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Inducing panchromatic absorption and photoconductivity in polycrystalline molecular 1D lead-iodide perovskites through π -stacked viologens

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ABSTRACT: As a consequence of their quantum- and electronically-confined inorganic lattices, molecular 1D lead-iodide perovskites are ill suited to photovoltaic (PV) applications. In order to circumvent these problems we utilized electron accepting viologen (*N,N'*-dialkyl-4,4'-bipyridinium) dications incorporating hydrogen bond donor functionalities, which served to induce π - π stacking interactions. The resulting 'viologen dimers' display enhanced charge-transfer (CT) interactions with the 1D lead-iodide nanowires. This manifests in extended light absorption (up to 800 nm), reduced band gaps (1.74 eV to 1.77 eV), and longer photoluminescence lifetimes. More importantly, we demonstrate significant photoconductivity behavior in polycrystalline molecular 1D lead-iodide perovskites for the first time. Thus, this work offers a strategy for inducing the properties required for PV applications in molecular 1D lead-iodide perovskites.

Molecular one-dimensional (1D) lead-iodide hybrid perovskites are an interesting class of solution-processed materials.¹⁻² Relative to the corresponding 3D materials, they have the advantages of being thermally, mechanically, and chemically stable, especially against moisture,³ whilst also being able to incorporate a much wider range of organic cations.⁴⁻⁷ However, due to narrower light absorption ranges, high excitonic binding energies and band gaps, as well as greatly compromised electrical conductivity,⁸⁻¹⁰ molecular 1D perovskites based on inert organic

cations are not suitable for photovoltaic (PV) applications. In particular, although good photoconductivity has been demonstrated in single crystals of molecular 1D perovskites,¹¹⁻¹³ it has never been observed in more defective settings, such as polycrystalline forms.

Figure 1. Molecular structures and notation of dicationic viologens used in this article. Systematic naming of the corresponding organics can be found in supporting information.

In an attempt to alleviate some of the aforementioned deficiencies, molecular 1D perovskites incorporating chromophoric protonated naphthalene diimide,¹⁴ and electronically active tetrathiafulvalene (TTF) radical,¹⁵ cyclic tropylium cation,¹⁶ and doubly charged viologens (*N,N'*-dialkyl-4,4'-bipyridinium)¹⁷ have been generated. However, these materials were found to exhibit either good light harvesting capabilities *or* to be semiconducting. Both properties are required for PV applications. In principle, it should be possible to meet these requirements by selection of appropriate organic cations and crystal engineering techniques.

The synthetic simplicity and versatility of viologens (V_{2+}), combined with the lead-iodide-to- V_{2+} charge transfer (CT) interactions they display, made them a particularly appealing platform for our purposes. More specifically, we sought to enhance the aforementioned CTs by inducing ordering (π - π stacking) of V_{2+} via introduction of N -alkyl substituents containing hydrogen bonding functionality. To this end, the hydroxyethyl and carboxyethyl viologens HyEtV $_{2+}$ and CaEtV $_{2+}$ (Figure 1) were synthesized, and the respective iodoplumbates, (HyEtV)Pb $_2$ I $_6$ (**1**) and (CaEtV)Pb $_2$ I $_6$ (**2**), prepared. To clarify the influence of the hydrogen bonding functionality and viologen moiety upon any properties observed for **1** and **2**, 1D perovskites templated by propyl viologen and bis(methylammonium)biphenyl, (PrV)Pb $_2$ I $_6$ (**3**) and (BpbmA)Pb $_2$ I $_6$ (**4**), were also studied.

Figure 2. (a) UV-Vis spectra of polycrystalline powders of (HyEtV)Pb $_2$ I $_6$ (**1**; red solid line), (CaEtV)Pb $_2$ I $_6$ (**2**; blue solid line), (PrV)Pb $_2$ I $_6$ (**3**; orange solid line), and (BpbmA)Pb $_2$ I $_6$ (**4**; green solid line). The dashed lines obtained by extrapolation of the linear part of each spectrum correspond to the band gaps of each material. (b) Schematic energy diagram of the molecular 1D perovskites **1-4**. Valence band energies were obtained from photoelectron spectroscopy in air (PESA) measurements (see SI) and optical band gaps from the UV-vis spectra.

Figure 2a shows the UV-Vis diffuse reflectance spectra (DRS) of **1-4**, and Table S1 summarizes absorption profiles of each hybrid perovskite. All compounds display sharp, high energy bands at 372 –

377 nm that are characteristic of the inorganic intrachain electronic transitions of 1D lead-iodide lattices.¹⁹⁻²⁰ In addition, the spectra of the V_{2+} -containing compounds **1-3** possess relatively broad absorptions centered in the visible region. Notably, this feature is significantly red-shifted in hydrogen bond donor-containing **1** and **2** relative to **3**, which renders the former two materials black and the latter red. The panchromatic absorptions displayed by **1** and **2** are reminiscent of the light absorption capability of methyl ammonium-based 3D perovskite²¹ (MAPbI $_3$; see Figure S1 for comparison), and greatly surpasses that of molecular 1D perovskites derived from conventional ammonium cations, as exemplified by **4**.

In analogy with studies conducted by Fujisawa, *et al.* on 1,1'-dimethyl-4,4'-bipyridinium (methyl viologen; MeV $_{2+}$)-based 1D lead-iodide perovskite, which concluded that type-II band alignment is adopted, the low energy transitions in the UV-Vis spectra of **1-3** can be assigned as CT bands between the valence band localized on the lead-iodide chains (donor) and the V_{2+} -centered conduction bands (acceptor).^{19, 22} Extrapolation of the linear parts of the CT transitions of **1-3**, yield band gaps of 1.74, 1.77 and 2.21 eV, respectively.^{19, 23}

Estimation of the valence band energies for compounds **1-4** using photoelectron spectroscopy in air (PESA) yielded similar values of -5.79, -5.68, -5.70, and -5.73 eV, respectively (Figure S2). Coupling this data with that obtained from the UV-Vis measurements, allowed construction of band energy diagrams, shown in Figure 2b (and Figure S3). Given the similarity of the valence band energies in all materials, the reduced band gaps in **1** and **2** relative to **3** and **4** are clearly a consequence of the lower energy of the lowest unoccupied molecular orbitals (LUMOs) of their constituent V_{2+} organic cations. Furthermore, the hydrogen bond donor groups in HyEtV $_{2+}$ and CaEtV $_{2+}$ are electronically isolated from the viologen moiety, so the low energies of the LUMOs in **3** and **4** can be safely ascribed to supramolecular effects.

X-ray crystal structures of **1**, **2** and **3** (Figure 3, Table S2) all show perpetual 1D lead-iodide chains surrounded by parallel-oriented organic cations (see SI for more detailed discussions). However, the relative packing arrangement of the viologens is observed to vary, depending on the N -alkyl substituents incorporated. More specifically, the viologens possessing hydrogen bonding functionality, in **1** and **2**, are found to exist as π - π stacked dimers with interplane distances ranging from 3.642 to 3.662 Å and from 3.593 to 3.687 Å, respectively (Figures 3a and 3b). The alcohol and carboxylic acid

functionality in their respective dications, HyEtV₂⁺ and CaEtV₂⁺, hydrogen bond to DMSO (dimethyl sulfoxide) solvent molecules incorporated into the lattice. In compound **3**, where such interactions are unavailable, the PrV₂⁺ dications adopt multiple orientations (Figure 3c).

In contrast, amongst the iodide salts of the viologen dications, π - π stacking of V₂⁺ is seen only in the X-ray structure of [PrV]I₂ (Figure S5, Table S3). Intriguingly, the iodide-to-V₂⁺ CT band observed in the UV-Vis spectrum of this compound, λ_{max} = 467 nm, is red-

shifted relative to those of [HyEtV]I₂ and [CaEtV]I₂ (Figure S4), for which λ_{max} = 405 nm. Thus, it appears that the observed shifts in anion-to-V₂⁺ CTs to lower energy are associated with formation of π - π stacked dimers. This can be attributed to resultant delocalization and attendant stabilization of the V₂⁺-based LUMOs.

Our assertion is reinforced by the UV-Vis absorption profiles of (HyEtV)Pb₂I₆ (**1a**) and (CaEtV)Pb₂I₆ (**2a**)

Figure 3. Crystal structures of (a) (HyEtV)Pb₂I₆ (**1**), (b) (CaEtV)Pb₂I₆ (**2**), and (c) (PrV)Pb₂I₆ (**3**). Left insets indicate the relative orientation of organic viologens in the crystal lattice. Right insets show the visual appearances of the polycrystalline 1D perovskites. Gray, purple, brown, red, blue, and yellow spheres represent Pb, I, C, O, N, and S atoms, respectively. H atoms are omitted for clarity.

recrystallized from DMF (dimethylformamide) solution. The X-ray structures of these compounds (Figure S6) exhibit face-sharing 1D inorganic backbone structures. In contrast to **1** and **2**, the incorporated solvent molecules do not hydrogen bond to the HyEtV₂⁺ and CaEtV₂⁺ cations and, as a consequence, π - π stacked V₂⁺ dimers are not formed. Commensurately, these materials exhibit attenuated absorption, with onsets at 550 and 650 nm, respectively (Figure S7).

Photoluminescence (PL) spectra of the viologen-based 1D perovskites (Figure S8a) show features that are fully consistent with the UV-vis absorption profiles. In particular, the emission spectra of **1** and **2** display broad bands centered at 647 and 649 nm, respectively, values that are significantly lower in energy than that of the corresponding feature in **3** at 544 nm. These features can be attributed to CT relaxation. The emissions related to the inorganic chain band transition appear for all compounds (**1-4**) at characteristically high energy.²⁰

To obtain further insight into the luminescent properties of polycrystalline samples of perovskites **1-3**, we performed time-resolved photoluminescence (TRPL) experiments. TRPL spectra recorded at the highest intensity emissions show that **3** exhibits much faster average charge carrier recombination than both **1** and **2** (Figure S8b). More specifically,

best fits (summarized in Table S4) reveal that while **3** exhibits a biexponential decay composed of 336 ps (89%) and 2.88 ns (11%) components, **1** and **2** display longer lifetime decay in both radiative (τ_1) and nonradiative (τ_2) processes. More specifically, 354 ps (79%) and 2.91 ns (21%) components in the former case, and 723 ps (70%) and 3.56 ns (30%) components in the latter. The longer average lifetime of charge carriers in **1** and **2** suggests a higher probability of generating free charge carriers compared to **3**.

Inspired by the aforementioned data, the photoconductivity of polycrystalline samples of **1-4**, plus **1a** and **2a**, were investigated via four-probe measurements (Figure 4a). Unsurprisingly, the polycrystalline 1D perovskites based on the ammonium cation **4** and V₂⁺ that do not form π - π stacked dimers (i.e., **3**, **1a** and **2a**) do not show enhanced photocurrent (Figure 4b, Figures S9 and S11). However, **1** and **2** exhibit a significant increase in charge transport under white light illumination (Figure 4b, Figure S10). At a bias as low as 3.0 V, the photocurrent increased from 24.4 pA (dark) to 159 pA (light) in the case of **1** and from 71.5 pA (dark) to 1470 pA in the case of **2**. This corresponds to on/off ratios of 6.4 and 20.6, respectively. Interestingly, the on/off ratio measured for **2** is comparable to that observed for 2D lead-iodide perovskites templated by

related isomeric organic dication, 4,4'-bis(ammonium-ethyl)-1,1'-biphenyl (~33.1, Figures

S12 and S13). This is the first example of

Figure 4. (a) Schematic diagram of the four-probe electrical conductivity measurements performed upon the polycrystalline samples. (b) I-V characteristics of (HyEtV)Pb₂I₆ (**1**; red line), (CaEtV)Pb₂I₆ (**2**; blue line), (PrV)Pb₂I₆ (**3**; orange line), and (BpbmA)Pb₂I₆ (**4**; green line) under white light irradiation (1 sun illumination). (c) Time-dependent photoresponses of the 1D perovskites at 2.0 V bias, upon repetitive on and off white light (1 sun AM1.5G) illumination (interval 10 s), measured for 300 s.

photoconductivity in a polycrystalline 1D lead-halide perovskite, and it demonstrates that such behavior can be induced by enhancement of CT between the inorganic anions and organic cations.

In order to probe the short-term stability of the materials to voltage and light, time-dependent photoconductivity studies were conducted. As shown in Figure 4c, over the course of 300 s, compound **2** consistently exhibits a much stronger photocurrent response than **1** upon repetitive on and off white light illumination (1 sun AM1.5G, interval 10 s). The increase in current obtained during the course of measurements is attributed to ion migration, which can be especially significant in defect-rich settings, such as polycrystalline samples. The greater photoconductivity response observed in **2**, relative to **1**, can be attributed not only to the former possessing a smaller inorganic band gap (2.83 vs. 3.08 eV) and significantly slower photodecay (1.576 ns vs. 0.891 ns), but also to it possessing better inherent conductivity. The latter is borne out by dark conductivity measurements for **2** yielding values approx. 3.3 times greater than for **1** (Table S4).

In conclusion, we have demonstrated for the first time that molecular 1D perovskites can be endowed with photoconductivity in randomly oriented (i.e., polycrystalline) samples. The requisite improvement in optical and electronic properties was attained via amplification of CT interactions between the lead-iodide lattice and organic counteranions. This was achieved using a molecular engineering approach that involved incorporation of hydrogen bonding functionality into *N*-alkyl substituents of viologens. As such, this work demonstrates a strategy that can be used to improve the optoelectronic characteristics of lower dimensional perovskites, thereby offering a route by which they might become of practical use in photovoltaic applications.

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Notes

The authors declare no competing financial interest. CIF data for associated crystal structures have been deposited in the Cambridge Crystallographic Data Centre under deposition numbers CCDC 1828821–1828830.

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