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Induced Chain Alignment, Efficient Energy Transfer, and Enhanced Light Emission in Functional Polyacetylene−Perovskite Hybrids

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Hybridization of organic and inorganic species at the molecular level has attracted much interest among scientists because it offers the potential of combining the best parts of the two classes of materials in a single molecular composite as well as creating new properties arising from the molecular interactions between the two kinds of building blocks. One promising group of organic−inorganic hybrids is the self-assembled multilayers of organic cations and inorganic anions, where the layers of organic ammonium salt alternate with the layers of corner-sharing metal halide octahedra.[1,2] Most of the organic moieties used in the construction of ammonium salt−metal halide perovskites have been nonfunctional groups such as alkyl chains that play a secondary role of merely helping to improve the processability of the hybrids.[1−3]

Hybridization of π-conjugated macromolecules with perovskites may generate new materials with novel properties. This possibility has been explored but met with only limited success. For example, Mitzi et al. have integrated α,ω-diaminated oligothiophenes into lead halide perovskites.[4] The light-emitting diodes fabricated from the oligothiophene−perovskite hybrids exhibited maximum power efficiency and external quantum efficiency of 0.1 lm/W and 0.1%, respectively.[4] A possible reason for the poor device performance is the efficient intersystem crossing in the oligothiophene system.

Polyacetylenes have traditionally been regarded as poor emitters, but our recent work has proven that the polymers can be excellent luminophors with photoluminescence (PL) quantum yields (Φ_{PL}) up to unity, provided that appropriate substituents or pendants are appended to the polyene backbone.[5] In this work, we hybridized a group of emissive polyacetylenes with lead bromide perovskites. In this communication, we demonstrate how the molecular hybrids benefit from synergistic interplay between organic and inorganic components: the soluble polymers endow the hybrids with solubility or processability, while the perovskite layers induce the polymer chains to luminesce more efficiently.

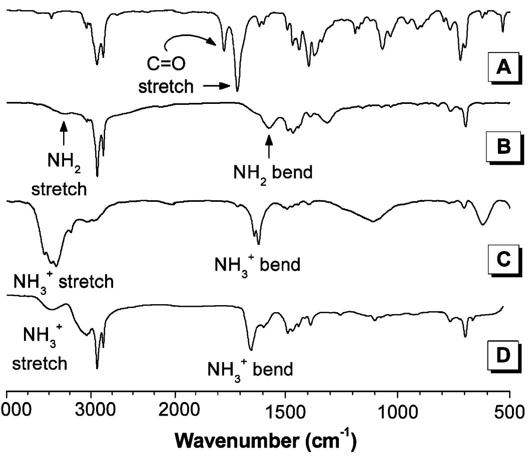
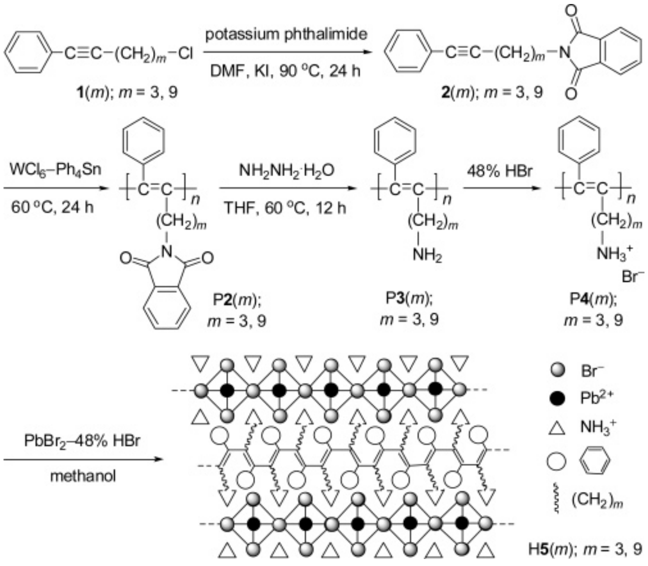


Figure 1. IR spectra of (A) polyimide P**2**(9), (B) polyamine P**3**(9), (C) polysalt P**4**(9), and (D) hybrid H**5**(9).

Scheme 1. Syntheses of Poly(1-phenyl-1-alkyne) Ammonium Salt−Lead Bromide Perovskite Hybrids



The synthetic routes to the polyacetylene−lead bromide hybrids [H**5**(m); $m = 3$, 9] are depicted in Scheme 1. ω-Chloro-1-phenyl-1-alkynes **1**(m) are prepared by palladium-catalyzed coupling of ω-chloro-1-alkynes with iodobenzene,[6] which are converted to **2**(m) by the reaction with potassium phthalimide. The monomers are isolated in high yields and characterized by spectroscopic methods, from which satisfactory analysis data are obtained [see Supporting Information (SI) for details]. The polymerizations of **2**(m) are effected by WCl$_6$−Ph$_4$Sn in toluene at 60 °C, giving yellow powdery poly“imides” P**2**(m) in good yields. The phthalimido group of P**2**(m) is hydrolyzed by hydrazine, producing poly“amines” P**3**(m) in high yields (>89%). Treatment of P**3**(m) with aqueous HBr gives rise to poly“salts” P**4**(m), the complexation of which with lead bromide results in the formation of the polyacetylene−perovskite hybrids in >83% yields.

The hybrids are soluble in common polar solvents such as DMF, DMSO, and water. They are thermally stable, losing little of their weight when heated to ~350 °C under nitrogen (e.g., SI, Figure S1). Their molecular structures are characterized spectroscopically. An IR spectrum of H**5**(9) is shown in Figure 1 as an example, with those of P**2**(9)−P**4**(9) given in the same figure for comparison. Two bands arising from stretching vibra-

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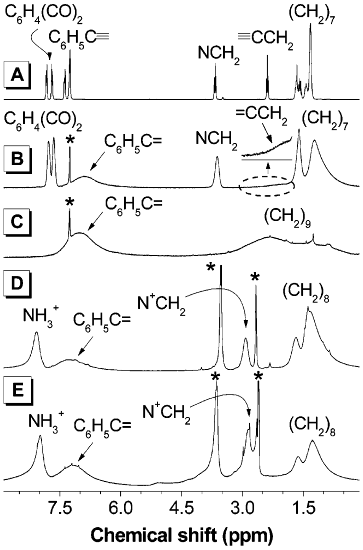

Figure 2. ^{1}H NMR spectra of solutions of (A) monomer **2**(9), (B) polyimide P**2**(9), (C) polyamine P**3**(9), (D) polysalt P**4**(9), and (E) hybrid H**5**(9) in chloroform-d (A–C) or DMSO-d_6 (D, E). The solvent and water peaks are marked with asterisks.

tions of phthalimido group of polyimide P**2**(9) appear at 1773 and 1713 cm^{-1} (Figure 1A),[7] which disappear after P**2**(9) has been subjeted to hydrolysis deprotection. In the spectrum of the hydrolysis product or polyamine P**3**(9), new absorption bands associated with stretching and bending vibrations of amine group are observed at 3379 and 1573 cm^{-1}, respectively. The ammonium ion of polysalt P**4**(9) absorbs at 3000 and 1615 cm^{-1}.[7] The absorption bands of the ammonium ion of hybrid H**5**(9) are observed in a similar spectral region (Figure 1D).[8]

Figure 2 shows ^{1}H NMR spectra of the solutions of monomer **2**(9), polymers P**2**(9)–P**4**(9), and hybrid H**5**(9) in chloroform-d or DMSO-d_6. The protons of ethynylphenyl ($\equiv CC_6H_5$) and propargyl groups ($\equiv CCH_2$) of the monomer resonate at δ 7.37–7.25 and 2.39, respectively. The resonances upfield shift when the ethynylphenyl and propargyl groups of **2**(9) are transformed to styryl ($=CC_6H_5$) and allyl groups ($=CCH_2$)[7] of P**2**(9) by the W-catalyzed acetylene polymerization. The peaks are broadened due to the rigid nature of the polyene backbone.[5,9] There are no peaks of phthalimido protons [$C_6H_4(CO)_2$] in the spectrum of P**3**(9) (Figure 2C), confirming that the hydrolysis has proceeded to completion. The spectrum of P**3**(9) is broad and structureless, possibly because the polymer chains have aggregated via hydrogen bonding of their amino pendnats. The resonance peaks of P**4**(9) and H**5**(9) are sharper and better resolved due to the blockage of the H-bonding channel as well as their good solubility in the polar solvent. New peaks are found at $\delta \sim 8$ in the spectra of P**4**(9) and H**5**(9), which are assignable to the resonances of the protons of their ammonium ions (NH_3^+).[7]

The polyacetylene backbone of polysalt P**4**(9) absorbs at ~340 nm (Figure 3A).[5,9] Upon hybridization with lead bromide, a new peak appears at 397 nm in the spectrum of H**5**(9). To identify the origin of this peak, we prepared a "model hybrid" $(C_4H_9NH_3)_2PbBr_4$[1] and measured its absorption spectrum. The model hybrid absorbs at 404 nm, verifying that the peak of H**5**(9) at 397 nm is associated with exciton absorption of its lead bromide perovskite component.[10]

While P**4**(9) is amorphous, its hybrid H**5**(9) displays reflection peaks at low 2θ angles of 4.1° and 7.7° (Figure 4). The d-spacing associated with the reflection at $2\theta =$ 4.1° is 21.5 Å, close to the molecular length of the repeat unit of the polymer chain in its fully extended conformation. The model hybrid $(C_4H_9NH_3)_2PbBr_4$ shows an intense reflection peak at $2\theta = 6.4°$. The broad refelction peak of H**5**(9) at $2\theta = 7.7°$ is probably a combination of the reflection of the perovskite layer and the secondary refelction of the polymer chain. The XRD pattern of the hybrid is similar to those of the liquid crystalline polyacetylenes developed in our laboratories[5,9,11] al-

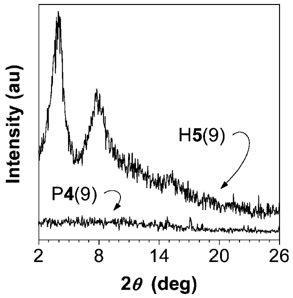

Figure 4. X-ray diffraction patterns of the thin solid films of polysalt P**4**(9) and hybrid H**5**(9) spin-coated on quartz substrates.

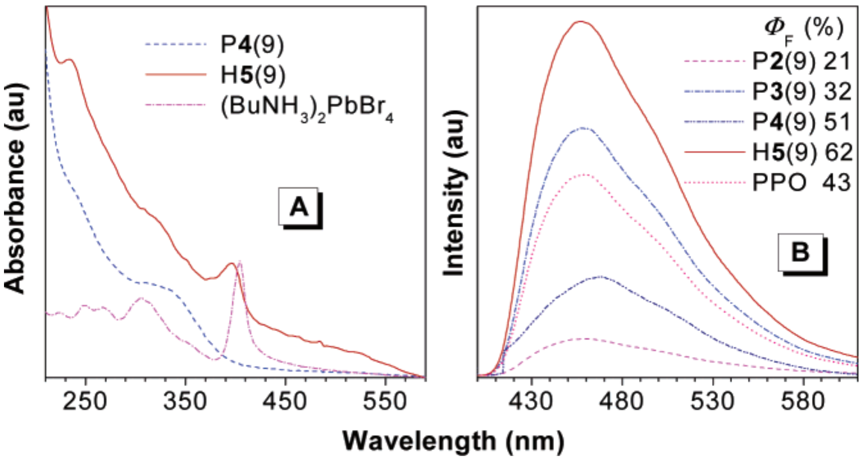

Figure 3. (A) Absorption spectra of thin solid films of polysalt P**4**(9), hybrid H**5**(9), and model hybrid compound $(BuNH_3)_2PbBr_4$. (B) Emission spectra of solutions of P**2**(9)–P**4**(9), H**5**(9), and poly(1-phenyl-1-octyne) (PPO) in THF. Polymer concentration: 0.05 mM; excitation wavelength (nm): 330 [P**2**(9)–P**4**(9) and H**5**(9)], 355 (PPO).

though the polymer in H**5**(9) carries no mesogenic units. The long-range order of the polymer chains thus must have been induced by the perovskite when they are intercalated into the lead bromide layers.

The PL peaks of the solid films of polyamine P**3**(9) and model hybrid $(C_4H_9NH_3)_2PbBr_4$ are located at 458 and 433 nm, respectively (SI, Figure S2). The PL spectrum of hybrid H**5**(9) peaks at 466 nm with no shoulder at 433 nm, indicating that an efficient energy transfer has taken place in the polyacetylene−perovskite hybrid. The violet light of 433 nm emitted from the perovskite framework has been absorbed by or transferred to the polyacetylene chains, the radiative decay of whose singlet excited state leads to the blue light emission at 466 nm.

To estimate PL efficiencies of the polymers and hybrids, their emission spectra are measured in dilute THF solutions. Similar to the solid films, the solutions of the polymers and hybrids emit blue light when photoexcited. Examples of the PL spectra are given in Figure 3B. Using 9,10-diphenylanthracene as standard,[12] Φ_{PL} of polyimide P**2**(9) is estimated to be 21%, which is about half of that of its parent form PPO.[13] This is probably caused by the quenching effect of its phthalimido pendant. Removal of the imido group leads to an increase in the Φ_{PL} [32% for P**3**(9)]. The quaternization and hybridization help to enhance Φ_{PL}, with Φ_{PL} of the hybrid being boosted to a value as high as 62%. When the polyamine is quaternized by the acid, the polymer is converted to a polysalt or polyelectrolyte. Electrical repulsion of the charged polyelectrolyte chains reduces the chain interaction of P**4**(9) and enhences its Φ_{PL}. When the polysalt chains are sheathed in the perovskite layers, the chain interaction is further weakened, hence the even higher Φ_{PL} of the hybrid.

The PL spectra of polymers P**2**(3)−P**4**(3) and hybrid H**5**(3) are similar to those of their congeners with the longer spacer ($m = 9$) discussed above. Their Φ_{PL} values are lower,[14] in agreement with our early observation that Φ_{PL} of a polyacetylene decreases with a decrease in its spacer length.[5,9,15] In this series again, quaternization and hybridization boost the emission efficiency: the Φ_{PL} (47%) of hybrid H**5**(3) is ~2-fold higher than that of its polyamine parent P**3**(3) (24%).

In summary, in this work, we succeeded in hybridizing functional polyacetylenes with lead bromide perovskite. The resultant hybrids H**5**(m) are soluble, film forming, and thermally stable. The provskite induces the nonmesogenic polyacetylene chains to align like liquid crystals within the inorganic layers. Photoenergy is efficiently transferred from the perovskite framework to the polyacetylene chains, and the chain interactions are supressed by the segregation of the polymer chains in separate perovskite layers. The energy transfer and chain separation both help enhance the light emission efficiency of the hybrids. To our knowledge, this is the first successful example of constructing a conjugated polymer−perovskite hybrid in which both organic and inorganic components play active, constructive roles in boosting their functional performances. Noting that the conjugated polyacetylene chains are electro- and photoactive and that the perovskite layers possess high charge mobilities, the hybrids are envisioned to serve as active layers for fabricating efficient light-emitting diodes and photovoltaic cells.[16] These possibilities are under exploration in collaboration with colleagues in the departments of physics and electrical and electronic engineering of our universities.

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Supporting Information Available: Synthesis and characterization details for **2**(m), P**2**(m)−P**4**(m), and H**5**(m); TGA thermograms of P**2**(9)−P**4**(9) and H**5**(m) and PL spectra of the films of P**3**(9), H**5**(9), and $(BuNH_3)_2PbBr_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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