2b). It was also found that the organic polymer can be isolated from the CPOP by an acid–base workup. The ¹H NMR of separated material in D₂O with a drop of HCl reveals the presence of cyclobutane protons at $\delta = 4.40$ and 3.92 ppm and the absence of olefinic protons indicating the quantitative conversion to a polymer (Fig. 3).

Furthermore, the longer ligand containing the butyl spacer was also found to form crystals of iso-structural complex 3, $[Ag(1b)(ClO_4)]_n$, when reacted with $AgClO_4$ in the abovementioned manner. The irradiation of these crystals resulted in the single crystals of complex 3'. The crystal structure analysis reveals that the content of the asymmetric unit of 3' is four times that of 3 (unit cell volume 2212 versus 4352 Å³) due to the doubling of the cell and change in the space group (C2/cto C2) with an overall compression of 1.6% of crystal volume. The cross-linked Ag(1) 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 dimensions 12.75 and 12.95 Å, which are doubly interpenetrated via the 2D-hydrogen bonding layer to result in a threedimensional structure (Fig. S21, see in the ESI[†]). We note here that the hydrogen bonding parameters remain almost similar for both the structures but several adjustments in the layers were



Fig. 3 ¹H NMR spectra in D_2O + HCl: (a) of **1a**, notice the doublets at 7.32 and 6.67 ppm for olefin protons; (b) of the isolated polymer of **1a**, notice the absence of doublets and the presence of signals for cyclobutane protons at 4.40 and 3.92 ppm.

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 the case of 2 and 2', the H-bonded amide planes are parallel to each other before reaction whereas they become angular after reaction. In the case of 3 and 3', the H-bonded amide groups are in plane before reaction, which become separated into two parallel planes after reaction.

To investigate the influence of anions, the reactions of 1a and 1b with AgNO3 were conducted in MeOH-DCM with a drop of NH₄OH to produce single crystals of 4, $[Ag(1a)(NO_3)]_n$, and 5, $[Ag(1b)(NO_3)]_n$, respectively. The crystal structures of 4 (triclinic, $P\bar{1}$) and 5 (monoclinic, C_2/c) were found to contain similar onedimensional chains, which are observed in 2 and 3. The onedimensional chains are interlinked by similar 2D-hydrogen bonding layers, which facilitate polymerization. In the case of 4, the asymmetric unit is constituted by two Ag(1) ions, one and two half units of 1a and two nitrate ions which are disordered. The Ag(I) ion exhibits linear coordination geometry and is connected to two 3-pyridyl units. The zig-zag chains pack in a crisscross 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 the same, in contrast to the above two examples, the content of 4' is reduced to half (unit cell volume 1874 versus 917 $Å^3$) indicating an overall compression of 2%. Interestingly, the hydrogen bonding layer remains intact during the entire course of reaction with albeit minor differences. In the case of 5, the quality of crystals as formed is very poor and they are small in size, and the butyl groups and nitrate ions are found to be severely disordered, therefore the crystal structure after irradiation could not be determined. However, quantitative conversion of 1b units to organic polymers was observed using ¹H NMR spectroscopy. We note here that both nitrate and perchlorate neither interfere with the hydrogen bonding nor strongly coordinate to Ag(I) ions, therefore in all four cases studied here, the formation of the 2D-hydrogen bonding layer which is required for polymerization is facilitated. Furthermore, complexes 2-5 can also be produced by a mechano-chemical dry grinding process of the corresponding components; the similarities between ground materials and conventionally produced materials were identified by comparing their XRPD patterns. The irradiation of these materials was found to produce 2'' 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 were recorded using 2,5-dihydroxybenzoic acid (DBH) as a matrix and sodium tri-fluoroacetate as a cationizing agent. In all the cases, the molecular weight corresponding to 7-mer was observed.

In summary, four examples of crystalline materials of coordination polymers of organic polymers were produced by [2+2] reaction of dienes in a 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 of the crystal. This reaction serves as a means of producing crystalline CPs of OPs otherwise impossible to produce. 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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