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Photochemical Structural Transformation of a Linear 1D **Coordination Polymer Impacts the Electrical Conductivity**

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Supporting Information

ABSTRACT: A pair of 4-(1-naphthylvinyl)pyridine (4nvp) ligands has been successfully aligned in head-to-tail fashion in a one-dimensional (1D) double chain ladder polymer $[Cd(adc)(4-nvp)_2(H_2O)]_n$ (1; H₂adc = acetylenedicarboxylic acid) that undergoes a photochemical [2 + 2] cycloaddition reaction accompanied by single-crystal to single-crystal (SCSC) structural transformation from a 1D chain to a 2D layer structure. These structural changes have a significant impact on the conductivity and Schottky nature of the compound.

C ingle-crystal to single-crystal (SCSC) structural transformation of coordination polymers (CPs) has attained a great deal of interest in solid-state chemistry, because the final products can be characterized unambiguously by single crystal X-ray crystallography, which may be otherwise unattainable in solution.^{1,2} Of these, structural transformation via photochemical [2 + 2] cycloaddition attains a special interest.³⁻⁵ Ditopic spacer 1,2-bis(4'-pyridyl)ethylene (bpe) and monotopic terminal ligand 4-styrylpyridine (4-spy) have been used in CPs for studying topochemical structural transformation.^{3–} Recently, monotopic 4-(1-naphthylvinyl)pyridine (4-nvp) has also been used for the same purpose.⁹ However, conversion of CP from one-dimensional (1D) to two-dimensional (2D) structure by photodimerization is still rare in the literature. One of the strategies of synthesizing 1D CP is to employ acetylenedicarboxylate $(-O_2CCCCO_2)$, which acts as a dianionic linear connector in the fabrication of CPs.^{10,11}

In the past few decades, successful attempts have been made for the topochemical structural transformation via photochemical $\begin{bmatrix} 2 \\ 2 \end{bmatrix}$ cycloaddition.^{3-5,12-16} However, despite having few reports in the literature, the effects of photodimerization on physical properties of CPs have remained largely unexplored.^{17–22} Additionally, CPs have currently emerged as an important class of solid-state materials and have been characterized with conductive properties for application in Schottky diodes as well as a photosensing devices.²³⁻²⁶ It is important to mention that the electronic properties of the CPs depend on a judicious choice of organic linkers as well as metal ions. CPs prepared from d¹⁰ metal ions $(Zn^{2+}, Cd^{2+} \text{ etc.})$ with conjugated carboxylate linkers are found to show semiconducting properties^{27,28} and can behave in a Schottky nature.²⁴⁻²⁶ MacGillivray et al. have demonstrated the effect of photodimerization on the conductivity of a metal-organic complex.²⁹ However, there is no example on how photodimerization affects the conductivity properties of CP. Herein, we report an acetylenedicarboxylate based 1D CP $[Cd(adc)(4-nvp)_2(H_2O)]_n$ (1; H₂adc = acetylenedicarboxylic acid), which undergoes photochemical [2 + 2] cycloaddition accompanied by SCSC structural transformation from 1D chain to 2D layer structure. Interestingly, this structural change on photodimerization has an impact on the Schottky nature of compound 1.

The pale yellow needle-like crystals of 1 were grown in 60% yield by slow diffusion of 4-nvp and H₂adc in ethanol into a solution of aqueous $Cd(NO_3)_2 \cdot 6H_2O$ and Et_3N in $H_2O/$ MeOH (Scheme S1). Single crystal X-ray diffraction (SCXRD) reveals that compound 1 crystallizes in the triclinic space group $P\overline{1}$ with Z = 2. Each Cd(II) center has a distorted octahedral geometry, being coordinated to two 4-nvp ligands disposed in trans fashion along with an adc ligand in a monodentate fashion and an aqua ligand. Two such Cd(II) centers are bridged by two bridging adc ligands to form a dimeric unit which propagates along the a axis to generate a 1D double chain ladder polymer (Figure 1) resembling with the structure reported by Lang group.³⁰ The Cd…Cd distance in the ladder is 4.81 Å. The axial 4-nvp ligands are projected on both sides of dimeric units of the ladder, resulting in the formation of empty spaces between 4-nvp ligands of the chain. This facilitates the 1D ladders to be mutually interdigitated to form a 2D layer structure (Figure S2).

Interestingly, 4-nvp ligand of one ladder is exactly aligned parallel in a head-to-tail fashion to the 4-nvp ligand of the adjacent ladder (Figure 1). There are $\pi \cdots \pi$ stacking interactions between pyridine and naphthalene groups with a centroid-centroid distance of 3.60 Å. The bond distance between the center of the adjacent C=C bonds is 3.67 Å, which indicates the possibility of photochemical [2 + 2]cycloaddition. However, of a pair of 4-nvp ligands of a dimeric unit, only one ligand undergoes alignment with that of the adjacent ladder, indicating 50% of 4-nvp ligands have the possibility of photodimerization. Furthermore, the 2D layers undergo strong intermolecular hydrogen bonding interactions

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Figure 1. A perspective view of alignment of 4-nvp ligands between adjacent chains in 1. Distances are in Å. Only selected atoms are shown for clarity.

between the aqua ligand and noncoordinated oxygen atom of adc with an O···O separation of 2.76–2.90 Å to form a threedimensional (3D) supramolecular aggregate (Figure S3).

The alignment of C==C bonds between the pair of 4-nvp ligands follows Schmidt's criteria (<4.2 Å) for photochemical cycloaddition, which prompted us to conduct photoirradiation of 1 using UV light.^{31,32} The single crystals of 1 were subjected to UV irradiation ($\lambda = 350$ nm) using a mercury lamp for 30 min. The ¹H NMR spectrum of compound 1 in d_6 -DMSO shows the appearance of the δ 5.17 cyclobutane proton of 1,3-bis(4'-pyridyl)-2,4-bis(naphthyl)cyclobutane (*rctt*-4-pncb), which is evident for the photodimerization as reported earlier.⁹ Moreover, the transparency and shape of the crystals remains intact after 30 min of UV irradiation, only the color of the dimerized product becomes intense. These results propelled us to investigate SCSC transformation of compound 1.

The SCXRD of the irradiated product $[Cd(adc)(4-nvp)-(rctt-4-pncb)_{1/2}(H_2O)]_{n\nu}$ (1') reveals a quantitative photodimerization of aligned 4-nvp ligands accompanied by SCSC structural transformation from a 1D ladder to a 2D layer structure (Figure 2). As a result, the distance between two Cd(II) centers attached to aligned 4-nvp ligands of adjacent ladders decreases from 14.80 Å in 1 to 14.44 Å in 1'. The $\pi \cdots \pi$ interactions between pyridine and naphthalene groups also decrease from 3.60 Å in 1 to 3.41 Å in 1'.

In this work, the direct optical band gap (E_g) of 1 and 1' were evaluated as 3.33 and 3.21 eV respectively, using Tauc's plot³³ (Figure S5), described in the Supporting Information. The optical band gaps essentially match well with the ΔE (HOMO–LUMO gap) values obtained from DFT computations (Figure S6). The obtained band gaps falling within the semiconductor limit motivated us to check further the inherent electrical conductivity of the compounds in terms of dielectric study from impedance spectroscopy (IS).

Figure 3A signifies the complex plane impedance plots, i.e., the Nyquist plots for 1 and 1', which reveal the prominent arc of a semicircle. From the radius of the semicircle, the charge transfer resistance R_{ct} (DC resistance) of the compounds was calculated. Here, 1' possesses a small semicircle arc which primarily signifies small charge transfer resistance (R_{ct}) and better conducting nature compared to 1. To extend this study, we have plotted Bode phase diagram of the compounds



Figure 2. A perspective view of two adjacent chains in 1 after UV irradiation. Only selected atoms are shown for clarity.



Figure 3. (A) Nyquist impedance plots. (B) Bode plots. (C) Dependency of AC conductivity on frequency. (D) Capacitance vs frequency graph of 1 and 1', respectively.

(Figure 3B), which represents the characteristic peak position and frequency related to the inverse of the electron lifetime (τ_n) of the compounds.²⁷ From this study it is obvious that the characteristic frequency is related to the electron lifetime and the longer electron lifetime corresponds to smaller frequency. We have studied the frequency (f) dependency of AC conductivity (Figure 3C), which gives an idea on the interior of the semiconductor, a region of relatively low conductivity when the conduction process is electrode-limited.³⁴ With the increase in frequency, the conductivity decreases when it depends on free carriers.³³ The relative dielectric constant was measured on disc shaped pellet of as-synthesized 1 and 1' (diameter 6.12 mm and thickness 1.4 mm) from the frequency (f) vs capacitance (C) plot at constant bias potential (Figure 3D). At room temperature, the frequency dependent capacitance of 1 and 1' decreases with increase in frequency and becomes saturated at higher frequency. At the saturation level, the relative permittivity of the compounds was calculated. All the measured parameters are listed in Table S4.

The impedance analysis further impelled us to look into the inherent electrical properties of 1 and 1'. Hence, the electrical

characterization was accomplished by fabricating an ITO/(1 or 1')/Al sandwich structured metal (Al)–semiconductor (1 or 1') (MS) junction, and the representative I-V characteristics are displayed in Figure 4. The conductivities of 1 and 1' were measured as 1.83×10^{-3} Sm⁻¹ and 3.91×10^{-3} Sm⁻¹, respectively, signifying a recognizable enhancement of 1' as compared to 1.



Figure 4. I-V characteristics curve for ITO/compound 1/Al and ITO/compound 1'/Al.

Evidently, the representative I-V characteristics of the compounds exhibited a nonlinear rectifying nature, which is the signature of a Schottky barrier diode (SBD).^{35,36} Hence, the rectification ratios (I_{on}/I_{off}) were calculated as 25.25 and 33.12, respectively, for 1 and 1' at ± 2 V. The values of ideality factors are obtained as 2.89 and 1.92 for 1 and 1', respectively. All the measured parameters, e.g., potential height $(\sigma_{\rm B})$, ideality factor (η), and series resistance (R_s) for 1', show better performance compared to 1 (Table S5). It is important to mention that the value of the ideality factor of 1' approached closer to 1, indicating a more ideal device. This is an indication of less interfacial charge recombination and better homogeneity of Schottky junctions.³⁷ Additionally, the higher rectification ratio for 1' is attributed to the lower barrier height. The lowered value of series resistance of 1' is attributed to the large increase of charge carriers. Here, the decrease in distance between the adjacent chains together with shrinkage of $\pi \cdots \pi$ stacking interactions between pyridine and naphthalene groups results in an increase in conductivty after photodimerization.²³ All these observations portrayed the dimerized product 1' as a good contender in the field of electronic devices.

To get insight into the charge transport phenomena, the I-V curves have been studied in detail. The characteristic I-V curves revealed the presence of two different regions marked as region I and region II (Figure 5A). In region I (slope is ~1), current follows with relation $I \propto V$, which refers to the Ohmic regime. In region II (slope is ~2), current is proportional to V^2 (Figure 5A), corresponding to the characteristic trap free space charge limited current (SCLC) regime.^{33,37}

Using this model, the mobility has been estimated for 1 and 1' as 1.92×10^{-9} and 3.93×10^{-9} m² V⁻¹ s⁻¹, respectively, from the higher voltage region of the *I* vs V^2 plot by Mott–Gurney law (Figure 5B).^{33,37} The effective carrier mobility, transit time, carrier concentration, and diffusion length have been depicted in Table S6, which clearly indicates that the



Figure 5. (A) log I vs logV curve. (B) I vs V^2 curve for 1 and 1'.

charge transport properties have been improved for 1'. All the diode parameters also demonstrate the enhanced charge transfer kinetics for 1' as compared to 1.

In summary, we have synthesized a linear 1D coordination polymer which undergoes photochemical [2 + 2] cycloaddition accompanied by SCSC topochemical structural transformation from a 1D double chain to a 2D layer structure. This structural transformation leads to a decrease in distance between the adjacent chains as well as $\pi \cdots \pi$ stacking interactions resulting in an increase in conductivity. To the best of our knowledge, this appears to be a rare example, where [2 + 2] cycloaddition has an impact on electrical conductivity and the Schottky nature of the CP. Therefore, this kind of material can be used as a promising candidate for future device application.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b00833.

Details of the synthesis, elemental analysis, device fabrication, Figures S1–S7, Tables S1–S7, PXRD, TGA, and NMR (PDF)

Accession Codes

CCDC 1831710–1831711 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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