

Supporting Information

Tuning Spin-Polarized Lifetime in Two-Dimensional Metal Halide Perovskite Through Exciton Binding Energy

Xihan Chen^{†*1,2}, Haipeng Lu^{†1,3}, Kang Wang^{†1,4}, Yaxin Zhai^{1,5}, Vladimir Lunin¹, Peter C. Sercel⁶ and Matthew C. Beard^{*1}

¹ *National Renewable Energy Laboratory, Golden, Colorado, 80401, United States*

² *Department of Mechanical and Energy Engineering, Southern University of Science and Technology, Shenzhen, Guangdong, 518055, China.*

³ *Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China (SAR).*

⁴ *State Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China*

⁵ *Key Laboratory of Low-Dimensional Quantum Structures and Quantum Control of Ministry of Education, Department of Physics, Hunan Normal University, Changsha 410081, China*

⁶ *Center for Hybrid Organic Inorganic Semiconductors for Energy, Golden, Colorado, 80401, United States*

†These authors contributed equally to this work

***Corresponding Authors**

Matt C. Beard (email: Matt.Beard@nrel.gov)

Xihan Chen (email: chenxh@sustech.edu.cn)

Exciton binding energy extraction using 2D Elliot's formula The linear absorption spectra can be modelled with generalized Elliot's formula taken in the form of:³

$$\alpha(h\nu) = \frac{A}{\zeta} \frac{\Gamma(E_{ex})}{\frac{\Gamma(E_{ex})^2}{4} + \left[\frac{h\nu - E_{ex}}{\zeta} \right]^2} + B \frac{1}{1 + \theta(h\nu - E_g) \exp \left\{ -2\pi \left[\frac{h\nu - E_g}{Ry} \right]^{-1/2} \right\}} \left\{ \frac{1}{2} + \frac{1}{\pi} \arctan \left[\frac{2(h\nu - E_g)}{\Gamma(E_g)} \right] \right\}$$

where, $E_{ex} = E_g - Ry$, ζ is a broadening parameter, A and B are the relative amplitudes of the exciton and free carrier absorptions and

$$\Gamma(E_x) = \frac{2(\Gamma_0)}{\exp[-3(h\nu - E_x)/k_B T] + 1}$$

This generalized equation is used to fit linear absorption spectra to extract exciton binding energy of synthesized 2D perovskite n = 1 single crystals.

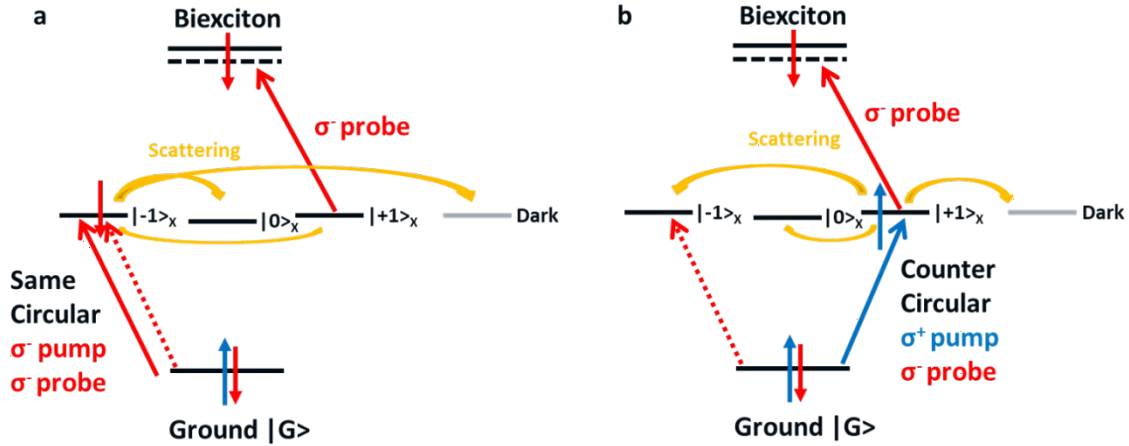


Figure S1: Exciton pictures in low dimensional perovskite materials. (a) Same Circular pump and probe. **(b)** Counter circular pump and probe. The ground state $|G\rangle$ is a singlet with 0 spin momentum. The first exciton will have four states with 1 dark state and triplet states with angular momentum projections $J_z = +1, 0, -1$. The circular polarized pump or probe could directly excite the $|-1>_x$ or $|+1>_x$ states since the circular polarized light will carry -1 (a) or +1 (b) angular momentum.

In **(a)**, the circular σ^- pump could populate the $|-1>_x$ exciton state from the ground state $|G\rangle$. The σ^- probe could also induce the same transition from ground state $|G\rangle$ to the $|-1>_x$ state as well as promoting the $|+1>_x$ state to the biexciton state. Initially after pump, the $|-1>_x$ exciton state will be populated at a level, p , while $|+1>_x$ state is unpopulated, and the ground state will be depleted by p . Thus, there will be bleach for the exciton transition with magnitude proportional to $2p$, where p is the ground state depletion. (The bleach comes from the sum of the bleach due to the depleted ground state, p , and stimulated emission, p , on the $|-1>_x$ to G transition). Then, the $|-1>_x$ exciton population can scatter into other exciton states and eventually reach an equal population of all four states ($0.25p$ each, assuming the scattering is much faster than exciton recombination). Then the σ^- probe will induce three transitions: One is the transition from ground $|G\rangle$ to $|-1>_x$ with bleach magnitude p due to the ground state depletion; the second has magnitude $0.25p$ due to stimulated emission on the transition from the now-populated $|-1>_x$ state to the ground state; and the third is the photo-induced absorption (opposite from bleach) from $|+1>_x$ state to the biexciton state with magnitude $-0.25p$. Therefore, the total bleach amplitude be will $p + 0.25p - 0.25p = p$. So, for case **(a)**, the bleach magnitude will decay from magnitude $2p$ to p after all spins reach equilibrium.

For case **(b)**, the circular σ^+ pump populates the $|+1>_x$ exciton state to an initial level, p , from ground state $|G\rangle$, which is depleted by p . The σ^- probe can induce the transition from ground state $|G\rangle$ to the $|-1>_x$ state and also from the $|+1>_x$ state to the biexciton state. Initially, the population of the $|-1>_x$ exciton state will be zero (gives bleach magnitude of 0), the $|+1>_x$ state will be fully populated (gives photo induced absorption magnitude of p), and the ground state will be depleted (gives bleach

magnitude of p), thus, there will a net bleach of 0 for the exciton transition (p bleach and $-p$ photo-induced absorption cancel each other). The final state will be the same with case **(a)** which has bleach magnitude of p . Therefore, for case **(b)**, the bleach magnitude will increase from 0 to p after all spins reach equilibrium. (Figure 2e)

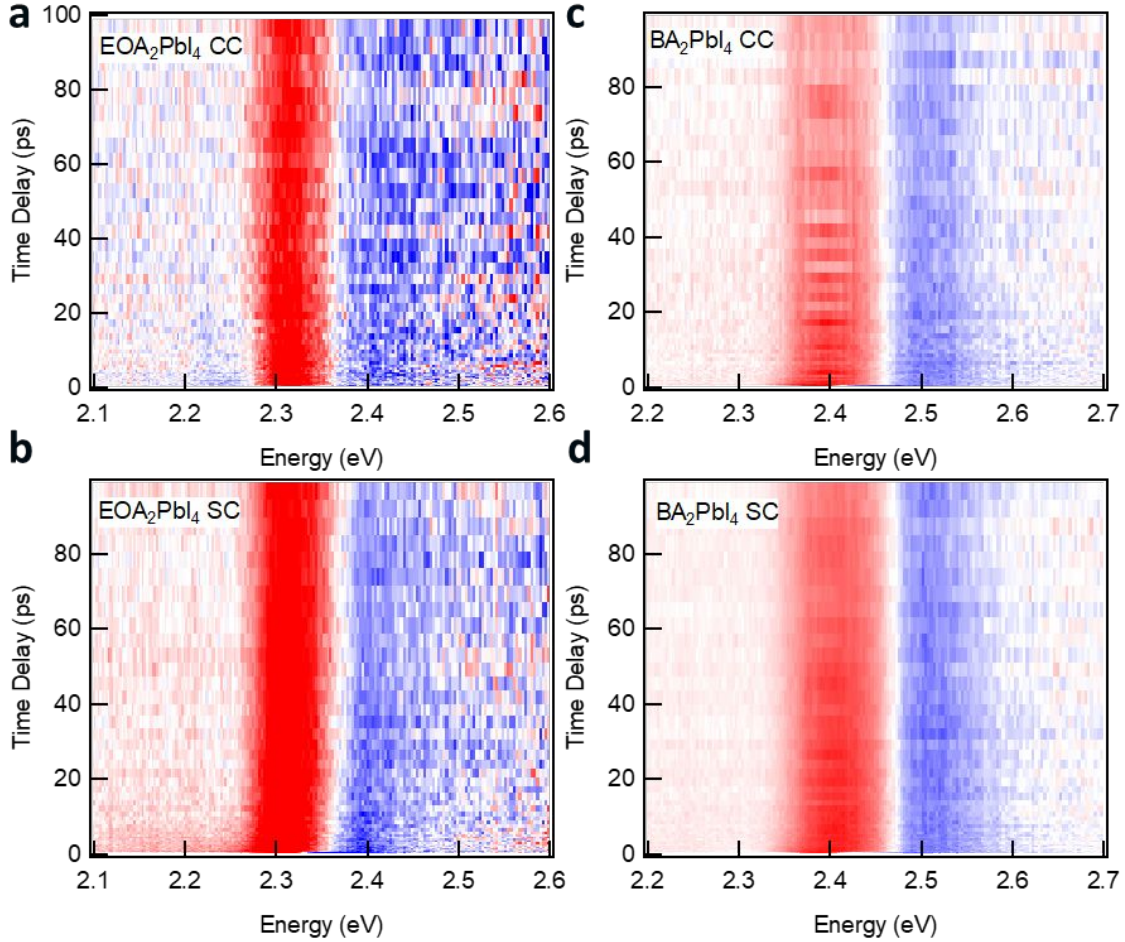


Figure S2: Pseudo color image of transient reflection of same and counter circular polarization for **(a,b)** EOA₂PbI₄ and **(c,d)** BA₂PbI₄. For EOA₂PbI₄, the two helicities show a difference in the color mapping at 2.23 eV near the biexciton (the blue color in CC). For BA₂PbI₄, the two helicities show nearly identical color image.

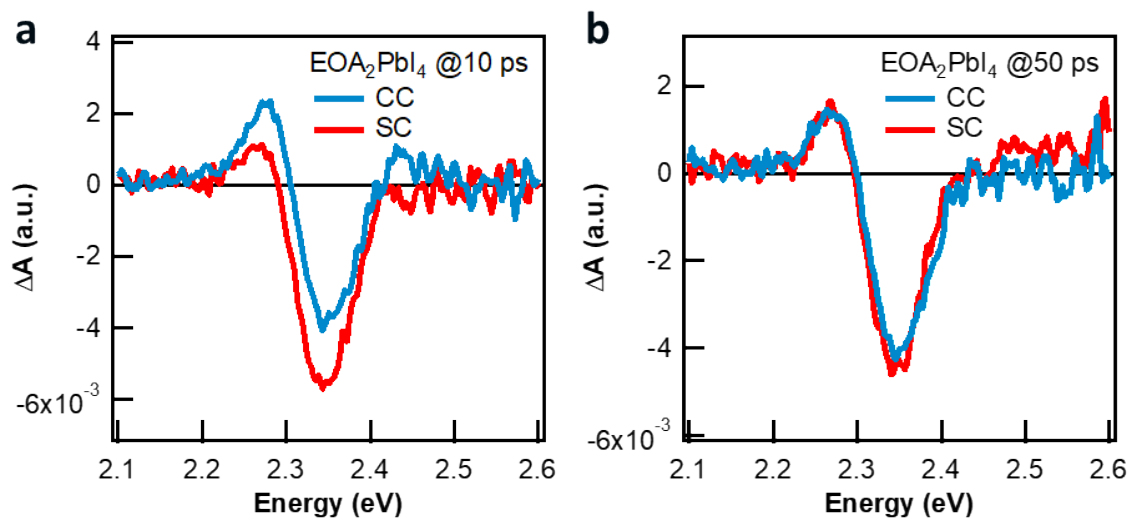


Figure S3: Kramer-Kronig transformed transient reflection spectra of same and counter circular polarization for EOA₂PbI₄ at 10 and 50 ps delay. The two helicities yield the same spectra at 50 ps time delay.

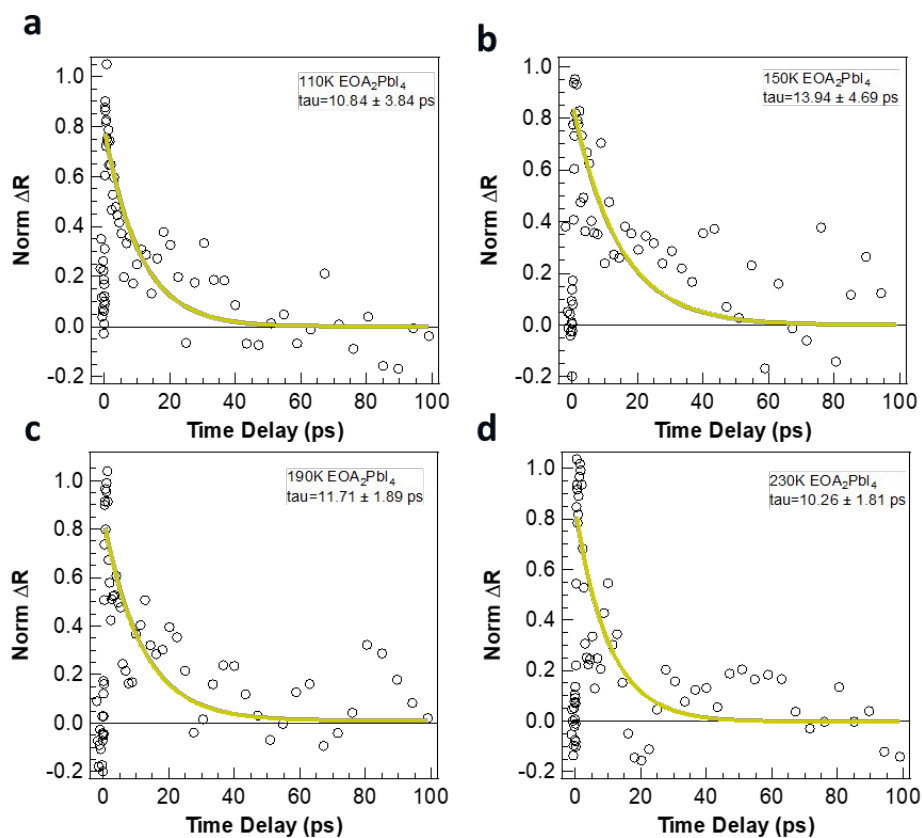


Figure S4. Transient difference kinetics for same and counter circular polarized pump and probe of EOA₂PbI₄ at **(a)** 110K, **(b)** 150K, **(c)** 190K and **(d)** 230K. The kinetics is fitted with a single exponential decay function to extract spin-dephasing time ($\tau_{1/2}$) to use in the plot shown in Figure 3b of the maintext.

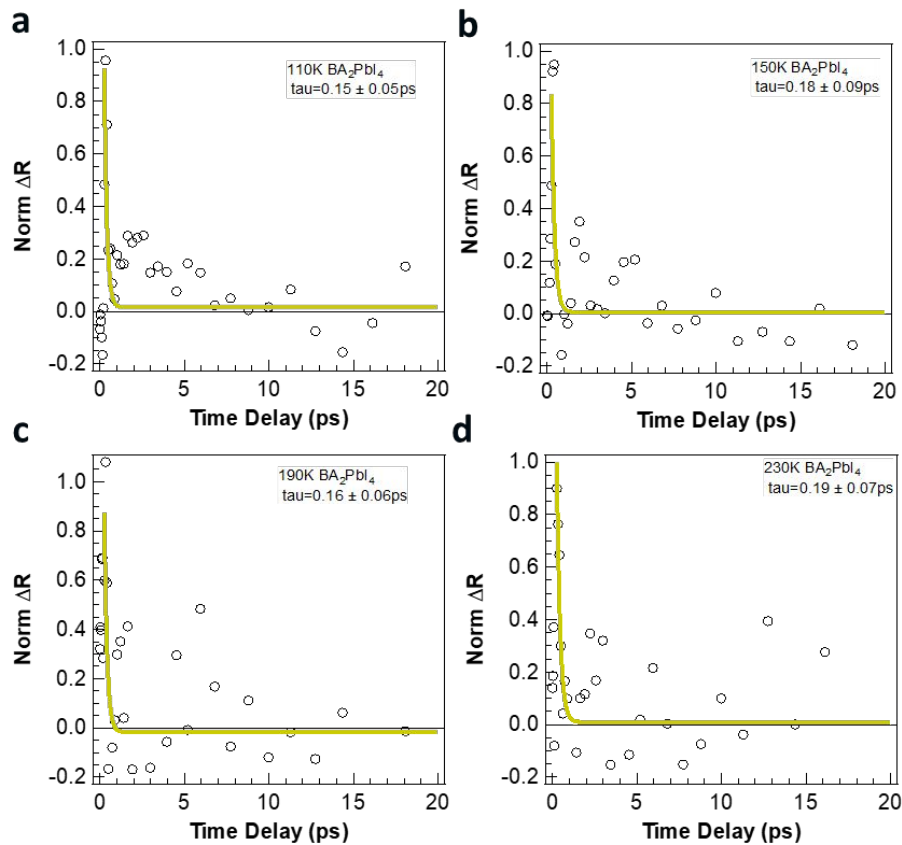


Figure S5. Transient difference kinetics for same and counter circular polarized pump and probe of BA_2PbI_4 at (a) 110K, (b) 150K, (c) 190K and (d) 230K. The kinetics is fitted with a single exponential decay function to extract spin-dephasing time ($\tau_{1/2}$) to use in the plot shown in Figure 3b of the maintext.

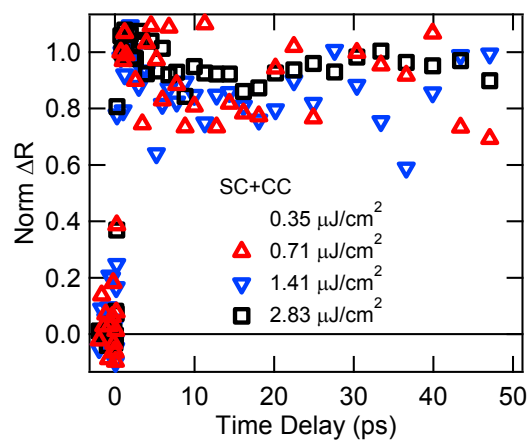


Figure S6. Transient sum kinetics for same and counter circular polarized pump and probe of EOA₂PbI₄ at different excitation fluence. The kinetics shows no differences in decay kinetics for the first 50 ps with various fluence.

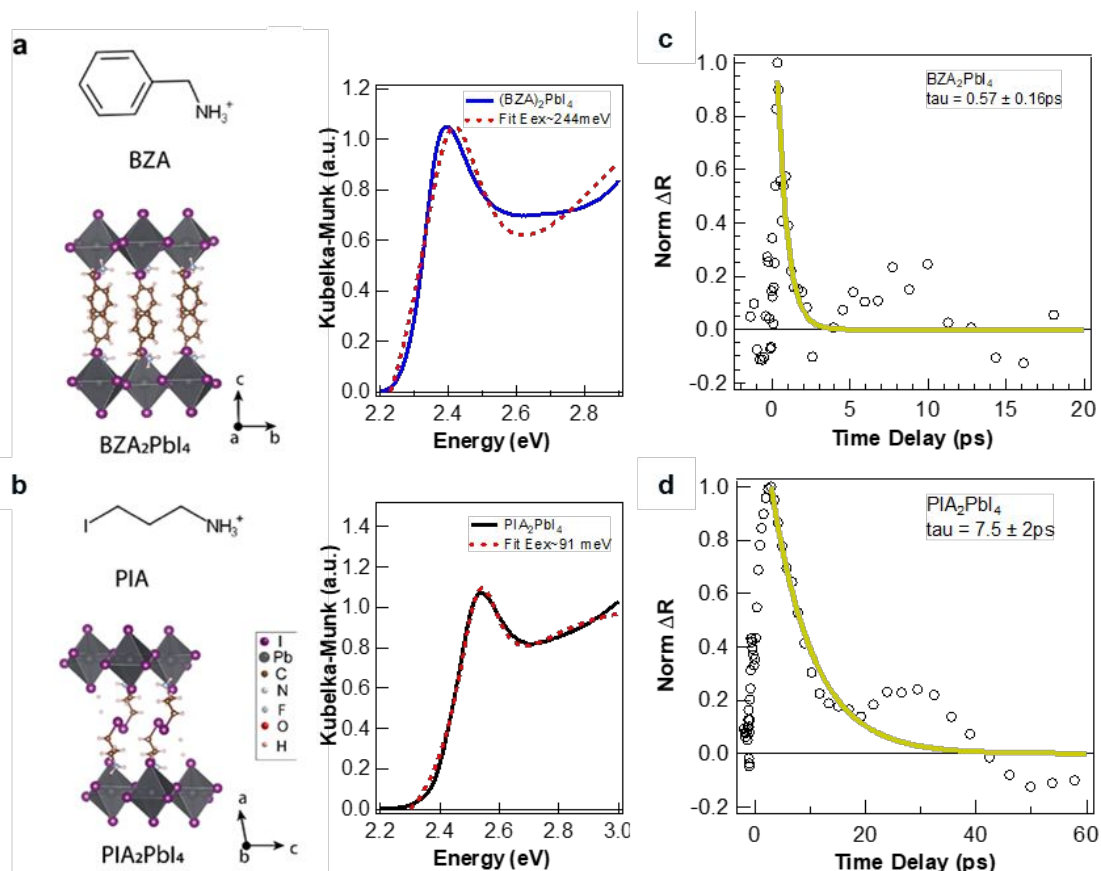


Figure S7. Chemical, crystal structures and absorption spectra of organic ammonium cations and corresponding hybrid 2D Pb-I perovskite (a), BZA_2PbI_4 and (b), $(\text{PIA})_2\text{PbI}_4$. The binding energy can be obtained through fitting. Normalized transient difference kinetics for same and counter circular polarized pump and probe of (c) BZA_2PbI_4 and (d) PIA_2PbI_4 . The kinetics is fitted with a single exponential decay function to extract spin-dephasing time ($\tau_{1/2}$).

References:

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