

Interlayer-Sensitized Linear and Nonlinear Photoluminescence of Quasi-2D Hybrid Perovskites Using Aggregation-Induced Enhanced Emission Active Organic Cation Layers

Chang-Keun Lim, Melissa Maldonado, Robert Zalesny, Rashid Valiev, Hans Ågren, Anderson S. L. Gomes, Jie Jiang, Ruth Pachter, and Paras N. Prasad*

A concept of interlayer-sensitized photoluminescence (PL) of quasi-2D hybrid perovskite (PVK) with a π -conjugated optically interacting organic cation layer is introduced and demonstrated. A rod-shaped aggregation-induced enhanced emission (AIEE) organic cation (BPCSA+), well fitted into the lattice size of 2D PVK layers, is designed and synthesized to prolong the exciton lifetime in a condensed layer assembly in the PVK. The BPCSA+ promotes the PL of this hybrid PVK up to 10-folds from that of a non- π -conjugated organic cation (OA) 2D PVK. Notably, different from PL of OA 2D PVK, the increased PL intensity of BPCSA 2D PVKs with an increase of the BPCSA ratio in the PVK indicates a critical photon-harvesting contribution of BPCSA. The films of BPCSA 2D PVKs are incredibly stable in ambient environments for more than 4 months and even upon direct contact with water. Additionally, due to the strong two-photon absorption property of BPCSA, the BPCSA 2D PVK displays superior emission properties upon two-photon excitation with a short wavelength IR laser. Thus, the AIEE sensitization system for quasi-2D PVK hybrid system can make a drastic improvement in performance as well as in the stability of the PVK emitter and PVK based nonlinear optical devices.

1. Introduction

2D perovskites (PVKs) have been considered as appropriate materials to upgrade water resistance and interfacial charge transfer efficiency of PVK solar cells.^[1] However, since they have

Dr. C.-K. Lim,^[+] Prof. P. N. Prasad Institute for Lasers, Photonics, and Biophotonics Department of Chemistry University at Buffalo State University of New York Buffalo, NY 14260, USA E-mail: pnprasad@buffalo.edu Dr. M. Maldonado, Prof. A. S. L. Gomes Physics Department Universidade Federal of Pernambuco Recife, PE 50670-901, Brazil

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.201909375.

^[+]Present address: Department of Chemical and Materials Engineering, Nazarbayev University, 53 Kabanbay Batyr Avenue, Nur-Sultan City, 010000, Kazakhstan

DOI: 10.1002/adfm.201909375

Adv. Funct. Mater. 2020, 1909375

1909375 (1 of 8)

superior charge carrier lifetime, photoluminescence (PL) quantum efficiency, and defect tolerance,^[2] their potential is not only in the photovoltaics applications but also as light emitter,^[3] lasing media,^[4] and photo detection^[5] devices. The absorption and the emission wavelengths (i.e., energy gap [Eg] between valence and conduction band) of 3D PVKs are usually tunable by substitutions of halide anions, metal cations, and organic or inorganic cations.^[6] Also, for the quasi-2D PVKs composed of alternative structures of 2D PVK layers and 2D interlayers of one-dimensionally bulky organic cations, an increase of the number of 2D PVK layers enlarges the Eg sequentially.^[6b,7] Hence, by the compositional and structural versatility of PVKs, we can achieve full-color PL in the visible and near-IR range. Typically, long aliphatic and small aromatic organic cations such as butylammonium,^[1c,d,3c,4b,5a,c,7] octylammonium,^[8] dodecylammonium,^[9] and phe

nylethylammonium^[3a,b,d] have been incorporated into quasi-2D PVKs as an insulator to confine photogenerated excitons in the 2D PVK quantum well. But, occasionally, some organic cations of extended π -conjugated molecules (e.g., naphthalene,^[10] oligothiophene,^[11] carbazole,^[12] pyrene,^[13] and polydiacetylene^[14])

Wroclaw University of Science and Technology Wyb. Wyspiańskiego 27, PL-50370 Wrocław, Poland Dr. R. Valiev Department of General and Inorganic Chemistry National Research Tomsk Polytechnic University 30 Lenin Avenue, Tomsk 634050, Russia Prof. H. Ågren Department of Theoretical Chemistry and Biology Royal Institute of Technology S-10691 Stockholm, Sweden Dr. J. Jiang, Dr. R. Pachter Air Force Research Laboratory Wright-Patterson Air Force Base

Wright-Patterson Air Force Ba Dayton, OH 45433, USA

Prof. R. Zalesny Department of Physical and Quantum Chemistry Wroclaw University of Science and Technology



have also been explored to improve the optical and conducting features of PVKs. Considering the superior absorption coefficient per mass for π -conjugated molecules, they have a strong potential as sensitizers to reinforce optical and optoelectronic properties of PVKs. However, concentration quenching of their PL could be a significant hurdle to realize an efficient sensitization process in 2D PVKs.

Here, we propose and demonstrate an efficient interlayer sensitization system in quasi-2D hybrid PVK consisting of aggregation-induced enhanced emission (AIEE) luminophores (LPs) and multi-layered 2D PVK alternatively. AIEE LPs are a novel class of LPs showing enhanced PL properties with an increase in the concentration of LPs.^[15] Due to the immunity of AIEE LPs to concentration quenching observed in conventional LPs, the lifetime of Frenkel excitons on the AIEE organic cation layer can be prolonged, which can promote energy transfer to subsequently generate Wannier excitons in PVK layers. In the present work, an organic cation of AIEE LP was successfully designed, synthesized, and integrated into quasi-2D PVKs to demonstrate efficient photosensitization. The AIEE 2D PVKs were synthesized as nanoparticles as well as thin films with a variation of the number of 2D PVK layers to tune the Eg of PVKs. They showed superior PL intensities under single- and two-photon excitations compared to those of nonsensitizing 2D PVKs with insulating octylammonium cations with the same trends of bandgap adjustments by stoichiometric control. Furthermore, the films of AIEE 2D PVKs are incredibly stable in ambient environment for more than several months and even against direct contact with a drop of water on the sample surface.

2. Results and Discussion

The precursor of the AIEE LP cation, (Z)-2-([1,1'-bipheny])-4-yl)-3-(4-(3-aminopropoxy)phenyl)acrylonitrile (BPCSA, see Figure 1a,b), was designed and synthesized. Among wellknown AIEE LP frameworks such as tetraphenylethene,^[16] cyanostilbene,^[17] bis(styryl)anthracene,^[18] and hydroxyphenylbenzoxazole,^[19] we selected a rod-shaped cyanostilbene derivative that has only 1D bulkiness and has a diameter well fitted to the 2D PVK lattice size, to facilitate the formation of a hybrid 2D PVK assembly. The propyl group at the top of the BPCSA structure provides a degree of freedom for energy minimization during cocrystallization between the 2D PVK compositions and the LPs, and allows the terminal amine group, the precursor of the ammonium cation, to interact with the 2D PVK layers. BPCSA was synthesized through Williamson etherification, Knoevenagel condensation, and acid-catalyzed deprotection of the protected amine group, consecutively (Figure 1a). As shown in Figure 1b, the synthesized BPCSA displayed a strong sky-blue emission in the solid state upon 365 nm UV illumination, while the solution of BPCSA in dimethyl sulfoxide (DMSO) was almost nonfluorescent, thus displaying the AIEE characteristic. The PL spectrum of the BPCSA powder $(\lambda_{max} = 470 \text{ nm})$ was slightly red-shifted from that of its water dispersion (λ_{max} = 450 nm), which can be related to a degree of I aggregation that induces band gap narrowing by a head-totail dipole alignment. The absorption spectrum of the BPCSA solution and the PL excitation spectra of its dispersion and its powder form showed a further red-shift of their maximum



Figure 1. a) Synthetic route of AIEE LP, BPCSA. b) PL image of BPCSA powder and solution in DMSO upon 365 nm illumination. c) Normalized absorption, PL, and PL excitation spectra of BPCSA solution in DMSO, dispersion in water, and powder.



ADVANCED FUNCTIONAL MATERIALS www.afm-journal.de

wavelength from 350 to 380 nm, and then to 420 nm, respectively. The appearance of a longer-wavelength PL excitation band in the aggregation state (the dispersion and powder) of BPCSA suggests that close stacking of the planarized LPs is potentially accompanied with fluorescence-enhancing *J* aggregation, often occurring in α -cyanostilbenes. Furthermore, the degree of *J* aggregation in the powder is higher than that in the water dispersion.^[17a] With this AIEE LP (BPCSA), we explored the interlayer-sensitized PL enhancement of quasi-2D PVKs.

The guasi-2D PVKs were synthesized under stoichiometric control of Pb2+ and a monovalent cation iodide for 2D PVK layers (methylammonium [MA] or formamidinium [FA] or cesium [Cs⁺], and the BPCSA cation [BPCSA+] iodide) to tune the layer structures (Figure 2a). As conceptually shown in Figure 2b, BPCSA in this hybrid 2D PVKs transfers its excitation energy after absorption of light to the 2D PVK layers that exhibit the typical PVK PL. On this hypothesis, the PL should have the PVK emission characteristics but predominantly the BPCSA excitation characteristics. BPCSA 2D PVK nanoparticles were synthesized with MA, FA, and Cs⁺ as the cations for the 2D PVK layers, by a simple precipitation method. Briefly, appropriate amounts of BPCSA, PbI2, MAI/FAI/Cs+, and hydriodic acid (HI) for two layers of 2D PVK (n = 2) were mixed and dissolved in dimethylformamide (DMF) with heating up to 60 °C, and then small portion of the mixture was injected into a poor solvent (toluene) for PVK, with vigorous stirring at room temperature (RT). The resulting suspensions showed strong red PL at a slightly different emission maximum wavelength, and a long PL lifetime component (about 200-300 ns) dependent on the cations (see Figure S1, Supporting Information), which are well-matched with common PL characteristics of lead iodide PVKs. Meanwhile, their PL properties are far different from the PL wavelength of 450 nm (see Figure 1c) and lifetime of 57 ns (see Figure S2, Supporting Information) for the BPCSA aggregates, which suggests that the 2D PVK layers are the main PL centers in these hybrid BPCSA 2D PVKs. Among these hybrid 2D PVKs, MA-incorporated PVK was selected for further studies because of its relatively higher stability (Figure S1, Supporting Information). For comparison, a conventional quasi-2D PVK (n = 2) was synthesized by the same precipitation method but using now a non- π -conjugated octylammonium (OA) as a reference (Figure 2c). The OA 2D PVK displayed further red-shift ($\lambda_{max} = 705$ nm) and 2.5-fold weaker PL than those of BPCSA 2D PVK (Figure 2d). Noticeably, the excitation spectrum of BPCSA 2D PVK almost entirely overlapped with that of the BPCSA powder, while the excitation spectrum of OA 2D PVK showed a pronounced peak at 605 nm attributable to layered 2D PVK absorption (Figure 2e). These results establish that the photoexcitation of BPCSA dominantly contributes to the PL of BPCSA 2D PVK, which proves efficient AIEE sensitization for the quasi-2D PVK. For further study, BPCSA 2D PVK with three of 2D PVK layers (n = 3) was also synthesized, and its photoinduced excitation/emission properties were studied. As shown in Figure 2f, with an increase of the number of 2D PVK layers, the PL red-shifted in the same manner as for typical quasi-2D PVKs; however, the primary excitation band still perfectly overlapped with that of BPCSA 2D PVK (n = 2) and with the BPCSA powder, which again verified the existence of AIEE-sensitized PL in this hybrid 2D PVK. The transmission electron microscopy (TEM) image of BPCSA 2D PVK (n = 2) mostly showed spherical nanoparticles with a 50-150 nm diameter (Figure 2g).

Since the nanosuspensions could not provide long-term stability for further studies (based on PL intensity, the half-life is



Figure 2. a) Schematic representation of BPCSA 2D PVK. Energy diagram and estimated photoinduced excitation/emission property in b) BPCSA and c) OA 2D PVKs. d) PL spectra of BPCSA 2D PVK (n = 2, (BPCSA)₂MAPb₂I₇) and OA 2D PVK (n = 2, (OA)₂MAPb₂I₇) nanosuspensions. e) PL excitation spectra of BPCSA 2D PVK (n = 2, (BPCSA)₂MAPb₂I₇) nanosuspension, OA 2D PVK (n = 2, (OA)₂MAPb₂I₇) nanosuspension, and BPCSA powder. f) Normalized PL and PL excitation spectra of BPCSA 2D PVKs nanosuspension with two different numbers of 2D PVK layers (n = 2 and 3). g) TEM image of BPCSA 2D PVK (n = 2) nanoparticles. Inset shows picture of PL of their nanosuspension upon 365 nm excitation.





about 20 h), we decided to prepare thin films of BPCSA 2D PVKs and OA 2D PVKs. The films were prepared on indium tin oxide (ITO)-deposited glass substrates by spin-coating of the precursor solution including lead iodide, MA iodide, BPCSA (or OA), and HI (at various stoichiometric ratio for quasi-2D PVK with n = 2, 3, 4 2D PVK layers). The chemical formula is, thus, BPCSA(or OA)₂MA_{*n*-1}Pb_{*n*}I_{3*n*+1}). Followed by thermal annealing at 100 °C for 10 min, we obtained brown transparent films (**Figure 3a**). Upon 365 nm illumination, both of the BPCSA/OA 2D PVKs films displayed decreased red PL with an increase in the number of 2D PVK layers (Figure 3a). But the increased number of 2D PVK layers induced a significant red-shift of the PL toward invisible near-IR region (Figure 3b–d; Figure S3, Supporting Information). At the same time, for both

of the BPCSA and OA 2D PVK films, the longer edge of the absorption spectra also shifted to a longer wavelength with the increase of the number of 2D PVK layers (Figure S3, Supporting Information). Again, this spectral red-shift with the increase of the 2D layers is well accorded with the typical quasi-2D PVK characteristic. However, the PL intensity of BPCSA 2D PVKs decreased with an increase of the number of 2D PVK layers, while that of OA 2D PVKs clearly showed an opposite trend (Figure 3b,c). These trends strongly support that the AIEE LPs efficiently sensitize the PL of their quasi-2D PVKs by strong light absorbance. In BPCSA 2D PVKs, the quantitative ratio of BPCSA in the PVK decreases with an increase of the number of 2D PVK layers; thus, the PL intensities are proportional to amounts of the AIEE LPs (BPCSAs). Meanwhile, in OA 2D



Figure 3. a) Photograph of BPCSA 2D PVKs (n = 2, 3, 4) and OA 2D PVKs (n = 2, 3, 4) films on ITO glass substrates under room light and 365 nm UV light. PL spectra of b) BPCSA 2D PVKs films and c) OA 2D PVKs films. d) Direct comparison of PL spectra between BPCSA 2D PVKs and OA 2D PVKs at the same 2D PVK layers. e) PL images of BPCSA 2D PVK (n = 2) film before adding water, with water, and after removal of water.

PVKs, the PL intensity of PVKs is proportional to the number of 2D layers. These results represent that light absorption in the BPCSA layer in BPCSA 2D PVKs, but that of the 2D PVK layer in OA 2D PVKs, are the primary contributors to the PL intensity of these quasi-2D hybrid PVKs (Figure S4, Supporting Information). As a result of the sensitized and nonsensitized system, the difference of the PL intensity between BPCSA 2D PVKs and OA 2D PVKs increased up to about 10-fold with a decrease of the 2D PVK layers.

The stability issue in PVK materials, mainly attributable to the high water solubility of their composition, is a significant problem in PVK research, and the quasi-2D PVKs with a hydrophobic organic cation layer is a leading solution for this issue.^[1] In this regard, the BPCSA layer in our study is a potential candidate for the hydrophobic layer. Although the stability of the BPCSA 2D PVK nanosuspensions was not satisfactory, the films are incredibly stable in ambient environment (average temperature: 25 °C, average relative humidity: 50%) for more than 4 months, without any inert gas blowing or encapsulation. We anticipate, in the nanosuspension, a solvated or suspended environment can have a dynamic character that can cause energy minimizing disassemble of the crystal lattice, while in a rigid environment of the film, the compositions are locked up after annealing. In addition, hydrophobic BPCSA substantially blocks penetration of humidity into the PVKs. To prove water resistance of the films, we added a water drop on the film. As shown in Figure 3e, we could not observe any significant change in the PL properties. Thus, we suggest that our AIEE LP, BPCSA, can sensitize as well as protect the quasi-2D PVKs from the moisture, when it is incorporated into the PVK as a bulky OAs layer.

We note that our results are consistent with density functional theory (DFT) calculations,^[20] where, for example, the excitation energy for the BPCSA molecule was calculated as 3.47 eV (see computational details in ref. [19]). This agrees well with the measured absorption peak energy of 3.54 eV for BPCSA in solution. In addition, the band alignment for the quasi-2D PVK, namely of BPCSA2MAPb2I7, was calculated as type I, consistent with no experimental evidence of a charge transfer exciton that would demonstrate type II band alignment in which the valence and the conduction bands in the inorganic layer are lower (or higher) than the HOMO and the LUMO levels in the organic cation, respectively. In the case of type I band alignment, the electrons and the holes are confined in either the organic or the inorganic parts. The calculated absorption spectrum for BPCSA2MAPb2I7 can be considered qualitatively consistent with the experimental PL excitation spectrum, and a discrepancy of 0.5 eV in the prediction of the wavelength can be attributed, in part, to the level of theory applied to the large material system.

For the applications of BPCSA 2D PVKs to nonlinear optical devices, we explored third-order nonlinear optical properties of their suspension and films. When a short-wavelength IR (1 μ m) laser was focused into the nanosuspension of BPCSA 2D PVK (n = 2) and OA 2D PVK (n = 2), interestingly, we observed about a 10-fold stronger PL from the BPCSA 2D PVK than that from OA 2D PVK (**Figure 4**a). This further promotion of two-photon-excited PL intensity in BPCSA 2D PVK is attributable to the superior two-photon absorption (TPA) capability

of π -conjugated organic materials to the TPA of inorganic materials of the same mass. The nonlinearity of TPA results in strong enhancement of the PL intensity in BPCSA 2D PVK upon two-photon excitation than the enhancement upon singlephoton excitation (Figure 2c). To verify the nonlinear optical character of the PL intensity, we measured the PL spectra under 1 µm laser illumination as a function of the excitation laser power. A two-photon process should show a guadratic dependence on the excitation intensity. As shown in Figure 4b, up to 1 mW cm⁻² pump power, no significant PL was observed from the BPCSA 2D PVK (n = 2) nanosuspension. However, for illumination intensities of 2 mW cm⁻² or higher, the PL intensity increased nonlinearly with an increase of excitation laser power. When plotted on a log-log scale, the power dependence fits well by a line with slope 1.96 (Figure 4b), consistent with a twophoton process.^[21]

To explore the third-order nonlinear optical property of the BPCSA 2D PVK thin film, we measured open- and closedaperture Z-scans of the film using an 800 nm femtosecond laser with 100 fs pulses at 1 kHz with intensities varying from 50 to 300 GW cm⁻² to obtain TPA and nonlinear refraction coefficient, respectively. We determined the thickness by crosssectional SEM imaging before the Z-scan. In the SEM image, we observed an evenly coated 147 nm thick BPCSA 2D PVK film (see Figure 4C). We regarded the film thickness as 150 nm and measured the Z-scan. The result yielded a TPA curve (Figure 4d) with the TPA coefficient, $\beta = 11.25 \pm 2.0$ cm GW⁻¹, and a nonlinear Kerr coefficient with a positive (self-focusing) sign (see Figure 4e) and $n_2 = 1.2 \pm 0.3 \times 10^{-13} \text{ cm}^2 \text{ W}^{-1}$. The values calculated using the equations described in reference articles^[22] are constant in this intensity regime and arise only from contributions of the imaginary and the real part of the third-order nonlinear coefficient $\chi^{(3)}$, respectively. The value of n_2 was corrected for the nonlinearity of the substrate, following a reference work by Zheng et al.,^[23] since there was no nonlinear absorption in the substrate, at these intensities, no correction was required for the β value.

To shed light on the electronic structure and TPA of the isolated (i.e., nonaggregated) BPCSA precursor and its cation, we performed DFT calculations using the CAM-B3LYP functional and the cc-pVDZ basis set. As demonstrated by the results shown in Table S1, Supporting Information (see also Figure S5, Supporting Information, for a clear comparison between oneand TPA spectra of both species), both BPCSA and BPCSA+ exhibit a strong one-photon transition to the first excited state and much weaker transitions to higher electronic excited states. However, the orbital character of the first allowed transition is different for the two species, that is, the $S_0 \rightarrow S_1$ electronic excitation is either dominated by the HOMO→LUMO (BPCSA) or HOMO→LUMO+1 (BPCSA+) one-electron orbital transition. There are also remarkable differences in the corresponding two-photon transition strengths of BPCSA and BPCSA+. Namely, the two-photon $S_0 \rightarrow S_1$ transition strength of BPCSA+ is much larger than the corresponding value for BPCSA. It is, thus, beneficial to use the BPCSA cation in the active organic layer, as it has much larger two-photon activity than its neutral precursor. The estimated two-photon cross section for the $S_0 \rightarrow S_1$ electronic transition of BPCSA+ is roughly 40 GM, or even higher considering that the CAM-B3LYP







Figure 4. a) PL spectra of BPCSA 2D PVK (n = 2, (BPCSA)₂MAPb₂I₇) and OA 2D PVK (n = 2, (OA)₂MAPb₂I₇) nanosuspensions under 1 µm laser illumination. b) PL spectra of BPCSA 2D PVK nanosuspension upon 1 µm laser illumination at various power and log–log plot of excitation power of 1 µm laser versus PL intensity of the BPCSA 2D PVK (n = 2) nanosuspension. c) Cross-sectional SEM image of BPCSA 2D PVK-coated ITO glass. Gold and platinum were sputtered on the 2D PVK film. d) The result from the open-aperture Z-scan measurement of BPCSA 2D PVK (n = 2) thin film (150 nm thick) at ≈193GW cm⁻¹. e) Closed-aperture measurement for the 2D PVK film as in panel (d), with an intensity of ≈197GW cm⁻².

functional systematically underestimates this property for organic chromophores. One can anticipate that after TPA to the higher lying electronic states, the molecular system will experience an ultrafast internal conversion decay to the S1 level. The lifetime of this level is very consequential for excited state energy injection into to the PVK part of the hybrid system, and we have, therefore, estimated its lifetime for free BPSCA using newly developed algorithms, namely as the inverted sum of the radiative decay rate (k_r) , the nonradiative (internal conversion) decay rate $(k_{\rm IC})$ and the intersystem singlet-triplet transfer rate $(k_{\rm ISC})$. The radiative rate constant (k_r) was estimated using the Strickler-Berg equation, which includes the oscillator strength and the de-excitation energy; the energy to the ground state internal conversion (k_{IC}) and intersystem crossing (k_{ISC}) rate constants were calculated in the Herzberg-Teller approximation using a formulation accounting for all vibrational degrees of freedom, including the calculated first- and second-order non-adiabatic coupling elements (for k_{IC}) and spin-orbit coupling and nuclear derivatives of the spin-orbit coupling elements (for k_{ISC}). The basic electronic structure theories were in this case time-dependent DFT and variational-perturbation theory (CASSCF and XMC-QDPT2 methods). An account of these methods as well as of detailed results for BPSCA and four related organic molecules and their cations will be given in a separate report. These rates are highly dependent on the precise energetics of the ground, excited singlet, and triplet states and can only be associated with qualitative significance—the prediction is 3.0×10^8 , 1.0, and 10.0 for the $k_{\rm P}$, $k_{\rm IC}$, and $k_{\rm ISC}$ constants, respectively. This gives an estimate of the S₁ level lifetime as long as 3 ns, thus into the nanoscale range, in fact not far from the expected natural decay rate of the compound. The overwhelming dominance of the radiative rate is a consequence of strong one-photon emission oscillator strength for the S₁ level, of the stiff skeleton of the BPCSA molecule and a relatively large HOMO-LUMO gap (small $k_{\rm IC}$ constant). A large singlet–triplet gap (small $k_{\rm ISC}$) together with a significant two-photon excitation cross section makes BPSCA very well designed for effective IR energy injection to the PVK system.

3. Conclusion

In summary, we have introduced the concept of interlayer sensitized PL of a quasi-2D hybrid PVK containing an AIEE organic cation layer. A rod-shaped AIEE organic cation, well fitted into the lattice of 2D PVK layers, was designed and synthesized to maximize the energy-sensitizing property. The produced cation precursor, BPCSA, emitted strong fluorescence in the solid state, while its solution was almost nonfluorescent, which is representative of the AIEE characteristic. When BPCSA was incorporated into quasi-2D PVKs as a bulky organic layer in between 2D PVK layers, it enhanced the PL of



PVK up to 10-folds compared to that of a non- π -conjugated OA containing 2D PVK. The PL excitation wavelength of BPCSA 2D PVKs well-matched with that of the BPCSA solid, but the PL was of typical quasi-2D PVKs, establishing sensitization by BPCSA to produce strong PL from 2D PVKs. Notably, the PL intensity of BPCSA 2D PVKs increased with a decrease of the number of 2D PVK layers, while that of OA 2D PVKs showed exactly an opposite trend, indicating the critical contribution of the amount of BPCSA for generating PL. The films of BPCSA 2D PVKs are incredibly stable in ambient environments for more than 4 months and even upon direct contact of water. Furthermore, the BPCSA 2D PVK displayed superior emission properties upon two-photon excitation by short-wavelength IR laser. Therefore, the AIEE sensitization system for quasi-2D PVK can reinforce the PL properties upon linear/nonlinear optical excitations for PVK as an emitter and for PVK based nonlinear optical devices.

4. Experimental Section

Material 4-Hydroxybenzaldehyde (98%), 3-(Boc-amino)propyl bromide (≥96%), 4-biphenylacetonitrile (97%), trifluoroacetic acid (CF₃COOH, 99%), tetrabutylammonium hydroxide solution (1.0 M in methanol), potassium carbonate (anhydrous, ACS reagent, ≥99%), sodium bicarbonate (ACS reagent, ≥99.7%), lead(II) iodide (99.999%, PVK grade), MA iodide (MAI, anhydrous, ≥99%), FA iodide (FAI, anhydrous, ≥99%), cesium iodide (CsI, 99.999%), octylamine (OA, 99%), HI (57 wt% in H₂O, stabilized, 99.95%), acetone (≥99.9%), tertbutanol (\geq 99.5%), dichloromethane (CH₂Cl₂, anhydrous, \geq 99.8%), DMF (anhydrous, 99.8%), and toluene (anhydrous, 99.8%) were obtained from Sigma-Aldrich. Acetone (certified ACS), hexane (ACS reagent grade, ≥98.5%), hexane (95%, HPLC grade), ethyl acetate (certified ACS), and methanol (certified ACS) were purchased from Fisher Scientific. All materials were used as received, without further purifications.

Instruments: ¹H NMR spectra were recorded on a Varian Inova-500 500 MHz spectrometer and referenced to tetramethylsilane as the internal standard, and ¹³C NMR spectra were recorded on a Varian Mercury-300 75 MHz spectrometer. The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, and br = broad. The steady-state UV-vis absorption spectra were measured by Shimadzu UV-3600 Plus UVvis-near NIR spectrophotometer. The steady-state PL spectra were measured using the HORIBA Scientific Fluorolog-3 spectrofluorometer equipped with xenon lamp. The lifetime was measured using HORIBA Scientific EasyLife X lifetime fluorescence spectrometer equipped with a 370 nm LED for excitation and 480 nm long-pass filter to minimize IRF. SEM images were taken using a Carl Zeiss AURIGA CrossBeam system at 2 kV accelerating voltage. The cross-sectional images were obtained by milling using the focused ion beam in the same microscope. The tilt angle was set at 54° and corrected by 36° when taking images. TEM images were obtained by using a JEOL-2100 microscope operating at 200 kV.

Synthesis of tert-butyl(3-(4-formylphenoxy)propyl)carbamate (1) (Figure 1a): 4-Hydroxybenzaldehyde (0.855 g, 7 mmol), 3-(Boc-amino)propyl bromide (2 g, 8.4 mmol), potassium carbonate (1.94 g, 14 mmol), and acetone (50 mL) were added to a 100 mL round-bottomed flask and then refluxed for 18 h. Then the reaction mixture was cooled to RT and diluted with 50 mL water to form precipitation. The precipitates were filtered and washed with water, and then dissolved in dichloromethane and dried with sodium sulfate. After removing the sodium sulfate by filtration, the solution of the product was condensed by solvent evaporation and then purified with silica gel column chromatography (ethyl acetate/hexane = 1:2) to obtain 1 as a colorless liquid (82% yield). ¹H NMR (500 MHz, CDCl₃), δ 9.885 (s, 1H), 7.831 (d, 2H, J = 11 Hz), 6.995 (d, 2*H*, *J* = 11 Hz), 4.752 (br, 1*H*), 4.108 (t, 2*H*, *J* = 6 Hz), 3.342 (q, 2*H*, *J* = 6.5 Hz), 2.023 (t, 2*H*, *J* = 6.5 Hz) 1.440 (s, 9*H*).

Synthesis of tert-butyl(Z)-(3-(4-(2-([1, 1'-biphenyl]-4-yl)-2-cyanovinyl) phenoxy)propyl)carbamate (**2**) (Figure 1a): **1** (1.5 g, 5.4 mmol), 4-biphenylacetonitrile (1.24 g, 6.4 mmol), and tert-butyl alcohol (90 mL) were added to a 150 mL round-bottomed flask and then were heated to 60 °C with stirring. Tetrabutylammonium hydroxide (1 M solution in methanol, 1 mL) was added dropwise into the reaction mixture and the mixture was stirred at 60 °C overnight. The resulting precipitate was filtered and washed with tert-butyl alcohol. A pale-yellow crystals of 2 (69% yield) were obtained by recrystallization from hot methanol solution. ¹H NMR (500 MHz, DMSO-d₆), δ 8.021 (s, 1H), 7.961 (d, 2H, J = 8.5 Hz), 7.813 (s, 4H), 7.731 (d, 2H, J = 7.5 Hz), 7.488 (t, 2H, J = 6.5 Hz), 7.392 (t, 1H, J = 7.5 Hz), 7.094 (d, 2H, J = 8 Hz), 6.911 (br, 1H), 4.067 (t, 2H, J = 6.5 Hz), 3.088 (q, 2H, J = 6.5 Hz), 1.850 (t, 2H, J = 6 Hz), 1.370 (s, 9H).

Synthesis of (Z)-2-([1,1'-biphenyl]-4-yl)-3-(4-(3-aminopropoxy)phenyl) acrylonitrile (BPCSA) (Figure 1a): 2 (1.68 g, 3.7 mmol) and 20 mL dichloromethane were added to a 100 mL round-bottomed flask and then 10 mL trifluoroacetic acid was added dropwise into the reaction mixture with stirring at RT. The mixture was stirred at RT for 2 h and the solvent was evaporated. A saturated aqueous solution of sodium bicarbonate was slowly added to the resulting mixture to form precipitation of the products. The precipitates were filtered and washed with water. A paleyellow powder of BPCSA (85% yield) was obtained by recrystallization from hot methanol solution. ¹H NMR (500 MHz, DMSO- d_6), δ 8.025 (s, 1H), 7.962 (d, 2H, J = 8.5 Hz), 7.814 (s, 4H), 7.731 (d, 2H, J = 7.5 Hz), 7.489 (t, 2H, J = 7.5 Hz), 7.394 (t, 1H, J = 7.5 Hz), 7.111 (d, 2H, J = 8.5 Hz), 4.135 (t, 2H, J = 6.5 Hz), 3.649 (br, 2H), 2.768 (t, 2H, J = 6.5 Hz), 1.859 (qui, 2H, J = 6.5 Hz). ¹³C NMR (75 MHz, DMSO- d_6), δ 160.271, 142.200, 139.35, 139.011, 133.135, 133.181, 129.044, 127.900, 127.304, 126.633, 126.434, 126.022, 118.361, 144.988, 106.731, 65.019, 36.631, 27.687.

Synthesis of Quasi-2D PVK Nanosuspension: In a general procedure, 0.01 mmol PbI₂, *x* mmol MAI (or FAI or CsI), *y* mmol BPCSA (or OA), *z* mmol HI, and 200 μ L DMF were added into a vial and all the chemicals were dissolved with heating (up to 80 °C) and stirring. For *n* = 2 (or 3), the *x*, *y*, and *z* were respectively 0.005 (or 0.0066), 0.007 (or 0.0033), and 0.008 (or 0.004). After 20 min stirring at 80 °C, 10 μ L of the mixture was injected into 5 mL toluene at RT with vigorous stirring, and then the stirring was stopped immediately to obtain nanosuspension of BPCSA (or OA) 2D PVKs.

Preparation of Quasi-2D PVK Films: The films were fabricated on the prepatterned ITO substrates, which were cleaned sequentially with the Hellmanex III solution, acetone, methanol, and isopropyl alcohol, with 10 min ultrasonication in each solvent. To prepare PVK precursor solutions, 0.05 mmol Pbl₂, *x* mmol MAI, *y* mmol BPCSA (or OA), *z* mmol HI, and 200 µL DMF were added into a vial and dissolved with heating (up to 80 °C) and stirring. The *x*, *y*, and *z* were 0.027, 0.033, and 0.014 for *n* = 2; 0.038, 0.013, and 0.015 for *n* = 3; and 0.04, 0.01, and 0.012 for *n* = 4, respectively. After 30 min stirring at 80 °C, the PVK precursor solution was spin-coated at 3000 rpm for 30 s and then annealed at 100 °C for 10 min to remove residual solvent and to crystallize the film.

Electronic-Structure Calculations: The geometries of BPCSA and BPCSA+ were optimized based on DFT, employing the B3LYP functional and the cc-pVDZ basis set. In doing so, we neglected environmental effects, that is, we considered molecules in vacuo. The minima on potential energy hypersurface were confirmed by evaluation of Hessian. Subsequently, the minimum-energy geometries were used for electronic-structure calculations using the CAM-B3LYP functional and cc-pVDZ basis set. All calculations were performed using GAMESS US program.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

ADVANCED SCIENCE NEWS_____ www.advancedsciencenews.com

Acknowledgements

The authors acknowledge the support from the Air Force Office of Scientific Research (no. FA9550-18-1-0042 and FA9550-18-1-0032). R.Z. thanks National Science Centre (Poland) for financial support (grant no. 2018/30/E/ST4/00457).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

aggregation-induced emission, energy transfer, nonlinear optics, photoluminescence, quasi-2D perovskites

Received: November 10, 2019 Revised: February 8, 2020 Published online:

- a) E. H. Jung, N. J. Jeon, E. Y. Park, C. S. Moon, T. J. Shin, T.-Y. Yang, J. H. Noh, J. Seo, *Nature* 2019, *567*, 511; b) Y. Liu, S. Akin, L. Pan, R. Uchida, N. Arora, J. V. Milić, A. Hinderhofer, F. Schreiber, A. R. Uhl, S. M. Zakeeruddin, *Sci. Adv.* 2019, *5*, eaaw2543; c) Z. Wang, Q. Lin, F. P. Chmiel, N. Sakai, L. M. Herz, H. J. Snaith, *Nat. Energy* 2017, *2*, 17135; d) H. Tsai, W. Nie, J.-C. Blancon, C. C. Stoumpos, R. Asadpour, B. Harutyunyan, A. J. Neukirch, R. Verduzco, J. J. Crochet, S. Tretiak, *Nature* 2016, *536*, 312.
- [2] E. Shi, Y. Gao, B. P. Finkenauer, A. H. Coffey, L. Dou, Chem. Soc. Rev. 2018, 47, 6046.
- [3] a) M. Yuan, L. N. Quan, R. Comin, G. Walters, R. Sabatini, O. Voznyy, S. Hoogland, Y. Zhao, E. M. Beauregard, P. Kanjanaboos, *Nat. Nanotechnol.* 2016, *11*, 872; b) J. Byun, H. Cho, C. Wolf, M. Jang, A. Sadhanala, R. H. Friend, H. Yang, T. W. Lee, *Adv. Mater.* 2016, *28*, 7515; c) C. C. Stoumpos, D. H. Cao, D. J. Clark, J. Young, J. M. Rondinelli, J. I. Jang, J. T. Hupp, M. G. Kanatzidis, *Chem. Mater.* 2016, *28*, 2852; d) X. Gong, O. Voznyy, A. Jain, W. Liu, R. Sabatini, Z. Piontkowski, G. Walters, G. Bappi, S. Nokhrin, O. Bushuyev, *Nat. Mater.* 2018, *17*, 550.
- [4] a) Y. Zhang, C.-K. Lim, Z. Dai, G. Yu, J. W. Haus, H. Zhang, P. N. Prasad, *Phys. Rep.* **2019**, *795*, 1; b) H. Zhang, Q. Liao, Y. Wu, Z. Zhang, Q. Gao, P. Liu, M. Li, J. Yao, H. Fu, *Adv. Mater.* **2018**, *30*, 1706186; c) M. Li, Q. Gao, P. Liu, Q. Liao, H. Zhang, J. Yao, W. Hu, Y. Wu, H. Fu, *Adv. Funct. Mater.* **2018**, *28*, 1707006.
- [5] a) Z. Tan, Y. Wu, H. Hong, J. Yin, J. Zhang, L. Lin, M. Wang, X. Sun,
 L. Sun, Y. Huang, J. Am. Chem. Soc. 2016, 138, 16612; b) D. Yu,
 F. Cao, Y. Shen, X. Liu, Y. Zhu, H. Zeng, J. Phys. Chem. Lett. 2017,



8, 2565; c) L. Li, Z. Sun, P. Wang, W. Hu, S. Wang, C. Ji, M. Hong, J. Luo, Angew. Chem., Int. Ed. **2017**, 56, 12150.

- [6] a) B. R. Sutherland, E. H. Sargent, *Nat. Photonics* 2016, *10*, 295;
 b) L. N. Quan, F. P. García de Arquer, R. P. Sabatini, E. H. Sargent, *Adv. Mater.* 2018, *30*, 1801996.
- [7] J.-C. Blancon, A. V. Stier, H. Tsai, W. Nie, C. Stoumpos, B. Traore, L. Pedesseau, M. Kepenekian, F. Katsutani, G. Noe, *Nat. Commun.* 2018, 9, 2254.
- [8] a) W. Chen, S. Bhaumik, S. A. Veldhuis, G. Xing, Q. Xu, M. Grätzel, S. Mhaisalkar, N. Mathews, T. C. Sum, *Nat. Commun.* 2017, *8*, 15198; b) S. Kumar, J. Jagielski, S. Yakunin, P. Rice, Y.-C. Chiu, M. Wang, G. Nedelcu, Y. Kim, S. Lin, E. J. Santos, *ACS Nano* 2016, 10, 9720.
- [9] a) E. P. Booker, M. B. Price, P. J. Budden, H. Abolins, Y. del Valle-Inclan Redondo, L. Eyre, I. Nasrallah, R. T. Phillips, R. H. Friend, F. Deschler, Adv. Opt. Mater. 2018, 6, 1800616; b) C. Quarti, N. G. Marchal, D. Beljonne, J. Phys. Chem. Lett. 2018, 9, 3416; c) E. P. Booker, T. H. Thomas, C. Quarti, M. R. Stanton, C. D. Dashwood, A. J. Gillett, J. M. Richter, A. J. Pearson, N. J. Davis, H. Sirringhaus, J. Am. Chem. Soc. 2017, 139, 18632.
- [10] a) K. Jemli, P. Audebert, L. Galmiche, G. Trippé-Allard, D. Garrot, J.-S. Lauret, E. Deleporte, ACS Appl. Mater. Interfaces 2015, 7, 21763;
 b) K. Ema, M. Inomata, Y. Kato, H. Kunugita, M. Era, Phys. Rev. Lett. 2008, 100, 257401.
- [11] a) D. B. Mitzi, K. Chondroudis, C. R. Kagan, Inorg. Chem. 1999, 38, 6246; b) K. Chondroudis, D. B. Mitzi, Chem. Mater. 1999, 11, 3028.
- [12] M. Era, T. Kobayashi, K. Sakaguchi, E. Tsukamoto, Y. Oishi, Org. Electron. 2013, 14, 1313.
- [13] J. V. Passarelli, D. J. Fairfield, N. A. Sather, M. P. Hendricks, H. Sai, C. L. Stern, S. I. Stupp, J. Am. Chem. Soc. 2018, 140, 7313.
- [14] C. Ortiz-Cervantes, P. I. Román-Román, J. Vazquez-Chavez, M. Hernández-Rodríguez, D. Solis-Ibarra, Angew. Chem., Int. Ed. 2018, 57, 13882.
- [15] G. Feng, R. T. Kwok, B. Z. Tang, B. Liu, Appl. Phys. Rev. 2017, 4, 021307.
- [16] Z. Zhao, J. W. Lam, B. Z. Tang, J. Mater. Chem. 2012, 22, 23726.
- [17] a) B.-K. An, J. Gierschner, S. Y. Park, Acc. Chem. Res. 2011, 45, 544;
 b) W. Shao, C.-K. Lim, Q. Li, M. T. Swihart, P. N. Prasad, Nano Lett. 2018, 18, 4922.
- [18] S. Kim, T. Y. Ohulchanskyy, H. E. Pudavar, R. K. Pandey, P. N. Prasad, J. Am. Chem. Soc. 2007, 129, 2669.
- [19] J. E. Kwon, S. Y. Park, Adv. Mater. 2011, 23, 3615.
- [20] J. Jiang, R. Pachter, C.-K. Lim, J. E. Haley, P. N. Prasad, J. Phys. Chem. C 2020, 124, 3224.
- [21] D. R. Larson, W. R. Zipfel, R. M. Williams, S. W. Clark, M. P. Bruchez, F. W. Wise, W. W. Webb, *Science* **2003**, *300*, 1434.
- [22] a) M. Sheik-Bahae, A. A. Said, T.-H. Wei, D. J. Hagan, E. W. Van Stryland, *IEEE J. Quantum Electron.* **1990**, *26*, 760; b) C. B. De Araújo, A. S. Gornes, G. Boudebs, *Rep. Prog. Phys.* **2016**, *79*, 036401.
- [23] X. Zheng, Y. Zhang, R. Chen, Z. Xu, T. Jiang, *Opt. Express* **2015**, *23*, 15616.