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Thousand-fold Conductivity Increase in 2D Perovskites by Polydiacetylene Incorporation and Doping

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Abstract: Two dimensional (2D) organic-inorganic perovskites have rapidly become an attractive alternative to traditional threedimensional (3D) perovskites solar cells absorbers due to their improved stability and processability. Despite their advantages, the insulating nature of the organic cations and diminished light absorption limit their overall performance. Herein, we demonstrate that the incorporation of conjugated diynes in hybrid 2D perovskites, and subsequent thermal treatment results in the formation of 2D perovskites that incorporate polydiacetylenes in their structure. Furthermore, we show that oxygen or iodine doping results in the formation of stable radicals within the material alongside a drastic shift of the bandgap from 3.0 to 1.4 eV and *in-plane* conductivity improvements of up to three-orders of magnitude, which lead to record conductivities for 2D halide perovskites (n = 1).

Two-dimensional (2D) organic-inorganic hybrid perovskites have recently attracted attention as viable alternatives to threedimensional (3D) perovskites solar cells absorbers such as MAPbl₃ (MA = methylammonium) and related materials. Compared to the 3D analogues, 2D perovskites have shown improved processability and stability towards water and light.^[1-6] This can be easily rationalized when considering the hydrophobic nature of the cations that replace the volatile and hydrophilic methylammonium.^[1-5] The insulating nature of the organic cations in 2D perovskites also disrupts the electronic structure of these materials which leads to diminished light absorption (larger bandgaps) and conductivities. This peculiar

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Supporting information for this article is given via a link at the end of the document. Detailed experimental procedures, crystallographic data, as well as the X-ray crystallographic file (CIF) of **1-as** is available in supporting information.

electronic structure which consists of alternating semiconducting and insulating layers has been described as a "quantum-well structure".^[7-9] In this work, we describe how the incorporation of conjugated diynes into 2D lead halide perovskites and subsequent thermal treatment results in the topochemical formation of 2D lead halide perovskites that incorporate polydiacetylenes into their structure. Furthermore, we show that by oxygen or iodine doping we can generate additional carriers that generate important changes in the properties of these materials, shifting the optical bandgap from 3.0 eV to 1.4 eV and improving the conductivity by up to three orders of magnitude, effectively inverting the traditional quantum-well structure (Figure 1a,b).



Figure 1. a) Schematic representation of heat-induced polydiacetylene formation and b) of the quantum-well structure before and after polymerization (CB = conduction band, VB = valance band and E_g = bandgap).

Seminal work by Tieke and collaborators^[10-13] showed that irradiating 2D perovskites with unsaturated organic cations resulted in the topochemical polymerization of such cations with retention of the 2D hybrid perovskite structure. Most studies by Tieke however, focused on the use of cadmium chloride layers and diene monomers, which have large bandgaps and form polymers without notable electronic properties. Later, Takeoka and coworkers incorporated polydiacetylenes in lead halide

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perovskites, yet, they used gamma radiation to induce polymerization, which makes this technique unpractical for most applications.^[14] Other attempts have been made to incorporate pre-synthesized conducting polymers into perovskites, however, they often result in poorly crystalline and ill-characterized materials.^[15,16] Moreover, no attention has been given to the electronic properties of these materials, nor have there been any reports on the effect that doping might exert in this kind of materials, despite being well-known in the field of conducting polymers that doping is essential to achieve high conductivities. We therefore sought out to study the effect of polydiacetylene incorporation and doping in the optical and electronic properties of 2D hybrid perovskites.

We started our studies by synthesizing the conjugated dialkynyl ammonium salt deca-3,5-diyn-1-amine: of (H₃N⁺CH₂CH₂C=CC=CC₄H₉) or DDA. The hydrochloric salt of DDA (or DDA•Cl) can be easily obtained from commercially available precursors in two synthetic steps and with good yields (See Supporting Information (SI) for details). DDA was incorporated into a 2D hybrid perovskite with formula: [DDA]₂PbBr₄ (1-as) which was characterized by IR, UV-Vis, single-crystal (SCXRD) and powder (PXRD) X-ray diffraction; all of which are consistent with the sought after 2D perovskite structure with an optical bandgap of 3.0 eV (Figure S11). The SCXRD structure clearly shows the presence of two neighboring triple bonds with C=C distances of 1.196 and 1.167 Å and intermolecular C(sp) to C(sp) distances that are as small as 3.79 and 3.85 Å, clearly in a distance range that could allow for topochemical polymerization (Figure 2a,b).[17,18]

Inspired by Tieke's work,^[10-13] we first tried to promote polymerization by irradiating samples of 1-as with UV light (250 and 354 nm). Such treatments did not result in any measurable change in PXRD pattern or UV-ViS absorbance. The lack of reactivity of 1-as towards UV light can be rationalized by considering the high absorption coefficients of lead bromide layers, particularly in the UV region, which prevents UV light from reaching the organic fragments and thus, preventing their polymerization. We then tried heating a crystalline sample of 1as at 160 °C (slightly below its decomposition temperature at 180 °C, Figure S12) for 24 hours under an inert atmosphere (N₂). Such treatment resulted in a highly crystalline yellow material, hereafter called 1-N2 (Figure 2d). 1-N2 shows an expanded unit cell when compared to 1-as. Particularly the c axis (which is directly related to the layer to layer distance) expands from 19.8 to 22.4 Å (Figure 2f). The color change and unit cell expansion come with the appearance of a C=C stretch at 1618 cm⁻¹ in the vibrational spectrum (Figure S13). All of these changes are consistent with polydiacetylene formation (Figure 1a).[14] Similarly, UV-Vis absorption data shows the appearance of a broad shoulder at about 520 nm, attributable to π - π * transitions in highly conjugated polydiacetylene fragments (Figure 2g).^[14] Importantly, regardless of the duration of the thermal treatment duration, we always observed remaining, non-polymerized DDA

cations in **1–N**₂, that can be identified by vibrational spectroscopy or by material's digestion followed by solution-state ¹³C nuclear magnetic resonance (NMR). The presence of unreacted diynes is consistent with a topochemical polymerization, which would be governed by a stochastic process that would inexorably leave some unpolymerized monomers.^[19] The ¹³C NMR of the organic fraction shows the appearance of new signals between 113 and 128 ppm attributable to C–C double bonds, as well as a new set of signals for aliphatic and vinylic carbons. Thus, solution NMR of the isolated organic, is also consistent with polydiacetylene formation (Figure S15).

To our surprise, when samples of **1-as** were heated under air instead of nitrogen, crystals turned black instead of yellow (Figure 2e). This material, hereafter called **1-O**₂, is still highly crystalline and has very similar PXRD pattern and IR spectrum as **1-N**₂, however, the UV-Vis-NIR absorption spectra of **1-O**₂ revealed that this material now absorbs well into the near-IR (NIR) region of the spectra with an optical bandgap of 1.4 eV, that is, 1.6 eV smaller than its parent compound, **1-as** (Figures S11 and S14). Notably, absorption in the NIR part of the spectrum is highly desirable for photovoltaic applications and it is indeed where most 2D, and some 3D, perovskites fail to absorb, which makes this an attractive alternative to increase light absorption.

Despite the striking differences in color, $1-N_2$ and $1-O_2$ have almost identical PXRD pattern and IR spectra. This suggests that structurally, similar materials were formed in both cases, and thus we hypothesize that the color differences can be attributed to the presence of oxygen, which caused partial oxidation of polydiacetylene moiety. Such oxidation could result in the generation of free carriers and a concomitant shrink of its optical bandgap. To probe this hypothesis, we performed the thermal treatment of 1-as under an iodine (I2) atmosphere. Due its volatility and lower redox potential than oxygen, molecular iodine is a commonly used oxidant for conducting polymers, as such, it could act as an alternative oxidant that could then confirm if oxygen is indeed responsible for the observed changes. Treatment of 1-as with iodine yielded 1-l₂, which has almost identical PXRD pattern and light absorption properties than 1-O₂ (Figures S16-S18). Alternatively, **1-N**₂, can also be exposed to iodine vapors at room temperature to yield 1-N₂/I₂; which also presents similar absorption and PXRD pattern to those of 1-O2 and I-I₂ (Figure S18). Importantly, neither 1-I₂ or 1-N₂/I₂, show evidence of iodine addition to triple or double bonds^[20] halide swap,^[21] nor does the observed effects can be explained by intercalation of I2.[22]

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b) c) a) 3.789 Å d) 3.854 Å e) **f)** g) Absorbance (a.u.) ntensity (a.u.) 1-0₂ 1-N₂ 1-0₂ 1-N₂ 1-as 1-as <u>2</u>0 **2**5 <u>3</u>0 <u>3</u>5 1000 1200 5 10 15 40 400 600 800 Diffraction angle (2θ) Wavelength (nm)

Figure 2. a) Room temperature single crystal X-ray structure of *as synthesized* [DDA]₂PbBr₄ (1-as). Pb–Br octahedra: green, Pb: green, Br: brown, N: blue, C: gray. Hydrogen atoms are omitted for clarity. b) Two neighbouring DDA cations within 1-as crystal structure. Thermal ellipsoids for non-hydrogen atoms is set at a 50% probability level. Dashed bonds highlight the two shortest intermolecular C(sp) to C(sp) distances. Photographs of crystalline samples 1-as (c), 1-N₂ (d) and 1-O₂ (e). f) Powder X-ray diffraction (PXRD) patterns and g) UV-ViS-NIR spectra of 1-as, 1-N₂ and 1-O₂.

The spectroscopic similarities between 1-I₂, 1-N₂/I₂ and 1-O₂, suggest that indeed, partial oxidation of 1–N₂ is responsible for the change in color. To further prove our hypothesis, we conducted solid-state X-band electron paramagnetic resonance (EPR) on samples of 1-as, 1-N₂, 1-O₂ and 1–I₂. EPR spectra of 1-as and 1-N₂, showed no signal whereas 1-O₂, and 1–I₂ showed a signal at a g-value of 2.0033 and 2.0025 respectively (Figure 3a and S19), both of which lie almost at the expected value for a free electron (2.0023) and clearly suggests the presence of an organic radical species within the material, likely delocalized across the π-conjugated polydiacetylene.

Using EPR spectroscopy, we were also able to quantify the number of electrons in $1-O_2$ and $1-I_2$, which showed a concentration of 1.62 and 2.35 x10⁻¹⁹ spins/mol respectively

(relative to the molar mass of the starting perovskite). While these doping levels can be considered small relative to other conducting polymers,^[23] the level of doping in our samples was obtained upon treatment with air (~21% O₂) or 10% molar I₂, which suggest that those values are likely to change depending on the O₂ or I₂ concentration and the specific technique used for doping. Thus, changing the doping agent and/or doping technique could provide a viable way to modify or adjust the carrier concentration and consequently, the electrical and optical properties of these materials. Importantly, the doping levels did not change over the course of time: storing samples of **1-O**₂ and **1-I**₂ under air for up to seven weeks did not change the spin density (Table S2–S3), showing that the materials and the radicals in them are quite stable.

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Finally, to assess the effect that polydiacetylene incorporation and subsequent doping has on the electrical conductivity of these materials; we performed *in-plane* single crystal conductivity studies on them. For these studies, we ensembled 18 devices (3 per sample) using single crystals of **1-as**, **1-N**₂, **1-O**₂, **1-I**₂, **1-N**₂/**I**₂ and a control material with no unsaturated fragments in the organic structure: $[OA]_2PbBr_4$ (OA = octylammonium). Our control, $[OA]_2PbBr_4$ showed typical inplane conductivity values for 2D lead bromide perovskites of approximately 2x10⁻⁵ S/m. The conductivity of **1-as** is one order of magnitude higher than that of the control material ($[OA]_2PbBr_4$) and is essentially identical to the one shown by **1-N**₂ (Figure 3d). The latter is interesting since it shows that the presence of polydiacetylenic fragments does not necessarily result in an increased conductivity.



Figure 3. (a) X-band electron paramagnetic resonance (EPR) of solid crystalline samples of 1-as, 1-N₂, 1-O₂ and 1-I₂ at 77 K. (b) Schematic of the experimental setup used for single crystal electrical conductivity measurements and representation of the layered hybrid perovskites orientation showing the direction of conductivity measurements; c) microphotograph showing a device made with a single crystal of 1-as, the scale bar represents 4 mm; and d) averaged values and standard uncertainties for *in-plane* conductivity of [OA]₂PbBr₄, 1-as, 1-N₂, 1-O₂, 1-I₂ and 1-N₂/I₂ at 423 K.

The presence of organic radicals in **1-O**₂, **1-I**₂ and **1-N**₂/**I**₂ has a significant effect on the conductivity, as it increased by about two orders of magnitude with respect to **1-as** and three orders of magnitude with respect to the control material ($[OA]_2PbBr_4$). To the best of our knowledge, the conductivities shown by **1-O**₂ and **1-I**₂ are the highest electrical conductivity reported for a 2D perovskite (n=1) and are comparable to those reported for MAPbl₃ (MA = methylammonium).^[24-29]

In conclusion, we have demonstrated that the incorporation of conjugated diynes in 2D hybrid perovskites allows for the thermally induced topochemical formation of polydiacetylenes in this class of materials. Unlike previous methods, the use of heat (instead of γ -rays) as the polymerization inducer makes this a realistic option for its implementation in optoelectronic devices. We have also shown that it is possible to dope the formed polydiacetylenes inside the perovskites which in turns leads to the formation of radicals and drastic improvement in light absorption and conductivity. The incorporation of polymeric species in 2D perovskites can also have positive effects in the stability and mechanical properties of the materials, effects that shall be studied in the near future. Similarly, attempts to use these materials in optoelectronic devices and further studies to better understand the electronics properties, and to modulate of optical and electronic properties of this materials by means of controlled doping are underway in our laboratories.

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Keywords: hybrid 2D perovskites • polydiacetylenes • singlecrystal conductivity • doping • conducting polymers

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COMMUNICATION

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Entry for the Table of Contents

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Page No. – Page No.

Thousand-fold Conductivity Increase in 2D Perovskites by Polydiacetylene Incorporation and Doping

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