Hybrid Organic/Inorganic Perovskite–Polymer Nanocomposites: Toward the Enhancement of Structural and Electrical Properties

Alberto Privitera,^{*,†,§} Marcello Righetto,[†] Michele De Bastiani,[‡] Francesco Carraro,[†] Marzio Rancan,^{†,§} Lidia Armelao,^{†,§} Gaetano Granozzi,[†] Renato Bozio,[†] and Lorenzo Franco[†]

[†]Department of Chemical Science and U.R. INSTM, University of Padova, Via Marzolo 1, I-35131 Padova, Italy

[‡]King Abdullah University of Science and Technology (KAUST), KAUST Solar Center (KSC), Division of Physical Sciences and Engineering (PSE), Thuwal 23955-6900, Kingdom of Saudi Arabia

[§]ICMATE-CNR and U.R. INSTM, University of Padova, Via Marzolo 1, I-35131 Padova, Italy

Supporting Information

ABSTRACT: Hybrid organic/inorganic perovskite nanoparticles (NPs) have garnered remarkable research attention because of their promising photophysical properties. New and interesting properties emerge after combining perovskite NPs with semiconducting materials. Here, we report the synthesis and investigation of a composite material obtained by mixing $\text{CH}_3\text{NH}_3\text{PbBr}_3$ nanocrystals with the semiconducting polymer poly(3-hexylthiophene) (P3HT). By the combination of structural techniques and optical and magnetic spectroscopies we observed multiple effects of the perovskite NPs on the P3HT: (i) an enlargement of P3HT crystalline domains, (ii) a strong p-doping of the P3HT, and (iii) an enhancement of interchain order typical of H-aggregates. These observations open a new avenue toward innovative perovskite NP-based applications.

Very recently there has been a huge growth of interest in hybrid perovskite materials.^{1–8} In analogy with confinement effects in conventional semiconductors, exciting new physical properties emerge with the miniaturization of hybrid perovskites materials to the nanometer scale.^{9–16} Among these properties, higher oscillator strength, size tunability of energy levels, Auger-assisted charge transfer, and phonon bottleneck multiexciton generation represent only a few of the many features which provide perovskite nanostructures an appealing interest for optoelectronic applications.^{17–22} Moreover, as discovered in conventional semiconductors, new properties can be triggered by coupling inorganic nanoparticles (NPs) with other semiconducting materials.²³ Among the many nanostructured composites, those including NPs and conducting polymers have played a pivotal role in the last two decades.^{23–25} For example, in organic solar cells, blending NPs with conducting polymers has contributed toward the enhancement of light absorption, fast exciton diffusion and dissociation, as well as balanced electron–hole transport.^{26–29} A similar success has been obtained also in thermoelectric applications, where NP incorporation improves device performances.³⁰ In Li-ion batteries, NP/polymer nanocomposites used at the cathode or anode have contributed to a significant improvement of capacity and cyclability of the devices.³¹ Finally, NP incorporation has facilitated high luminous yield, color tunability, and low operation voltage for organic light-emitting diodes.³²

Despite the promising response of inorganic NP/conducting polymer nanocomposites in optoelectronic devices, only few examples have so far examined the benefits given by hybrid perovskite nanostructures to the crystallinity, morphology, and photophysics of polymers.³³ In particular, the control over crystallinity in partially disordered materials is of paramount importance for achieving highly performing optoelectronic devices.^{34,35} Indeed, the formation of larger ordered polymer domains has a strong impact on photophysical processes, such as exciton and polaron dynamics.^{36–39}

Within this scenario, we investigated a nanocomposite material of methylammonium lead bromide ($\text{CH}_3\text{NH}_3\text{PbBr}_3$) perovskite nanoparticles (PNPs) blended with poly(3-hexylthiophene) (P3HT) (hereafter P3HT/PNPs). We explored the effect of the PNPs on the morphology and the photophysics of P3HT by combining optical and magnetic spectroscopies with X-ray diffraction, electron microscopy/spectroscopy, and elemental analysis. Our study disclosed a triple influence of the PNPs on the P3HT properties. First, the P3HT crystalline domains notably increased in dimensions when blended with the PNPs with respect to the pristine conditions. Second, a strong p-doping of the P3HT is induced by the PNPs. Third, a large area of π -stacking between adjacent monomers of P3HT, forming H-aggregates, is generated by the presence of the

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Figure 1. (a) TEM image of a thin film of the P3HT/PNPs blend. (b, c) Pb 4f and Br 3d photoemission raw spectra and total fit of PNPs (black circles, orange line) and P3HT/PNPs (black triangles, red line) samples, respectively. (d) PXRD spectra of pristine P3HT film (blue line) and P3HT/PNPs blend (red line).

PNPs. The combination of these effects might open the way to novel functionalities of the composite material and to the development of highly efficient optoelectronic devices.

We synthesized PNPs following the well-established ligand-assisted reprecipitation (LARP) technique.²⁰ The suspended NP solution was centrifuged to discard the precipitates, and a bright blue-green photoluminescence, fingerprint of PNPs, was observed in the supernatant solution (more details on the synthesis are reported in the [Supporting Information](#)). The as-synthesized PNPs show an absorption edge at 510 nm with an intense photoluminescence peak at 520 nm, blue-shifted with respect to bulk $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and in agreement with the quantum confinement effect (see [Figure SI_1a](#)). Powder XRD (PXRD) of PNPs matches well the cubic phase ($Pm\bar{3}m$) of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (see [Figure SI_1b](#)).²⁰

With the aim of investigating the effects induced by the PNPs on the morphology and the optoelectronic properties of an embedding conducting polymer, we prepared a composite material P3HT/PNPs by mixing PNPs and P3HT (details in the [Supporting Information](#)).

TEM images of the P3HT/PNPs composite clearly exhibit a uniform dispersion of the PNPs in the polymer matrix ([Figures 1a](#) and [SI_2b](#)), indicating a homogeneous mixing in the composite material. In addition, the presence of perovskite nanoplatelets of average side of 10–30 nm is observed. Their presence is also confirmed by XRD and optical analysis (see below). Additional evidence of the uniform PNPs dispersion is provided by SEM micrographs ([Figure SI_3](#)) and energy dispersive X-ray spectroscopy (EDS, [Figure SI_4](#)) which confirms a homogeneous distribution of Br and Pb with a matching ratio corresponding to hybrid perovskites (Br/Pb = 3.5).

We also determined the chemical composition of pristine PNPs and the P3HT/PNPs composite by X-ray photoemission spectroscopy (XPS). Surface elemental composition (atom %) determined by XPS quantitative analysis confirmed the presence of the PNPs with a calculated ratio Br/Pb of 2.5 and 3.3 for the PNPs and P3HT/PNPs, respectively, in good agreement with EDS results. The small difference in the calculated surface Br/Pb ratio can be attributed to the presence of P3HT and to surface effects in the composite material. Pristine PNPs showed two symmetric peaks attributed to Pb 4f_{7/2} and Pb 4f_{5/2} level at binding energies (BE) of 138.5 and 143.4 eV, respectively ([Figures 1b](#) and [SI_5](#)). The deconvolution of the Pb 4f confirms that no undesired Pb oxides phases were formed.⁴⁰ Interestingly, we observe a shift of 0.4 eV to lower BE of the perovskite's photoemission lines ([Figures 1c](#) and [SI_6](#)). This shift can be induced by the presence of an electronic interaction between the PNPs and the P3HT which generates an excess of negative charges on the PNPs, thus lowering the binding energy.

To further characterize the effect of the interaction between PNPs and the polymer, we recorded the PXRD patterns of P3HT/PNPs and pristine P3HT. The pristine P3HT shows an intense reflection at 5.4° (100) and two smaller ones at 10.6° (200) and 16.0° (300) commonly attributed to the lamellar ordering of the polymer chains induced by the π -stacking of the aromatic rings ([Figure 1d](#)). The P3HT/PNPs composite shows a clearly different diffraction pattern with respect to the pristine polymer. In particular, a severe narrowing of the XRD reflections and a shift to lower angles are observed. The narrowing of the peaks is attributed to a structural rearrangement of the polymer with the formation of larger crystalline domains. Concerning the shift of the peaks, some possible

explanations are reported in the literature. Doping of P3HT (p-doping) has been reported to produce a shift of the low-angle reflections with respect to the pristine condition,^{41,42} and it was also demonstrated that when the doping overcomes a critical threshold, P3HT can undergo a deep structural rearrangement.⁴³ These explanations do not seem to be fully applicable to our case. However, for our purposes, the most important result from XRD is the detection of an enhanced P3HT crystallinity in the blend.

Finally, by magnifying the region between 10° and 50° (Figure SI_7), a series of very low-intensity peaks is visible. These low-intensity peaks are associated with the PNPs. Similar features for PNPs were observed in the presence of perovskite nanoplatelets.⁴⁴

To further investigate the increased crystallinity of the P3HT in the blend with PNPs, we applied electron paramagnetic resonance (EPR) spectroscopy, which can provide structural and dynamical information about charge carriers (polarons) in P3HT blends.⁴⁵

The EPR spectra of the neat P3HT film and the P3HT/PNPs blend, recorded at 80 K, are reported in Figure 2a. In the

the blend. From the EPR results, the PL quenching can be attributed to the electron transfer from the P3HT to the PNPs. A multitude of different causes that promote this electron transfer can be envisaged. A relevant role can be represented by trap states induced by surface defects in PNPs, which are reported to affect the photophysical properties of the NPs.^{48,49} These trap states may act as interfacial sink for the transferred electrons, providing an excess of positive charges left on the P3HT. Additionally, the generated polarons are stabilized by the high dielectric permittivity of the perovskite that hinders the back electron-transfer process. As well as the increased number of polarons, a secondary effect induced by the presence of PNPs is represented by an anomalous narrowing of EPR line width. We rationalize this evidence as being due to a motional narrowing regime of the polarons in the blend induced by a higher mobility with respect to the neat P3HT film.⁵⁰

We confirm such an explanation by investigating in more detail the dynamics of the polarons in the blend recording EPR spectra in a broad range of temperatures, from 80 to 240 K (Figure 2b). When the temperature is increased from 80 K, a contraction of the EPR line width is observed, while the g-tensor anisotropy is substantially unvaried. This observation is likely due to a thermally activated charge carriers diffusion along and between polymer chains.⁵⁰ The higher charge diffusion rate induces a more efficient averaging of broadening due to hyperfine coupling and an EPR line width narrowing.⁵⁰ However, if the motion of the polarons occurs within equally oriented molecules in a crystalline domain, it does not result in an averaging of the g-anisotropy. Therefore, in the presence of a high crystallinity of the sample, which allows a high charge mobility, the resulting EPR spectrum of the polarons shows the full g-tensor anisotropy with a narrow line width. Electron spin relaxation time measurements provide further confirmation of the temperature-dependent enhanced mobility of polarons in the P3HT/PNPs blend. Figure 2c,d shows a decrease of electron spin–lattice and spin–spin relaxation times as a function of temperature. In the P3HT/PNPs blend, polaron electron spin relaxation is governed by spin dynamics. Indeed, in organic systems, electron spin relaxation is caused by local magnetic field fluctuations mainly due to magnetic dipole–dipole interactions.⁵⁰ A faster charge carriers' diffusion along and between polymer chains increases the rate of the local magnetic field fluctuations experienced by the polaron unpaired electron. A higher rate of these fluctuations is the cause of the decrease of the polaron spin relaxation times. Therefore, at increasing temperatures, a faster polaron diffusion lowers both electron spin–lattice and spin–spin relaxation times.

The polaron diffusion along and between P3HT chains is strongly influenced by the packing of the polymer chains within the crystalline domains, which in turn can be determined by the relative orientation between the P3HT chains. We used ultraviolet–visible (UV–vis) spectroscopy to investigate the degree of interchain order and the relative orientation of transition dipoles associated with P3HT units. This analysis takes advantage of the coupled Frenkel excitons model developed by Spano for semiconducting polymers.⁵¹ In particular, models involving H- and J-aggregates were proposed to predict optical properties of P3HT films.^{51,52} Upon deposition, interactions between monomers can be either interchain or intrachain. Hence, the competition between through-bond and through-space excitonic coupling contains information on the aggregation of P3HT. In particular, a dominant interchain coupling, associated with a high degree of

Figure 2. (a) EPR spectra of the neat P3HT film (blue line) and P3HT/PNPs blend (red line) recorded at 80 K and best fit spectral simulation (light blue and orange dotted lines). (b) Normalized EPR spectra of P3HT/PNPs blend recorded at various temperatures. The inset illustrates the narrowing of the EPR line at increasing temperatures. (c, d) T_1 and T_2 electron spin relaxation times as a function of temperature for P3HT/PNPs blend.

neat P3HT film (blue line), only a weak EPR peak is detected. From the spectral simulation the g-tensor typical of spin 1/2 positive charge carriers (polarons) in P3HT is obtained (g-tensor principal values: 2.001, 2.002, and 2.003).⁴⁶ The presence of this small signal is attributed to a partial intrinsic oxidation of the polymer in air.⁴⁷ In contrast, the P3HT/PNPs blend shows a strong EPR line with the same g-tensor indicating a much stronger oxidation, i.e., a p-doping, of the polymer.⁴⁶ The p-doping of P3HT in the blend is consistent with the observed XPS shift previously discussed. We explain the excess of positive polarons on the P3HT as the result of either a thermal or an ambient light-induced electron transfer from the P3HT to the perovskite NPs. The presence of an electronic interaction between the two components of the blend is demonstrated also by PL quenching measurements (Figure SI_8). We observed a complete quenching of the PL of both the P3HT and the PNPs when they are mixed together in

interchain order, would result in cofacial H-aggregate signatures in the optical spectrum. On the other hand, a dominant intrachain coupling, reflecting higher intrachain order, would result in J-aggregate signatures. Spano et al. demonstrated that electronic dispersion of molecular levels, associated with aggregate formation, results in vibronic bands.^{51,52} The relative intensities of vibronic bands are a sensitive probe for polymer inner structure. Indeed, the ratio of the first two vibronic peak intensities in the absorption spectrum (I_{00}/I_{01}) is correlated with the degree of inter/intrachain order, i.e., the lower this ratio, the higher the interchain order. UV-vis spectra recorded for pristine P3HT and P3HT/PNP film are shown in Figure 3a.

Figure 3. (a) UV-vis absorption spectra of P3HT (black) and P3HT/PPs blend (blue). (b) Difference between UV-vis spectra of P3HT with and without perovskite NPs. Changes in the vibronic structure of P3HT account for different aggregation, while appearance of novel absorption peaks on the blue absorption tail are ascribed to perovskite nanoplatelets.

In Figure 3b, we present the difference between the spectrum of P3HT with and without PNPs to magnify the differences. This subtraction reveals a redistribution of relative intensities of vibronic bands, associated with a microscopic ordering of the aggregated polymer. The strong decrease of I_{00} suggests an augmented interchain order, confirming EPR and XRD data. According to refs 51 and 52, we can quantitatively estimate the exciton bandwidth associated with H-aggregates formation using relation 1:

$$\frac{I_{00}}{I_{01}} \approx \frac{n_{01}}{n_{00}} \left(\frac{1 - 0.24W/E_p}{1 + 0.073W/E_p} \right)^2 \quad (1)$$

where W is the exciton bandwidth and E_p is the frequency of the coupled normal mode; n are the refractive indexes. By using parameters similar to those in ref 51, we estimate a 3-fold increment in the exciton bandwidth, from 24 to 67 meV, when PNPs are blended with P3HT. This result indicates that the presence of PNPs directs crystallization toward the formation of H-aggregates.

Moreover, two additional peaks observed at shorter wavelength are assigned to perovskite nanoplatelets.⁴⁴ We suggest that these features originate from the exfoliation of PNPs during the deposition process which results in the formation of mono- and bilayered perovskite nanoplatelets in agreement with the layered nature of perovskite materials.⁴⁴

Clearly, together with standard parameters (such as the choice of solvent and of film deposition conditions²³), the

interfacial regions between the PNPs and the P3HT rule the crystallization process of the polymer and actively modify the P3HT aggregation. The combination of the good miscibility between the two components of the blend, the nanometric size of PNPs, and the presence of perovskite nanoplatelets increases the interfacial regions and bolsters the formation of large crystalline domains of H-aggregates.

To conclude, in this work we presented an in-depth study of a polymer/nanoparticle composite material, based on semiconducting polymer P3HT and methylammonium lead bromide perovskite nanoparticles. After having demonstrated the good miscibility between the P3HT and PNPs and the optimal homogeneity of the composite by using TEM, SEM, EDS, and XPS analysis, we investigated how the morphological and electrical properties of the P3HT are enhanced by the presence of PNPs. The combined use of X-ray diffraction, EPR spectroscopy, and optical analysis revealed a 3-fold contribution of the PNPs on the properties of P3HT: (i) an increment of the P3HT crystalline domains, (ii) a p-doping of the P3HT, and (iii) the extended formation of π -stacking between adjacent monomers of P3HT (H-aggregates). Our results may be potentially extended to other semiconducting polymers blended with hybrid organic perovskite NPs. Further experimental work is currently underway to test this hypothesis. In addition, because the structural and electronic control of conducting polymers is of paramount importance for achieving high-performance optoelectronic devices, our composite material is promising for the design of new highly performing devices.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b03077.

Details of experimental methods, characterization of PNPs, EDS elemental maps, XPS spectra, and PXRD patterns of the studied samples (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: alberto.privitera@phd.unipd.it.

ORCID

Alberto Privitera: 0000-0002-7062-8077
 Marcello Righetto: 0000-0001-5507-1445
 Francesco Carraro: 0000-0001-8485-4676
 Gaetano Granozzi: 0000-0002-9509-6142
 Renato Bozio: 0000-0001-7274-9190
 Lorenzo Franco: 0000-0003-3548-4423

Notes

The authors declare no competing financial interest.

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330 ■ REFERENCES

- 331 (1) Brenner, T. M.; Egger, D. A.; Kronik, L.; Hodes, G.; Cahen, D.
332 Hybrid Organic-Inorganic Perovskites: Low-Cost Semiconductors
333 with Intriguing Charge-Transport Properties. *Nat. Rev. Mater.* **2016**,
334 *1*, 15007.
- 335 (2) Zhao, Y.; Zhu, K. Organic-Inorganic Hybrid Lead Halide
336 Perovskites for Optoelectronic and Electronic Applications. *Chem. Soc.*
337 *Rev.* **2016**, *45*, 655–689.
- 338 (3) Shi, Z.; Guo, J.; Chen, Y.; Li, Q.; Pan, Y.; Zhang, H.; Xia, Y.;
339 Huang, W. Lead-Free Organic-Inorganic Hybrid Perovskites for
340 Photovoltaic Applications: Recent Advances and Perspectives. *Adv.*
341 *Mater.* **2017**, *29*, 1605005.
- 342 (4) Chen, Q.; De Marco, N.; Yang, Y.; Song, T.-B.; Chen, C.-C.;
343 Zhao, H.; Hong, Z.; Zhou, H.; Yang, Y. Under the Spotlight: The
344 Organic-Inorganic Hybrid Halide Perovskite for Optoelectronic
345 Applications. *Nano Today* **2015**, *10*, 355–396.
- 346 (5) Ye, M.; He, C.; Iocozzia, J.; Liu, X.; Cui, X.; Meng, X.; Rager, M.;
347 Hong, X.; Liu, X.; Lin, Z. Recent Advances in Interfacial Engineering
348 of Perovskite Solar Cells. *J. Phys. D: Appl. Phys.* **2017**, *50*, 373002.
- 349 (6) He, M.; Zheng, D.; Wang, M.; Lin, C.; Lin, Z. High Efficiency
350 Perovskite Solar Cells: from Complex Nanostructure to Planar
351 Heterojunction. *J. Mater. Chem. A* **2014**, *2*, 5994–6003.
- 352 (7) He, M.; Li, B.; Cui, X.; Jiang, B.; He, Y.; Chen, Y.; O'Neil, D.;
353 Szymanski, P.; Ei-Sayed, M. A.; Huang, J.; et al. Meniscus-Assisted
354 Solution Printing of Large-Grained Perovskite Films for High-
355 Efficiency Solar Cells. *Nat. Commun.* **2017**, *8*, 16045.
- 356 (8) He, M.; Pang, X.; Liu, X.; Jiang, B.; He, Y.; Snaith, H.; Lin, Z.
357 Monodisperse Dual-Functional Upconversion Nanoparticles Enabled
358 Near-Infrared Organolead Halide Perovskite Solar Cells. *Angew. Chem.,*
359 *Int. Ed.* **2016**, *55*, 4280–4284.
- 360 (9) González-Carrero, S.; Galian, R. E.; Pérez-Prieto, J. Organometal
361 Halide Perovskites: Bulk Low-Dimension Materials and Nanoparticles.
362 *Part. Part. Syst. Charact.* **2015**, *32*, 709–720.
- 363 (10) Gonzalez-Carrero, S.; Galian, R. E.; Pérez-Prieto, J. Organic-
364 Inorganic and All-Inorganic Lead Halide Nanoparticles [Invited]. *Opt.*
365 *Express* **2016**, *24*, A285–A301.
- 366 (11) Luo, B.; Pu, Y.-C.; Yang, Y.; Lindley, S. A.; Abdelmageed, G.;
367 Ashry, H.; Li, Y.; Li, X.; Zhang, J. Z. Synthesis, Optical Properties, and
368 Exciton Dynamics of Organolead Bromide Perovskite Nanocrystals. *J.*
369 *Phys. Chem. C* **2015**, *119*, 26672–26682.
- 370 (12) Zheng, K.; Židek, K.; Abdellah, M.; Messing, M. E.; Al-Marri, M.
371 J.; Pullerits, T. Trap States and Their Dynamics in Organometal
372 Halide Perovskite Nanoparticles and Bulk Crystals. *J. Phys. Chem. C*
373 **2016**, *120*, 3077–3084.
- 374 (13) Schmidt, L. C.; Pertegás, A.; González-Carrero, S.;
375 Malinkiewicz, O.; Agouram, S.; Mínguez Espallargas, G.; Bolink, H.
376 J.; Galian, R. E.; Pérez-Prieto, J. Nontemplate Synthesis of
377 $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Perovskite Nanoparticles. *J. Am. Chem. Soc.* **2014**,
378 *136*, 850–853.
- 379 (14) Mittal, M.; Jana, A.; Sarkar, S.; Mahadevan, P.; Sapra, S. Size of
380 the Organic Cation Tunes the Band Gap of Colloidal Organolead
381 Bromide Perovskite Nanocrystals. *J. Phys. Chem. Lett.* **2016**, *7*, 3270–
382 3277.
- 383 (15) Privitera, A.; Righetto, M.; Bozio, R.; Franco, L. The Central
384 Role of Ligands in Electron Transfer from Perovskite Nanocrystals.
385 *MRS Advances* **2017**, *2*, 2327.
- 386 (16) Lamberti, F.; Litti, L.; De Bastiani, M.; Sorrentino, R.; Gandini,
387 M.; Meneghetti, M.; Petrozza, A. High-Quality, Ligands-Free, Mixed-
388 Halide Perovskite Nanocrystals Inks for Optoelectronic Applications.
389 *Adv. Energy Mater.* **2017**, *7*, 1601703.
- 390 (17) Huang, H.; Susha, A. S.; Kershaw, S. V.; Hung, T. F.; Rogach, A.
391 L. Control of Emission Color of High Quantum Yield $\text{CH}_3\text{NH}_3\text{PbBr}_3$
392 Perovskite Quantum Dots by Precipitation Temperature. *Adv. Sci.*
393 **2015**, *2*, 1500194.
- 394 (18) Martinez-Sarti, L.; Koh, T. M.; La-Placa, M.-G.; Boix, P. P.;
395 Sessolo, M.; Mhaisalkar, S. G.; Bolink, H. J. Efficient Photoluminescent
396 Thin Films Consisting of Anchored Hybrid Perovskite Nanoparticles.
397 *Chem. Commun.* **2016**, *52*, 11351–11354.
- (19) Sichert, J. A.; Tong, Y.; Mutz, N.; Vollmer, M.; Fischer, S.;
Milowska, K. Z.; García Cortadella, R.; Nickel, B.; Cardenas-Daw, C.;
Stolarczyk, J. K.; et al. Quantum Size Effect in Organometal Halide
Perovskite Nanoplatelets. *Nano Lett.* **2015**, *15*, 6521–6527.
- (20) Zhang, F.; Zhong, H.; Chen, C.; Wu, X.-g.; Hu, X.; Huang, H.;
Han, J.; Zou, B.; Dong, Y. Brightly Luminescent and Color-Tunable
Colloidal $\text{CH}_3\text{NH}_3\text{PbX}_3$ (X = Br, I, Cl) Quantum Dots: Potential
Alternatives for Display Technology. *ACS Nano* **2015**, *9*, 4533–4542.
- (21) Veldhuis, S. A.; Boix, P. P.; Yantara, N.; Li, M.; Sum, T. C.;
Mathews, N.; Mhaisalkar, S. G. Perovskite Materials for Light-Emitting
Diodes and Lasers. *Adv. Mater.* **2016**, *28*, 6804–6834.
- (22) Chen, Y.; Yang, D.; Yoon, Y. J.; Pang, X.; Wang, Z.; Jung, J.; He,
Y.; Harn, Y. W.; He, M.; Zhang, S.; et al. Hairy Uniform Permanently
Ligated Hollow Nanoparticles with Precise Dimension Control and
Tunable Optical Properties. *J. Am. Chem. Soc.* **2017**, *139*, 12956–
12967.
- (23) Saini, P. *Fundamentals of Conjugated Polymer Blends, Copolymers*
and Composites: Synthesis, Properties, and Applications; Wiley: Beverly,
MA, 2015.
- (24) Eftekhar, A. *Nanostructured Conductive Polymers*; Wiley:
Chichester, U.K., 2011.
- (25) Pan, S.; He, L.; Peng, J.; Qiu, F.; Lin, Z. Chemical-Bonding-
Directed Hierarchical Assembly of Nanoribbon-Shaped Nanocompo-
sites of Gold Nanorods and Poly(3-hexylthiophene). *Angew. Chem.,*
Int. Ed. **2016**, *55*, 8686–8690.
- (26) Carey, G. H.; Abdelhady, A. L.; Ning, Z.; Thon, S. M.; Bakr, O.
M.; Sargent, E. H. Colloidal Quantum Dot Solar Cells. *Chem. Rev.* **2015**,
115, 12732–12763.
- (27) Kamat, P. V. Quantum Dot Solar Cells. Semiconductor
Nanocrystals as Light Harvesters. *J. Phys. Chem. C* **2008**, *112*,
18737–18753.
- (28) Kamat, P. V. Quantum Dot Solar Cells. The Next Big Thing in
Photovoltaics. *J. Phys. Chem. Lett.* **2013**, *4*, 908–918.
- (29) Sargent, E. H. Colloidal Quantum Dot Solar Cells. *Nat.*
Photonics **2012**, *6*, 133–135.
- (30) McGrail, B. T.; Sehirlioglu, A.; Pentzer, E. Polymer Composites
for Thermoelectric Applications. *Angew. Chem., Int. Ed.* **2015**, *54*,
1710–1723.
- (31) Sengodu, P.; Deshmukh, A. D. Conducting Polymers and Their
Inorganic Composites for Advanced Li-Ion Batteries: A Review. *RSC*
Adv. **2015**, *5*, 42109–42130.
- (32) Buckley, A. *Organic Light-emitting Diodes (OLEDs): Materials,*
Devices and Applications; Elsevier Science & Technology: Cambridge,
U.K., 2013.
- (33) Masi, S.; Colella, S.; Listorti, A.; Roiati, V.; Liscio, A.; Palermo,
V.; Rizzo, A.; Gigli, G. Growing Perovskite into Polymers for Easy-
Processable Optoelectronic Devices. *Sci. Rep.* **2015**, *5*, 7725.
- (34) Bansal, N.; Reynolds, L. X.; MacLachlan, A.; Lutz, T.; Ashraf, R.
S.; Zhang, W.; Nielsen, C. B.; McCulloch, I.; Rebois, D. G.; Kirchartz,
T.; et al. Influence of Crystallinity and Energetics on Charge Separation
in Polymer-Inorganic Nanocomposite Films for Solar Cells. *Sci. Rep.*
2013, *3*, 1531.
- (35) Kumar, V.; Kalia, S.; Swart, H. C. *Conducting Polymer Hybrids*;
Springer International Publishing: Cham, Switzerland, 2016.
- (36) Liu, Y.; Zhao, J.; Li, Z.; Mu, C.; Ma, W.; Hu, H.; Jiang, K.; Lin,
H.; Ade, H.; Yan, H. Aggregation and Morphology Control Enables
Multiple Cases of High-Efficiency Polymer Solar Cells. *Nat. Commun.*
2014, *5*, 5293.
- (37) Chang, J.-F.; Sun, B.; Breiby, D. W.; Nielsen, M. M.; Sölling, T.
I.; Giles, M.; McCulloch, I.; Sirringhaus, H. Enhanced Mobility of
Poly(3-hexylthiophene) Transistors by Spin-Coating from High-
Boiling-Point Solvents. *Chem. Mater.* **2004**, *16*, 4772–4776.
- (38) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.;
Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R.
A. J.; Meijer, E. W.; Herwig, P.; et al. Two-Dimensional Charge
Transport in Self-Organized, High-Mobility Conjugated Polymers.
Nature **1999**, *401*, 685–688.
- (39) Silva, C.; Russell, D. M.; Dhoot, A. S.; Herz, L. M.; Daniel, C.;
Greenham, N. C.; Arias, A. C.; Setayesh, S.; Mullen, K.; Friend, R. H.

- 467 Exciton and Polaron Dynamics in a Step-Ladder Polymeric Semi-
468 conductor: The Influence of Interchain Order. *J. Phys.: Condens. Matter*
469 **2002**, *14*, 9803.
- 470 (40) Lindblad, R.; Bi, D.; Park, B.-w.; Oscarsson, J.; Gorgoi, M.;
471 Siegbahn, H.; Odelius, M.; Johansson, E. M. J.; Rensmo, H. Electronic
472 Structure of $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Solar Cell Interfaces. *J.*
473 *Phys. Chem. Lett.* **2014**, *5*, 648–653.
- 474 (41) Varga, A.; Endrődi, B.; Hornok, V.; Visy, C.; Janáky, C.
475 Controlled Photocatalytic Deposition of CdS Nanoparticles on
476 Poly(3-hexylthiophene) Nanofibers: A Versatile Approach to Obtain
477 Organic/Inorganic Hybrid Semiconductor Assemblies. *J. Phys. Chem.*
478 *C* **2015**, *119*, 28020–28027.
- 479 (42) Endrodi, B.; Mellar, J.; Gingl, Z.; Visy, C.; Janaky, C. Reasons
480 Behind the Improved Thermoelectric Properties of Poly(3-hexylth-
481 iophene) Nanofiber Networks. *RSC Adv.* **2014**, *4*, 55328–55333.
- 482 (43) Duong, D. T.; Wang, C.; Antono, E.; Toney, M. F.; Salleo, A.
483 The Chemical and Structural Origin of Efficient p-Type Doping in
484 P3HT. *Org. Electron.* **2013**, *14*, 1330–1336.
- 485 (44) Weidman, M. C.; Seitz, M.; Stranks, S. D.; Tisdale, W. A. Highly
486 Tunable Colloidal Perovskite Nanoplatelets through Variable Cation,
487 Metal, and Halide Composition. *ACS Nano* **2016**, *10*, 7830–7839.
- 488 (45) Niklas, J.; Poluektov, O. G. Charge Transfer Processes in OPV
489 Materials as Revealed by EPR Spectroscopy. *Adv. Energy Mater.* **2017**,
490 *7*, 1602226.
- 491 (46) Aguirre, A.; Gast, P.; Orlinskii, S.; Akimoto, I.; Groenen, E. J. J.;
492 El Mkami, H.; Goovaerts, E.; Van Doorslaer, S. Multifrequency EPR
493 Analysis of the Positive Polaron in I2-Doped Poly(3-hexylthiophene)
494 and in Poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenyleneviny-
495 lene. *Phys. Chem. Chem. Phys.* **2008**, *10*, 7129–7138.
- 496 (47) Camaioni, N.; Tinti, F.; Franco, L.; Fabris, M.; Toffoletti, A.;
497 Ruzzi, M.; Montanari, L.; Bonoldi, L.; Pellegrino, A.; Calabrese, A.;
498 et al. Effect of Residual Catalyst on Solar Cells Made of a Fluorene-
499 Thiophene-Benzothiadiazole Copolymer as Electron-Donor: A
500 Combined Electrical and Photophysical Study. *Org. Electron.* **2012**,
501 *13*, 550–559.
- 502 (48) Pan, J.; Quan, L. N.; Zhao, Y.; Peng, W.; Murali, B.; Sarmah, S.
503 P.; Yuan, M.; Sinatra, L.; Alyami, N. M.; Liu, J.; et al. Highly Efficient
504 Perovskite-Quantum-Dot Light-Emitting Diodes by Surface Engineer-
505 ing. *Adv. Mater.* **2016**, *28*, 8718–8725.
- 506 (49) Pan, J.; Sarmah, S. P.; Murali, B.; Dursun, I.; Peng, W.; Parida,
507 M. R.; Liu, J.; Sinatra, L.; Alyami, N.; Zhao, C.; et al. Air-Stable
508 Surface-Passivated Perovskite Quantum Dots for Ultra-Robust, Single-
509 and Two-Photon-Induced Amplified Spontaneous Emission. *J. Phys.*
510 *Chem. Lett.* **2015**, *6*, 5027–5033.
- 511 (50) Krinichnyi, V. I. *Multi Frequency EPR Spectroscopy of Conjugated*
512 *Polymers and Their Nanocomposites*; CRC Press LLC: Boca Raton, FL,
513 2016.
- 514 (51) Spano, F. C. The Spectral Signatures of Frenkel Polarons in H-
515 and J-Aggregates. *Acc. Chem. Res.* **2010**, *43*, 429–439.
- 516 (52) Clark, J.; Silva, C.; Friend, R. H.; Spano, F. C. Role of
517 Intermolecular Coupling in the Photophysics of Disordered Organic
518 Semiconductors: Aggregate Emission in Regioregular Polythiophene.
519 *Phys. Rev. Lett.* **2007**, *98*, 206406.